Robert H. Armon
Osmo Hänninen *Editors*

Environmental Indicators

Springer

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ISBN 978-94-017-9498-5 ISBN 978-94-017-9499-2 (eBook)
DOI 10.1007/978-94-017-9499-2
Springer Dordrecht Heidelberg New York London

Library of Congress Control Number: 2014954799

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

An indicator is like a lighthouse, if we don’t pay attention we’ll end up crashing on the rocks.

To my current grandchildren Yahli, Ivri and Ori and to those to be born in a cleaner world! And also in the memory of my best friends, my late parents Dorothea and Theodor.

Preface

While on sabbatical leave at Kuopio University, Finland, and being involved with the organization called ISEI (International Society of Environmental Indicators), I reached the conclusion that a concentrated effort articulated in a book on various environmental indicators does not exist on the global bookshelf, and this is the time to put one together!

Following discussions with my ISEI colleague Prof. Em. Osmo Hänninen from Finland, a veteran and highly active member of our organization (ISEI), an outlook list was composed, which was intended to be covered later by various international authors (known as experts in their field). Now, in retrospect, we should say that it was not an easy task, as we had to decide which subjects to cover and which to leave for alternative future opportunities. When the subject list had been consolidated, it was communicated to various international scientists, and, following their approval, the book "assemblage" was on its way. I do recall today that in a phone conversation with Dr. Paul Roos (Editorial Director of Environmental Sciences, Springer Dordrecht), besides expressing his interest, he told me that he thought the proposed project a very ambitious one, basically meaning that our venture would not be an easy task.... As scientists, we are never hindered by difficulties, but rather the contrary is true: they make our work more challenging, and therefore, we attacked the task seriously and stubbornly.

Indeed, after more than a year's work, the present book represents the efforts of 80 authors, expressed in 15 subjects and 58 chapters on a large variety of environmental issues, starting from thermodynamics and ending in health issues! The subjects that are covered were selected based on European and US environmental databases, as the important issues that raise critical environmental concerns had been emphasized along the years by these leading entities.

We are happy to bring this compilation to the reader involved in environmental issues, as well as to those who wish to use it as the first textbook on environmental indicators as such. We as well as our academic colleagues always touch upon the indicator issue in our courses, although merely as related to our own specific professional field. The present book is the first effort to present the most important indicators together and consolidate a unifying line between the various subjects. We hope that this volume achieves this task well and can be used by many thousands of scientists involved in environmental research.

Haifa
April 2014

Prof. Robert H. Armon, Faculty of Civil and Environmental Engineering, Technion (Israel Institute of Technology), Department of Environmental, Water and Agricultural Engineering, Haifa 32000, Israel. Board Member of IWA Specialist Group-HRWM (Health-Related Water Microbiology).

Kuopio
April 2014

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Acknowledgement

We would like to thank Ms. Liz Yudim for her help with English style editing of each book chapter. To Technion (Israel Institute of Technology) for financial support and the vast references data base (SciFinder) that allowed reading of hundreds of published articles to be used in the consolidation of the chapters. And finally to Dr. Paul Roos (Editorial Director, Environmental Sciences, Springer) and to Ms. Betty van Herk and Ms. Judith Terpos for their help in bringing this volume to production.

And finally to all authors that contributed to this book with their intellectual knowledge, effort and time.

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Introduction

Perhaps the finest analogy to the role of indicators can be found in the physician's preliminary examination of a patient. Any respectful physician will start his or her diagnosis of a patient with simple and fast tests that are easy to perform, e.g., temperature, blood pressure, physical contact to detect pain, etc., and only later will apply the more sophisticated tests, such as CT, MRI, or the simpler X-ray radiography, in order to reach a final diagnosis. We should bear in mind this analogy when handling environmental indicators.

Environmental indicators are simple events that let us know what is happening in different surrounding environments. Because of its complexity, environmental measurement should be performed using a less expensive and cumbersome approach involving a large variety of indicators. For example, to measure the presence of a pathogen in potable water in order to ensure the safety of a water supply, a large battery of expensive materials and methods are required that in some cases are useless and in others practically and economically almost impossible to accomplish! In most cases, those pathogens are found in low numbers, therefore requiring a concentration step, which will increase the economic burden (especially since thousands of such tests are required annually) to the extent of leading to economic bankruptcy! On the other hand, for health people, what is the epidemiological significance of one viral/bacterial particle in 1,000 L? Consequently, the indicator system makes our lives easier and is a matter of choice, both economically and scientifically. Below, we present two historical examples of "classical indicators" and their introduction and use.

Historically, microbiological indicators of the sanitary quality of water were introduced at the end of the nineteenth century. In 1880, Von Fritsch described *Klebsiella pneumonia* and *Klebsiella rhinoscleromatis* as characteristic human fecal bacteria, and in 1885 Percy and Grace Frankland introduced the first routine bacteriological examination of London's water, using Robert Koch's solid gelatin media for bacterial enumeration. The same Frankland, in 1891, came up with the idea that sewage microorganisms should be characterized in order to give warning of a potential sanitary hazard. In 1885, Escherich described *Bacillus coli*

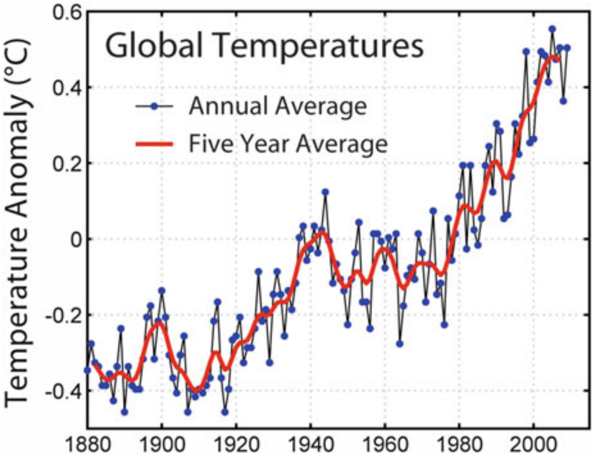

Fig. 1 An example of an environmental indicator: Trend in global temperature anomalies of the last 150 years as an indicator of climate change (Source: National Aeronautics and Space Administration, Goddard Institute for Space Studies (http://data.giss.nasa.gov/gistemp/graphs_v3/); Hansen et al. 2006)

(now called *Escherichia coli* in his memory) as a typical bacterium originating from the feces of breast-fed infants. Then, starting at the beginning of the last century (1900 and on), *Bacillus coli* was used as an indicator in the UK of potential water contamination with fecal material. To make a long story short, specific human fecal bacteria became the standard indicators of potable water safety! Together with the introduction of chlorination, waterborne diseases were significantly reduced worldwide. Today, those bacteria are used as the common indicators of water pollution, in spite of their many drawbacks.

Another example of an important indicator, which marked the way to apprehending climate change, is the temperature rise over time as an indicator of global warming (Fig. 1)! Temperature measurements are easy to perform and have been conducted for more than 100 years. Therefore, using their anomalies frequency as an indicator, it can be concluded that there is an essential shift in global temperatures.

Both examples show the use of simple, fast, and cost-effective parameters that have a real potential to indicate with a certain percentage of accuracy that our environment is polluted or is facing a problem!

This book presents many such indicators covering a large area of environmental issues that affect the human population globally. It is our pleasure to bring to the attentive environmentalist reader a large panel of indicators that are in use, or whose potential as such is proposed, to achieve a more livable and cleaner planet (Maher 2011).

The editors would like to thank all contributors and the Springer publishing house, especially Dr. Paul Roos for his support and encouragement and Ms. Betty van Herk for her editorial support. We would like to thank the authors' families for their equability and for understanding the value of our contribution, in spite of long hours and days in the office.

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Maher B (2011) The new rules: a funny look at how everybody but me has their head up their ass. New rule: oil companies must stop with the advertisements implying they're friends of the environment. 'At Exxon Mobil, we care about a thriving wildlife.' Please – the only thing an oil executive has in common with a seagull is they'd both steal French fries from a baby. Blue Rider Press

The International Society of Environmental Indicators: Historical Overview

The International Society of Environmental Indicators (ISEI) is an international network of scholars who support and promote the development and use of biological, chemical and physical environmental indicators in environmental assessments and environmental management. Environmental indicators are critical components of monitoring efforts worldwide, and because many environmental indicators are relatively inexpensive to monitor, ISEI makes efforts to work with scientists in developing countries to enable them to better integrate environmental indicators in their environmental assessment and monitoring efforts. This overview describes its formation and development.

The ISEI traces its origin to a series of sessions on bioindicators, or biomarkers, organized by myself and Jim Newman at the Annual International Conference on Contaminated Soils, Sediments and Water held at the University of Massachusetts, Amherst in 2002–2005. Abstracts from the inaugural session are available at: http://scholarworks.umass.edu/cgi/viewcontent.cgi?article=1001&context=soils_conf_abstracts. In 2003, we published a paper on *Bioindicators – Essential tools for realistic site assessment and remediation cost control* in the March/April issue of The Association for Environmental Health & Sciences (AEHS) magazine, *Soil Sediment & Water*. It was in Amherst during this period when several new journals were being launched by Amherst Scientific Publishers, an affiliate of AEHS. I was having lunch with Paul Kostecki, the co-founder of AEHS, and suggested that there was a need for a journal on environmental bioindicators and that AEHS should consider adding such a journal to their portfolio. Paul responded with, "Why don't you do it?" This was not something I had contemplated before and it took a couple weeks to get used to the idea. I contacted Jim Newman to see if he would be interested in partnering with me on the venture and found him to be enthusiastic. I then called a contact at Taylor & Francis Group, LLC (T&F). A short time later, Jim and I were invited to meet with the publishing staff of T&F at their corporate offices in Philadelphia. We were advised that the chances of such a journal being a success would be greatly enhanced if we were to form a scientific society to support it.

The first meeting of the new International Society of Environmental Bioindicators was held in concert with the Thirteenth International Conference on Environmental Bioindicators of the International Union of Biological Scientists (IUBS), International Commission on Bioindicators at the Vila Porthemaka Praha, Czech Republic, 6–10 June 2005. The formation of the new society was proposed and agreed to by the participants. (The name of the new society was formally changed to the International Society of Environmental Indicators [ISEI] in 2009 to reflect the broader scope of the interests of its members.)

The inaugural issue of a new international journal, *Environmental Bioindicators*, was published by T&F in the first quarter of 2006 in print and online (ISSN 1555–5275, and 1555–5267, respectively). The print version of the journal continued to be published quarterly through October-December 2009. A brief history of the changes and milestones in the structure of the journal and in the development of the society was reported in an editorial at the completion of its first 4 years of publication (Zillioux EJ, 2009, *Environmental Bioindicators* [EBI] to *Environmental Indicators* [EI] and other Developments: the evolution of a journal. Vol. 4, pp. 283–285). Beginning with volume 5 in 2010, *Environmental Indicators* became a stand-alone on-line open-access journal. Complete contents of all issues of both print and subsequent on-line volumes are accessible at www.environmentalindicators.net.

Following the Prague conference, the ISEBI and subsequent ISEI Conferences continued on an annual basis from 2005 through 2011. At the 2011 conference it was decided to hold future conferences on a biennial basis. The first biennial conference was held in 2013 and the next is planned for 2015. All ISEI conferences are listed with details on Table 1; in addition, a related and linked conference, held in Moscow in 2013, is also listed.

Table 1 Conferences sponsored by ISEI, 2005–2015

Conference		Theme	Location & sponsoring institute
	21st International Conference on Environmental Indicators 9th ISEI International Conference 2–5 August 2015	Water Quality Indicators	Windsor, Canada – University of Windsor and the Agriculture and Agri-Food Canada
	20th International Conference on Environmental Indicators 8th ISEI International Conference 16–19 September 2013	Monitoring Indicators to Inform and Diagnose Environmental Hazards and their Impacts	Trier, Germany – Trier University
	An ISEI-Related and Linked Conference 4–6 February 2013	Bioindication in the Ecological Assessment of Soils and Related Habitats	Moscow, Russian Federation – Moscow State University

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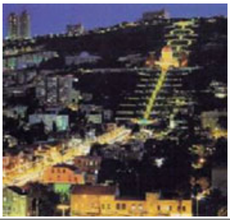	19th International Conference on Environmental Indicators 7th ISEI Annual Meeting 11–14 September 2011	Environmental Indicators with a Global View	Haifa, Israel – *Technion-Israel Institute of Technology*
	18th International Conference on Environmental Indicators 6th ISEI Annual Meeting 13–16 September 2010	Polar & Marine Environmental Changes and Pollutants & Other Anthropogenic Impacts	Hefei, China – University of Science and Technology of China
	17th International Conference on Environmental Indicators 5th ISEI Annual Meeting 18–20 May 2009	Global Indicators	Moscow, Russian Federation – Moscow State University
	16th International Conference on Environmental Indicators 4th ISEI Annual Meeting 11–14 November 2008	Management Metrics	Orlando, Florida, USA – Environmental Indicators Foundation, LLC
	15th International Conference on Environmental Indicators 3rd ISEI Annual Meeting 7–9 June 2007	Bioindicators for Environmental Management	Hong Kong, SAR, China – City University of Hong Kong
	14th International Conference on Environmental Indicators 2nd ISEI Annual Meeting 24–26 April 2006	Indicators of Performance and Trends	Linthicum Heights, Maryland – Maritime Institute
	13th International Conference on Environmental Indicators 1st ISEI Annual Meeting 6–10 June 2005	Large-scale Biomonitoring	Prague, Czech Republic – University of South Bohemia

ISEI is governed by an elected Board currently headed by: President: Diane Henshel, Ph.D., Indiana University, Bloomington, IN, USA, dhenshel@indiana.edu, and Vice President: Zhi-Qing (ZQ) Lin, Ph.D., Southern Illinois University, Edwardsville, IL, USA, zhlin@siue.edu. Other Officials of the Society include: Secretary: Nancy Denslow, Ph.D., University of Florida, Gainesville, FL, USA, ndenslow@ufl.edu; Editor-in-Chief: Nicholas V.C. Ralston, Ph.D., University of North Dakota, Grand Forks, ND, USA, nralston@undeerc.org; Treasurer: Edward Zillioux, Ph.D., Environmental Indicators Foundation LLC, Fort Pierce, FL, USA, zillioux@bioindicators.org; and Board Members: Robert Armon, Ph.D., Technion, Haifa, Israel; Jill Jenkins, Ph.D., Geological Survey, Lafayette, LA, USA; Roland Klein, Ph.D., Trier University, Trier, Germany; James Newman, Ph.D., Normandeau Associates, Inc., Gainesville, FL, USA; and Carla Ralston, Ph.D., University of North Dakota, Grand Forks, ND, USA.

The ISEI journal and society website is in the process of being upgraded to make it more efficient to use and easier to access and to submit papers. The Board is currently conducting a Membership Drive to strengthen the vitality of ISEI and to carry forward the critical mission of this society:

Mission Statement and Objective

The International Society of Environmental Indicators (ISEI) and its journal, *Environmental Indicators* (JEI), seeks to explore the scientific bases and uses of indicators (biological, chemical, physical) and biomarkers as they relate directly to specific measurable effects in ecological and human populations from environmental exposures. Emphasis is placed on the application of molecular to landscape level indicators as tools to help in understanding the probability that the presence of a contaminant(s) or other disturbances in the ambient environment that may produce an adverse effect in exposed receptors or populations, the degree of harm that may be indicated, and the integration of these data to characterize environmental health. Environmental indicators range from molecular and genetic indicators to landscape-level indictors reflecting the conditions of the human and ecological environments.

It is the objective of the Society to provide an empirically-derived foundation in the use of indicators to help define environmental health and requisite protection or restoration needs, and from which responsible action, including informed and cost-effective regulatory endpoints, can be developed.

The ISEI membership application (which is also available on the Society website: http://www.environmentalindicators.net/) is attached for the convenience of prospective renewal and new membership applicants. Please copy the application and follow submittal instructions. Thank you.

Acknowledgements Thanks are due to Drs. Diane Henshel, Nicholas Ralston, and Zhi-Qing (ZQ) Lin for their reviews and helpful suggestions which have substantially improved this chapter.

Fort Pierce, FL, USA Edward J. Zillioux

2014–2015 ISEI Membership Application

International Society of Environmental Indicators (ISEI) http://www.environmentalindicators.net.

Year of Renewal or New Member Application: ________________

(Memberships are accepted on a calendar-year basis only; dues include subscription to the on-line journal, free manuscript submissions, and conference registration fee discount)

Please check category and amount paid:

❒ Renewal ❒ New

❒ Regular Membership: US**$100.00** per year

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* "Developing Countries" are those categorized as "Low-Income," "Lower-Middle-Income," and "Upper-Middle-Income" by the World Bank; see http://go.worldbank.org/D7SN0B8YU0

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PayPal: Payments for membership can be processed through PayPal. **Option 1:** Interested individuals who have a PayPal account can send payments to zillioux@bioindicators.org. **Option 2:** Interested Individuals who do not have a PayPal account, should send an email to **zillioux@bioindicators.org** requesting payment through PayPal. I will forward your request and PayPal will contact you and ask for your credit card information. Your card information is protected by PayPal.

Check or money order: Make payable to "Environmental Indicators Foundation, LLC" in US funds. Send to ISEI, 207 Orange Avenue, Ste. G, Fort Pierce, Florida, 34950, USA

Member Information:

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Affiliation: ____
Title/Position: ______________________________________
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City: _____________________ State/Province: ___________________ Zip/Country Code: ________________
Country: ___________________________ E-mail:____________________________

Print and complete this form and mail to: Edward J. Zillioux, Treasurer and ISEI Business Manager, 207 Orange Avenue, Ste. G, Fort Pierce, FL 34950, USA, or send a scanned copy by email to: **zillioux@bioindicators.org**.

Part I
Environmental Thermodynamics

Chapter 1
Non-renewable Resources as Indicator of Thermodynamic Changes in Environment

Wenjie Liao and Reinout Heijungs

Abstract Natural resources are the non-substitutable biophysical basis for our economy growth. Transforming current unsustainable economies requires changes to technologies that are thermodynamically speaking a conversion of natural resources from the ecosphere into products and services to meet human needs in the anthroposphere. Certain conditions of thermodynamic change should be respected to ensure the environmental sustainability of technologies. This chapter presents how to use natural resources, particularly non-renewable resources, as a basis to formulate such an environmental indicator. Cumulative exergy demand of non-renewable resources is introduced as an environmental indicator that measures the thermodynamic change in the environment caused by technologies in terms of the extraction of exergy of fossil fuels, nuclear fuels, metal ores, and minerals from the environment and the emission of heat to the environment. The case of global liquid biofuel production is studied to demonstrate the feasibility of the environmental indicator.

Keywords Non-renewable resources • Exergy • Biofuels • Anthropogenic heat

1.1 Introduction

According to the online Oxford dictionary, natural resources are materials or substances occurring in nature which can be exploited for economic gain. They are the ultimate inputs to our civilization and the non-substitutable basis for economic growth (Daly 1991; Ayres 1998). Today, the world economy utilizes gigatons of metals and fossil fuels and about one third of the land surface (Kleijn 2012;

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_1

Lambin and Geist 2006). More than half of all accessible fresh water is used by humans (Pauly and Christensen 1995). More atmospheric nitrogen is fixed by humans than by all natural terrestrial sources combined (Vitousek et al. 1997). The scale of human activities and human-driven changes are comparable to that of natural processes and major changes in the geological past (Zalasiewicz et al. 2011). The current era may be viewed as being sufficiently different from other parts of the Holocene to refer to it as the Anthropocene, as proposed by Crutzen (2003).

In the Anthropocene, humans have been pursing economic growth and creating wealth in an unsustainable way, which is illustrated by various environmental problems that we have faced since the onset of the Industrial Revolution around two centuries ago. Transforming such unsustainable economies requires changes to technologies that are essentially a conversion of natural resources from the ecosphere into products and services to meet human needs in the anthroposphere (Beinhocker 2006; Liao 2012). For the sake of environmental sustainability, natural resources should not run out and emissions, mainly in terms of heat and waste, should not endanger the ecosphere or transcend the ecospherical carrying capacity (Dewulf et al. 2000; Rockström et al. 2009).

This chapter aims at introducing non-renewable resources as an indicator to measure thermodynamic changes in the environment in the context of environmental sustainability analysis of technologies. In the following sections, we present the system boundary as defined by Liao (2012), explain the method to develop the environmental indicator, and demonstrate its application in the case study of global liquid biofuel production.

1.2 Method

1.2.1 System Boundary

The principle of system definition is that it should include all relevant processes. Figure 1.1 shows the four different levels of boundary, labeled A, B, C, and D, of the conceptualized system. Flows of energy carriers (referred to below as energy without further specification) and non-energetic materials (referred to below as materials without further specification) are indicated. The anthroposphere is the boundary of most environmental indicators for natural resources, including both energy and materials. The conversion of natural resources into products and services can be at the level of the foreground system or the supply chain of a techno-system, or the whole anthroposphere.

Level A (the ecosphere) principally includes the planetary processes that provide renewable resources, i.e., natural resources that are generated on a human time scale (mainly flows of renewable energy, such as tidal, biomass, solar, hydro, wind, geothermal, and wave), and non-renewable resources, i.e., stocks of natural resources that have been accumulated on a geological time scale (fossil and nuclear fuels, metal ores, and minerals). Level B (the anthroposphere) includes all the

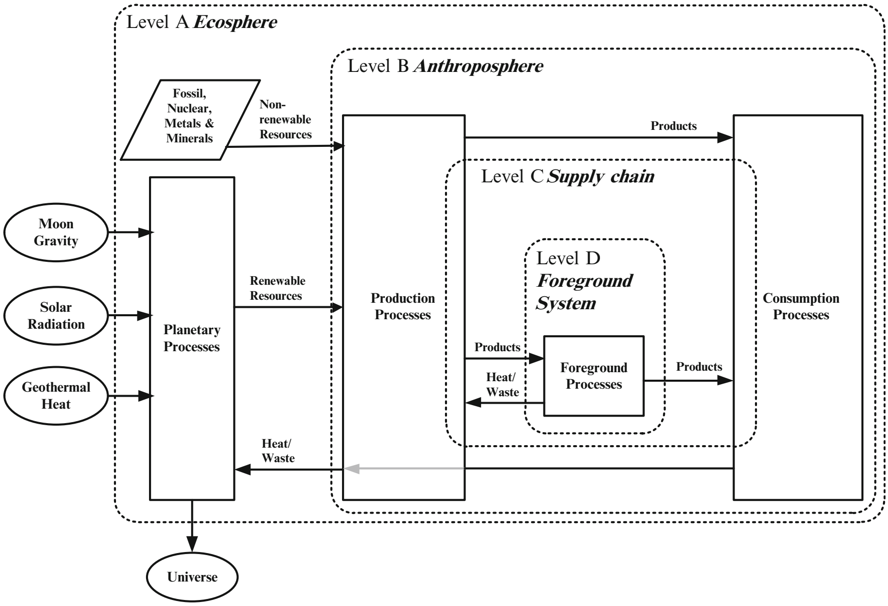

Fig. 1.1 Systems diagram showing the conversion of natural resources into products at different levels. The *ellipses* stand for sources or sinks, the *parallelogram* for stocks, and the *rectangles* for processes, i.e., conversion steps. *Dashed lines* represent the boundaries of the levels of analysis

human activities, mainly production and consumption processes. Level C (the supply chain) includes part of the production and consumption processes that supplies the intermediate products. Level D (the foreground system) is defined to account only for the direct inputs of the foreground processes (Liao 2012)

1.2.2 Exergy-Based Resource Indicator

1.2.2.1 Exergy

Exergy is a thermodynamic metric rooted in the first and second laws of thermodynamics. The first law of thermodynamics expresses the conservation of energy; the second law describes the degradation of the quality of energy. While thermodynamics basically is the study of the relation between heat and work (Keenan 1941), we uses the term of thermodynamics in a broad sense, extending to transformations of energy and materials, since material flows and conversions are accompanied by energy flows and conversions in various processes of the ecosphere. From this, the concept of exergy that takes into account the availability or quality of both energy and materials can be derived.

Exergy is defined as the maximum amount of work that can be obtained from a flow of energy or materials when it is brought into equilibrium with a reference environment (for a commented history of the concept, see Sciubba and Wall (2007)). It has the same unit as energy, i.e., Joules. This study adopted the reference environment proposed by Szargut (2005) with the ecosphere subsystem by Gaggioli and Petit (1977), which is defined as the global average environment that has average chemical compositions of the atmosphere, seawater, and the crust under a temperature of 298 K and atmospheric pressure of 1.01325 E+05 Pa. Exergy is recognized as a proxy of the physical value of a natural resource since all production and consumption processes in the anthroposphere require energy and material resources from the ecosphere that feature exergy. The exergy value of a natural resource represents the minimal work that is needed to form the resource. Exergy is consumed in all real processes in proportion to the entropy being generated. Exergy analysis is being applied in various fields of human-environment systems where social and ecological aspects are interacting at multiple scales (Sciubba and Wall 2007; Dincer and Rosen 2005; Dewulf et al. 2008; Liao 2012).

1.2.2.2 Cumulative Exergy Demand

Cumulative exergy demand (CExD) expresses the gross exergy of all natural resources required to deliver a product (Bösch et al. 2007). CExD is equivalent to the definition of cumulative exergy consumption of Szargut (2005). In Fig. 1.1, CExD measures the exergy value of all natural resources (both renewable and non-renewable) at the interface of level A and level B that are needed to deliver the final product at level D. We define the cumulative exergy demand of non-renewable resources ($\mathrm{CExD_{NRR}}$) as the sum of exergy of all fossil fuels (F), nuclear fuels (N), metal ores (O), and minerals (M) that are needed to deliver a product (Eq. 1.1).

$$CExD_{NRR} = m_F \times \beta_F \times HHV_F + m_N \times \beta_N \times HHV_N + m_O \times Ex_{ch,O} + m_M \times Ex_{ch,M} \tag{1.1}$$

where, m stands for the cumulative amount of a natural resource that is needed to deliver the final product (in m^3 for natural gas and kg for other non-renewable resources), β for the exergy-to-energy ratio of a fuel (dimensionless), HHV for the higher heating value of a fuel (in MJ/m^3 or MJ/kg), and Ex_{ch} for the specific chemical exergy of a metal ore or mineral (MJ/kg).

1.2.2.3 Data Sources and Calculation

Data on the cumulative amount of a natural resource required for a specific product are provided in ecoinvent database v2.2 (Swiss Centre for Life Cycle Inventories 2010) or approximated by using the cumulative degree of thermodynamic perfection of the corresponding intermediate products (Szargut and Morris 1987; Szargut 2005). Data on the exergy-to-energy ratio are available in Szargut (2005). Higher heating values can be obtained from Frischknecht et al. (2004). The specific chemical exergy of a material resource Ex_{ch} is calculated based on its composition of different substances (Eq. 1.2)

$$
\begin{aligned}
Ex_{ch} &\approx Ex^{o}_{ch} \\
Ex^{o}_{ch} &= \sum_i n_i ex^{o}_{ch,i} / \sum_i n_i w_i \\
ex^{0}_{ch,i} &= \Delta G^{o}_{f} + \sum_k v_k ex^{o}_{ch,k}
\end{aligned}
\tag{1.2}
$$

where, Ex^{0}_{ch} is the standard specific chemical exergy of a material resource (in kJ/g), n_i the molar fraction of substance i in a material resource (dimensionless), w_i the molar weight of substance i (in g/mol), $ex^{0}_{ch,i}$ the standard molar chemical exergy of substance i (in kJ/mol), ΔG^{o}_{f} the standard Gibbs energy of formation of substance i (in kJ/mol), v_k the number of element k in substance i (in mol), and $ex^{o}_{ch,k}$ the standard molar chemical exergy of element k (in kJ/mol).

Data on $ex^{o}_{ch,k}$ are provided in Szargut (2005) and data on ΔG^{o}_{f} are available in thermodynamics handbooks, e.g., Atkins (2001) and Lide (2004).

1.2.3 Anthropogenic Exergy Demand

As shown in Fig. 1.1, solar radiation, moon gravity, and geothermal heat are three main primary exergy sources supporting all processes in the ecosphere. The exergy of solar radiation received by the Earth can be approximated once the flux density of solar radiation received by the Earth (i.e., the solar constant) is determined and associated with the β-value given by Petela (1964). Part of the exergy of solar radiation reaching the Earth is immediately reflected and backscattered by the atmosphere. A small percent of the incident exergy is also reflected by the Earth's surface. Moon gravity, together with solar gravity, interacts with the rotating Earth and causes tides as the motion of sea levels. Specific tidal exergy is equivalent to the gravitational potential energy due to the height difference between the tidal maxima and minima over the tidal record (Hermann 2006). Geothermal heat to the ecosphere comes from three sources, i.e., lithospheric heat, heat from the core, and heat from radioactive decay. Conversion of these heat flows into exergy flows depends on the Carnot efficiency that in turn is determined by the temperature of a geothermal heat flow and the temperature of the reference environment. The uncertainty of various geothermal heat flows makes the determination of global geothermal heat quite challenging. The evaluation of the exergy values of solar radiation and moon gravity is characterized by different uncertainties due to the lack of sufficient knowledge of the ecosphere dynamics. Various estimations of global exergy sources (to level A) that were reported in different studies were summarized by Liao (2012). It is indicated that by far the dominant primary exergy source to the ecosphere is the net solar exergy input of 3.60 E+18 MJ/year. The other two independent primary exergy sources, i.e., geothermal heat and moon gravity, with values of 1.198 E+15 MJ/year and 9.5 E+13 MJ/year, respectively, are several orders of magnitude less than net solar exergy input and thus their contribution is negligible.

Liao (2012) also summarized global energy flows to the anthroposphere in 2008 (from level A to level B). It is shown that the exergy demand of the anthroposphere is considerably smaller than that of the ecosphere. $CExD_{NRR}$ of the anthroposphere amounts to 4.15 E+14 MJ/year and accounts for 85.2 % of the exergy of global anthropogenic natural resource demand. This value includes 3.89 E+14 MJ/year from fossil fuels and 2.59 E+13 MJ/year from nuclear fuels. Assuming that the exergy extracted from non-renewable energy resources is completely consumed in various production and consumption processes, a corresponding heat of 4.15 E +14 MJ/year is added to the planetary processes.

1.3 Case Study

1.3.1 Liquid Biofuels

Biofuels are derived from biomass, in solid state, such as biochar, liquid, such as biodiesel and bioethanol, or gaseous, such as biogas and biohydrogen. The biggest difference between biofuels and petroleum feed-stocks is oxygen content (Demirbas 2009). Biofuels are widely regarded as a promising fuel alternative to petroleum-derived fuels to offset the decline of oil production and to mitigate the increase in greenhouse gas emissions. The use of liquid biofuels for transportation is already being promoted as a (supra-) national policy, for instance in the United States (Energy Independence and Security Act 2007) and in Europe (Directive 2009/28/EC 2009). Such liquid biofuels includes mainly biodiesel and bioethanol. Biodiesel is monoalkyl esters of long chain fatty acids derived from vegetable oil or animal fat. Bioethanol is ethanol derived exclusively from the fermentation of plant starches.

The global biofuel economy is an aggregation of a dozen of national markets. Each market provides various kinds of biofuels in terms of different feed-stocks of biomass, agricultural cultivation methods, industrial conversion technologies, and the process energy to power the industrial conversion. The global biofuel production is primarily based on the first generation technologies, i.e., using sugar, starch, and vegetable oil as feed-stocks. Production of advanced biofuels, i.e., biofuels derived from non-food crops and algae, has not taken place on a large scale yet. In 2008, the global production of liquid biofuels for transport was dominated by 19 producers.

According to a review of the production capacities of liquid biofuels of 19 key producers, i.e., the US, Brazil, China, Canada, Australia, Japan, and some EU member states, by Liao (2012), the global production of liquid biofuels totaled 7.85 E+07 m^3 in 2008, including 1.19 E+07 m^3 of biodiesel and 6.66 E+07 m^3 of bioethanol, which accounted for 1.8 % of total transport fuels in 2007, as shown in Table 1.1. Over 99 % of the capacity has been based on the first generation

Table 1.1 Summary of production capacities of key biofuel producers in 2008, in E+03 m^3 /year

	Biodiesel				Bioethanol					
Producer	Soybean	Rapeseed	U.S.[a]	Total	Corn	Sugar cane	Wheat	Sugar beet	U.S.[a]	Total
USA	2,650			2,650	36,300					36,300
Brazil	1,100			1,100		24,497				24,497
China	60			60	1,958		490			2,448
Germany		3,180		3,180				730		730
France	248	743		991			116	462		578
Spain		926		926			578			578
Netherlands		1,372		1,372						0
UK		347		347	153					153
Austria			252	252					13	13
Poland			91	91					151	151
Portugal			227	227						0
Ireland		63		63			85			85
Belgium			108	108						0
Denmark			103	103						0
Norway			39	39						0
Finland				0					3	3
Canada		60	40	100	670		200			870
Australia			260	260		64	100			164
Japan	10			10						0
Total	4,068	6,691	1,120	11,879	39,081	24,561	1,569	1,192	167	66,570

[a]U.S. = unspecific feed-stocks

technologies, using soybean and rapeseed as the main feed-stocks for biodiesel production, and corn, sugar cane, wheat, and sugar beet for bioethanol.

The foreground system (at level D in Fig. 1.1) of liquid biofuels consists mainly of two processes, the agricultural production and industrial conversion. Inflows for the agricultural production are seeds, lime, fertilizers, pesticides, fuels for the operation of agricultural machinery, and steel for the production of agricultural machinery. Inflows for the industrial conversion are fuels, chemicals, and various feed-stocks. Figure 1.2 shows an exemplified diagram of ethanol produced from corn stover as studied by Liao (2012).

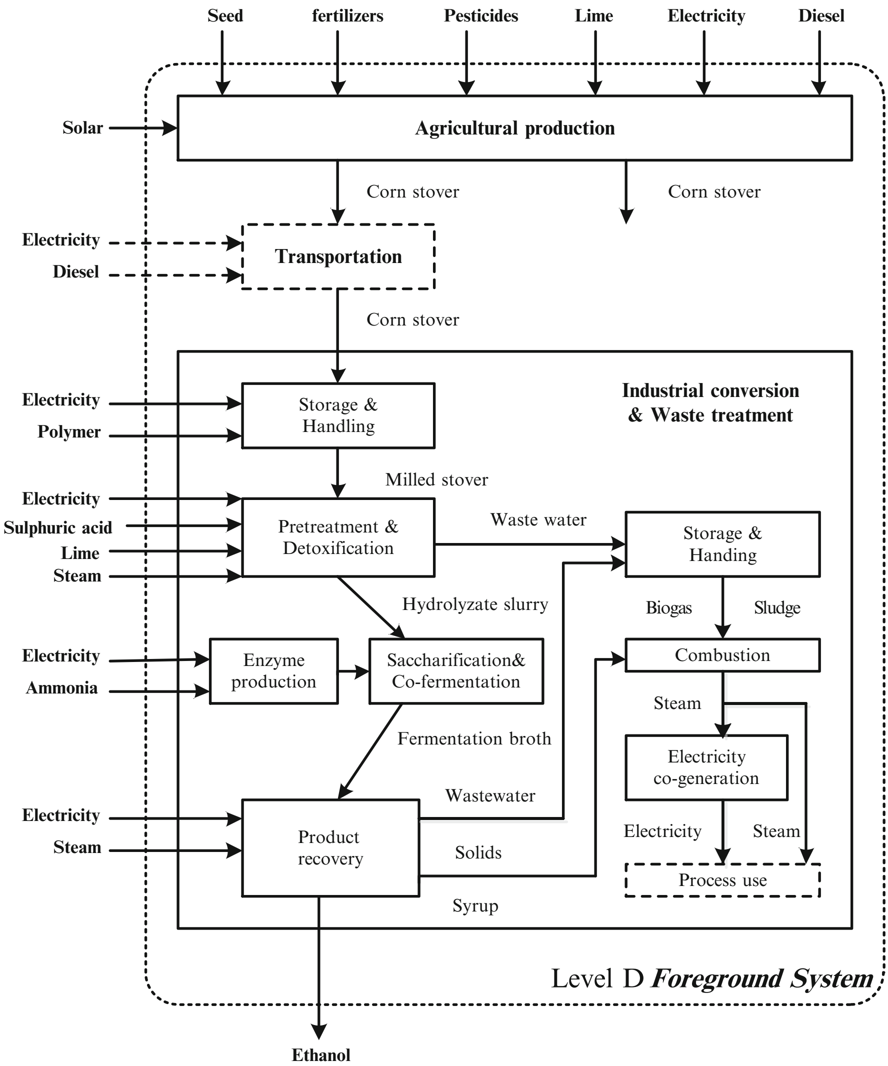

Fig. 1.2 Systems diagram showing the foreground system at level D for the product of corn stover-derived ethanol

1.3.2 *Results*[1]

1.3.2.1 Non-renewable Resource Demand

Table 1.2 summarizes the $CExD_{NRR}$ values of non-renewable resources that are required in the supply chain of various inflows to deliver a specific type of biofuel. It is indicated that the production of the first generation liquid biofuels, i.e., biodiesel and bioethanol, by key producer countries in 2008 consumed 9.32 E+11 MJ of exergy from non-renewable resources. Comparing the result of $CExD_{NRR}$ of global biofuel production with that of the anthroposphere (4.15 E+14 MJ/year), the normalization shows that global production of the first generation liquid biofuels in 2008 would account for 0.23 % of the total anthropogenic non-renewable resource demand.

1.3.2.2 Heat Emission

Anthropogenic heat generated by various human activities and emitted to the ecosphere (from level B to level A) is neglected in current global climate models, likely because it is considered as a much smaller contributor to global warming than greenhouse gases and aerosols. However, the heat that is introduced by deriving exergy from non-renewable resources would not otherwise have been added on relevant timescales, thus should constitute a climate forcing (Chaisson 2008; Flanner 2009). An outgoing ecospherical radiation flux of 238 W/m^2 at an equivalent blackbody temperature of 255 K is reported (Chen 2005; Peixoto et al. 1991). The global anthropogenic exergy demand and the $CExD_{NRR}$ of global biofuels correspond to a heat emission to the ecosphere of 4.87 E+14 MJ/year and 9.32 E+11 MJ/year, respectively. With an average Earth's surface temperature of 288 K and Earth's surface area of 5.1 E +14 m^2, they generate heat flux of 0.03 W/ m^2 and 5.79 E-05 W/m^2 and entropy at a rate of 5.36 E+10 W/K and 1.03 E+08 W/K, respectively, as shown in Table 1.3. Although the anthropogenic heat is small compared to the ecospherical radiation, its addition might lead to a new equilibrium with a higher temperature (global warming). Besides, as compared to greenhouse gases that have a climate forcing of 2.9 W/m^2 (Intergovernmental Panel on Climate Change 2007), the contribution to climate change of heat emission due to the exergy consumption of global biofuels is about 0.002 % of global greenhouse warming and could be negligible at level A.

Table 1.2 Summary of $CExD_{NRR}$ of different biofuels, in MJ/year (from level C to level D)

Biofuel	Soybean methyl ester	Rapeseed methyl ester	Corn-derived ethanol	Sugar cane-derived ethanol	Wheat-derived ethanol	Sugar beet-derived ethanol
$CExD_{NRR}$	6.13 E+10	1.00 E+11	6.62 E+11	7.36 E+10	2.82 E+10	7.97 E+09

[1] Based on the Chap. 4 of Liao (2012).

Table 1.3 Summary of heat emission of the ecosphere, the anthroposhere, and global biofuels (from level B to level A)

System	Heat flux W/m^2	Entropy generation rate W/K	Temperature K
Ecosphere	238	6.17 E+14	255
Anthroposphere	0.03	5.36 E+10	288
Biofuels	5.79 E−05	1.03 E+08	288

Conclusion
We presented how to use non-renewable resources as a basis to formulate an environmental indicator. A framework was defined to depict the conversion of natural resources by technologies at four levels: the foreground system, the supply chain, the anthroposphere, and the ecosphere. Cumulative exergy demand of non-renewable resources was introduced as an environmental indicator that measures the thermodynamic change of the environment caused by the extraction of natural resource and emission of heat. Its feasibility was tested in the case study on global liquid biofuel production, which showed that global production of first generation liquid biofuels accounted for 0.23 % of the total anthropogenic non-renewable resource demand and the induced heat flux would reach up to 0.002 % of global greenhouse warming, if anthropogenic heat flux is treated as a climate forcing. We anticipate that the usefulness of the environmental indicator based on non-renewable resources can be understood better if the indicator is applied to other technologies besides biofuels.

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Chapter 2
Photon Dissipation Rates as an Indicator of Ecosystem Health

Karo Michaelian

Abstract Ecosystems arise and evolve predominantly through the thermodynamic imperative of dissipating the solar photon flux into heat. Organic pigments coupled to water inside cyanobacteria, algae, and plants provide the dissipative structures for this entropy production. Viruses, bacteria, insects, and animals play the role of diversifiers and nutrient and seed dispersers in favor of the proliferation and dispersal of pigments over Earth's entire surface. The past few decades has seen an enormous negative human impact on the majority of Earth's ecosystems, antagonistic to human nominal supportive role in photon dissipation. Discerning whether or not efforts to reverse the damage are having the desired effect requires an accurate measure of ecosystem health. This chapter describes an indicator of global ecosystem health based on the entropy production of the ecosystem as a whole, which recognizes solar photon dissipation as its ultimate thermodynamic function. Thermodynamic justification for using the "red-edge" as an even simpler remotely sensed indicator of ecosystem health is also given.

Keywords Ecosystems • Ecosystem health • Albedo • Entropy production • Red edge

2.1 Introduction

We are only recently, and very reluctantly, coming to understand that, although we are, and have been since our existence, an integral part of natural ecosystems, our newly acquired ability to perturb them through technological innovation, and our ability to over exploit them through consumer economies, although providing for our own enormous proliferation and a naïve sense of "well-being", is the greatest threat to ecosystem health and stability and thus to our own very existence. Our recent assault on ecosystems has been relentless, from deforestation over the globe, the extinction or near extinction of many of Earth's large animals, ocean surface contamination with oil, plastics and other chemicals, coral reef destruction throughout the oceans, to the continually rising levels of contaminant aerosols and

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_2

CO_2 in the atmosphere, which has recently passed the psychologically important 400 ppm mark (Shukman 2013).

Destruction of Earth's ecosystems proceeds at an alarming rate while sterile debate rages over whether the perturbations are man-made or whether ecosystems can absorb the blows. The fiercest confrontations pit free market entrepreneurs and governments intent on short term profit and development against an enlightened and pro-active public with a genuine concern for the environment but without sufficient expertise to disentangle the complexities. Scientists, unfortunately, have been employed by both camps in order to simulate legitimacy in favor of corresponding interests. In reality, however, the situations are extremely complex and not easily understood, even by the specialists, leaving room for uncertainty and skepticism, and thus providing a cover for the continued assault on the environment by industry, governments, and individuals.

There are, however, reasons for optimism in this rather bleak scenario. Dire predictions for the fate of the human species made by renowned scientists such as James Lovelock (2007) have fomented a keen interest in the subject. We have seen the creation of a new field of multidisciplinary research coined "Ecohealth," along with many new multidisciplinary journals, such as EcoHealth (2004), Earth System Dynamics (2010), and Ecosystem Services (2012), among many others. These journals are devoted to understanding the complex dynamics of ecosystems, identifying specific dangers, and bringing together scientists and policy makers in order to achieve a long term healthy coexistence of humans with their environment.

We may finally have begun to recognize our fundamental role as protectors and proliferators of ecosystems. Scientists have embarked on international projects to characterize the destruction of ecosystems and are attempting to quantify the relation to global climate change (Hall et al. 2008). What is urgently needed at this time, as a precursor to embarking upon serious corrective intervention, be it preventative or restorative, is a simple indicator of ecosystem health. The indicator should be accurate and reproducible, easy to implement through remote sensing, and, of course, accepted as being scientifically sound by the majority of experts.

In this chapter, building on the work of Prigogine (1967) and Prigogine et al. (1972), Ulanowicz and Hannon (1987), Schneider and Kay (1994), and some of my own work (Michaelian 2005, 2011, 2012), I present a general thermodynamic framework for addressing ecosystem health. The generality of this framework derives from the fact that all irreversible processes in nature, from the water cycle, hurricanes, ocean and atmospheric currents, human societies, to ecosystems, arise, persist, and evolve to dissipate a general thermodynamic potential; to disperse the conserved thermodynamic quantities (energy, momentum, angular momentum, charge, etc.), over ever more microscopic degrees of freedom, or, in thermodynamic terms, to produce entropy. Although a rigorous theoretical derivation is still lacking, there is ample empirical evidence indicating that the evolutionary trend of nature is towards a structuring and coupling of material into irreversible processes that augment the global entropy production, as long as there exists a driving force over the system, the generalized thermodynamic potential (for example, the solar photon flux in the case of ecosystems). Therefore, "healthy" irreversible processes, those robust processes with small probability of collapsing, have sustained and copious entropy production, while those vulnerable, unstable, processes will generally have smaller and fluctuating, or even a decreasing, entropy production.

This thermodynamic framework to be presented for gauging ecosystem health, based on the entropy production of irreversible processes, has its foundations in the formalism of the *thermodynamics of irreversible processes*, which was developed during the first half of the last century by deDonder, Onsager, Prigogine, and Nicolis among others. Although non-equilibrium thermodynamics is still a specialty subject and normally not part of the curricula of most scientists, the thermodynamics of irreversible processes has been steadily advancing our understanding of the origin, persistence, proliferation, and evolution of complex dissipative processes and structures. Irreversible thermodynamics is an indispensable tool for understanding the complexities and addressing the uncertainties in earth system dynamics, and it is therefore incumbent on practitioners in the field to ensure that knowledge of this subject becomes widely disseminated. I have, therefore, included a brief introduction to the thermodynamics of irreversible processes in Sect. 2.4.

2.2 Traditional Indicators of Ecosystem Health and Their Limitations

Ecosystem health, although still lacking a concise and practical definition, has traditionally been associated with ideas such as, ecological integrity, capability of self-restoration, biodiversity, and resilience. Evaluations of poor ecosystem health have included one or more of the following indicators.

1. Extinction of a "keystone" species, such as, for example, a top predator, allowing smaller predators to proliferate, thereby stressing the herbivore species.
2. Dieback of particular plant species indigenous to an area.
3. General reduction in biodiversity of a region.
4. Migration of foreign species into a region, or of native species out of a region.
5. Greater vulnerability to disease and temporary stress, such as that produced by insects, drought, flooding, or fire.
6. Reduction in nutrient content of the soils or the accumulation of wastes or contaminants.

Such local indicators of ecosystem health require difficult and expensive monitoring at the ground level and can therefore provide only coarse grained measurements. Local surveillance is also prone to delayed assessment, individual subjectivity, and may miss important global changes. Furthermore, although the above indicators are certainly indicative of change, they do not necessarily register poor health. For example, in both the natural processes of species migration and ecosystem succession there are rather abrupt changes in the composition of species in a given region. Also, many species, particularly insects, have a natural many year cycle of accelerated proliferation and succumbing to disease or starvation, which, in turn, has an important impact on the local populations of specific plants and animals. An example demonstrating how traditional local indicators are of relatively little value in real ecosystem surveillance, due to coarse graininess and delayed assessment capability, is the recent surprising finding of "massive aspen dieback" in our northern boreal forests attributed to severe drought, which may be related to climate change (Michaelian et al. 2011). So sketchy are our present surveillance techniques, in fact, that there is still unresolved controversy over whether recent climate change has led to a "greening" or "browning" of North American boreal forests (Alcaraz-Segura et al. 2009).

More general and global indicators of ecosystem health have been proposed, such as gauging primary productivity using, for example, remote detection of chlorophyll density (Wong and He 2013) or the novel detection of large tree trunks using 70 cm radar reflection with the satellite "Biomass" to be launched by ESA in 2020 (Quegan et al. 2013). In remote detection of chlorophyll, one observes, from above the ocean surface or the tree canopy using planes or satellites, the amount of solar light reflected in the green at 550 nm or the fluorescent photochemical quenching signal of chlorophyll at 685 nm (Babin et al. 1996). An example of this is the now routine satellite technique to measure the extent and density of cyanobacteria and algal blooms on the ocean surface (Shen et al. 2012). Although locally high chlorophyll levels on the ocean surface are often thought to negatively affect the underlying ecosystem health, since these blooms remove oxygen and can add lethal toxins (Shen et al. 2012), seeding of the ocean surface with iron nutrients to stimulate growth of cyanobacterial blooms has been suggested as a means of sequestering excess carbon dioxide from the atmosphere and thereby stabilizing global ecosystems (Lovelock 2007). Remote sensing of chlorophyll density focuses on plants, phytoplankton, and cyanobacteria, and thus correctly recognizes the overwhelming importance of these organisms as primary components of the biosphere, at the base of the food chain of all organisms. These phototrophs also constitute, by far, the greatest biomass of the biosphere and are at the base of photon dissipation and thus should be duly considered in any reliable indicator of ecosystem health.

Although the remote sensing of chlorophyll density to ascertain ecosystem health is relevant and relatively easy to implement, from the more general thermodynamic perspective it is deficient since it fails to recognize that photosynthesis is only one very small portion of the total thermodynamic work that plants and cyanobacteria perform, perhaps only as little as 0.2 % (Gates 1980). Chlorophyll is only one of many organic pigments involved in photon dissipation. All phototrophic organisms contain a vast assortment of pigments (see Table 2.1, Sect. 2.7), which absorb and dissipate over the entire range of the solar spectrum, from the ultraviolet to the infrared (although generally limited to wavelengths shorter than the "red-edge" at approximately 700 nm; see Sect. 2.7). The thermodynamic importance of the dissipative function of these pigments has been universally ignored and their existence has instead been rather cursorily assigned to "antenna" molecules or to "protectors" of the photosynthetic system (Owens 1996). This, however, is inconsistent with a number of facts: (1) photosynthesis saturates in plants and surface cyanobacteria at about 100 Wm^{-2}, only approximately 10 % of midday solar photon intensities; (2) the carotenoids, the so-called "protective pigments," have, in reality, little effect on chlorophyll bleaching by UV light (Zvezdanovic and Markovic 2008); and (3) photosynthesis is not optimized in plants under variation of external conditions, but rather transpiration is optimized (Wang et al. 2007). The great assortment of pigments finds a much more plausible reason for being in the thermodynamic imperative of nature to form dissipative structures that augment the global entropy production of the Earth in its solar environment (Michaelian 2011, 2012); the greater the absorption and dissipation of photons of highest entropy-producing potential (the short wavelength region), the greater the entropy production of the ecosystem and thus the greater the thermodynamic imperative for its existence. Global entropy production, rather than chlorophyll density, is the variable that correctly characterizes ecosystem health.

2.3 Entropy Production and Ecosystem Health

Boltzmann (1886) first suggested that all life was surviving off entropy production. Schrödinger (1944) emphasized this succinctly in his motivating book "What is Life," and Prigogine (1967) and Prigogine et al. (1972) suggested how living processes could be treated within a precise mathematical formalism, which would become known as *classical irreversible thermodynamics*. However, it was not until the publication of a seminal paper by Ulanowicz and Hannon (1987) that it was realized that entropy production was an important ecosystem variable that could be used to study the dynamics of ecosystem succession and evolution. Ulanowicz proposed using remote sensing to determine the entropy production as the difference in the integrated entropy spectrum of the photons leaving and entering an ecosystem. The entropy flux was calculated by Ulanowicz at a given wavelength λ to be approximately the energy in the photon flux at that wavelength, $e(\lambda)$, divided by a temperature, $T(\lambda)$, i.e., $S(\lambda) = e(\lambda)/T(\lambda)$. The temperature was determined by assuming the photon flux to be a Bose-Einstein gas in thermal equilibrium giving $T(\lambda) = hc/k\lambda$, where h and k are the Planck and Boltzmann constants, respectively, and c is the speed of light. Ulanowicz suggested that "mature" ecosystems would have a more red-shifted emitted spectrum and thus greater entropy production. According to Ulanowicz and Hannon, not only would the emitted spectrum of ecosystems be red shifted with respect to that of areas barren of life, but the albedo (ratio of the reflected to incident light integrated over the visible region of the spectrum) measured over living areas would be lower than over areas barren of life.

Schneider and Kay (1994) took up the proposal of Ulanowicz and Hannon and applied the thermodynamic formalism to remotely sensed temperature data obtained by Luvall and Holbo (1991). Given a constant incident photon spectrum and assuming a black-body spectrum for the emitted radiation, ecosystems measured at a lower temperature would have a more red-shifted emitted black-body spectrum and hence greater entropy production. In this way, Schneider and Kay demonstrated that old growth forest ecosystems had a greater entropy production than new growth forests and, in turn, the latter had a greater entropy production than clear cut areas. A reverse trend was found, as Ulanowicz had predicted, for the albedo, for example, the albedo over old growth forest was measured to be as low as 5 % while that over clear cut areas increased to 25 % (see also Betts and Ball 1997). This work showed that it was indeed possible to distinguish between stages of ecosystem succession using thermodynamic principles and employing simple remote sensing temperature measurements. In summary, for a given incident photon flux, older, more established, ecosystems have greater entropy production and thus a lower black-body temperature, and this relation between entropy production and the maturity of the ecosystem is now well corroborated.

Wang et al. (2007) have shown that under variation of external conditions, and even under stressful situations, plants optimize transpiration rather than photosynthesis. Transpiration removes the heat of the dissipated photons at the leaf surface by converting it into latent heat of the evaporation of water and thus is directly associated with photon dissipation. Together, photon dissipation and transpiration account, by far, for the greatest free energy dissipation performed by plants (Hernández Candia 2009; Michaelian 2012). If, by extension, it is also true that ecosystems optimize the rate of solar photon dissipation under variation of external conditions, as Ulanowicz proposed and the empirical analysis of Schneider and Kay suggests, and therefore that healthy ecosystems have greater entropy production than unhealthy or stressed ecosystems, then a measure of ecosystem entropy production should be a reliable indicator of its health.

The author is not aware of any published data with regard to remote temperature sensing comparing healthy with unhealthy ecosystems. Although using recorded temperature values as a measure of ecosystem health should not be discounted *a priori*, there are, however, a number of complications and problems related to such an approach: (1) ecosystem temperatures are a function of the intensity of the incoming solar radiation; (2) comparisons of the temperature must be made over extended periods and therefore are prone to atmospheric and seasonal variations; and (3) ecosystems do not emit light in a black-body spectrum (Gates 1980) and therefore an equilibrium temperature is not even a well-defined concept for ecosystems. Here, instead, I consider a more accurate determination of the true entropy production of an ecosystem and define this number as the best possible indicator of its present state of health.

The true entropy production due to photon dissipation can be directly obtained from the differences between the incident and emitted entropy flux of the light spectra as Ulanowicz suggested. However, it is not necessary to assume that ecosystems are black-bodies, an approximation in error of between 30 and 40 % (Michaelian 2012), and which, in fact, can be questioned on the grounds that ecosystems are out of equilibrium structures. After providing a brief introduction to non-equilibrium thermodynamics in Sect. 2.4, in Sect. 2.5 of this chapter I determine an accurate value for the entropy production of an ecosystem using equations for the entropy of a photon flux derived by Planck (1913), including a contribution for photon scattering without absorption. The analysis takes as input the incident and emitted photon spectra and produces a single number, our "indicator" of ecosystem health, for the entropy production of the global area under observation.

In Sect. 2.7, I describe an alternative indicator of ecosystem health, still based on total entropy production, but now obtained through a more simple remotely sensed determination of the *red-edge*; the wavelength at which the absorption of light by plants, algae, and cyanobacteria decreases rapidly from very high values (which occurs at wavelengths of around 700 nm). The proposed thermodynamic justification for the association of the red-edge with ecosystem health is that, under nutrient or other physical stresses, photosynthetic organisms would prioritize the production and maintenance of primarily those organic pigments that dissipate the highest energy photons available, since this maximizes entropy production under the given restrictive conditions. The entropy production of an ecosystem may thus be directly related to the remotely sensed position of its absorption red-edge (Michaelian 2013, 2014). The red-edge is therefore a simple and reliable indicator of ecosystem health, not requiring full spectrum integration over wavelength and independent of atmospheric conditions, although, as with a full calculation of entropy production by integrating over wavelength, it has a detectable seasonal variation (Gates 1980) related to nutrient flow variations.

2.4 Thermodynamics of Dissipative Systems

Before discussing the photon dissipation process in plants, algae, and cyanobacteria, it is first relevant to describe the formalism of irreversible thermodynamics that is needed to treat out of equilibrium dissipative processes in general.

There are two types of structures in nature: equilibrium structures and dissipative structures. Equilibrium structures arise as the result of nature minimizing a potential (such as, for example, the Gibb's free energy) for an isolated, or near-isolated, system. Examples are, crystalline structures, protein folded structures, and the spherical shape of the Earth. Dissipative structures, on the other hand, arise as the result of the application of a generalized thermodynamic potential over a system, such as a gradient of heat, material concentration, or an electric or photonic potential. Under such a potential, material tends to organize into dissipative structures, or as more correctly stated, into dissipative *processes*, which foment the dissipation of these potentials. Examples of dissipative processes are hurricanes, ocean and atmospheric currents, convection cells, the water cycle, ecosystems, and human societies. One such dissipative process, only recently considered in detail (Michaelian 2011, 2012) and of fundamental importance to us here, is the formation, proliferation, and propagation over Earth's surface of organic pigments and water, which together dissipate the solar photon flux.

Equilibrium thermodynamic formalism is strictly applicable only to isolated, or near isolated, systems, and deals with the relations between the macroscopic variables of a system, for example, temperature, pressure, volume, and energy, which become uniquely specified, homogeneous and constant in the time relaxed state of the system known as the "equilibrium state." For systems that are isolated, but not initially in equilibrium, another variable of interest is the entropy, which measures the progress of evolution towards the equilibrium state of the system. Entropy is a measure of how well the conserved quantities of an isolated system, e.g., energy, momentum, angular momentum, charge, etc., are distributed over the microscopic internal degrees of freedom of the system. The width of this distribution tends to increase through time-dependent processes in nature. The second law of thermodynamics states that an isolated system will evolve towards a state in which the dispersion of the conserved quantities over the microscopic degrees of freedom is maximal. For example, for the case of the conserved variable "energy" in material systems, these microscopic internal degrees of freedom are the translational, vibrational, rotational, and electronic degrees of freedom of the atoms or molecules composing the system. In the equilibrium state, the entropy of any macroscopic system is at a global maximum.

The relations between the microscopic degrees of freedom and the macroscopic variables measured in the laboratory that uniquely define the macro-state of the system in equilibrium (e.g., temperature, pressure, volume, energy, entropy) were obtained by Boltzmann, under some particular, but surprisingly universal, assumptions, through a probabilistic analysis, which is now known as *statistical mechanics*.

For discussing non-isolated open systems, such as ecosystems, which can exchange matter, energy, momentum, angular momentum, charge, etc. with their environment, the formalism at our disposal is somewhat more limited, having been founded since only the middle of the last century. For most practical situations, under the physical conditions prevalent on Earth's surface, we can use an extension of equilibrium thermodynamics known as *classical irreversible thermodynamics*, which was formulated by Lars Onsager, Ilya Prigogine, and others. Basically, this approach is applicable to systems in which *local* equilibrium can be assumed, i.e., although the system as a whole is out of equilibrium, very small, but still macroscopic regions (on the order of 10^{23} particles) within the system can be considered, to a good approximation, to be in equilibrium. Thus, the normal thermodynamic variables of equilibrium thermodynamics, and the equations relating these variables (e.g., the Gibb's equation), retain their validity on a local space and time scale, and thus become functions of position and time. The utility of this approach has been adequately demonstrated in more than half a century of successful application to a great variety of dissipative systems (Lebon et al. 2008).

Specifically, application of classical irreversible thermodynamic formalism is valid if the system meets the following conditions.

1. That the external constraints, the generalized thermodynamic potentials, over the system are relatively constant in time, with respect to natural decay times of the induced dissipative processes.
2. That even though the system as a whole is out of equilibrium, every small, but still macroscopic part of the system, is at a "local equilibrium." This ensures, as mentioned above, that all the normal equilibrium thermodynamic variables

retain their usual significance, but now are functions of position and time within the system. It also implies the validity of the Gibbs equation relating these local variables, $ds = \frac{de}{T} - \frac{P}{T}dv + \sum_i \mu_i dn_i$, where all variables have their usual thermodynamic meaning, but are now functions of position and time. For this condition of local equilibrium to be satisfied for chemical reactions, it is required that the reactions are sufficiently slow that the reactants retain a Maxwell-Boltzmann distribution of their velocities. For diffusion and transport processes, it is required that the material is sufficiently dense that there are enough collisions to ensure local equilibrium, which can be shown to be valid for all but the most rarefied gases.

The change in entropy in time of open systems can be written as a sum of two parts, that of the internal production of entropy within the system due to irreversible process occurring therein, and a part describing the exchange of entropy of the system with its external environment,

$$\frac{ds}{dt} = \frac{d_i s}{dt} + \frac{d_e s}{dt}. \tag{2.1}$$

The second law of thermodynamics extended to open systems states that the entropy production due to irreversible processes occurring inside the system must be positive definite, $\frac{d_i s}{dt} \geq 0$, while the flow, into or out of the system, $\frac{d_e s}{dt}$, has no definite sign.

The entropy production of any system can be written as a sum over the generalized forces X_k times their corresponding flows J_k,

$$\frac{d_i s}{dt} = \sum_k X_k J_k, \tag{2.2}$$

where the sum is over all irreversible processes occurring within the system. For example, for the irreversible process of heat flow in a discrete two component system with temperatures T_1 and T_2, the generalized flow is that of heat, $\frac{dQ}{dt}$, and the generalized force is $\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$, so that the entropy production is

$$\frac{d_i s}{dt} = \frac{dQ}{dt}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \tag{2.3}$$

For a continuous (non discrete) system, this equation for the entropy production σ due to heat flow becomes (Prigogine 1967)

$$\sigma = -\sum_i \frac{Q_i}{T^2}\frac{\partial T}{\partial x^i}, \tag{2.4}$$

where Q_i is the heat flow in coordinate direction x^i.

For systems in which the external constraints are constant (fixed forces over the system), it can be shown that the system will eventually come to a *stationary state* in which all the local thermodynamic variables (e, s, T, p, etc.) remain constant in time, although they may be functions of position. In the case that the flows are linearly related to the forces, it was shown by Prigogine (1967) that there is a unique stable stationary state and that this state occurs at a minimum of entropy production with respect to variation of the free forces (those non-fixed forces that arise in a system due to the applied external force, for example, a concentration gradient arising due to an imposed heat flow). However, if there are non-linear relations between the flows and forces, then there may be many locally stable stationary states with different entropy production that are available to the system. The tendency of such systems is to evolve from one stationary state to another through bifurcations, generally in the direction of increasing entropy production (Prigogine 1967). This evolution through bifurcations implies that the system or process acquires a history. For example, in ecosystems this evolution is observable and is known as *succession*. This thermodynamic evolution is also, most probably, an accurate explanation of general biotic, and coupled biotic-abiotic, evolution. There is an empirical trend over time observed in many Earth systems, both biotic and abiotic, towards greater entropy production (Kleidon and Lorenz 2005).

In Sect. 2.5 of this chapter, it will be shown that, since by far the most important external generalized thermodynamic potential over ecosystems is the photon potential, the entropy production due to all processes occurring in an ecosystem, $\frac{d_i s}{dt}$, can be determined from an analysis of the spectrum of solar light incident on the ecosystem and the spectrum of light emitted back into the atmosphere by the ecosystem. The conversion of UV and visible light into infrared light is the dissipation that ecosystems perform, and the rate of dissipation, or the entropy production, is related to the magnitude of the shift integrated over wavelength of the emitted spectrum towards the infrared with respect to the incident solar spectrum. The technique proposed here for determining ecosystem health is therefore simply integrating over the difference between the incident and emitted spectra and carrying out a straight forward analysis, taking into account specific details, such as the albedo and emissivity of the organic material in ecosystems and the coupling of ecosystems to other dissipative processes, such as the water cycle (Michaelian 2012).

2.5 Entropy Production as an Indicator of Ecosystem Health

Photon dissipation by ecosystems is a coupled process involving various stages. In the first stage, a high energy photon from the sun is absorbed on an organic pigment molecule of plants, algae, or cyanobacteria. The electronic excitation energy is dissipated through various de-excitation processes, the principal of which is known as internal conversion, to the translational and vibrational modes of the surrounding water molecules, thereby increasing the local temperature of the water. A certain amount of liquid water is thus converted into gas, removing the latent heat of vaporization from the organism. The H_2O gas rises in the atmosphere to a height at which the temperature is low enough for condensation around microscopic particles, leaving part of its heat of condensation to escape into space in the form of many infrared photons. A single high energy photon (visible or ultraviolet) is thus converted into many (20 or more) infrared photons, conserving the total energy but producing entropy in the process, since the initial photon energy has been distributed over the many more degrees of freedom of the numerous infrared photons. Most of the entropy production, about 63 % (Kleidon and Lorenz 2005), occurs at the surface of Earth during the first stage of the process where the incident photon is absorbed and dissipated by organic pigments. A further approximately 2.6 % can be attributed to the latent heat flux of the ensuing water cycle (Kleidon and Lorenz 2005). Details of how biology catalyses the hydrological cycle can be found in Michaelian (2012) and will not be discussed further here except to say that this coupling is important to keep in mind when determining our indicator of ecosystem health based on remote sensing satellite data that detects light emission from both the ecosystem and the atmosphere.

The entropy production of a specific area of the Earth's surface can be determined by considering the change in the frequency ν or wavelength λ distributions of the radiation incident from the Sun, $I_{in}(\nu)$ [Jm^{-2}] or $I_{in}(\lambda)$ [Jm^{-3} s^{-1}], and that radiated by the area, $I_{rad}(\nu)$ or $I_{rad}(\lambda)$, including the change in the directional isotropy of the radiation. Planck (1913) determined that the entropy flux $L(\nu)$ [Jm^{-2} K^{-1}] due to a given photon energy flux $I(\nu)$ takes the following form (Wu and Liu 2010)

$$L(\nu) = \frac{n_0 k \nu^2}{c^2}\left[\left(1+\frac{c^2 I(\nu)}{n_0 h \nu^3}\right)\ln\left(1+\frac{c^2 I(\nu)}{n_0 h \nu^3}\right) - \left(\frac{c^2 I(\nu)}{n_0 h \nu^3}\right)\ln\left(\frac{c^2 I(\nu)}{n_0 h \nu^3}\right)\right] \tag{2.5}$$

where n_0 denotes the polarization state, $n_0 = 1$ or 2 for polarized or unpolarized photons, respectively, k is the Boltzmann constant, c is the speed of light, and h is Planck's constant. In terms of wavelength ($\lambda = c/\nu$), the corresponding expression is (Wu et al. 2011)

$$L(\lambda) = \frac{n_0 k c}{\lambda^4}\left[\left(1+\frac{\lambda^5 I(\lambda)}{n_0 h c^2}\right)\ln\left(1+\frac{\lambda^5 I(\lambda)}{n_0 h c^2}\right) - \left(\frac{\lambda^5 I(\lambda)}{n_0 h c^2}\right)\ln\left(\frac{\lambda^5 I(\lambda)}{n_0 h c^2}\right)\right] \tag{2.6}$$

which has the units [Jm^{-3} K^{-1} s^{-1}]. The entropy flux (per unit area) passing through a given surface is thus

$$J = \int_0^\infty d\lambda \int_\Omega L(\lambda)\cos(\theta) d\Omega \tag{2.7}$$

where θ is the angle of the normal of the surface to the incident photon beam, and Ω is the solid angle subtended by the source at the surface. The total entropy flux crossing the surface is then just Eq. (2.7) integrated over the entire surface area.

The total entropy production per unit area of the ecosystem is then

$$J = J_{rad} - J_{in}. \tag{2.8}$$

The radiated part J_{rad} is composed of two parts, that due to emission after absorption J^e_{rad} and that due to reflection without absorption J^r_{rad}. For the ecosystem, we may assume isotropic emission into a 2π solid angle and predominantly Lambertian reflection also into a 2π solid angle, since scattering from leaves is predominantly diffuse (Gates 1980) and multiple scattering from many leaf surfaces occurs in ecosystems. Therefore, with Eq. (2.7), Eq. (2.8) becomes

$$J = \int_0^\infty d\lambda \left[2\pi L_{rad}(\lambda) - \int_\Omega L_{in}(\lambda) \cos(\theta_{in}) d\Omega_{in} \right] \tag{2.9}$$

where θ_{in} is the angle of the incident solar radiation with respect to the normal of the detection surface and Ω_{in} is the solid angle subtended by the sun as seen from the surface of Earth. For example, if we take the sun directly overhead ($\theta_{in} = 0$) and the detection surface perpendicular to the zenith, then Eq. (2.9) can be simplified to give

$$Health = J = \int_0^\infty 2\pi L_{rad}(\lambda) - 0.04 L_{in}(\lambda) d\lambda \tag{2.10}$$

where $L_{rad}(\lambda)$ is obtained from Eq. (2.6) with $\mathrm{I_{rad}}(\lambda)$ measured by the detecting spectrometer and $L_{in}(\lambda)$ obtained from Eq. (2.6) with $\mathrm{I_{in}}(\lambda)$ the solar spectrum at Earth's surface with the sun directly overhead. The factor of 0.04 accounts for the solid angle subtended by the Sun at the Earth's surface. The [SI] units of this indicator of ecosystem health (entropy production) are [J $\mathrm{K^{-1}}$ $\mathrm{m^{-2}}$ $\mathrm{s^{-1}}$].

The distance above the ecosystem at which the spectrometer is flying, and the solid angle of the detector, will determine the extent of the ecosystem considered. Satellite measurements are most global, but will include other coupled abiotic dissipative processes as mentioned above, such as the water cycle and ocean and wind currents, which are spawned by the heat generated through photon dissipation in the ecosystem. One would also have to consider photon dispersion by clouds and the atmosphere.

A few remarks are in order with respect to this measure of ecosystem health based on Eq. (2.10), or more generally (2.9). First, it is an instantaneous measure, which will vary throughout the day and is not completely accurate since part of the energy absorbed by the ecosystem during the day is released at night, and this radiation is not included in the instantaneous measure. A more accurate measure would integrate Eq. (19) over the 24 h diurnal cycle, but would be significantly more complex to perform. The same applies to the annual cycle. Second, Eq. (2.9) is more accurate than simple temperature measurements, since there is no assumption of thermodynamic equilibrium (a black-body spectrum) and the entropy production is not based on heat flow equations, which can result in up to 40 % error in the calculated entropy production (Michaelian 2012). Third, by considering the full spectrum of the radiated entropy flow as the emitted plus reflected, $L_{rad}(\lambda) = L^e_{rad}(\lambda) + L^r_{rad}(\lambda)$, the above calculation also takes into account the entropy production due to the Lambertian scattering of the component that is reflected and referred to as the albedo, which accounts for roughly 8.3 % (assuming a wavelength independent albedo) of the total entropy production integrated over the whole of Earth's surface (Michaelian 2012).

2.6 Albedo as an Indicator of Ecosystem Health

Bond albedo, α, is a measure of the ratio of the reflected solar radiation to the incoming solar radiation. It is specified once the limits on the wavelengths, λ_1 and λ_2, for the integration are specified:

$$\alpha = \frac{\int_{\lambda_1}^{\lambda_2} I_r(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} I_i(\lambda) d\lambda},$$

where $I_i(\lambda)$ and $I_r(\lambda)$ are the incident (solar) and reflected (over the same wavelength region) energy fluxes, respectively. The limits of integration, λ_1 and λ_2, are usually confined to the visible region of the Sun's spectrum and must be specified in quantitative statements.

Earth's albedo has been determined mainly by satellite observations but also by measuring the lunar Earth shine (Goode et al. 2001). Its accepted value integrated over Earth's surface in the visible range 400–700 nm is 0.296 ± 0.002, implying that 29.6 % of incident light in the visible range is reflected back to space. Although there is no dissipation to longer wavelengths (more photons), there is still entropy produced due to the isotropic expansion of the directed solar photon beam into a 2π solid angle. As an example, in the case of Venus, more than one half of its total entropy production is due to simple Lambertian reflection off the clouds (Michaelian 2012).

As originally proposed by Ulanowicz and Hannon (1987), albedo itself may be an approximate indicator of ecosystem health. This is related to the fact that absorption with dissipation (to longer wavelengths) into a 2π solid angle always produces more entropy than simple dispersion into a 2π solid angle. Thus, the higher the albedo, the lower the potential entropy production of an area. This fact can be used to gauge ecosystem health. For example, Ollinger et al. (2008) have found an interesting anti-correlation between nitrogen in the forest canopy and forest albedo, which deserves to be studied in more detail.

2.7 The Red-Edge as an Indicator of Ecosystem Health

It is a curious fact that the great majority of phototropic organisms have strong absorption throughout the UV and visible regions of the sun's spectrum but a sudden pronounced drop in absorption at approximately 700 nm. This sudden drop in absorption is known as the "red-edge." Beyond the red-edge, almost all light is either reflected or transmitted by the organism until around 1,400 nm, where the strong absorption bands of water in the organisms become important. See Fig. 2.1.

The red-edge has been attributed to a gap in the molecular energy levels between the lowest energy vibrational state of the 1st electronic excited state and the highest energy vibrational state of the electronic ground state (Gates 1980). A second explanation, which is also given by Gates (1980), is that it may be an evolved characteristic since plant leaves would heat up to beyond optimal temperatures for photosynthesis if the leaves also absorbed the solar energy beyond the red-edge. However, these explanations do not appear convincing, particularly given the fact that photosynthesis is most efficient at wavelengths around the red-edge. The first explanation can now be rejected, since there have now been found many deep ocean living bacteria that have strong electronic absorption within the gap beyond the red-edge and that, in fact, use the faint very red light from deep sea hydrothermal

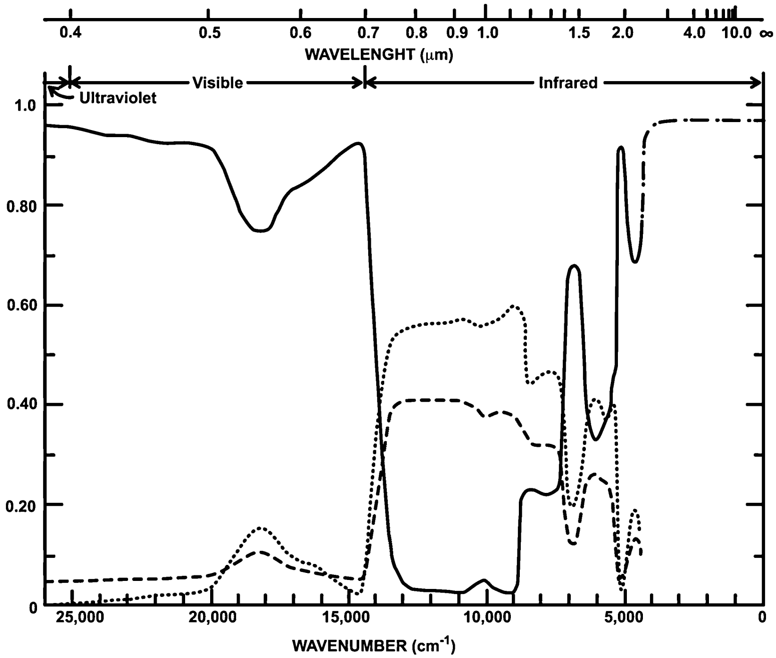

Fig. 2.1 Absorption spectrum (*solid line*) of a cottonwood leaf showing the red-edge, the pronounced drop in absorption at approximately 700 nm. The reflection of the upper surface (*dashed line*) and transmission through the leaf (*dotted line*) are also given (From Gates 1980)

vents for efficient photosynthesis (Kiang et al. 2007; Beatty et al. 2005). Anoxygenic photosynthesis has been discovered using wavelengths as long as 1,015–1,020 nm (Trissl 1993; Scheer 2003). The second explanation of Gates appears also to be lacking, since plants could have equally well evolved to reflect the UV and blue light with only a strong absorption peak centered around 700 nm where, in fact, photosynthesis is most efficient (Kiang et al. 2007).

Here I present a simple and approximate calculation to show instead that the red-edge can be explained given the finite size and dead-time (excited state decay time) of present day organic pigments under the premise of the optimization of entropy production in organisms dissipating the solar photon flux. The solar photon flux integrated over the whole spectrum at the Earth's surface at the equator and at midday is of the order of 2×10^{26} photons per square meter per second. This copious flux saturates present day organic pigments given their finite size and dead-time. It would thus be most profitable, from the viewpoint of entropy production, to dedicate resources to absorption and dissipation only at those shorter wavelengths where dissipation has the greatest potential for entropy production. Below, I show how the position of the red-edge in wavelength can indeed be determined accurately from the incident photon flux, the finite size of the common pigments, and their measured dead-times.

If plants, cyanobacteria, and algae have evolved for producing entropy through the dissipation of the solar photon flux, then if these organisms were in some way stressed, through nutrient limitation, climate, or disease, the first pigments to be foregone would be those dissipating towards the red since these have relatively less entropy production potential per unit photon. It therefore follows that healthy organisms or ecosystems will have a red-edge more towards the red, while unhealthy organisms or ecosystems would have their red-edge shifted from nominal values towards the blue.

Plants, cyanobacteria and algae absorb strongly from the far ultraviolet (240 nm) to the red-edge (700 nm). Some of the major pigment groups involved in the absorption are listed in Table 2.1 along with their respective absorption maxima wavelength, size, and approximate non-fluorescent de-excitation time. (Note that there are usually many

Table 2.1 Average size and excited state decay times for the major pigment groups

Pigment	Abs. Max. λ [nm]	Size [nm^2]	De-excitation time [ns]	Organisms
Nucleotides	260	1.5	0.005	All
Aromatic amino acids	280	1.0	0.5	All
Mycosporines	300–450	1.5	0.4	Algae, cyanobacteria
Carotenoids	450	2.5	<0.1	Plants, algae
Porphyrinas	400–430, 600–700	5.25	1.0	Plants, algae, cyanobacteria
Flavanoides	265, 530	1.5	<10	Plants
Ficobilines	550–600	3.5	–	Algae, cyanobacteria

different pigments within a group and different decay channels, which are strongly environment dependent for these molecules. Table 2.1 lists average values of the group and non-radiative decay times, where these are available.)

Table 2.1 indicates that pigments that dissipate in the region of the solar spectrum reaching Earth's surface today (300–2,000 nm) have an average size of less than about 5 nm^2 and an average lifetime in the excited state of about 0.5 ns, during which they have an almost zero probability for absorbing another photon. Pigments, however, need a support structure, for example, chlorophyll is bound to proteins and lipids of thylakoide membranes (Hoshina et al. 1984). They also need a water environment to attain rapid de-excitation through internal conversion (the times listed in Table 2.1) and to provide a solvent for delivering nutrients and removing damaged pigments. For example, for the pigment chlorophyll, each molecule occupies an area of 5.25 nm^2 and they make up only 5 % of the chloroplasts by weight. This means that each chlorophyll pigment needs a minimum effective surface area of approximately $5.25\ nm^2/(0.05)^{2/3} = 38.7\ nm^2$, which implies a maximal effective areal density of chlorophyll pigments of $2.6 \times 10^{16}\ m^{-2}$.

If we now consider the fact that the average finite dead-time of organic pigments that absorb in the visible range is approximately 0.5 ns (Table 2.1), then the maximum photon flux that present day organisms could handle (absorb and dissipate) is $2.6 \times 10^{16}\ m^{-2}/0.5 \times 10^{-9}\ s = 5.2 \times 10^{25}\ m^{-2}\ s^{-1}$, which is only about 26 % of the actual photon flux at Earth's surface at midday at the equator.

Given this thermodynamic explanation for evolutive change, it may be reasonable to presume that plants, algae, and cyanobacteria would dedicate this dissipation potential to the higher energy region of the surface solar spectrum where the resulting entropy production per photon from dissipation would be greatest. By considering the intensity distribution (number of photons per unit wavelength interval) of the surface spectrum, it is, therefore, possible to determine what should be the approximate location of the red-edge in wavelength given the maximum photon flux manageable of $5.2 \times 10^{25}\ m^{-2}\ s^{-1}$. To calculate this position, we use the approximation of a black-body incident solar spectrum at the top of the atmosphere with a temperature of the sun's surface (5,800 K) and include the effect of absorption and scattering due to the gasses in Earth's atmosphere (see Fig. 2.2).

The red-edge in the absorption spectrum, as determined using the simulated solar spectrum at Earth's surface obtained from a black-body solar spectrum and including absorption mainly due to water in Earth's atmosphere (Fig. 2.3b), is very close to the actual measured red-edge in the absorption spectrum measured for a real leaf (Fig. 2.3a). This provides a plausible thermodynamic explanation of the red-edge, which should be corroborated in further, more detailed, studies. It also suggests that the red-edge could be used as an indicator to measure ecosystem health under the premise that ecosystems have evolved to optimize entropy production through photon dissipation and that the first pigments to be forgone when an ecosystem is perturbed or under stress are those that absorb and dissipate towards the red, since these have the smallest entropy production potential.

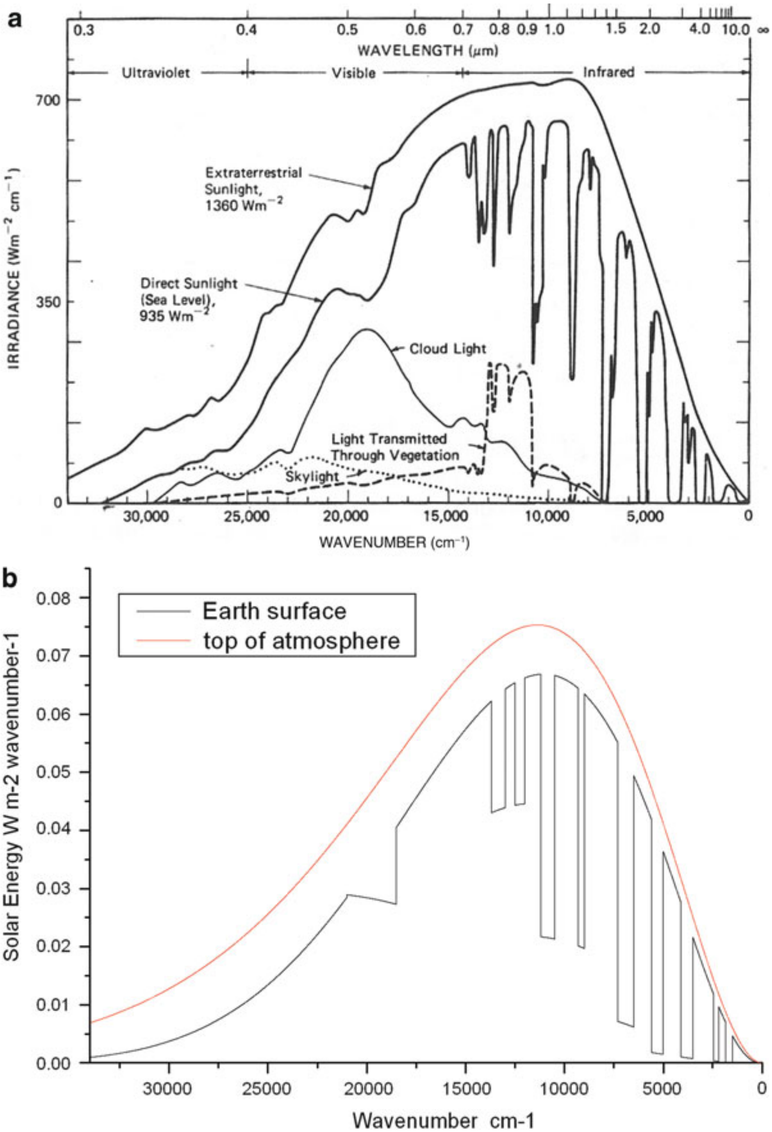

Fig. 2.2 (**a**) Measured solar photon spectrum at the top of Earth's atmosphere and at Earth's surface. Taken from Gates (1980). (**b**) Corresponding simulated solar spectrums making a black body assumption and including absorption by water in Earth's atmosphere. The integrated energy flow for the simulation is calculated to be 1,353 Wm^{-2} at the top of the atmosphere and 891 Wm^{-2} at Earth's surface

Even without the hindsight of this thermodynamic explanation, the red-edge had already been recognized as a useful indicator of plant and ecosystem health (Carter and Miller 1994; Carter et al. 1996; Eitel et al. 2011). Carter et al. (1996) showed that for loblolly pine and slash pine, the narrow band 694/760 nm reflectance ratio

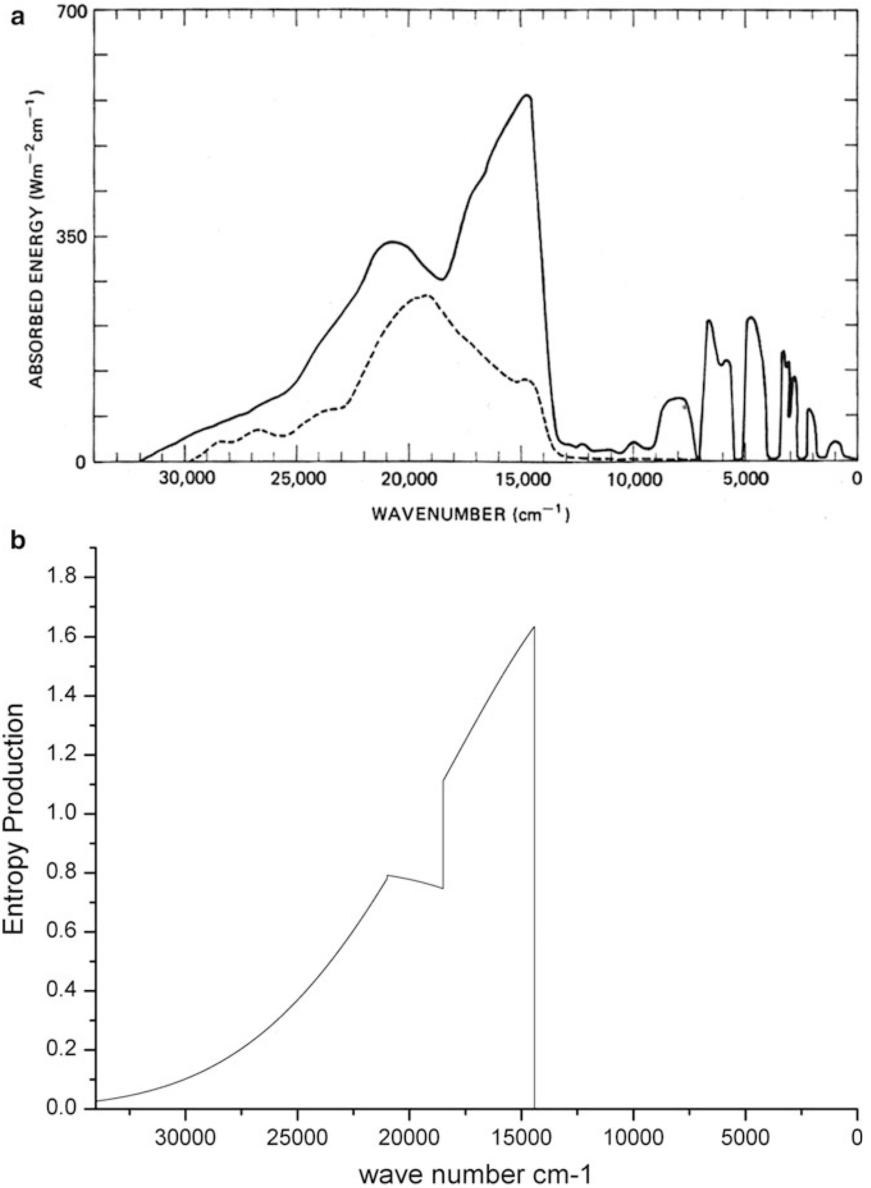

Fig. 2.3 (**a**) The measured absorption of a leaf convoluted with the incident solar spectrum showing the pronounced red-edge. Taken from Gates (1980). (**b**) The calculated position of the red-edge assuming that pigments can handle 5.2×10^{25} photons m^{-2} s^{-1} (26 % of the total, see text)

(red-edge/near infrared) allowed plant stress to be detected 16 days prior to signs of stress becoming visually apparent. By measuring the difference in the remotely (satellite) sensed wavelength intervals (690–730 nm), known as band 4, and (760–850 nm), known as band 5, Eitel et al. (2011) were able to detect stress in a

New Mexico conifer woodland 16 days earlier than by using any other remotely sensed measurements based on measuring reflection. They conclude "broadband satellite data containing the red-edge band is useful and important as a sensitive indicator for monitoring forest health at the landscape scale" (Eitel et al. 2011). It is hoped that the above thermodynamic explanation of the red-edge will help to refine these remotely sensed measurements into an even more sensitive indicator of ecosystem health.

2.8 Discussion

In a previous article (Michaelian 2012), we applied Eqs. (2.6, 2.7, and 2.8) above to determine the global entropy production on Earth and its nearest neighbors, Venus and Mars. Our results showed that Earth's entropy production per unit surface area is approximately twice that of either Venus or Mars, and thus, using our entropy production indicator of ecosystem health, we could humorously claim that the ecosystems on Earth are healthier than those on either Venus or Mars. However, ecosystems are just one form of dissipative system and since the measures of the incident and emitted spectrum were global in the above article, we can really only claim that global dissipative processes on Earth are stronger than the dissipative processes on either Venus or Mars.

This also leads us to the important point that if the conditions are not identical or very similar, e.g., constituent nutrients and water, incident photon intensity, etc., then a comparison of absolute entropy production does not say much about the respective health. For example, it is well known that tropical forests dissipate more photons per unit area than boreal forests, but it would be meaningless to claim that tropical forests are therefore "healthier" than boreal forests. However, it is well known that tropical forests are much more resistant to insect and disease (generally more stable) than boreal forests, and this type of resilience or stability must certainly be related to greater entropy production if the tendency of nature is towards greater global entropy production. For example, the coupling of the water cycle to ecosystems is much more pronounced in tropical regions. Entropy production is simply the product of a generalized thermodynamic flow times a generalized thermodynamic force (Prigogine 1967). It is much harder to perturb strong flows and cause a system to collapse than it is to perturb weak flows and cause a collapse (or, more precisely, to cause a change into a new non-equilibrium thermodynamic stationary state).

Finally, since the red-edge is a very distinctive characteristic of living organisms that can be remotely detected from space, it has been proposed as an indicator for scanning extra-solar system planets for life (Seager et al. 2005). However, the analysis above indicates that we should not expect to find the red-edge at the same or similar wavelengths as we do on Earth. The position of the red-edge on an extra-solar planet would depend on the details of the spectrum (intensity-wavelength distribution) of the star at the surface of the planet and the elapsed time of evolution of pigment size and excited state lifetime since the beginning of life on the planet. It may be, however, that a pronounced drop in absorption could be clearly distinguishable in the reflection data of a planet, even if we would have to call this a "blue-edge," for example.

Conclusions

Rapid deterioration of Earth's ecosystems due to human excesses has left us in a dangerous situation in which, unless we respond and change our ways, our own survival is at risk. Any response will first require a careful assessment of ecosystem health and a measure of the effect of our intervention. Such an approach requires a reliable and remotely sensed indicator of ecosystem health.

This chapter has been dedicated to describing an indicator of ecosystem health based on the most important thermodynamic function of all life, that of the dissipation of the solar photon flux. The indicator measures the global entropy production of the ecosystem, which is determined by integrating over the difference in the entropy flow in the incoming and outgoing photon fluxes. It is suggested that the red-edge can be used as a simplified indicator of ecosystem health since it is probably a good measure of the total entropy production. The validity of various assumptions used in deriving this relationship remains to be investigated in more detail in subsequent works.

The dissipation of the solar photon flux is an entropy producing process in which energy is dispersed over ever more microscopic degrees of freedom. As such, the dissipation process has a natural thermodynamic imperative and non-equilibrium thermodynamic principles indicate that nature will arrange material into structures and processes that tend to augment this entropy production. The whole of biological evolution, and even coupled biotic-abiotic evolution, can be described in these terms. There is no better indicator of biological evolution than the evolution in the increase in spectral absorbance range and dissipative efficiency of the organic pigments along with their dispersal (together with water) over an ever greater surface area of Earth.

It is only through the principles of non-equilibrium thermodynamics that we find a reason for the existence and evolution of ecosystems and for the existence and evolution of our own species, and it is these principles that we must learn to understand and respect if we are to attain stability through thermodynamic harmony with our environment.

Acknowledgements The author is grateful for the financial assistance afforded by DGAPA-UNAM, project number IN103113.

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Part II
Climate Change

Chapter 3
Environmental Indicators of Climate Change: Phenological Aspects

Anders Pape Møller

Abstract Recent climate change has caused an increase in mean temperature on earth by 0.8 °C during the last century with spatially heterogeneous change. Patterns of precipitation, wind and extreme weather have likewise changed considerably. These changes have prompted an enormous interest in the potential impact of climate change (and other components of global change) on all living beings. Environmental indicators of climate change should be easy to apply, consistent over time and space, reliable, and informative. The biological impact of climate change has been assessed with the help of environmental indicators such as change in phenology and change in distribution. Indicators of change in phenology include advanced spring arrival date of migratory birds, advanced first date of singing by birds and advanced first flowering date of plants in response to change in temperature. Indicators of change in distribution include change in the northernmost range limit of butterflies and birds. While there is a huge literature on responses to climate change, there is little assessment of the indicator ability of different biological responses to climate change. Here I briefly review environmental indicators of climate change; rank the response of different species in terms of their indicator ability; test for consistency in indicator ability over time; and test for consistency in indicator ability among indicators. Finally, I provide a list of research areas in need of further development.

Keywords Birds • Climate change • Phenology • Plants • Range expansion • Repeatability

3.1 Introduction

Climate change has been dramatic during the last three decades with particularly strong responses at high latitudes (IPCC 2007). Climate change has been measured as increased temperature, increasingly extreme temperatures, change in precipitation, change in wind speed and patterns, and change in frequency of storms

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_3

(IPCC 2007). All these changing climatic factors may directly or indirectly affect the distribution and the abundance of animals and plants either through effects on food or effects on interacting species (reviews in Møller et al 2010; Parmesan 2006; Parmesan and Yohe 2003; Root et al 2003), with weaker responses at higher trophic levels in the ecosystem (Thackeray et al 2010). While climatic factors can be measured directly, there is also good reason to measure biological responses to climate change because such responses may reflect the ability of organisms to cope with changing environmental conditions. Such responses may affect the prospects of maintaining viable populations and ultimately communities and ecosystems. Humans may be directly or indirectly impacted by such changes in natural ecosystems through agriculture, forestry and fisheries, but also through changes in the frequency and the distribution of infectious diseases of domestic animals and humans themselves.

Responses to climate change are based on decisions by individuals at particular sites. Individuals are the main units of selection, because individuals either die or survive, and because individuals through their reproduction differentially contribute to the nest generation. However, responses to climate change are rarely studied at the level of individuals, but instead typically studied at the population, species or ecosystem levels. As a rare example of the individual-based approach to study responses to climate change Møller (2008a) showed that individual barn swallows *Hirundo rustica* differed in their response to increasing spring temperatures at individual breeding sites. While barn swallows at some sites advanced their breeding phenology considerably during the last 30 years, breeding date barely changed or was even delayed at phenologically late breeding sites. However, overall across all sites there was a significant advancement in time of breeding. Thus it is the combined response of individuals in a population that represent the population level response to climate change.

Responses to climate change can either be phenotypic plasticity or micro-evolutionary change. A phenotypic plastic response occurs when for example individuals reproduce early in years with warm springs and late in years with cold springs. In contrast, a micro-evolutionary change occurs as a consequence of differences in genotype among individuals, with individuals with alleles coding for early phenology increasing in frequency across generations as a consequence of a selective advantage. Many studies have shown that the extent of change in phenology, for example, is fully explained by the extent of phenotypic plasticity suggesting that there is no reason to invoke additional explanations (e. g. Balbontín et al. 2009, for an example on spring arrival date of barn swallows), and there is only little direct evidence of micro-evolutionary change so far (Sheldon 2010).

Environmental indicators of climate change (or any other factor) should be easy to apply, consistent over time and space, reliable, and informative. While there is already a huge literature of thousands of papers dealing with changes in phenology and distribution range in response to climate change, there are very few papers dealing with methodological aspects including the ability of indicators to provide reliable and relevant information. Environmental indicators that are easy to apply include arrival date of migratory birds or emergence of flowers. The use of these phenology indicators dates back to the days of Linnaeus, when they were used as early indicators of the appropriate time for sowing crops (Lehikoinen et al 2004), and they are still widely used today.

Environmental indicators should be consistent over time and space if they reliable reflect change in environmental conditions. Statistically, this implies that they are repeatable among sites and periods. Repeatability is an estimate of the amount of variation among individuals relative to the total variance, with estimates ranging from one when subjects show complete consistency across samples to zero when subjects show no consistency (Falconer and Mackay 1996). When subjects are individuals, repeatability provides an upper limit to the heritability of a given trait. For example, Rubolini et al. (2007) tested for and found consistency in response to climate change as reflected by change in spring arrival date among European populations of migratory birds.

Environmental indicators should be reliable so there is little bias due to low detection probability (so-called false negatives) although such effects could be controlled statistically (e.g. Mackenzie et al 2004). For example, sessile organisms may be less prone to false negatives than mobile species because the former can be found in the same area in subsequent years. A different problem applies to migrants that live in different environments at different times of the year. Such species may be exposed to different climate systems that partly fluctuate independently of each other, making it difficult to pinpoint whether an environmental indicator reflects changing climate at the breeding grounds, on migration or during winter, or all of these combined. In contrast, resident species should be superior indicators of local climatic change because they are exposed to the same climate system year-round (Rubolini et al 2010) for an example of change in song phenology of resident, short distance and long distance migratory birds). Reliability of environmental indicators also implies that they are specific to the impact of a given environmental factor. For example, Gregory et al. (2009) presented information on the reliability of the European breeding bird monitoring program showing consistency between population trends and the predicted change in potential range forecasted by climate envelope models. However, many other factors such as urbanization, intensified agriculture, forestry and fisheries, and pollution also change simultaneously. Therefore, the null hypothesis is that there will be linear trends, and that the partial influence of other factors should be controlled statistically in tests of the reliability of climate change indicators.

Finally, environmental indicators should be informative in the sense that they should provide information that is relevant in the biological context. Early phenology is associated with considerable increased reproductive success because early phenology (be it arrival date of migratory birds or emergence of insects or plants in spring) equates with early start of reproduction, which is advantageous in terms of probability of recruitment to the next generation (Møller 1994). Likewise a distributional range under favorable climatic conditions is associated with a larger total population size and hence greater standing genetic variation, which will allow greater microevolutionary response to selection (Wakeley 1998). Thus if we can rank species with respect to their indicator ability, this will be helpful in terms of our continued ability to monitor the biological consequences of altered climatic conditions.

The objectives of this chapter are to (1) identify environmental indicators of climate change; (2) rank the response of different species in terms of their indicator ability; and (3) test for consistency in indicator ability over time. Here we attempt to address these issues mainly relying on birds as study organisms, although we cite the literature on other organisms whenever possible.

3.2 Environmental Indicators of Climate Change

3.2.1 Identification of Environmental Indicators of Climate Change

The most commonly used environmental indicators of climate change are change in phenology and range expansion. Figure 3.1 shows the frequency distribution of responses to climate change as an example of these two indicators.

It is evident from the frequency distributions that there has been a mean change over time, but also that there is considerable variation among species, and some species have even shown trends that are opposite to the predicted response. However, these are far from the only possible indicators. Body condition, reproductive output, survival and change in population size are indicators that are supposed to be more closely related to fitness. A list of advantages and disadvantages of different environmental indicators of climate change is provided in Table 3.1.

Generally, indicators that are more closely associated with fitness and maintenance of stable populations such as indices of reproduction, survival and population size are the most difficult and costly to obtain, while the easiest indices like change in phenology and range margin are easy to obtain, but less closely associated with fitness components. However, the observation that bird species that have responded the least to climate change are also the species that have the most negative future population trend suggests that change in phenology can be an informative indicator (Møller et al. 2008).

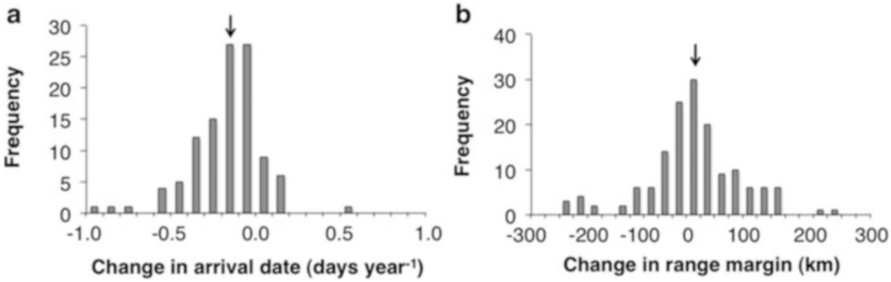

Fig. 3.1 Frequency distributions of (**a**) change in mean spring arrival date of migratory bird species (days year^{-1}) in Europe and (**b**) change in range margin of breeding bird species in Finland. *Arrows* indicate mean values

Table 3.1 Environmental indicators of climate change and their properties in terms of ease of use, consistency in response over time and space, reliability and degree of informative properties

Indicator	Ease of use	Consistency over time and space	Reliability	Informative
Change in phenology	Easy	Yes	Partly	Weakly
Change in distribution range	Easy	Yes, weakly	Partly	Weakly
Change in body condition	Relatively easy	?	Yes	Partly
Change in reproductive success	Time consuming	No	Yes	Yes
Change in survival	Time consuming	?	Yes	Yes
Change in population size	Time consuming	Yes	Yes	Yes

3.2.2 Ranking of Indicators in Terms of Their Indicator Ability

A first step in analyzing the indicator ability of an index of response to climate change is that there has been a response. Indeed mean arrival date of migratory birds has advanced considerably in recent years (mean (SE) = −0.16 (0.02) days year^{-1}, t = 7.58, P < 0.0001). The species with the strongest response to climate change are the short distance migratory stock dove *Columba oenas* −0.971 days year^{-1}, jackdaw *Corvus monedula* −0.833 days year^{-1} and snow bunting *Plectrophenax nivalis* −0.739 days year^{-1}. The species that have delayed arrival the most are the long distance migrants common tern *Sterna hirundo* +0.605 days year^{-1}, wood warbler *Phylloscopus sibilatrix* +0.249 days year^{-1} and common cuckoo *Cuculus canorus* +0.249 days year^{-1}.

Which factors determine the response of indicators to climate change? We can predict that advance in arrival date and other indicators of environmental change will increase with increasing population size for at least two different reasons. First, large populations will have larger amounts of standing genetic variation (Wakeley 1998), and they may hence respond more readily to climate change and other major selection pressures. Second, large populations are generally denser (Brown and Lomolino 1998), and since dispersal is density-dependent (Clobert et al 2001), we can expect greater dispersal distances in such populations resulting in greater range expansion. Mean arrival date has advanced the most in species with large population sizes (Fig. 3.2a; F = 10.17, df = 1,106, r^2 = 0.09, P = 0.0019, estimate (SE) = −0.07 (0.02) in a model that accounted for effects of body mass). There was no improvement in fit by addition of total range size (F = 6.55, df = 1,105, r^2 = 0.06, P = 0.012, estimate (SE) = −0.06 (0.02)). Thus there is evidence for a significant effect of population size.

Migratory species of birds spend part of their annual cycle in the breeding area and part in the winter quarters that may be more than 10,000 km away, and significant

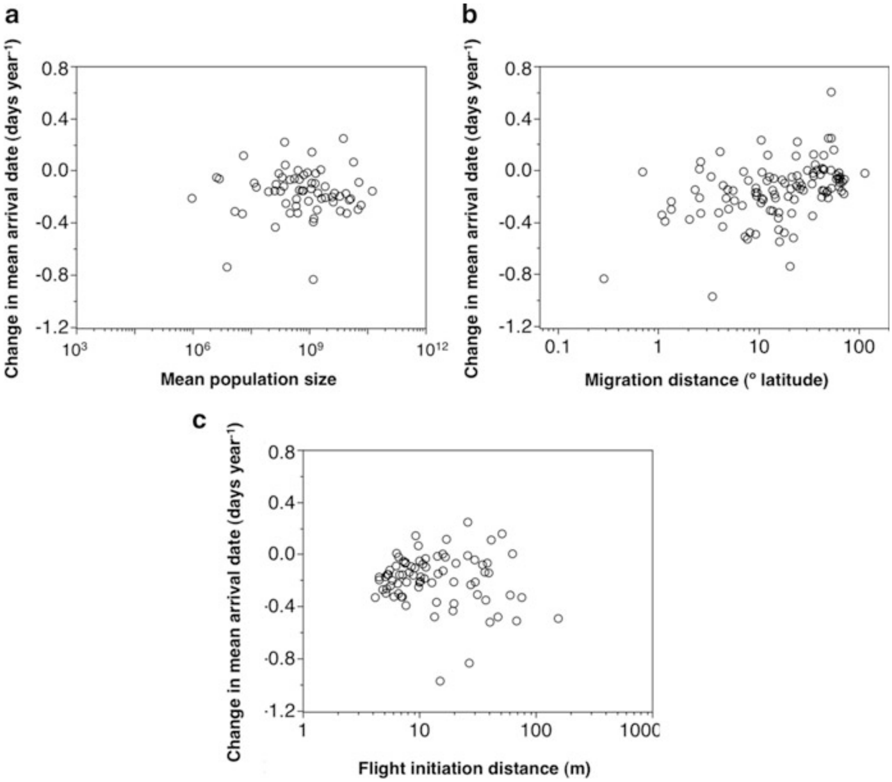

Fig. 3.2 Change in mean spring arrival date of migratory birds (days year^{-1}) in Europe in relation to (**a**) mean population size in the Western Palearctic, (**b**) migration distance (° latitude) and (**c**) flight initiation distance (m)

amounts of time is spent in between on migration. Migratory birds are known to respond less to climate change in the breeding areas than residents (Rubolini et al 2007, 2010; Lehikoinen and Sparks 2010). Indeed, in the European database spring arrival date advanced the most in resident and short distance migratory species, with long distance migrants showing little or no response (Fig. 3.2b; $F = 18.75$, $df = 1,110$, $r^2 = 0.15$, $P < 0.0001$, estimate (SE) = 0.16 (0.04).

Flight initiation distance is an important behavioral estimate of the risk that individual animals are willing to take when confronted with a potential predator (Hediger 1934; Burger and Gochfeld 1981). Different species of birds have average flight initiation distances that reflect their population trends with declining species having relatively long flight distances apparently because they require large tracts of undisturbed habitat, while stable or increasing populations of birds have relatively short flight distances for their body size (Møller 2008b). Indeed, species with long flight initiation distances have hardly changed their mean arrival date, while species with short flight distances have advanced their arrival date (Fig. 3.2c; $F = 7.40$, $df = 1,74$, $r^2 = 0.09$, $P = 0.008$, estimate (SE) = 0.26 (0.09)). Therefore, there is evidence of a significant effect of flight initiation distance.

Brommer and Møller (2010) reviewed evidence that the southernmost ranges of birds are significantly moving northwards based on studies in Finland, UK and USA, while there was less evidence for a change in northernmost ranges.

3.2.3 Testing for Consistency in Indicator Ability Across Spatial Scales

Environmental indicators of response to climate change may differ in indicator ability. Even change in phenology can be strongly affected by the choice of indicator. For example, first arrival date is difficult to estimate with any precision because it is a point estimate at the extreme left tail of a normal frequency distribution. Rubolini et al. (2010) have shown that first arrival date of migrating birds is repeatable across study sites, although much less so than a central estimate such as mean or median arrival date. This finding is as expected because a mean or a median is based on numerous point estimates that add up to a more reliable central estimate. This result mirrors the old saying that one swallow does not make a summer! It is also possible to investigate the relationship between first arrival date and mean arrival date across species to quantify the ability of these two indices to reflect the same phenomenon. Across 112 species of birds analyzed by Rubolini et al. (2007) first arrival date did not significantly predict mean arrival date ($F = 0.13$, $df = 1{,}110$, $r^2 = 0.001$, $P = 0.72$).

3.2.4 Testing for Consistency in Indicator Ability Over Time

If particular species are superior colonizers, then we should see consistent similarities in range expansion previously and now. This prediction has never been tested. Voous (1960) provided the first major atlas of the worldwide distribution of any group of organisms in his treatise of the birds of Europe. Cramp and Perrins (1977–1994) provided a second atlas of the breeding birds of the Western Palearctic. There was a significant increase towards the north in breeding distribution between the period before 1960 and the period before 1990 (mean change in northernmost distribution: +0.67° latitude, $SE = 0.20$, $N = 168$ species) differing significantly from zero ($t = 3.33$, $df = 167$, $r^2 = 0.06$, $P = 0.0011$), while there was no consistent change for the southernmost distribution range (−0.25° latitude, 0.43, $t = -0.59$, $df = 167$, $r^2 = 0.002$, $P = 0.56$). The indicator ability of northernmost range expansion estimated as the difference in northernmost latitude between 1960 and 1990 was positively correlated with range expansion in Finland between 1974–1979 and 1986–1989 (the latter data reported by Brommer and Møller (2010); $F = 5.04$, $df = 1{,}53$, $r^2 = 0.09$, $P = 0.029$, estimate (SE) = 2.40 (1.94)) after controlling for change in abundance. To conclude, there is weak, but significant consistency in range expansion over time. There are no similar data currently available for phenology.

3.2.5 Testing for Consistency in Indicator Ability Among Indicators

If there were multiple traits that all reliably indicated response to climate change, the task of assessing the response of living beings to climate change would be rendered much easier. From a theoretical point of view it is fully possible that characters that promote dispersal and hence range expansion would also promote change in phenology. For example, longer-winged insects have shown a greater response to climate change in terms of range expansion compared to species without or with shorter wings (Thomas et al 2001). It would not be difficult to argue that specific wing morphology in birds would facilitate range expansion, but also early arrival in spring from the tropical winter quarters. Surprisingly, there has been no empirical test of whether species that have advanced phenology are the same species that have expanded their range the most.

Change in spring phenology in terms of mean arrival date for different species of birds was not significantly related to range expansion in Finland (models that included mean distribution as a covariate and models that were weighted by number of mean arrival estimates; southernmost distribution: $F = 1.99$, $df = 1{,}51$, $r^2 = 0.04$, $P = 0.16$; northernmost distribution: $F = 2.09$, $df = 1{,}9$, $r^2 = 0.19$, $P = 0.18$). A similar conclusion was reached for range expansion in the UK (southernmost distribution: $F = 2.41$, $df = 1{,}24$, $r^2 = 0.09$, $P = 0.13$; northernmost distribution: $F = 0.58$, $df = 1{,}67$, $r^2 = 0.01$, $P = 0.34$). These tests provide no evidence for a species-specific indicator ability to respond to climate change. I conducted a second test of the prediction by relating mean change in spring arrival date to mean change in winter range of birds in Germany according to temporal changes in locations of banded birds (Fiedler et al 2004). Indeed there was a weak, but significant relationship ($F = 4.58$, $df = 1{,}21$, $r^2 = 0.18$, $P = 0.044$, estimate (SE) $= -0.185$ (0.086)). Therefore, bird species that now winter closer to their breeding grounds in Germany have advanced their spring arrival date the most.

3.3 General Discussion

The main findings of this chapter were that different environmental indicators of climate change were weakly consistent across spatial and temporal scales, and that different indicators were at best only weakly positively correlated. This implies that there is little evidence of general indicators.

Weak effects as reported in this chapter for environmental indicators of climate change are typical of biological research. On average biologists typically have $r^2 = 0.05$–0.07 in meta-analyses of biological phenomena as diverse as plant responses to increasing CO_2, intensity of sexual selection and parasite manipulation of hosts (Møller and Jennions 2002). Although such effects may seem small compared to effects in other natural sciences than biology, on an evolutionary time scale of thousands or more generations they can readily result in considerable phenotypic change.

Repeatability of environmental indicators of climate change across spatial and temporal scales is weak at best and often almost completely lacking. An absence of repeatability can be attributed to a lack of response in one area/period, but not the other. Alternatively, it can be attributed to the lack of a species-specific response with changes in response differing among areas/periods. In general phenotypic traits of species are highly consistent across spatial and temporal scales with external phenotype, life history, physiology, ecology and behavior of say Japanese and Irish great tits *Parus major* being more similar than say Irish great tits and closely related Irish blue tits *Cyanistes caeruleus*. This similarity is the basis for why bird watchers can readily distinguish between species with a pair of binoculars. The lack of repeatability for indicators of environmental change is all the more surprising.

Advancing spring phenology and range expansion are statistically largely independent environmental indicators according to the analyses reported here. Although there is a clear average biological signal in the predicted direction for both spring phenology and range expansion, this signal is specific for a particular location or a particular period.

Many aspects of global change such as urbanization, intensified agriculture, forestry and fisheries, and pollution all change simultaneously as does climate change. Thus there is a good reason for testing if environmental indicators of climate change are specific to climate, or whether such indicators reflect other components of global change. Surprisingly only few such tests exist, suggesting that there is reason for caution when assessing the effect of climate change on biological phenomena (Møller 2013).

3.4 Future Prospects

Future studies should attempt to pinpoint the reliability of environmental indicators, but should also further investigate the information content of such indicators. It would be interesting to test a range of different indicators for their ability to indicate climate change. Such a test should rely on reliability, but also on cost effectiveness.

Given that indicators of climate change are poorly correlated with each other we need to better understand what they are reflecting. We also need to quantify to which extent these indicators reliably reflect the reproductive potential and hence the persistence of populations. It is generally assumed, although not explicitly tested, that species with the strongest response to climate change will be the species that suffer the least from climate change. This may not always be the case because different taxa may respond at a different rate. Indeed, predators may fare better when exploiting populations of prey that have an inferior condition due to negative effects of climate change. The same may apply to parasites. It is clear that natural environments have always been affected by environmental change including climate change although the rate of change has rarely if ever been greater than today. Thus, there is every reason to identify the taxa that will be most affected by climate change, and the phenotypic traits of such taxa that will provide the most reliable information on future response to climate change.

Acknowledgments J. A. Shykoff helped crystallize some of the ideas presented here.

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Chapter 4
Carbon Footprint – An Environmental Sustainability Indicator of Large Scale CO_2 Sequestration

Dragoljub Bilanovic

Abstract To slow down the degeneration of the planetary life support system atmospheric CO_2 concentration must be reduced. There are no insignificant CO_2 emissions since all CO_2 ends-up in a single atmosphere of finite size. To minimize anthropogenic CO_2 emissions and to bring its atmospheric concentration to 320 ppm, the world economies should replace fossil fuels with alternative energy sources and construct large facilities for reduction of atmospheric CO_2.

Environmental indicators (EIs) gauge the burden of goods and services on the environment. The carbon footprint (CF) is the EI of greenhouse gas emissions and is measured in terms of CO_2 equivalent.

This chapter brings preliminary estimation of CFs for the following CO_2 reduction technologies: photosynthetic or microalgae CO_2 sequestration (MCS), artificial photosynthesis (AP), ocean iron fertilization (OIF), oceanic CO_2 sequestration (OCS), and terrestrial CO_2 sequestration (TCS).

OIF, OCS, and TCS should not be considered when constructing the large facilities for reduction of atmospheric CO_2 because each of these technologies could easily become a source of greenhouse gases. The large facilities for reduction of atmospheric CO_2 should rely on MCS and AP technologies and reforestation.

Keywords Carbon footprint • CO_2 reduction technology • Microalgae

Abbreviations

ACO2	atmospheric CO_2
CF	carbon footprint
CFA	carbon footprints of affluence
CFP	carbon footprints of population
CFT	carbon footprints of technology
CF^{AP}	carbon footprint of artificial photosynthesis

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_4

CF^{MCS}	carbon footprint of photosynthetic or microalgae CO_2 sequestration
CF^{OCS}	carbon footprint of oceanic CO_2 sequestration
CF^{OIF}	carbon footprint of ocean iron fertilization
CF^{TCS}	carbon footprint of terrestrial CO_2 sequestration
CHC	cost of chemicals
COC	construction costs
CO2E	carbon dioxide equivalent
EIs	environmental indicators
EQI	equivalent inhabitant
GHG	greenhouse gas
GDP	gross domestic product
GWP	global warming potential
LAC	labor costs
MCF	median carbon footprint
MPI	marketable product income
OEN	cost of energy consumed, excluding energy used to transport CO_2 or Fe
OMC	operation and maintenance expenses
OTC	other expenses
PI	pollution intensity
TRC	cost of energy to transport CO2 or Fe via pipeline, tanker or both

4.1 Introduction

Carbon dioxide (CO_2) is the major greenhouse gas (GHG) warming the Earth and accelerating global climate change. Atmospheric CO_2 (ACO2) and anthropogenic CO_2 emissions must be reduced to slow down the degeneration of the planetary life support system. This chapter presents preliminary comparative estimation of carbon footprint for five technologies for reducing ACO2 and CO_2 emissions.

Fossil fuels provide about 85 % of the world's primary energy today, a share is expected to drop to 79 % by 2035 (USEIA 2011). Growing population and rising energy demands could bring increase in CO_2 emissions (i.e. of 40 %, probably higher) within the next two decades.

The world economy discharged about 34 Gt CO_2 in 2011 of which the China emitted 9.7, the US 5.4, and the European Union 3.9 Gt (Olivier et al. 2012). About 8.5 Gt CO_2 was emitted from coal-fired plants to make 1,600 GW electricity (IEA 2012); coal rich countries will continue adding these plants for as long as such electricity is cheaper than electricity from alternative energy sources.

No goods or service in the fossil fuel economy produces CO_2 emissions that are insignificant; small and large emissions are both important, since all CO_2 ends-up in a single atmosphere of finite size; (Tables 4.1 and 4.2). Alternative energy sources could eliminate two-thirds of the CO_2 emissions produced by fossil fuels.

At least 97 % of scientists agree that anthropogenic CO_2 emissions are the cause of global warming (Cook et al. 2013). Increasing ACO2 by 1.0 ppm raises the air

Table 4.1 Emissions from 1,000 MW power plant firing fossil fuels

Fuel	CO_2	CO	SO_2	NO_x	VOC	PM	Hg	PI	CF
Coal	100	100	100	100	100	100	100	700	100
NGas	46	16	0.1	32	32	0.008	8	134	46.2
Oil	76	17	176	67	75	13	0.5	424	76.1

Emissions from coal plant (ton day^{-1}): 24,571 CO_2, 3.43 CO, 67.14 SO_2, 49 NO_2, 1.05 VOC, 2.38 PM, 570 ash, 880 smokestack sludge. 0.37 kg Hg day^{-1}. The plant uses: 1.0 to 3.0*10^9 m^3 cooling water day^{-1}; and only 33–35 % of heat available in coal (EEA 2012, UCSUSA 2013). Pollution Intensity (PI) = (CO_2 + CO + SO_2 + NO_x + VOC + PM + Hg). Carbon Footprint (CF) = (CO_2 + NO_x).

Table 4.2 Small and large CO_2 emissions

CO_2 source	EI
1. Private car (kilometrage: 20 km L^{-1}; 5,000 km year^{-1})	0.12
2. 10^9 cars on Earth in 2013 ("1" above)	1.64*10^9
3. Single 500 MW coal-fired plant	0.41 –0.52*10^6
4. 818 coal-fired plants with total installed capacity exceeding 1,077 GW to be built by China and India (Yang and Cui 2012, "3" above)	0.89–1.12*10^9
5. Beef production – 0.2 kg meat person^{-1} day^{-1} (Röös et al. 2013)	0.41
6. Beef for 7*10^9 people ("5" above)	2.87*10^9
7. Chicken production – 0.2 kg meet person^{-1} day^{-1} (Röös et al. 2013)	0.04
8. Chicken for 7*10^9 people ("7" above)	0.28*10^9
9. EQI = Equivalent Inhabitant 4.9 t CO_2E year^{-1} (World Bank 2013)	1.0
10. World population	7*10^9
11. World population & its partial needs (i.e. "10 + 2 + 4 + 6" above)	12.63*10^9

temperature by $0.013 \pm 0.002°$ (i.e., Eq. 4.1 from Boeker and Van Grondelle 2011; ACO2 from 1778 to 2013 adapted from SIO 2013). Today's temperature is on average 0.6 °C higher than in the 1950s (NASA 2013); without CO_2 reductions the temperature in 2035 could be 2.08 ± 0.45°C higher than today.

$$\Delta T = 9.833 * \log([CO_2]/[280]) \tag{4.1}$$

where:

ΔT = air temperature increase (degree K),
9.833 = proportionality factor (degree K per W m^2), and
$[CO_2]$ = atmospheric CO_2 concentration (ppm)

ACO2 has increased by 43 % since 1778 when James Watt improved the steam engine (Table 4.3). Some falsely claim the percentage is insignificant on a planetary scale but today:

Table 4.3 Atmospheric CO_2

Year	1778	1850	1950	1997	2013
Atmospheric CO_2 ppm (SIO 2013)	280	287	310	363.7	400
Temperature increase (K $year^{-1}$) – Eq. 4.1	0.000	0.001	0.002	0.011	0.019
Calculated ACO2 increase if no NS[a] (ppm $year^{-1}$)	0.25	0.37	1.26	5.05	6.77
Observed ACO2 increase (ppm $year^{-1}$)	0.01	0.08	0.28	1.47	2.71
% of Anthropogenic CO_2 emissions absorbed by NS	96.00	78.38	77.78	70.89	59.97

[a]NS stands for natural CO_2 sinks (SIO 2013)

- ACO2 concentration is rising 9.7 times faster than in the 1950s (Observed ACO2 in Table 4.3), consequently
- The temperature is increasing yearly 9.5 times faster than in the 1950s (see Temperature Increase in Table 4.3), and
- Natural sinks (NS) absorbed almost 80 % of anthropogenic CO_2 emissions in 1950s and less than 60 % today (% of Anthropogenic CO_2 emissions absorbed by NS in Table 4.3).

Environmental indicators (EIs) gauge the burden of goods and services on the environment; more than 300 EIs germane to agriculture, energy, industry, and other subjects of environmental and social impact are in use (EEA 2012; EPA 2013; World Bank 2013).

The carbon foot print (CF) is the EI of greenhouse gas (GHG) emissions and is measured in terms of carbon dioxide equivalent (CO2E). GHG emissions are converted into CO2E by multiplying emission by a factor called global warming potential (GWP). The GWP of methane is 72, meaning that 1.0 kg of CH_4 induces the same amount of global warming as 72 kg of CO_2 over 20 years; N_2O's GWP is 289. The CF of a 500 Mw plant burning coal is twice the CF of a 500 Mw plant burning natural gas which makes coal twice as polluting as natural gas (CO_2 Table 4.1). Coal's pollution intensity is five times higher than that of natural gas (PI in Table 4.1). Replacing coal with natural gas could apparently reduce CO_2 emissions by 4.6 Gt. However, both the CF and PI of natural gas would exceed those of coal if just 1.39 % of the CH_4 produced escaped into the atmosphere in hydraulic fracturing; CH_4 escape rate is in the 3.9–7.9 % range (Howarth et al. 2011).

Carbon footprint, expressed in ton of CO2E per capita, is of help when debating who pays for the reduction of excess CO_2, but because global warming and global climate change (GCC) are rapidly causing the planetary life support system to degenerate it is next to irrelevant which country is a larger polluter. To continue, the world economies should focus on reducing atmospheric CO_2 and its emissions, – a truly global job of massive proportions. About $7.7*10^9$ ton CO_2 should be removed from the atmosphere to cut ACO2 by 1.0 ppm; closing 91 % of the world's coal-fired plants would have the same effect.

There seems to be little political and financial willingness to reduce ACO2 and anthropogenic CO_2 emissions. "Adaptation to GCC" is argued and ACO2 higher than 500 ppm is espoused. "Doubling of ACO2 has emerged as a political target and a focal point for scientific analysis in most climate change models" (Graedel and Allenby 2010). The annual costs of "adaptation to GCC" are estimated at 2 % of the world GDP. Without emission cuts the world would be losing 5 % of its GDP per annum (Stern 2007); the losses would keep increasing with rising ACO2.

Qualitative and quantitative changes throughout Earth's environment show that the concept of "adaptation to GCC" via "stabilization at higher ACO2 concentration" is a very bad idea. ACO2 should be reduced from the current 400–350 ppm or lower (Hansen et al. 2008, 2011). Deceleration of global warming and reversal of GCC necessitates:

- Transition from fossil fuels to alternative energy sources, and
- Construction of large facilities for reduction of ACO2.

This chapter presents preliminary comparative estimation of carbon footprint (CF) for five CO_2 reduction technologies; CO_2 removal efficiency for a particular technology was calculated from [1– (ton CO_2 invested /ton CO_2 avoided)*100] where "CO_2 invested" is technology's CF.

4.2 Methodology

Carbon footprints (CF) were estimated for: photosynthetic or microalgae CO_2 sequestration (CF^{MCS}), artificial photosynthesis (CF^{AP}), ocean iron fertilization (CF^{OIF}), oceanic CO_2 sequestration (CF^{OCS}), and terrestrial CO_2 sequestration (CF^{TCS}). Other GHG emissions were not considered.

($\Delta CO_2/\Delta t$) is the rate of atmospheric CO_2 increase where ΔCO_2 is the change in ACO2 concentration, and Δt is time elapsed in years.

4.2.1 Estimation of Carbon Footprints for Population, Affluence, and Technology

Carbon footprints of population (CFP), affluence (CFA), and technology (CFT) were estimated from:

CFP = [ton CO_2 to be removed from atmosphere to reduce it to 280 ppm]/[world population];
CFA = [$ GWP * ton CO_2/ton coal] / [$/ton coal];
CFT = [World energy consumption GJ] * [ton CO_2/ton coal] / [GJ/ton coal].

The average cost of US coal was \$39.00 ton^{-1}; a ton of coal yields 2.11 ton of CO_2; and the average heat content is 22.75 GJ per ton coal (EIA 2013).

4.2.2 Estimation of Carbon Footprints of CO_2 Reduction Technologies

The CF estimation procedure consists of the following steps:

1. Assessment of minimal and maximal costs to remove 1 ton of atmospheric CO_2 using:

$$\text{Cost} = \text{CHC} + \text{COC} + \text{LAC} + \text{OMC} + \text{OTC} + \text{OEN} + \text{TRC} - \text{MPI}$$

   where: • CHC is the cost of chemicals on which technology relies, • COC is construction costs, • LAC is labor costs, • OMC is operation and maintenance expenses, • OTC is other expenses, • OEN is energy consumed, excluding energy used to transport CO_2 or Fe, • TRC is energy to transport CO_2 or Fe via pipeline, tanker or both, • MPI is marketable product income from a particular technology.
2. The costs were divided by the average cost of US coal to obtain coal equivalent (Sect. 4.2.1.).
3. The coal equivalent was multiplied by 2.11 to obtain CO2E (Sect. 4.2.1.).
4. Sum of minimal CO2E equals minimal CF; sum of maximal CO2E equals maximal CF for a particular technology (Tables 4.4 and 4.5).

   Additional assumptions pertinent to estimation of CF were:

4.2.2.1 Artificial Photosynthesis (AP) Carbon Footprint (CF^{AP})

AP construction costs assumed to be 5–30 % of installed photovoltaic costs in 2013 (Table 4.4).

Table 4.4 Estimated construction costs (COC) and sources

Technology	Construction costs (\$/ton CO_2 avoided)
TCS	\$0.85–\$1.35 (NETL 2010; Fujioka et al. 1997; Weber and Matthews 2008)
OCS	\$5.29–\$7.24 (Fujioka et al. 1997; Weber and Matthews 2008)
AP	\$2.66–\$17.06 (Feldman et al. 2012)
OIF	\$2.59–\$3.88 (Cost of fleet of 800 or 1,200 tankers at 5 % interest over 30 years from UNCTAD 2011; Weber and Matthews 2008; Johnston et al. 1999)
MCS	\$0.82–\$7.61 (Bilanovic, Holland, and Armon 2012)

Table 4.5 Other cost categories – assumptions and sources

Cost category	Technology				
	TCS	OCS	AP	OIF	MCS
CHC (%COC-Table 4.4)	See Sect. 4.2.2.5	See Sect. 4.2.2.4	0	See Sect. 4.2.2.3	MCS-Table 4.4
LAC (% COC-Table 4.4)	15–30	15–30	5–15	15–30	5–15
OMC (%COC-Table 4.4)	15–25	15–25	3–6	15–25	3–6
OTC (% COC-Table 4.4)	10–15	10–15	3–6	3–6	3–6
OEN (% COC-Table 4.4)	See Sect. 4.2.2.5	See Sect. 4.2.2.4.	0	3–6	MCS-Table 4.4
TRC (% COC-Table 4.4)	See Sect. 4.2.2.5	See Sect. 4.2.2.4.	0	See Sect. 4.2.2.3.	0
MPI (\$/ton CO_2 avoided)	0	0	136–410	0	136–410

4.2.2.2 Microalgae CO_2 Sequestration (MCS) Carbon Footprint (CF^{MCS})

MCS (Bilanovic et al. 2009) and AP could operate at any CO_2 concentration. Reactors would be air-sparged to provide CO_2 and mixing; sparging costs and chemical expenses for microalgae harvesting are combined under OEN costs (Bilanovic et al. 2012). This eliminates costly operations such as concentration, purification, and transport of CO_2.

4.2.2.3 Ocean Iron Fertilization (OIF) Carbon Footprint (CF^{OIF})

Iron would be sprayed over 17,000,000 km^2 of the Pacific Ocean to stimulate phytoplankton to consume 1.47 Gt of CO_2 yearly using 1/5 of sprayed Fe. $FeCl_3$ (\$1,000/t FOB, 33 % Fe) and $FeSO_4$*$4H_2O$ (\$500/t FOB, 20 % Fe) prices were used to find the chemical costs (CHC). A fleet of tankers would spray Fe over the Pacific 40–70 times per year at 2,500 and 5,000 km from the nearest port (Table 4.4, UNCTAD 2011; Weber and Matthews 2008; Johnston et al. 1999; Fujioka et al. 1997).

4.2.2.4 Oceanic CO_2 Sequestration (OCS) Carbon Footprint (CF^{OCS})

Monoethanol amine, MEA, is used to extract CO_2 from flume gases. Up to 6 % of MEA degrades per extraction cycle; a ton of MEA extracts 0.5 ton of CO_2. MEA costs of \$1,800–\$1,935/ton are used to find CHC. Two options are considered when estimating the costs of CO_2 storage in deep-waters (TRC in Table 4.5): (1) CO_2 transported 500 km via pipeline and then 100 km by ship, and (2) CO_2 transported 1,000 km via pipeline and then 500 km by ship (Weber and Matthews 2008; Johnston et al. 1999; Fujioka et al. 1997).

4.2.2.5 Terrestrial CO_2 Sequestration (TCS) Carbon Footprint (CF^{TCS})

See MEA/CHC costs in Sect. 4.2.2.4 above. Two options are considered to estimate TRC costs: (1) CO_2 transported via 500-km pipeline, and (2) CO_2 transported via 1,000-km pipeline prior to its storage in geological formations (Weber and Matthews 2008; Johnston et al. 1999; Fujioka et al. 1997).

4.3 Carbon Footprints of Population, Affluence and Technology

The rate of ACO2 buildup was: • below 0.28 ppm year^{-1} from the times of James Watt until the end of WWII, • in 0.51–1.00 ppm year^{-1} range from 1951 to 1968, • in 1.06 to 1.63 ppm year^{-1} range from 1969 to 2000, and •1.9 ppm in 2002 to increase to • 2.71 ppm in 2012 (Fig. 4.1).

Natural sinks are, apparently, absorbing the increasing quantities of CO_2 (see CO_2 curve in Fig. 4.1 and Table 4.3). However the size of the "peak to peak" amplitude on the CO_2 curve after the 1950s appears smaller than that before the 1950s, indicating that the capacity of natural CO_2 sinks cannot cope with the rising CO_2 emissions. Their capacity seems to have been exceeded in the 1950s when ACO2 started accumulating 2–3 times faster than previously (CO_2 in Fig. 4.1). Today ACO2 accumulates 9.7 times faster than in the 1950s (CO_2 in Fig. 4.1). At that time ACO2 was in the 310–319 ppm range and the sinks were apparently removing 80 % of the CO_2 emitted (CO_2 in Fig. 4.1). To decrease the burdens on the sinks, anthropogenic CO_2 emissions should be returned to the 1950s level and ACO2 reduced to 320 ppm instead of 350 ppm (Kharecha et al. 2010).

As compared to the 1950s, today's population's CF is 78 % bigger; technology's CF is 375 % bigger, and affluence's CF increased roughly 1,200 % (P, T and A in Fig. 4.1). The annual CO_2 increase is directly proportional to rising P, A, and T carbon footprints:

$$\text{Population CF}\left[\text{t R-CO}_2/\text{capita}\right] = 31.46 \times \left[\text{CO}_2\,\text{ppm year}^{-1}\right] + 57.48;\ R^2 = 0.698.$$

$$\text{Affluence CF}\left[\text{Gt C-CO}_2\right] = 1,392.77 \times \left[\text{CO}_2\,\text{ppm year}^{-1}\right] - 326.31;\ R^2 = 0.903.$$

$$\text{Technology CF}\left[\text{Gt C-CO}_2\right] = 20.62 \times \left[\text{CO}_2\,\text{ppm year}^{-1}\right] + 1.64;\ R^2 = 0.974.$$

Where, t R-CO_2 is t CO_2 to be removed from the atmosphere to decrease ACO2 to 280 ppm, and Gt C-CO_2 is Gt CO_2 emitted by world's economy assuming coal is the only fuel.

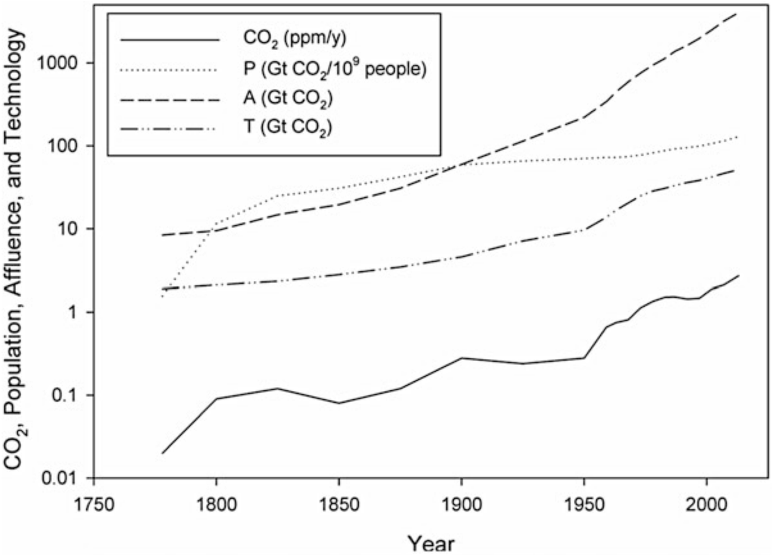

Fig. 4.1 Carbon dioxide emission rate (CO_2) and carbon footprints of: population (*P*), affluence (*A*), and technology (*T*) (Adapted from: SIO 2013; UN 2004; OECD 2012; BP 2013; Smil 2010)

P, A, and T are projected to grow: by 2050, the population could reach 10.6 billion (UN 2004) and affluence could be three times higher than today (OECD 2012). If technology continues growing at its present rate (i.e., technology growth approximated here to consumption of fossil fuels) by 2050 ACO2 could easily be in the 750–1,000 ppm range. Technology is the key for reduction of ACO2 to 300–350 ppm, and for minimization of anthropogenic CO_2 emissions.

4.4 Technologies for Reduction of Carbon Dioxide

The median carbon footprint of terrestrial carbon sequestering (CF^{TCS}) is 40 % smaller than CF^{MCS} and is much smaller than the CFs of three other technologies (MCF – Table 4.6). Maximal CF^{TCS} is significantly smaller than the maximal CF of other technologies (Max – Table 4.6).

The minimal carbon footprint of microalgae CO_2 sequestering is four times smaller than the minimal CF of other technologies (Min – Table 4.6). AP and MCS are closed system technologies, meaning both technologies have built-in mechanisms to control the fate and transport of CO_2 and of generated biomass. These two technologies yield a marketable product(s) that the other three do not (MPI in Table 4.6). The products would replace goods that are currently made from fossil fuels (i.e. polymers, building blocks and other chemicals, and fuels) and,

Table 4.6 Carbon footprint of technologies for reduction of carbon dioxide

Preliminary carbon footprint (kg CO_2 emitted per ton CO_2 eliminated)										
	TCS		OCS		AP		OIF		MCS	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
CHC	17.5	33.9	17.5	33.9	0	0	0.2	0.3	−6	10.1
COC	50	70	290	390	150	920	140	210	40	410
LAC	10	20	40	120	10	140	20	60	0.6	6.1
OMC	6.9	18.3	15.7	21.1	4.5	92	14	42	0.9	3.5
OTC	0.1	10	30	40	4.5	55.2	0.1	10	0	0.1
OEN	0.4	1.9	0.5	2	0	0	4.2	8.4	7.9	35.2
TRC	4.9	9.7	4.9	10.1	0	0	30	60	0	0
MPI	0	0	0	0	−21.1	−63.4	0	0	−21.1	−63.4
CF	89.8	163.8	398.6	617.1	147.9	1,143.8	208.5	390.7	22.3	401.6
MCF	126.8 ± 52.3		507.8 ± 154.5		645.8 ± 704.2		299.6 ± 128.8		211.9 ± 268.2	

Median carbon footprint (MCF); CF = CHC + COC + LAC + OMC + OTC + OEN + TRC + MPI; other abbreviations see Sect. 4.2

being carbon negative, decrease the carbon footprints of AP and MCS. These technologies work at any CO_2 concentration, and therefore there is no need for extraction, purification, or transport of CO_2, which brings OEN&TRC costs to zero (Table 4.6).

OIF, OCS and TCS are open system technologies, meaning they do not have any mechanisms to control the fate and transport of injected CO_2 or of generated biomass. Lack of the control mechanisms means these technologies could become a large sources of CO_2 instead of being CO_2 sinks.

4.4.1 Limitations of Terrestrial CO_2 Sequestration (TCS)

CO_2 is about 40 times more soluble in crude oil than in water (Diamond and Akinfiev 2003). Large scale TCS would benefit enhanced oil recovery, but would also increase CO_2 emissions. CO_2 injected into geological formations would migrate into crude oil to increase its CO_2 emissions up to 8 % while decreasing oil heat content. TCS is not "leak proof"; large and sudden releases of CO_2 sequestered in geological formations appear unavoidable (Celia and Bachu 2003). Chemical properties of CO_2 inflict additional limitations on TCS technology, some of which are:

- The drop in pH following CO_2 injection would increase the mobility and concentration of ions and alter the salinity of ground water;
- Pressure build-up, a consequence of CO_2 injection, can trigger CO_2 leakage via natural faults and man-made structures;
- Leakage into shallow geological formations could contaminate both ground and surface waters;
- CO_2 could be a health hazards if it were to leak into man-made structures;
- A drop in pH could alter permeability and porosity, reducing CO_2 storage capacity;
- The CO_2 might corrode sealing cement and perforate aquitards;
- Procedures for tracking and monitoring CO_2 plume are lacking;
- To regenerate MEA, power plants would consume even more water than today (Johnston and Santillo 2002; Court et al. 2011; Farrelly et al. 2013 and references therein).

The CO_2 reduction efficiency of TCS would drop to zero if the energy and material costs needed to resolve TCS limitations increased CF^{TCS} by 0.84 ton CO_2 invested per ton CO_2 avoided.

Average N_2O flux from the world's top soils is 33.8 ± 19.3 kg N_2O $km^{-1}year^{-1}$ (Zhuang et al. 2012). Leaking CO_2 could inhibit nitrification and denitrification to increase N_2O flux; if the soil's pH dropped by 0.5 units following CO_2 acidification, microbes would increase the flux by 6.92 kg N_2O $km^{-1}year^{-1}$, probably more, which is the equivalent of increasing the soil's CO_2 emissions by 2.0 ton $km^{-1}year^{-1}$. CO_2 leakage could also result in higher CH_4 emissions from the top soils and further limit TCS (see Sects. 4.4.2 and 4.4.3).

4.4.2 Limitations of Oceanic Iron Fertilization (OIF)

The average carbon footprint of OIF is: smaller than those of AP and OCS, much larger than that of TCS, and 40 % smaller than that of MCS. Being an "open system technology" OIF does not have mechanisms to control the transport and fate of the microalgae biomass produced following iron fertilization. This makes OIF problematic since:

- A ton of decaying phytoplankton biomass subject to anaerobic digestion yields 0.73 ton CO_2 and 0.27 ton CH_4 (i.e., $C_6H_{12}O_6 \rightarrow 3CH_4 + 3CO_2$) which is equivalent to emitting 20.17 ton CO_2 (i.e., 20-year horizon) per ton of CO_2 avoided,
- Oversupply of carbon (i.e. CO_2 and organic carbon from decaying biomass) and water acidification (Sprent 1987; Huesemann et al. 2002) would inhibit both denitrification and nitrification to increase N_2O emissions. OIF would become a GHG source if microbes made just 3.36 kg N_2O per ton CO_2 avoided. To make 3.36 kg N_2O nitrifiers need 0.067 kg CO_2, and therefore, there would be no nitrifier-phytoplankton competition for CO_2. To make 3.36 kg N_2O denitrifying microbes need about 2.0 kg of carbon in the form of small organic compounds (Bilanovic et al. 1999); they would turn OIF into a GHG source upon consuming just 4.0 kg of decaying phytoplankton. Rising iron concentration in oligotrophic water also stimulates microbial N_2O production (i.e., $4Fe^{2+} + NO_3^{-} + 9.5H_2O \rightarrow 4Fe(OH)_3 + 0.5N_2O + 7H^{+}$). If OIF is to sequester $1.47 * 10^9$ ton CO_2, about 470,000 ton of iron should be added to the ocean of which phytoplankton would consume at most one quarter. There would be at least 325,000 ton of iron left for use in various microbiological and chemical processes; OIF would become a GHG source if microbes other than microalgae used just 10.7 % of the iron applied or when just 1.39 % of the decaying plankton biomass underwent anaerobic digestion.

4.4.3 Limitations of Oceanic CO_2 Sequestration (OCS)

Carbon dioxide could be dispersed through bulk oceanic water or be injected into deep waters to form CO_2 lakes at the sea floor (Johnston and Santillo 2002; Stewart and Hessami 2005). Clathrate (CO_2 hydrate) would form at the floor and, probably, slow down CO_2 migration into overlying water (Johnston and Santillo 2002). The sections of sea floor beneath a CO_2 lake would change from slightly aerobic into anaerobic-reducing environments. Various ions from the floor would dissolve into the lake and then migrate into overlying water permanently changing water biology and chemistry. CO_2 from the top side of the lake would diffuse and acidify overlying water, intensifying biological and chemical changes including the generation of CH_4 and N_2O. Dispersing CO_2 through the bulk of ocean water would be as detrimental as the formation of CO_2 lakes. OCS, like OIF and TCS, does not have mechanisms to control the fluxes of organic and inorganic carbon and to eliminate pH changes/acidification in either aquatic or terrestrial environments. The risk of increasing N_2O and CH_4 emissions cannot be eliminated implying that these technologies could become large CO_2 sources (see Sects. 4.4.1 and 4.4.2).

4.4.4 Limitations of Artificial Photosynthesis (AP)

Current research on artificial photosynthesis focuses on the development of an efficient and inexpensive water oxidation catalyst that would require less frequent repairs than natural photo-catalysts (McConnell et al. 2010; Kalyanasundaram and Graetzel 2010). Efficient hydrogen generation from water could probably be achieved on an industrial scale within a decade or so; AP would employ a variety of water-splitting catalysts during the first phase of industrial application. Some of the catalysts could be toxic and hard to dispose of, and, as a consequence the AP carbon footprint could be even higher than estimated (Table 4.6). The CF^{AP} would probably be in the CF^{MCS} range following the development of green catalysts. However; AP would reach its full potential upon the integration of hydrogen production and CO_2 fixation to make 3-phosphoglycerate or similar small organic compounds. The integration could happen within the next few decades and would immensely benefit the planetary environment and world economies by ending the era of fossil fuels.

4.4.5 Limitations of Microalgae CO_2 Sequestration (MCS)

Microalgae CO_2 sequestering in freshwater could have large negative effects on agriculture and, perhaps, forestry. To preclude competition for land and water, MSC should rely exclusively on marine algae, and be constructed on non-arable lands and offshore, like the Omega System (Omega NASA 2013). Uncontrolled discharge of effluents after microalgae harvesting could trigger eutrophication of coastal waters. Proper water management and recycling routines, currently used in coastal municipalities, would eliminate this problem. MSC and AP are closed system technologies (i.e., relying on man-made structures such as ponds and reactors), which have good control of biomass harvesting and processing. MCS and AP generated materials (i.e., biomass or small organic molecules) would not be left to decay in either aquatic or terrestrial environment. The materials are also environmentally inert in comparison to both concentrated and diluted CO_2. Technological limitations arising from environmental acidification and increasing N_2O/CH_4 emissions are inherent and unavoidable at reasonable cost in OIF, OCS and TCS technologies in stark contrast to MCS and AP that do not suffer from these limitations.

Conclusions

To minimize anthropogenic CO_2 emissions and to decrease its atmospheric concentration to 320 ppm, world economies should replace fossil fuels with alternative energy sources and establish large CO_2 reduction facilities. Alternative energy sources should be put into service at a rate high enough to eliminate up to 100 % of current and 80–90 % of projected fossil fuel demand in 15 or at most 25 years. Some OIF, CST and TCS limitations could be eliminated, but the costs of elimination are likely to bring their CO_2 reduction efficiency to zero. OIF, OCS, and TCS technologies should not be considered for CO_2 reduction facilities because each technology could easily become a GHG source. Facilities for CO_2 reduction should rely on MCS and AP technologies and reforestation. Roughly 1,100,000 km^2 of MCS facilities should be built to eliminate 2 ppm ACO2 per annum given a biomass yield of 75 t ha^{-1}; for comparison the MCS area is just 6.7 % of deserts suitable for microalgae cultivation. An investment of 0.88–2.53 trillion dollars is needed to build MCS facilities of this size (Bilanovic et al. 2012), which, if spread over 10 years, equals 1.06–3.04 % of the world GDP in 2012 (CIA 2013). The construction and operation of large MCS facilities would yield millions of new jobs and establish new environmentally benign markets (Bilanovic, unpublished data).

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Chapter 5
Urban Heat Islands

Keiko Masumoto

Abstract As global warming continues, we are facing another significant issue: the temperature increases during summer in urban areas due to a factor other than global warming. The urban heat island (UHI) is a phenomenon that occurs when the temperature in an urban area becomes higher than that in a suburban area. Moreover, as urbanization advances year by year, the area of the high-temperature zone continues to increase.

The regional difference and time change of the temperature, which vary from hour to hour, are typical indexes used to indicate the UHI. While there are geographical factors that cause long-term fluctuations, artificial factors that cause short-term fluctuations also exist; therefore, we cannot fully understand this phenomenon by simply monitoring the temperature.

Due to this, the numbers of days classified according to the day-to-day minimum and maximum temperatures in a year or in several months are sometimes used as a standard of climate change and the UHI. Furthermore, the degree hour (DH), which is an index for quantitative evaluation that uses both intensity and the number of hours beyond a certain constant temperature (the threshold), can show the characteristics of an urban area better.

Keywords Urban heat island • Air temperature • Thermal pollution • Urban climatology

5.1 Introduction

"Global warming" is a large scale climate change caused by greenhouse gases; as is increasingly widely known, many experts, including the Intergovernmental Panel on Climate Change (IPCC), are now clarifying this. Global warming progresses on the long-term scale, and therefore, our concern is that the warming progresses so slowly that people easily become accustomed to the temperature change and do not

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_5

recognize the problem in daily life. The day may come when we get into serious situations unawares and unprepared.

Changes in the thermal environment do not, however, necessarily occur only on a global scale. We cannot ignore the likelihood that a thermal environment change may occur in a local urban area. This phenomenon is called the "urban heat island (UHI)," where the temperature of a specific urban area greatly increases as compared with the neighboring areas of the suburbs by a mechanism different from global warming. The name "heat island" is based on the characteristics of the phenomenon, being such that the high-temperature area looks like a '(thermal) island' in the isothermal chart drawn on a map. We can call this "local" warming as opposed to "global" warming. This phenomenon is gaining attention as an environmental problem specific to urban areas (Saitoh et al. 1996).

In global warming, the climate of the medium latitude region is coming to resemble that of the low latitude region; furthermore, warmer tropical temperatures are experienced in urban areas with a high population density and large energy consumption.

Even though not located in the tropical zone, the hot summer night of Japan is called "Nettaiya" (a tropical night in Japanese). There is no doubt that cities are following a path to the high-temperature environment no one has ever experienced.

The climate change, in an urban area caused by the UHI changes, results in changes also in people's lifestyle. Energy consumption is increased in the summer, and the influence on people's health is becoming a worrisome environmental problem with which the whole of society must cope.

5.2 Factors Influencing the Temperature

People can look back on a short-term temperature change and say that, for example, last summer was hot. However, since the temperature fluctuate over a year, the long-term change in the gradually-increased average temperature can be identified only by taking measurements. Therefore, it is necessary to continue measurements at specified places and times over a long period. Furthermore, the measurement points must be well chosen according to the purpose. The temperature index depends on both the increment due to global warming and the increment due to local warming. For example, it is important to compare cities and suburbs to extract heat island effects.

The temperature observation points that IPCC cites to monitor global warming are chosen such that they exclude urban areas in order to remove the influence of urbanization.

In addition, the characteristics of the geography–for example, the closeness to the sea, rivers, or mountains–greatly affect the temperature. Furthermore, an urban area contains industrial, business, and residential areas, where there are differences in the ground surface structure and the amount of artificial exhaust heat. It is thus important to measure the temperature and the temperature difference in the various areas to decide whether the temperature increase is caused by the natural geography or the artificial difference in the environment, and to take measures to prevent its worsening due to human activities.

5.3 What Causes the Problem?

As the heat island effect increases during the day in summer, the temperature of the building surfaces and the road surface in an urban area becomes high, and the energy consumed by the air-conditioners for cooling buildings and cars increases. The energy consumption per unit area becomes large in the urban area, where buildings are concentrated and there is a large population. Furthermore, due to the influence of heat storage in the day, the time during which air-conditioners are used at night increases.

In particular, in the urban area, windows are normally closed for crime prevention and thus buildings do not actively take in fresh air early in the morning when the temperature is low.

The increase in the energy consumption is not the only problem. If extremely hot days continue, more patients with heat stroke are seen. In recent years, the statistics for the number of patients transported by ambulance services have been publicized (see Table 5.1).

It should be noted that the number of patients does not include the non-emergency patients to whom appropriate treatment for a medical condition is provided by medical institutions or those who personally avoid the crisis by taking appropriate measures. In particular, in a densely populated urban area, it is considered that more people become sick in places such as event sites, amusement parks, and sports stadiums, where many people congregate.

Table 5.1 Increment of heat stroke patients transported to hospitals in Osaka City. The resident population in Osaka City is about 268 million people

Year	Number of patients			Patients per million		
	Male	Female	Total	Male	Female	Total
2002	137	47	184	107.2	35.2	70.4
2003	105	21	126	82.1	15.7	48.1
2004	135	66	201	105.5	49.1	76.6
2005	129	43	172	100.8	31.9	65.4
2006	173	67	240	135.1	49.5	91.1
2007	230	109	339	179.0	80.2	128.3
2008	308	105	413	239.2	77.0	155.8
2009	144	49	193	111.5	35.8	72.6
2010	684	300	984	528.7	218.7	369.2
2011	510	267	777	393.5	194.3	290.9
2012	510	238	748	392.5	172.7	279.4
2013	799	472	1,271	613.7	341.6	473.6

Data source: National Institute for Environmental Studies Japan

It is not an exaggeration to say that the lives of elderly people, patients with diseases, e.g., cardiac disease, and infants with imperfect thermoregulation, are in danger due to the extreme heat in the urban area, even in ordinary homes.

To mitigate the seriousness of the heat island effects, it seems essential to take effective measures to prevent health damage due to the "thermal pollution" before attempting to create a comfortable environment. In addition, it has been pointed out that it is possible that, due to global warming, insects, and microbes of the tropical zone, which cannot live in colder areas, live and reproduce in the middle latitude zone (Bradley et al. 2005). Furthermore, in sewage pipes and underground shopping areas, it is suggested that the temperature increase of urban areas has affected the native habitat of living things.

5.4 Monitoring the Temperature

In order to measure the temperature distribution in the urban area exactly, it is necessary to equalize the conditions of the thermometers placed at multiple measurement points. The temperature measurement is easily affected by the sunlight and light reflection from the ground. In order that the box or tube housing a thermometer is not heated by the sunlight, it is necessary to use a reflective material and a natural or forced ventilation system.

For accurate comparison between measuring points, it is necessary to arrange the installation of instruments at a specified height from the ground, where the ground is covered by neatly trimmed grass, and the wind speed and direction are typical of the area. However, it is difficult to secure a large number of measurement locations with equivalent conditions in the urban area where buildings are concentrated. Therefore, as a relatively appropriate measurement point, we use a thermometer shelter placed in an elementary school for the study of weather. In addition, it would be appropriate for the measurement to be taken every 10 min or less to evaluate the temperature quantitatively.

If we focus on the measurement of the summer temperature, the hottest month may vary with the year. In Japan, we need to measure the temperature for at least 3 months. In Japan, August is the hottest month on average, but the timing of hot days may shift to the end of July, or early in September. The reason for this is that the El Nino and La Nina climate patterns vary with the year, and the westerly winds, the windy areas, and the pressure patterns also vary from year to year. Moreover, the number of typhoons and their courses influence the temperature of that year.

Although we can grasp the temperature distribution in the area through observations at given times, we can average the temperature over a fixed period of time through consecutive measurements to grasp the temperature distribution in the area more accurately. In addition, the space-time distribution, in which the time is divided into time zones (day and night), is important for predicting the mechanism of the phenomenon (Masumoto et al. 2006).

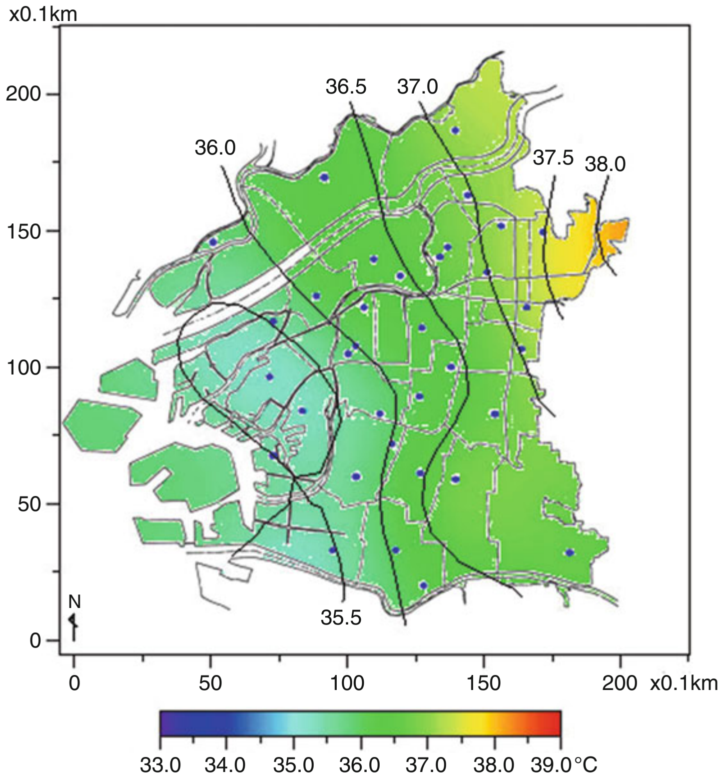

Fig. 5.1 Contour map in Osaka City of air temperature, Aug. 16, 2007 at 14:00 by 43 monitoring stations. In the daytime, the sea breeze blew from the west to the east and it was cool around the harbor

In the daytime temperature distribution of a particular day, the temperature was low in the western area close to the sea and high in the east inland region. On the other hand, it is indicated that the temperature was highest in the central part of the city during the night to early morning (Masumoto 2009b) (Figs. 5.1 and 5.2).

5.5 Evaluating the Temperature

It was shown in earlier studies that the size of the urban area is related to the heat island intensity, in other words, the temperature difference between the urban and suburban areas (Oke 1973). This is an indicator to show us the UHI. However, it is important to carefully select locations and times that are representative of their thermal environment when using this indicator.

For evaluating the temperature, the simplest method is to count the number of days in which the daily maximum temperature and the daily minimum temperature

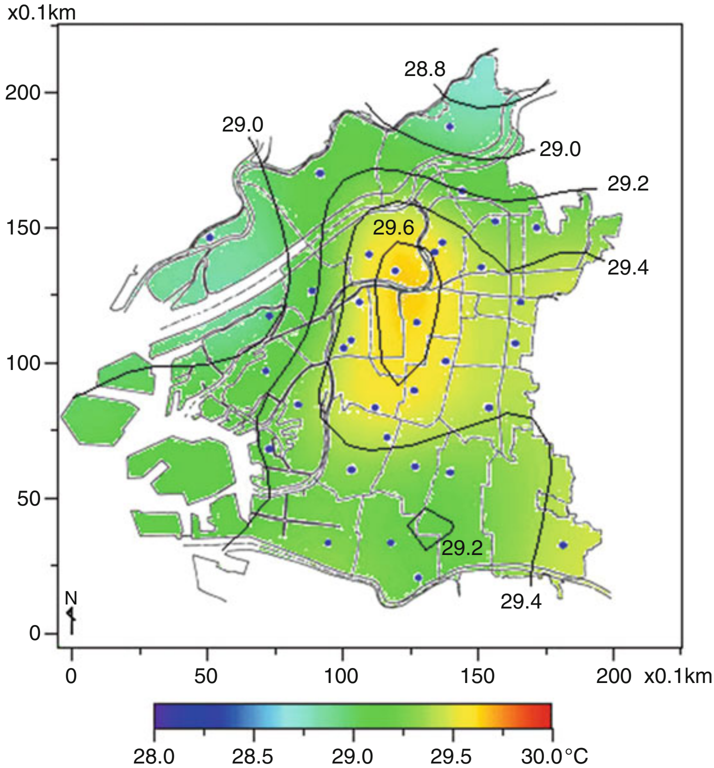

Fig. 5.2 Contour map in Osaka City of air temperature, Aug. 17, 2007 at 2:00 by 43 monitoring stations. In the nighttime, the wind was calm and it was hot in the central area

exceed the respective threshold values. The index by class is actually reported with an expression such as "This year was hotter than last year," so that ordinary people can easily understand. The Meteorological Agency (JMA) of Japan defines some classes of summer temperature.

Regarding daytime temperature, we call a day when the highest temperature is equal to or over 30 °C "Manatsubi," which means "midsummer's day" in Japanese. Furthermore, we call a day when the highest temperature is equal to or over 35 °C "Moushobi," meaning "extremely hot day." On the other hand, we call a night when the lowest temperature is equal to or above 25 °C "Nettaiya," which means "tropical night." However, these expressions are not good enough to be used as indexes to classify the recent hot summer nights of the cities. During the last few decades, almost every August night has become sultry. Thus, it is necessary to examine the change in a number of consecutive tropical nights using another index. For example, a new index may be evaluated using another class for the analysis: "Extremely hot night", where the daily minimum temperature is equal to or over 28 °C.

In the urban area, heat islands may be formed even in the winter season; we call the night when the lowest temperature is less than 0 °C “Fuyubi,” which means “winter night” in Japanese. However, evaluation by the number of nights or days is not good enough for quantitative analysis without considering the thermal intensity and the period.

Using the degree hour, DH, as an index for a more quantitative evaluation, it becomes clear that there are areas with different thermal intensities within an area where every night is hot (Masumoto 2009a). The DH value was calculated for each class using

$$\text{Degree Hour} = \int_{h_1}^{h_2} (\text{temperature} - \text{Tc})\, dh \quad (^{\circ}\text{C hour}) \tag{5.1}$$

where T_c is used by each class, as shown in Table 5.2;

We evaluated the number of days or nights and the DH distribution contour map, according to class in August in the city of Osaka (see Figs. 5.3, 5.4, 5.5, and 5.6) (Osaka City Institute of Public Health and Environmental Sciences 2011).

Table 5.2 Four classes used for evaluation of daily air temperature

Time zone	Class “Defined name in Japanese”	T_c (°C)
Day h = 7:00–19:00	“Manatsubi”: midsummer’s day	$T_{max} \geq 30$
	“Moushobi”: extremely hot day	$T_{max} \geq 35$
Night h = 19:00–7:00	“Nettaiya”: tropical night	$T_{min} \geq 25$
	Extremely Hot Night[a]	$T_{min} \geq 28$[b]

[a]Undefined by Japan Meteorological Agency
[b]Japan Ministry of the Environment recommends that the temperature of air conditioning should be set to 28 °C in the summer

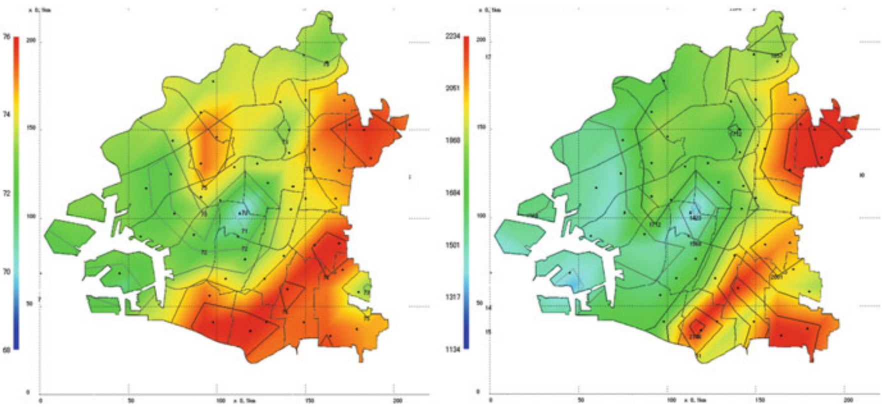

Fig. 5.3 Contour maps in Osaka City of “Manatsubi” days (*left*) and the DH (*right*) accumulated during the summer (July, August and September in 2010)

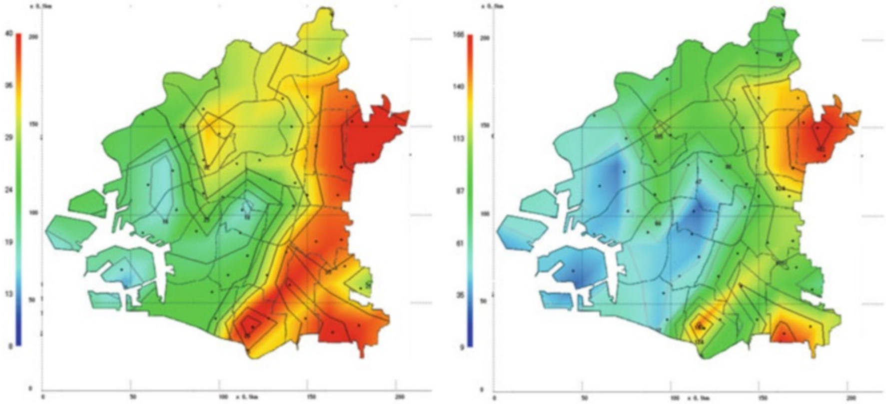

Fig. 5.4 Contour maps in Osaka City of "Moushobi" days (*left*) and the DH (*right*) accumulated during the summer (July, August and September in 2010)

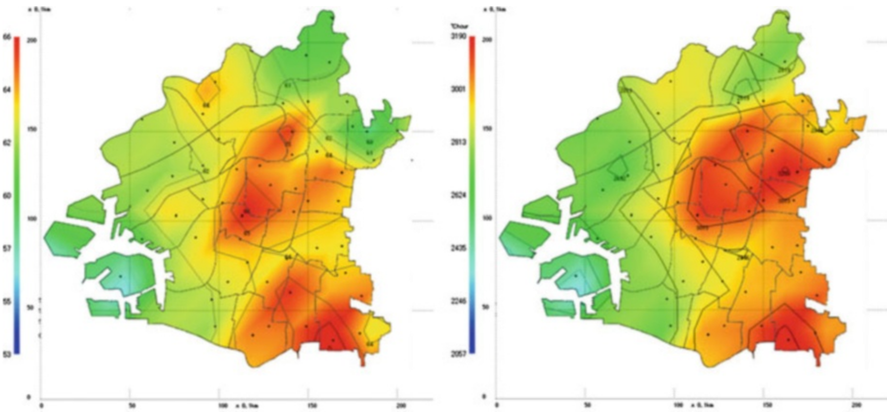

Fig. 5.5 Contour maps in Osaka City of "Nettaiya" nights (*left*) and the DH (*right*) accumulated during the summer (July, August and September in 2010)

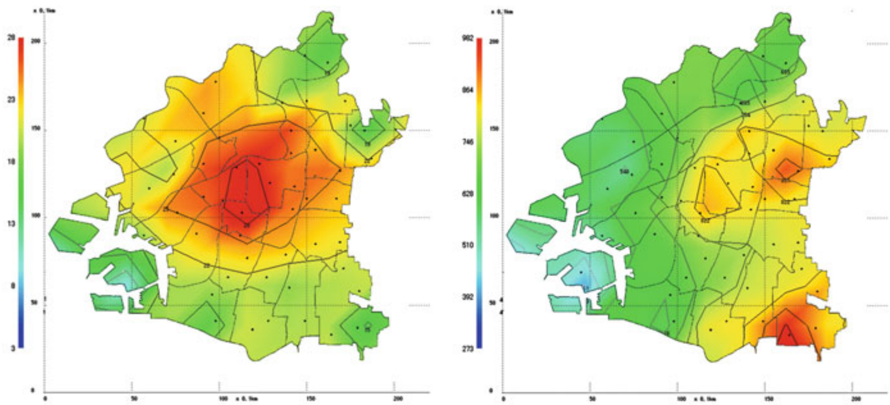

Fig. 5.6 Contour maps in Osaka City of Extremely Hot Nights (*left*) and the DH (*right*) accumulated during the summer (July, August and September in 2010)

For example, the DH is compared with the number of nights for the class of "Extremely hot nights"; although not remarkable, the DH showed that the temperature in east area was high (see Fig. 5.6).

This situation showed that the daytime heat may influence also nighttime temperatures. In other words, the results according to the quantitative index, DH, are different from those of the temperature distribution at a specific time and the index of the number of days or nights according to classes. Thus, as an index of UHI, the DH according to the temperature class can express the local characteristics more accurately than can the number of days. In addition, the evaluation of hot nights is as important as that of hot days, and, depending on the area, it is necessary to use the index to choose appropriate measures.

5.6 The Measures to Solve the Problem

In order to suppress UHI, it is necessary to take short-term measures in a relatively small area that are different from anti-global warming measures: using high-reflection materials to cover the building and the ground surface of roads, increasing the green space and the water surface, and creating an area well-ventilated by land and sea breezes.

In order to judge whether the measures for the area are appropriate and whether they achieve fruitful results, an effective means is a quantitative evaluation using the temperature indexes discussed above.

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Chapter 6
Tsunami

Robert H. Armon

Abstract Tsunami is a sudden, rapid and disastrous phenomenon that is very difficult to forecast earlier. However, with the development of GPS and other satellite linked system it is possible to detect/indicate potential tsunami formation based on ocean waves increased pressure or other phenomena such as: earthquakes or volcanic eruption that may release compounds that can be detected with certain sensors.

Keywords Tsunami • Harbor wave • Earthquakes • Volcanic eruptions • Magnitude • Radon

6.1 Background

Undersea earthquakes can displace large volumes of water, generating waves. Tsunami (in Japanese "harbor wave") is an abnormal sea wave with a very long wavelength that is caused by such undersea earthquakes, reminiscent of a fast rising tide. Tsunami wave heights can reach tens of meters along a time interval from minutes to hours. Offshore, a tsunami displays a small amplitude with a very long wavelength up to hundreds of kilometers (regular ocean wavelengths are in the range of 30–200 m!), which is difficult to detect when on board a ship. In shallow waters (close to shore), the tsunami wave amplitude increases significantly, which explains its destructive power. Figure 6.1 describes the formation of tsunami schematically. Briefly, when two tectonic plates located under the sea move abruptly, a large volume of water is displaced upward forming a wave that can move in all directions (concentric circles). There are many articles describing this phenomenon that generates a highly destructive power (e.g., 2004 Indian Ocean tsunami caused >230,000 casualties in 14 countries bordering this ocean) (Stein and Okal 2005). Different data on the 2004 Indian Ocean tsunami revealed several remarkable facts: (1) the earthquake energy was equivalent to a 23×10^3 Hiroshima-type atomic bomb ranked 9.0 (Richter scale); (2) the tectonic plates in the area built up the pressure for thousands of years and still continue the process, increasing the feasibility of future tsunamis;

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_6

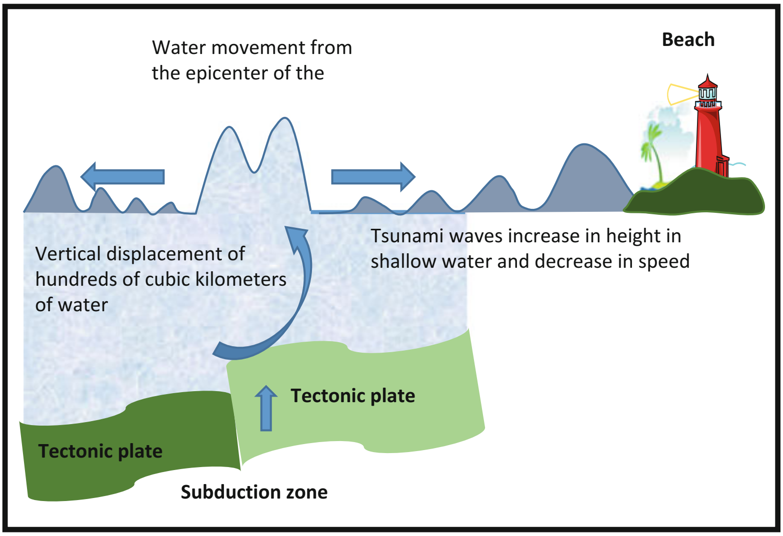

Fig. 6.1 Schematic representation of tsunami formation with its epicenter

(3) the rupture caused by tectonic movement was >600 miles long with a possible seafloor displacement of 10 yards horizontally and several yards vertically, resulting in the movement of trillions of tons of rock along hundreds of miles; and (4) due to its power, the Indian Ocean tsunami traveled as far as 3,000 miles to Africa with sufficient force to be environmentally destructive (human lives and property destruction) (Anonymous 1 2013; Anonymous 2 2013).

6.2 Phenomena Linked to Tsunami Formation

The events that can trigger tsunamis are listed in Table 6.1. There are five events that have enough energy to produce waves of tsunami magnitude: landslides, earthquakes, volcanic eruptions, underwater explosions (mainly atomic tests), and meteorites.

6.3 Scales of Intensity and Magnitude

As for earthquakes, it is important to determine different measures of intensity and magnitude for tsunamis to allow events comparison. The intensity scale used by NGDC/NOAA is the Soloviev-Imamura tsunami intensity scale according to the following formula:

$$I = \frac{1}{2} + \log_2 H_{av} \quad \text{or} \quad i_s = \log_2\left(\sqrt{2}\,H\right)$$

where H_{av} is the average wave height along the nearest coast (Soloviev 1970). This scale is used in the global tsunami catalogues as the main parameter for the size of

Table 6.1 Phenomena (sources) capable of forming tsunami or tsunami-like waves

Phenomena	Location	Year	Magnitude	Damage	Reference
Landslide	USA, Lituya Bay, Alaska	1958	Unknown; maximum wave height of ~ 518.16 m	2 dead 60 m inland zone of stripped vegetation	Tocher and Miller (1959)
Earthquake	Near the east coast of Honshu, Japan; Tōhoku earthquake and tsunami	2011	9.0 Mw = Moment magnitude Centred 129 km east of Sendai, Honshu, Japan, at a depth of 30 km	18,184 dead 2,668 missing	Urabe et al. (2013)
Volcanic eruption	Indonesia, Krakatau in the Straights of Sunda, between Java and Sumatra	1883		36,417 dead	Carey et al. (2001), Verbeek (1884)
Underwater explosion	USA, Marshall Islands	1940–1960	Nuclear experiments		Stanley (1999)
Meteorite impact	Mexico, Yucatan Peninsula	Cretaceous Period, ~ 65 Ma ago	Unknown	Deposits all along the Gulf coast of Mexico and the United States	Schulte et al. (2012)

the tsunami expressed as intensity. The ML scale proposed by Murty and Loomis (1980) based on the potential energy (ergs) was the first scale that genuinely calculated a magnitude of a tsunami, rather than its intensity at a particular location.

$$\mathbf{ML} = \mathbf{2} \left(\mathbf{log}\ \boldsymbol{E} - \mathbf{19}\right)$$

where E is the tsunami potential energy. However, measuring potential energy is not an easy task, and therefore, Shuto (1993) proposed a particular scale measuring tsunami size, considering it as an intensity scale:

$$\mathbf{i} = \mathbf{log_2}\, \boldsymbol{H}$$

where H is the local tsunami height (in m). This is still a magnitude scale, and therefore, Shuto proposed defining H in relation to its possible impact; accordingly, H is taken as the tsunami crest height above the ground level at the shoreline for the tsunami profile and damage to fishing boats, the inundation height for damage to an individual house and the effectiveness of a tsunami control forest, and H as the

Table 6.2 Potential correlation between the proposed intensity domains, I, and the quantities H and I introduced in formula $i = \log_2 H$ by Shuto (1993)

I (intensity proposed)	Effects on humans, objects, nature and buildings	H (m)	*i*
I–V	Not, scarcely, weakly felt, largely observed, and strong	<1.0	0
VI	Slightly damaging	2.0	1
VII–VIII	Damaging, heavily damaging	4.0	2
IX–X	Destructive, very destructive	8.0	3
XI	devastating	16.0	4
XII	Completely devastating	32.0	5

maximum tsunami crest height above the m.s.w (mean sea waves) level at the raft location for damage to an aquaculture raft (Table 6.2) (Shuto 1993).

Technical hitches in calculating the tsunami's potential energy meant that this scale was rarely used. Abe introduced the *tsunami magnitude scale* M_t, which is calculated according to

$$M_t = a \log h + b \log \Delta + D$$

where h is the maximum tsunami-wave amplitude (in m) measured by a tide gauge at a distance R from the epicenter, Δ is the distance (in km) from the earthquake epicenter so that make the M_t scale matches the moment magnitude scale as closely as possible (Abe 1995a, b).

6.4 Tsunami Real Time Warning/Indicator System

Perhaps the best warning/indicator system available today is the DART® (Deep-ocean Assessment and Reporting of Tsunamis) system that is able in real time to detect abrupt changes in an ocean wave's height (Fig. 6.2) (Green 2006). The system uses satellite technology to transmit online seafloor bottom pressure. An anchored seafloor bottom pressure recorder (BPR) and a companion moored surface buoy are connected through an acoustic link that provides real-time communications. The BPR collects temperature and pressure measurements at 15-s intervals. The pressure values are corrected for temperature effects and the pressure converted to an estimated sea-surface height (height of the ocean surface above the seafloor) by using a constant 670 mm/psi. The system has two data reporting modes, standard and event. The system operates routinely in standard mode, in which four spot values (of the 15-s data) at 15-min intervals of the estimated sea surface height are reported at scheduled transmission times.

When the internal detection software identifies an event, the system ceases standard mode reporting and begins event mode transmissions. In event mode, 15-s values are transmitted during the initial few minutes, followed by 1-min averaged values. Event mode messages also contain the time of the initial occurrence of the event. The system returns to standard transmission after 4 h of 1-min real-time transmissions if no further events are detected (Gonzalez et al. 1998).

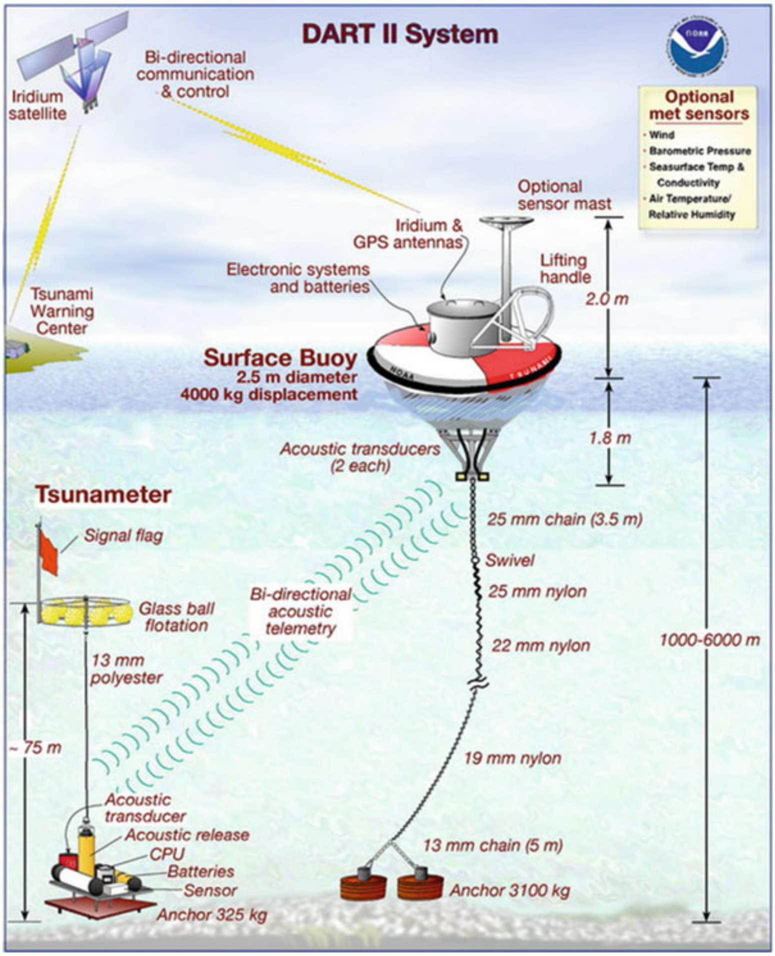

Fig. 6.2 DART® (Deep-ocean Assessment and Reporting of Tsunamis) warning system to detect sudden changes in ocean waves height (With permission from NOAA-National Oceanic and Atmospheric Administration)

6.4.1 Tsunami Potential Indicators

It is difficult to talk about certain tsunami indicators since this phenomenon is a sudden, unpredicted event whose duration is very short on the geological time scale (a classic wave period of a destructive tsunami is about 12 min). Consequently, almost all indicators are merely warnings and do not fit accurately the indicator role. Some of them can be used as indicators of potential future tsunami events based on sedimentology, tectonic plates, chemical composition alterations, etc.

From the surveillance point of view, shore wave behavior can be a mark indicative of a tsunami, according to the wave arrival form. Waves have positive and negative peaks (ridges and troughs), and therefore, the first form to reach the land will impact the event. For example, when a ridge arrives, the first event will be a massive breaking wave or a sudden flood; however, if a trough arrives a dramatic drawback of the shoreline will be observed, exposing submerged coastline. The shoreline retreat can exceed hundreds of meters. Again, these are short lived warnings and cannot be considered long term indicators; however, they may be considered as indicators of sudden ocean geophysical changes, which is the case of tsunami!

Ruiz et al. (2010) described the taphonomical analysis of ostracods records as tsunami tracers in holocene tsunami deposits. Based on salinity changes due to sea water floods during a tsunami, these authors showed several phenomena, such as temporal colonization of brackish species, presence of bioclastic layers with increasing diversity, and littoral erosion with sandy spits and azoic ridges deposition. Another taphonomical study revealed that foramenifera can also be used as tsunami indicators in a shallow arid system lagoon (Pilarczyk and Reinhardt 2012). In this study, predominant marine taxa (Amphistegina spp., Ammonia inflata, and planktics) were found to be abundant in tsunami beds indicating a marine source for the sediment. The authors concluded that "foraminiferal analysis, when combined with other proxies (e.g. mollusc taphonomy, particle size distribution), can be used to delineate tsunami units from normal background sedimentation in intertidal systems" and hence to detect older tsunami events.

Inan et al. (2012) reported a chemical analysis over ~5 month (from September 2011 to January 2012) of the spring water of a natural spring located <20 km from the epicenter of an earthquake (Mw = 7.2) that took place on October 2011 in the eastern part of Turkey. Pre-earthquake samples revealed an increase in Ca^{+2}, Mg^{+2}, K^+ and Cl^- content and a decrease in Na+ and $SO_4{}^{-2}$. Post-earthquake (3 months after the seismic event) samples showed an opposite trend (Ca^{+2}, Mg^{+2}, K^+, Cl^- ↓ and Na+, $SO_4{}^{-2}$ ↑). The authors suggest that these measured chemical anomalies could be used as geochemical pre-earthquake indicators.

Jankaew et al. (2008) suggested swales (a marshy depression between ridges) stratigraphy as an indicator of a tsunami prone area. In their article, the authors described a sand layer, 5–20 cm thick, along a 20 km plain, which coated ridges and intervening swales during the 2004 Indian Ocean tsunami. A study of deeper layers in the peaty soils of two marshy swales found that a precedent sand layer has been preserved as the remains of previous tsunami events, with the most recent occurring "about 550–700 years ago." A related concept based on ocean sedimentology was proposed as an indicator of tsunami potential occurrence (Tachibana 2013). Lonestones had attracted attention as glacial indicators in paleoclimatic studies and were usually inferred to be iceberg-rafted dropstones. The author described lonestones found in deposits from Early Miocene deep-sea sedimentary rocks present around the Chita Peninsula of central Japan, but suggested a different explanation for their presence not related to icebergs and cold climate. Tachibana's (2013) explanation is that "tsunami-induced flows or high-energy episodic currents on the sea bottom may also form lonestones." According to their deposition formation, lonestones are associated with sandy to gravelly deposits (in the form of multiple stacking of normally graded units, and the laterally discontinuous distribution of coarse-grained clastic material such as sand and gravel) consistent

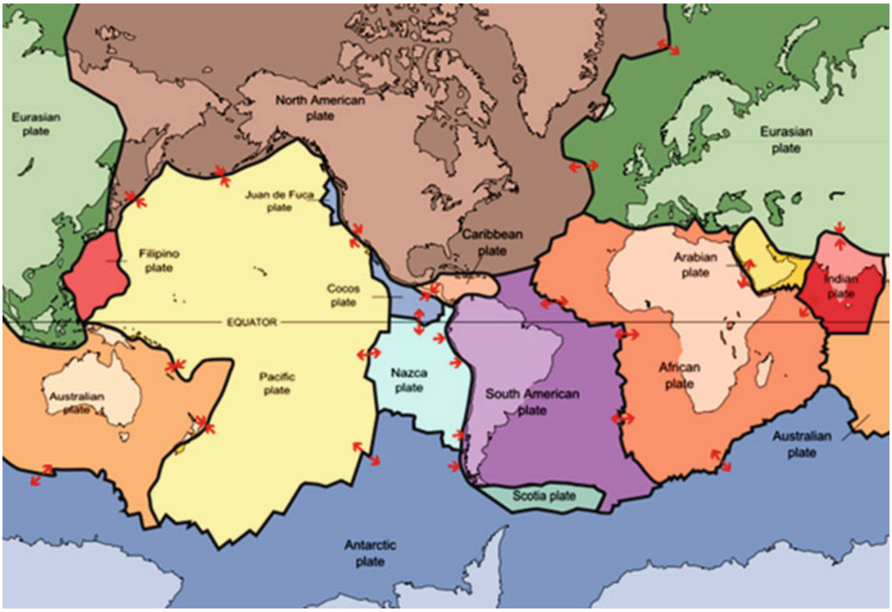

Fig. 6.3 Global tectonic plates and their convergent boundaries (With permission from USGS)

with tsunamis' deposition! On the macro-scale of tectonic plates, the subduction process occurs at convergent boundaries (Fig. 6.3). The subduction rate is commonly measured in centimeters/year with the convergence average rate of ~2 to 8 cm per year. Cummins (2007) showed several indicators that suggest a high potential for a giant earthquake along the coast of Myanmar. The proposed indicators were a tectonic environment, as compared to other subduction zones, and stress and crustal strain observations that indicate a locked seismogenic zone.

Another interesting tracer/indicator of tsunami formation that should be taken in consideration is the inert gas of radon. ^{222}Radon, or in short ^{222}Rn (half-life of 3.8 days) is the decay product of radium ^{226}Ra (a stable isotope with a half-life of 1,601 years) released into the environment from earth crust volcanic and earthquake activities. The usefulness of ^{222}Rn, a radioactive inert gas, as a tracer for mixing rate studies in fluid boundary layer regions has been well demonstrated (Chung and Kim 1980). The measurement of radon in water is relatively simple as compared to that in air. The rate and magnitude of variations are much lower, and there are fewer sampling problems. All methods require correction for decay of radon during the decay between sampling and analysis (Cothern and Smith 1987). In their study, Chung and Kim (1980) showed excess ^{222}Rn in the benthic boundary layer (50–100 m) in the western and southern parts of the Indian Ocean. A comparison of the Atlantic and Pacific oceans revealed that ^{226}Ra is uniformly distributed in the surface water of both (4×10^{-14} g/l). However, the deep Pacific has a four times higher concentration of ^{226}Ra and the Atlantic twice higher as compared with their surface water concentrations (Broecker et al 1967). Their explanation for this

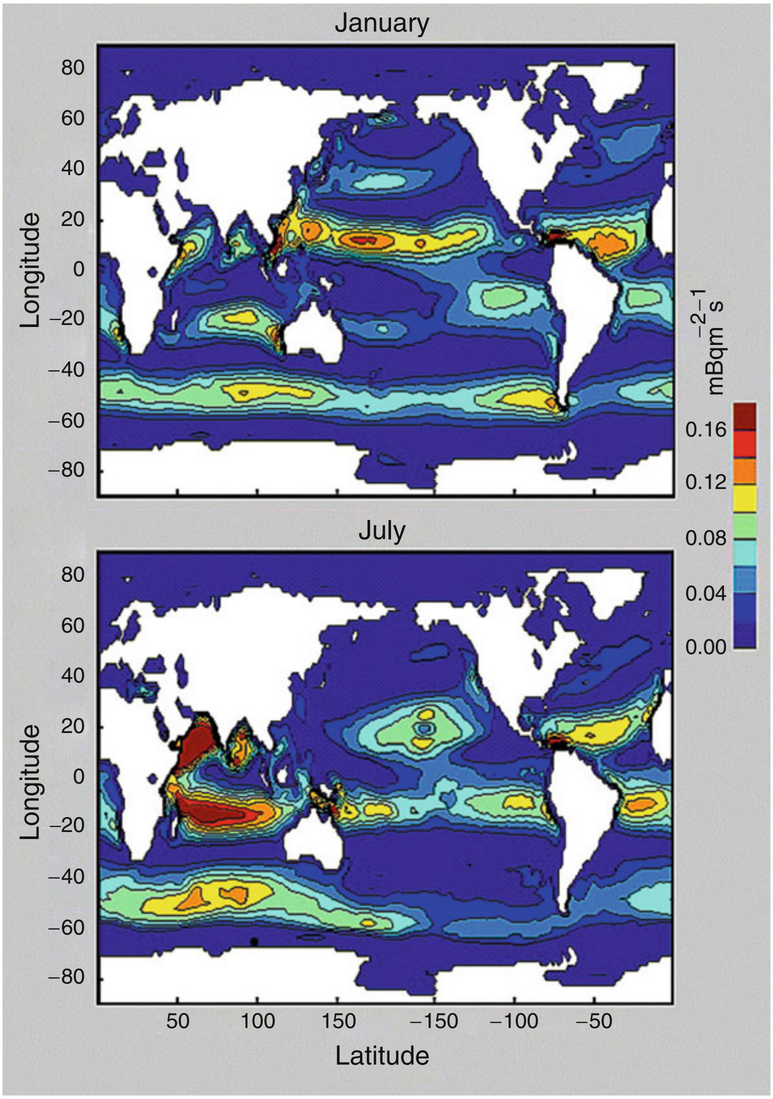

Fig. 6.4 Global radon flux density (for January and July) based on model predictions (With permission from Schery and Huang 2004)

phenomenon was that the Pacific Ocean has a threefold longer deep water residence time as compared to the Atlantic for ^{226}Ra, and its ^{222}Rn coefficient of vertical eddy diffusion is more than twice as high. Schery and Huang (2004) estimated the global distribution of radon emission from oceans. The estimated radon flux showed a high variation between seasons (January and July) strongly dependent on surface winds. However, it is interesting to see that, in July, an increased flux of ^{222}Rn can be found in the Indian Ocean where the most devastating Tsunami took place (Fig. 6.4).

The suggestion that that this increased flux of radon is linked to seismic activity in this region, in combination with Chung and Kim's (1980) data, is interesting. It may be possible that radon is an efficient indicator of deep ocean seismic activity that can be used to predict/indicate tsunamis formation! Supporting evidence of this phenomenon has been presented by Gervino et al. (2012), who measured radon emission from soil located at Stromboli Island from 2002 up to 2007. The authors observed that major eruptions were preceded by radon emission anomalies at three summit stations (reaching values of 20,000 Bqm^{-3}). The main question still to be answered is: is radon emission in the deep ocean a good indicator of tectonic activity in a subduction zone?

6.5 Biota Behavior as a Potential Indicator of an Approaching Tsunami

There is some apparent evidence that animals may sense natural disasters (i.e., seismic activity, tsunamis, fires, etc.) (Bhargava et al. 2009; Grant and Halliday 2010; Grant et al. 2011). However, there is no conclusive evidence as to how animals may be able to sense earthquakes, and therefore, the U.S. Geological Survey (USGS) officially states: "changes in animal behavior cannot be used to predict earthquakes" (Tiwari and Tiwari 2011). Several concepts have been suggested to explain how animals may be able to detect natural disasters based on: ground tilting (vibrations), humidity changes, earth gases release, electrical currents, and magnetic field variations.

For example, Wikramanayake et al. (2006) presented data from two satellite-collared Asian elephants that ranged close to the tsunami impact area in Sri Lanka during the Asian tsunami of 26 December 2004. Their data indicated "that neither elephant behaved in a manner consistent with a "sixth sense" that allowed an early detection of the approaching tsunami". Garstang (2009) pointed out that there is "no need to call upon some unknown sixth sense to explain how elephants might detect and respond to such an event," emphasizing that a tsunami of the magnitude of that occurring on December 26, 2004 could produce signals that elephants can detect. According to the scientific literature, it is likely not only that elephants would react to unusual stimuli but also that they have the cognitive capability to draw deductions from simultaneous multiple inputs (Bates et al. 2008).

An interesting concept was presented by Kirschvink (2000) in a brief review titled "Earthquake Prediction by Animals: Evolution and Sensory Perception." The author emphasized the evolutionary potential of animals to predict earthquakes based on the general rule "that genes that control evolutionarily ancient processes evolve much more slowly, and are influenced far less by genetic drift, than are more recent additions to the genome". Hence, one would expect a seismic escape response system to be evolutionarily conserved. It is generally accepted that many animals sense an earthquake some minutes before humans do. Briefly, most

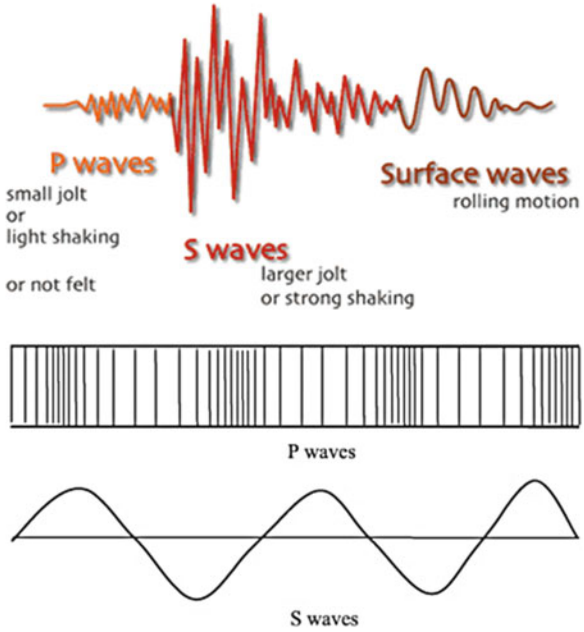

Fig. 6.5 P waves and S waves have different speeds and wave actions

unusual animal behavior reported before earthquakes coincides with the arrival of P-waves, which travel faster than the damaging S-waves (2–4 km/s faster) (Fig. 6.5). Subject to distance from the epicenter, P-waves can be felt seconds to minutes before an earthquake. The response to P-waves is not a real predictive response, but rather an "early warning system" (Kirschvink 2000; Grant and Halliday 2010).

Finally, the author suggested enhancing the scientific foundation by creating dense monitoring networks in seismically active regions based on animals' tilt, hygroreception (humidity), electric, and magnetic sensory systems. This concept has been recently supported by Meenakshi and Juvanna (2013), based on their recommendation to monitor unusual animal behavior as a predictor of tsunami through analysis of the sensory organs of animals that are able to monitor and sense stimuli preceding an earthquake. Yet, hard evidence is still missing, and therefore, animals' behavior monitoring prior to earthquake is still circumstantial.

6.6 Summary

As indicated earlier, there are two roles for indicators of tsunami occurrence: (1) indication of past tsunami events through taphonomical analysis and ocean sedimentology; and (2) direct, real-time detection of tsunamis through monitoring deep ocean earthquakes, online seafloor bottom pressure (DART®), and prospective radon released from tectonic activity at subduction zone. For the time being, in spite of local reports, there are no organisms that may be used as tsunami indicators, and more scientific research is needed.

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Part III
Conservation

Chapter 7
Species Extinction Indicators

Robert H. Armon

Abstract There are many environmental causes to species extinction. Some foreseeable and some unpredictable; those foreseeable are mainly of human activity origin such as pollution while those unpredictable are Mother Nature vagaries such as earthquakes or volcanic eruption. Species extinction is the process whereby a last member of a species dies and therefore no individuals able to reproduce and continue the genetic entity preserved in their genes remain. The definition includes also the situation where only a few individuals from a certain species persist lacking reproduction capability. It should be mentioned that, while species extinction has been a normal part of evolution measured in thousands of years, under human activities and modifications the evolutionary time scale has dropped to a few centuries. This acceleration was caused by several drivers, among which habitat loss, overharvesting, pollution, and climate change are the principle ones. The first three drivers are frequently caused by human activity, while the fourth is also constantly affected by humans. Among the primary consequences of rapid extinction are disruptions to pollination, seed dispersal, scavenging potential, and vital ecological processes.

Keywords Species • Extinction • Endemism • Taxonomic groups • Fragmentation • Consumption • Biodiversity • Evolution

7.1 Background

By definition, species extinction is the process whereby a last member of a species dies and therefore no individuals able to reproduce and continue the genetic entity preserved in their genes remain. The definition can be extended even to the situation where only a few individuals from a certain species persist, which, however, lack reproduction capability, and therefore, no new generations are produced (attributable to scant distribution, poor health, and disparity in sexes, in case of sexual reproduction). There are many causes/threats leading to species extinctions as summarized in Table 7.1. Nevertheless, it should be mentioned that, while

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_7

Table 7.1 Threats that impact species extinction processes

Threat	Additional factors linked to	Examples	Forms	Organisms affected	References
Human settlement	Urban, industrial, and recreational areas	The Javan tiger (*Panthera tigris sondaica*) *Acalypha rubrinervis* (string tree or stringwood) from the spurge family (*Euphorbiaceae*) 1860	Cities, highways, dams, bridges, electricity, transportation, etc.	Mammalian, birds, reptiles, amphibians, fish, insects	McKee et al. (2004) and Park et al. (2003)
HPD (human population density)					
Intensive agriculture	(Silviculture, Mariculture Aquaculture)	The Hokkaidō wolf, known in Japan as the Ezo wolf (*Ezo Ōkami*, *Canis lupus hattai*) 1889	Annual & perennial non-Timber crops; Wood & pulp plantations; Livestock farming & ranching; Marine & freshwater Aquaculture	Plants, fish, amphibians	Ceballos and Ehrlich (2002), Szabo et al. (2012), de Baan et al. (2013), and Lenzen et al. (2012)
Energy production & mining	Environmental destruction		Oil & gas drilling; Mining & quarrying; Renewable energy	Plants, mammalians, birds	de Aquino-Silva et al. (2010) and Pisarsky et al. (2005)
Transportation & service corridors	Fragmentation and obstruction	The Texas wolf (*Canis lupus monstrabilis*), also known as the Texas gray wolf, 1942	Roads & railroads; Utility & service lines; Shipping lanes, Flight paths	Mammalians, fish, birds, plants	Cagnolo et al. (2009) and Vandergast et al. (2007)
Biological resource use	Mainly human economic activities	Cry Violet, (*Viola cryana*) grew in restricted limestone outcrops in the region of Cry, France southeast of Tonnerre in department Yonne	Hunting & collecting terrestrial animals; Gathering terrestrial plants; Logging & wood harvesting; Fishing & harvesting aquatic resources	Plants, mammalians, fish and birds, insects, amphibians	Bar-Oz et al. (2011), Szabo et al. (2012), and Machado and Loyola (2013)

Human intrusions & disturbance	Mainly human economic activities	The Middle Eastern Ostrich or Arabian Ostrich (*Struthio camelus syriacus*) 1966	Recreational activities; War, civil unrest & military exercises; Work & other Activities	Mammalian, birds, reptiles, amphibians, fish, insects	Pisarsky et al. (2005)
Natural system modifications	Mainly human economic activities		Fire & fire suppression; Dams & water management/use; Other ecosystem modifications	Mammalian, birds, reptiles, amphibians, fish, insects	de Baan et al. (2013)
Invasive & other problematic species & genes	Enhanced agriculture and human economic needs (e.g., control of rat population in Hawaii by the introduction of mongoose in 1883 by sugar cane farmers; however, mongoose primarily preyed upon birds and their eggs, driving those species to extinction!)	*Nesoryzomys darwini*, also known as Darwin's Nesoryzomys or Darwin's Galápagos (its extinction was probably caused by the introduction of black rat) 1930	Invasive non-native/alien species; Problematic native species; Introduced genetic material	Birds, amphibians, fish, insects	Occhipinti-Ambrogi (2007) and Galil (2007)
Pollution	Mainly human economic activities	*Vanvoorstia bennettiana* (Bennett's Seaweed, an extinct red alga from Australia) 1886	Household sewage & urban wastewater; Industrial & military effluents; Agricultural & forestry effluents; Garbage & solid waste; Air-borne pollutants; Excess energy	Mammalian, birds, reptiles, amphibians, fish, insects	Subramanian and Amutha (2006) and Cravens (1996)

(continued)

Table 7.1 (continued)

Threat	Additional factors linked to	Examples	Forms	Organisms affected	References
Geological events	Sporadic but titanic events	Conodonts all marine reptiles except ichthyosaurs and plesiosaurs and invertebrates like brachiopods, gastropods, and molluscs were severely affected. End of the Triassic period, 252.2 ± 0.5 to 201.3 ± 0.2 Ma ago, mass extinction, particularly in oceans	Volcanoes; Earthquakes/ tsunamis; Avalanches/ landslides	Mammalian, reptiles, amphibians, fish	Barash (2012)
Climate change & severe weather	Partial human activity, partial external factors (not all known)	The golden toad (*Bufo periglenes*), also known as *Incilius aurarius*, 1989	Habitat shifting & alteration; Droughts; Temperature extremes; Storms & flooding	Mammalian, birds, reptiles, amphibians, fish, insects	Puschendorf et al. (2011)
Disease/ Epidemics	Impacted by human activity and climate change	Honshū wolf (*Canis lupus hodophilax*); mostly extinct by rabies and other factors 1905	Loss of immunological defense due to external factors	Mammalian, birds, reptiles, amphibians, fish	Pounds et al. (2006)

species extinction has been a normal part of evolution measured in thousands of years, under human activities and modifications the evolutionary time scale has dropped to a few centuries. This acceleration was caused by several drivers, among which habitat loss, overharvesting, pollution, and climate change are the principle ones (Erwin 2009). The first three drivers are frequently caused by human activity, while the fourth is also constantly affected by humans. Among the primary consequences of rapid extinction are disruptions to pollination, seed dispersal, scavenging potential, and vital ecological processes. An excellent example of the vital disruption of ecological processes is the extinction of a species involved in the spread of another species through its digestive system or its motility capability (usually between vertebrates and plants). Unfortunately, a recent study by Butchart et al. (2010) showed that most indicators of the biodiversity status (covering, e.g., species' population trends, extinction risk, habitat extent and condition, and community composition) declined, while pressure indicators on biodiversity (e.g., resources consumption, invasive alien species, nitrogen pollution, overexploitation, and climate change impacts) showed increases. It can therefore be concluded that the rate of biodiversity loss (or in other words extinction rates) does not appear to be slowing down! The extinction process linked to taxonomic groups is a remarkable topic (Fig. 7.1). There are taxonomic groups that are more threatened than others, possibly because of their ecological niche specialization as well as human impact on these particular niches, or, as will be shown later, because of specific conditions in the tropics, where most of diversity is located, mainly in the plant kingdom (Vamosi and Vamosi 2008).

According to the International Union for Conservation of Nature (IUCN), there are four criteria that impact the species extinction process: (A) reduction of land cover and continuing threat, (B) rapid rate of land cover change, (C) increased fragmentation, and (D) highly restricted geographical distribution. Using these criteria, one can predict the extent of species extinction and establish related indicators, as shown below.

Here, it should be emphasized that different indicators may change according to the species' kingdom, e.g., plants, mammals, birds, and marine organisms, under study (Fig. 7.1). These differences are based on motility, growth requirements, climate, geographical distribution, human habitation, etc. all being important factors in this "equation".

7.2 Potential Indicators

Vandergast et al. (2007) suggested the use of the southern California endemic Jerusalem cricket (Orthoptera: Stenopelmatidae: *Stenopelmatus*), focusing on this large flightless insect (more precisely the mahogany Jerusalem cricket, *Stenopelmatus 'mahogani,'* which has low vagility), as an indicator of recent habitat fragmentation, given its impact on biodiversity and subsequent link to species extinction. This insect seems to be an ideal indicator species for monitoring the genetic effects of anthropogenic habitat fragmentation in Cismontane, southern

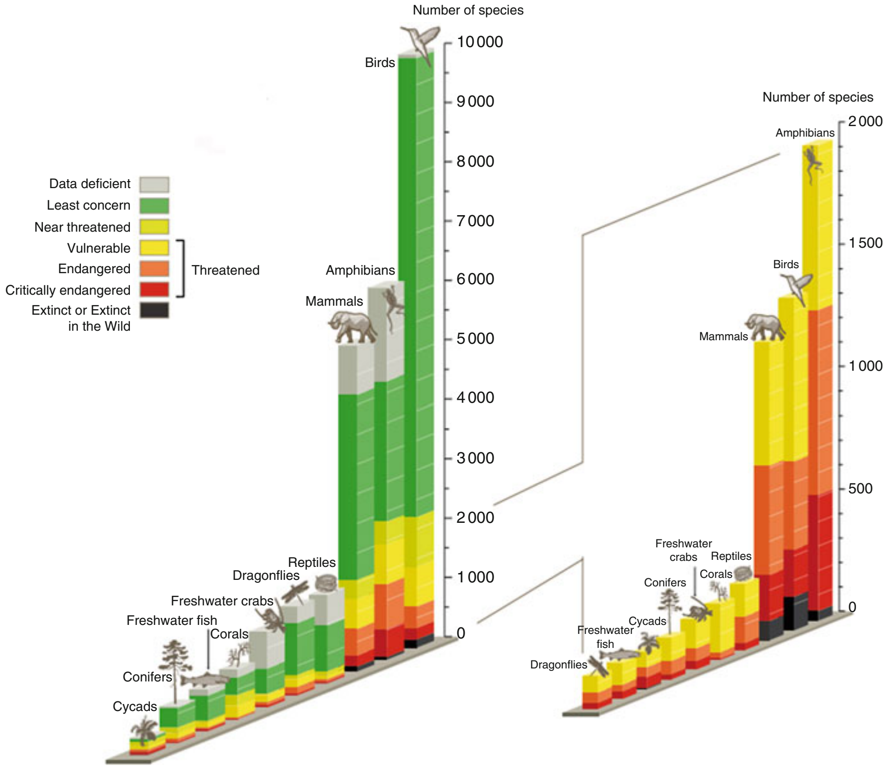


Fig. 7.1 Threat status of species in comprehensively assessed taxonomic groups (The number and proportion of species in different extinction risk categories in those taxonomic groups that have been comprehensively assessed, or (for dragonflies, freshwater fish, and reptiles) estimated from a randomized sample of species. For corals, only warm water reef building species are included in the assessment (Source: IUCN))

California. The insect analysis was performed through mitochondrial DNA (mtDNA) sequence variation in *S. mahagoni* combined with phylogenetic and population genetic approaches, simulation models, and geographical information system (GIS) to address specific questions such as: (1) Do prehistoric levels of habitat fragmentation have any impact on current patterns of genetic differentiation? (2) Has recent fragmentation increased genetic differentiation? (3) Has genetic differentiation increased significantly in the short time of the urbanization time scale? (4) Is genetic variability correlated to fragmentation magnitude?

As a result of increasing fragmentation caused by human habitat constructions, the genetic diversity has been reduced, decreasing the ability of populations to evolve and respond to ecological perturbations (as listed in Table 7.1), e.g., climate change, disease and parasites, introduced predators or competitors, habitat fragmentation, etc.

A more holistic approach has been described by Rodríguez et al. (2007), who suggested using the following criteria (indicators?) for the development of “objective, repeatable, and transparent criteria for assessing extinction risk”: (I) reduction of land cover and continuing threat, (II) rapid rate of land cover change, (III) increased fragmentation, and (IV) highly restricted geographical distribution, based on remotely sensed data (GIS). According to the authors, this approach is open to scientific debate; however, it allows a global versus regional analysis from data already present in the evaluation of species extinction risk assessment.

Geographic range is a good indicator of extinction susceptibility in fossil marine species and higher taxa (Heim and Peters 2011). In this study, covering North American and European occurrences of marine genera from the Paleobiology database and the areal extent of marine sedimentary cover in North America, these authors showed "that those endemic and cosmopolitan fossil marine genera have significantly different range-duration relationships and that broad geographic range and longevity are both predicted by regional environmental breadth." Consequently wide environmental tolerances within a distinct region predict both broad geographic range and increased longevity in marine genera over the evolutionary time interval.

Invasive species can be used as indicators of species extinction, too. An excellent example, based on invasiveness characteristics, is the crayfish *Pacifastacus leniusculus* that excluded the native white clawed crayfish *Austropotamobius pallipes*. Haddaaway et al.'s (2012) results indicate that the per capita difference (i.e., functional response) between these two species may contribute to invader success and extinction of the native species, as well as decreased biodiversity and biomass in invaded rivers. A second example is the introduction of exotic grasses in Central and South America extensive savannas by Europeans (D'Antonio and Vitousek 1992). As dominant native grasses were unable to support intensive grazing, new C_4 grasses, such as *Hyparrhenia rufa*, *Melinis minutiflora*, *Panicum maximum*, and *Brachiara* spp., were introduced to support grazing and replace cleared forests. All the above species burn readily and resprout rapidly following fire, and therefore, are capable of maintaining cleared forests and savannas as grassland, and thus preventing the return of the native flora. Another result found after the biological invasion was that *H. rufa* and *M. minutiflora* were able "to invade intact native-dominated savanna ecosystem."

On another plane, it is clear today that international trade affects biodiversity and escalates species extinction. Consequently, it can also be considered as an indicator of species extinction in developing countries (Lenzen et al. 2012). The authors, through examination of biodiversity loss as a global systemic phenomenon, found that 30 % of global species' threats (impacting extinction) are due to the international trade of coffee, sugar, tea, textiles, fish, etc. from developing to developed countries. Therefore, international trading in certain goods may indicate an endangered species threat in areas modified to boost international trade (Fig. 7.2).

Such a potential extinction indicator has been described by Morrison et al. (2007), who followed the persistence of large mammals (>20 kg) in different geographical areas, as indicators of global human impacts. Large mammals are much more vulnerable to extinction due to human activities (e.g., wolves in the UK). The study was based on historical range maps (from 1,500 A.D.) of range areas occupied by large mammals as compared with current maps, and the changes that were found. The comparison revealed that less than 21 % of the earth's terrestrial area carries all of the large mammals once held, with varying proportions from 68 % (Australasia) to 1 % in Indomalaya. Although the presence of large mammals is not a guarantee of that of all smaller animals, their absence represents an ecologically-based measurement of human impacts on biodiversity.

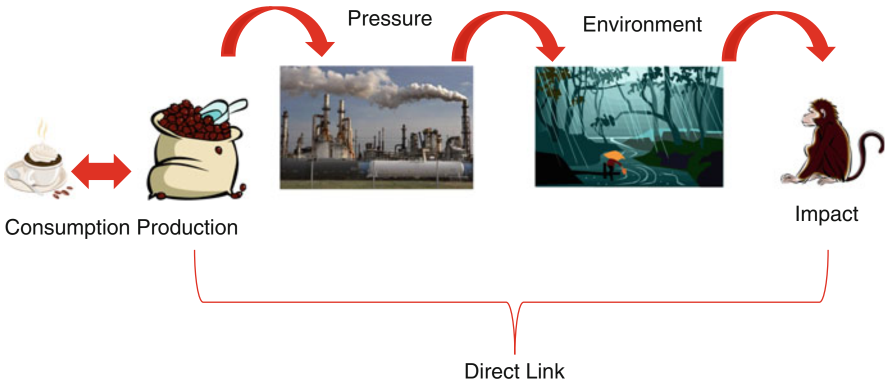


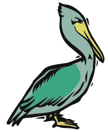
Fig. 7.2 Production, trade, and consumption links to biodiversity loss, and pressures exerted by these activities. E.g., Mexico's spider monkey, *Ateles geoffroyi*, listed as a protected species, owes its survival potential to consumers being aware of the coffee plantations' invasion (registered as a biodiversity-implicated commodity) of its habitat (Adapted from Lenzen et al. 2012)

The ecological state called ***Endemism*** (defined as a specific organism species unique to a defined geographic location, e.g., animals or plants growing and developing only on an island such as Galapagos) can be considered as an indicator of biodiversity. Reaka et al. (2008) using mantis shrimps (*e.g.*, *Gonodactylaceus falcatus* and *Gonodactylellus incipiens*, two stomatopod crustaceans, important members of the benthic community) and their distribution extent across Indo-Australian archipelago, Indian Ocean continental, central Indian Ocean, and central Pacific found that percent endemism among these stomatopods correlates positively with species diversity and inversely with species body size. The authors suggested that, since body size constrains reproductive traits and dispersal, it can be used as a reliable indicator of the speciation and extinction potential of reef stomatopods, and most likely of other marine organisms as well. Another observation made by these authors was that body size declines toward the CP (Central Pacific), especially in atoll environments. In these environments, the wheels of speciation and extinction again spin rapidly but in the opposite direction (extinction > speciation), yielding low diversity and moderate endemism.

In another geographical environment, Williams et al. (2009) supported the above findings while studying terrestrial vertebrates (mammals, birds, reptiles, frogs) in the rainforests of the Australian Wet Tropics (AWT). Their results emphasized that "geographic rarity should increase the probability of extinction as a result of environmental change" and "demographic rarity (low and/or patchy abundance) contributes independently to extinction risk by making species more vulnerable to stochastic population fluctuations," concluding, based also on other studies, that species that are rare, both geographically and demographically, face a double threat of extinction and should be at especially high risk. Therefore geographical and demographical rarity can be used as indicators of extinction.

Another way to detect extinction processes is through the surveillance of indirect environmental processes, as illustrated in Table 7.2, as related to bird's nutrition.

Table 7.2 Environmental consequences as potential extinction indicators based on bird groups' nutritional behavior

Negative consequences of species extinction that can be used as indicators of species extinction	Birds functional group						All species
	Frugivores	Nectarivores	Scavengers	Insectivores	Piscivores	Raptors	
							
Plant seeds dispersion, germination and reduced gene flow; dependent plant species reduction/extinction.	+++[a]	+	+	+	–[b]	–	+/–
Pollination decline; increased inbreeding and reduced fruit yield	+	+++	+	+	–	–	+/–
Disease outbreaks; slow decomposition and carcasses accumulation	–	–	+++	+	–	++	+/–
Pest outbreaks; affected crops	–	–	+	+++	–	–	+/–
Guano reduction; trophic cascade perturbation.	–	–	+	–	+++	+	+/–
Rodent population increase and agricultural impact	–	–	+	–	–	+++	+/–
Ecological unpredicted consequences	+	+	+	+	+	+	+++

Adapted from Şekercioğlu et al. (2004)
[a]Significant impact
[b]Minor impact

In relation to different bird species that feed on different nutrient sources, it can be seen that a reduction of individuals of a certain species that carries a highly nutritive niche (e.g., insectivores) results in pest copiousness that in turn can be related to as an indicator of these insectivores species' extinction in the immediate or near future.

7.3 Summary

It is beyond our reach, but species extinction has occurred for millions of years, before humanoids spread and conquered the globe. In 1973, the prominent evolutionary biologist, Theodosius Dobzhansky, while lecturing in front of a biology teacher, emphasized the role played by evolution in biology and species extinction (Dobzhansky 1973). It is clear that biological evolution brings extinction to some species due to continuous or sudden environmental changes (climate, natural disasters, etc.). However, humans are the catalyst enhancing this process. In a recent publication, Vamosi and Vamosi (2008) reporting on non-angiosperm plant species found species extinction process to be critical (higher extinction rate) in species-rich nations where their abundance is high, a fact at odds with the notion that tropic areas are plants biodiversity museums ! On the one hand, these authors found a significant difference between islands and mainland (with mainland leading the process) in relation to latitude; on the other hand, island nations exhibited high levels of extinction threat regardless of latitude. Looking at these threats and based on the geographical range that impacts the extinction risk of any particular species, as well endemism that determines the proportion of at-risk species, it can be seen that isolated island nations with high levels of endemic species are susceptible to high extinction rates. Nevertheless, the most thought-provoking finding of these authors was that "the risk of extinction is higher in biodiversity hotspots regardless of, and not because of, the influences of human impact." Consequently, human impact seems not to be the major factor in extinction patterns albeit its importance and species in tropical regions appear to be more susceptible to a certain amount of disturbance! However, the authors pointed out that this deviation from previous scientific research is a result of different factors impacting extinction rates in plants from those in bird and amphibian species (Vamosi and Vamosi 2008). In summary, even if the extinction process is a natural one (which we as humans cannot do much to ameliorate), certainly we are not allowed to enhance it by our deeds, and continuous monitoring is required, including clear indicators of the process.

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Chapter 8
Indicators of Pollinator Decline and Pollen Limitation

Yuval Sapir, Achik Dorchin, and Yael Mandelik

Abstract Pollination is a crucial process for maintaining plant reproduction, and is responsible to the yield of about two third of the world's crops. In recent years, there are growing concerns over pollinator declines and global pollination crisis. A decrease in pollinator populations also affects plants' reproductive success, and alters the composition of wild plant communities. The main drivers for pollination decline are agriculture intensification and the subsequent fragmentation and loss of habitats, as well as introduction of non-native species and indirect effects of global climate change. Specialist pollinators and self-incompatible plants are seemingly in higher vulnerability. Our current knowledge of environmental effects on pollination processes is limited by the relatively little knowledge of the ecological requirements of pollinators and plants, and by the shortage of studies on the response of populations and communities to changes in land use. In this chapter we provide indices for estimating pollinator decline in both local and landscape scale, and discuss the relative efficiency of taxonomic and environmental indicators and indicators for estimating pollination services. We propose that future research should include developing and testing cost-effectiveness of indicators for patterns of pollinators' diversity and of indicators for pollination services. These indicators should be tested in various ecological and spatial scales.

Keywords Biodiversity decline • Ecological services • Ecosystem function • Plant-pollinator interactions • Pollen limitation • Taxonomic index

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_8

8.1 Introduction

8.1.1 What Is Pollination?

Pollination is the transfer of pollen grains to the stigma of a flower. Pollen grains are the male germ line cells of the plant, and once they arrive at the stigma, they imbibe water and germinate, producing a pollen-tube that penetrates the stigma surface, growing through the style to the ovary (Proctor et al. 1996). There, the gamete (haploid nucleus) unites with the female gamete in the ovule and this fertilized ovule creates the zygote. The zygote develops into an embryo, which matures to become a seed. The process is totally dependent on the movement of pollen from the male organs (stamens) to the female organs (pistils). This movement can be spontaneous, or, as in many plant species, mediated by animal pollinators (Ollerton et al. 2011).

8.1.2 What Are Pollinators?

Of the ~300,000 animal species that visit plant flowers (Kearns et al. 1998) only a subset are true pollinators that actually transport the pollen grains to the stigma. Pollinators are flower visitors that transfer pollen sequentially to the stigma of conspecific flowers while collecting rewards, usually pollen and nectar as food (Willmer 2011).

8.1.3 A-biotic Pollination

Some plants have evolved a dependency on non-biotic media for pollination, namely wind or water. The main characteristics shared by these plants are small inconspicuous flowers with reduced perianths and exposed anthers and stigmas, as well as diverse adaptations for exploiting the properties of the mediating media for efficient delivery of pollen (Willmer 2011).

8.1.4 Insects

Insects comprise the great majority of pollinators, including some generalist food-foragers, such as beetles, carrion and dung flies, wasps and ants, as well as various unusual flower visitors, such as cockroaches and thrips. Other insects, including mainly bees, hoverflies (Syrphidae) and bee-flies (Bombylidae), moths and butterflies, are floral specialists, showing morphological, sensorial, and behavioral adaptations for collecting and carrying nectar and pollen (Willmer 2011). Members of these groups can provide more reliable and frequent pollination services, and bees in particular are considered the most important pollinators in many ecosystems due to their total reliance on flowers for both adult and larval nutrition (Minckley and Roulston 2006; Wcislo and Cane 1996).

8.1.5 Vertebrates

The most common vertebrate pollinators are birds and bats. Both groups had evolved less specialized interactions with flowers as compared to those of insects (Willmer 2011), with some exceptions, such as the Caribbean hummingbird species (e.g., Temeles and Kress 2003). Other, unusual, pollinators include arboreal marsupial and eutherian mammals from all southern continents, and several lizards and geckos typically found on islands (Willmer 2011). Plants pollinated by vertebrates often have large and robust conspicuous flowers, with sufficient nectar to provide the energy requirements of the animals.

8.1.6 Importance of Pollination for Nature and Agriculture

Animal pollination is crucial for the persistence of natural ecosystems, as more than 87 % of the world's angiosperm species require animal pollination for sexual reproduction (Ollerton et al. 2011). A decrease in pollinator populations can affect the reproductive success of these plants, and alter the composition of wild plant communities (Ashman et al. 2004; Christian 2001). Animal pollination is critical also for maintaining agricultural ecosystems. Animal pollination, provided mainly by bees (Delaplane and Mayer 2000), is required for more than two thirds of the world's leading fruit and seed crops, and collectively accounts for 35 % of the global food production (Klein et al. 2007). The demand for pollination services increases continuously with the increasing need for agricultural products due to human population growth (Aizen and Harder 2009). Without adequate pollination, the human diet would be greatly diminished, both nutritionally and culturally (Klein et al. 2007; Steffan-Dewenter et al. 2005). Hence, pollinators play a key role in maintaining both natural ecosystems and human food supply.

8.2 Environmental Threats

Growing anthropogenic disturbance in natural ecosystems directly threatens plant–pollinator interactions via several environmental stressors, commonly including habitat degradation and loss, fragmentation, agricultural intensification, and the introduction of non-native species, as well as indirect effects, such as climate change (Potts et al. 2010a). A quantitative synthesis of 54 studies showed that habitat fragmentation and loss is the most important disturbance factor having a significant negative effect on the richness and abundance of pollinator bees (Winfree et al. 2009). A comparable negative effect of habitat fragmentation has been demonstrated also among flowering plants and was found to be particularly strong among self-incompatible plant species (Aguilar et al. 2006). Studies on the effects of herbicides and insecticides (Brittain et al. 2010; Holzschuh et al. 2007), cattle grazing (Sjödin et al. 2008; Yoshihara et al. 2008), and fire (Potts et al. 2003) reported varying effects on pollinators that were dependent on the disturbance intensity, sampling period, and pollinator taxon studied. In addition, the changes in pollinator richness and abundance in these studies were largely mediated by the diversity and abundance of the flowering plants. The introduction of non-native invasive plant species can either facilitate or reduce pollinator visitation through competition with native plants for pollination services, but their effects on the local pollinator communities are not yet clear (Bartomeus et al. 2008).

Also in debate is the extent to which the introduction of the European honeybee (*Apis mellifera*), the most important managed pollinator and an exotic species in most ecosystems, affects native bee species (Paini 2004). There is already an indication of competitive suppression of native bumble bees by non-native honey bees in North America (Thomson 2004). In addition, an indirect effect of honey bees, through faster and more efficient pollen removal, was shown to reduce pollination of the endangered plant Iris atropurpurea by native longhorn bees (of the genus *Eucera*; Watts et al. 2013). The honeybee, *A. mellifera*, being a habitat generalist opportunistic species, largely benefits from anthropogenic disturbance (Carré et al. 2009). It is, however, more susceptible to other factors, namely infestation by pests and pathogens (Genersch 2010).

Finally, multiple global change pressures are currently impacting animal-mediated pollination (González-Varo et al. 2013). For example, climate change is a factor that has been commonly associated with latitudinal shifts in the distribution ranges of butterflies (Chen et al. 2011). A particularly large effect of climate change on butterfly populations has been demonstrated in lower elevation areas that also comprised a disturbed habitat (Forister et al. 2010), emphasizing the importance of interacting disturbance factors. Global warming was found to shift phenology in both plants and insects (e.g., Calinger et al. 2013; Ovaskainen et al. 2013). Plants are more likely than insects to advance phenology in response to springtime warming (Forrest and Thomson 2011), and a mismatch of flowering and the emergence of the pollinators may cause population declines if the plants flower at times when effective pollinators are unavailable (Rafferty and Ives 2012).

8.3 Pollinator Decline

8.3.1 Evidence for Pollinator Decline – Pollinators Diversity

In recent years, there are growing concerns over pollinator declines and global pollination crisis (Potts et al. 2010a). However, scarcity of long-term data on the status of domesticated and wild pollinators, in particular bees hampers attempts to evaluate trends in wild pollinators' abundance and diversity (National Research Council 2007). In the last few decades, the number of domesticated honey bee colonies declined in some central European countries, but increased in other countries (Potts et al. 2010b). Overall, the global stock of domesticated honey bees is growing more slowly than the agricultural demand for pollination, stressing the global pollination capacity (Aizen and Harder 2009). As for native pollinators, studies have shown declines in populations of some bumble bee (*Bombus*) species (Cameron et al. 2011; Colla and Packer 2008; Goulson et al. 2006), while other bumble bee species have shown stability or even expansion in range (Williams et al. 2009). Studies on long term trends in the status of pollinator species other than honey bees and bumble bees are scarce. Among these few studies are that of Biesmeijer et al. (2006), who demonstrated significant declines in native bee populations, other than bumble bees, in Britain and the Netherlands, and of Burkle et al. (2013) who found an extinction of 50 % of the native bee species in Illinois forests, as well as subsequent degradation in bee-plant interactions in these communities. However, a comparable study by Bartomeus et al. (2013) did not find such significant declines in other regions of the northeastern United States. The status of wild pollinators in most other regions around the world is largely unknown.

8.3.2 Evidence for Pollination Decline – Pollen Limitation

Limited female success due to inadequate pollen receipt appears to be a common phenomenon in plants (Ashman et al. 2004; Burd 1994). This pollen limitation can be the result of one of two components. First, pollen quality can reduce fruit-set and seed-set due to genetic factors, even when pollinator services are sufficient (Aizen and Harder 2007; Sapir and Mazzucco 2012). For example, Segal et al. (2007) showed that reduced fruit-set and seed-set in *Iris bismarckiana* occurs in crosses within population, relative to crosses between populations, suggesting that genetic similarity within a population reduces reproduction. Similarly, the plant *Hymenoxys herbacea* showed reduced reproductive success because of mate limitation, despite sufficient pollination services (Campbell and Husband 2007). In addition, a plant's mating system also affects its fecundity and intensifies the pollen limitation in plants that rely on cross pollination, as compared to self-pollinated plants (Larson and Barrett 2000).

Second, pollen limitation can be the result of reduced pollen quantity, due to reduced pollinator services. Pollinator decline reduces fruit-set due to reduced pollen transfer to stigmas. To assess the effect of pollinator decline on pollen limitation, it is important to partition the effects of pollen quality and quantity (Aizen and Harder 2007). The recent development of a standardized modular approach to measure pollinator effectiveness and efficiency (Ne'eman et al. 2010) is an important step toward assessing the effect of pollination decline on pollen limitation and plant's reproductive success.

Although pollen limitation is a relatively common phenomenon in natural ecosystems, it is accelerated by anthropogenic disturbance, such as habitat loss, grazing, logging, and agriculture. For example, habitat fragmentation led to a decline in pollination and subsequent fruit set in wild plant populations and an even stronger decline in cross-pollinated species (Cunningham 2000; Winter et al. 2008). The anthropogenic decline of natural areas results in the decline of pollinator populations, leading to a collapse of pollination webs and to seed production failure in specialized plants (Cunningham 2000; Klank et al. 2010; Pauw 2007).

8.4 Methods to Detect Pollinator Decline

The direct assessment of pollinators' diversity, and even more so, the assessment of pollinators' function requires large investments of time, money and expertise. Hence, there is a need for surrogate measures (indicators) that will provide the necessary data inexpensively, quickly, and reliably (Mandelik et al. 2010). The two main categories of surrogates used to assess patterns of species diversity are environmental indicators, which are the physical characteristics of the environment that are expected to affect species distribution, and taxonomic indicators, which are the assessment of a taxon or a subset of taxa that are expected to reflect a wider range of taxa in the ecosystem (Mandelik et al. 2012a; Rodrigues and Brooks 2007).

8.4.1 Environmental Indicators

8.4.1.1 Local-Scale Environmental Indicators of Pollinators

Many studies have found a strong positive relationship between the abundance and species richness of flowers and bees at a given site (e.g., Gotlieb et al. 2011; Grundel et al. 2010; Persson and Smith 2013). This may be especially true during periods of limited availability of bloom (Mandelik et al. 2012b). Similar positive relationships were found between the number and diversity of nesting sites and substrates and wild bee richness (Grundel et al. 2010) and bee community structure (Lonsdorf et al. 2009; Murray et al. 2012; Potts et al. 2005). Hence, the overall amount and diversity of the main limiting resources of bees, foraging plants and nesting sites and substrates, may be used to assess diversity patterns of bees at local (field) scales.

8.4.2 Landscape-Scale Environmental Indicators of Pollinators

Spatial characteristics of the landscape, such as patch size, land-use distribution, and degree of fragmentation, were found to affect the richness and abundance of wild bees (e.g., Grundel et al. 2010; Hinners et al. 2012; Potts et al. 2010b; Winfree et al. 2009). Accordingly, spatial indices of land-use intensification and fragmentation may be used to evaluate the number and diversity of bee populations in different landscapes (Sheffield et al. 2013a).

8.4.3 *Taxonomic Indicators*

Subsets of pollinators, e.g., a single species or a few functional groups, may be used to reflect the diversity patterns of additional pollinators. Cleptoparasitic bees, in particular, hold promise as representatives of the status of bee communities and as indicators of environmental disturbances (Sheffield et al. 2013b).

Diversity patterns of high taxonomic levels, such as genus, sub-families etc., may reflect species-level diversity patterns of pollinators. The efficiency of genus level data in reflecting species patterns of wild bees is variable (Van Rijn 2012) and depends on community characteristics and sample size (Neeson et al. 2013). Such genus and even subgenus level-based analyses should be made with caution considering the high ecological diversity found within some groups of pollinators, for example among members of the bee tribe Osmiini (Müller 2013).

Overall, knowledge about the efficiency of the different possible indicators of pollinator patterns is very limited. Much of the current knowledge is based on speculative assessments rather than direct tests of the efficiency and cost-benefit ratio of the different indicators. Studies of the relative efficacies of the different indicators are urgently needed in order to develop reliable monitoring programs and allow better conservation of pollinator communities.

8.5 Pollination Services Indicators

8.5.1 *Pollination Measurement*

Pollination rates can be used to assess the decline of pollinator communities indirectly. Pollination rates are assessed either by pollinator(s) behavior indices or by indices of pollination success. Pollinator activity on flowers includes visitation rate per plant/inflorescence or per flower, duration of stay in the flower, and foraging type (Dafni et al. 2005). The most common foraging behavior is food collection, usually nectar or pollen, but other behaviors exist, such as night sheltering (Sapir et al. 2005), mating (Fishman and Hadany 2013), or behaviors associated with deception (Schiestl 2005).

The comparison of historical data on pollination rates with current pollination rates is a tool for assessing pollination decline in an ecosystem over time. For example, Pauw and Hawkins (2011) estimated the reduction in visitation rates to orchids using estimates of pollinia removal from herbarium specimens as compared to current pollinia removal in the same region, and showed through time-series analysis that pollination services to these orchids have declined. On a larger scale, Biesmeijer et al. (2006) showed a concerted diversity decline of both bees and animal-pollinated plant species, based on a multi-year database from Britain and the Netherlands.

A different approach, replacing space with time, compares pollination rates in disturbed or destructed areas with that in nearby areas that are still relatively natural and undisturbed (e.g., Aizen et al. 2008; Lopes and Buzato 2007). However, this approach has been criticized on the basis of the high spatial variation of pollination rates, suggesting that the results may be confounded with spatial comparisons (Pauw and Hawkins 2011).

8.5.2 Post-Pollination Measurements in Plants

The pollen deposition on a stigma measured after a single visit can estimate the relative efficiency of pollinators in transporting pollen (Watts et al. 2013; Winfree et al. 2007). This way, not only the pollination services can be assessed, but also the integration of such services for different types of pollinators that may differ in their relative efficiency (Conner et al. 1995).

Fruit-set can be measured in the level of inflorescence, plant, or population (e.g., González-Varo et al. 2009; Gonzalez-Varo and Traveset 2010). To quantify pollen limitation in natural populations, pollen supplementation experiments are conducted, in which the reproductive success of control plants is compared with that of plants receiving supplemental pollen. If more fruits or seeds are produced when pollen is supplemented, then it is usually concluded that reproduction is limited by pollen receipt (Ashman et al. 2004; Knight et al. 2005). Pollen limitation can be quantified by the Pollen Limitation Index (PLI; Campbell and Husband 2007):

$$PLI = \left(fruit\text{-}set_{Suppl.} - fruit\text{-}set_{Open}\right)/fruit\text{-}set_{Suppl.}$$

Or:

$$PLI = \left(seed\text{-}set_{Suppl.} - seed\text{-}set_{Open}\right)/seed\text{-}set_{Suppl.}$$

In this index, the excess fruits or seeds produced with supplementary hand pollination as compared to those of open-pollination flowers is divided by the reproductive success when pollen is not limited, i.e., with supplementary hand pollination. The cumulative pollen limitation is achieved when the probability of a flower to set a fruit and the number of seeds are multiplied (González-Varo et al. 2009):

$$PLI_{Commulative} = \left(fruit\text{-}set_{Suppl.} x\ seed\text{-}set_{Suppl.} - fruit\text{-}set_{Open} x\ seed\text{-}set_{Open}\right) / \left(fruit\text{-}set_{Suppl.} x\ seed\text{-}set_{Suppl.}\right)$$

Pollen limitation measurements with supplementary pollination treatment may be a cheap and quick surrogate for the tedious and time-consuming pollinators' observations, because a plant's reproduction is determined by an integration of pollination events throughout the plant's flowering season. However, special caution should be taken when the mating system or the genetic structure of the plant population may affect reproductive success (Aizen and Harder 2007).

8.6 Summary and Prospective

Recent studies found empirical evidence for the decline of pollinator-plant systems, particularly in intensified regions of Western Europe and the US. The main drivers for pollination decline are agriculture intensification and the subsequent fragmentation and loss of preexisting habitats. Some studies indicated the higher vulnerability of specialists, such as self-incompatible plants, and mutual obligates, such as many bee species. Our current understanding of environmental effects on pollination processes in both natural and human-dominated ecosystems is limited mainly by two factors. One is the relatively little knowledge of the ecological requirements of pollinators and plants, and the other is shortage of studies on the response of populations and communities to landscape change. Future research should include not only long-term monitoring schemes for pollinator-plant systems but also manipulation experiments in order to elucidate potential mechanisms of decline. For example, manipulating nesting-associated variables of various pollinators can contribute new insights into pollination processes, such as limitation in pollination services. For the conservation of pollinators and plants in disturbed human dominated ecosystems, comprehensive solutions should be explored that improve not only the dominant attractive pollinator and plant species but also rare and less enchanting species. Finally, there is a great need to develop and test the cost-effectiveness of possible indicators of pollinators' diversity patterns and their pollination services. These indicators will enable the execution of long-term monitoring programs to detect patterns and changes in pollinator communities.

Acknowledgements We thank Robert Armon and Osmo Hänninen for the invitation to write this chapter. Studies related to this chapter were supported by the Israel Science Foundation (YS and AD, YM), the Nekudat Hen program for promoting agricultural – Ecological projects (YS and AD, YM), and Porter School for Environmental Studies at Tel Aviv University (YS).

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Chapter 9
Coral Bleaching

Jeremiah G. Plass-Johnson, Ulisse Cardini, Nanne van Hoytema, Elisa Bayraktarov, Ingo Burghardt, Malik S. Naumann, and Christian Wild

Abstract Bleaching of corals (reversible loss of endosymbiotic zooxanthellae) is an unspecific indicator for a range of environmental stressors including too high or too low water temperatures, sedimentation, high irradiance or turbidity, mechanical disturbance, or infection by microbial pathogens. Coral bleaching may result in the death of affected corals depending on the severity and duration of the environmental stressor that induced bleaching. We know that the frequency and extent of high temperature-induced coral bleaching increased over the last century with recent large-scale events and resulting mass coral mortality in the Indian Ocean (1998), the Pacific Ocean (2002), the Caribbean (2005), and even all the world oceans (1998 and 2010). This may lead to major changes in the benthic community composition (i.e., phase shifts) of coral reefs and pronounced modifications of biogeochemical cycles that support coral reef functioning.

Keywords Bleaching • Coral • Benthos • Reef • Climate change • Biogeochemical

9.1 Introduction

Coral bleaching is a dynamic process that includes multiple levels of systemic causes and effects. Interactions of the environment at multiple spatial and temporal scales affect coral reef systems. Coral bleaching can be effective as an indicator of large-scale, exogenous environmental processes, or alternatively, there can be indicators of bleaching at the level of the organism up to the ecosystem indicating endogenous processes. Likewise, there can be temporal processes at the scale of the

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_9

organism or ecosystem that allow differing indications of bleaching cause and effect. Because of the multiple spatial and temporal scales that interact with the processes of bleaching, we try to identify (1) early warning indicators of bleaching and/or bleaching as an early warning indicator, (2) indicators of direct impacts on corals, and finally, (3) indicators of long-term changes under specific conditions within and among communities. To clarify these ideas, below are examples of each group of indicators.

1. Early warning indicators of bleaching can be species or environmental parameters that can be highly susceptible to environmental changes, providing insight into developing issues before they affect the system as whole. For example, many corals are highly susceptible to changing water conditions, specifically changes in temperature. These changes in water conditions may be used as indicators of possible wide-scale, coral reef bleaching (see Sects. 9.3 and 9.6). Likewise, coral reefs are seen as indicators for global environmental change because they are found in environments at their physiological thresholds (see Sect. 9.3). Therefore, coral bleaching can be seen as an indicator of global processes (see Sect. 9.2).
2. Indicators of direct impacts are used to ascertain a process that is currently taking effect. For example, corals may release their symbiotic zooxanthellae prior to and during bleaching events. These changes in zooxanthellae numbers can work as indicators of direct effects (see Sect. 9.4).
3. Finally, indicators of long-term changes provide evidence of an event that has already taken place. There is a range of susceptibility to bleaching in coral reef organisms with some species being highly robust. Post-bleaching examination of coral reef species composition can provide insight into bleaching that has not been directly witnessed (see Sect. 9.6)

We start this chapter by exploring the definition and historical knowledge of coral bleaching. The following three sections provide information about the causes of bleaching and the physiological processes. The final three sections cover the ecological consequences of bleaching, including some brief ideas on conservation and management strategies. The processes that induce bleaching in corals and the response of these organisms are closely linked, and an indication of the bleaching processes at any level of organisation may help us to understand patterns and processes of local and global coral reef systems.

9.2 Definition and Occurrence of Coral Bleaching

The most conspicuous, rapid and destructive impact of global climate change on coral reef ecosystems is reflected by a physiological stress response of reef corals, a phenomenon called *coral bleaching*. The term coral bleaching is derived from the

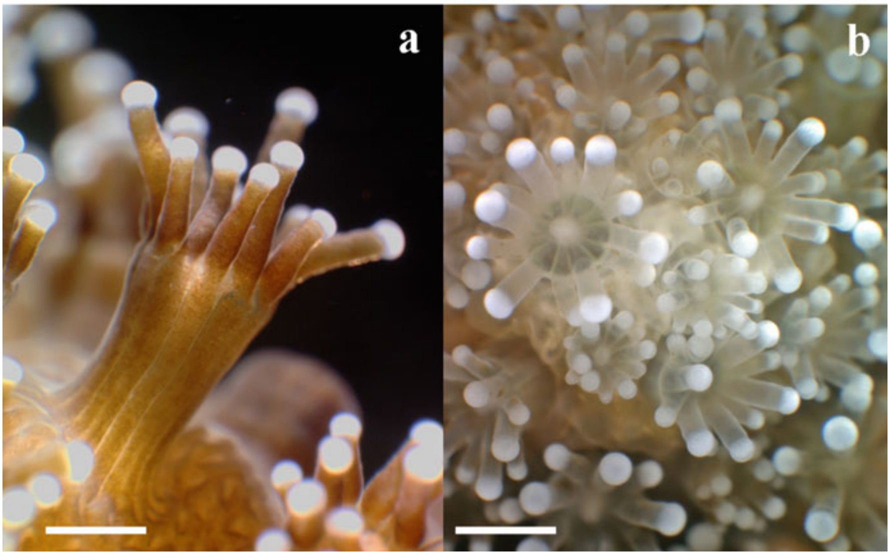

Fig. 9.1 Macro photographs showing unbleached and bleached polyp tissue of the scleractinian coral *Stylophora pistillata*. Panel (**a**): lateral view of protruded unbleached polyps with visible zooxanthellae population, panel (**b**): overhead view of protruded bleached polyps with nearly transparent tissue; scale bars: 0.25 mm (**a**) and 0.5 mm (**b**) Photography: E. Tambutté (Centre Scientifique de Monaco)

whitening of the tissue of reef corals that host endosymbiotic *Symbiodinium* microalgae (i.e., zooxanthellae) (Fig. 9.1a). This whitening results from the expulsion of the zooxanthellae and/or the loss of photosynthetic, algal pigments, allowing the white aragonite skeleton to become visible through the transparent coral tissue (Fig. 9.1b). Coral bleaching disrupts the mutualistic symbiosis between zooxanthellae and their cnidarian host, entailing the loss of an essential, internal photosynthetic energy transfer from the algal symbionts to the coral (Hoegh-Guldberg and Smith 1989) (Sect. 9.4). At times, bleaching may be reversible, but rapid mortality of weakened and/or diseased corals is common with repetitive or intense events. In extreme instances, consequences for the functioning of coral reefs can be severely negative, as bleaching can lead to systemic failures and serious ecosystem degradation caused by usually irreversible phase shifts of benthic reef communities (Douglas 2003; Wild et al. 2011).

The primary environmental factor triggering coral bleaching is elevated water temperatures, which cause physiological thermal stress (Hoegh-Guldberg 1999). Extreme levels of solar irradiance, including visible (Hoegh-Guldberg and Smith 1989; Banaszak and Lesser 2009) and ultraviolet radiation (Lesser et al. 1990; Shick et al. 1996), can create additional physiological stress to increase the deleterious impact of thermal bleaching. Furthermore, coral bleaching can result from a range of abiotic and biotic stressors as a product of their typical coastal, shallow water distribution (Sect. 9.3). Often, many stressors act in concert to increase susceptibility of corals to thermal bleaching further by lowering their temperature threshold and, subsequently, exacerbating the degree of coral mortality (Lesser 2004, 2006).

Considering the main environmental factors that induce reef corals to bleach (temperature and light), the stability of the coral-zooxanthellae symbiosis can serve as a sensitive environmental indicator, in particular, for temperature anomalies, which are included in climate change projections (Hoegh-Guldberg et al. 2007). Because corals often live in environments where temperatures are close to their physiological thermal threshold, they are highly vulnerable to bleach at temperatures 1 °C above the historical mean summer maximum in many regions (e.g., Toscano et al. 2000) (Sect. 9.3). Satellite sea surface temperature data have shown that bleaching of variable severity can be expected if this warming persists for several weeks or increases, and this correlation is now used to forecast the global spatiotemporal distribution and intensity of coral bleaching events (Strong et al. 2006). Given the low thermal tolerance of many reef coral taxa, temperature anomalies can trigger widespread bleaching events posing serious threat to coral reefs world-wide (Hoegh-Guldberg 1999; Pandolfi et al. 2003, 2011).

The phenomenon of coral bleaching has been known for more than 100 years; however, the first comprehensive report on a temperature-induced bleaching event originates from 1929 when Yonge and Nichols (1931) recorded widespread coral bleaching and mortality on reef flats within the Great Barrier Reef. Thereafter, regular reports on bleaching observations can be found in the literature. The first Caribbean thermal "mass bleaching" event of the early 1980s had a widespread impact and led to increased awareness of other bleaching events induced by elevated water temperatures and high solar irradiance (Glynn 1983, 1996; Lessios et al. 1983; Glynn and D'Croz 1990). Region-wide mass coral bleaching can affect thousands of square kilometres of reef-covered seafloor over relatively small time scales (i.e., within weeks) and thus, constitute a major cause for large-scale coral mortality and the simultaneous decline of coral reef ecosystems (Hoegh-Guldberg et al. 2007).

On a global scale, mass bleaching events can be associated with extended periods of elevated water temperatures generally associated with anomalies in the Southern Pacific Oscillation (i.e., El Niño or La Niña events), which can affect multiple oceanic regions (Hoegh-Guldberg 1999). In 1998, the first, and to date most severe, of four global bleaching events (Fig. 9.2a) affected reefs in all tropical and subtropical latitudes causing a loss of 16 % of corals world-wide (Wilkinson 2008). During this event, 80 % of all corals in the Western Indian Ocean bleached and nearly 50 % died, with up to 95 % mortality at some sites (Lindén and Sporrong 1999; Souter et al. 2000). Another global event occurred in 2002, where the Great Barrier Reef represented the major bleaching hotspot (Fig. 9.2b; e.g. Berkelmans et al. 2004). In 2005, the Caribbean was most severely affected resulting in more than 80 % of corals bleached and over 40 % mortality (Fig. 9.2c; Eakin et al. 2010). The most recent global bleaching event in 2010 (Fig. 9.2d) significantly impacted many regions throughout the Indo-Pacific (Burke et al. 2011; Krishnan et al. 2011; Guest et al. 2012; Furby et al. 2013), including Western Australia, which

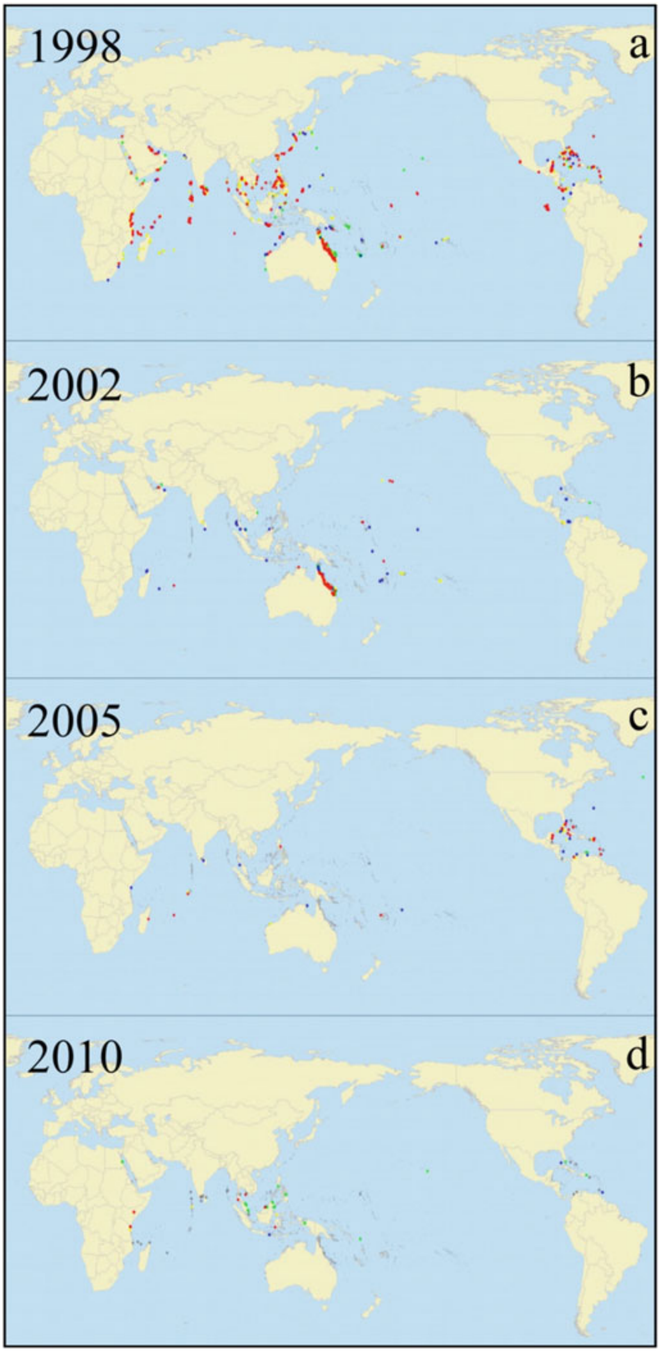

Fig. 9.2 Overview of bleaching reports covering the four global mass bleaching events since 1998. Panels (**a–d**): 1998, 2002, 2005 and 2010, respectively. Bleaching severity indicated by colour coding: *red* = high, *yellow* = medium, *blue* = low, *grey* = severity unknown, *green* = no bleaching (Maps adopted and modified from ReefGIS online services (http://www.reefgis.reefbase.org) based on the comprehensive ReefBase database (2013) compiled by contributions of UNEP-WCMC, The WorldFish Center, National Oceanographic and Atmospheric Administration (NOAA), Great Barrier Reef Marine Park Authority, Australian Institute of Marine Science and coral-list (http://coral.aoml.noaa.gov/mailman/listinfo/coral-list/) maintained by NOAA)

experienced up to 95 % bleaching and 84 % mortality in certain reef areas (Moore et al. 2012).

Intensity and frequency of world-wide coral bleaching events may be recognised as biological indicators for consequences of global climate change on coral reefs (Hughes 2000). If current rates of CO_2 emission and ocean warming persist, model predictions for the coming decades project the intensity and frequency of bleaching events may increase with possible annual occurrences (Hoegh-Guldberg 1999, 2011; Sheppard 2003; Donner et al. 2007; Hoegh-Guldberg et al. 2007; Lesser 2007; Eakin et al. 2009). One of the latest models predicts that preserving >10 % of coral reefs world-wide would require limiting warming to <1.5 °C relative to pre-industrial levels, a figure considerably less than the globally agreed 2 °C (Frieler et al. 2013). This prospect clearly constitutes a massive threat to the existence of present-day coral reef ecosystems. Due to the lack of human observers and limited reporting effort in remote locations, the analysis of global bleaching observation databases (e.g., ReefBase) is limited in spatial and temporal terms (Burke et al. 2011). As a consequence, many bleaching events remain unobserved and unreported, masking their actual global frequency and intensity.

These contrasting results have stimulated further research, which has suggested differing levels of thermal stress tolerance and acclimatisation of particular coral taxa, or possibly entire reef communities, acquired from past stress exposures and/or local mitigating environmental, abiotic factors (e.g., shading, current speed, upwelling zones or depth; Maynard et al. 2008; Brown and Cossins 2011) (Sect. 9.7). Nevertheless, the capacity for stress resistance and bleaching resilience appears highly variable and limited, as evidenced by recent mass bleaching events that affected much of the occurring coral taxa, and a subsequent, marginal recovery of these systems (Grimsditch and Salm 2006; Baird and Maynard 2008; Baker et al. 2008; Sheppard et al. 2008; Somerfield et al. 2008; Veron et al. 2009). Finally, the physiological capacity for stress acclimatisation may also be closely related to the actual type of active stressors, which will be addressed in more detail in the following sections.

9.3 Causes of Coral Bleaching

Although the mechanisms of coral bleaching are still not completely understood, various factors that may trigger this process have been the subject of intense research (Brown 1997a, b; Lesser 2011; Wooldridge 2013). Corals undergo bleaching if the environmental conditions that contribute to the stability of the relationship between *Symbiodinium* and the coral host fail (Sect. 9.2). Many field and laboratory studies found increased seawater temperature to be the major factor for the breakdown of the symbionts-host environment, leading to the subsequent occurrence of bleaching events (e.g. Hoegh-Guldberg and Smith 1989; Jokiel and Coles 1990; Lesser et al. 1990; Fitt et al. 1993; Glynn 1993). Temperature increases of 1–2 °C above the mean summer maximum, persisting for several consecutive weeks, can lead to coral bleaching (Jokiel and Coles 1990; Bruno et al. 2001) indicating that many coral species are living close to their upper thermal limits (Jokiel and Coles 1990). Therefore, thermal thresholds have been studied as early warning indicators of potential bleaching events. Rankings of susceptibility of different taxa to thermal stress have been published (Fitt et al. 2001; Loya et al. 2001; Marshall and Baird 2000; Okamoto et al. 2005) (Sect. 9.6). However, thermal thresholds vary among areas and it is not clear how these limits apply *in situ* where several processes (e.g., wind, wave action, and upwelling) can work synergistically to alter the effects of thermal stress (Abdo et al. 2012; Berkelmans and Willis 1999).

While thermal stress is viewed as the principal cause of coral bleaching, several other biotic and abiotic factors have been found to impact the stability of the symbiosis, including: reduced seawater temperatures (Muscatine et al. 1991; Gates et al. 1992; Kobluk and Lysenko 1994; Saxby et al. 2003); supra-optimal levels of visible or ultraviolet radiation (Gleason and Wellington 1993; Lesser and Farrell 2004; Brown and Dunne 2008); ocean acidification (Sect. 41.3) (Anthony et al. 2008); salinity fluctuations (Meehan and Ostrander 1997; Kerswell and Jones 2003); nutrient enrichment (Wiedenmann et al. 2013); bacterial infection (Rosenberg et al. 2009); and cyanide exposure (Jones and Hoegh-Guldberg 1999). Hoegh-Guldberg (1999) added copper ions and pesticides, while Glynn (1996) included sub-aerial exposure, sedimentation, and oil as contributory factors.

However, of critical importance is that mass coral bleaching events, such as those recorded in 1998, 2002, 2005, and 2010 (Goreau et al. 2000; Berkelmans et al. 2004; Guest et al. 2012) (Sect. 9.2), have been associated with the effects of anthropogenic global warming (Hughes et al. 2003; Donner et al. 2005), which has resulted in a steady rise of marine baseline temperatures. Consequently, forecasts of warming events on a global scale such as the occurrence of El Niño events serve as early warning indicators of potential bleaching of wide areas of coral reefs. Likewise, a sudden drop in seawater temperature induced by either atmospheric chilling or intense upwelling may also result in coral bleaching across wide areas (Hoegh-Guldberg et al. 2005) and should be monitored and used as an early warning indicator. Finally, ocean acidification and changes in solar radiation have the potential to cause mass bleaching across large spatial scales as climate change occurs (Anthony et al. 2008; Lesser 2011). These are indicators of long-term changes in coral reef communities and may be monitored with the use of time series data. All the large scale stressors mentioned above and their combined effects may have dramatic consequences on the geographic extent, increasing frequency, and regional severity of future mass bleaching events.

Local stressors such as pollutants, nutrient loading or sedimentation result in localised bleaching events (tens to hundreds of kilometres) because of the constrained nature of the stress source. However, these can act synergistically by effectively lowering the threshold temperature at which coral bleaching occurs, thereby reducing coral resistance and resilience to global climate change (Lesser 2004, 2006; Carilli et al. 2012; Wooldridge 2009; D'Angelo and Wiedenmann 2014). Consequently, these local stressors should also be monitored as they can act as indicators of subsequent bleaching events, especially if they occur simultaneously with high summer water temperatures.

While there is consensus in identifying the above described environmental drivers (e.g., temperature, light) as (direct or indirect) causes of coral bleaching, the scientific community is not in agreement on the role of bacteria as potential causative agents of bleaching. Most coral biologists contend that changes in the microbial community of bleached corals are a mere result of the process. Indeed, during a bleaching event, coral-associated microbial communities show major shifts in their composition and metabolism (Bourne et al. 2007), with an increase in microorganisms capable of pathogenesis (Littman et al. 2011). This has been confirmed by reports that found a positive link between coral bleaching events and subsequent coral disease epizootics (Miller et al. 2006; Muller et al. 2008; Brandt and McManus 2009; Cróquer and Weil 2009; McClanahan et al. 2009). Consequently, the occurrence of coral diseases might be an indicator of an effect of coral bleaching on both the organism and the ecosystem level, or otherwise bleaching can be used as early warning indicator of subsequent susceptibility of the coral community to disease outbreaks.

However, bleaching has also been found to occur as a direct result of bacterial infection in the coral tissue, particularly by gram-negative bacteria of the genus *Vibrio*. Kushmaro et al. (1996) found that bleaching of the Mediterranean coral *Oculina patagonica* was caused by *Vibrio shiloi*, which produces extracellular proline-rich peptides referred to as Toxin P, which blocks photosynthesis and bleaches and lyses zooxanthellae. However, the mere presence of the *Vibrio* bacterium is not sufficient to cause coral bleaching: virulence factors for adhesion and ingress into the coral and Toxin P are produced by the bacterium only at elevated seawater temperatures (Kushmaro et al. 1998; Toren et al. 1998; Banin et al. 2000). Similarly, *V. coralliilyticus* in combination with elevated temperature caused bleaching in the coral *Pocillopora damicornis* (Ben-Haim and Rosenberg 2002; Ben-Haim et al. 2003). These observations led to the Bacterial Bleaching Hypothesis (Rosenberg and Falkovitz 2004; Rosenberg et al. 2009), which proposes a microbial infection as the primary trigger of coral bleaching. Conversely, Ainsworth et al. (2007) found no evidence to support this hypothesis and argued against its generalisation, suggesting that the bacterial infection is opportunistic rather than a primary pathogenic cause of bleaching and that non-microbial environmental stressors trigger coral bleaching in *O. patagonica*. Nevertheless, a recent experiment with the coral *Montipora digitata* demonstrated that corals exposed to thermal stress in synergy with external bacterial challenge (by different inoculated strains of *V. coralliilyticus, V. harveyi, Paracoccus carotinifaciens, Pseudoalteromonas sp.,* and *Sulfitobacter sp.*) undergo more severe bleaching than colonies exposed to thermal stress alone (Higuchi et al. 2013). Conversely, a ‘healthy’ microbial community (i.e., the microbial community found in healthy colonies) increases the thermal tolerance of the holobiont compared to that of coral colonies whose bacterial community was treated with antibiotics (Gilbert et al. 2012).

From these findings, it appears likely that environmental drivers act on the coral microorganisms as well as the coral host, causing a change in the microbial community that in some cases contributes directly or indirectly to bleaching (Rosenberg et al. 2009). Finally, these studies stress the importance of the interaction between abiotic and biotic factors and of the stability of the coral microbiota for the resilience of the holobiont to bleaching, calling attention to a more careful consideration of bacteria as fundamental players in the bleaching process. Because of the present development of molecular techniques (e.g., qPCR, CARD-FISH), which are becoming accessible to more researchers every day, monitoring of the bacterial community or of a particular bacterial bioindicator (such as *Vibrio*) may serve as an early warning indicator of bleaching events or as an indicator of direct impact on corals once the bleaching process occurs.

As we come to understand the causes of bleaching and the interaction between different biotic and abiotic stressors across spatial and temporal scales, at both the organism and the ecosystem level, it is fundamental to develop environmental indicators that help in managing and protecting coral reef ecosystems from degradation. Finally, monitoring of these indicators, on both a global and local scale should be implemented and response protocols need to be developed if we are to save these ecosystems in the coming decades.

9.4 Mechanisms of Coral Bleaching

Coral bleaching is primarily induced by two factors: photoinhibition and oxidative stress. A clear indicator for coral bleaching is that the coral's zooxanthellae are experiencing either one or both of these stressors. Photoinhibition is the process in which a constantly high absorption of excitation energy and a decrease in photosynthetic electron transport combine to cause damage to the photosystem II reaction centre of photosynthetic organisms (Hoogenboom et al. 2012). Photoinhibition can be caused by exposure to thermal stress and increased ultraviolet radiation (UVR). It leads to a reduced yield from photosynthesis and energy expenditure on the repair of damaged tissues (Long et al. 1994). Oxidative stress occurs within an organism when the production and accumulation of Reactive Oxygen Species (ROS) exceed the organism's capacity to control their levels (Fridovich 1998). ROS are a group of compounds (superoxide radicals, hydrogen peroxide, hydroxyl radicals, and ions) that, when they accumulate in the cells, can damage lipids, DNA, and proteins. They are normally controlled by anti-oxidants produced by the organism. ROS production can increase rapidly in photosynthetic organisms such as zooxanthellae when they are exposed to increased temperature and UVR (Suggett et al. 2008; Lesser and Farrell 2004). As these two factors increase, the production of ROS overwhelms the antioxidant defences and causes extensive damage (Martindale and Holbrook 2002). Besides being transferred to the host from the zooxanthellae (Suggett et al. 2008), ROS are also produced by the cnidarian hosts as a response to thermal stress (Dykens et al. 1992). A build-up of ROS in coral tissues might be monitored as an indicator for a potential future bleaching event. As the host cells are exposed to, and damaged by, the built up ROS, there are several ways in which the symbiosis can be uncoupled. In apoptosis, a programmed cell death pathway is initiated due to exposure to ROS or extensive damage to the DNA or other cell components. In necrosis, the cell's functioning is disrupted to a degree where it disintegrates without a controlling pathway (Martindale and Holbrook 2002). Additionally, zooxanthellae can be expelled from the host tissue by exocytosis into the gastrovascular cavity, or the cell can be detached from the endoderm as a whole (Gates et al. 1992). For an extensive review of coral bleaching mechanisms, the authors refer the reader to Lesser (2011).

Photosynthesis by zooxanthellae can provide the coral host with a significant proportion of its energy demand (Tremblay et al. 2012). A loss of this contribution due to bleaching severely impacts coral fitness, reducing reproductive output and growth (Manzello 2010; Cantin et al. 2010; Brown 2012). Calcification can be "light enhanced" during the day (Gattuso et al. 1999; Schutter et al. 2012), and although the precise physiological mechanism behind this process is still under debate, a loss of zooxanthellae has a clear adverse effect on calcification (Moya et al. 2008). Coral bleaching can also increase the occurrence of growth anomalies, disturbing the normal development of coral colonies (McClanahan et al. 2009). The reproductive capability of the coral is influenced in the period following a bleaching event, with a reduced number of gametes being produced by bleached coral tissue (Armoza-Zvuloni et al. 2011). Coral reproduction is further impacted by increased water temperatures through reduced fertilisation success (Albright and Mason 2013), and reduced larvae survivorship and settlement (Randall and Szmant 2009a, b). There are, however, factors that seem to reduce the impact of thermal stress on coral reproduction. Cox (2007) found no change in reproductive parameters after a bleaching in *Montipora capitata* and hypothesized that this was due to the coral's capacity to increase its heterotrophic feeding. Along with carbon fixation by the zooxanthellae, heterotrophic feeding is an important source of energy for corals, and Grottoli et al. (2006) found that some corals are able to meet 100 % of their daily metabolic requirements through heterotrophic feeding. Corals of the species *M. capitata* were able to replenish their energy reserves within 6 weeks after a bleaching event when exposed to naturally available zooplankton. Plasticity in heterotrophic feeding has been found to help corals in both resistance to thermal stress (Borell et al. 2008) and recovery from a bleaching events (Connolly et al. 2012) (Sect. 9.7). The status of a reef's coral energy reserves in the time following a bleaching event would be a useful indicator of the chance of full recovery.

9.5 What Can We Learn from Bleaching of Other Symbiont-Bearing Organisms?

Research and literature addressing the symbiosis with *Symbiodinium* and bleaching has primarily focused on hard corals as indicators of bleaching, as these are the main builders of tropical coral reefs. However, symbioses between organisms other than corals and *Symbiodinium* remain poorly understood despite the fact that these relationships may help to provide clarification on processes within scleractinian corals and act as indicators for bleaching of various levels. Such symbioses are widespread within various ecologically relevant taxa of marine invertebrates and protists: Cnidaria (Hexa- and Octocorallia, some Scyphozoa such as *Cassiopea*), Mollusca (e.g., Bivalvia of the genera *Tridacna* and *Hippopus*: Hernawan 2008; Nudibranchia: Burghardt et al. 2008), Acoelomorpha (the genus *Waminoa:* Barneah et al. 2007), Porifera (Steindler et al. 2002), and Foraminifera (Lee et al. 1979). Similar to scleractinian corals, symbiosis with *Symbiodinium* in other organisms has evolved as a strategy to complement nutrition; these relationships can be either facultative or obligatory.

Despite many similarities (such as the cultivation of photosynthetically active and proliferating *Symbiodinium* in specific organs, specialised cell structures of host and symbiont, exchange of certain metabolites/chemicals), there are still important differences between corals and other symbiotic systems, particularly on the host side. In most symbioses, *Symbiodinium* lives intracellularly as endosymbionts; in Cnidaria, *Symbiodinium* are found within the cells of the endoderm, and in Nudibranchia, they reside within the digestive gland. In contrast, *Symbiodinium* in many bivalves (e.g., *Tridacna* spp.) are harboured extracellularly in specialised structures (Norton et al. 1992). Within the Acoelomorpha, they occur in parenchyma cells (intracellular) or in the lumen (extracellular; Barneah et al. 2007). In the unicellular Foraminifera, they reside in the endo- and ectoplasma (Köhler-Rink and Kühl 2000).

There is an abundance of literature on the impacts of a changing environment and the effects on scleractinian corals leading to their bleaching (e.g., Berkelmans and van Oppen 2006; Fitt et al. 2000). Throughout various non-coral taxa, investigations of other symbioses and bleaching susceptibility are, nevertheless, unfortunately scarce. Only a few studies have demonstrated that a large variety of *Symbiodinium* symbioses can suffer, and therefore indicate bleaching (octocorals: Goulet et al. 2008; Prada et al. 2010; Strychar et al. 2005; *Tridacna*: Buck et al. 2002; Norton et al. 1995; Porifera: Fromont and Garson 1999; Vicente 1990; Foraminifera: Talge and Hallock 2003). Bleaching mechanisms in these symbioses seem similar to coral systems and are mainly triggered by factors such as high water temperature and irradiance. Thus so far, non-coral symbiotic systems have rarely been used as indicators for bleaching, although they have an important ecological role and their examples in coral reef ecosystems are common. It would be crucial to include these symbioses in bleaching studies, since they reflect various host-symbiont-assemblages that might react differently from corals to bleaching conditions. Therefore, they represent an ideal array of indicators to monitor bleaching.

Many previous studies on corals highlight the importance of symbiont genotype in bleaching susceptibility, and the high diversity in *Symbiodinium* may be the key to the survival of coral reefs in times of coral bleaching. Diversity of *Symbiodinium* differs in various invertebrate hosts. Most scleractinian corals house clades A-D of *Symbiodinium*, but other symbiotic invertebrates and protozoans potentially house an even wider range of types. For example, in Foraminifera six different clades can be detected (A, C, F-I; Carlos et al. 1999; Pawlowski et al. 2001; Pochon and Gates 2010). Acoelomorph flatworms house clades A and C (Barneah et al. 2007), the jellyfish *Cassiopea* spp. houses clades A, B and D (LaJeunesse 2001; Lampert et al. 2011; Santos et al. 2002), sponges contain clades A, C and G (Hill et al. 2011), and various solar-powered nudibranchs cultivate clades A-D (Fitzpatrick et al. 2012; Loh et al. 2006; Wägele and Johnsen 2001). Symbiont acquisition is either vertical, which is the transfer of symbionts through oocytes or clonal cell division as seen in a few scleractinian corals, one species of *Waminoa* and foraminferans, or more commonly, they are acquired horizontally where every generation needs to acquire new symbionts. Vertical transmission of symbionts offers a reliable pool of certain zooxanthellae suited for stable environmental conditions. Alternatively, this acquisition mode offers less flexibility. In contrast, horizontal transmission offers flexibility such that each new generation takes up suitable *Symbiodinium* types. Depending on the specificity of the symbiosis, this could be a disadvantage, since needed *Symbiodinium* types might not always be available in the environment. Since most symbioses practice horizontal symbiont transmission, they depend on pools of *Symbiodinium* available in the environment (free-living stages in the water column and sediment) and in other symbiotic organisms (connected by expulsion of living symbionts).

Both *Symbiodinium* diversity and symbiont acquisition seem to be important for bleaching susceptibility of the holobiont. Bleaching susceptibility has most often been attributed to the thermal tolerance of the algal symbiont (Ulstrup et al. 2006). *Symbiodinium* display significant differences in physiological performance both within and among clades (Baker 2003; Hennige et al. 2009; Robison and Warner 2006; Savage et al. 2002). These dissimilarities obviously affect host performance (Berkelmans and van Oppen 2006) and influence the holobiont's ability to handle environmental stresses such as increased temperature (D'Croz and Mate 2004; Goulet et al. 2005). It has been suggested that the high diversity in *Symbiodinium* might be the key to survival of coral reefs in times of coral bleaching. Most research has focused on whether or not corals are able to associate flexibly with diverse symbionts whose different physiologies impart greater resistance to environmental extremes (Baker 2003; Berkelmans and van Oppen 2006). This model has been called the 'Adaptive Bleaching Hypothesis' (ABH: Buddemeier and Fautin 1993). According to the ABH, zooxanthellae may enter the host from exogenous sources (symbiont 'switching') or, if multiple zooxanthellae already concurrently exist within the host, a shift in symbiont dominance may occur (symbiont 'shuffling'; Baker 2003). The ABH has been a point of contention with ambiguous results coming from studies largely based on reef-building corals. Nevertheless, the high diversity of *Symbiodinium* in various invertebrate taxa might be important in times of bleaching, since they offer pools of potentially resistant *Symbiodinium* genotypes to bleached corals. Additionally, many non-coral symbioses are mobile and could act as vectors for spreading genotypes that are better adapted to alternative environmental conditions. For instance, a study by Stat and Gates (2008) demonstrated that symbionts can be introduced to new geographic locations vectored by mobile symbiotic invertebrate hosts. They showed that new *Symbiodinium* genotypes were introduced into Hawaiian waters by *Cassiopea* sp.

In contrast to the many studies that focus on the responsibility of the symbiont in bleaching, divergences in host tolerance or, particular host-symbiont-assemblages, have been examined far less frequently as possible causes of bleaching (Brown et al. 2002; D'Croz and Mate 2004; Goulet et al. 2005). Studies have demonstrated that holobionts consisting of identical *Symbiodinium* types but differing in coral hosts react differently to environmental stressors and could, therefore, be used as indicators for bleaching with different sensibility (Baird et al. 2009; Barshis et al. 2010; Bellantuono et al. 2012; Bhagooli and Hidaka 2004). Another recent study by Oliver and Palumbi (2011) indicated that only the combination of heat-resistant symbionts with heat-acclimatised/adapted hosts resulted in thermal tolerant holobionts. Thus, the interplay of both partners seems to determine bleaching susceptibility (Fitt et al. 2009; Ralph et al. 2001).

Concerning bleaching tolerance, generally, the relative role of the host is better understood than the one of the symbiont (Abrego et al. 2008; Baird et al. 2009). Due to the diverse phylogenetic origins of different invertebrate hosts, micro-environments offered to symbionts can vary (Jimenez et al. 2011). Factors such as host tissue thickness appear crucial in holobiont susceptibility to bleaching (Ainsworth et al. 2008; Loya et al. 2001; Stimson et al. 2002), and furthermore, host-driven protective mechanisms that could contribute to the regulation of the holobiont's bleaching response include the production of anti-oxidant enzymes (Baird et al. 2009; Lesser et al. 1990), fluorescent pigments (Salih et al. 2000), and mycosporine-like amino acids (MAAs; Dunlap and Shick 1998).

In summary, there are four main reasons to focus more on non-coral symbioses with *Symbiodinium* as indicators for bleaching in the future. (1) The wide variety of *Symbiodinium* genotypes (with significant differences in physiological performance and thus thermal tolerance) in various invertebrate symbiotic systems might act as potential *Symbiodinium* pools by offering symbiont types that are better suited for post-bleaching conditions. (2) Many non-coral symbiotic systems are (in contrast to corals) mobile. Mobile symbiotic systems are of particular interest since they can potentially adapt to changed environmental conditions by escaping to areas with more suitable environmental conditions (vertically and horizontally). They can potentially function as mobile *Symbiodinium* vectors by spreading symbiont types that are better suited for post-bleaching conditions by means of expulsion. (3) Since the relative contribution of the host in terms of bleaching tolerance is still unclear (Abrego et al. 2008; Baird et al. 2009), it is crucial to perform comparative studies investigating different symbiotic systems that share *Symbiodinium* as a symbiont. How do various host/symbiont-assemblages react to environmental stressors? (4) Non-coral symbiotic systems can be used as indicators to trace bleaching conditions early. Some of these systems are already used as bio-indicators for other purpose, for instance foraminiferans (subfamily Soritinae) are important in mineral and calcium cycles (Fujita et al. 2000; Murray 1991) and are used as bio-indicators in reef monitoring programs (Hallock et al. 2003). Another example is the jellyfish genus *Cassiopea*: Niggl et al. (2010) demonstrated that organic matter derived from the jellyfish *Cassiopea* sp. may function as a newly discovered pathway for organic matter from the benthic environment to pelagic food chains in coral reefs. Thus, a combination of organism traits and ecosystem processes could be utilised as indicators for bleaching.

9.6 Ecological and Biogeochemical Consequences of Coral Bleaching

The impact of coral bleaching on fundamental physiological processes, such as coral growth, calcification, and reproduction, results in broad-scale consequences for the ecosystem functions and services provided by this ecosystem engineer (Wild et al. 2011). Reduced growth and reproduction may thereby result in reduced resilience of coral-dominated reef communities. Similarly, reduction in the abilities of corals to compete with other invertebrates or reef algae (Hughes 1994) can lead to fundamental changes in the community structure of tropical benthic assemblages. Branching, framework-building corals, including the genera *Acropora, Seriatopora, Pocillopora*, and *Stylopora,* are morphologies that are more sensitive to thermal stress and bleach more often than massive and encrusting growth forms (Loya et al. 2001; Marshall and Baird 2000; McClanahan et al. 2002). In addition, larger branching colonies are more susceptible to thermal stress than their smaller counterparts (Bena and van Woesik 2004; Mumby et al. 2001a; Nakamura and van Woesik 2001). Consequently, mass coral bleaching events will likely change the coral reef landscape from one supporting a diversity of coral colony morphologies and species to a landscape dominated by fewer species with robust, small, massive, and encrusting coral forms. Therefore, coral morphology and species composition across the benthic reef community are potential proxies for the ecological effects of bleaching events.

Coral-generated production of inorganic materials (i.e., framework structures and calcareous sands) will decrease substantially with increasing bleaching frequency and extent because of the bleaching-induced inhibition of calcification (Sect. 9.4). Parameters such as reef rugosity may therefore also act as potential indicators reflecting the reef ecosystem consequences of coral bleaching. The calcifying activities of reef-building corals ultimately result in a three-dimensional matrix that provides space, shelter, and food for many reef associated organisms (Sale et al. 2005). Coral reefs are therefore associated with high abundances of fishes (McClanahan and Shafir 1990) and other animals. Coral bleaching may reduce the framework building and habitat generation capacity of reef corals. The resulting reduction in structural complexity also reduces the availability of habitat space at a variety of scales and leads to a considerable reduction in coral reef fish diversity (McClanahan and Shafir 1990). This highlights fish abundance and diversity as good indicators for coral bleaching consequences on the associated organisms.

Scleractinian corals continuously release particulate and dissolved organic matter (POM and DOM) (e.g., Wild et al. 2004). During thermal-induced bleaching, two different kinds of organic matter are increasingly released: (1) POM as zooxanthellae, and (2) POM derived from the coral host (Niggl et al. 2009). Degradation of these two POM sources by reef microbes is much lower for the released zooxanthellae (<1 % h^{-1}) than for the coral-derived POM (>5 % h^{-1}) (Wild et al. 2005). The very low microbial degradation rates for the cellulose-containing zooxanthellae indicates that most of the suspended zooxanthellae released during coral bleaching are not degraded and recycled by the reef microbes fast enough to allow recycling to take place in the reef. Alternatively, zooxanthellae are exported from the reef via the prevailing water currents. Thus, from a biogeochemical point of view, coral bleaching most likely involves a considerable loss of energy and essential nutrients from the reef ecosystem. In contrast, coral-derived POM may function as an energy carrier and particle trap (Huettel et al. 2006; Wild et al. 2004). This material, because of its fast microbial degradation rates, potentially stays within the reef system and is recycled, particularly by the benthic community (Wild et al. 2004). Histological analyses (Fitt et al. 2009) indicate that internal mucus production in the coral tissue is depleted during bleaching so that mucus-POM release by corals is most likely stimulated only during the early phase of bleaching, but drops to lower levels the longer the bleaching event lasts. This dynamic flux of POM was confirmed by the study of Piggot et al. (2009), who demonstrated that the number of mucus-producing cells (i.e., mucocytes) in coral tissue is potentially a good indicator for bleaching because they decline after an initial bleaching response. Coral bleaching thereby largely reduces the metabolic exchange between corals and all reef organisms that feed on coral-derived organic matter (e.g., microbes, filter feeders, fish) while also reducing the capacity of corals to trap organic matter. This may lead to further loss of POM from the reef system with subsequent important biogeochemical consequences.

Corals can recover from bleaching (Sect. 9.4), which also allows the reoccurrence of organic matter release by this key ecosystem engineer. The respective recovery time scales range from weeks to months (Gates 1990; Jokiel and Coles 1990), so that short- to mid-term effects on organic matter cycles driven by the corals can be expected from a brief impedance of the coral engineer during reversible bleaching. However, this may include long-term changes in the reefs nutrient recycling capacity. The initiation of carbon and nutrient cycles by coral-derived organic matter will, therefore, likely be reduced by coral bleaching.

Bleaching-induced mortality of the coral polyp also results in the exposure of bare skeletons. These structures are particularly sensitive to physical, chemical, and biological erosion processes (Stoddart 2008). In addition, colonisation of these stable surfaces by microbial biofilms, algae, or other invertebrates may not only reduce coral recruitment success (e.g. Webster et al. 2004), but also change important biogeochemical processes in the reef, such as nitrogen fixation (Davey et al. 2008).

9.7 Coral Susceptibility and Resilience to Bleaching and Subsequent Reef Degradation

9.7.1 Susceptibility and Resilience

In corals, photosynthesis of endosymbiotic zooxanthellae is significantly affected by light availability and water temperature. These environmental factors can affect coral susceptibility and resilience to bleaching, and because of this, considerable work has gone into understanding the parameters that influence light and temperature conditions in coral reef ecosystems (reviewed in: Brown 1997a, b; Hoegh-Guldberg 1999; Loya et al. 2001; Baker et al. 2008; Van Woesik and Jordán-Garza 2011). Given the spatial and temporal heterogeneity in marine environments and in climatic processes, and their dynamic interactions that are potentially confounding, it has not been easy to unequivocally discern all environmental processes affecting coral reef systems.

Ecological resilience is the potential of an ecosystem to absorb repeating disturbances and adapt to change while keeping its function and structure (Holling 1973; Nyström et al. 2000, 2008; Scheffer et al. 2001). Resilience of corals against coral bleaching encompasses the processes of resistance and recovery (Pimm 1984; West and Salm 2003), which represent two important environmental indicators of how corals cope with climate change and direct anthropogenic and natural disturbances. Resistance describes the capability of corals to withstand or to survive bleaching and bears an extrinsic (function of environmental factors) and an intrinsic, species-specific component (West and Salm 2003). Recovery is the process of regeneration after a severe bleaching event that resulted in significant mortality, and is directly associated with the growth and the replenishment of communities via coral recruitment (Marshall and Schuttenberg 2006; Diaz-Pulido et al. 2009).

At the ecosystem level, there is a degree of overlap in resilience and susceptibility, because those factors that make a coral reef susceptible can also increase systemic resilience depending on temporal and spatial occurrence of impacting factors. Research addressing the environmental factors that can mitigate coral bleaching and enhance recovery potential and resilience has identified several environmental indicators. Factors that mitigate thermally induced coral bleaching (Brown 1997a, b; Hoegh-Guldberg 1999. Hughes et al. 2003; van Oppen and Lough 2009) include decreased temperature stress during warm periods through either local seasonal upwelling (Glynn 1996; Riegl and Piller 2003; Chollett et al. 2010) or long amplitude internal wave pulses (Wall et al. 2012). Currently, upwelling-induced mitigation of coral bleaching, and consequently resilient reefs were observed in the western coast of Mexico (Glynn and Leyte-Morales 1997; Reyes-Bonilla 2001; Reyes-Bonilla et al. 2002), the Gulf of Panama (Glynn et al. 2001; Podestá and Glynn 1997), the Gulf of Papagayo/Costa Rica (Jiménez et al. 2001), the Bahamas (Riegl and Piller 2003), South Africa (Riegl 2003), Northern Madagascar (McClanahan et al. 2007a, b), and the Colombian Caribbean (Rodríguez-Ramírez et al. 2008; Bayraktarov et al. 2012, 2013). In addition, Wall et al. (2012) observed that corals of the Andaman Sea/Thailand exposed to deep-water intrusions by long amplitude internal waves were less susceptible to coral bleaching than corals at sheltered sites. Less coral bleaching and faster recovery was also observed in regions with exposure to a naturally high water flow (Bayraktarov et al. 2013; Nakamura and van Woesik 2001; Nakamura et al. 2003; West and Salm 2003). Hydrodynamics enhance water flow-induced mass exchange (e.g., respiration or uptake of nutrients) and molecular transport processes (Huettel et al. 2003), and have considerable consequences for coral physiology (Atkinson et al. 1994; Mass et al. 2010; Wild et al. 2012). They play a role in the removal of toxic Reactive Oxygen Species (ROS) and its derivatives, which are produced during bleaching (Nakamura and van Woesik 2001; Lesser 2006) (Sect. 9.4).

Bleaching can also be influenced by the amount and type of irradiance that arrives at the corals through the atmosphere and water. An increase in particle concentrations within either environment results in the scattering of light and the lessening of its intensity. This has been demonstrated in the Tuamotu Islands, where the absence of bleaching was attributed to high cloud cover (Mumby et al. 2001b). Likewise, coastal reefs with high levels of suspended terrigenous material display less bleaching than reefs further from shore (West and Salm 2003). Similarly, coral bleaching was less in areas that received shading, such as reefs near tall cliffs in the Pacific (Salm et al. 2001). However, it is not just the quantity of light that reaches the corals, but also the quality of light can have strong impacts. Increases in ultraviolet radiation can cause photoinhibition (Sect. 9.4) and this can be a concern for corals in shallow water or in geographical areas with a damaged atmospheric layer (Shick et al. 1996). Bleaching has also been attributed to other factors including reduced salinity (Kerswell and Jones 2003) and exposure to toxins (Jones et al. 1999) (Sect. 9.3), and although these can present localised confounding factors, most managers assessing bleaching susceptibility consider the mediation of high water temperatures of most importance due to its widespread implications (Sect. 9.8). Faster recovery from bleaching and thereby higher resilience in the long term was attributed to corals that increased their heterotrophically acquired carbon budget (Grottoli et al. 2006) (Sect. 9.4).

Understanding the effect of varying environmental conditions on corals is becoming increasingly important, because climate change is likely to increase the spatial and temporal variability of these factors, some of which are directly related to coral bleaching. When high temperature anomalies are severe and prolonged, as can be experienced during El Niño years, regional-scale bleaching can be pronounced (Glynn 1993) (Sect. 9.3). In some regions, the frequency and intensity of tropical storms may also increase (Hughes et al. 2003), although, there are indications that storms may provide a net benefit to coral reefs because they mix warming surface layers with deeper waters (Riegl 2007). Changes in global weather patterns will lead to more extreme rainfall in some areas (Hoegh-Guldberg et al. 2007). This, combined with increasing coastal populations, may increase pollution and eutrophication on near-shore reefs (Glynn 1996), reducing overall coral fitness and making them more susceptible to bleaching. Moreover, thermal expansion of the oceans indicates that sea levels will continue to rise, and further redistribution of heat in the oceans may lead to changes in the dominant currents known as the “global conveyor belt” (Hoegh-Guldberg and Bruno 2010). Although not a direct factor of coral bleaching, ocean acidification may lead to a reduction in carbonate accretion and density, resulting in a decrease in overall coral fitness (Hoegh-Guldberg et al. 2007). The synergistic effects of these factors, and the changes on spatial and temporal scales, indicate that reefs will experience increasingly variable environmental conditions, and thus, increasing stress that promotes the likelihood of coral bleaching events. This is particularly true for reefs with pre-existing environmental factors, such as land-based pollution of areas with limited cold water exchange, which may increase their susceptibility and make them less resilient to bleaching events.

9.7.2 Reef Degradation

In worst case scenarios, combined stressors will interact before, during and after bleaching events leading to increased degradation of reefs. Within coral reef communities, there is taxonomic variation in susceptibility to bleaching (van Woesik et al. 2011) (Sect. 9.6). Coral reefs are generally resilient to localised disturbances because depleted populations can be repopulated by unaffected populations (Sale 1991). However, the extent of coral bleaching can vary depending on population composition and susceptibility (Sect. 9.6), and community effects can vary based on the extent of bleaching events. Immediate ecological responses to bleaching events are less studied than longer-term responses, but studies have shown that other (non-coral) species are affected by their degree of specialisation to corals and their ability to shift resources during alternative ecological states (Pratchett et al. 2009). Specifically, species that rely on corals for food or habitat, such as fish, show the quickest changes in populations, while reduction in coral populations may have sub-lethal effects on coral-specific organisms because later generations are not able to find habitat for recruitment. For example, butterfly fish and certain damselfish populations that experienced losses after extreme bleaching events were able to shift to bleached coral for habitat, but declined because the impacted reef was not suited for larval recruitment (Wilson et al. 2006). Therefore, it may be possible to use species that react strongly to changes in coral communities as pre-bleaching indicators of potential, post-bleaching, coral reef health.

Bleaching-induced changes in habitat can lead to the long-term loss of species and function and overall degradation of reefs. On the community level, continuing function depends on the pre- and post-condition of the reef. In the Caribbean, reefs that existed in equilibrium state between corals and algae became algae-dominated after a relatively minor bleaching event due to an already reduced herbivore community (Ostrander et al. 2000), indicating that the pre-bleaching status of the ecosystem leads to higher levels of susceptibility. Sub-lethal effects on coral reef species, or inter-generational effects, depend on the recovery of the current system.

Although the susceptibility of coral reefs to degradation in relation to coral bleaching events is not easy to understand fully, many indications of possible effects can depend on the environment (changes in light attenuation and water temperature) and the community composition (present groups of organisms). It may be possible to use these conditions as an indication of susceptibility and the possible effects on these vulnerable ecosystems.

9.8 Management Strategies Against Coral Bleaching

Coral survival and recovery prospects can be promoted through appropriate marine protected area (MPA) design (Salm et al. 2001). Conservation priority is often focused on areas of high-biodiversity (hotspots) that are currently exposed to local anthropogenic stressors (Myers et al. 2000). The disadvantage of this conservation strategy is that the influence of climate change is hardly manageable because local processes such as overfishing or pollution reduce reef resilience prior to climate change driven impacts. Therefore, West and Salm (2003) suggested identifying areas with low exposure to climate threats and reducing human impact on these particular regions (Sect. 9.7). This would assure the potential for corals to persist in "refugia" and resist bleaching in times of changing climate (Glynn 2000; Riegl and Piller 2003). Current conservation strategies should take into account reef resilience assessments during climate change in order to define management priorities (Maynard et al. 2010; Obura and Grimsditch 2009). McClanahan et al. (2012) recently proposed an evidence-based framework for the identification of climate change resilience of coral reefs to define conservation priorities. This novel framework includes the measurement of 11 key factors selected by perceived importance, empirical evidence, and feasibility of measurement (McClanahan et al. 2012). Rau et al. (2012) go one step further and encourage marine science and management communities to actively evaluate all marine management strategies, including unconventional ones such as shading of local reefs from solar radiation during increased thermal stress (Jones et al. 1998; Jones 2008; Hoegh-Guldberg 1999), low-voltage direct current, which has been proposed to stimulate coral growth (Sabater and Yap 2002, 2004; Goreau et al. 2004), and wave- or tidal powered artificial upwelling (Kirke 2003; Hollier et al. 2011). In times of dramatic climate change, our hope lies in the most resilient reefs and the increase of reef resilience through management actions, which should, therefore, be considered as essential conservation priorities.

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Chapter 10
Invasive Alien Species and Their Indicators

Robert H. Armon and Argyro Zenetos

Abstract Biodiversity is obstructed not only by climate change but also, among other factors, by invasive alien species (IAS). The infiltration/invasion, overgrowth, and control of IAS is linked to many elements, such as human activities that change our environment in such a way that, together with climate change, new opportunities for alien species to conquer new territories are realized. The successful take over by IAS of new geographic areas is orchestrated by the ability to grow fast and spread rapidly without "real competition." The environmental/ecological impact of IAS has still to be defined; however, there is plenty of research that can be performed to assess this facet. Presently, the global awareness of IAS is rising, as expressed in the many international committees/organizations looking for IAS's indicators and economical solutions to the problem.

Keywords Invasive alien species (IAS) • Invasion • Tropicalization • Climate change • Streamlining European Biodiversity Indicators (SEBI) • Delivering Alien Invasive Species Inventories for Europe (DAISIE) • Marine Strategy Framework Directive (MSFD)

10.1 Introduction

Perhaps the most invasive species known to science today is the human race. Starting ~200,000 years ago somewhere in Africa, our species conquered almost every territory/niche on this planet. Like all invasive species, humans developed two main characteristics of an invasive species, that is, the ability to: (1) grow in diverse ecological niches, and (2) reproduce successfully. As seen later in this chapter, the human invasion has both positive and negative aspects. To justify our

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_10

impact on our environment, our entrance into the history of the universe brought amazing positive developments (i.e., computer technology), control over some parts of the nature (i.e., agriculture), and control over other organisms (i.e., disease control), although coupled with some highly negative aspects such as wars (i.e., self-destruction), pollution, annihilation of other species, and overcrowding of the planet earth! The present chapter is not intended to describe the human species as such but rather to describe other organisms that have invaded our environment and the methods using specific indicators that we are expecting to use to allow us to issue warning about them. However, we must bear in mind that we constitute a very important, sometimes even crucial factor, in species invasion.

From the historical point of view, almost all cultivar plant species are invasive species spread mainly by humans! Most of our edible plants have been transferred from one place to another along the centuries in parallel with human global colonization, e.g.: the potato (*S. tuberosum* sp.), domesticated in Peru-Bolivia and later brought to Europe; the tomato (*Solanum lycopersicum* sp.), a native of South and Central America subsequently distributed all over the world; maize (*Zea mays subsp. Mays*), domesticated in the Tehuacan Valley of Mexico and later dispersed globally; and wheat (*Triticum* spp.), originally cultivated in the Near East and Ethiopian Highlands and now disseminated globally. It should be pointed out that the spread of and invasion by an organism is controlled by several factors: (1) distance; (2) climate; (3) nutrient sources; and (4) genetics. It is clear that an endemic plant growing in one continent has to be transported to another continent in order to prosper and invade. Nevertheless, when dealing with motile or marine organisms (birds, mammalians, fish, crustaceans, etc.), transport is facilitated by their motility without direct human intervention (Fig. 10.1). Therefore the invasion process should be defined carefully in order to distinguish it from other ecological processes. Basically, species invasion should be examined from our perspective and linked to the environmental/ecological balance and its beneficiary/detrimental impact (Kelly and Hawes 2005; Whitman 2000).

The definition of the term ‘alien’ species varies (Warren 2007). Alien: an organism occurring outside its natural past or present range and dispersal potential, whose presence and dispersal is due to intentional or unintentional human action. In Europe, natural shifts in distribution ranges (due, e.g., to climate change or dispersal by ocean currents) do not qualify a species as an alien (Ojaveer et al. 2014). In contrast, immigration due to climate changes is considered biological invasion in USA. Invasive species are a subset of those alien species that are established and have an impact (positive or negative) on ecosystems and/or ecosystem functioning.

In Europe, invasive species are defined as species that are external to their natural distribution and also threaten biological diversity (EEA 2012; Genovesi et al. 2012; Anonymous 2011a). There are additional definitions, such as that which relates to native species able to overspread in the absence of natural control (deer, family Cervidae) or that which relates to a species that is globally widespread and therefore is considered non-indigenous to a specific environment (e.g., the plants mentioned above among flora, or the common goldfish, *Carassius auratus* among fauna).

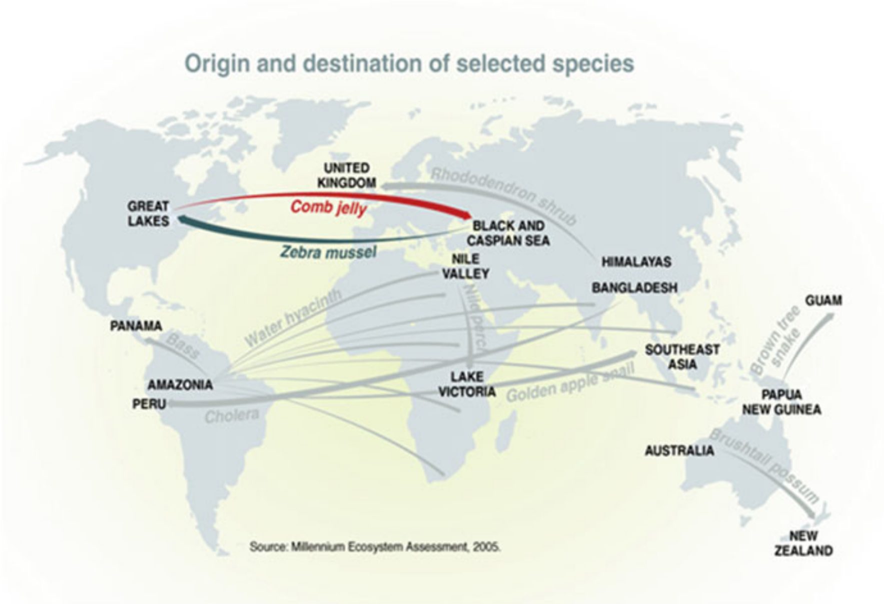


Fig. 10.1 Invasive Species around the World (With permission from Source: Philippe Rekacewicz, UNEP/GRID-Arendal)

To summarize the definition incoherence, it can be said that "the term **invasive** has been used to describe among other things: (1) any introduced non-indigenous species; (2) introduced species that spread rapidly in a new region; (3) introduced species that have harmful environmental impacts, particularly on native species" (Ricciardi and Cohen 2007); and (4) introduced species that have a socio-economic impact (economy, tourism, human health) (EEA 2009).

To accentuate these definitions, a bird species is considered as an alien invasive species under the following conditions: (1) it has been introduced (intentionally or accidentally) to a site previously unknown to it; (2) it becomes proficient to breed without extra human involvement; (3) it spreads and develops as a pest impacting the local biodiversity, environment, the economy, and/or society, as well as human health. Perhaps the best known examples are the European Starling (*Sturnus vulgaris*), Common Myna (*Acridotheres tristis*), and the Red-vented Bulbul (*Pycnonotus cafer*), which are among the "100 of the World's Worst Invasive Alien Species" (a subset of the Global Invasive Species Database) (Anonymous 2014a, b, c). The "Delivering Alien Invasive Species Inventories for Europe" (DAISIE) project selected the Canada goose (*Branta canadensis*), ruddy duck (*Oxyura jamaicensis*), rose-ringed parakeet (*Psittacula krameri*), and sacred ibis (*Threskiornisa ethiopicus*) as among the 100 most invasive species in Europe (Anonymous 2013). In USA, among plants, *Lygodium microphyllum* (generally known as climbing maidenhair fern), a fern originating in tropical Africa, South East Asia, Melanesia, and Australia, became an invasive weed in Florida and

Alabama's open forest and wetland areas (Pemberton 1998; Volin et al. 2004). Here is the place to ask a straightforward question: is every alien species a hazard to its newly invaded environment?

According to DAISIE (Delivering Alien Invasive Species Inventories for Europe, a project supported by the European Commission under the Sixth Framework Program) among the ~11,000 alien species encountered in Europe, the majority are interim innocuous, while ~15 % cause economic damages and ~15 % harm biological diversity (the environment, habitats of animals, plants and microorganisms) (Anonymous 2013; Vilà et al. 2011). Table 10.1 shows several invasive alien species that belong to those ~30 % that are hazardous in a certain geographic area: Florida, USA (Anonymous 2006).

A look at the anti-IAS's organizations and their published material makes it clear that we are increasingly aware of this environmental phenomenon (at the national and international level) and many environmental organizations are involved in IAS problem definition, its state, and response through database organization, real time reports, indicator systems, and response/combat when needed.

However, at present, trying to find a more precise definition of an invasive species, we envision the introduction of flora and fauna that harmfully affect bioregions (economically, environmentally, and ecologically); however, not only these.

10.2 Factors Enhancing/Limiting IAS

Invasive alien species can be divided in two major groups: one that is characterized by mobility and can move freely along a wide range of geographic distribution (even very long distances, in the case of migratory birds), and a second that is characterized by immobility (e.g., plants) and can be transported only by animals/human activity or air/water currents. The first group is less reliant on human activity but can be affected by it in terms of their invasiveness. The second group is dependent mostly on human global activity, as shown in Table 10.2.

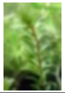
Among the factors that impact IAS distribution can be found: landscape use (deforestation; aquaculture; canals, i.e., Suez); global trade (ships ballasts and fouling); tourism (recreational boats, angling, botanical gardens, parks); aquarium trade] armed conflicts and reconstruction; regulatory regimes; biological control of pests and public health and environmental concerns. All these are orchestrated by humans (Kettunen et al. 2009). The last factor, environmental concerns, includes climate change; perhaps the only one for which human activity cannot be absolutely blamed, regardless of many scientific studies that have shown our central role in climate change fluctuations! A good example of climate change impact has been seen in the present-day Mediterranean marine biodiversity. This marine biodiversity is undergoing a rapid alteration through the increased occurrence of warm-water biota, tagged Mediterranean "tropicalization" (Zenetos et al. 2011). Together with the Atlantic influx, Suez Canal (lessepsian) migration, and humans' introduction of alien species, the Mediterranean Sea harbors an increased tropical

Table 10.1 Some examples of aggressive invasive alien species in Florida

Name	Type	Origin	Extent	Damage	Benefits
Brazilian Pepper (*Schinus terebinthifolius*) 	Shrub	Brazil & Paraguay; introduced in nineteenth century	Central & South Florida 700,000 acres	Shades out other plants, toxic to wildlife, causes poison ivy-like reaction	Ornamental plant; melliferous flower; spices
Cane toad (*Rhinella marina*) 	Amphibian	Amazon basin to the Rio Grande Valley; introduced accidentally in 1955	Spread via canals, found in 21 counties, Florida	Toxic secretions can kill pets or native predators; competes with native amphibians, eat insects	Predators' food including humans; biological pest control; laboratory animals
Chinese tallow (*Triadica sebifera*) 	Tree	China; introduced in eighteenth century	Northern & Central Florida, 38 counties	Displaces native trees; falling leaves contribute to nutrient loading in streams; oily seeds toxic to cattle	Ornamental honey plant for beekeepers; soap production;
Citrus canker (*Xanthomonas axonopodis*) 	Bacterium	Southeastern Asia; first found in USA in 1910	Florida's 11 counties currently quarantined	Highly contagious disease that causes citrus trees to drop their leaves and fruit. 2.9 million trees have been destroyed	

(continued)

Table 10.1 (continued)

Name	Type	Origin	Extent	Damage	Benefits
Cogon grass (*Imperata cylindrica*) 	Grass	Southeast Asia; introduced in 1920s and 1930s for forage and soil stabilization	Roadsides, fields & woods in Central & North Florida	Displaces native plants; little food value for wildlife; creates severe fire hazards	Ornamental; roof thatching; ground cover and soil stabilization; food; paper-making
Hydrilla (*Hydrilla verticillata*) 	Aquatic plant	Africa & Southeast Asia; introduced in Tampa area as an ornamental in 1950s	50,000 acres; 140,000 acres of tubers that could still resprout	Clogs waterways, restricting recreation; kills other aquatic life by blocking sunlight and consuming oxygen; promotes breeding of mosquitos	Bioremediation hyper-accumulator of Mercury, Cadmium, Chromium and Lead, and as such can be used in phytoremediation; high resistance to salinity; ornamental
Melaleuca 	Tree	Australia; introduced 1906 for windbreaks, timber & landscaping	South Florida 400,000 acres	Displaces native plants; alters water flow in everglades; oily leaves promote serious fires	Essential oil with medicinal qualities; drains low-lying swampy areas
Water hyacinth (*Eichhornia crassipes*) 	Aquatic plant	South America; introduced in 1880s	120,000 acres in 1960s, reduced to 2000 acres	Kills fish through anoxia; promotes breeding of mosquito; blocks waterways and crowds out native species	Biomass; wastewater phytoremediation, food and medicine

Adapted from Florida Fish and Wildlife Conservation Commission and Defenders of Wildlife (Anonymous 2014a, b; FLEPPC 2013)

Table 10.2 Factors impacting IAS global spread (FAO 2005)

Factor	Details	Examples	References
Land use changes including forest activities	Deforestation, reforestation, plantation, and timber industry	*Melaleuca quinquenervia* a native tree of Australia introduced into southern Florida (USA) invaded Florida's Everglades National Park; *Prunus serotina* a native tree of North America introduced into Europe, today an aggressive invasive species, mostly in Germany; Re-emergence of infectious diseases (leishmaniasis, yellow fever, trypanosomiasis (both African sleeping sickness and Chagas disease) through increased forest activity and human contact	Porazinska et al. (2007), Dassonville et al. (2008), Doren et al. (2009), Anonymous (2005)
Economics and trade	Globalization, material trade, vehicles (cars and trucks) trains, planes, ships, railways	A major source of forest pests and diseases originate from unprocessed wood, wood products, and nursery stock. For example, in the United States: chestnut blight (*Cryphonectria parasitica*), Dutch elm disease (*Ophiostoma ulmisensulato*), and white pine blister rust (*Cronartium ribicola*)	Bryner et al. (2012), Santini et al. (2005), McKinney et al. (2009), Robinet et al. (2009), Hummel (2003), Meyerson and Mooney (2007) and Vilà et al. (2010)
		The pinewood nematode (*Bursaphelenchus xylophilus*), the pine wilt disease agent spread from its native North America to Asia and Europe in wooden packing materials	
Climate change and changes in atmospheric composition	Human activities releasing greenhouse gases: (CO_2), methane, nitrous oxide, halocarbons, and ozone into the atmosphere. Consequently, the annual temperature rises causing species to spread into higher latitudes and altitudes	Climate warming trends may also allow for longer breeding seasons for invasive species, as observed in populations of the collared dove (*Streptopelia decaocto*) in Europe	Crooks and Soulé (1999) and Sheppard et al. (2014)
Tourism	Travelers can intentionally transport plant and animal species that can turn into invasive, or unintentionally they can transport fruits and other living or preserved plant materials that harbor insects and diseases that can have hazardous effects on agriculture, forestry and other sectors	For instance, Arctic species such as chickweed and yellow bog sedge have been found in Antarctica, able to tolerate low temperatures	Chown et al. (2012) and McNeely et al. (2001)

(continued)

Table 10.2 (continued)

Factor	Details	Examples	References
Conflicts and reconstructions	Wars and military conflicts lead to the collapse of controls and management systems (for plants and animals health), loss of supply lines for materials, the displacement of extensive numbers of people, lack of inspections and border controls increasing the unregulated movement of military personnel and refugees	During World War II, American troops inadvertently introduced the root rot of the pine tree (*Heterobasidio nannosum*) into Italy, causing an unprecedented mortality rate of stone pines (*Pinus pinea*). It is assumed that this pathogen was transferred in transport crates, pallets, or other military equipment made from untreated lumber from infected trees. Foreign food aid has been blamed for introducing agricultural pests into several African countries, such as the larger grain borer (*Prostephanus truncatus*), e.g., into the United Republic of Tanzania in a food aid shipment in 1979	Gonthier et al. (2004), FAO (2001a)
	Displaced people and their belongings can be a dispersal mechanism for, or the source of, alien invasive species		
	Increased smuggling can relocate alien species to new regions		
	Inflows of food aid may be contaminated with pests and diseases		
	Difficulties in obtaining access to border areas because of landmines and other hazards make these areas difficult to survey		
Regulatory regimes	Regulatory systems for managing alien invasive species are strongly dependent on the actions of both the government and private sectors. Its effectiveness is determined by the national resources' level and technical capacity provided by the government	New Zealand Ministry of Primary Industries site, http://www.biosecurity.govt.nz/regs/imports, shows a variety of regulations for controlling IAS introduction in this country. Most developed countries have regulatory systems controlling trade and transport of plants and animals species over international borders	FAO (2001a) and Kettunen et al. (2009)

Biological control of pests	Alternative source of IAS is the intentional importation and release of insects, snails, plant pathogens, and nematodes for pests biological control (biocontrol)	The coccinellid beetle *Harmonia axyridis* has been introduced as a biological control agent in Europe and the USA. Since its introduction, it has established and spread, and is now regarded as an invasive alien species	Raak-van den Berg et al. (2012)
Public health and environmental concerns	Concerns about human health and pesticides/herbicides application (e.g., organic agriculture) may promote the unchecked spread of IAS	*Rhinocyllus conicus*, a seed-feeding weevil, was introduced to North America to control exotic thistles (Musk and Canadian). However, the weevil does not target only the exotic thistles; it also targets native thistles that are essential to various native insects that rely solely on native thistles and do not adapt to other plant species	FAO (2001a) and Rand and Louda (2006)

marine biota (Raitsos et al. 2010; Anonymous 2011b). In connection with waterways, European inland waterways provide new prospects for the spread of nonnative aquatic species or IAS. The introduction pathways of IAS in Europe through aquatic networks have been defined, e.g., shipping (passage of ships or port), canals (within river basin or else), wild fisheries (commercial fishery exists in the area-stock movements, population reestablishment, releases of organisms intended as living fish food supplements, movement of fishing equipment), culture activities (aquaculture), ornamental and live food trade (garden centers, ornamental ponds, public aquaria or live food trade), leisure activity (marina or leisure craft visit with festivals; sporting events -including angling-SCUBA diving), alteration to natural water flow (hydrotechnical activities: creation of reservoirs, dams, dredging activities), thermal pollution (discharges of heated waters from power plants, untreated wastewater discharges), research and education (research activities with alien organisms or demonstration cultures of alien organisms), biological control (known biological control activities), and others (organic and chemical pollution, habitat modification, discharged live packing material, etc.) (Panov et al. 2009; Ojaveer et al. 2014).

An examination of the factors affecting IAS global spread shows that the effectiveness of IAS prevention is debatable (as our world is not a sterile environment), although well-established national and international regulations can reduce IAS spread and its consequences (Table 10.2).

10.3 An Issue of Global Concern

Aichi Target 9 states that "by 2020, invasive alien species and pathways are identified and prioritized, priority species are controlled or eradicated, and measures are in place to manage pathways to prevent their introduction and establishment"; Target 5 of the EU Biodiversity Strategy (EC 2011) is similar.

The EU Biodiversity Strategy (EC 2011) specifically stresses the need to assess pathways of biological invasions through its Target 5: "By 2020, invasive alien species and their pathways are identified and prioritized, priority species are controlled or eradicated, and pathways are managed to prevent the introduction and establishment of new invasive alien species."

Recognizing the need for a comprehensive instrument at EU level to tackle biological invasions effectively, the European Commission has recently issued a Communication presenting policy options for an EU Strategy on Invasive Species (EC 2008a). Furthermore, the Marine Strategy Framework Directive (MSFD; EC 2008b), which is the environmental pillar of EU Integrated Maritime Policy, sets as an overall objective to reach or maintain "Good Environmental Status" (GES) in European marine waters by 2020. It specifically recognizes the introduction of marine alien species as a major threat to European biodiversity and ecosystem health, requiring member States to include alien species in the definition of GES and the setting of environmental targets to reach it. Hence, one of the 11 qualitative descriptors of GES defined in the MSFD is that "non-indigenous species introduced by human activities are at levels that do not adversely alter the ecosystem" (Descriptor 2).

Currently a dedicated legislative instrument is being developed by the Commission as dictated by Action 16 of the Biodiversity Strategy. Among the indicators adopted to assess this descriptor are "trends in abundance, temporal occurrence and spatial distribution in the wild of non-indigenous species, particularly invasive non-indigenous species, notably in risk areas, in relation to the main vectors and pathways of spreading of such species" (Cardoso et al. 2010).

The SEBI (Streamlining European Biodiversity Indicators) 2010 process was established "to streamline national, regional and global indicators and, crucially, to develop a simple and workable set of indicators to measure progress and help reach the 2010 target" (EEA 2012). The SEBI process was initiated by generating >140 possible biodiversity indicators, a number that was later reduced to 26 through rigorous criteria by 2007 (Table 10.3).

In 2005, based on the report titled "Invasive alien species indicators in Europe, a review of streamlining European biodiversity (SEBI) Indicator 10," three indicators or "elements of an indicator" were submitted to the SEBI coordination team (EEA 2012):

1. Cumulative numbers of alien species in Europe since 1900;
2. Selected worst IAS threatening biodiversity in Europe;
3. Selected impacts/abundance of IAS;

Table 10.3 SEBI[a] 2010 indicators within CBD[b] focal areas and EU headline indicators

CBD focal area	Headline Indicator	SEBI 2010 specific indicator
Status and trends of the components of biological diversity	Trends in the abundance and distribution of selected species	1. Abundance and distribution of selected species
		(a). Birds
		(b). Butterflies
	Change in status of threatened and/or protected species	2. Red list Index for European species
		3. Species of Europe interest
	Trends in extent of selected biomes, ecosystems, and habitats	4. Ecosystem coverage
		5. Habitats of European interest
	Trends in genetic diversity of domesticated animals, cultivated plants, and fish species of major socioeconomic importance	6. Livestock genetic diversity
	Coverage of protected areas	7. Nationally designated protected areas
		8. Sites designated under the EU Habitats and Birds Directives
Threats to biodiversity	Nitrogen deposition	9. Critical load exceedance for nitrogen
	Trends in invasive alien species (numbers and costs of invasive alien species)	10. Invasive alien species in Europe
	Impact of climate change on biodiversity	11. Impact of climatic change on bird population

(continued)

Table 10.3 (continued)

CBD focal area	Headline Indicator	SEBI 2010 specific indicator
Ecosystem integrity and ecosystem goods and services	Marine Trophic Index	12. Marine trophic
	Connectivity/fragmentation of ecosystems	13. Fragmentation of natural and semi-natural areas
		14. Fragmentation of river systems
	Water quality in aquatic ecosystems	15. Nutrients in transitional, coastal and marine waters
		16. Freshwater quality
Sustainable use	Area of forest, agricultural, fishery and aquaculture ecosystems under sustainable management	17. Forest: growing stock, increment and fellings
		18. Forest: deadwood
		19. Agriculture: nitrogen balance
		20. Agriculture: area under management practices potentially supporting biodiversity
		21. Fisheries: European commercial fish stocks
		22. Aquaculture: effluent water quality from finfish farms
	Ecological Footprint of European countries	23. Ecological footprint of European countries
Status of access and benefits sharing	Percentage of European patent applications for inventions based on genetic resources	24. Patent applications based on genetic resources
Status of resources transfers	Funding to biodiversity	25. Financing biodiversity management
Public opinion (additional EU focal area)	Public awareness and participation	26. Public awareness

[a]SEBI = Streamlining European Biodiversity Indicators
[b]CBD = Convention on Biological Diversity

4. Awareness of IAS;
5. Cost of IAS.

Among the above three suggested indicators, only two were selected: (1) "cumulative numbers of alien species in Europe (since 1900)," and (2) "selected worst IAS threatening biodiversity in Europe"; the other three were rejected on the basis of weaknesses and uncertainty. From the database collection for the years since 1900 and its analysis, it was found that the suggested indicator No. 1, based on the cumulative decadal database and geographical spread, clearly shows that there is a steady increase in the numbers of alien species in Europe (Figs. 10.2 and 10.3). However, two weaknesses of this indicator were recognized: "a) invasive alien species are not distinguished and b) there is limited geographical coverage for the

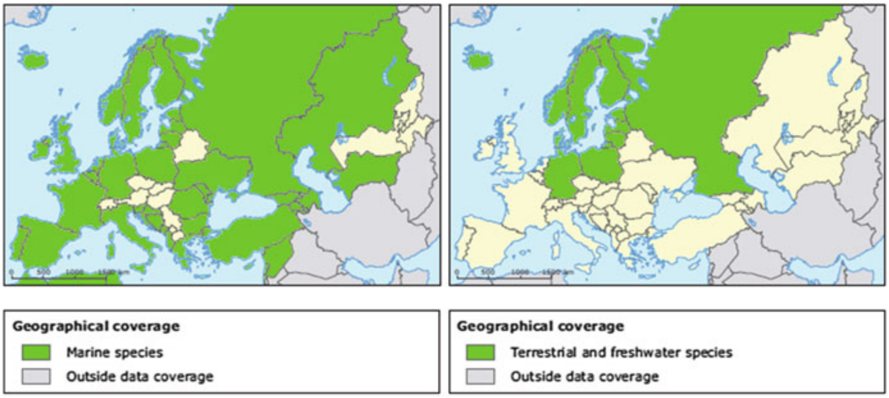


Fig. 10.2 Geographical coverage of the "Cumulative number of alien species established in Europe since 1900" (With permission from EEA 2012)

terrestrial and freshwater data set" (EEA 2012). The second indicator (selected the worst IAS threatening biodiversity in Europe) produced a large database; however, it failed to answer the posed key policy question: which IAS should be targeted by management actions? This indicator has two main recognized weaknesses: a) subjectivity in selection of species, and b) limited measurement of precise impacts of IAS (Fig. 10.4). In spite of its serious limitations ("the main conclusion drawn from the map was that fairly high numbers of listed species can be found in all European countries"), it served well for raising public awareness (EC 2012).

10.4 Justification for Indicator Selection and Potential Indicators

The policy questions such as "is the number of alien species in Europe increasing?" and "which invasive alien species should be targeted by management actions?" were answered using two indicators, which were the "cumulative number of alien species established in freshwater, terrestrial and marine environments," and the "worst invasive alien species threatening biodiversity in Europe." As the 2010 biodiversity target was not met, new global and European targets have to be determined.

In order to confront this relatively new threat successfully, it should be clear that the most hazardous IAS members are those that threaten the biological diversity and habitat destruction. Those species are fast multiplying, growing, and spreading, and thus, altering the eco-habitat and everything encompassed in such a system (Hulme 2007). One of the main indicators of an ecosystem's health is its biodiversity parameter, which may be hampered by IAS, e.g., the sea squirt *Didemnum vexillum* that may cover many square kilometers of sea floor while overgrowing

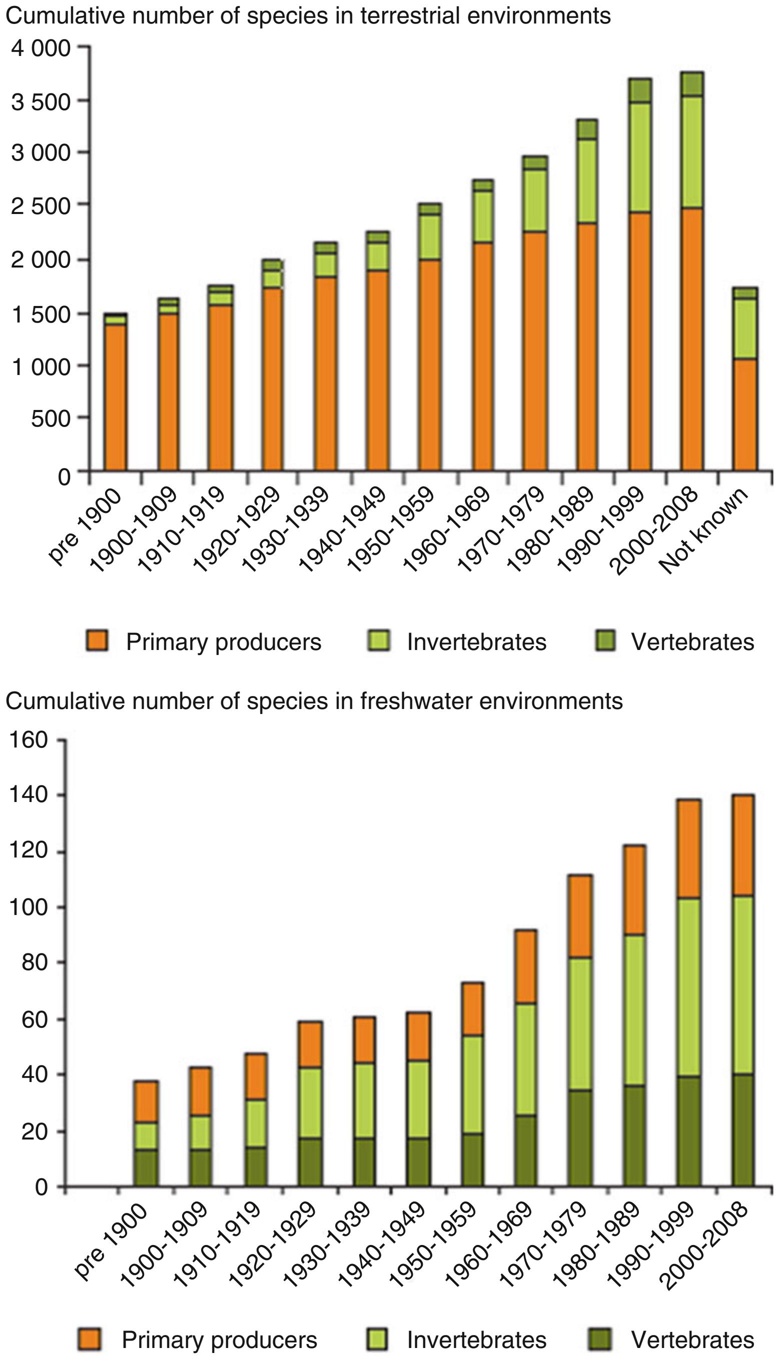


Fig. 10.3 Cumulative numbers of established alien species in Europe (since 1900) (With permission from EEA 2012). **Note:** The geographic coverage for data from the terrestrial and freshwater environments is: Denmark, Estonia, Finland, Germany, Iceland, Latvia, Lithuania, Norway, Poland, Russia and Sweden (With permission from EEA 2012)

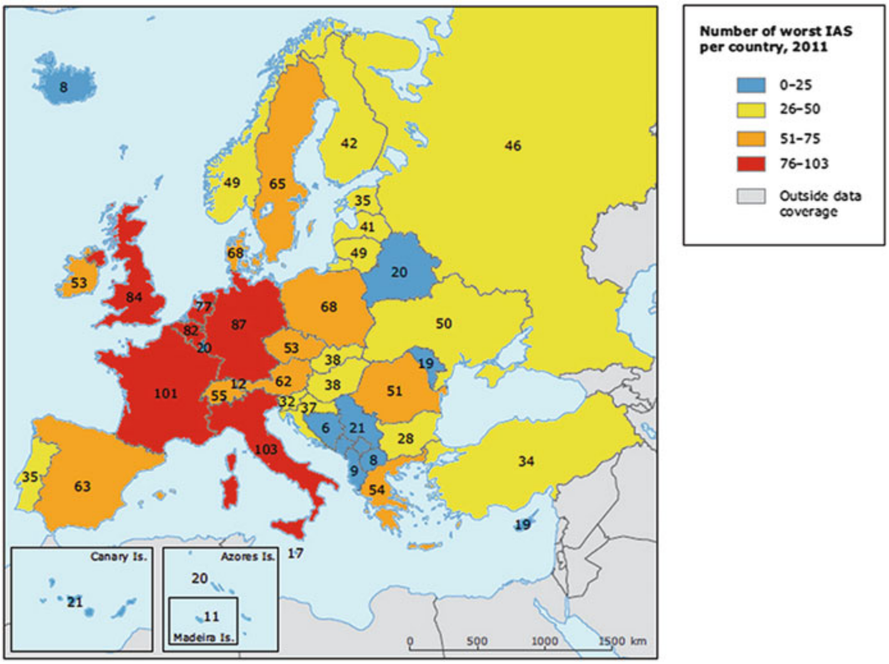


Fig. 10.4 Number of the worst IAS per country and an approximate estimate of their density. **Note:** A few of the worst IAS and some countries are not included in DAISIE, and country distributions are known to be incomplete for several species (With permission from DAISIE, queried November 2011, EEA-SEBI 2012)

other species. This bottom colonizing tunicate can expand over sand, gravel, and cobble, and is capable of growing over other organisms in order to expand (according to its morphology it was also named “marine vomit”!).

Nevertheless, some indicators have been suggested for IAS based on the pressure-state-response model (McGeoch et al. 2010). These indicators are intended to monitor: (1) the size or extent of the threat posed by IAS (pressure), (2) the impact of IAS on biodiversity (state), and (3) the progress towards reducing the threat (via policy or management interventions) (response) (Table 10.4). The following indicators have been selected: number of IAS/country, red list index for impacts of IAS, and international and national policy adoption. It is clear that first we should know “who is who” and, due to the extensive numbers of species, the database should be collected by country on plants, animals, and if possible smaller organisms. Then, a red list of IAS that are harmful to our environment (according to our principles!) should be built in order to warn the national network and also receive field information for database construction. Finally, action should be taken accordingly at the national and international levels (Fig. 10.5).

At a SEBI 2020 meeting held in Copenhagen in 2011, the following indicators were discussed

Table 10.4 Pressure-state-response (model) of invasive alien species (IAS) indicators (McGeoch et al. 2010)

Model parameters	Indicator	Details	References
Pressure	Number of IAS/country	Species impacting biodiversity negatively	Hulme (2009)
		IAS taxa: mammals, birds, amphibians, plants, freshwater fish, marine organisms (algae, corals, invertebrates and fish)	Ricciardi (2001), Cronk and Fuller (1995), Havird et al. (2013), Lonsdale (1999) and Winfield et al. (2011)
		Prospective trends therein at national, regional and global scale	EEA (2009), Stoett (2009), UNEP (2002a,b) and Rabitsch et al. (2013)
State	Red List Index for impacts of IAS	Trends in extinction risk driven by IAS to different taxa	Butchart et al. (2005, 2007)
		Taxa impacted: Birds, mammals, amphibians	Bird Life International (2008), Rodriguez-Cabal et al. (2009) and Anonymous (2009)
Response	International and national policy adoption	Agreements, legislation and policy relevant to reducing IAS threats to biodiversity	Shine et al. (2005, 2009) and Levin and D'Antonio (1999)
		Trends in number thereof and adoption by countries	Vilá et al. (2009)

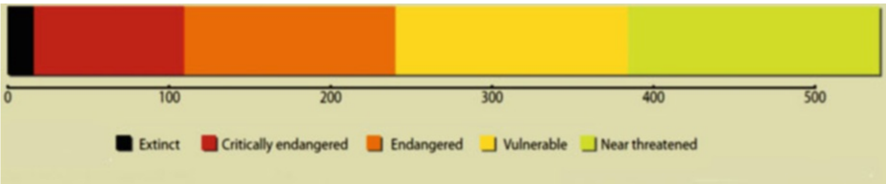


Fig. 10.5 Number of species in International Union for Conservation of Nature (IUCN) Red List categories from Mediterranean countries. Note: included Amphibians, Birds, Cartilaginous fishes, Crabs and Crayfish, Endemic freshwater fishes, Mammals, Dragonflies and Reptiles (Source: IUCN, *The Mediterranean*, a Biodiversity Hotspot Under Threat 2008)

1. Red list index and IAS: The red list index shows trend of red list status changes over time due to IAS. It was done globally, but could be done at the European level as well. It is probably more sensitive for detecting changes as the cumulative number of AS. In addition, the percentage of species impacted based on red list criteria may be useful, as well as the number of protected species threatened by IAS. Ideally, we have an indicator showing a positive trend due, e.g., to management actions.
2. Trends in management pathways: Analyses of management actions vs pathways and numbers of species over time may help prioritize pathways. This can be done for all IAS or for a selected list of species and for different environments. There were two different views about primary and secondary pathways: One is

that primary and secondary introduction pathways should be separated; the other that primary pathways across the biogeographical barrier should be focused on only because secondary pathways are out of our control.

3. Impact indicator: An indicator on impact is needed, although impact is hard to define or standardize, e.g., the red list index, or the impact in habitats of European interest (links to directives), impact on ecosystem services, and impact on economy or socio-economy. There is a need for an indicator for the impact on socio-economy, a work to be done by economists.

   In addition, impact on ecosystem services (ES) may be developed over time by using EASIN and the Vilá et al. (2010) article. Constraints for quantifying and mapping the impact of marine alien species include (1) the lack of coverage and resolution in the available natural and socio-economic data (e.g. habitat mapping, spatial distribution of native and alien species), (2) the gaps for assessing marine ecosystem services (Katsanevakis et al. 2014)
4. ES-s are also included as targets in the EU vision 2050. It should be checked whether the Economics of Ecosystems and Biodiversity (TEEB)-framework can be applied to alien species and assessment of services. Although it seems difficult, at least some of the ES can be identified and linked to IAS in a long term approach.

Newly introduced species indicator can eventually be done by a map showing number of first records per country. Such a map can also be produced for different time periods as trend over time; this would support prevention and rapid response. Nunes et al. (2014) have investigated the gateways of initial introductions of marine alien species in the European Seas. Marked geographic patterns depending on the pathway of introduction were revealed, with specific countries acting as gateways to alien invasions. For example France and Italy were the countries mostly responsible for introductions by aquaculture.

Based on DAISIE data and others, the UNEP-WCMC (2011) suggested four tentative IAS indicators tailored to Aichi Target 9* that relate to ecosystem services: (1) dollar value impact of IAS on crops (pests/disease/pollinators) or % yield; (2) fish and wildlife production; (3) dollar value of impacts of IAS on water availability and (4) daily impacts of IAS on human health (Table 10.5). These indicators are mainly linked to ecosystem-economy and as such are less precise when dealing with systems at higher resolution (Deudero et al. 2011).

More accurate indicators related to operability, relation and policy questions, and indicators are as follows. Hotspot indicators (IAS that are concentrated on specific spots, such as islands), which describe different alien arthropods to be used as indicators of invasion (see Fig. 10.6). Single group indicators that are centred on specific IAS groups, such as invasive alien bird index (based on the Birds Directive) or an invasive alien fish index (based on the WFD) (Brochier et al. 2010). A single species indicator is an excellent alarm system of a specific IAS but less, if at all, effective as a trend indicator (only if it is ecologically connected to more single species indicators) (Ghahramanzadeh et al. 2013). Alien species and climate change: according to most models, IAS will continue to spread, since their opportunism and generalistic character (as species) are able to outperform native species under climate and environmental changes. The amount, colonization, or sweep of

Table 10.5 Potential “new” IAS indicators as related to their operability, relation to policy questions and to operational indicators

Indicator[a]	Operability	Policy questions	Operational indicators
IAS and ecosystem Services	B-C	P	Trends in the economic impacts of selected IAS
Biopollution indexes	B-C	P	Trends in number of IAS
Hotspot indicator	B-C	P,R	Trends in number of IAS; Trends in IAS pathways management
Single group indicator	C	P	Trends in number of IAS
Single species indicator	n/a	R	Trends in number of IAS
Alien species and climate change	C	P	Trends in number of IAS
Animal and plant health	B	P,R	Trends in incidence of wildlife diseases caused by IAS; Trends in IAS pathways management
Important alien areas	C	P	Trends in number of IAS

Operability: A = Priority and ready to use; B = Priority to be developed; C = For consideration; n/a = not applicable
Policy questions: P = Pressure; R = Response
[a]All indicators relate to Aichi Target 9. (See the Strategic Plan for Biodiversity 2011–2020, adopted during the 10th meeting of the Conference of the Parties of the Convention on Biological Diversity (CBD COP 10) which took place in Nagoya, Aichi Prefecture, Japan, in October 2010)

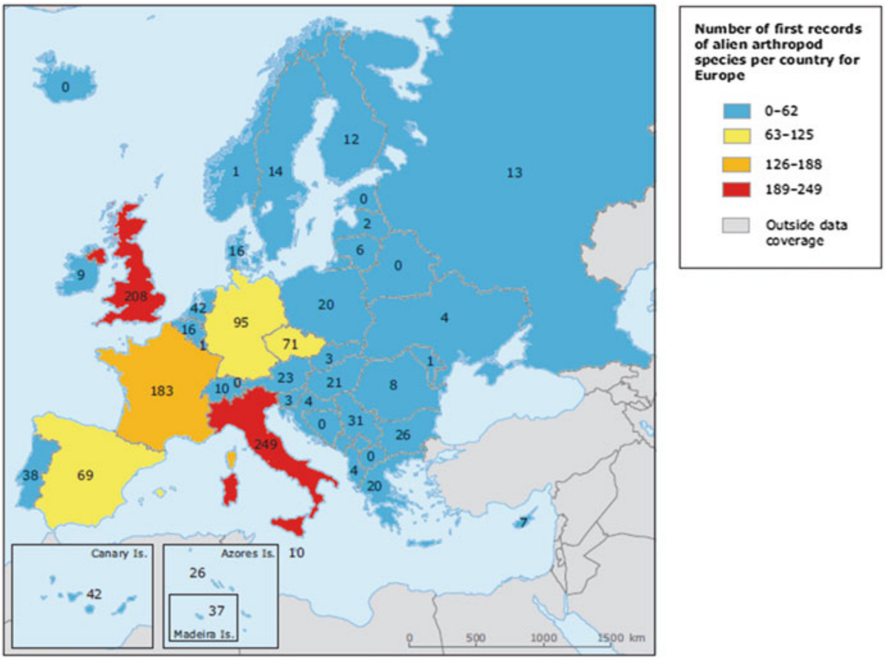


Fig. 10.6 Alien arthropod species per country for Europe (number of first records) (With permission from Roques 2010)

IAS whose presence is approximately related to temperature (e.g., palms, cacti, parakeets or the red-eared slider) may function well as “surrogate indicators” in this category. Nevertheless, in general these IAS patterns are driven by compound factors and rarely based on “clean” climate change phenomena (e.g., extreme cold or draughts) and rarely observed as such; Animal and plant health: according to Aichi Target 9, an indicator on “Trends in incidence of wildlife diseases caused by invasive alien species” should be developed. At the moment such an indicator is not available; nonetheless it may be developed using current data reported to the Animal Disease Notification System (ADNS). ADNS is a notification system to ensure rapid exchange of information between national authorities responsible for animal health. This system is based on a certain list of animal diseases (Annex I of Directive 82/894/EC) (EC 2012) without automatic update of the list for new or emerging diseases. Contained by the Animal Health Strategy, there are several supportive instruments such as TRACES “(a unified database including information on all veterinary matters), improved border biosecurity (revision of import legislation and risk management) and surveillance (including training support)” (EC 2012). In the plant health sector, a similar project has been established with regular updates being carried out. In summary, wildlife diseases’ indicators are of high priority (based on present data and strict methodology to be developed). Important alien areas for example relate to IBAs (Important Bird Areas) that describe important bird sites at the national level, those of including IAS. Following a continuous observation regime, the accumulated data can be used as an indicator of IAS impact at a regional scale within protected areas, e.g., national parks. A similar approach has been taken by EC with plants (IPAs-Important Plant Areas) and is hoped that useful data will be collected to define IAS spread and impact. Applying the concept of “Important Alien Areas,” the monitoring and measurement of IAS can be successful, especially when import hubs, such as airports or harbor and ecosystems (i.e., lagoons, gardens and parks in cities, forest plantations and national parks), are selected as “hot spots” rich in alien species. When talking about import hubs, the New Zealand example is one of the best: New Zealand has shown stabilization in IAS increase vs. Europe since its strict biosecurity measures were enforced! (Fig. 10.7).

10.4.1 Raising Public Awareness – Involvement of Citizen Scientists

Institutes often lack funds and manpower to perform large-scale biodiversity monitoring. Citizens can be involved, contributing to the collection of data, thus decreasing costs. Citizen Science has become to contribute to the wealth of information about alien species. Terrestrial and Aquatic resource managers have taken advantage of volunteer networks such as the Invasive Plant Atlas of New England IPANE (Simpson et al. 2009). Volunteers are trained to look for new incursions of both known and anticipated alien invaders, and to gather and submit basic ecological information on invasive plants that encounter on the New England

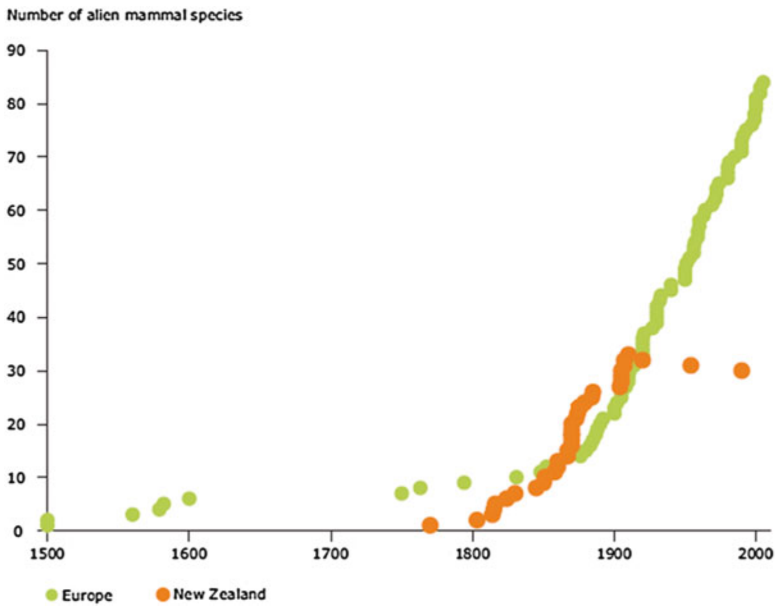


Fig. 10.7 Comparison of the number of alien mammals' species in Europe and New Zealand (1500–2000 BC). Note: New Zealand shows stabilization in IAS increase vs. Europe since its strict biosecurity measures had been enforced! (With permission from P. Genovesi, unpublished data, from http://www.eea.europa.eu/legal/copyright)

landscape via the IPANE Web site (http://www.ipane.org). Considerable citizen science support on alien species is also provided by ornithologists (Delaney et al. 2008); divers (Zenetos et al. 2013).

10.5 Case Studies: Indicators Based on IAS

10.5.1 Indicator: Trends in IAS

Selecting the "most" invasive species is a difficult task which can attract debate During the SEBI 2010 exercise, trends in alien species was used as a proxy to Trends in IAS. Approximately 1,400 alien species have been introduced in European Seas, 1,200 of them since 1950. The vast majority are invertebrates (mostly crustaceans and molluscs), followed by plants and vertebrates (mostly fish) (Fig. 10.8-left). The rate of introductions is continually increasing, with almost 300 new species reported since 2000. The introduction rate is relatively high in the North Sea, the Bay of Biscay and Iberian shelf, Celtic Seas, while the lowest is the contribution of new aliens in the Baltic Sea. This does not imply that the Baltic is less impacted.

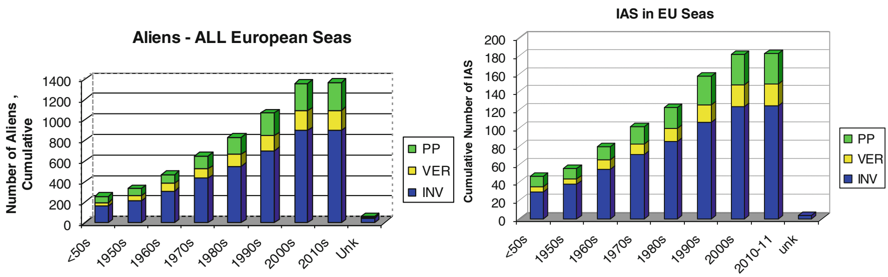


Fig. 10.8 Cumulative number of aliens in the European Seas by 2013. *left*: all aliens; *right* invasive species only (Data source: HCMR/EEA database)

Similarly, the high number of alien species in the Mediterranean does not imply higher overall impact, because many of them are harmless, while a number of them (fish, crabs, and shrimps) are commercially exploited.

Here we take a step toward presenting the trends in marine IAS in European Seas as compared to the trends of all introduced species. A list of target species was compiled by combining and updating the '100 of The Worst' list of DAISIE (Delivering Alien Invasive Species Inventories for Europe; http://www.europe-aliens.org/speciesTheWorst.do), the NOBANIS fact sheets on Invasive Alien Species (European Network on Invasive Alien Species; http://www.nobanis.org/Factsheets.asp), the SEBI 'List of worst invasive alien species threatening biodiversity in Europe' (Streamlining European 2010 Biodiversity Indicators; http://biodiversity.europa.eu/topics/sebi-indicators), and the datasheets of CABI's Invasive Species Compendium (CABI-ISC; http://www.cabi.org/isc/).

10.5.2 Indicator: Species per Country

Based on a thorough review of the scientific and grey literature, the country and year of initial introduction of marine alien species in Europe by February 2014 was identified (for approximately 1,400 species). The country through which a species was first introduced in Europe will hereafter be called 'recipient country.' For 31 species, more than one recipient country was associated with their introduction into European Seas. This may happen when a species data have been collected independently in the same year from different countries. In some cases, recipient countries can be identified with certainty (e.g., most commodity species introduced through aquaculture), while in other cases the country of first observation of the species in Europe was assumed to be the recipient country. The date of first observation of an alien species in Europe was used as the best available estimate of the year of its initial introduction, when the latter could not be determined with certainty. The information on the country and year of first introduction of each species is publicly available through the species search widgets of EASIN (http://

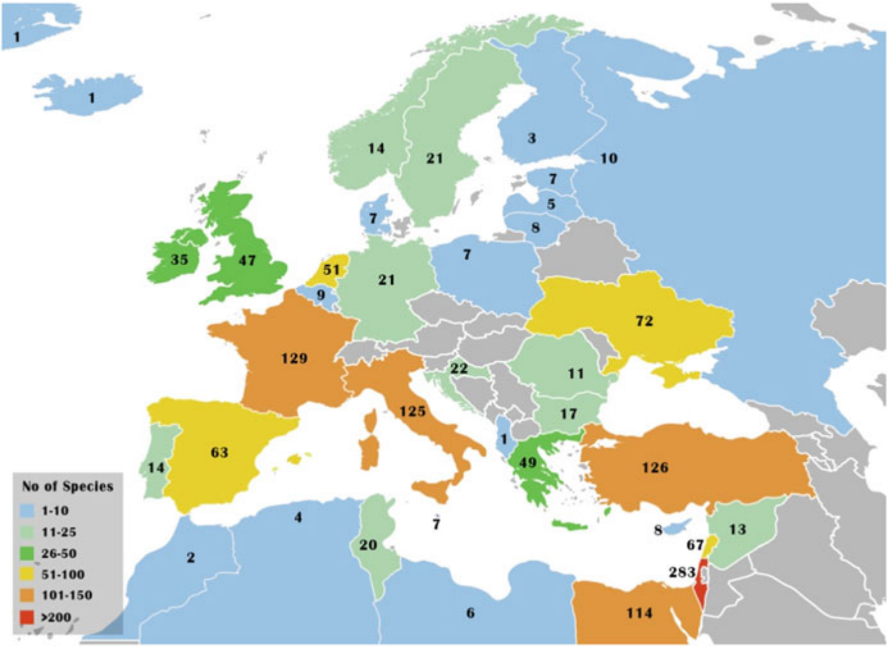


Fig. 10.9 Number of marine/estuarine alien species introduced for the first time in European waters through different pathways of introduction, per recipient country (i.e. countries of initial introduction in Europe) (Source: HCMR/EEA database)

easin.jrc.ec.europa.eu/use-easin/species-search). Figure 10.9 illustrates the number of aliens first recorded per recipient country.

Israel is the country with the highest number of recorded first introductions in European Seas, followed by Turkey, France, Italy, and Egypt (Fig. 10.9). The number of new invaders in Israel, Egypt, and Turkey is justified by their vicinity to the Suez Canal (Lessepsian immigrants), whereas Italy and France first host many invaders presumably due to extensive aquaculture activities.

10.5.3 Indicator: Trends in Pathways/Vectors

Assessing pathways of introduction of marine alien species is essential for identifying management options and evaluating management decisions to regulate and prevent new introductions. On reviewing critically related information in scientific/grey literature and online resources, 1,360 alien marine species in European seas were identified by 2012, of which 1,269 were linked to the most probable pathway (s)/vector(s) of primary introduction. Aquaculture was the only pathway for which there was a marked decrease in new introductions during the last decade, presumably due to compulsory measures implemented at a national or European level.

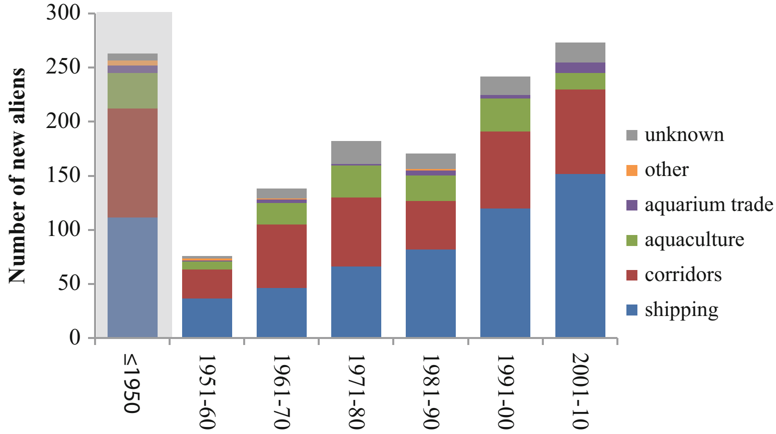


Fig. 10.10 Temporal trends in the numbers of new recorded marine aliens in Europe in relation to the pathways of introduction (Source: Katsanevakis et al. 2013)

Introductions via all the other pathways have been increasing, aquarium trade being the pathway with the most striking observed increase (Fig. 10.10). Many more species are expected to invade the Mediterranean Sea through the Suez Canal, as it has been continuously enlarged and the barriers to the invasion of Indo-Pacific Sea species have been substantially decreased. It has been estimated that approximately a new species is introduced in the Mediterranean every two weeks (Zenetos et al. 2012). Whereas lessepsian migration cannot be managed, in addition to the existing regulations on aquaculture, the implementation of appropriate management measures on shipping and aquarium trade could reverse the increasing trend in new introductions.

10.6 Summary

At present, the IAS indicators situation still needs improvement based on new databases and broader geographical areas. For example, the European Commission on IAS recommended increasing the cumulative numbers of alien species in their geographical area to 1500–1800 species to be included in the list to be covered scientifically. Prioritizing IAS is included in the new EU Regulation. Interestingly, the EC agreed to continue to cover the costs of IAS in Europe (the economic indicators) to be used further in combination with other indicators. The central recommendations have been the development of new indicators and elaboration of the two novel indicators already proposed: (a) the red list Index and (b) the combined index of invasion trends. Furthermore, quantification and mapping of impacts will assist stakeholders in their decisions for prevention or mitigation actions. Engaging citizen scientists to survey local biota detect and report new incursions of both known and anticipated alien is expected to result in the collection of significant data sets, which could potentially be used for an early-warning system *inter alia*.

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Part IV
Environmental Degradation

Chapter 11
Marine Eutrophication

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Abstract Eutrophication is one of the key local stressors for coastal marine ecosystems, particularly in those locations with many estuaries, intense coastal development or agriculture, and a lack of coastal forests or mangroves. The land-derived import of not only inorganic nutrients, such as nitrate and phosphate, but also particulate and dissolved organic matter (POM and DOM) affects the physiology and growth of marine organisms with ensuing effects on pelagic and benthic community structures, as well as cascading effects on ecosystem functioning. Indicators for marine eutrophication are therefore not only key water quality parameters (inorganic and organic nutrient concentrations, oxygen and chlorophyll availability, and biological oxygen demand), but also benthic status and process parameters, such as relative cover and growth rates of indicator algae, invertebrate recruitment, sedimentary oxygen demand, and interactions between indicator organisms. The primary future challenge lies in understanding the interaction between marine eutrophication and the two main marine consequences of climate change, ocean warming, and acidification. Management action should focus on increasing the efficiency of nutrient usage in industry and agriculture, while at the same time minimizing the input of nutrients into marine ecosystems in order to mitigate the negative effects of eutrophication on the marine realm.

Keywords Nutrient thresholds • Upwelling • River runoff • Discharge • Fertilization • Submarine groundwater discharge • Algal blooms • Hypoxia

11.1 Introduction

Environmental indicators can predict and assess processes and changes at different levels. In order to address the different levels of indicators, we use three different classes of indicators: (a) early (warning) indicators; (b) indicators of direct impact; and (c) indicators of long-term changes induced by eutrophication.

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_11

Early (warning) indicators can be species or parameters that are highly susceptible to environmental changes and are able to display an emerging change before that change influences the system on a broader scale. For instance, phytoplankton species and their respective toxins in water samples can be used as early (warning) indicators for algae blooms (see Sect. 11.5.1.1).

Indicators of direct impact are used to detect events or processes that have already occurred or started, but, in contrast to those detected by long-term indicators, have not been active for a long time period, or whose phenomena do not last long. Fast nutrient induced shifts in planktonic communities, such as diatoms to cyanobacteria and dinoflagellates, are an example of indicators of direct impacts (see Sect. 11.5.1).

Lastly, indicators for long-term changes display differences where an event or process has already had an effect for a certain time period. Examples of this can be (slower) changes in benthic coral reef community composition, such as seaweeds that take over formerly hard coral dominated reefs (see Sect. 11.5.2.2).

When listing indicators in this chapter, we will state to which level they belong, although overlapping may occur. It is important to be aware that an indicator can be a direct impact indicator for one event or process, but for another, it will be an early warning indicator.

We start this chapter with the definition and thresholds of eutrophication. We will discuss which molecules are involved and the thresholds at which eutrophication occurs. The second section deals with the different sources (anthropogenic and natural) of eutrophication, and lists their estimated input on a global scale. The fourth and fifth sections explain the effects of increased nutrients on the organism and the ecosystem level. We provide information on how marine organisms are affected on the physiological and community level. Lastly, we present an outlook on future scenarios by describing upcoming trends in nutrient input to the sea and how emerging climate change will likely influence these fluxes and their impacts.

11.2 Definition and Thresholds

11.2.1 Definition

Over the past few decades eutrophication has increasingly been recognized as a major threat to marine ecosystems worldwide (e.g., Nixon 1995; GESAMP 2001). Eutrophication typically refers to the enrichment of a given aquatic environment by inorganic or organic nutrients, particularly forms of nitrogen and phosphorous, leading to a change in its nutritional state (Richardson and Jørgensen 1996; Andersen et al. 2006). However, it should be emphasized that eutrophication is a process rather than a state parameter, and our concern over excess nutrient input is typically due to its impact on organic carbon supply rather than nutrient levels themselves. Thus, eutrophication can be defined as the increase in the rate of organic matter supply to an ecosystem (Nixon 1995, 2009). This definition emphasizes eutrophication as a process and separates it from its causes, such as increased nutrients, and its consequences. However, such a broad definition is problematic from a management perspective, as it is difficult to apply (Andersen et al. 2006). For this reason, the definition used for monitoring and management purposes remains focused on an increase in nutrient availability and the resulting negative consequences for the ecosystem of interest (e.g., OSPAR 2003). While the most immediate effect of eutrophication is increased primary production via phytoplankton or macrophytes (Richardson and Jørgensen 1996), eutrophication can lead to changes in the energy flow of aquatic food webs and can have wide-reaching ecosystem effects (Carpenter et al. 1998; Smith et al. 2006; Worm and Lotze 2006) (see Sect. 11.5).

11.2.2 Nutrient Limitation and Critical Molecules

Eutrophication occurs when a limiting factor on the rate of growth and production of primary producers is released, most frequently via an input of inorganic or organic nutrients (Smith 1984; Howarth 1988). A variety of essential micro and macronutrients are required for plant growth. The macronutrients, nitrogen (N), phosphorous (P), potassium (K), calcium (Ca), magnesium (Mg), and sulfur (S), are required in larger quantities, while micronutrients, including iron (Fe), boron (B), chlorine (Cl), manganese (Mn), zinc (Zn), copper (Cu), nickel (Ni), and molybdenum (Mo), are required only in trace amounts (Raven et al. 2005). The two primary nutrients most limiting to growth in both aquatic and terrestrial primary producers are N and P (Hecky and Kilham 1988; Howarth 1988), as these are needed in large amounts and are typically short in supply. However, other molecules, such as Fe and Zn, can also play an important role in limiting primary production, as can factors such as light, hydrology, and grazing (Smith et al. 2006). Historically, P has been considered to be the principal molecule limiting primary production in freshwater lakes (Schindler 1977; Hecky and Kilham 1988), while N is generally believed to be limiting in most marine ecosystems (Vitousek and Howarth 1991; Howarth and Marino 2006). A recent meta-analysis, however, found strong widespread evidence for the co-limitation of P and N in all marine, freshwater, and terrestrial ecosystems examined (Elser et al. 2007), indicating that both nutrients play an interactive role in nutrient limitation. Which nutrient is most limiting in a given marine habitat is ecosystem-dependent, with N limitation dominating in most coastal, nutrient-polluted and temperate systems, while P limitation may dominate in pelagic, unpolluted, and tropical systems or when nutrient inputs have high N:P ratios (Downing et al. 1999; Smith et al. 2006).

The most common reactive forms of N and P considered by eutrophication studies are dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorous (DIP). The forms of DIN found in marine waters are nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+), while DIP is found as phosphate (PO_4^{3-}). These are typically the most abundant molecules containing N and P in marine waters and are also the most bioavailable to marine primary producers. However, in many systems, NO_3 and PO_4 are typically found at concentrations that limit plant growth. In addition to these dissolved inorganic forms, there are significant amounts of N and P found in dissolved organic matter (DOM) as dissolved organic N and P (DON and DOP), (Bronk 2002; Karl and Björkman 2002; Voss et al. 2013). The general importance of the nutrients in DOM to phytoplankton nutrition remains mostly unknown, as much DOM is refractory and therefore likely unavailable to marine organisms (Fabricius 2011; Davidson et al. 2012). However, there is evidence that DOM can be utilized by some phytoplankton organisms, including harmful algal bloom (HAB) species and therefore has the potential to be an important factor in eutrophication (Lomas et al. 2001; Glibert et al. 2006; Davidson et al. 2007). The particulate organic matter (POM) pool is small and is dominated by plankton and detritus. While this material is likely not directly usable by most plankton and macroalgae, the remineralization of this particulate material is an additional source of inorganic nutrients (Fabricius 2011; Davidson et al. 2012).

11.2.3 Thresholds and Indicators

As eutrophication has become an increasing global concern, there is growing need to identify nutrient thresholds and accurate indicators of eutrophication for monitoring and management purposes. However, due to high variation in natural conditions and the interaction of multiple factors influencing eutrophication, ecosystem responses to nutrient enrichment are frequently non-linear making it difficult to determine widely applicable thresholds at which eutrophication produces undesirable changes in community structure and function (Howarth and Marino 2006; Duarte 2009; Nixon 2009). Despite this, attempts have been made to define nutrient thresholds for eutrophication for some marine ecosystems. However, dissolved inorganic nutrients alone may be poor indicators of eutrophication as they do not represent the entire pool of bioavailable nutrients, are often taken up so quickly that it can be difficult to detect increases in DIN and DIP, and cannot increase primary production at concentrations in excess of nutrient limitation (McCook 1999; Fabricius 2011). Measurements of total N (TN) or total P (TP) may be better indicators than DIN and DIP, as all forms of N and P are taken into account, and thus these measurements are widely employed in monitoring programs. Chlorophyll *a* (Chl *a*), a proxy for phytoplankton biomass, is another widely used indicator of eutrophication, as phytoplankton biomass rapidly responds to changes in nutrient concentrations (Reynolds and Maberly 2002). However, the use of Chl *a* as an indicator has its own drawbacks, as there can be no increase in Chl *a* after nutrient concentrations have exceeded the threshold beyond which they are no longer limiting. Additionally, Chl *a* measures indicate only changes in the abundance of primary producers and cannot indicate any changes in community composition that may occur simultaneously (Devlin et al. 2007; Lugoli et al. 2012).

A global critical limit for TN of 0.5–1.5 mg L^{-1} may prevent eutrophication and harmful toxicological effects by inorganic N pollution in many aquatic systems; however, these data are based more on freshwater than marine systems (Camargo and Alonso 2006; Durand et al. 2011; Sutton et al. 2013). In nutrient-poor (oligotrophic) tropical coral reef ecosystems, lower nutrient threshold concentrations of 1.0 μM DIN and 0.1–0.2 μM DIP, as well as a Chl *a* threshold of 0.5 μg L^{-1}, may indicate the onset of eutrophication (Bell 1992; Lapointe 1997). However, the mean nutrient concentrations for over 1,000 reefs worldwide are above these values (Kleypas et al. 1999), and nutrient enrichment does not always result in increased algal biomass, probably due to compensatory feeding by herbivores (Belliveau and Paul 2002; Burkepile and Hay 2009). Therefore, considering bottom-up thresholds, such as nutrient concentrations, without taking into account the impact of top-down controls on community structure, such as herbivore grazing, will limit understanding of how eutrophication will impact benthic communities (McCook 1999; Szmant 2002; McClanahan et al. 2004; Jessen et al. 2013a). The interaction of these two effects and their relative roles in structuring benthic communities also depends on a variety of other factors, such that a robust threshold for eutrophication in coral reefs and other benthic ecosystems may require a suite of multi-index indicators that provide information on a variety of biological responses rather than just nutrient concentrations and phytoplankton production rates. Macrobenthic assemblages have been used as an indicator for eutrophication for coral reefs (Littler and Littler 1984, 2007) and other coastal and estuarine benthic ecosystems (e.g., Rakocinski 2012; Verissimo et al. 2012). Other successful indicators include tissue C:N:P ratios and nitrogen stable isotopes ($\delta^{15}N$) in macroalgae, gastropods (rather long-term responding), and epilithic biofilms (rather short-term responding) (Vermeulen et al. 2011; Carballeira et al. 2012).

In benthic ecosystems, the sediment-water interface is sensitive to eutrophication due to the settling and decomposition of the increased biomass of primary producers in the water column. Lehtoranta et al. (2009) proposed eutrophication thresholds for this organic carbon input to coastal ecosystems which result in a shift in microbial sedimentary processes leading to anoxic conditions and a shift from iron reduction to sulfate reduction, thereby increasing the efflux of P from the sediment. This alters the biogeochemical cycling of P and may have wider ecological implications (Lehtoranta et al. 2009). For example, Hyland et al. (2005) found that total organic carbon (TOC) concentrations in sediments in a range of temperate coastal ecosystems were a good indicator for benthic health based on benthic species richness. The authors found that sediment TOC concentrations of less than 10 mg g^{-1} corresponded to a low risk of decreased species richness, while concentrations greater than 35 mg g^{-1} corresponded to a high risk of decreased species richness, suggesting that TOC may be a good preliminary nutrient indicator of benthic health.

11.3 Causes and Distribution

Sources of marine eutrophication can be divided into natural and anthropogenic sources, though disentangling their relative contributions is sometimes challenging. If not specified, N in this text always refers to the reactive form (i.e., all N species

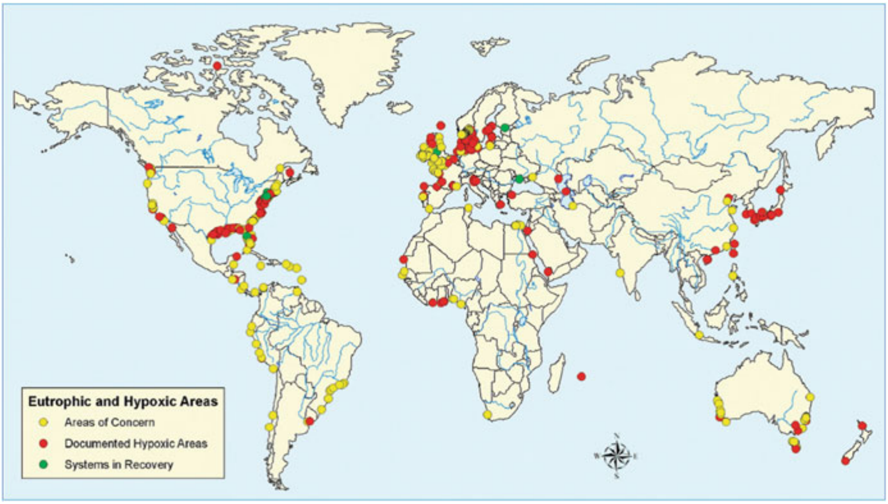

Fig. 11.1 Global map of known eutrophic and hypoxic areas (Taken from Selman et al. 2008 WRI)

except dinitrogen - N_2). Most scientific studies only covered inorganic N forms, whereas information on dissolved organic N (DON) is very limited. However, DON is rather uniformly distributed in the water column, but increases substantially towards coastal areas (Voss et al. 2013). While most anthropogenic pollution consists primarily of inorganic nutrients, the input of organic forms occurs as well and can be potentially more important in that it comprises between 18 and 85 % of total nitrogen (TN) (Davidson et al. 2012; Voss et al. 2013).

The main natural sources comprise atmospheric deposition, upwelling, river runoff, and submarine groundwater seepage, while the main anthropogenic contributors are fertilizers, sewage, and industrial runoffs. There are signs of increased nutrient discharges to the marine environment everywhere in the world where data are available, particularly in coastal areas adjacent to human settlements (GESAMP 2001, Fig. 11.1).

Though, not considered as eutrophication, internal sources can deliver a major portion of new or recycled N to marine ecosystems. Biogenic fixation of N_2, for example, provides the largest single source of new N via diazotrophs (Voss et al. 2013) (Table 11.1). However, Burkepile et al. (2013) showed for a Caribbean coral reef that carnivorous fish excretions largely exceeded other biological and abiotic sources of N.

In the following, we list the main eutrophication sources, their composition, and tracers used for their detection. Table 11.1 displays global sources of marine nutrient enrichment.

Table 11.1 Overview of the most important sources of marine nutrient input. If not stated otherwise, numbers are in Tg year^{-1}

Source	N	P
Atmospheric deposition	46–67 (Voss et al. 2013)	0.5 (Krishnamurthy et al. 2010)
River export	40–66 (Voss et al. 2013)	8.6 (Seitzinger et al. 2010)
	40 % DIN	1.4 DIP
	40 % PN	6.6 PP
	20 % DON	0.6 DOP
Sewage[a]	6 (Billen et al. 2013)	1.3–3 (Van Drecht et al. 2009; Van Vuuren et al. 2010)
Agricultural surplus	138 (Billen et al. 2013)	n.a.
Total anthropogenic N	210 (Voss et al. 2013)	n.a.
SGD	4 (Voss et al. 2013)	n.a.
Upwelling[b]	330–390 (Messié et al. 2009)	21–25 (Messié et al. 2009)
N fixation by oceans	140 (Voss et al. 2013)	–

[a]Discharge into rivers
[b]In the tropical and southern open ocean; based on estimation of new C production using the Redfield ratio of 106:16:1 for C:N:P

11.3.1 Atmospheric Deposition

Atmospheric deposition can provide mainly N, P, and Fe to the coastal and open ocean (Duce et al. 2008; Mahowald et al. 2009; Krishnamurthy et al. 2010). Studies have shown that 10–70 % of fixed N input to many coastal regions is delivered via the atmosphere, sometimes from sources more than 1,000 km away (Paerl and Whitall 1999; GESAMP 2001; Duce et al. 2008). Despite an increase of 50–200 % over the last 50 years (Paerl 1995), in attempts to mitigate eutrophication events, total atmospheric fixed N has barely been considered (GESAMP 2001).

The transport of atmospheric TP (total phosphate = organic and inorganic forms) is different from that of N, as P does not have a stable gaseous phase and it cannot be fixed from the atmosphere (Mahowald et al. 2008). TP is mainly restricted to aerosols (e.g., Graham and Duce 1979). As a result, perturbations to atmospheric TP are less than to atmospheric C or fixed N (Schlesinger 1997). Nonetheless, atmospheric TP is being altered: 5 and 15 %, respectively, of atmospheric P and PO_4 that enter the ocean, are estimated to be anthropogenic (Mahowald et al. 2008). On a global averaged basis, TP export by rivers to the coastal oceans (8.6 Tg year^{-1}) largely exceeds atmospheric inputs (0.5 Tg year^{-1}) (Table 11.1). However, the riverine inputs may be trapped in coastal zones, making the atmospheric P source more important in the open ocean (Krishnamurthy et al. 2010). Primary sources of atmospheric N and P are not always clear; however, studies suggest an important fraction is anthropogenic (Jickells 2006; Duce et al. 2008; Mahowald et al. 2008) produced from fossil fuel combustion by industries and vehicles as well as from livestock farming (GESAMP 2001; Graham et al. 2003; Baker et al. 2006).

11.3.2 Upwelling

Upwelling describes the rising of cold water masses from the deep that are enriched with nutrients, including NO_3, and $Si(OH)_4$ (Wilkerson and Dugdale 2008) that originate from OM rematerialized by bacteria on the seafloor. In contrast, NH_4^+ is not enriched in the deeper waters, and therefore, not transported by upwelling, but rather originates from zooplankton and nekton in surface waters (Wilkerson and Dugdale 2008). To reconstruct the intensity of upwelling events, ^{18}O isotopes in planktonic organisms of deep-sea sediments are used (Prell and Curry 1981).

There are no studies available that estimated global nutrient contributions of upwelling. However, approximations based on estimates of upwelling-driven new C production and the Redfield ratio (Table 11.1) suggest enormous local and regional nutrient contributions that outnumber by far all other sources. Regional studies confirm this (e.g., Szmant and Forrester 1996), although not for all regions (e.g. Lamb-Wozniak 2008). Besides upwelling, other oceanographic processes, such as winter mixing or eddies, may transport large amounts of nutrients to ocean surface water. The Atlantic Ocean, for example, receives about 30 % of the total N flux by eddy transport (Voss et al. 2013).

11.3.3 River Runoff

Originally, this term described discharged freshwater that became nutrient-enriched by flowing through mineral loaded rocks. Today, this natural effect is often enhanced by anthropogenic sources, such as industrial runoff, sewage, and agricultural fertilizer discharge, and is further facilitated by the loss of riparian wetlands that can greatly reduce the nutrient loading in rivers (Mitsch et al. 2001; EPA Science Advisory Board 2007).

According to estimates by Billen et al. (2013), around 70 % of the N that originally enters a river is denitrified on the way to, or in the estuary. Nevertheless, anthropogenic nutrient fluxes in rivers may be at least equal to, and probably greater than, the natural fluxes (GESAMP 2001).

11.3.4 Submarine Groundwater Discharge (SGD)

Within the last few decades, recognition has emerged that SGD into the sea may be both volumetrically and chemically important (Johannes 1980; Moore 1999;

Charette and Sholkovitz 2002). SGD is patchy, diffuse, and temporally variable, and can occur wherever coastal aquifers are interconnected to the ocean (Burnett et al. 2006). However, nutrient fluxes of SGD can rival inputs via rivers (Krest et al. 2000; Charette et al. 2001; Paytan et al. 2006). Accordingly, insufficient consideration of this source can result in serious misinterpretations of coastal pollution (Johannes 1980).

Besides nutrients (e.g., N, P, Si), metals and organic compounds can be introduced into the sea (Corbett et al. 1999; Burnett et al. 2001; Ji et al. 2013). Several isotopes such as B, O_2, hydrogen (H), radon (Rn), and radium (Ra) are used as tracers for SGD (Cable et al. 1996; Burnett and Dulaiova 2006; Burnett et al. 2008; Ben Moussa et al. 2010; Ben Hamouda et al. 2011; Dimova et al. 2013).

The importance of nutrient sources varies widely between regions. Agricultural products are the main contributors to eutrophication in North America and the EU, with sewage and industrial run-off as secondary sources since they usually receive some treatment before being discharged. However, in other parts of the world, such as Asia, Africa, and Latin America, where sewage and industrial wastewater is typically not treated, these sources exceed agriculture waste as the main anthropogenic source of eutrophication.

11.3.5 Fertilization and Agriculture Activities

Synthetic fertilizer application is the largest anthropogenic nutrient source (Table 11.1). High agricultural nutrient consumption is caused by growing populations and because usage is typically much higher than the uptake by the plants. On average, over 80 % of N and 25–75 % of P applied as fertilizer is lost to the environment (Fowler et al. 2013; Sutton et al. 2013). Particularly NO_3, but also NH_4 and PO_4, are flushed into rivers and groundwater by irrigation systems, rain, or floodings, so that high amounts of these inorganic nutrients finally reach the sea. Since the 1960s, global human use of synthetic fertilizers has increased drastically: N 9-fold (from 12 to 105 Tg) and P 3-fold (from 12 to 38 Tg) (FAO 2012).

Isotopic analysis is used for the detection of fertilizer input. Due to their atmospheric origin, synthetically produced fertilizers typically have $\delta^{15}N$ values of around 0 ‰ (Heaton 1986), and can therefore be distinguished from animal wastes that exhibit characteristic $\delta^{15}N$ values of 10–20 ‰ (Kendall et al. 2007).

11.3.6 Sewage and Industrial Runoff

Estimates show that in North America and Europe 90 and 66 %, respectively, of urban wastewater is treated, while this is much less in Asia (35 %), Latin America including the Caribbean (14 %), and in Africa, where waste water is usually not treated at all (Martinelli 2003). Nonetheless, sewage treatment seldom includes reduction of inorganic nutrients. Even in North America, the primary aim of sewage treatment is to reduce OM components that can contribute to biological oxygen (O_2) demand, but this procedure is not very effective in removing N (mostly in the form of NH_4) and PO_4 (Chopra et al. 2005). Consequently, global sewage emissions of N and P are predicted to double by 2050 (Van Drecht et al. 2009).

Generally, studies found that sewage emissions led to an elevation in the $\delta^{15}N$ signals in the sediment and tissue of a variety of organisms, such as seagrasses, macroalgae, fish, oysters, corals, and other invertebrates (Costanzo et al. 2001; Savage and Elmgren 2004; Piola et al. 2006; Carlier et al. 2007; Risk et al. 2009). Other tracers that have been used to detect sewage emissions comprise boron, carbon, carbamazepine, and coprostanol (Bachtiar et al. 1996; Piola et al. 2006; Cary et al. 2013).

11.4 Impacts on Marine Organisms

11.4.1 Algae

Eutrophication in marine coastal systems directly affects benthic and pelagic marine algae. Some of the early signs of eutrophication include excessive growth of bloom-forming macroalgae and phytoplankton (Duarte 1995; Valiela et al. 1997; Cloern 2001). The range of eutrophication effects on these primary producers depends partly on their morphology, physiology, and nutrient requirements. Because eutrophication is stimulated by inorganic and organic nutrient inputs, the algae that often benefit are those with high nutrient requirements and rapid nutrient uptake rates (Peckol and Rivers 1995; Pedersen and Borum 1997; Valiela et al. 1997). For example, benthic green macroalgae of the genus *Ulva* are by far the most commonly cited bloom-forming species under eutrophic conditions worldwide (Sfriso et al. 1992; Rafaelli et al. 1998; Morand and Merceron 2005; Teichberg et al. 2010). These macroalgae are known for their high nutrient uptake and growth rates under high nutrient supply (Pedersen and Borum 1997; Naldi and Viaroli 2002) and can also take up forms of DON, such as urea and amino acids (Tyler et al. 2005).

The growth and photosynthetic responses of different species of macroalgae and phytoplankton depend not only on light availability, but also on the supply of the limiting nutrient in a particular environment (see Sect. 11.2.2). Nutrient contents, including % N and P, of macroalgae are often used as indicators of nutrient supply, and C:N:P ratios may reveal the limiting nutrient of a particular environment (Lapointe et al. 1992; Lapointe et al. 2005). However, in addition, these ratios also indicate the species-specific nutrient uptake, assimilation, and storage capacity of macroalgae, and can be used to determine which species may benefit under certain nutrient conditions (Fujita 1985; Pedersen and Borum 1997).

N isotopic signatures of macroalgae have also been used to access eutrophication and trace the source of nutrient pollution (McClelland and Valiela 1998; Lapointe et al. 2005) (see Sect. 11.3.6). Although there is some degree of isotopic fractionation from the nutrient source, macroalgae generally do exhibit little, but more, constant fractionation (Deutsch and Voss 2006) as compared to the variable and large range in fractionation in phytoplankton (Needoba et al. 2003). Macroalgae therefore are more reliable indicators of N sources. The $\delta^{15}N$ signature of faster-growing species, such as *Ulva* sp., can indicate changes in their environment or nutrient supply relatively quickly, in a matter of days (Teichberg et al. 2007; Teichberg et al. 2008), while slower growing species such as *Fucus* sp. are better long-term indicators of nutrient supply (Savage and Elmgren 2004). Therefore, taxon-specific differences in rates of N uptake, turnover, and growth may mediate how quickly the $\delta^{15}N$ signatures of macroalgae change in the presence of new N supply (Deutsch and Voss 2006).

11.4.2 Seagrasses

Seagrasses are usually more severely impacted by eutrophication among the macrophytes. Nutrient enrichment itself is not the main problem and can either be positive, negative, or have no direct effects on their growth and physiology (Burkholder et al. 2007). While low levels of nutrient enrichment may stimulate seagrasses through increased photosynthesis and production, high nutrient enrichment generally leads to negative effects (Burkholder et al. 2007). Excessive ammonium may be toxic (Van Katwijk et al. 1997; Cabaço et al. 2008), while nitrate may inhibit growth due to carbon limitation in some seagrass species (Burkholder et al. 1994).

Although nutrient stress is not highly detrimental to seagrasses, reduction of light due to algal overgrowth is considered one of the most detrimental indirect effects of eutrophication on seagrasses (Duarte 1995; Burkholder et al. 2007). Therefore, most studies examining eutrophication impacts on seagrasses focus on light availability and competition among seagrasses, epiphytes, and drifting macroalgae (Hauxwell et al. 2001, 2006 Armitage et al. 2005). For seagrasses that have high light requirements (Dennison et al. 1993), lower light levels result in a negative carbon balance due to decreased photosynthetic rates and increased respiration rates, which then influences growth rates, shoot density, and below-ground biomass (Sand-Jensen 1977; Hauxwell et al. 2006; Burkholder et al. 2007) and can control depth distribution (Ralph et al. 2007).

11.4.3 Corals

Corals can also be highly susceptible to eutrophication (Fabricius 2005), but some results of scientific studies contradict each other (Wiedenmann et al. 2012;

Fabricius et al. 2013). Increases in zooxanthellae density, chlorophyll content, and photosynthesis with increasing NO_3^- (Marubini and Davies 1996) and NH_4^+ (Snidvongs and Kinzie 1994) availabilities have been observed. However, increases in zooxanthellae may lead to decreases in calcification (Marubini and Davies 1996), possibly due to increased CO_2 usage by zooxanthellae for photosynthesis and, therefore, decreased availability for calcification of the coral host. A recent review and study discussed mixed outcomes for nutrient stress on corals, in which increased nutrients may either increase the nutritional status of corals, which in turn protects the coral from thermal stress and onset of bleaching, or lead to higher bleaching due to higher endosymbiont division rates, production of more harmful O_2 radicals, and photoinhibition, which then increases the susceptibility of corals to heat stress (Fabricius et al. 2013). Increased turbidity due to phytoplankton or macroalgal overgrowth in combination with increased sedimentation can also reduce photosynthetic and growth rates in corals (Rogers 1979), and has been linked to high losses in coral cover and mortality rates (Fabricius 2005). However, some studies suggest that corals may continue to grow even under high nutrient conditions, despite net reef erosion (Edinger et al. 2000).

11.4.4 Microbes

In addition to increases in dissolved inorganic nutrients associated with eutrophication, increases in organic nutrients may stimulate bacterial production and activity that can be harmful to corals and other marine organisms (Kline et al. 2006) and lead to the spread of disease-associated bacteria, such as those found in black band disease (BBD) (Voss and Richardson 2006). High nutrient supply can also lead to changes in associated microbial communities. For example, coral-associated microbe abundances increase under eutrophic conditions (Sawall et al. 2012) which favors those microbes that benefit from nutrient rich waters (Jessen et al. 2013b). In the Red Sea coral *Acropora hemprichii*, microbes of the genus *Nautella* and *Defluvibacter*, particularly benefitted from inorganic nutrient enrichment (Jessen et al. 2013b).

To detect eutrophication, changes in microbial activity using simple measurements of biological O_2 demand can be used. In addition, eutrophication often leads to changes in microbial processes in the water column and sediment, such as denitrification and nitrification, N_2 fixation, and sulphate reduction. An increase or decrease in these processes may also be used as indicator of eutrophication. Furthermore, a variety of molecular techniques, such as microarrays and quantitative PCR, to measure microbial diversity and productivity in coastal waters have made the use of microbes as early warning indicators of eutrophication more promising (Paerl et al. 2003; Glaubitz et al. 2013).

11.4.5 Invertebrates and Fish

The effects of eutrophication on invertebrates and fish can either be direct through toxicity via high concentrations of inorganic nitrogenous compounds, such as NH_4^+ and NO_2^-, or indirect from changes in composition and abundance of primary producers leading to decreases in water quality and shifts in food availability (Camargo and Alonso 2006). Toxicity from high NH_4^+ concentrations can cause asphyxiation, stimulation of glycolysis, inhibition of ATP (adenosine triphosphate) production, and disruption of blood vessels and osmoregulation in marine animals, particularly fish, which can then lead to reduced feeding activity and fecundity along with increased mortality (Camargo and Alonso 2006).

Loss of seagrasses and declining coral cover may have severe consequences for many invertebrate and fish species that live and feed in these habitats (Baden et al. 1990; Valiela et al. 1992; Chabanet et al. 1995; Halford et al. 2004; Feary et al. 2009). Shifts to other habitats, such as macroalgae, may not offer the same food quality or habitat complexity, and large algal blooms may lead to hypoxic or anoxic conditions that are especially harmful to sessile organisms or smaller invertebrates that cannot escape so easily (Diaz and Rosenberg 1995; Cheung et al. 2008; Fox et al. 2009). Fish, although more mobile, can also be affected by low O_2 concentrations (Chang et al. 2012). Harmful algal blooms, often stimulated by nutrients, can lead to extensive fish kills (Glibert et al. 2002).

Some frequently observed impacts of eutrophication on consumer communities are decreases in organism abundance, loss in species richness, and shifts in benthic community structure, as well as in important functional groups (Valiela et al. 1992; Tagliapietra et al. 1998; Cardoso et al. 2004). Often, more sensitive species, such as the polychaetes *Alkmaria romijni* and *Capitella capitata* and the bivalve *Scrobicularia plana*, are used as indicator species: their loss from a system indicates deteriorating eutrophic conditions, and their recovery indicates improvement (Verdelhos et al. 2005; Cardoso et al. 2007). However, many of the changes in fauna species composition are due to hypoxia, an indirect effect of eutrophication, which causes increased respiration, reduced growth, feeding, and overall fitness of many marine animals (Wu 2002).

Eutrophication impacts on marine animals can also be seen in their growth rates, reproduction, and metabolism, although impacts may differ depending on the organism. Many suspension feeders, such as bivalves, may benefit from higher primary productivity and organic-rich material, and have faster growth rates, as they have more food availability (Weiss et al. 2002; Kirby and Miller 2005). Small crustaceans, such as amphipods and shrimp, and many herbivorous fish can benefit from shifts in macroalgal food choice, exhibiting increasing abundance, growth rates, or fecundity with higher nutrient quality food (Kraufvelin et al. 2006; Martinetto et al. 2010). However, these benefits are generally limited to conditions of high O_2 concentrations, as these organisms are all sensitive to hypoxia (Wu 2002; Carmichael et al. 2004; Fox et al. 2009). Despite some positive effects of eutrophication on consumer communities, the majority of studies show detrimental effects with significant losses in species diversity and changes in community structure.

11.5 Consequences for Marine Ecosystems

Coastal eutrophication has become a major threat to the structure and functioning of marine ecosystems. The stimulation of primary production provides an increased food supply, and subsequently, it can increase biomass at higher trophic levels (Jørgensen and Richardson 1996). However, where nutrient enrichment exceeds the capacity of primary consumers (e.g., grazers) to absorb the enhanced primary production, marine ecosystems can be significantly impacted and destabilized through the loss of habitat, species diversity, and changes in community structure (Rabalais et al. 2002). The occurrence of algal blooms and the generation of hypoxia (O_2 concentrations in the water lower than 2 ml O_2 L^{-1}) in the water belong to the most severe impacts and their distribution and intensity has grown dramatically over the last several decades in areas with increased nutrient input. Therefore, these events can provide strong indicators for direct eutrophication impacts on marine ecosystems (Anderson et al. 2002; Tett et al. 2007).

11.5.1 Algal Blooms

Algal blooms are characterized by the proliferation and dominance of specific phytoplankton or macroalgal species. As a consequence of marine eutrophication, phytoplankton communities can shift from diatoms toward dinoflagellates or cyanobacteria species, and macroalgae communities can shift from slow-growing perennial toward fast-growing opportunistic species (Anderson et al. 2002; Conley et al. 2009). Changes in the primary producer composition, which represent the basis of marine food webs, will subsequently affect the diet and community composition of primary and secondary consumers, and therefore, the entire trophic structure and energy transfer within an ecosystem (Conley et al. 1993; Riegman 1995; Turner et al. 1998).

11.5.1.1 Phytoplankton Blooms

Marine phytoplankton blooms are a natural phenomenon in marine systems. However, human-induced nutrient enrichment in coastal areas strongly increased their intensity and frequency (Anderson et al. 2002). Subsequently, such blooms can cause severe environmental problems either directly, through toxin production, or indirectly, through their high biomass (Purdie 1996).

Toxic algal blooms occur in relatively low densities, but can cause mortality of wild fishes, sea birds, marine mammals, and humans when their toxins become accumulated in filter-feeders (e.g., shellfish) and are transported up to higher trophic levels in the food chain (Anderson 2009; Davidson et al. 2011). Shellfish-poisoning induces sub-lethal responses in humans, such as diarrhea, eye/skin irritation, or breathing difficulties. Approximately 300 people die annually as a result of consuming contaminated shellfish (Richardson 1997). Non-toxic phytoplankton blooms are events that produce large amounts of biomass and are visibly detectable through the formation of foam along shorelines and the coloration of the seawater, commonly known as red tides. High phytoplankton biomass in the water column significantly reduces light and O_2 availability in bottom waters with a subsequent reduction in the depth distribution or elimination of the benthic vegetation. This can have dramatic impacts on coastal ecosystems due to habitat destruction and mass mortality of benthic and pelagic organisms (Glibert et al. 2005). In 1998, a red tide event in Hong Kong killed around 90 % of fish farm stocks, causing economic damage of 40 million USD and red tides in US coastal waters caused damage of around 500 million USD between 1987 and 1992 (Anderson et al. 2000; Selman et al. 2008). Today, according to estimates, these blooms cause global damages of billions of dollars each year (Smith and Schindler 2009).

Changes in phytoplankton biomass (i.e., Chl *a*) or the occurrence of harmful phytoplankton species and their respective toxins in water samples can be used as early warning indicators for such blooms (Sellner et al. 2003).

11.5.1.2 Macroalgal Blooms

Fast-growing opportunistic macroalgae (seaweeds) species can reach high abundance in nutrient-enriched, near-shore areas in situations where grazing pressure is low and phytoplankton growth is suppressed (e.g., due to short water residence time). Macroalgal blooms typically last longer than phytoplankton blooms and they can have profound effects on marine ecosystems by overgrowing and outcompeting slow-growing perennial species (e.g., seagrasses, corals, and brown and red algae; Valiela et al. 1997). As compared to perennial species, seaweeds fix carbon in excess and subsequently release large amounts of dissolved organic matter into surrounding water (Velimirov 1986; Haas et al. 2010a). This organic matter quickly enters the microbial food web, thereby stimulating microbial activity, increasing the biological O_2 demand of bottom waters, and causing hypoxic conditions to occur (Haas et al. 2010a, b; Niggl et al. 2010) (see Sect. 11.5.2). Hypoxia and changes in the composition of primary producer species are in turn responsible for the major fauna community shifts that accompany macroalgal blooms in eutrophic areas. They can be particularly harmful to seagrass and tropical coral reef ecosystems as they are highly adapted to low nutrient waters, support a high biodiversity, and are important nurseries for many juvenile fish species (Grall and Chauvaud 2002; Fabricius 2005). In contrast, the reaction of marine ecosystems that lie within estuaries or upwelling areas is likely to be less sensitive, since these regularly experience elevated nutrient concentrations.

11.5.2 Hypoxia

11.5.2.1 Causes and Distribution

Die-off, sedimentation, and subsequent microbial decomposition of the high algal biomass considerably enhance O_2 consumption in bottom water, subsequently leading to hypoxic (O_2 depleted) or even anoxic (no O_2) conditions near the sediment-water interface (Diaz and Rosenberg 1995; Glibert et al. 2005). Hypoxia is described as the most serious effect of excess eutrophication, because it causes major geochemical and biological shifts within marine ecosystems. Selman et al. (2008) identified 415 eutrophic coastal systems worldwide, of which 169 are documented as hypoxic, 233 are areas of concern, and 13 areas are in recovery (Fig. 11.1). Marine coastal environments that are near nutrient-rich rivers (e.g., the Mississippi River and the Gulf of Mexico; the Susquehanna River and the Chesapeake Bay) or located in geographically constrained areas with low water exchange and high stratification of the water column (e.g., the Baltic Sea, the Black Sea) can be highly affected, and subsequently represent the largest hypoxic areas worldwide (Rabalais 2002). The impact on the functioning of marine life and ecosystems also depends on the system's duration of exposure to hypoxic events (e.g., seasonal exposure in upwelling areas, permanent exposure in the Baltic Sea and the Gulf of Mexico).

11.5.2.2 Consequences on Marine Ecosystems

With decreasing O_2 availability, the redox potential (the tendency of chemical species to either acquire or lose electrons) in the sediment changes, thereby increasing fluxes of NH_4^+, silica (SiO_2), and particularly PO_4^{3-} from the sediment into overlaying waters. This increased nutrient supply further fuels phytoplankton production and accelerates hypoxia and the effects of eutrophication (Howarth et al. 2011). O_2 respiration can be completely replaced by bacterial sulfate respiration leading to the generation of hydrogen sulfide, which is toxic to most of the benthic macrofauna, including functionally important species such as bioturbators. The loss of bioturbation reduces the downward transport of O_2 into the sediment and makes the sediment less cohesive and more susceptible to resuspension. Consequently, water turbidity increases and the potential growth of the O_2 producing phytobenthic community is reduced (Rabalais et al. 2010). This implies a dramatic change in ecosystem functioning by reducing the buffer capacity against benthic hypoxia and making the system more vulnerable to the development and persistence of hypoxic events.

Furthermore, in hypoxic areas microbial pathways can quickly dominate the food web, thereby reducing the energy transfer toward higher trophic levels (Diaz and Rosenberg 2008). This leads to an overall decline of biomass, changes in species composition, and loss of habitat and biodiversity (Selman et al. 2008).

Large, long-lived, less tolerant organisms (e.g., demersal fish, macrobenthos, and suspension feeders) are eliminated first, and then the benthic community will shift toward higher abundances of small, short-lived, tolerant organisms (pelagic fish, meiobenthos and deposit feeders) in successive stages, depending on the extent of hypoxia (Grall and Chauvaud 2002). Successive changes in the benthic community structure and changes in the ratio of pelagic to benthic and demersal fish biomass represent useful long-term indicators for hypoxia-stressed areas (Rabalais 2002; Wu 2002; Hondorp et al. 2010), where community structure can provide insight into the level of hypoxia-driven degradation. Under prolonged hypoxia, the total loss of benthic and pelagic fauna can occur creating so-called dead zones, which have grown dramatically in size and distribution over the last decades. Globally, the observed number of dead zones has increased from 9 in the 1960s to 540 today, and is still tending to grow (Galloway et al. 2013; Fig. 11.1). These areas can have detrimental effects on commercially important species, thereby affecting local economies and markets that rely on these natural resources (Grall and Chauvaud 2002; Diaz and Rosenberg 2008; Rabalais et al. 2009). Therefore, regularly monitoring of dissolved O_2 concentrations in the water provides an important direct indicator to measure the actual state of oxygenation and thus the health of marine ecosystems. Recently, specific sulfur-oxidizing bacteria (SUP05) have been found worldwide in O_2-depleted marine environments, and hence their presence can serve as early warning indicator to detect the development of dead zones (Glaubitz et al. 2013).

11.6 Outlook

In the future, the world's marine ecosystems will likely be simultaneously affected by a range of global (ocean acidification and warming) and local factors, particularly marine eutrophication (e.g., Voss et al. 2013). This particularly applies to tropical coastal areas of developing countries, because here coastal ecosystems that are already at their upper temperature threshold often meet coastal regions with high population pressure so that marine ecosystems are likely affected by both warming and eutrophication. Ocean warming will also very likely enhance the above-mentioned eutrophication-induced O_2 depletion that is particularly critical in tropical areas with already high water temperatures. The upper limit of low O_2 water has already moved up to 90 m closer to the surface off North America's west coast (Stramma et al. 2008). Almost no information is available about the potential interaction of ocean acidification and eutrophication, but there is some indication that acidification may affect the bioavailability of essential nutrients in the marine realm (Shi et al. 2010). In turn, marine eutrophication may stimulate ocean acidification by facilitation of CO_2 uptake by phytoplankton. Furthermore, certain N species, particularly NO_2 contribute to the greenhouse effect, in contrast to the fertilization effects of N that cause additional CO_2 uptake from the atmosphere. The net effect of N is probably cooling, but this is highly uncertain (Galloway et al. 2013).

Knowledge of the interaction between such global and local factors and their consequences for ecosystem functioning is obviously scarce, but a few existing related studies indicate cumulative aggravating effects (e.g., Lloret et al. 2008). Good science-based management of marine coastal ecosystems and their resources should include these aspects and consider biogeochemical cycles of C, N and P in particular.

The ability to define nutrient threshold concentrations is crucial to the management and monitoring of marine ecosystems. However, our current understanding of nutrient enrichment and specific nutrient thresholds cannot be improved without reference to a biological response. Ecological monitoring and management decisions should not be based on nutrient concentrations and Chl *a* measurements alone (Devlin et al. 2007; Nixon 2009). Rather, more comprehensive ecosystem level indicators, which take into account the interaction of nutrients, primary production, and evidence of biological disturbance, are required to provide the information necessary to manage marine ecosystems successfully.

Generally, it has become clear that all measures (e.g., more efficient use of fertilizers in coastal agriculture, reduction in atmospheric emissions, conservation of coastal forests and mangrove areas, and establishment and improvement of waste water treatments; please see Sutton et al. 2013) that reduce both inorganic and organic nutrient input into coastal waters will likely benefit the functioning of coastal marine ecosystems. The challenge for the current century is indeed to optimize the use of nutrients such as N, but at the same time to minimize their negative effects (Galloway et al. 2013).

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Part V
Environmatics

Chapter 12
Framework for Analyzing Environmental Indicators Measurements Acquired by Wireless Distributed Sensory Network – Air Pollution Showcase

Barak Fishbain

Abstract Distributed continuous in situ monitoring of the environment is an essential component in assessing environmental indicators as their changes take place on different spatial and temporal scales. Recent sensory and communication technological developments have led to the emergence of Wireless Distributed Environmental Sensing Networks (WDESNs) that consist mainly of Micro-Sensory-Units (MSUs). The set of skills and expertise that are called for developing these WDESNs are from different fields and research disciplines, where each discipline has its own jargon. To allow cross-disciplinary discussion, a comprehensive, yet simple framework for discussing data acquired by WDESNs is presented. The terminology presented here allows for describing complex multi-modal environmental sensory networks and the integration of the observed environmental indicators' into a holistic understanding of the environment. The usage of the presented framework is demonstrated in describing a recently reported data acquired by air-pollution WDESN.

Keywords Enviromatics • Environmental informatics • Distributed sensing • Sensory networks • Environmental sensing • Environmental data analysis • Environmental data fusion

12.1 Introduction

Continuous in situ monitoring of the environment is an essential component in assessing environmental indicators. Air, water and land characteristics and quality, and their change over time is fundamental to most environmental applications. Quantifying changes in environmental indicators over time is a most challenging

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_12

task as their changes take place on different spatial and temporal scales. Local system characteristics and behavior affect overall system, while system level parameters govern the local scale processes.

Recent sensory and communication technological developments have led to the emergence of Wireless Distributed Environmental Sensing Networks (WDESNs) that consist of Micro-Sensory-Units (MSUs), mainly in air and atmospheric assessments (Mead et al. 2013; Chen 2008; Dutta et al. 2009; Williams et al. 2013; Etzion et al. 2013; Broday et al. 2013) and aquatic systems (Kroll and King 2007; Hall et al. 2007; Pickard et al. 2011; Research and Development, National Homeland Security Research Center 2005; Kramer 2009; Storey et al. 2011). These have greatly enhanced monitoring of complex infrastructure and the natural environment, allowing the study of fundamental processes in the environment, as well as hazard warnings, such as flood (Hart and Martinez 2006; Martinez and Hart 2004; Zhou and Roure 2007) and pollution alerts (Hochbaum and Fishbain 2011), in a new way. In conjunction new hardware designs and algorithmic approaches to support these networks have emerged (Ramanathan et al. 2006; Budde et al. 2012; Denzer 2005; Kranz et al. 2010; Bakken et al. 2001). The focus of most of these studies is an efficient operation of the network and failure tolerance and therefore they do not provide new insights on the monitored environments. Further, many problems studied in the field, have their roots in the desire to emulate cognitive capabilities of a human (e.g., Ramanathan et al. 2006; Chen 2008; Dutta et al. 2009). With the rapid advances in hardware technology, this anthropocentric and somewhat limited paradigm may no longer be the only source for inspiration. The variety and availability of sensors have made the accessible data much greater in quantity than the data that can be gathered and interpreted by a human being. However, considering the sheer amount of data and its diversity, building such multi-sensors systems becomes a great challenge.

Field deployments of low-cost air quality MSU-based WDESN have been recently reported (Mead et al. 2013; Williams et al. 2013). Williams et al. (2013) showed the use of metal-oxide micro-sensors for measuring ambient O_3 levels and Mead et al. (2013) used electrochemical probes for measuring CO, NO and NO_2. These studies do not present a network configuration for air pollution measurements. Therefore, their ability to capture the spatial pollutant variability has not been shown.

The ability and potential of WDESN to capture spatial and temporal variation in field campaigns has been recently demonstrated (Broday et al. 2013; Shashank et al. 2013). These studies regard only one indicator (pollutant) in their analysis. The integration of different modalities possesses the ability to exploit the sensors' cross-selectivity and to compensate each modality's inherent deficiencies by utilizing the strengths of the other modalities. This is still a relatively new discipline, and little effort has so far been devoted to the implementation of fully operational devices for environmental applications as seen in other fields such as computer vision and robotics. Such spatial and temporal analysis of several indicators on a well-defined environment, through WDESN, has been recently reported by Moltchanov et al. (2015).

This new emerging field, enviromatics (environmental informatics), calls for a new set of algorithms and methodologies originating from several distinct disciplines – chemistry, environmental sciences, optimization, multi-dimensional signal processing, data fusion and data communication. To facilitate any discussion between scholars from these different research fields, there is a need to build a comprehensive, yet simple, framework. Here such framework is presented. Section 12.2 presents the framework, its components and its lexis foundations. Section 12.3 demonstrates the usage of the presented lexis in the context of air-pollution distributed sensory network by describing the results reported by Moltchanov et al. (2015). Section 12.4 concludes this chapter.

12.2 Framework

12.2.1 Lexis

This section introduces the lexis that facilitates the Environmental Multimodal Distributed Sensory Network framework. *An environmental episode* is a disruption in the environmental conditions. To this end, an episode can be a major environmental happening, such as high or irregular gamma radiation levels (Hochbaum and Fishbain 2011), volcanic eruptions (Werner-Allen et al. 2006) or mass fish death (CNN Wire Staff 2011). It can also be a typical happening such as traffic rush hours. Such environmental episode consists of recorded *events*. Events are a set of *incidents*, which are recorded by a single or a set of sensors, and are found to be related to an environmental episode. Events in those cases are, for example, the deviations from the regular background radiation; the seismic-acoustic recordings and the oxygen levels in the aquatic system. Each incident represents one or more measured environmental indicators (Fig. 12.1). In the context of air-pollution, this can be ozone (O_3), nitrogen dioxide (NO_2) or particular matter (PM). This formulation ensures, by definition, the following:

Corollary 1

- Each environmental episode has a well-defined spatial and temporal window.
- An environmental episode manifests itself in the sensors' acquired data.

Events are extracted from streams of *incidents* and only then are cross-referenced. The key justification behind this dichotomy is that different set of algorithms are called for extracting events from a stream of incidents, and for relating these events. The separation of these tasks also allows for distributed processing, as the event extraction can be held on the sensing platform itself. The

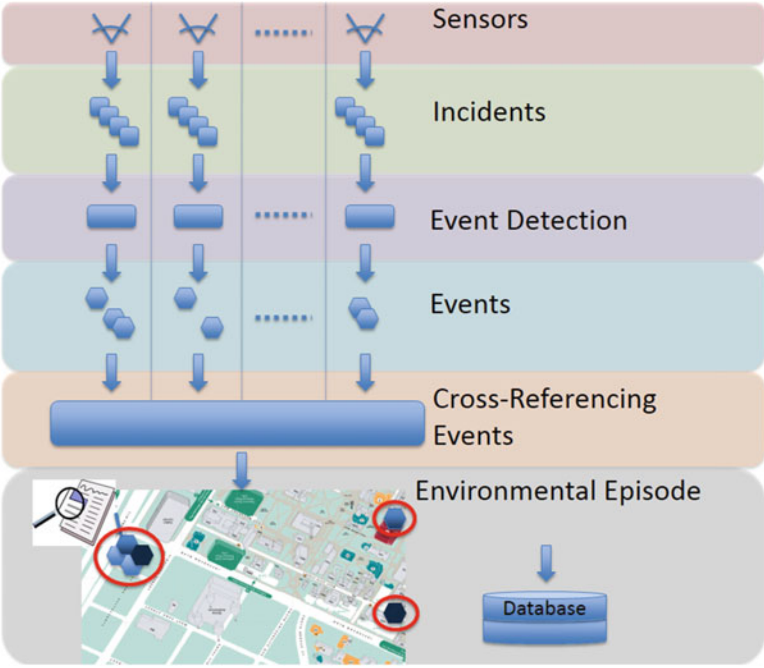

Fig. 12.1 Multimodal distributed sensory networks dataflow and terminology

set of extracted events is processed by a set of analytics tools for individual data streams as well as multiple data streams of various types. Both kinds of analytics are needed for unveiling the information embedded within each data stream/source as well as the information that is spread across various data sources. This formulation facilitates an efficient and reliable processing of exceptionally large environmental data sets (of size in the tens of thousands or millions entries).

12.2.2 Event Detection in Streams of Incidents

The small size and low power-consumption of MSU allow for mobile measurements. Placing these units on vehicles enables the coverage of a wider area with a lower number of units, while keeping the spatial and temporal resolution high enough. Few recent studies showed the possibility and advantages of such use, and the relatively easy adaptation of such MSU's to function as mobile sensing units, with the addition of GPS (Al Ali et al. 2010; Devarakonda et al. 2013; Levy et al. 2012). Thus, WDESN may consist of stationary and mobile nodes. Therefore the discussion is a dual-facet one, where incident streams generated from stationary and mobile WDESN nodes should be addressed differently. The following sections address event detection in streams received from stationary and mobile nodes.

12.2.2.1 Event Detection in Streams of Stationary WDESN Nodes

The common practice for extracting events from a set of incidents is finding a deviation from a pattern that represents the normal or routine set of incidents. The patterns may be computed from the indicators' time series themselves (e.g., Hall et al. 2007; Pickard et al. 2011), or from any representation of the data. Typical data representation techniques are Principal Component Analysis (PCA) (e.g., Huang et al. 2010), spectral exploration (e.g., Eder et al. 2012; Koscielny-Bunde et al. 1998; Whitcher and Jensen 2000) or De-trended Fluctuation Analysis – FDA (e.g., Koscielny-Bunde et al. 1998; Talkner and Weber 2000). All aforementioned methods require that the data samples are acquired in a uniform fashion, i.e., with the same time and spatial intervals between samples. However, this requirement, typically, does not hold for the dataset in hand. To tackle this hurdle, data interpolation methods that interpolate the data in a regular grid fashion from the non-uniform samples are sought. These methods include, for example, the Discrete Sampling Theorem (Yaroslavsky et al. 2009) and, in the context of air pollution, the Inverse Distance Weighted (IDW) (Moore et al. 2008) and Kriging (Sarigiannis and Saisana 2008) interpolations.

Regardless of the representation method, an incident can be regarded as an event if the deviation from the pattern is above a certain threshold. The threshold can be set manually (e.g., Pickard, et al. 2011) or inferred in an automatic fashion based on the acquired data and trends observed (Arad et al. 2013). This approach, however, is vulnerable to faulty measurements that present a large deviation from the pattern.

Classification approaches such as Support Vector Machine (SVM) (e.g., Oliker and Ostfeld 2012), Minimum Volume Ellipsoid (MVE) (Becker and Gather 1999) or the Supervised Normalized Cut (SNC) (Yang et al. 2013) present a more robust event detection schemes as they allow for the integration of several environmental indicators into one recorded incident. SVM aims at separating events from the background stream of incidents. The SVM method consists of two stages – At the first stage, incidents that are known to be an event and incident that are known to be non-event (i.e., routine) are applied on an environmental indicators space. Then, based on the pre-classified data, a classifier is constructed on this space. At the second stage each new incident is compared against the classifier and tagged accordingly. SVM requires that normal and abnormal incident patterns are known before-hand. While routine patterns can be extracted from continuous streams of incidents (e.g., Kroll and King 2007; Hall et al. 2007; Pickard et al. 2011), considering all possible abnormal indicators' conditions and values is not a tractable task.

MVE solves this problem by using only the non-event incidents in the training phase (Becker and Gather 1999). The MVE, in its training phase, constructs a minimum volume ellipsoid on the indicators space, which includes all non-event incidents. Then any measurement that falls outside this ellipsoid is considered to be an event.

The SNC method forms the event detection task as graph-cuts optimization problem. In this formulation an undirected graph, *G(V,E)*, is constructed, where

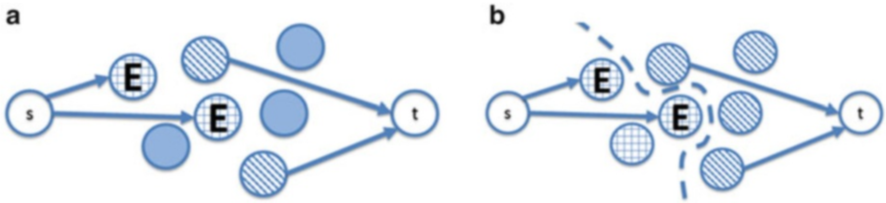

Fig. 12.2 SNC procedure

V is the set of incidents and E is the set of edges connecting adjacent incidents. The set of incidents contains both tagged (either as event or as non-event) and untagged incidents. A node that corresponds to an event-incident, is referred to as an event-node. Each edge $[i, j] \in E$ carries a similarity weight, w_{ij}, that represents the similarity between incidents i and j. The method is more generalized than SVM and MVE as adjacency (i.e., what characteristic qualifies two incident to be considered adjacent) and the similarity measures are not dictated by the SNC formulation and can be set by the characteristics of the specific problem in hand. Once the graph is constructed two additional nodes, s and t, are added to the graph. An arc with infinite weight is drawn from s to all event-nodes and from all non-event nodes to t. The construction of the graph is illustrated in Fig. 12.2a, where event-nodes are marked with an "E", non-event nodes are presented with diagonal markings and untagged nodes are solid.

The classification is then held by solving the s-t minimum-cut problem (Ford and Fulkerson 1956) on the graph. The minimum s-t cut problem partitions the nodes in the graph into two partitions, S and T, such that $s \in S$ and $t \in T$ and the sum of similarity weights on edges going between S and T (i.e., the cut) is minimized. After the partition, all incidents that correspond to nodes in S, are considered as an event and all incidents that are associated with nodes in T are tagged as non-event. The classification process is illustrated in Fig. 12.2b. All untagged nodes are now tagged based on the cut.

12.2.2.2 Event Detection in Streams of Mobile WDESN Nodes

Streams received from portable sensors are obtained from the same sensor in different locations at different times. Thus, mobile sensors' measurement are time-space variant. While networks that consist of mobile sensory platforms (Al Ali et al. 2010; Devarakonda et al. 2013; Levy et al. 2012) have been suggested, little effort has been invested in fusing the readings (i.e., incidents) into one holistic spatio-temporal patterns. Pattern recognition in mobile sensory networks has been suggested through the *concentrated alert* (CA) *problem*. The CA problem aim at optimizing two goals: One goal is to identify a small region; another goal is to have a large number of sensors indicating high pollution levels. These two goals are potentially conflicting – focusing on a large number of sensors reporting high levels of pollution within an area is likely to result in the entire region; on the other hand focusing on concentration alone would result in a single block of the area containing the highest number of sensors reporting high concentrations, thus disregarding information provided by other detectors in neighboring areas. The goal then is to identify, at every period of time, a region that relatively to its size has high concentration of sensors reporting high pollution levels. One way to achieve this is by minimizing a ratio function of the size divided by the number of detected events in the region. Another, is to optimize a weighted combination of the goals. As was shown in (Hochbaum and Fishbain 2011) the latter problem is efficiently solvable in polynomial time.

One iteration of the CA problem finds one region with the highest concentration of sensors reporting highest levels of pollution, hence a binary decision, which is based on solving a minimum-cut problem on an associated graph (Hochbaum and Fishbain 2011). After each iteration the region that was tagged as risky with its corresponding sensors are removed and the process is repeated so equi-pollution contour lines are produced. The final output is the patterns and deviations from these patterns are events.

Another graph-theory based method, firstly presented here, for generating patterns from distributed sensory network is based on Markov Random Fields (MRF) (Hochbaum 2001). The MRF optimization problem aims at finding a value such that two functions are minimized: a deviation cost function that depends on the distance between an observed value and a modified one; and a penalty function that grows with the distance between values of related (adjacent) pairs, i.e., *a separation function*. Specifically, within the suggested framework, the goal is to modify the indicators' values so that an objective function, consisting of one term due to the deviation of the events' values from the measurements, and a second term that penalizes differences in assigned values to adjacent spatial sensors, is minimized. This is illustrated in Fig. 12.3.

Adjacency is not mandated by the method and can be derived from the characteristics of the problem in hand. For example incidents can be considered to be adjacent if they are less than a predefined distance from each other. Once adjacency is determined, one has to assign the deviation and separation weights. This implies that for computing the separation cost function one should extract the affinity function for all adjacent incidents pairs.

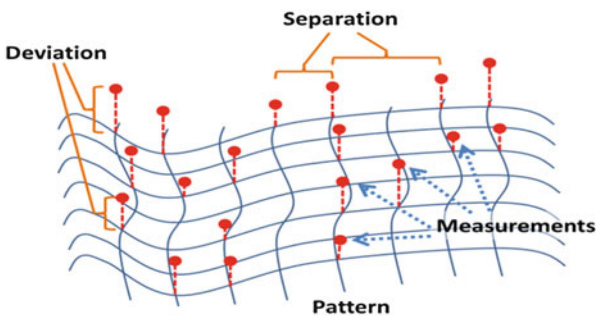

Fig. 12.3 Markov Random Field

For *G()* and *F()* the deviation and separation cost functions respectively, g_j – events value in node *j*, the problem is to find a pattern *X* that consists of a set of $x_i \in X$ that minimizes the following objective function:

$$min_X \left\{ \sum_{i \in V} G_j(g_i, x_i) + \sum_{(i,j) \in A} F_{ij}(x_i - x_j) \right\}$$

When the separation function is linear and the deviation function is linear, quadratic or piecewise linear convex, the MRF problem can be solved efficiently (in strongly polynomial time) through network flow algorithm (Hochbaum 2001).

12.2.3 Cross Referencing Events

In order to understand the nature of the entire environmental episode based on all extracted events, one has to find a set of events that co-align with each other and best explain the observed environmental episode. To this end, the common methods are the Maximum Likelihood Estimation (MLE) (e.g., Álvarez, et al. 2005), Artificial Neural Networks (ANN) (Reich, et al. 1999; Gardner and Dorling 1998) and the Dempster-Shafer Theory (D-S) (e.g., Wang, et al. 2006; Yadav, et al. 2013).

The MLE approach assumes an underlying model and aims at finding the model's parameters that are most probable, given the observations. For example, Álvarez et al. present a Markov chain model to study air pollution, where daily maximum ozone measurements in Mexico City are assumed to follow a Markov chain of order $K > 0$. The parameter K is then inferred using MLE (Álvarez et al. 2005). The necessity of a model is a drawback of these types of methods as describing environmental and atmospheric phenomena by an accurate model is an extremely difficult task.

In its most general formulation ANN consists of a system of simple interconnected neurons, or nodes (as illustrated in Fig. 12.4), which represent a nonlinear mapping between an input vector (events in this case) and an output vector (episodes). The nodes are connected by weights and output signals which are a function of the inputs to the node modified by a simple nonlinear transfer, or activation, function. It is the superposition of many simple nonlinear transfer functions that enables the multilayer perceptron to approximate extremely non-linear functions. The output of a node is scaled by the connecting weight and fed forward to be an input to the nodes in the next layer of the network. This implies a feed-forward neural network, where each input, I_i, goes through several such functions. Each *i*th transfer function in layer L,f_i^L, can be of a different form. Due to its easily computed derivative a commonly used transfer function is the logistic function, $y = (1 - e^{-x})^{-1}$, but any other function would work. As both the input

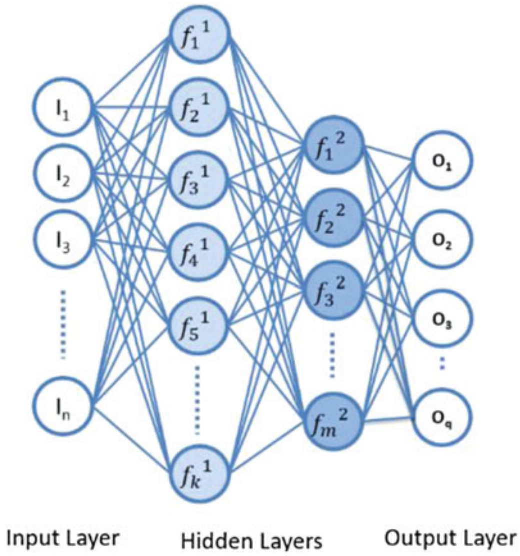

Fig. 12.4 Artificial neural network for associating events with episodes

events $\{I_1, I_2, I_3, I_4, \cdots, I_n\}$ and observed episodes $\{O_1, O_2, O_3, \cdots, O_q\}$are known, the goal is to find the various functions' parameters that explain best the linkage between the events of episodes. The resulted network and its parameters explain the role of various events in the observed episodes. Thus the goal is not to detect the happening of an episode, but to infer the events that contribute to its happening.

In its core the D-S methodology is a generalization of the Bayesian theory of subjective probability. For illustration of the problem, let us consider an episode, O, and a set of related events, Ω. All subsets of events, $\{\omega\} \subseteq \Omega$, are assigned with a probability [0,1] that represents their post-priori probability to actually happen given observation O, such that $\sum_{\omega \subseteq \Omega} P(\omega) = 1$. Two values are then calculated for each subset, ω_i:

- **Belief Value** – the sum of probabilities of all subsets that include ω_i, i.e., $Bel(\omega_i) = \sum_{\omega_j \supseteq \omega_i} P(\omega_j)$.
- **Plausibility value** – the sum of probabilities of all subsets that intersect with, ω_i, thus $Pl(\omega_i) = \sum_{\omega_j \cap \omega_i \neq \phi} P(\omega_j)$.

$Bel(\omega_i)$ represents the evidence we have for ω_i directly. So $P(\omega_i)$ cannot be less than this value. $Pl(\omega_i)$ represents the maximum share of the evidence, if, for all sets that intersect with ω_i, the part that intersects is actually valid. Thus, $Pl(\omega_i)$ is the maximum possible value of $P(\omega_i)$. The difference, $(Pl(\omega_j) - Bel(\omega_j) \geq 0)$, called the *belief interval*, represents how certain a belief, ω_i is. Thus, how accurate is the initial assumption about its post-prior conditional probability given O.

12.3 Neighborhood Scale Air-Quality Environmental Indicators

Next we illustrate the use of the suggested framework within the context of air-quality monitoring by describing the results of (Moltchanov et al. 2015) in the above terminology. In their study Moltchanov et al. (2015) report ambient measurements of gaseous air pollutants by a WDESN of MSUs that have been deployed in three urban sites, about 150 m apart. This study of Moltchaqnov et al. is the first time a network's capability to capture spatiotemporal variations is demonstrated at a sub-neighborhood spatial resolution, which suits the requirement for highly spatiotemporal resolved measurements at the breathing-height when assessing exposure to urban air pollution.

12.3.1 Study Design

The study region is the city of Haifa, located in the north of Israel with a population of ~265,000. The city is located at the northern part of the Israeli Mediterranean Sea shore, ranging from sea level to the Carmel mountain ridge at ~500 m above sea level (ASL). The Haifa bay area is a busy metropolitan, combining both densely populated residential areas and a large industrial complex which includes a primary sea-port, petrochemical industries and oil refineries. The entire region is burdened with traffic, including heavy vehicles, cargo trains and a large number of diesel buses, as Haifa functions as a transportation center for the entire northern region of Israel.

Specifically, the study was performed at the Neve Sha'anan neighborhood – a residential neighborhood located on a relatively leveled region of the Carmel Ridge, about 200 m ASL. The neighborhood is roughly divided by a major road (Trumpeldor Ave.), which also serves as the main commercial center for the residents of this area (Fig. 12.5).

In the study described in (Moltchanov et al. 2015), six units were deployed at three different locations some 100–150 m apart – sites A, B and C in Fig. 12.5. The campaign took place for 71 days in the summer of 2013 (between 16/06/2013 and 26/08/2013), a season that is characterized by meteorological stability and persistence. Site A is a balcony on small residential street. The units were placed 3 m high above ground level (AGL) and 5 m off the centerline of the road, which experience sparse traffic density. Site B is a second story balcony. The first story of the building houses a pizzeria with an exhaust at the rear side of the building. The units were placed 4 m AGL and 7 m off an adjacent busy street. The building is a corner building of the Ziv junction, which is a busy local (neighborhood-scale) commercial zone (see Fig. 12.5b and c). Site C is located on the Trumpeldor Blvd., the main street of the neighborhood, ~80 m NE from a busy bus stop. The units were placed on a roof of a kindergarten courtyard, 3 m AGL and 4 m off road.

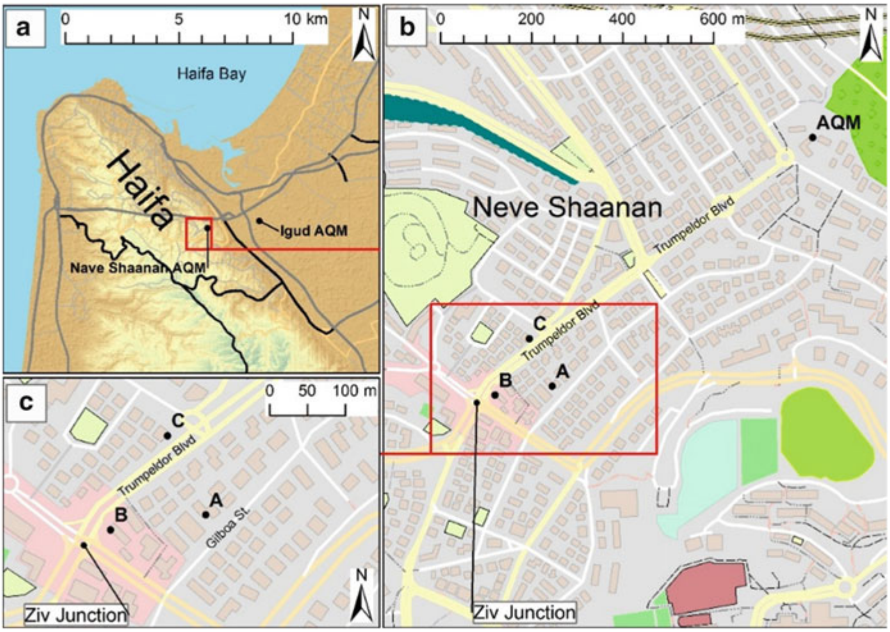

Fig. 12.5 Map of the study region showing the Haifa bay area and the Carmel Ridge (**a**), Nave Shaanan neighborhood (**b**) and the Ziv Junction area in greater detail (**c**)

Wind data were obtained from the Nave Shaanan AQM station (marked AQM in Fig. 12.5b), located 750 m down the road from site C.

12.3.2 *Incident Streams*

The incident streams are produced by CanarIT™ air quality MSUs (Airbase Systems LTD). Each unit generates streams of ambient levels of the following indicators – O_3, NO_2, total VOC (tVOC), Total Suspended Particles (TSP), noise, temperature (Temp) and relative humidity (RH). In this analysis we focus on NO_2 and O_3 measurements only. Each apparatus gauges the indicators' level over a short time period (Meas.T) and reports the average level, computed over Meas.T, at a given Frequency (Freq). Thus, Meas.T is shorter than the time between reports (1/Freq). The technical specifications of the various sensors are detailed in Table 12.1. Measurements are transmitted to a cloud-based storage, by an on-board GSM embedded chip.

Throughout the campaign, one unit was fixed at each site. The three remaining units were rotated twice between the sites, on days 28 and 51 from the beginning of the campaign, so that each of these three units operated at each of the three sites. The rotation allowed for comparison within and between the sites, thus enabling to

Table 12.1 Sensors technical specifications

Stream	Man.	Model	Meas.T [s]	Freq. [Hz]	Dyn.R [ppb]	Res. [ppb]
O_3	Aeroqual	SM50	1	60	0–150	1
NO2	AppliedSensors	iAQ-100	2	20	0–2,000 ppb	5
tVOC[1]	AppliedSensors	iAQ-100	2	20	0–2,000 ppm[2]	
TSP			0.5	20		
Noise			0.25	20		
Temp.			0.5	20		
RH			0.5	20		

Man. manufacturer, *Meas.T* acquisition time, *Freq.* reports frequency, *Dyn.R* sensors' dynamic range, *Res.* the sensors' resolution

Table 12.2 Location of units during each of the study periods

Site	Fixed units	Period I – days 1–28	Period II – days 28–50	Period III – days 50–71
		Jun. 16 – Jul. 14	Jul. 14 – Aug. 5	Aug. 5 – Aug. 26
A	418	422	413	424
B	420	424	422	413
C	414	413	424	422

compare the obtained streams across the different locations and the sensor nodes. Table 12.2 details the sensors' location throughout the field campaign. Because of the persistent meteorological conditions over the region in the summer, 21–28 days' time periods are assumed sufficient to characterize the pollution levels at each of the microenvironments.

As detailed in (Moltchanov et al. 2015), in general, high correlations were found among incidents of collocated WDESN nodes, suggesting consistency across different MSUs' measurements. In contrast, low correlations are depicted between concentrations of both NO_2 and O_3 measured by MSUs at different locations, indicating that the measured concentrations echoed some local conditions and responded to the specific microenvironment where the nodes were placed.

12.3.3 Events Detection in Streams of Incidents

Diurnal patterns of NO_2 and O_3 concentrations among collocated MSUs were highly correlated. NO_2 and O_3 daily patterns are presented in Fig. 12.6. Figures (a) and (c) depict weekday's pattern of NO_2 and O_3 respectively. Figures (b) and (d) present the corresponding weekend's patterns. Both NO_2 and O_3 reveal distinct patterns in each site. The reason for this is twofold – first each microenvironment is governed by different conditions. Second, the sensors themselves present inherent biases.

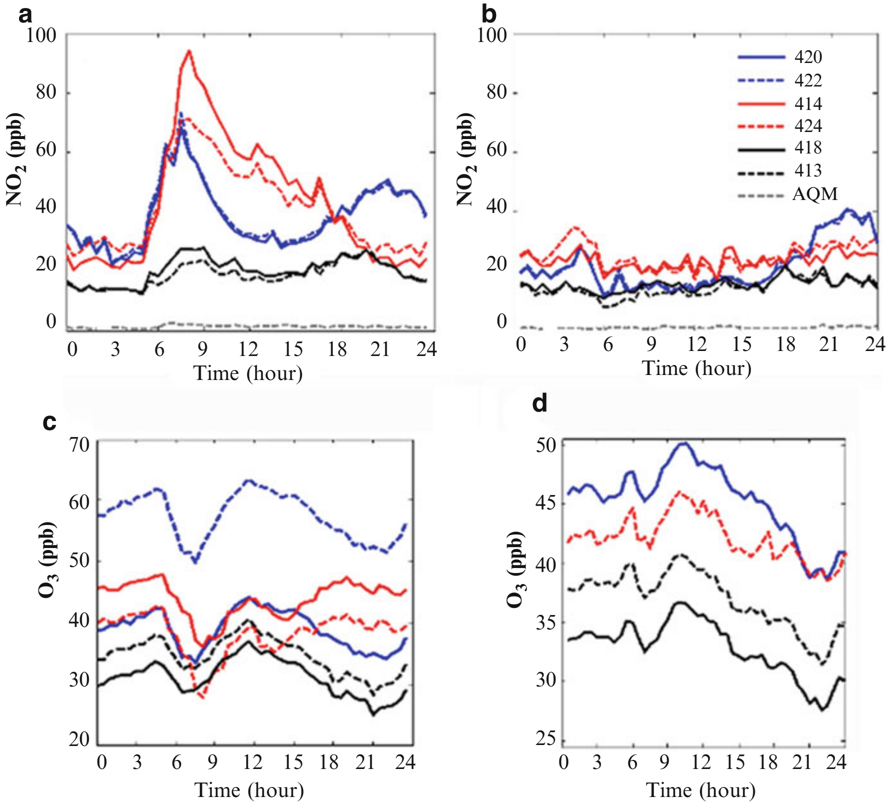

Fig. 12.6 Daily patterns of NO2, (**a**) and (**b**), and O3, (**c**) and (**d**), concentrations (30 min. averages) measured by collocated nodes in locations A (*black lines*), B (*blue lines*) and C (*red lines*) during Period II. Plates (**a**) and (**c**) are weekdays (Sunday–Thursday) patterns, plates (**b**) and (**d**) weekends (Saturdays) patterns. *Dashed grey lines* – simultaneous AQM monitoring data (Source Moltchanov et al. 2015)

This is especially true for O_3 sensors (see Fig. 12.6c and d). Regardless of the reason for these differences, the phenomenon itself emphasizes the advantage of extracting events from each stream of incidents separately.

In the study of Moltchanov et al. (2015), the goal was to assess the MSUs' capability to capture real-life phenomena. Therefore, let us consider incidents acquired from a specific stream as events if they present values that are higher or lower (by a standard deviation) than the specific stream's average. This should correspond to higher and lower values of NO2 and O3 respectively during morning and evening traffic peaks (Levy et al. 2012; Nazaroff and Alvarez-Cohen 2001; Zalel et al. 2008). On weekday, events were recorded, for example, between 7 and 8 am. On weekends, on the other hand, the daily peaks diminish (Fig. 12.6b, d) and therefore no events are recorded.

Site A is located in a small residential street with little traffic and is characterized by lower NO_2 concentrations than the two other sites (See sensor # 413 and 418 in Fig. 12.6a and b). Nevertheless, events are recorded at site A at morning (7:00–7:30) and at evening (~19:30) rush hour peaks. Site B is located at a busy junction in a commercial area. Indeed, the diurnal NO_2 patterns on weekdays reveal a dual-peak daily pattern (Fig. 12.6a), where events are indeed recorded around these peaks. On Saturdays the concentrations remain low and constant until ~19:00, when traffic resumes (Fig. 12.6b). However no events are recorded on weekends. The signature of traffic is revealed also in the weekday ozone concentration patterns that show a dramatic decrease from 05:30 am and reach a minimum at about 07:00–07:30, in parallel to a peak in NO_2 concentrations. Typically, O_3 concentrations increase afterwards and reach peak values at around noon (Fig. 12.6c). Likewise, events extracted from NO_2 and O_3 streams at site C indicate traffic related origin. Peak NO_2 concentrations and minimum O_3 concentrations occurred between 08:00 and 09:00 am.

12.3.4 Cross Correlating Events

Once the set of events are extracted one can cross-correlate them and infer the observed episode. Based on the recorded events, the morning episode at sites A and B starts on average at 7:00 am. Thus, the morning episode's spatial boundaries contain both sites. The episode at site C starts somewhat later than that, forming a different episode. It is worthwhile noting that the suggested reasoning, given in (Moltchanov et al. 2015), is that while the episodes in A and B are due to traffic behavior, the episode at site C is due to children drop off at the kindergarten, located at C. The association of events recorded in sites B and C with the same morning episode is supported by the low mean wind speed (Fig. 12.7a) and the high traffic volume at the Ziv junction, which result in high concentrations at both B and C.

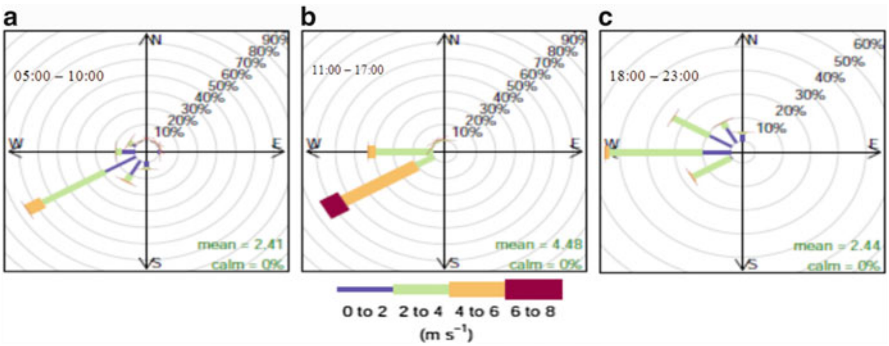

Fig. 12.7 Wind rose plots based on data measured at the AQM station on period I. (**a**) Morning, (**b**) noon and afternoon, and (**c**) evening (Source Moltchanov et al. 2015)

In the afternoon, however, reduced traffic volume and higher wind speeds (Fig. 12.7b) result in significantly lower concentrations at site B whereas site C maintains its relatively higher concentrations. Thus, the evening episode is bounded to site C only.

This detailed discussion demonstrates the capability of the suggested framework to capture both spatial and temporal boundaries of an environmental episode – traffic pollution in this case. The episodes correspond to intra-urban pollutant “hot-spots”, which in return can be treated. The aggregation of the events into set of episodes allows for investigating the episode separately, while incorporating all supporting relevant data in the process and eliminating all non-relevant data. Hence, the use of the suggested framework has a huge potential for providing a comprehensive, yet simple framework for capturing environmental indicators’ impact and their dynamic spatial and temporal variability. As such it presents a great potential to become a common tool in examining environmental indicators acquired through WDESN.

Conclusion

In this chapter a framework and its lexis foundations for analyzing measurements acquired by Wireless Environmental Distributed Sensory Network (WDESN) is presented. A set of sensors acquire observations of environmental indicators. These are formed by the sensing platform as streams of incidents. Incidents that deviate from the normal pattern are regarded as events. The event extraction can be held on the sensing platform itself, which facilitates distributed analysis of the acquired data. Then the events are cross-referenced for inferring environmental episodes. This formulation ensures, by definition, that an environmental episode is well defined in time and space and manifests itself in the recorded incidents by the sensors. Algorithms and methods that constitute the framework are also described.

A practical example of using this framework for describing the results of (Moltchanov et al. 2015) is given. In this example, it is shown how the framework set the spatial and temporal boundaries of an environmental episode and how it captures its dynamic behavior. This shows the great potential of such framework for any future environmental research that is based on WDESN.

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Chapter 13
Environment Benefits Quantification Through Statistical Indicators

Giani Gradinaru

Abstract In the absence of markets for evaluating environment benefits, alternative methodologies must be found to measure them. Indirect estimation allows a value to be assigned to an environmental good by using data about the real choices made by individuals in related markets (markets of substitution). In the absence of the market data, the availability to pay (AP) can be estimated with the help of some substituting goods sold on a market. The behavior of individuals on the related markets reveals the value they assign to the environmental improvements. For example, if pollution levels influence the utilization of a park, the individual AP to travel to another area may be used in estimating damage avoidance for that park. In this chapter, ***enviro-statistical indicators*** are developed**,** which are estimated by applying techniques used to evaluate the need for recreation, preventive behaviour, and cost of illness.

Keywords Environment benefit • Market • Statistics • Economy

13.1 Introduction

The statistical approach for environmental benefits involves considering them complex, atypical mass phenomena resulting from the combined and repeated action of a great number of influence factors. The objective tendencies of the manifestation of environmental benefits require that all individual cases be traced, and that everything unessential and accidental in their being generated in succession be turned into abstraction and eliminated. This means that the environmental benefits are analyzed from the point of view of quantity and specific conditions of time, space, and organization, and they are interpreted as probable phenomena (Gradinaru 2011).

In order to facilitate the reader's understanding of the proposed concepts, in this chapter, we shall refer to aspects extracted from one of my own studies called *Environmental benefits obtained by terminating a tip and neutralizing its effects.*

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_13

This study is complex, for which reason we are only going to highlight the issues suggested for this paper. The study targeted a community located in a Romanian mountain area. The existence of a tip in the very close neighborhood affects the quality of the lake water, potable water, air, and soil, having different effects on the community. The populations covered by the study are the community of the people grouped in 50 households located at a distance of 7 km from the tip, at the most, and the community of the tourists coming in and out of the area.

The objectives of the study referred to throughout the paper are:

- *The effects of the tip on the attractiveness of the touristic area:* data referring to the duration of the trip were collected. Tourists were grouped according to the number of days spent in the area;
- *Effects of the tip on the quality of the drinkable water:* The existence of the tip has adverse effects on the quality of the drinking water. The area is not connected to a centralized network providing drinking water, and the population therefore uses spring water for consumption in their households. Observations were focused on two aspects:
  - *Estimating the disease indirect cost:* The statistical characteristic considered was the number of days covered by the medical leaves that the community employees were given as a consequence of their having fallen ill due to the drinking water contamination. The data were gathered from the family physicians' registers. For each employee the domain of activity was recorded.
  - *Studying consumption behavior*: interest focused on how the people living in 14 households less than a kilometer away from the tip perceive the deterioration in the fountain water quality. The frequency of using the fountain water, bottled water, or water brought from fountains located further away from the tip was monitored. A score was summed according to these considerations.
- *Degree of perceiving foul smell:* the frequency of using air conditioning devices, although the outside air did not require it, was monitored.
- *The behavior of the community's members as far as self-consumption agriculture is concerned:* Scores were given according to the land assigned to self-consumption agriculture.

13.2 Valuation Techniques Used for Enviro-statistical Indicators Estimation

Direct estimation of environmental benefits may be used whenever there is a market for environmental good and services. The benefits resulting from a change in the quantity of a good are estimated using the transaction data on the market. By knowing the way goods are sold, the way people appreciate the respective goods can easily be inferred. In this situation, market value-based tools can be used in the statistical analysis of the environmental benefits (Ioan and co. 2010).

Moreover, there are no direct markets for environmental good and services. In the absence of such markets, alternative methodologies must be found to measure the environmental benefits. Indirect estimation allows a value to be assigned to an environmental good by using data about the real choices made by individuals on related markets (markets of substitution). In the absence of the market data, the availability to pay (AP) can be estimated with the help of some substituting goods sold on a market. The behavior of individuals on the related markets reveals the value they assign to the environmental improvements. For example, if pollution levels influence the utilization of a park, the individual AP to travel to another area may be used in estimating damage avoidance for that park. The techniques used for ***enviro-statistical indicators estimation*** are: need for recreation; preventive behaviour; and cost of illness.

13.3 Enviro-statistical Indicators Estimation Through Technique of Need for Recreation

Improvements in the quality of the environmental elements can increase the recreational opportunities in a certain area (destination). The technique of the need for recreation focuses on choosing certain destinations for recreational purposes. The basic exchange taken into consideration is that between the satisfaction gained after staying in that area and the value expressed in money and time allocated. The number of tourists in the respective area, the duration of their stay and the money spent, including transportation, provide information on how individuals rank the place or certain aspects of the area (such as the quality of the environmental elements).

For the statistical analysis of the environmental benefits offered by an area through the need of recreation technique, the following stages are suggested:

- characterization of the reference area based on the statistical variables considered;
- estimation of the environmental benefit through comparing the reference area with other similar areas (having the same environmental characteristics), from the perspective of the statistical variables considered.

13.3.1 Characterization of the Reference Area

The analysis of how tourists are distributed according to the researched variables suggests information on the attractiveness of the area. If the data series contains a great number of individual values, then the frequency polygon satisfactorily

Table 13.1 Descriptive statistics as regards the duration of stay

Indicators of distribution series	Value
Arithmetical average	4.44
Median	4
Module	3
Square average deviation	2.8
Coefficient of asymmetry	1.4
Coefficient of flatness	2.4

approximates the distribution density graph. In the case of the quantitative variables, the indicators of flatness and asymmetry can be determined. In order to quantify the asymmetry and flatness of distribution, the values of the central tendency (average, median, mode) are used, as well as the moments focusing on various sequences.

Reference is made to the objective: *The effects of the tip on the attractiveness of the touristic area* of the study *Environmental benefits obtained from shutting down the tip and neutralizing its effects*. The characteristics that are followed refer to the tourists' duration of stay and daily expenses. An analysis of the tourists' distribution asymmetry and flatness was made depending on their duration of stay in the area. Thus, the asymmetry and flatness coefficients have values of 1.4 and 2.4, respectively. The descriptive statistics are presented in Table 13.1.

The conclusion is reached that *the majority of tourists would rather stay in the analyzed area for short time periods, as according to the variable analysed their distribution is not uniform. Their choice to stay for a short period stay, 3 days, may be explained by the influence the tip has on the quality of the environmental elements in the area. Shutting down the tip and neutralizing its effects would lead to an increase in the duration of stay for the majority of tourists choosing the area for recreational purposes, which would trigger an increase in the average expenses per duration of stay.*

13.3.2 Comparing the Reference Area to Similar Areas

For the analysis of the environmental benefit generated by the tip's disappearance and neutralization of its effects, **a comparison between the reference area and other similar recreational areas is drawn.** The stages of the analysis are:

– A multi-criteria hierarchy of the similar recreational areas is built;
– A quantification of the environmental benefits is calculated by comparing the reference area to an area most visited by tourists.

The multi-criteria hierarchy of the similar recreational areas presupposes the following steps:

Table 13.2 Multi criteria hierarchy of similar areas

Area	Modal duration of stay		Number of tourists in a year		Daily average expenses		Score	Rank
	Days	Rank	Persons	Rank	Lei	Rank		
A	**3**	**8**	**1,073**	**9**	**175**	**8**	**25**	**9**
B	12	2	1,011	10	184	7	19	5
C	10	4	1,245	8	171	9	21	7
D	2	9	1,498	4	165	10	23	8
E	1	10	1,310	7	207	3	20	6
F	4	7	1,387	6	191	6	19	5
G	**12**	**3**	**1,732**	**1**	**210**	**2**	**6**	**1**
H	5	6	1,547	3	215	1	10	3
I	14	1	1,609	2	201	4	7	2
J	8	5	1,432	5	196	5	15	4

– Selecting the indicators to be applied in the elaboration of the multi-criteria hierarchy;
– Selecting the form in which to express the comparison result and elaborating temporary hierarchies based on each indicator selected; and finally
– Determining the method of aggregation in a single indicator of simple, one-criterion comparisons.

The reference area is compared to the other similar areas in terms of the modal duration of stay, number of tourists in a year, and daily average expenses of the tourist.

A rank is successively assigned to each area according to each indicator covered by the analysis: The area with the maximum qualitative performance receives rank 1, and the following units receive ever higher ranks, until the highest rank is assigned to the area recording the minimum qualitative level for each variable.

An overall score is obtained by summing the ranks corresponding to each area. The area receiving the lowest score is the best performing from all the points of view included in the multi-criteria analysis (Table 13.2).

The method of assigning of ranks has the advantage of being quickly and easily applied, and it generally provides the correct information on the area hierarchy. In addition, the results can be included in the analyses based on the non-parametrical methods of measuring the intensity of the relationship between variables. One deficiency of the method is related to the double leveling of the variable size of the differences between units by replacing them with an arithmetical progression having the ratio 1 unit. The first leveling occurs with the assigning of ranks to each of the characteristics included in the analysis, and the second with replacing the score by the row of final ranks. Thus, a good part of the information quality is lost. A second deficiency is that two or more areas frequently happen to obtain the same score (B and F). They cannot be differentiated unless the analyst intervenes and introduces an additional criterion.

Table 13.3 Gaps between the reference and the most attractive area

Indicator	Area A	Area G	Gap
Modal duration of stay (days)	3	12	9
Number of tourists	1,073	1,732	659
Daily average expenses (lei)	175	210	35

Tourists favor area G the most. To estimate the environmental benefits, a comparison between the reference area (A) and area G is drawn (Table 13.3).

The estimation of the environmental benefit generated by the tip's disappearance and neutralization of its effects, from the perspective of the indicators, aims at the following targets:

– *In area A, the same number of tourists would come and would spend equal daily average amounts, but the majority would rather extend their stay for another 9 days;*
– *In area A, the same number of tourists would come and spend a daily average of 35 lei more, but the majority would rather stay for 3 days;*
– *In area A, the same number of tourists would come and spend a daily average amount of 35 lei more and the majority would rather extend their stay for another 9 days;*
– *In area A, 659 more tourists would come and spend a daily average in equal amounts and the majority would rather stay for 3 days;*
– *In area A, 659 more tourists would come and spend a daily average in equal amounts and the majority would rather extend their stay for another 9 days;*
– *In area A, 659 more tourists would come and spend a daily average amount with 35 lei more and the majority would rather extend their stay for another 9 days.*

13.4 Enviro-statistical Indicators Estimation Trough Technique of Preventive Behavior

Through the preventive behavior technique, values can be obtained from observing how people change their behavior (using air filters, boiling water before drinking it, applying health care treatments) as a response to the modifications in the quality of the environment.

The technique of the preventive behavior presupposes an analysis of the way in which the individuals facing a certain level of environmental risk adopt a preventive behavior to reach an optimum level of health. This technique refers to the fact that individuals will behave preventively as long as the benefit thus obtained exceeds the cost triggered by their action.

Hypothetically, if each preventive action triggers a health risk reduction, the individual will continue to adopt a preventive behavior until its cost equals the AP for the health risk reduction (Shogren and Crocker 1991). Thus, the estimation of the benefits through this technique is performed based on two groups of information:

- Cost triggered by the adoption of the preventive behavior;
- Efficiency of the individual's actions given the way he/she perceives the compensation for quality deterioration in environmental elements.

The individuals for whom the environmental benefits are analyzed fall into two main categories: those who do or do not adopt a preventive behavior as a response to the deterioration in the quality of the environmental elements. There is obviously a third category between these two: those whose behavior is indifferent.

13.4.1 Typical Characteristics of the Individual

There are many variables that can be used to analyze the way people change their behavior, for which reason it is necessary to search for as small a number of explainable variables as possible to express the separation of the individuals into classes best. This is, in fact, the descriptive purpose of the discriminatory analysis. In addition, based on such an analysis, the extent to which any individual, not yet categorized, resembles the individuals in a certain class can be checked, and, if this resemblance does exist, his/her distribution in the respective class can be determined.

A discriminatory analysis highlights the connections existing between the explainable quantitative characteristics and a characteristic to be explained (Bouroche and Saporta 1980). The method allows this to be achieved through visualizing the characteristics on a factorial level. At the same time, it includes the modalities of the explained characteristic, beginning with the values assumed by the explainable characteristics.

Let us consider a group of individuals and monitor a qualitative characteristic having q modalities. Each individual will be identified by a single modality of that characteristic, part of the group of individuals being defined in q disjunctive classes. On this group, the quantitative p characteristics are measured and, whether the q classes differ in the ensemble of quantitative characteristics is studied. Thus, a new characteristic is determined through some linear combinations of the old characteristics.

A discriminatory analysis will lead to a decision rule with the help of which, depending on the values of the explicative variables, the individuals belonging to a certain class will be established; based on these results, forecasts for other individuals belonging to classes will be made.

Reference is made to the objectives of the study *Environmental benefits generated by shutting down the tip and neutralizing its effects: Studying consumption behaviour; degree of perceiving foul smell; and the behavior of the community people as far as self consumption agriculture is concerned*. The focus was on how the fountain water, air, and soil quality deterioration for self-consumption agriculture is perceived

Table 13.4 Assessment of preventive behaviour

Real estate property	Fountain water usage x_1	Air filtering device usage x_2	Self-consumption soil cultivation x_3
Individuals with preventive behavior			
1	7	8	9
2	8	9	10
3	9	10	9
4	7	9	9
5	10	9	9
6	8	7	8
7	9	8	8
8	8	9	7
Average assessment	8.25	8.62	8.62
Individuals without preventive behavior			
9	3	6	7
10	2	6	7
11	6	2	5
12	2	3	2
13	2	5	4
14	2	2	2
Average assessment	2.83	4.00	4.50
Difference between the average assessments	5.42	4.62	4.12

by the individuals living on the 14 real estate properties located at a distance of 1 km from the tip. The following were monitored: Frequency of using the fountain water; use of air conditioning devices to filter the air in the house, and cultivation of the land surface around the house for self-consumption.

It was considered that the members of a family adopted preventive behavior if the frequency of their usage of the fountain water was low (bottled water or water brought from the more distant fountains was used), the frequency of their usage of air-conditioning devices, although not required by the outside air, was high, and the surrounding land surfaces were not fully cultivated (Table 13.4).

Monitoring the stages of the discriminating analysis the thresholds were determined by which individuals can be grouped depending on the importance they give to the deterioration of the environmental elements quality (Fig. 13.1).

13.4.2 *Identifying the Target Group*

Based on the equation of the multiple linear discriminant, which has the form $D = a X_1 + b X_2 + c X_3$, it can be determined whether an individual whose behavior has not

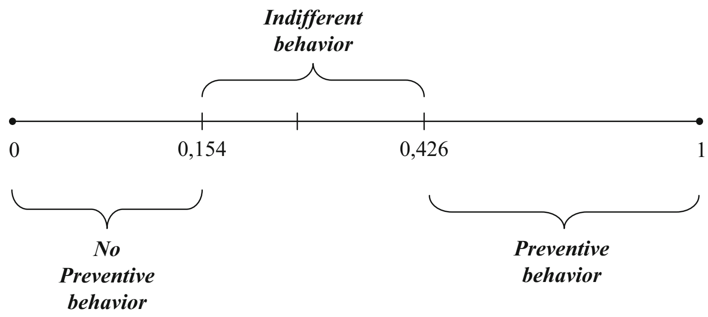

Fig. 13.1 Grouping of individuals by the importance given to the deterioration in the quality of the environmental elements

Table 13.5 Selecting individuals in the target group

Individual	Criterion			Δi	Preventive behavior
	X_1	X_2	X_3		
1	6	6	3	0.333	Indifferent
2	10	8	9	0.461	Yes
3	10	4	2	0.408	Indifferent
4	8	7	6	0.397	Indifferent
5	9	9	9	0.459	Yes
6	7	7	7	0.357	Indifferent
7	7	8	9	0.368	Indifferent
8	8	9	8	0.437	Yes
9	9	9	9	0.459	Yes
10	9	9	9	0.459	Yes
11	2	2	2	0.102	No
12	2	3	3	0.122	No
13	3	3	3	0.153	No
14	10	9	9	0.49	Yes

yet been studied directly attaches any importance to the environmental elements' quality deterioration through his/her adoption of a preventive behavior. The criteria considered are assessed, and then the threshold given by the equation of the multiple linear discriminant is determined $\Delta i = 0.031\ X_1 + 0.029\ X_2 - 0.009\ X_3$.

In this case three situations can be discussed:

– If $\Delta i < 0.154$, the individual does not behave preventively;
– If $\Delta i > 0.426$, the individual does behave preventively;
– If $0.154 < \Delta i < 0.426$, the individual behaves indifferently.

In Table 13.5, the assessments of the above-mentioned criteria made by a representative of each household included in the research are presented. For each, the threshold was determined as given by the equation of the multiple linear discriminant, thus determining the behavior type.

The expenses incurred by all the individuals who adopted a preventive behavior to purchase water from sources other than the contaminated fountains, to use the air-conditioning devices although the outside temperature does not require it, and to procure the food that might have been obtained by cultivating land surface the house surrounding represent a measure of the environmental benefit obtained by shutting down the tip and neutralizing its effects.

13.5 Enviro-statistical Indicators Estimation Trough Technique of Cost of Illness

The technique of the cost of illness is frequently used in statistical research on morbidity. This technique estimates the costs resulting from a modification to the incidence of a certain illness. Two types of costs are measured in an analysis on the cost of illness: direct costs (such as diagnosis, treatment, recovery, rehabilitation) and indirect costs (including the work time spent).

The theoretical basis of the cost of illness technique stands on two major hypotheses:

– Direct costs of morbidity reflect the economic value of goods/ products and services used to treat the illness;
– A person's income reflects the economic value of his/her lost potential achievements because of illness.

13.5.1 Model of Indirect Cost of Illness

Indirect costs are estimated on the basis of time spent for working or household production. These costs are assessed according to the average salary (per hour, day, and month) corresponding to the social and professional category.

In order to analyze the implications of incomplete usage of working time, indicators expressed in absolute and relative measures can be used. These indicators express the time wasted in man-hours (T_h) and man-days (T_z) that trigger salary losses representing the indirect cost of illness. In order to determine the indirect cost of illness, we suggest the following indicators:

– Coefficient of applying the working month normal duration;
– Working time affected by illness;
– Indirect cost of illness.

The coefficient of applying the normal duration of a working month is calculated as $\overline{K}_{dl} = \frac{\overline{d}_l}{\overline{d}_{nl}} \times 100$, where $\overline{d}_l$ represents the average duration of the working month for the employee community being studied, and $\overline{d}_{nl}$ represents the normal duration of the working month, considered to constitute 22 days.

The level of the indicator characterizes the proportion in which the normal duration of the working month was used by an employee, and the difference up to 100 represents in a relative expression the average losses of full working days per each employee of the community.

Working time affected by illness, expressed in man-day $\left(\Delta_{T_z}^{d_l}\right)$ is calculated as $\Delta_{T_z}^{d_l} = \left(\overline{d}_l - \overline{d}_{nl}\right) \times \sum T$, where ΣT is the number of employees in the community.

Working time affected by illness, expressed in man-hours $\left(\Delta_{T_h}^{d_l}\right)$ is calculated as $\Delta_{\sum T_h}^{\overline{d}_l} = \left(\overline{d}_l - \overline{d}_{nl}\right) \times \sum T \times \overline{d}_{nz} = \Delta_{\sum T_z}^{\overline{d}_l} \times \overline{d}_{nz}$, where $\overline{d}_{nz}$ represents the normal duration of the working day, considered to be 8 h.

The indirect cost of illness (ICI) based on incomplete usage of the working month normal duration $\left(CIB^{\overline{d}_l}\right)$ is determined by applying $CIB^{\overline{d}_l} = \left(\overline{d}_l - \overline{d}_{nl}\right) \times \sum T \times \overline{s}_z = \Delta_{\sum T_z}^{\overline{d}_l} \times \overline{s}_z$, where $\overline{s}_z$ is the daily average salary of the community. This is determined on the basis of the daily average salaries corresponding to the business sectors in which the community members are employed.

Referring to the objective *Estimating the disease indirect cost* of the research study *Environmental benefits obtained from shutting down the tip and neutralizing its effects,* data for the number of days effectively worked in the month of September 2012 and for the daily average salary corresponding to each employee who benefited from medical leave as a consequence of some illness caused by the water quality were collected. Through processing the data, one can obtain the values of the indicators of interest (Table 13.6).

At the level of the target group, the working month normal duration was used in a proportion of 58.9 %. Thus, the time not worked due to illnesses was 199 man-days and 1,592 man-hours. The indirect cost of illness estimated on the basis of the daily average salary is 12,036 lei.

If there are any data for the hours in a day not worked by a community employee, due to the discomfort caused by minor illnesses generated by inadequate water quality, then this loss-generating source (incomplete usage of the working day) can

Table 13.6 Statistical indicators for determining the indirect cost of illness

Indicators	Measuring unit	Value
Daily average salary at the level of target group	Lei	60.48
Average duration of the working month	Days	12.95
Coefficient of usage of the working month	%	58.88
Un-worked time	Man-day	199
	Man-hours	1,592
Indirect cost of illness	Lei	12,036

also easily be taken into consideration; hence, overall time loss indicators can be determined and, implicitly, the indirect cost of illness.

Time loss $\left(\Delta_{\sum T_h}^{\overline{d}_z, \overline{d}_l}\right)$ due to incomplete usage of the average normal working day duration and the average normal working month duration is determined as $\Delta_{\sum T_h}^{\overline{d}_z, \overline{d}_l} = \Delta_{\sum T_h}^{\overline{h}} = \left(\overline{h} - \overline{h}_n\right) \times \sum T$ and the indirect cost of illness $\left(CIB^{\overline{d}_z, \overline{d}_l}\right)$ is determined as $CIB^{\overline{d}_z, \overline{d}_l} = CIB^{\overline{h}} = \left(\overline{h} - \overline{h}_n\right) \times \sum T \times \overline{s}_h$.

In the previous relations, $\overline{h}$ represents the working month duration expressed in hours, $\overline{h}_n$ represents the normal duration of the working month expressed in hours, and $\overline{s}_h$ represents the average hourly salary for the community analyzed.

The proposed models do not represent a sufficient measure of AP analysis. When this technique is used, AP is underestimated, because the analysis does not include unused time associated with restlessness, pain, and suffering, or prevention costs.

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Part VI
Intensive Farming

Chapter 14
Environmental Indicators of Dryland

Martin Wiesmeier

Abstract Desertification in arid and semi-arid ecosystems is an unsolved environmental problem affecting 1.5 billion people and 25 % of drylands worldwide. Due to various definitions of desertification there is as yet no agreement on a common assessment of the phenomenon. Several environmental parameters related to vegetation, soil, animals, water, and topography that could serve as indicators for degradation and desertification in drylands were proposed. Among the key indicators, the net primary productivity, presence/absence of indicative plant species, vegetation cover, soil organic matter, and further chemical and physical soil properties were recommended. The most promising and effective way to indicate desertification in its early stages is the determination of vegetation/bare soil patterns by remote sensing. In intact drylands, a heterogeneous pattern of vegetation patches separated by bare soil, which is homogenized in the course of degradation, can often be found. On the other hand, there are homogeneously distributed drylands that become patchy in the early stages of desertification. Thus, a change in the spatial distribution of vegetation and related soil properties constitutes a valuable desertification indicator. However, due to the complexity of the processes summarized under the term desertification, a set of different environmental core indicators should be used that is able to capture all aspects of land degradation in drylands.

Keywords Dryland • Desertification • Arid zone • Vegetation • Remote sensing • Spatial distribution • Land degradation

14.1 Introduction

Desertification, land degradation in arid, semi-arid, and sub-humid regions, is one of the major environmental problems of the world. About 45 % of earth's land surface is covered by drylands and is home to over two billion people. Globally, about 25 % of drylands and 1.5 billion people are affected by severe land

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_14

degradation (Reynolds et al. 2007; UNCCD 2011). Despite the significance of this environmental problem, there is as yet no consensus about the precise extent and assessment of desertification (Veron et al. 2006). This is related to the various definitions of desertification, which were proposed in the last decades (Geist 2005; Reynolds and Stafford Smith 2002). Desertification attracted worldwide attention in the course of the severe drought in the Sahel between 1969 and 1973 (UNCCD 1977). At the beginning, the discussion about desertification was associated with the image of encroaching deserts based on Stebbing's reports about the "encroaching Sahara" in the 1930s (Reynolds and Stafford Smith 2002). In the following decades, numerous definitions for desertification were proposed, which differed in terms of the human and the climatic contribution to the problem. The most accepted definition was proposed by the United Nations Convention to Combat Desertification (UNCCD) in 1977: "Land degradation in arid, semi-arid and dry sub-humid areas resulting from various factors, including climatic variations and human activities." As a result of this wide definition, a huge number of different parameters were suggested, which might be indicative of the various processes associated with the term desertification.

In addition to several promising indicators of the degradation of vegetation and soil in drylands, further indicator parameters were suggested that are related to the climate. However, several authors pointed out that desertification in drylands is mainly caused by human activities, particularly intensive grazing, and climatic variations only aggravate land degradation (Dregne 1983; Hellden 1991; Hiernaux and Turner 2002; Manzano and Navar 2000; Schlesinger et al. 1990). Therefore, climatic parameters cannot be regarded as indicative of desertification (Mabbutt 1986; Reining 1978). Due to the complexity of desertification, many authors recommended that several different indicators be combined to create comprehensive monitoring systems (Kosmas et al. 1999; Reed et al. 2011; Reynolds et al. 2011; Sepehr et al. 2007; Sommer et al. 2011; Winslow et al. 2011). In addition to environmental parameters as key indicators, the importance of socioeconomic variables was emphasized (Leemans and Kleidon 2002; Sommer et al. 2011; Veron et al. 2006). This paper reviews the most important environmental indicators for desertification in terms of vegetation, soil, animals, water, and topography.

14.2 Environmental Indicators for Dryland Degradation and Desertification

14.2.1 Vegetation

Vegetation-related parameters are long-established indicators of the condition of grazing land in arid and semi-arid environments and constitute key indicators for desertification (Mabbutt 1986). These indicators refer to the function, composition,

Fig. 14.1 Overgrazing is the major cause of desertification in drylands (*left*); severe erosion in a desertified semi-arid steppe of Inner Mongolia, Northern China (*right*)

and structure of vegetation. The most established functional vegetation indicator is biomass, measured as above- and/or belowground net primary productivity (NNP). A decrease in NNP was observed in many drylands affected by overgrazing and early stages of desertification (Fig. 14.1) (Guodong et al. 2008; Holzner and Kriechbaum 2000; Ibanez et al. 2007; Prince 2002; Tong et al. 2004; Wiesmeier et al. 2012). However, the suitability of NPP is limited, as it is largely influenced by climatic variations and associated compensatory growth even in intensively grazed drylands (Schönbach et al. 2010; Wiesmeier et al. 2012; Xie and Sha 2012). It was proposed that rain use efficiency (RUE), which is the ratio of NPP and precipitation, as well as the difference between potential and actual NPP (DNPP) and locally scaled NPP (LSNPP), are more suitable indicators, being more independent of short-term fluctuations (Prince 2002; Symeonakis and Drake 2004; Veron et al. 2006). Further important functional vegetation indicators are leaf area index, tiller density, seed germination, growth rate, mortality and disease susceptibility (Mouat et al. 1997; Rubio and Bochet 1998; Wiesmeier et al. 2012).

Several indicators related to the composition of the vegetation were proposed. In many drylands of the world, the distribution and frequency of key species were used as early warning indicators for desertification (An et al. 2007; Bertiller et al. 2002; Keya 1997; Liu et al. 2003; Manzano and Navar 2000; Seghieri et al. 1997; Wang et al. 2002). In particular, an increase in weedy, xerophytic, or unpalatable species was observed in degraded drylands (Holzner and Kriechbaum 2000; Reining 1978). In addition to single species, also a change in the proportion of plant functional types was identified as a useful indicator (Jauffret and Lavorel 2003; Navarro et al. 2006). In this context, the encroachment of woody plants into grasslands, e.g., the invasion of mesquite (*Prosopis glandulosa*) and creosote bush (*Larrea tridentate*) in the Chihuahuan Desert of south-western United States, is often linked to desertification (D'Odorico et al. 2012; Dahlberg 2000; Schlesinger et al. 1990; Van Auken 2000). However, a recent review revealed that the link between shrub encroachment and degradation of drylands is not universal (Eldridge et al. 2011a). As further suitable indicators related to the composition of vegetation, the proportion of C3/C4 plants and simply the species diversity were proposed (Rubio and Bochet 1998; Wang et al. 2002).

Most promising vegetation indicators of desertification are related to the structure of the vegetation. In many drylands of the world, the cover of vegetation (trees, shrubs, grasses, and cryptogamic soil crusts), as well as the percentage of bare soil, was used as an indicator of severe degradation and nascent desertification (Dregne 1983; Eldridge et al. 2011b; Manzano and Navar 2000; Reining 1978; Rubio and Bochet 1998; Yang et al. 2005). The vegetation cover can be derived by remote sensing using several vegetation indexes, such as the normalized difference vegetation index (NDVI), and is thus an effective indicator for detecting desertification also in larger scale and remote areas (Jabbar and Chen 2006; Symeonakis and Drake 2004; Xu et al. 2009). However, vegetation cover is also influenced by natural variations in rainfall.

In addition to the percentage of vegetation cover, the spatial pattern of vegetation and bare soil seems to be a resilient and effective early-warning indicator (Ares et al. 2003; Imeson and Prinsen 2004; Kefi et al. 2007; Ludwig et al. 2000; Ludwig et al. 2004; Maestre and Escudero 2009; Reynolds et al. 2011). In many arid and semi-arid ecosystems, vegetation is arranged in patches separated by bare soil areas (Aguiar and Sala 1999; Augustine 2003; Burke et al. 1998; Maestre and Cortina 2002; Valentin et al. 2001). Vegetation patches change the microenvironment, as they act as surface obstructions that increase water infiltration, reduce radiation and surface temperatures, and accumulate water and windborne sediments, seeds, litter and other organic materials (Bhark and Small 2003; Garner and Steinberger 1989; HillerisLambers et al. 2001; Hook et al. 1991; Ludwig et al. 1999a; Ludwig et al. 2005; Puigdefabregas 2005; Saco et al. 2007). These heterogeneously distributed "islands of fertility" are important for ecosystem stability, as low amounts of precipitation in drylands are redistributed from bare soil areas to vegetation patches where they enable primary production. This is referred to as "functional heterogeneity" (Aguiar and Sala 1999; Ludwig et al. 1999b; Noy-Meir 1973; Tongway and Ludwig 1990, 2001, 2005). In intensively grazed, degraded drylands a change from a heterogeneous to a more homogeneous vegetation pattern was often observed (Adler and Lauenroth 2000; Hiernaux 1998; Ludwig and Tongway 1995; Wiesmeier et al. 2009). On the other hand, in drylands with a naturally homogenous vegetation pattern, degradation was associated with the formation of a heterogeneous vegetation pattern (Asner et al. 2004; Barbier et al. 2006; Schlesinger et al. 1990; Stock et al. 1999). Thus, a change in the vegetation-bare soil pattern, which can easily be monitored by remote sensing, is a promising indicator for beginning desertification. In this regard, several indices for the structure and connectivity of vegetation/bare soil and the landscape in drylands were proposed (Bastin et al. 2002; de Soyza et al. 1998; Kepner et al. 2000; Lin et al. 2010; Ludwig et al. 2002; Sun et al. 2007).

14.2.2 Soil

As soil degradation is one of the main issues of desertification, several soil-related parameters were proposed as sensitive indicators. The amount of soil organic matter

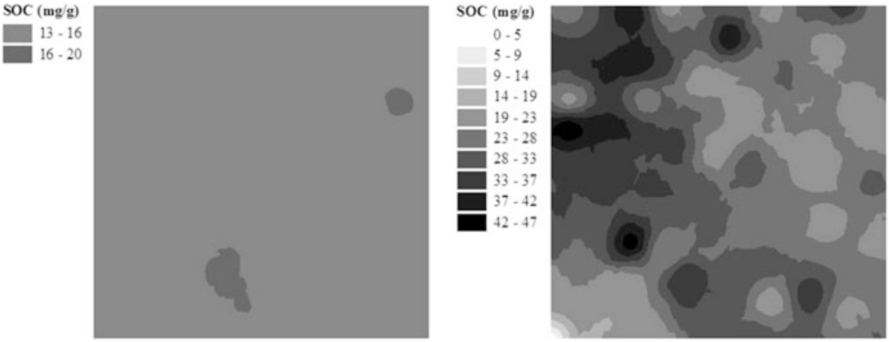

Fig. 14.2 Homogeneous pattern of SOC in degraded semi-arid steppes (*left*) and heterogeneously distributed SOC patches at adjacent intact sites (*right*) (Wiesmeier et al. 2009)

(SOM) is a key indicator, as it is of decisive importance for several key soil functions, e.g., nutrient availability and supply, and soil structural stability and water holding capacity (Reining 1978; Rubio and Bochet 1998). The determination of soil organic carbon (SOC) and/or nitrogen (N) is a well-established, routine method to assess the status of SOM. In several studies, a decrease in SOC and N was detected in degraded drylands, and thus SOC and N concentration were proposed as early-warning indicators for desertification (Fig. 14.2)(Asner et al. 2003; Bell and Raczkowski 2008; Guodong et al. 2008; Wiesmeier et al. 2012; Zhou et al. 2008). Moreover, it was proposed that soil microbial biomass and litter cover might be an earlier and more sensitive indication of degradation in drylands than SOC (Holt 1997; Mouat et al. 1997). As soil degradation in drylands is associated with a deterioration of soil structure, several soil physical properties, such as infiltration, bulk density, aggregate stability, shear strength, porosity, texture and water content, were identified as being sensitive to the early stages of desertification (Bell and Raczkowski 2008; Bergkamp 1995; Manzano and Navar 2000; Rubio and Bochet 1998; Sepehr et al. 2007; Wiesmeier et al. 2012; Yang et al. 2005). Moreover, desertification is often associated with a degradation of chemical soil properties. Soil salinization and alkalinization are indicators of degradation, particularly in irrigated drylands, which can be identified by electrical conductivity, salt crusts, or depth to groundwater or by remote sensing of changes in the albedo (Prince 2002; Reining 1978; Rubio and Bochet 1998). Soil erosion is a further indicator of an advanced state of desertification, which can be directly detected by rill or gully density or indirectly by runoff and soil loss rates, slope length, soil morphology, or sediment transport (Mouat et al. 1997; Prince 2002; Rubio and Bochet 1998; Symeonakis and Drake 2004; Vanmaercke et al. 2011).

However, due to the natural patchiness of many arid and semi-arid ecosystems, degradation phenomena, such as soil erosion or deteriorated chemical and physical soil properties, are also existent in intact drylands.

Heterogeneously distributed vegetation patches are intimately connected to soil patches of favorable structural, biological, and chemical characteristics separated by bare soil areas with deteriorated soil properties (Cross and Schlesinger 1999; Wiesmeier et al. 2009). The destruction of vegetation patches in degraded drylands is associated with homogenization of soil patches (Allsopp 1999; Lechmere-Oertel et al. 2005; Li et al. 2008; Nash et al. 2004; Wiesmeier et al. 2009). Therefore, a change in the spatial distribution of sensitive soil properties such as SOM, is a promising early-warning indicator of desertification (Cross and Schlesinger 1999; Havstad et al. 2000; Imeson and Cammeraat 2000; Schlesinger et al. 1996; Tongway and Hindley 2000). The spatial patterns of soil properties are probably better indicators of desertification in drylands than vegetation parameters, as they are not influenced by short-term climatic variations (Asner et al. 2003; Imeson and Prinsen 2004; Schlesinger et al. 1990; Tongway and Hindley 2000).

14.2.3 Animals

Changes in the distribution of the fauna in arid and semi-arid ecosystems can be indicative of desertification, but the value of animals as indicators is limited due to the competition with other species and their ability to migrate, particularly in the case of larger mammals. Key species which are sensitive to degradation and desertification in drylands include birds, reptiles, and small mammals, particularly rodents (Reining 1978). For example, in the Chihuahuan Desert the banner tailed kangaroo rat (*Dipodomys spectabilis*) and in South Australian shrublands the central netted dragon (*Ctenophorus nuchalis*) are regarded as keystone species (Krogh et al. 2002; Read 2002). Moreover, there are some key invertebrate species, such as tenebrionid beetles and scorpions (Reining 1978). Further, soil organisms, such as nematodes, bacteria and also biological soil crusts, are regarded as promising indicators due to their ubiquity, abundance, trophic specificity, and sedentary nature (Bowker et al. 2008; Klass et al. 2012). Besides key species, the number and distribution of domestic animals, such as cattle, sheep, goats, camels, donkeys, and horses, as well as the herd composition (e.g., the sheep-goat ratio) can be used as indicator parameters (Reining 1978). Finally, it should be mentioned that several animal species and certain patterns of animal behavior, but also different plant species, are used by indigenous people of drylands as grassroots indicators of desertification (Hambly and Angura 1996).

14.2.4 Water and Topography

Water is one of the main limiting factors in drylands and thus a lack or misuse of water is often a fundamental cause of degradation and desertification. Several hydrological indicators were identified that are sensitive to the early stages of desertification. Effective and easily determinable indicators are a reduction in water bodies and changes in the flow of water courses. Further indicative parameters are changes in the depth and quality of groundwater, as well as sequential changes in the groundwater table, increased runoff, decreased infiltration of rainwater, and increased sedimentation (Bergkamp 1995; Dregne 1983; Mabbutt 1986; Qi and Luo 2006; Reining 1978; Sepehr et al. 2007; Sharma 1998). Further, more indirect parameters that might be indicative of desertification are related to the topography and the climate in arid and semi-arid regions. As topography-related parameters, length, shape, aspect and position of slopes, as well as the slope angle, were proposed (Rubio and Bochet 1998).

14.3 Summary

Degradation and desertification in arid and semi-arid regions can be detected by a large number of environmental indicators related to vegetation, soil, animals, water, topography, and climate. Key indictors include various parameters of net primary productivity, indicative plant species, vegetation cover, soil organic matter, and several chemical and physical soil properties. Thereby, a change in the spatial distribution of these vegetation and soil parameters at various scales is the most promising approach for detecting desertification in its early stages. In particular, patterns of vegetation cover and bare soil areas are of great value, as they can be easily determined by remote sensing. Thus, the assessment of vegetation/bare soil patterns is an effective approach for detecting desertification worldwide, even in larger areas and remote regions. However, due to the complexity of desertification and its related processes, key indicators should be connected with further indicative parameters to a set of indicators in order to capture all the environmental changes associated with desertification and minimize the masking effects induced by the naturally high climatic variability in drylands.

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Chapter 15
Pesticide Drift: Seeking Reliable Environmental Indicators of Exposure Assessment

Christos A. Damalas

Abstract Pesticide drift, the physical movement of the pesticide droplets or particles through the air at the time of pesticide application or soon thereafter from the target site to any non-target site, is a constant concern in pesticide use because it inevitably occurs even in the most careful applications, and thus, can increase the possibility of detrimental effects of pesticide use on the environment. Numerous factors can affect the occurrence and the extent of pesticide drift, but the main ones are the application method and the spraying equipment used, the canopy type and height, the weather conditions, the physicochemical properties of the spray liquid, and the decisions made by the applicator. Several pesticide risk indicators have been developed so far to predict the potential environmental impact of agrochemicals (including pesticide drift), many of which have the advantage of requiring a small amount of inputs, being rather fast to calculate and easy to interpret, allowing comparisons both in space and time, and representing an integration of different processes in rather complex systems. However, the information to be included in such indicators varies widely among the different indicators utilized, with the selection process often reflecting to a great extent the specific background of the developers. Thus, different indicators may provide different results, depending on the compartments and effects taken into account, often resulting in difficult judgements about which results are most accurate. Assessing the contribution of each single pesticide to potential environmental problems, in addition to eco-toxicological aspects of the products, requires consideration of the method and the timing of application, without ignoring other aspects of pesticide use. Yet, a major problem in such assessments is the lack of reliable quantitative exposure information, a fact which is also related to the paucity of appropriate pesticide usage data, including the behavioural variable of the pesticide applicator. Nevertheless, it appears that indicators for assessing pesticide impact on the environment will presumably proliferate as long as more complete datasets and indicator prototypes are produced and as long as the pioneering efforts are continuously criticized and improved.

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_15

It should be kept in mind, however, that the potential negative consequences of pesticide use are largely displaced both spatially and temporally, and also that the effects on humans or other organisms may show up far from the site of application or often are not manifested for many years. Taking into account all the above, environmental indicators for the assessment of exposure by pesticide drift, albeit useful instruments for a relative risk rating among pesticides, can be questioned from both a technical and a practical point of view.

Keywords Pesticide • Drift • Spray • Agrochemical • Environment • Weather • Crop

15.1 Introduction

Pesticides are considered a significant component of modern farming, playing a major role in maintaining high agricultural productivity (Cooper and Dobson 2007; Damalas 2009). Pesticides allow the maintenance of current crop yields and thus contribute to economic viability. However, concerns about potential human health and the environmental effects of pesticides have increased over the past several years (Van der Werf 1996; Pimentel 2005; Damalas and Eleftherohorinos 2011). Pesticide residues, the pesticides that may remain on or in food after application to food crops for pest management, are also of great concern for public health (Jackson 2009; Kantiani et al. 2010). With increasing legislation and environmental pressure, it is essential that everything possible is done to ensure that pesticides are used correctly to obtain the maximum benefit with the minimum of risk for the human and the environment. In this context, an increasing number of environmental effects of pesticide applications are taken into account by regulatory bodies, leading to increased restrictions on the use of pesticides or to their banning. The impact of a pesticide on the environment will depend to a large extent on (a) the amount of active ingredient applied and site of application, (b) its level of partitioning to and concentration in the air, soil, surface water, and groundwater compartments, (c) its rate of degradation in each of these compartments, and (d) its toxicity to the species present in these compartments. It is well known that only a small proportion of the pesticides applied to crops actually reach the target (Pimentel 1995). Normally, the rest can enter into the environment gratuitously, contaminating air, water, and soil, where it can be poisonous or otherwise harmful to non-target organisms. Moreover, many pesticides can persist for long periods in an ecosystem (Jablonowski et al. 2012) and can accumulate in the body tissues of living organisms (Wang et al. 2012). Pesticide application refers to the practical way in which pesticides are delivered to their intended biological targets. During the application of pesticides, some losses occur as a result of several mechanisms, such as runoff, leaching, vapour spray drift, and droplet spray drift. The escape of these chemicals during or after the application represents inefficient pest control, economic loss to the pesticide user, and introduction of possible environmental contamination.

Accuracy and timeliness of spraying determine to a great extent the effectiveness of any pesticide application (Matthews 2004). Thus, greater awareness of the details of an application will surely lead to better use of pesticides within integrated farming systems. The objective of this chapter is to summarize basic concepts of pesticide drift and difficulties that arise in the assessment of exposure with appropriate risk indicators, taking into account the special nature of pesticide risk assessment, and to highlight concerns that challenge the development of environmental policy for pesticides.

15.2 A Synopsis of Pesticide Drift, Determinants, and Potential Effects

15.2.1 Definition of Pesticide Drift

Pesticide drift can be generally defined for the purpose of this chapter as: the movement of pesticide residues via air masses during and after application outside the target area where the pesticide was intended to be applied. However, there several other definitions of pesticide drift. Vencill (2002) defines pesticide drift as the downwind movement of the airborne spray droplets beyond the intended area of application originating from aerial or ground-based spraying operations. De Schampheleire et al. (2009) define pesticide drift as the quantity of plant protection product that is deflected out of the treated area by air currents at the moment of pesticide application. Felsot et al. (2011) define pesticide drift as the movement of measurable concentrations of agrochemicals generated during spray application from targeted sites to non-target receptor sites. A more detailed definition is provided by U.S. EPA (1999), which defines pesticide drift as the physical movement of a pesticide through the air at the time of application or soon after application, to any site other than that intended for application (often referred to as off-target). It should be noted, however, that this definition does not include the movement of pesticides to off-target sites caused by other related factors such as erosion, migration, volatility, or contaminated soil particles that are windblown after pesticide application, unless specifically addressed on the label of the pesticide product with respect to requirements for drift control. When the pesticide solution is applied (sprayed) by ground spray equipment or by aircraft, some droplets produced by the nozzles can be so small that they stay suspended in the air and carried by air currents, until they come into contact with a surface or eventually drop to the ground. Pesticide drift can be in the form of liquid droplets, dust particles (if the pesticide was applied as a dust), or vapour. However, pesticide drift is not limited only to the period during or immediately after an application, but can occur hours or even days later. Post-application drift (distinguished as secondary or indirect drift) occurs after an application is completed and may be the result of an illegal application (e.g., an application of a fumigant that does not follow rules) or the result of correct applications, where pesticides evaporate into a gas days or even weeks after application. Post-application drift from legal pesticide applications is difficult to predict, as it depends on factors such as weather conditions even days after the application.

15.2.2 Determinants of Pesticide Drift

Several factors are important in determining how much pesticide spray will eventually drift (Fig. 15.1). These primarily involve the method of application and the droplet size. The latter can be modified by several other factors, such as nozzle types, pesticide formulation, wind direction, wind speed, air stability, air temperature, relative humidity, and height of spray release relative to the crop canopy (Arvidsson et al. 2011; Bretthauer 2011; Felsot et al. 2011; Dorr et al. 2013; Hilz and Vermeer 2013).

As shown in Fig. 15.1, the factors overlap and interact, which practically means that a change in one factor requires reconsidering another. The operator can affect all the factors, illustrating that the skill and attitude of the operator can greatly improve the accuracy of an application. Meteorology plays an important role in determining the movement of spray droplets in the atmosphere as well as where these droplets land. Wind speed and direction are critical meteorological factors that influence spray deposition considerably. With other factors remaining constant, pesticide drift will increase linearly as wind speed increases (Thistle 2004). Relative humidity and high air temperature can reinforce evaporation by decreasing the size of small spray droplets, subsequently decreasing their sedimentation velocity and making them more prone to drift. Drift risk is correlated with the size of the spray droplet, in particular, with the percentage of fine spray droplets. The fate of the spray

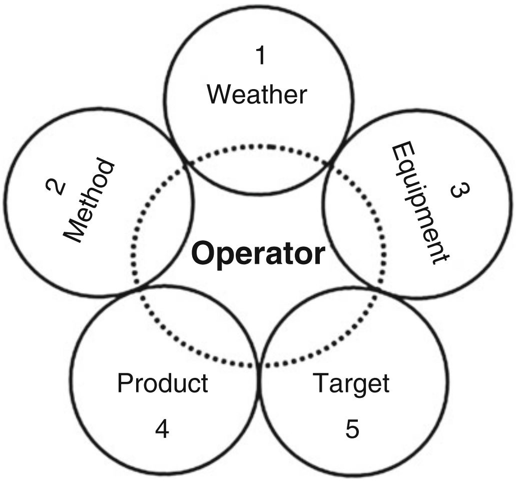

Fig. 15.1 Factors affecting pesticide drift

droplets is influenced by operating conditions such as application height, driving speed of sprayer, and nozzle spacing, as well as other factors. The three primary factors in drift are droplet size, release height, and meteorology (Hewitt et al. 2002). Droplet size is critical because as smaller droplets are considered, the role of gravity is lessened and the role of the ambient wind is increased. As the release height of the spray solution increases, droplets spend longer in the atmosphere and the ambient wind will have a longer time to displace them laterally away from the initial target (Thistle 2004). When dependencies between related variables are considered, meteorology is practically responsible for drift to a great extent. Actually, the role of meteorology in the determination of the position of droplet deposition is generally proportional to the amount of time the droplet remains in the atmosphere. In low boom ground sprayer applications, where the nozzles are pointed downwards, the vast majority of the spray material is not resident in the atmosphere for a long period and thus is not much influenced by meteorology. Even in this scenario, however, there is a small fraction of the total mass of the spray material in very fine drops that does not reach the surface and is available to drift.

15.2.3 Potential Impact of Pesticide Drift

Pesticide drift is a common yet often unseen problem whenever pesticides are applied. In addition, several factors can interact and influence pesticide loss (Gil and Sinfort 2005). Non-target receptors (water, plants and animals, also including humans) may be acutely exposed and therefore face great risk of adverse effects during and immediately after spray application (Felsot et al. 2011). In addition, residues from pesticide drift can become concentrated in inversions or stable air masses and be transported over long distances. Thus, the risk likelihood of an adverse impact will depend on the magnitude of exposure and the toxicity of the chemical to the non-target receptor affected. Over the last decades, concern has focused on contamination of water resources. Direct contamination of water bodies by spray drift has been found to be far less than the contaminant loads by surface runoff (Huber et al. 2000; Dabrowski and Schulz 2003). However, the average amount of pesticides reaching water resources varies largely among regions and highly depends on the characteristics of pesticides, the application doses, and the environmental conditions during application. Exposure via pesticide drift can have a risk impact on local residents, bystanders, livestock, and terrestrial and aquatic ecosystems. There are several potential routes of pesticide exposure for humans associated with spray applications in the field (Butler Ellis et al. 2010). These include direct exposure to spray drift at the time of application, both dermal and inhaled; indirect exposure for a period of time following the application through contact with contaminated surfaces and inhalation of volatilised active ingredient. Farm workers and residents in rural areas were found to have the highest rate of pesticide poisoning from drift exposure (Lee et al. 2011). Additionally, although aerial applications were the most frequent method associated with drift events, soil fumigations also were identified as a major hazard causing large drift incidents.

15.3 Environmental Indicators as Evaluation Tools of Pesticide Impact

Evaluation of the environmental impact of pesticide use and the development of an appropriate policy to reduce the impact remain a constant concern in many countries (Falconer 2002). Methods that allow a relative evaluation of the off-site impact of pesticides can be of great value to many people as an aid in choosing the pesticides and practices with the minimum detrimental effects on the environment (Levitan et al. 1995; Van der Werf 1996). Several approaches have been proposed for carrying out relative assessment of pesticide impact on the environment (Van der Werf 1996; Ramos et al. 2000; Sanchez-Bayo et al. 2002; Reus et al. 2002; Vercruysse and Steurbaut 2002; Brown et al. 2003; Kookana et al. 2005; Alister and Kogan 2006; De Schampheleire et al. 2007; Greitens and Day 2007; Hernández-Hernández et al. 2007; Juraske et al. 2007; Stenrod et al. 2008). The objectives of these approaches are quite variable, including assessments of pesticide toxicity to a particular organism (e.g., honeybees), potential consequences of pesticides on the health of farm workers, the suitability of a pesticide product for an Integrated Pest Management (IPM) system, or the use of the approach as a decision-making tool for choosing a pesticide with minimum potential for environmental contamination. In the last few years, the risk assessment approach has also been frequently used for ranking pesticides in terms of the hazard they pose to the environment according to risk indicators. Pesticide risk indicators are regarded as useful tools in minimising the off-site impact of pesticides and can greatly assist in decision making and policy formulation (Reus et al. 2002; Finizio and Villa 2002; Feola et al. 2011).

In general, the purpose of risk indicators is to simplify a complex system so as to make it easily accessible to the users, in the form of a diagnostic or decision aid tool (Girardin et al. 2008). The basic objective of the various risk indicators for pesticides is to provide an estimate of the environmental performance of the pesticides and an assessment of the risk of pesticide impact on water quality and non-target organisms. Risk indicators for pesticides can also be used to compare farming systems, provide farmers with suggestions to adapt their crop protection practices, and advise policy-makers. A generally acknowledged feature of risk indicators is simplicity. This feature makes them acceptable, easily usable even with a sparse amount of data, quick to calculate, and easy to communicate, although at the expense of a more realistic representation of pesticide impact (Van der Werf 1996; Feola et al. 2011). Risk indicators are developed by giving scores to a set of physical-chemical properties of the substances under consideration, and these scores are combined through an appropriate algorithm to obtain a synthetic number (an index) for comparative purposes. Ideally, an appropriate risk indicator needs to deal not so much with the inherent hazard of a pesticide, but rather with the potential risk it poses. This involves taking into account the rate and the method of application of the pesticide, the environmental and site conditions (Reus et al. 2002), and taking into consideration the specific asset threatened by the use of that pesticide. Pesticide risk indicators are often broad in scope covering, i.e., they may cover impact on aquatic organisms, soil organisms, bees, occupational exposure, and also human health effects.

15.4 Complexity in Evaluation of Pesticide Drift Impact

The likelihood of the risk of an adverse impact will depend directly on the magnitude of exposure and the toxicity of the chemical to the non-target receptor affected. Spray drift can be quantified as a function of surface area deposition relative to downwind distance and the resulting function can be empirically obtained or estimated using deterministic and stochastic models (Felsot et al. 2011). Further, exposure assessment is combined with dose response functions [or singular toxicity benchmarks like No Observable Adverse Effects Levels (NOAELs)] to characterize the risk of toxicity. The use of computer models and mathematical simulations could be an important complement to heavy tests, where many environmental variables and technical conditions are in constant change in time as well as space (Gil and Sinfort 2005). Nevertheless, drift models cannot be considered as a substitute for determination in the field, but rather as a powerful complement that is an aid for understanding the phenomenon and adapting practice implementation to decrease the contamination risks.

As shown in Fig. 15.2, the risk assessment process includes the characterization of the risk based on an evaluation of the evidence to estimate the likelihood and consequences of an adverse event. Particularly for pesticide drift, even if the potential hazard can be identified with sufficient accuracy, the estimation of the likelihood of occurrence and the magnitude of consequences is difficult, in particular, when the behaviour of the applicator, the specific conditions under which a pesticide has been applied, and the environmental conditions after application are unknown.

Harrison (2011) summarizes some technical limitations inherent to risk assessment that may inhibit the ability of risk assessments to estimate adequately the risks that chemicals pose to human health. First, the predictive capacity of risk assessment is fundamentally and inherently constrained by the fact that it is used to study singular chemicals, actually single doses of single pesticides on single individuals of single species (Levitan 2000). Second, risk assessments are widely compromised by data gaps. For example, most risk assessments do not include data on the health effects of chronic exposure to low levels of pesticides, which is the most common way that residents of the rural community usually experience pesticide exposure. Third, risk assessments are limited by standard scientific norms in the sense that when some uncertainty exists in terms of a relationship between two variables, researchers should misjudge on the side of assuming that the relationship does not

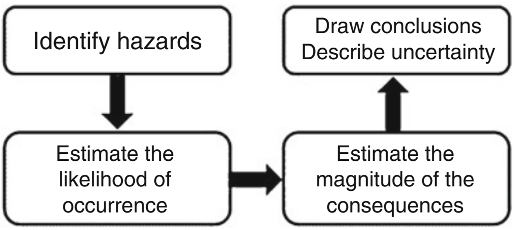

Fig. 15.2 A general overview of pesticide risk assessment process

exist even though in fact it might exist, rather than assuming that the relationship does exist when in fact it may not exist. Additionally, it should be kept in mind that the potential negative consequences of pesticide use are largely displaced both spatially and temporally, and also that the effects on humans or other organisms may show up far from the site of application or often are not manifested for many years (Harrison 2011).

15.5 Limitations to Pesticide Indicator Development

Similar agrochemicals are registered throughout the world, yet quite diverse methods are employed to estimate both the magnitude of spray drift and its potential impact (Felsot et al. 2011). However, each of the methods varies significantly in estimates of spray drift due to many factors, such as environmental conditions, cropping system, equipment used, and the tracer used (Donkersley and Nuyttens 2011). This variation usually leads to divergent perspectives on spray drift hazards. In this context, the information to be included in the indicators varies widely, with the selection process reflecting to a great extent the specific background of the developers. Obviously, each discipline can appreciate the complexities of its own area, but has difficulty realizing that other disciplines also face the same or even higher levels of complexity (Levitan 2000). Thus, various tools of assessment use diverse approaches for incorporating indicators of exposure and often they assign different weights to different aspects of the environment. As a result, the proposed indicators provide different results, depending on the compartments and the effects that are taken into account, often resulting in difficult judgements about which results are most accurate (Levitan 2000; Maud et al. 2001; Reus et al. 2002).

Assessing the contribution of each pesticide to potential environmental problems, in addition to eco-toxicological aspects of the products, requires consideration of the method and the timing of application, without ignoring other aspects of pesticide use. Yet, a major problem in such assessments is the lack of reliable quantitative exposure information, a fact that is also related to the paucity of appropriate pesticide usage data, including the behavioural variable of the pesticide applicator. While some information such as pesticide fate properties may be easy to acquire, others may be difficult to obtain. Even if the data for human and environmental exposure during the use can be considered solid, being based on science, the behavioural variable of the pesticide applicator cannot be taken into account (Calliera et al. 2013). Operational behaviour includes unpredictable changes in operator activities with regard to uncontrollable factors such as wind speed and direction, as well as the characteristics of the adjacent environment, which can all be critical for an accurate risk assessment, especially for pesticide drift. In this context, the reality of the risk management process is very subjective, influenced by human behaviour and human understanding or knowledge of the different aspects of pesticide use. The difficulty in defining appropriate risk indicators is to find the best set of data that can measure as accurately as possible the shift in the random behaviour of pesticide users and the shift in their knowledge and awareness, as well as the efficiency of the various mitigation measures. This practically means that not only environmental, but also potential social and economic consequences and benefits need to be measured and judged to meet the definition of sustainability (Calliera et al. 2013).

Conclusions

Several indicators have been used to assess the potential risk of pesticides to human health and the environment. However, their use revealed uncertainty, underlying the need for the development of alternative indicators that should increase the accuracy and reliability of pesticide risk assessment and thus contribute to a reduction in the possible adverse effects of pesticides on human health and the environment. Due to complexities in the assessment of risk by pesticides, currently, no universally accepted indicators are available to measure potential risks. Knowledge of actual pesticide use will be crucial to calculate risks using appropriate indicators. It should be kept in mind, however, that the potential negative consequences of pesticide use are largely displaced both spatially and temporally, and also that the effects on humans or other organisms may show up far from the site of application or often do not manifest themselves for many years. Taking into account all the above, environmental indicators for exposure assessment by pesticide drift, albeit useful tools for a relative risk rating among pesticides, can be questioned from both a technical and a practical point of view.

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Part VII
Land Degradation

Chapter 16
Environmental Indicators of Land Cover, Land Use, and Landscape Change

Gerald J. Niemi, Lucinda B. Johnson, and Robert W. Howe

Abstract The combination of land cover and land use functions as a pressure indicator resulting from natural and human-induced disturbances or drivers. Land use within patches and landscape change can be represented by primary, secondary, and higher order state indicators in the above and below ground terrestrial, aerial, and aquatic environments. Land cover represents the physical properties of the land surface; land use, in contrast, is the manifestation of human activities. Land cover is primarily detected by remote sensing imagery, while land use by humans modifies natural land cover and requires more detailed information for accurate detection. Changes in habitat status can be measured by a plethora of state environmental indicators that range from effects on the distribution and abundance of individual organisms to shifts in ecological processes, such as nutrient dynamics, hydrological cycles, and predator-prey dynamics. Applications of these pressure and state indicators have greatly improved over the past 30 years with the advancements in computer technology. New development of indicators should examine their merit as compared to that of existing indicators and scrutinize what they are indicating.

Keywords Land cover • Remote sensing • Nutrient dynamics • Hydrological cycle • Predator-prey

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_16

16.1 Introduction

The exponential increase in the world's human population from one billion in 1800 to over seven billion in 2013 (Worldometers 2013) has led to vast changes in land cover and use as well as irreversible change in the juxtaposition of habitat patches across the landscape mosaic. Natural vegetation has largely been converted to metropolitan, urban, residential, industrial, forestry, and agricultural lands, habitats that have never previously existed or have not existed to the extent found today. Landscape changes have led to massive changes in all aspects of air, land, and water as well as the ecological processes and the organisms that inhabit these environs (National Research Council 2000). Unfortunately, we were unable to visualize or quantify these changes until the advent of satellite-based remote sensing technology, geographic information systems (GIS), geo-positioning systems (GPS), and powerful digital imaging tools with the computer age, which began in the late 1960s (Lee et al. 2011).

Our purpose here is to review the types of environmental indicators that have been developed as a consequence of computer-based analysis of land cover, land use, and landscape change. We focus environmental indicators on what is commonly referred to as the DPSIR framework (Drivers-Pressures State-Impact-Responses) (e.g., Smeets and Weterings 1999; US EPA 2013a); however, we limit our consideration of environmental indicators to the DPS portion. It is beyond the scope of this chapter to review the vast array of physical, chemical, biotic, and ecological changes that result from land and landscape change or to provide an extensive, comprehensive review of the literature on this topic. Many publications have summarized the environmental and ecological connections among land cover, land use, and landscape change with respect to aquatic systems (Allan 2004; Niemi and McDonald 2004; Brazner et al. 2007; Burcher et al. 2007; Johnson and Host 2010; Kelly and Yurista 2013; Maloney and Weller 2011), terrestrial systems (Morrison 1986; Gregory et al. 2005), air quality (Brandão et al. 2011; Milne et al. 2013), or ecosystem services (Haines-Young 2000; Syrbe and Walz 2012; Van Oudenhoven et al. 2012).

16.2 History of Land Use and Landscape Indicators

The concepts of mapping the land are as old as human history, but they have evolved dramatically during the past 100 years and especially in the past 30 years (Tomlinson 1984; Foresman 1998; DeMers 2008). Past views of land or the landscape were limited to ground surveys or to aerial photography once airplane flights became common; remote sensing technology has only recently emerged as satellites such as Landsat were launched in the early 1970s (Cohen and Goward 2004). As these technologies continue to improve, our ability to quantify details about land cover, land use, and landscape configurations will concurrently improve.

Nevertheless, technology that exists today enables researchers to link land cover and land use change over time with changes in the biota, ecological processes, and other environmental indicators of interest to society. Among the limitations on mapping land cover/use and landscape change is the lack of appropriate and consistent imagery over time (Dunn et al. 1991). Some of these barriers have recently been overcome by studies such as Wolter et al.'s (2006) analysis of changes in the watershed of the Great Lakes from 1992 to 2001 and Hansen's et al.'s (2013) changes in global forest cover from 2000 to 2012. Two programs, Google Earth (2013) and LANDFIRE (2013), have made available through programs like ArcGIS (ESRI 2011) and FRAGTATS (McGarigal et al. 2012) a host of tools for quantifying land cover and the ability to download data to calculate landscape characteristics. Examples of simple land cover indicators include the proportion of the landscape having natural vegetation (Hasse and Lathrop 2003), total area of core habitat (Forman and Godron 1981), coverage of impervious surfaces (Arnold and Gibbons 1996), and coarse-resolution change vectors (Lambin and Strahler 1994).

16.3 Chain of Indicators

Land cover and land use represent the physical properties of the vegetation and other features of the earth's surface. Land cover is primarily detected by remote sensing imagery, while land use generally requires more detailed information for accurate detection, such as more labor-intensive examination of regional or local data sources (National Research Council 2000). We use land cover/land use (LC/LU) together as the primary pressure indicator that result from natural and human-induced disturbances or drivers. Natural disturbances with major influences on land cover include forest fire, hurricanes, tornadoes, insect damage, flooding, earthquakes, or long-term phenomena such as plate tectonics. Anthropogenic disturbances to land cover include conversion of natural vegetation, such as forests or wetlands, to alternate uses, such as to cropland, residential areas, or industrial development. The influence of these resultant disturbances on LC/LU can have profound effects on the organisms that inhabit these landscapes, as well as the ecological processes that sustain them. The process of change is described in Fig. 16.1.

Many terms have been applied to this progression or chain of events in the published literature (e.g., Smeets and Weterings 1999; Niemi and McDonald 2004; Niemeijer and de Groot 2008). Niemeijer and de Groot (2008) emphasized the network complexity of direct and indirect effects of the DPSIR framework. Here we simply indicate that a variety of disturbances (natural or human-related) result in LC/LU change. As LC/LU changes, habitat within the patch of LC/LU and landscape pattern also change (Turner and Gardner 1991; Turner et al. 2001).

We distinguish LC/LU change that alters the within-patch characteristics versus changes that alter the configuration of the landscape. Any change in a patch, however, also potentially affects other patches at the landscape scale. For instance,

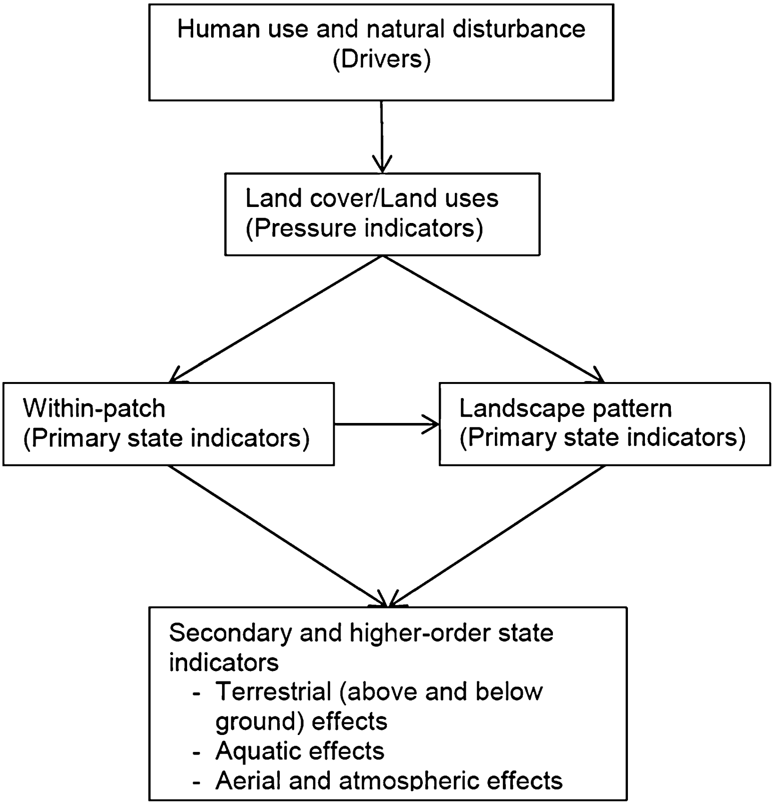

Fig. 16.1 The driver-pressure-state (DPS) framework in land cover, land use, and landscape pattern

local-scale changes may affect the hydrology within a patch, which can affect the flow of water across the landscape (Germer et al. 2010; Burcher et al. 2007). Similarly, extirpation or reduction in density of organisms within a patch will affect the metapopulation dynamics of immigration and emigration among neighboring patches because of the potential inability to disperse across inhospitable habitat (Syrbe and Walz 2012). Studies of source-sink dynamics among populations in the landscape mosaic have become well-developed in the landscape ecology literature, especially as the human footprint on the landscape via the process of fragmentation has intensified (Pulliam 1988; Eriksson 1996; Hanski 1998).

An understanding of the linkages between human and natural disturbances and the ultimate effects on the biotic and abiotic structure and function of ecosystems is critical. A state indicator that is not linked with a pressure indicator or driver is far less useful because management or policy action cannot be implemented to potentially rectify the problem (Niemi and McDonald 2004; Rapport and Hilden 2013). This is crucial because without a potential causal linkage we cannot understand what environmental indicators are indicating.

16.4 Drivers of Environmental Change

The ultimate causes of changes in LC/LU and landscape patterns emanate from various natural and human disturbances; often these changes are part of a recurring disturbance regime (Pickett and White 1985; Forman 1995; Turner et al. 2001) (Table 16.1). A critical area of research is to weigh the impacts of these disturbance patterns, especially comparisons of the variability of responses of environmental indicators to natural versus human-induced disturbances (Hannah et al. 1995). In general, many natural disturbances, such as for hurricanes, tornadoes, or high-intensity forest fires, tend to be intense, but they also tend to be of short duration and

Table 16.1 Summary of duration, frequency, intensity, and recovery time for major natural and human disturbances that change land cover, land use, and landscape patterns

Disturbance: Drivers of land change	Duration	Frequency	Intensity	Recovery time	Comments
Natural					
Forest fire	Short, <1 year	Variable	Variable	Moderate	Frequency and intensity depends on location and climate
Hurricane / Typhoon	Short, <1 week	Low	High	Moderate	–
Tornadoes	Short, <1 day	Low	High	Moderate	–
Drought	Moderate, yrs	Moderate	Variable	Variable	Intensity increases with duration; recovery varies with intensity
Succession	Long, hundreds of yrs	Low	Low	Variable	Rate of succession depends on location
Anthropogenic					
Urban and industrial development	Long, hundreds of yrs	Low	High	Long	Generally permanent change to land use
Agriculture	Long, tens of yrs	Variable	High	Variable	Frequency and recovery depend on location
Forest Harvesting	Short, <1 year	Moderate	Variable	Moderate	Intensity varies with harvest technique & location (e.g., clear-cut vs selective cut)
Climate change – temperature	Long, tens of yrs	Variable	Low	Long	Frequency can be constant or short-term as in the case of drought
Both natural and anthropogenic					
Flooding	Short, <1 year	Variable	Moderate	Moderate	Frequency is variable depending on location and climate

low frequency. In comparison, many anthropogenic disturbances, such as urban development and agriculture, tend be of long duration, and from these the native habitat may never be allowed to recover. For example, the longest recovery times or lack of recovery in a review of aquatic systems that have been altered by a variety of disturbance types were for those in which permanent changes occurred to the habitat, while short recovery times were noted for disturbances such as oil or chemical spills (Niemi et al. 1990). Documenting the legacy effects of land use change on ecosystems is an important area of research (e.g., Foster et al. 2003; Maloney and Weller 2011).

16.5 Environmental or Pressure Indicators of LC/LU

The capacity to quantify LC/LU has greatly improved over the past 100 years. The field has progressed from crude aerial photography to advanced satellite imagery that can sense land cover and other vegetation characteristics at < 1 m using such techniques as Very High Spatial Resolution (VHSR) and LiDAR (Mora et al. 2013). Barrett (2013) and Richards (2013) have recently reviewed the status of this remote sensing technology. Efforts to quantifying land use are subject to many scale-related phenomena, such as the spatial and temporal dimension of interest, resolution of the imagery, and grain size (Turner and Gardner 1991; Gustafson 1998; Turner et al. 2001). For instance, the scale of interest greatly depends on the resolution required for the questions being addressed. The scale of analysis for the global analysis of changes in forest used by Hansen et al. (2013) was much larger than the resolution required for detailed estimates of forest stand height and crown-level metrics used by Mora et al. (2013).

The primary pressure indicators for individual patches of LC/LU include measurements such as cover type (e.g., forest, cropland, pasture, or wetland), patch shape, patch area, and core area of a patch (Table 16.2). These are measurements that characterize the current land use of the patch and are highly dependent on the grain of the methods used. For instance, if the questions of interest require detailed information on cover type in an agricultural setting, then knowing that the cropland is a corn, wheat, or soybean field will require the appropriate level of precision. A significant gap in characterizing land use, and a current area of research, is the development of methods to characterize land use "intensity," particularly for urbanized regions.

16.6 Environmental or Primary State Indicators of LC/LU

Primary state indicators are responses to the pressure indicator changes in LC/LU. They represent the abiotic and biotic characteristics of the patch, such as the abundance, richness, biomass, productivity, or diversity of organisms and ecological processes of the patch (e.g., nutrient cycling or predation rates)

Table 16.2 Examples of primary pressure and primary state indicators in the process from disturbance to land use and landscape changes

Indicator	Type	Environmental indicator	Examples
Pressure: Primary	Land cover/land use (LC/LU)	Cover type of patch	Deciduous forest, cropland, bare ground[a]
–	–	Area of patch	–
–	–	Shape of patch	Edge to perimeter ratio or fractal dimension of patch[a]
State: Primary	Landscape	Patch richness	Number of habitat patches[a]
–	–	Patch diversity	Number of different LU/LC types[a]
–	–	Patch evenness/ homogeneity	Size and type distribution of patches[a]
–	–	Interspersion/ Juxtaposition	IJI[a]
–	–	Connectivity	Gamma index[d], Flow distance[f]
–	–	Texture or graininess	Contagion metric[e]
State: Primary	Within-patch	Species richness	Number of plant species per unit area[a]
–	–	Species diversity	Shannon-Wiener diversity index[a]
–	–	Ecological condition	Indices of biotic integrity or ecological condition[b]
–	–	Population indices	Abundance of species[a]
–	–	Below-ground characteristics	Mycorrhizal biomass[c]

[a]Turner and Gardner (1991), Turner et al. (2003), McGarigal et al. (2012)
[b]Karr (1981), Howe et al. (2007)
[c]Vogt et al. (1993)
[d]Forman and Godron (1981)
[e]Turner et al. (2001)
[f]VanSickle and Johnson (2008)

(Table 16.2). There is a rich history of information on the effects of both human and natural disturbance on organisms and ecological processes (Johnson and Miyanishi 2007; Chapin et al. 2011). The array of potential state indicators at a local patch scale is vast, and indices have often been developed to combine the responses of many organisms (Karr 1981; Howe et al. 2007).

16.7 Environmental or Primary State Indicators of Landscape Pattern

Changes in LC/LU result in changes to primary state indicators of a landscape (Turner 1989). These indicators define the characteristics of the landscape, such as number of patches, cover type richness, cover type evenness, or metrics that represent combinations of these variables, such as connectivity or juxtaposition (Table 16.2). Landscape patterns can be considered on a mean or area-weighted basis depending on whether the analyses are to be interpreted on a patch-centric or landscape-centric basis (Turner et al. 2001). Many of these metrics tend to be highly correlated because they are using the same basic measurements, and hence, individual variables should be selected *a priori* on the basis of focused hypotheses, or, alternatively, multivariate techniques can be used to reduce the dimensionality (Turner et al. 2001).

Changes in the configuration of patches within the landscape can have profound effects on both biotic and abiotic processes within the landscape and adjacent landscapes (Turner and Gardner 1991; Turner et al. 2001; Wiens 2002). Watershed studies that incorporate the spatial position of patches can increase the predictive level of models (King et al. 2005; VanSickle and Johnson 2008). Biodiversity patterns of organisms are affected by disruptions in dispersal among patches within the landscape via the colonization and extinction of local populations (Pulliam 1988; Hanski 1998). Most environmental processes with a landscape component, such as hydrology, succession, foraging, predator–prey interactions, and nutrient dynamics, are altered with changes in the landscape mosaic. The massive worldwide concerns about non-point source pollution impacts on water bodies are primarily a result of excessive soil erosion, contaminated water, and flooding from increased speed of runoff from land conversion at a landscape scale (Young et al. 1989; Wiens 2002). Significant legislative action has been implemented in response to this form of pollution worldwide to protect the quality of aquatic ecosystems from land use and landscape change (e.g., European Commission 2002; Quan 2002; US EPA 2013b). The large scale of these and other landscape-level processes, however, makes effective actions very challenging.

In the United States, FRAGSTATS (McGarigal et al. 2012) is one of the most widely used, publically available programs for the calculation of spatial characteristics of the landscape. FRAGSTATS has the capability to calculate many landscape metrics quantitatively and each can represent an environmental indicator of a landscape. Calculated over time, these metrics measure changes in the landscape configuration that can be related to specific changes in patches of land use and, subsequently, potential changes in higher order state indicators (Fig. 16.1). Gustafson (1998) emphasized that analyses of changes in the landscape pattern were most useful when applied and interpreted in the context of the organism and ecological processes of interest. He also emphasized the need for careful thought on the use of appropriate spatial scales; a critical point echoed by many landscape scientists (O'Neill et al. 1989; Turner and Gardner 1991; Wu and Loucks 1995; Turner et al. 2001).

Conclusions

Applications of LC/LU variables as pressure indicators have greatly improved over the past 30 years with the advancements in computer technology, including data storage, remote sensing imagery, GIS, GPS, and many other developments. Quality analyses still rely on well-defined hypotheses, solid experimental designs, application of appropriate technology, careful scrutiny of data, and the use of the proper models or statistical tests. Environmental state indicators typically range from individual measurements, such as pH or the population status of an endangered species, to more complex measurements that combine data for many species or phenomena into environmental indices. Borja and Dauer (2008) emphasized that informative environmental indicators are not in short supply, and this applies to the plethora of metrics available for land cover, land use, and landscapes. Selection of the appropriate environmental indicators for use such as for effects of land management on ecosystem services is critical (Van Oudenhoven et al. 2012). Moreover, because many of these variables are highly correlated, the latitude for errors in interpreting environmental indicators is often large. Borja and Dauer (2008) suggest any new development of potential environmental indicators should first examine the merit of existing indicators and what improvements are forthcoming with the new indicator. We agree with this suggestion.

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Chapter 17
Desertification and Desertification Indicators Classification (DPSIR)

Robert H. Armon

Abstract Desertification is one of the main driver of global famine and intensive urbanization. Fertile soil that passes the process of desertification cannot be reversed and it is lost for many decades. Basically the process is the degradation of soil. Soil degradation is not necessarily continuous. It may take place over a relatively short period between two states of ecological equilibrium. The processes of soil degradation are mainly water erosion, wind erosion, salinization and/or sodification, chemical degradation, physical degradation, and biological degradation. The concept of DPSIR (driver, state, impact, and response) has been adopted by the European Environment Agency and other organizations for soil strategy. For example, in this model: *state indicators* are soil water availability, land suitability, erosion vulnerability, etc.; *pressure indicators* are human and environmental harmful effects, such as deforestation, ground water overexploitation, forest fire, etc.; *response indicators* are represented by corrective measures, such as sustainable farming, ground water recharge, terracing, storage of runoff water, etc.; *driving forces indicators* represent human activities that impact land degradation, such as intensified agriculture, overgrazing, uncontrolled tourism, and population increase; and finally *impact indicators* of the desertification process, e.g., loss of plant productivity and farm income, flooding of low land, dam sedimentation, etc.

Keywords Desertification • Evapotranspiration • Soil • Crust • Desertification indicators classification (DPSIR) • Deforestation • Urbanization

17.1 Background

There are many definitions of the desertification process; however, the next two seems to best describe the process: *"Desertification is land degradation in arid, semi-arid and dry sub-humid areas resulting from various factors including climatic variations and human activities"*; and *". . .desertification is best reserved for the ultimate step of land degradation, the point when land becomes irreversibly*

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_17

sterile in human terms and with respect to reasonable economic limitations" UNCOD (1978).

In most cases, a typical desert is directly linked to diurnal high and low temperature variations, as well to precipitation deficit, and therefore continental deserts are dry and hot. However, it should be mentioned that the area at the poles and the Himalayas (or other high altitude zones) are also deserts, to be precise, cold deserts, due to their continuous frozen state and the subsequent low water availability. In terms of water budget, defined by the equation $P - PE \pm S$ (where P is precipitation, PE is potential evapotranspiration rate, and S is surface storage capacity of water), deserts receive very low precipitation while evapotranspiration surpasses it by several folds, creating a high water deficit expressed by specific or the lack of vegetation. The water balance and hydrological cycle can also be connected by a similar equation called the water balance equation:

$$\mathbf{R = P - ET - IG - \Delta S}$$

where R = runoff P = precipitation, ET = evapotranspiration, IG = deep/inactive groundwater, and ΔS = the change in water storage in soil and rocks in a certain area and time. The interrelations between these parameters can be used as an indicator of how much water is available (from runoff or groundwater) in the soil.

In general, deserts can be divided into five forms: (1) mountain and basin; (2) plateau landforms called Hamada deserts [mainly barren, hard, rocky plateaus, with very little sand, i.e. *northwest Sahara desert*]; (3) regs [with rock pavement surface covered with closely mesh packed, angular or rounded pebble and cobble size fragments, i.e. *Mojave Desert*]; (4) ergs [called also sand/dune sea or sand sheet if flat, is an extensive, flat desert area covered with wind-swept sand and almost no vegetation, i.e., *Issaouane erg, Algeria*]; and (5) intermontane basins [a semi-arid geologic structural basin filled with sedimentary rocks and an annual precipitation of 15–25 cm, i.e., *Bighorn Basin, Wyoming*]. Most of these forms are a result of æolian deflation caused by wind attributable to lack of vegetation due to low precipitation.

The easiest approach to understanding the actual meaning of the desertification concept is to walk and live in this extreme environment. There are several specific characteristics of "the desert" that fit the accepted definition of these geographical regions: (1) daily high temperature variations (>45 °C/113 °F in summer and <0 °C/32 °F at nighttime in the winter); (2) severe water deficit through evaporation, and lack of water resources (in spite of some flow of groundwater) and rain; (3) lack of ground vegetation due mainly to the first two points; and (4) poor soil quality that does not allow agricultural development (Dregne 1983; UNEP 1994).

17.2 Land Degradation

Land degradation describes how one or more of the land resources, such as soil, water, vegetation, rocks, air, climate and relief, has changed for the worse (Stocking and Murnaghan 2001). The change may prevail only over the short term,

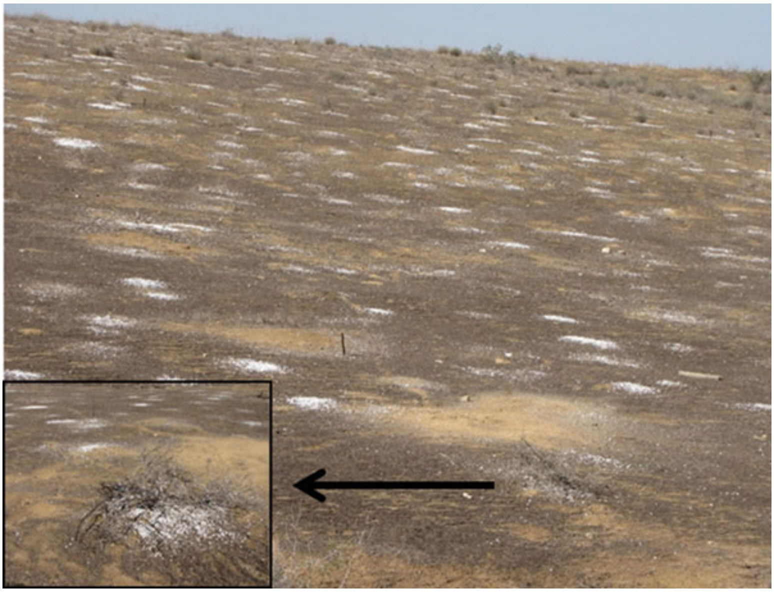

Fig. 17.1 Land degradation in the northern part of the Negev semi-arid zone, as a result of rain shortage, death of certain shrubs and their companion snails (seen as ground white spots) (Courtesy of Dr. E. Zaady, Agriculture Research Organization – Volcani Center, Israel, 2013)

with the degraded resource recovering quickly. Alternatively, it may be the precursor of a strong deterioration process, causing a long-term, permanent change in the status of the resource. It therefore includes changes to soil quality, the reduction in available water, the diminution of vegetation sources and of biological diversity, and the many other changes caused by inappropriate uses that challenge the overall integrity of land. An excellent example of such a condition has been described in the northern part of the Negev (a semi-arid area located in the southern part of Israel) (Zaady et al. 2012; Sher et al. 2012). The annual average precipitation in this area was ~200 mm; however, in the last decade it has dropped to half this amount. As a result, a process of shrub death occurred leaving behind white spots of dead white snails (gastropods reliant on shrubs as a habitat). The disappearance of these shrubs affected many ecological parameters: rain accumulation, soil biocrust changes, nitrogen loss, and the departure of animals associated with the shrubs' existence! (Fig. 17.1).

17.3 Soil Degradation

Soil is defined as a natural, three-dimensional body with definable boundaries that commonly, but not always, consists of horizons made up of mineral and organic materials, contains living matter, and can support vegetation (Soil Survey Staff 1996; Denti 2004).

Soil degradation is defined by FAO/ UNEP/ UNESCO (1979) as "A process which lowers the current and/or the potential capability of soil to produce (quantitatively and/or qualitatively) goods or services. Soil degradation is not necessarily continuous. It may take place over a relatively short period between two states of ecological equilibrium." The processes of soil degradation are mainly water erosion, wind erosion, salinization and/or sodification, chemical degradation, physical degradation, and biological degradation. Soil degradation is considered the most critical component of land degradation and, in the framework of irreversible land degradation, the main factor of desertification (Mainguet 1994).

17.4 Proposed Framework for Desertification Indicators Classification (DPSIR)

A search among the vast mass of publications on desertification indicator systems found the concept of DPSIR (driver, state, impact, and response) has been adopted by the European Environment Agency and other organizations for soil strategy (Rubio 1990). Figure 17.2 schematically presents the main five components (each owning its special indicators) of the DPSIR approach and their interrelations. For example, in this model: *state indicators* are soil water availability, land suitability, erosion vulnerability, etc.; *pressure indicators* are human and environmental harmful effects, such as deforestation, ground water overexploitation, forest fire, etc.; *response indicators* are represented by corrective measures, such as sustainable farming, ground water recharge, terracing, storage of runoff water, etc.; *driving forces indicators* represent human activities that impact land degradation, such as intensified agriculture, overgrazing, uncontrolled tourism, and population increase; and finally *impact indicators* of the desertification process, e.g., loss of plant productivity and farm income, flooding of low land, dam sedimentation, etc.

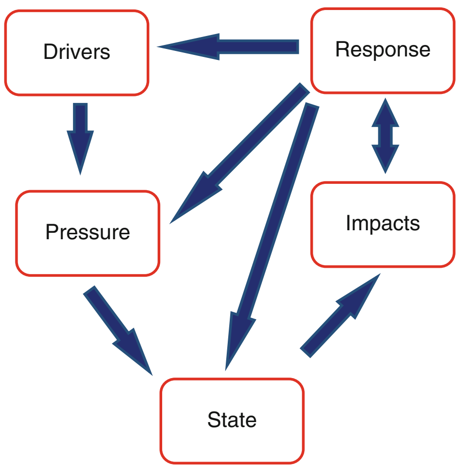

Fig. 17.2 DPSIR framework for system conditions used for classification of indicators (Gentile 1998, 2003)

A detailed description of indicators of desertification is presented in Table 17.1. Among the many suggested, the most valuable indicator of desertification is the lack of water (Imeson 2012; Berry and Ford 1977). Global water scarcity is obvious from the map showing the vast global areas of dry lands (Fig. 17.3). It is interesting to note that many urban systems overlap dry land systems (North America, Middle East, and parts of the Indian peninsula), contributing to an enhanced desertification process. Another important parameter linked to water and desertification is the constant process of deforestation in certain areas of the globe (Fig. 17.4). Continuous loss of forested areas without replacement (absence of reforestation) may cause water and soil loss, global warming, and biodiversity decline.

17.5 Other Indicator Concepts (Imeson 2012)

Beside the DPSIR approach for desertification indicators, some other concepts have been suggested, as follows:

1. *Rangeland Health* – use of physical and biological indicators to assess soil health (state and transition; resilience and functions), soil and site stability, hydrologic function, and/or biotic integrity (Pellant et al. 2005, Herrick et al. 2010) defined as:

   – **Soil and site stability** is the capacity of a site to limit redistribution of loss of soil resources (including nutrients and organic matter) by wind and water.
   – **Hydrologic function** characterizes the capacity of the site to capture, store, and safely release water from rainfall, run-off, and snowmelt (where relevant), to resist a reduction in this capacity, and to recover this capacity following degradation.
   – **Biotic integrity** is defined as the capacity of a site to support characteristic functional and structural communities in the context of normal variability, to resist loss of this function and structure caused by disturbance, and to recover following such a disturbance.

2. *Functions and ecosystem services* (de Groot 1992) – defines ecosystem functions as "*the capacity of natural processes and components to provide goods and services that satisfy human needs, directly or indirectly*." Ecosystem services can be simply defined as a set of ecosystem functions that are useful to humans (Kremen 2005; Herrick et al. 2010).
3. *Soil conservation function* – soil aggregation behavior, infiltration characteristics (clay dispersion as indicator), and soil response to slopes and catchments to extreme rainfall (Hunsaker and Carpenter 1990).
4. *Soil quality* – represented by soil functions and stability (Table 17.2)
5. *Land and soil habitat functions* – explained as the loss of fertile topsoil that produces important crops vital for humans and animals (Huxley 1890).

Table 17.1 List of candidate indicators related to causes or processes of land/soil degradation and desertification (Adapted from Anonymous 2008)

Indicator	Parameters					
Climate	**Air temperature**	**Rainfall**	**Aridity index**	**Potential evapotranspiration [ETo]**	**Rainfall seasonality**	**Rainfall erosivity**
	(° C) nearby hot spot areas	Yearly av. (mm) nearby hot spot areas	Bagnouls-Gaussen Index (BGI)	Penman-Monteith modified method[a]	Walsh and Lawler equation[b]	Fournier index (FI)
			$\mathbf{BGI} = \sum_{\mathbf{i=1}}^{\mathbf{n}} (\mathbf{2ti{-}Pi})\mathbf{k}$		$\boldsymbol{SIi} = \frac{1}{\boldsymbol{Ri}} \sum_{n=1}^{n=12} \boldsymbol{Xin} - \frac{\boldsymbol{Ri}}{12}$	$\mathbf{FI} = \sum_{i=1}^{12} \mathbf{Pi}^2/\mathbf{p}$
					$\boldsymbol{Ri}$ = particular annual precipitation	$\boldsymbol{Pi}$ = total precipitation in month i
			$\boldsymbol{ti}$ = monthly av. temperature (°C); $\boldsymbol{PI}$ = monthly precipitation (mm); $\boldsymbol{k}$ = proportion of month during which 2ti−Pi > 0		$\boldsymbol{Xin}$ = monthly precipitation for month **n**	**p** = mean annual precipitation

Water	**Quality**	**Quantity**	**Ground water exploitation**	**Water consumption/water demands**
	Low salinity (low ratio of Na^+ to Ca^{+2} Mg^{+2}), sodium adsorption ratio (SAR) (mol/L), conductivity (μS)	Surface and groundwater estimates	Measured by: (1) water consumption by sector; (2) rivers, springs, and groundwater flow reduction; (3) appraisal of recharge rate in the hydrological area	Indicator is determined by dividing total consumption (WC) by total demands (WD) in all sectors (WC/WD)
	SAR = $[Na^+]/\{([Ca^{2+}] + [Mg^{2+}])/2\}$** (1/2).			Low-WC/WD <0.5
				Moderate- WC/WD = 0.5–1
				High- WC/WD = 1–2
				Very High- WC/WD >2

Soil	Drainage	Parent material	Rock fragments	Slope aspect	Slope texture	Water storage capacity	Exposure of rock outcrop	Organic matter in surfaces horizon	Degree of soil erosion	Electrical conductivity
	Defined by the depth of hydro-morphic features (Fe, Mn) and groundwater depth	Site geo-logical map	From rock fragments of 2 mm and up in soil surface	Relative to magnetic North; NW, NE, SW, SE and plain	Related to its silt, sand, and clay components	The amount of water stored in soil available for plants growth	Bedrock exposure on soil surface	Percentage of plant material	Different exposure of parental material	Salt content of soil called salinization
Vegetation	**Major land use**	**Vegetation cover type**	**Plant cover**	**Deforested area**						
	Agriculture, pasture, shrub land, forest, min-ing, recreation, urban areas, etc.	Vines, olives, cereals, pine/oak forest, almonds, oranges, vegetables, cotton, bare land, etc.	Percentage of soil covered by green vegetation. Leaf area index (LAI) is also an expression that can be measured.	Annual deforested area as a percentage of the total land surface (mainly according to satellite-based earth observation and field data collection)						
Water runoff	**Drainage density**	**Flooding frequency**	**Impervious surface area**							
	The length of streams in a drainage basin/area of the basin	Yearly probability of damaging flood occurrence	Changes in soil use such as urbanization. Soil sealing by housing, industry, transport, waste disposal, and military that makes soil impervious							
Forest fires	**Fire frequency**	**Fire risk**	**Burned area**							
	Historic fire frequency	Structure and dominant vegetation as related to flammability and combustion capacity and recovery efficiency	Average area burned/decade on a defined territorial surface							
Agricultural	**Farm ownership**	**Farm size**	**Net farm income**	**Parallel employment**						
	The percentage of rented agricultural land (the Σ of arable land, kitchen gar-dens –“horticulture,” permanent pas-tures, meadows, and permanent crop) in the owner-farmed agricultural area	The ratio between the number of farms belonging to size classes of less than 2 ha and the number of farms belonging to size classes of more than 50 ha	Defined as Net Farm Income (NFI) = Total Output (A) − All Inputs(B) + net public receipts (subsidies-farm taxes)	The percentage of off-farm income of the Total Family Income (Farm + Off-Farm incomes)						

(continued)

Table 17.1 (continued)

Cultivation	Tillage operations	Frequency of tillage	Tillage depth	Tillage directions	Mechanization index
	Cultivation practices using the various tillage implements (e.g., mouldboard, chisel, duck foot chisel, harrow, etc.)	Tillage operations number/year by farmer	The depth effected by tillage operations (mouldboard and chisel plough, cultivator, harrow, etc.) that disturb the soil	The soil tillage directions such as: parallel, perpendicular, or in oblique lines, depending on the slope gradient, farm size and shape.	The motor vehicles, machinery, and plant used by the farm expressed as horsepower/hectare of the utilized agricultural area.

Husbandry	Grazing control	Grazing intensity
	Management of an equilibrium between herbivores and the resource base of rangeland to achieve a sustainable production (number of grazers, fencing, no grazing in very wet soils, fire protection of grazing area, etc.)	The pressure imposed on the growing vegetation by grazers. It can be calculated by assessment and comparison of stocking rate (SR) and grazing capacity (GC)
		$\boldsymbol{SE} = \frac{Number\ of\ grazing\ animals\ (SE)}{Area\ grazed\ (ha)}$
		$\boldsymbol{GC} = \frac{Area\ grazed\ (ha)\ \times\ maximum\ forage\ production\ \left(\frac{kg}{ha}\right)}{Monthly\ equivalent\ of\ a\ SE\ (kg) x\ Grazing\ period\ (months)}$
		E.g., High grazing intensity SR > 1.5GC

Land management	Fire protection	Sustainable farming	Reclamation of affected areas	Soil erosion control measures	Soil water conservation measures	Terracing (presence/absence)
	Presence of protective infrastructure against forest fires	Agricultural system favorable to humans and other species	Application of various methods to recover areas affected by acidification, salinization, and heavy metals contamination	Actions to reduce soil erosion: e.g., contour farming, stabilization structures, vegetated waterways, strip cropping, terraces, and small water reservoirs	Techniques such as: mulching, weed control, temporary storage of runoff in small ponds, soil surface management for maximum water vapor adsorption, cultivation, etc.	Terraces presence to reduce water erosion of cultivated erodible soil and also for water conservation

Land use	Land abandonment	Land use intensity	Period of existing land use	Urban area	Rate of change of urban area	Distance from the sea shore
	Decreased land productivity resulting in land use: from agriculture to pasture	The degree of mechanization and application or not of fertilizers and pesticides. Estimation of intensity is:	Related to cumulative long effects on land protection/degradation by present and past land use	Mainly along the cost, urban expansion into semi-natural and agricultural areas	Dispersal of built-up structures within semi-natural/agricultural areas (ha/10 years/10 km^2)	Assessment of water quality effect on soil salinization risk
		$\mathbf{SSR = X \cdot P \cdot F/R}$				
		SSR-sustainable stocking rate				
		R-required annual biomass/animal (sheep, goat)				
		X-fraction of grazed and non-grazed soil				
		P-averaged palatable biomass after dry season				
		F-averaged fraction of soil covered with annual plant species				

Water use	Irrigation percentage of arable land	Runoff water storage	Water consumption per sector	Water scarcity
	The irrigated land area as a percentage of total arable land	Volume of runoff water stored into soil or in small ponds	Annual water consumption for: domestic, industrial, and agricultural uses (m^3/year)	Assessment of the change between water availability per capita and the water consumption per capita in the past 10 years
				WAC-water availability/person
				WCC-water consumption/person
				WHO (World Health Organization) standard to identify risk of water scarcity is 1,000–2,000 m^3; < 1,000 m^3 areas are considered as water scarcity

Tourism	Tourism intensity	Tourism change
	Defined as number of overnight stays by tourists/10 km^2/year at peak season	Assessment of tourism destination changes in the last 10 years in a specific area. Comparison of number of overnight stays in a specific area/year to the average number of tourists overnight stays in the last 10 years

(continued)

Table 17.1 (continued)

Social	Human poverty index	Old age index	Population density	Population growth rate	Population distribution
	UN Development Programme (UNDP) defines human poverty index as follows:	The percentage of population > 65 divided to total population	Indicates the level of human pressure on natural resources	Defines population growth rate that impacts long-term sustainability of natural resources	Defines population distribution related to land management, e.g., Urban vs. Rural, Mountainous vs. Lowland, Coastal vs. Inland populations
	$HPI-2=[0.25\,(P2^3+P4^3+P5^3+P6^3)]^{0.33}$	$R=\frac{Population\ 65\ years\ old\ and\ older}{Total\ population}\cdot 100$	$\text{Population Density}=\frac{No.\ of\ individuals}{Area\ of\ the\ region\ in\ which\ they\ live}$	$PGR=\frac{(Birthrate+Immigration)-(Mortality\ Rate-Emigration)}{Population\ Size}$	
	P2-illiteracy rate P4- % of people not expected to survive over 60 years	R -old age index	$=\frac{People}{km^2}$	PGR-Population growth rate	
	P5-% of people with disposable income < 50 % of the median				
	P6-% of people in long term unemployment				

Institutional	Subsidies	Protected area	Policy enforcement
	Assessment of CAP (Common Agricultural Policy) structure impacts farmers' choice of agricultural use and management practices	Area of protected land expressed as a percentage of the total land. Protected areas commonly include: biodiversity conservation, cultural heritage, scientific research, recreation, natural resources maintenance, etc.	The effectiveness of implementation/enforcement of regulations/actions by environmental protection bodies

[a]Allen and Pruitt (1986)
[b]Walsh and Lawler (1981)

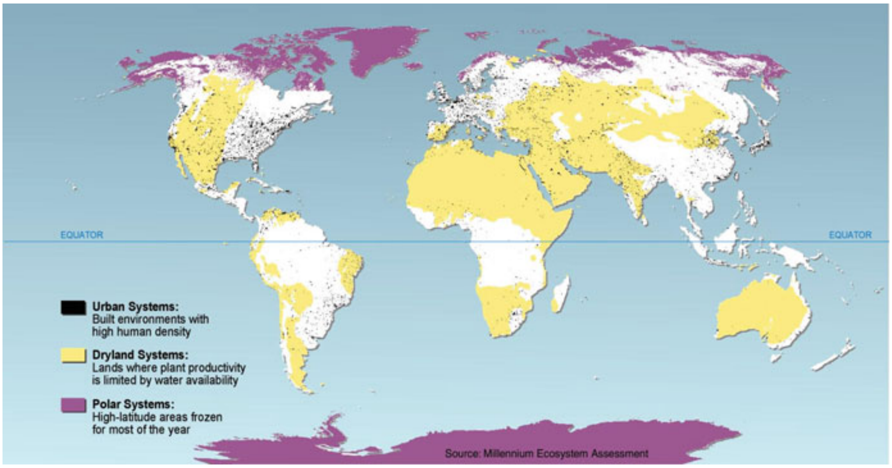

Fig. 17.3 The association between global dry lands and high density urbanization (with permission of: Millennium Ecosystem Assessment)

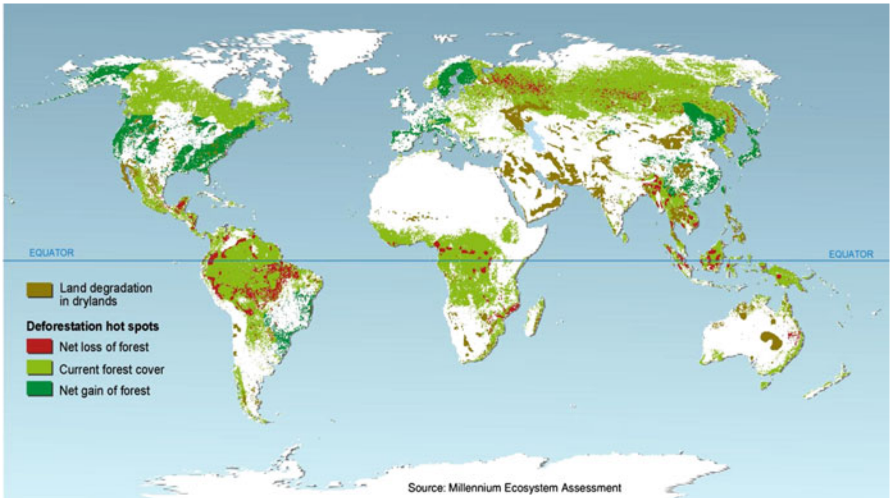

Fig. 17.4 Deforestation as one of the main causes of land degradation (with permission of: Millennium Ecosystem Assessment)

6. *Hydrology and water balance* – based on indicators such as soil moisture, infiltration, erosion, and sediment load.
7. *Dynamic and complex systems (Desertification Response Units – DRU)* – based on hierarchy theory applied in semi-arid regions for interlinked structures from microscopic soil level to general landscape level (Imeson et al. 1996).
8. *Adaptive management and panarchy* – based on hierarchy theory and resilience, it integrates policy, processes in interacting human terms, and physical

Table 17.2 Soil quality indicators: measures of soil functional state (After Doran and Parkin 1996)

Indicator category	Related soil function	Measurement methods
Chemical	Nutrient cycling, water relations, buffering	Electrical conductivity, soil nitrate phosphate and potassium, soil reaction (pH)
Physical	Physical stability and support, water relations, habitat,	Aggregate stability
		Available water capacity
		Bulk density
		Infiltration
		Slaking
		Soil crusts
		Soil structure and macropores
		Soil texture and stone content
Biological	Biodiversity, nutrient cycling, filtering	Earthworms
		Particulate organic matter
		Potentially mineralizable nitrogen
		Respiration
		Soil enzymes
		Total organic carbon
		Root Health Rating

systems (Imeson 2012). In France, for example sediment flows are managed by taking into consideration the interaction between hill slope and river channel dynamics to conserve soil. Another form of management includes watersheds treatment as a whole system with feedbacks from land use, hydrology, and sediment transport.

9. *Human use and appropriation of environment, land, and water* – as humans use most land and water sources, thus contaminating them, the key indicators are the disappearance of rivers and spread of desertification.
10. *Sustainable land use and traditional knowledge* – based on many indicators directly related to field assessment and vectorial change.
11. *Key indicators* – such as soil stability, runoff, water balance, sediment yield, subsidies, and ignorance that represent single complex system behavior with feedback to anthropogenic actions (see Table 17.1).

17.6 Summary

Desertification is a natural continuous process intensified by human activity (FAO/UNESCO/WMO 1977). Indeed, humans are to some extent able to combat this natural process with some success (see Israel experience, Boeken 2008; Carmi and Berliner 2009; Rewald et al. 2011). In order to detect desertification processes there is an obvious prerequisite for well-established indicators (Imeson et al. 1996). As previously shown in this chapter, the desertification process is a highly complex system that needs a comprehensive indicators concept (Table 17.1). Among these indicators, the DPSIR approach seems to be the most accurate and has been embraced globally. However, while organizing the present chapter on desertification indicators, it became very clear that water is a key indicator of the process, interrelated with soil and human agricultural activity. In the context of "you cannot milk the cow and not feed her," any agricultural activity has to take into account that nowadays "sustainability" is the name of the game in modern agriculture in order to prevent soil and land degradation. Furthermore, consistent with certain well-selected indicators, even non-agricultural desertification-related processes can be prevented.

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Part VIII
Soil

Chapter 18
Soil Conservation

Paolo Giandon

Abstract Soil fertility relies primarily on the presence of organic matter in soil, as it is the substrate for the vital processes needed for plant growth. Organic matter is the most important component of soils because of its influence on soil structure and stability and it plays the principal role in maintaining soil functions. For many relevant problems, such as physical soil degradation, soil carbon (C) concentrations in the topsoil are more meaningful than total carbon content. From the C storage point of view (C sequestration), ideally, changes in the SOM should refer to equivalent soil masses (C stocks).

Keywords Topsoil • Conservation • Soil organic matter (SOM)

18.1 Definition

Soil is the result of a combination of weathered parent material, climate influence on physical site factors, and vegetation, which affect soil properties by adding organic matter to the soil. Soil development depends on various processes, the key ones of which are the decomposition and accumulation of organic matter.

The physical and chemical characteristics of soil are strictly related to the quality and quantity of organic materials and the way they are linked to and aggregated with mineral soil to build up the so-called organo-mineral complexes, which constitute the main active surfaces with respect to interaction with solutes of soil water and with living organisms.

Soil fertility relies primarily on the presence of organic matter in soil, as it is the substrate for the vital processes needed for plant growth. For this reason, we can assume that soil conservation is attainable only through preventing the depletion of the soil's organic matter and maintaining its concentration at a level higher than the minimum that is required for soil conditions to be adequate for plant growth.

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_18

Therefore, the practices that comply with the aim of soil conservation are those that permit an adequate level of organic matter concentration to be maintained, that is, the concentration needed for adequate support to plant life and growth.

Organic matter is the most important component of soils because of its influence on soil structure and stability, water retention, cation exchange capacity, ecology, and biodiversity, and as a source of plant nutrients. Soil organic matter (SOM) plays the principal role in maintaining soil functions. It has the particular function to provide the physical environment that allows roots to penetrate the soil, excess water to drain through the soil profile but sufficient water to be retained to meet the physiological demands of the plants, and the flux of gases through the soil to maintain a well aerated environment. The soil organic fraction also provides a great variety of habitats and a food source for the living organisms within the soil. These organisms are very important for the breakdown of the organic materials and the release of plant nutrients, give significant support for maintaining the physical conditions of the soil, and facilitate the plants to access nutrients from otherwise unavailable sources.

Although the quantitative evidence for critical thresholds of organic matter content is slight (Körschens et al. 1998; Loveland and Webb 2003), it is widely believed that soil cannot function optimally without adequate levels of SOM (Van-Camp et al. 2004). SOM quality is related to the nature and properties and relative proportions of different organic compounds that are part of it and their combined influence on soil functions.

From the quality point of view, attention is mainly focused on a set of attributes linked to soil functions rather than the chemical characteristics of single organic constituents. For instance, changes in SOM quality may impact soil biodiversity, transport of substances within and through the soil, water availability, microbial activity, etc. (Van-Camp et al. 2004).

Soil formation and organic matter evolution are driven by living organisms, and therefore the interaction between SOM and biodiversity is strong.

The decline in SOM is of particular concern in tropical areas. The problem is not, however, limited to these areas because the loss of SOM can be relatively high even in temperate climates (Bellamy et al. 2005).

Several of the factors responsible for a decline in SOM are related to human activity: conversion of grassland, forests and natural vegetation to arable land, deep ploughing and other intensive tillage operations of arable soils, high application rates of nitrogen fertilizers that increase mineralization of organic matter, cultivation of peat soils, crop rotations with reduced proportion of grasses, soil erosion, and wild fires (Kibblewhite et al. 2005). Declining organic matter content in soil is also strongly associated with ongoing desertification.

18.2 Soil Conservation Description and Monitoring

The factors that control the dynamics of organic matter in the soil determine the changes in the SOM content. Some of these factors are inherent soil properties, such as the clay content, which protects organic matter against mineralization and therefore influences the rates of change in organic matter content; others are external, such as climate, or human-induced factors, for example, land cover, land use, agricultural practices, etc.

SOM levels and its nature and quality determine different soil functions. There are still gaps in our detailed knowledge and understanding of the nature, properties, and ecological significance of the overall SOM levels and its different pools, despite the fact that this topic area has been the subject of considerable research over many decades.

There are also still many gaps in our knowledge with respect to the relationships between SOM levels and quality and soil biodiversity nature and function. While the maintenance and improvement of biodiversity are recognized to be an important target of current policies and conventions, it is important to establish the roles of a diverse community of organisms within the soil.

There is a need to establish the nature of the relationships present under a range of conditions, how these relationships vary across them, what the natural variations in these relationships are, and how stable the relationships are under climate and environment changing scenarios (Smith 2004).

To assess the change in total SOM in agricultural land, changes not only in its concentration but also in bulk density and ploughing depth have to be taken into account. However, for many relevant problems, such as physical soil degradation, soil carbon (C) concentrations in the topsoil are more meaningful than total carbon content. From the C storage point of view (C sequestration), ideally, changes in the SOM should refer to equivalent soil masses (C stocks). In that case, reliable information on the bulk density and stone content of soils is required.

Although significant time scale changes of SOM were observed only in the topsoil of arable land, deeper soil layers should be investigated as well.

Since the topsoil is the most important part for crop and forest production, and it shows a high spatial and temporal variability (Jones et al. 2004), a careful and accurate description of the morphological topsoil properties offers important initial information for assessing the SOM status and quality, and thus for observing the effects of soil management.

Since most existing classifications focus mainly on stable subsoil properties, a new and comprehensive rationale for classifying topsoil properties was developed (FAO 1998). Exemplary parameters are soil color, distribution of coarse roots, ectohumus horizons, stone content, thickness of humus horizons, etc.

In particular in forests, but also in grassland and cropland topsoils, humus forms/humus types characterize the topsoil morphology on the basis of genetic and/or functional properties in a holistic manner. The well established national systems (Baritz 2003; Katzensteiner et al. 1999) of humus forms should be included in any monitoring system that focuses on SOM, especially in extensively managed ecosystems such as pastures and, in particular, forests.

18.3 Indicators

18.3.1 Organic Matter Status Indicators

There is wide concern in the world about the possibility that the decline in organic matter in the soils in intensively cultivated areas could lead to an irreversible decline in soil fertility, structural stability, and biodiversity. Total soil organic carbon is an overall measure of the state of the soil, and responds relatively rapidly (<10 years) to changes in pressures, and thus, it could be considered as a response variable. Organic carbon and nitrogen are widely measured as standard properties in most soil laboratories. They give a broad indication of the soil capacity to host biodiversity. Considering bulk density allows adequate comparisons of data between different soils.

For general purpose monitoring of SOM decline, it is recommended that the following parameters are measured:

– Total organic carbon,
– Total (organic) nitrogen,
– C:N ratio (derived from the previous two),
– Bulk density.

Successive evaluations lead to only organic carbon being considered, as nitrogen content is not a parameter that can give information about SOM status.

Therefore the following two main indicators can be proposed:

– Topsoil organic carbon content,
– Soil organic carbon stocks.

The topsoil organic carbon content indicator has some advantages:

– It can be measured directly,
– It is an indicator that is relevant to the potential risk of soil erosion and soil biodiversity decline, as well as to desertification,
– Data on the organic carbon content in topsoils are available in most countries.

At the same time some disadvantages can be underlined:

– Data are dispersed, not always easily accessible, and not harmonized;
– Discrepancies between data from different regions or countries can arise from differences in analytical methods and/or in sampling depth;
– As changes in soil organic carbon content are rather slow, the minimum time interval over which changes can be observed (and therefore measurements are justified) is typically > 5 years;
– As topsoil organic carbon content is highly variable in space, small changes (<5 %) at a given site cannot be detected without using a large (more than 100) number of replications (Conen et al. 2004; Smith 2004).

Soil organic carbon content is measured routinely in surface horizons during soil surveys and on experimental sites, and hence, there are sufficient data to apply this indicator at the national scale.

The soil organic carbon stocks indicator has some advantages:

– It is more relevant than organic carbon content for assessing the role of soils in the global C cycle and monitoring overall changes in SOM,
– It can be calculated from two direct measurements,
– Measurement of density is also relevant to the risk of soil compaction, soil biodiversity decline, and desertification.

On the other hand, soil organic carbon stocks require a greater sampling effort because of the need to determine bulk density, which is even more spatially and temporally variable than organic carbon content, particularly in soils under arable crop use. It is an important indicator of soil condition, especially under the influence of climate change.

18.3.2 Organic Matter Dynamic Indicators

The European Commission (Joint Research Centre) developed a set of Soil Organic Carbon Status Indicators (SOCSI) to support the EU policies related to SOC (Stolbovoy 2008). It was set up in order to investigate OC trends in different soil types and land uses. The SOCSI are knowledge-based and can be derived from available soil data at a regional scale. SOC content results from the combination of the Soil Typological Unit (STU) and land use/management. Each combination has specific SOC margins and therefore the SOC content change is limited. Moreover, the potential for the change depends on the actual OC content.

When a data set for each STU is too small to allow statistical analysis, the application of SOCSI can be determined for functional soil groups obtained by grouping STUs on the basis of texture, coarse fragment content, drainage, and physiography.

The set includes:

– Data-derived parameters (mean, minimum, and maximum values),
– Knowledge-derived parameters (CSP-Carbon Sequestration Potential, PCL-Potential Carbon Loss, CSR-Carbon Sequestration Rate, CLR-Carbon Loss Rate and capability classes for OC change).

The minimum and maximum values represent the margins of the OC range of change. The potential for the change depends on the actual OC content.

According to the Joint Research Centre's procedure, the low/medium/high capability classes of CSP and PCL are defined for each functional group:

- Low (L): < [Min + (Max – Min)/3]
- Medium (M): between [Min + (Max – Min)/3] and [Min + 2(Max – Min)/3]
- High (H): > [Min + 2(Max – Min)/3]

These SOCSI can be drawn on maps (one for CSP and one for PCL) to show the areas in the low, medium, or high PCL/CSP classes.

18.4 Baseline and Thresholds Values

Quantitative relationships exist between SOM and many soil properties and functions, but these relationships are complex in nature and rarely linear in their relationships (Loveland and Webb 2003). There may be threshold values for soil organic matter content above which the function may operate optimally (for example 1.5–2 % C for aggregate stability or desertification), but the task is to establish the nature of these thresholds and the extent to which they vary with the nature of the soil mineral fractions and environmental context. These threshold values should be defined in the context of a given soil property or function, within a climatic zone, and for a given soil type (texture).

As the different SOM fractions do not have the same roles in influencing soil properties, a fractionation of organic matter may be a way to establish the nature of the relationships with soil properties, and such an approach should be adopted as part of the soil monitoring process.

It is also of critical importance to consider SOM management, because SOM turnover and decomposition play significant roles in determining many soil properties (e.g., aggregation). It is important to recognize that stabilized composts or manures do not necessarily have the same effect on these properties as fresh plant residues, which are often left at the soil surface by the new practices in agriculture; such practices may have a role in influencing soil physical properties and contributing to soil protection.

18.5 Primary Indicator: Estimation of Soil Organic Carbon Stock. A Study Case

In order to manage soil information correctly, a new approach that exploits soil data and expertise available at the local level is required, and this is the basis for the development of the Multi-Scale European Soil Information System (MEUSIS).

SIAS (that stands for Development of Soil Environmental Indicators) is a pilot project developed in Italy, which is promoted by the National Environmental Protection Agency (APAT, now ISPRA) and involves Regional Soil Survey Services and the European Soil Data Center (ESDAC, at the EC DG JRC). All Italian regions were required to assess soil organic carbon stock data in order to build up the indicator for organic matter decline. The most accurate and up-to-date soil data were used and analyzed directly by institutions and experts involved in soil surveys at the local level to build a coherent picture, which is useful also at the national level, since it is harmonized according to a common infrastructure for data sharing.

18.5.1 Reference Grid

To overcome harmonization problems across borders, it was decided to assess and present output data on a reference grid, with a common coordinate reference system, setting up a common infrastructure for data sharing. The reference grid was built following the recommendations of the Eurogrid/INSPIRE Directive. For the SIAS project, the chosen grid is 1 km $\times$ 1 km in size, which seemed to offer the best compromise between the information quality, operability, and goals of the project.

18.5.2 Exchange Format

To collect pixel data and meta-information, an exchange format was set up jointly by the working group. The format was then developed as a database with an explanatory guide in which harmonized codes, suggested methodologies, and examples are collected.

Information about soil organic carbon stock and pixel coverage is stored in the so-called pixel-table. Some data quality indicators were also defined and shared by the working group, both as quantitative indexes of data availability in the pixel (number of available observations, number of analyzed observations, scale of available soil maps, etc.) and as specific confidence levels for each indicator in each pixel.

The special emphasis of the project lies in the exploitation of local expert judgment (“bottom-up” approach), so that local experts can follow the most adequate assessment procedures according to their judgment (to cope, for instance, with different levels of data availability and/or reliability) as long as all the procedural paths are recorded into three metadata tables. These tables constitute the project value-added information, and any kind of input data or assessment procedure is recorded in them, both through codified items and free descriptions.

18.5.3 Methodology

Organic carbon stock (t/ha) was calculated for three different layers, 0–30 cm, 0–100 cm and for hologanic layers (i.e., formed mainly by organic material consisting of undecomposed or partially decomposed litter, that has accumulated on the surface, not saturated with water for prolonged periods), through the following formula, applied for each profile or Soil Typological Unit (STU):

$$O.C. = \sum_{1}^{n} o.c.* b.d. * depth * \frac{(100 - sk)}{100}$$

where:

O.C. = profile/STU organic carbon content (t/ha);
o.c. = horizon organic carbon content (%);
b.d. = fine earth bulk density of the horizon (g/cm3);
depth = horizon depth (cm) within the given section;
sk = horizon rock fragment content (%);
n = number of horizons within the given section.

In order to allow a comparable assessment, organic carbon data obtained by means of local analytical methods were converted into ISO method results, according to specific regression functions. Concerning bulk density, some regions (5 out of 12) used both measured data and the pedotransfer function (PTF); among these, 4 regions used the original PTF calibrated on their own measured dataset (Ungaro et al. 2005); the others used the PTF found in the literature.

To assess organic carbon content within the pixel, different pathways were followed, as every Regional Soil Service could choose the most suitable one for its specific situation:

– by means of a soil map, calculating the weighted average of STUs in the SMU (soil mapping unit), or the average of single profiles in the SMU;
– using geostatistical analysis, usually by means of kriging with varying local means calibrated on SMUs (Ungaro et al. 2005; Ungaro et al. 2010). As the final step, the organic carbon stock within the pixel was intersected with a land-cover map, Corine Land Cover, or a more detailed regional map, to obtain the final value of t/ha, subtracting no-soil surfaces.

All information on methods and data (analytical-measurement methods, PTFs and regressions used, data time span, spatialization and up-scaling methods, land-cover scale and year) was recorded in the metadata section of the exchange format.

18.5.4 Results

The organic carbon stock for the two layers, 0–30 cm and 0–100 cm, for 11 regions out of 20 are shown in Figs. 18.1 and 18.2. The approaches used for organic carbon stock evaluation were different in different regions, and sometimes even in different areas of the same region, depending on data availability and observation density. In the areas where a soil map at a scale of at least 1:250.000 was available, carbon stock could be calculated by means of the weighted average of STUs in the SMU (i.e., Veneto region mountain area) or as the average value of observations within

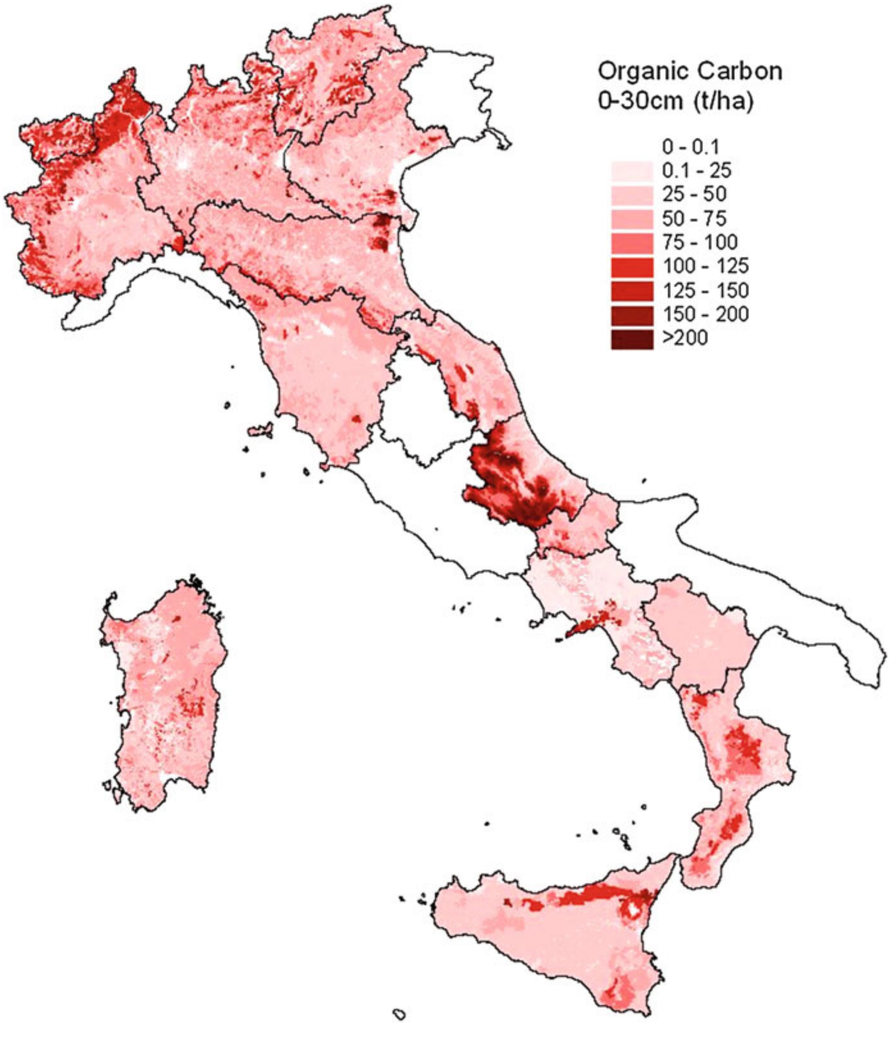

Fig. 18.1 Organic carbon stock 0–30 cm (t ha^{-1})

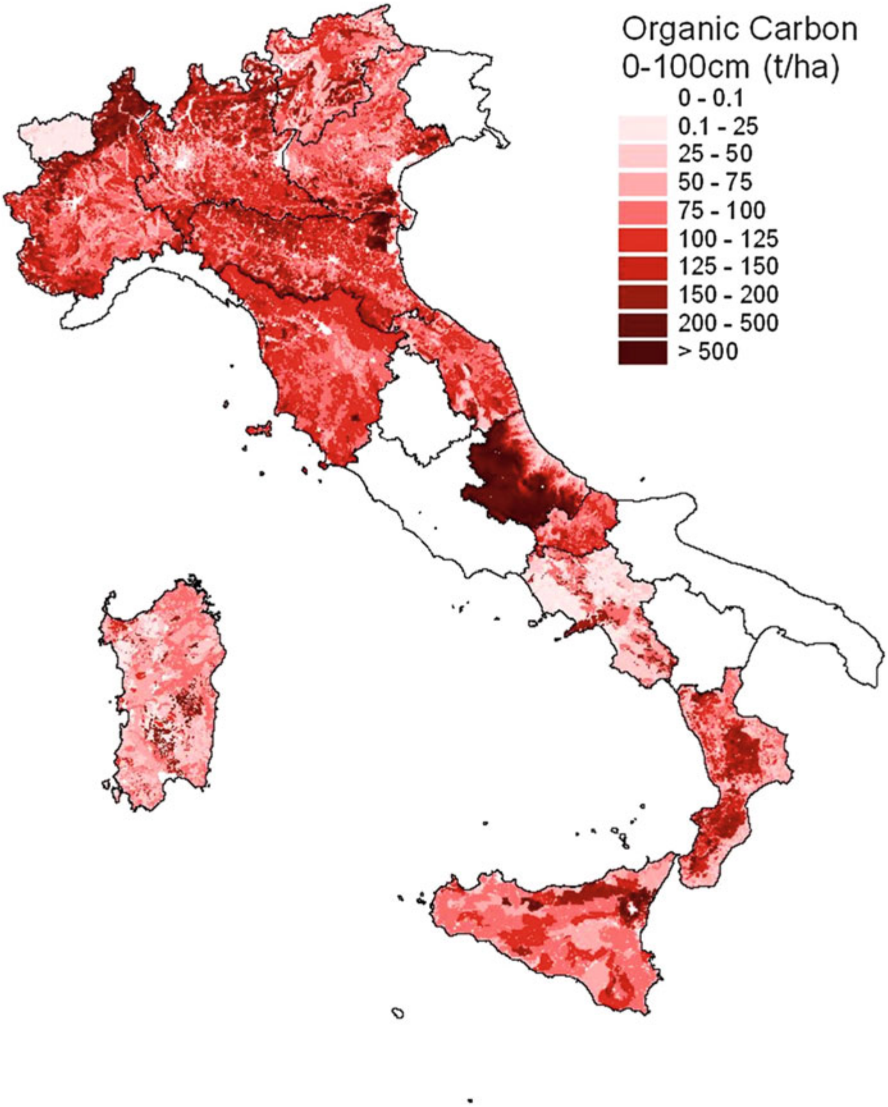

Fig. 18.2 Organic carbon stock 0–100 cm (t ha^{-1})

the SMU (i.e., Tuscany and Piemonte region). The procedure was worked out by overlaying three different layers, such as the European Reference Grid, the soil map (with attached OC data calculated for SMU), and a land cover map (simplified into a few classes, as soil, no-soil, extra-region, extra-country, and sea). All the operations were usually conducted by the regions in their own projection system, with some regions using raster layers, while others using vectors.

Where more detailed maps were available and the observation density was higher (Veneto and Emilia Romagna alluvial plain), geostatistical analysis could be applied for data spatialization (kriging with varying local means calibrated on functional groups of STUs), requiring data such as single observation organic carbon percentages, measured bulk density (where available), or estimated bulk density calculated by means of pedotransfer-functions. STUs and their observations were grouped into so-called "organic carbon functional groups," according to some characteristics that influence organic carbon dynamics in soils (i.e., rock fragment content, surface texture, drainage, mollic/organic horizon presence), and their significance was tested using statistical analysis. Through the geostatistical approach, functional group organic carbon values were spatialized according to statistical rules that take into account the spatial structure of the variable and mean organic carbon content of the geographic context to which the variables belong (SMU), as reference thresholds.

Bulk density assessment was found to be a weak point, since different PTFs often give very different results, strongly depending on the environment where they were developed and calibrated. Due to this variability, it was found advisable to provide the organic carbon percentage content, as well as t/ha, as required for the organic carbon soil indicator.

The graphs in Figs. 18.3 and 18.4 show the mean regional carbon stocks separately total and mountain and plain areas. According to the first results (10 regions out of 20), the average organic carbon content in plain areas ranges between 34 and 60 t/ha in the 0–30 cm section, with the lowest values in southern Italy (34 t/ha) and the highest (51–60 t/ha) in the north (Po plain). Average OC stock in the 0–100 cm section ranges from 78 to 154 t/ha in the plain, with the same geographical trend. In the Alps, the content is quite variable, from 59 to 103 t/ha, on average, for the 0–30 cm section and from 87 to 160 t/ha for the 0–100 cm section. Central and southern mountain areas (Appennini) have an average content of 50–58 t/ha within 30 cm and 95–114 t/ha within 100 cm.

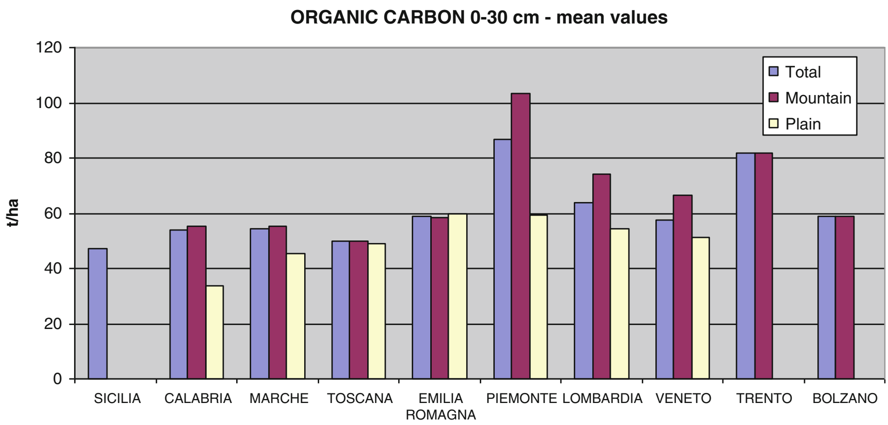

Fig. 18.3 Mean organic carbon values for 0–30 cm

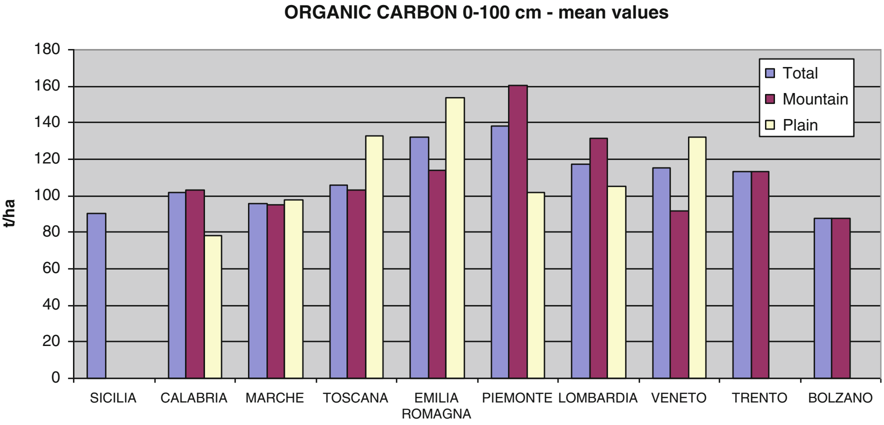

Fig. 18.4 Mean organic carbon values for 0–100 cm

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Chapter 19
Soil Erosion

Paolo Giandon

Abstract Soil erosion is a natural process that is exacerbated by human activities. Most actual concerns about soil erosion refer to accelerated erosion, where the natural rate has been increased significantly by human activities. In the past, a number of proxy-indicators were proposed for erosion. Accurate estimates of soil loss can be obtained from erosion models that already exist.

Soil erosion should be assessed by up-dating the baseline produced through modeling at regular time intervals. This will be achieved by collecting updated land cover/land use information, improved geomorphological data (DEM's, etc.), more detailed soil information, and improved rainfall data. Attempts have been made to map soil erosion in a number of areas worldwide, but to establish an accepted overall baseline for erosion remains a challenging task.

Keywords Erosion • Water • Geomorphological data • Land cover • Soil loss

19.1 Definition

Soil erosion is a natural process that is exacerbated by human activities. It is driven mainly by natural causes but often also by anthropogenic ones, which increase the magnitude and frequency of the process. It has been largely responsible for the distribution of weathered materials produced by geomorphic processes.

Soil erosion can be defined as: "The removal of soil particles away from the land surface by physical forces such as rainfall, flowing water, wind, ice, temperature change, gravity, or other natural or anthropogenic agents, and their deposit from one point on the earth's surface to elsewhere" (Eckelmann et al. 2006).

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_19

Most actual concerns about soil erosion refer to accelerated erosion, where the natural rate has been increased significantly by human activities. These activities include: intensification of land cultivation and management; inappropriate land use, for example through poor maintenance of terrace structures and cultivation of steep slopes; clearing of forests for cultivation; other changes in land cover through cultivation; grazing; controlled burning or wildfires; and leveling of land surface.

Agriculture is one of the primary drivers of unnatural soil erosion, since many farming practices are soil-unfriendly and wide areas of the territory covered by vegetation are intensively farmed, often in an unsustainable way. As a result, pressures on the environment are increased by changes in land structure (land leveling or removal of landscape elements, such as hedges, shelterbelts, etc.), changes in crop patterns, and inappropriate agricultural practices (Van-Camp et al. 2004).

The increase in forested areas in some developed countries, such as the Mediterranean countries, can be considered a positive driving force. However, a more detailed analysis is needed because changes in land structure may impact the hydrogeological cycle and increase wildfire risk.

Soil erosion is due primarily to water and secondarily to wind. Soil erosion by water occurs through rills, interrills, and gullies, as a result of rainfall or snowmelt. It involves the detachment of material essentially by two processes: raindrop impact and flow traction. Runoff by rainfall and from snowmelt is the most important direct driver of severe soil erosion by water. The dominant effect is the loss of topsoil, which is potentially very damaging and irreversible, in view of the fact that most soil pedogenesis in Europe took place in the last 10,000 years.

19.2 Soil Erosion Description and Monitoring

The European Soil Thematic Strategy Technical Working Group on Soil Erosion undertook a detailed analysis of the monitoring of soil erosion (Van-Camp et al. 2004) and concluded that it should be based on an indicator-based approach, where any proposed indicator should be derived from:

1. Estimated (or predicted) soil loss calculated by an appropriate tool (e.g., an erosion model);
2. Measurements of actual soil erosion rates (t ha^{-1} yr^{-1}) at a limited number of representative sites. The measurement sites (plots and catchments) should include those with a moderate to high erosion risk and be representative of an agro-ecological zone.
3. Upscaling of results from local measurements to larger areas and extrapolation to assess the state of soil erosion in areas where no measurements have been made, whilst accounting for local conditions of the factors affecting soil erosion.

19.3 Indicators

19.3.1 Criteria for Indicator Choice

In the past, a number of proxy-indicators were proposed for erosion. Gobin et al. (2004) reviewed a number of these and concluded that the most appropriate indicator for erosion by water is a regional model that estimates the risk of soil erosion combined with periodical monitoring of actual soil erosion in selected test areas.

In the Envasso project (Huber et al. 2008), the highest ranking selection criteria (according expert judgment) resulting from a panel evaluation were:

1. Acceptability or the extent to which the indicator is based on "sound science";
2. Practicability or the measurability of the indicator;
3. Policy relevance and utility for users;
4. Geographical coverage.

The first three criteria are similar to those proposed by the OECD (2003).

On the basis of these criteria, the indicators proposed by the Envasso project for water driven erosion were:

(i) Estimated and measured soil loss by rill, inter-rill, and sheet erosion;
(ii) Measured suspended sediment load in river and streams;
(iii) Extent of erosion features caused by overland flow.

19.3.2 Soil Loss Evaluation and Soil Erosion Risk

Accurate estimates of soil loss can be obtained from erosion models that already exist, for example: PESERA (Kirkby et al. 2004); USLE (Wischmeier and Smith 1965, 1978); RUSLE (Renard et al. 1997); Morgan et al. (1984) and Morgan (2001). These estimates exist for the major part of the world.

There are some aspects that make an accurate evaluation of erosion risk difficult:

1. Rill, inter-rill, and sheet erosion is difficult to estimate because of the complexity of the erosion processes involved and a lack of sufficiently accurate data;
2. Gully erosion is not estimated – there is no reliable method or model for estimating soil erosion by gully erosion;
3. Modeling errors contribute to the uncertainty of estimated values;
4. Very few sites exist in the world where water erosion has been measured systematically enough to provide sufficient data for model calibration and validation.

Thus, the primary indicator for water erosion by rill, inter-rill, and sheet erosion should be the estimated soil loss obtained by a calibrated model, which is subsequently backed up by a secondary indicator of measured soil loss by water erosion for continuing model validation, and quantification of data uncertainty.

The WG Monitoring of European Soil Thematic Strategy agreed that soil monitoring through on-the-ground measurements should not be done for erosion at present.

Soil erosion should be assessed by up-dating the baseline produced through modeling at regular time intervals. This will be achieved by collecting updated land cover/land use information, improved geomorphological data (DEM's, etc.), more detailed soil information, and improved rainfall data. This modeling approach will allow the land surface to be stratified into areas of actual erosion risk, potential erosion risk, and small erosion risk. In this way, effort invested in on-the-ground monitoring will be directed in a cost-effective and focused way. Such an approach does not preclude the future establishment of specific monitoring initiatives for soil erosion at dedicated sites.

Given this background, the following topics might have to be considered:

– Land use data and land management data (vegetation cover),
– Meteorological data,
– Topographical data,
– Soil data: surface particle size class, soil depth, soil type.

19.4 Baseline and Threshold Values

A baseline is defined as the "minimum or starting point of an indicator value." Therefore, a detailed inventory is required to define a baseline for soil erosion in a particular area. In areas that are not currently experiencing erosion, the baseline is $0\ \mathrm{t\ ha^{-1}\ yr^{-1}}$. The remaining land is subject to varying degrees of soil erosion where the baseline values are greater than zero.

Attempts have been made to map soil erosion in a number of areas worldwide, but to establish an accepted overall baseline for erosion remains a challenging task. These approaches more commonly produce assessments of erosion risk rather than estimates of actual soil loss, with baseline and/or threshold values rarely being mentioned. In the context of soil erosion, the true baseline is the amount of soil or sediment that is lost from a defined spatial unit under current environmental conditions. However, it is not practicable to measure the actual loss of soil caused by erosion processes over the whole territory to determine a universal baseline. It is more realistic to estimate baseline data by modeling the factors known to cause erosion. The estimated baseline soil losses should then be validated, using actual measurements at the few experimental sites that currently exist, augmented in the future by measurements from additional "benchmark" sites. This leaves undefined the spatial unit over which any baseline would apply.

The search for a baseline of soil loss in Europe leads to an examination of the concept of an average rate of soil erosion, because most baselines are established following a study of averages. Pimentel et al. (1995) reviewed erosion rates around the world and suggested an average of 17 t ha^{-1} yr^{-1} for Europe. This is a crude approximation, since it is based on plot data, which are in acute shortage. Furthermore, data from plot experiments are not a good basis for regional generalization. Several researchers quote soil erosion rates in Europe as being between 10 and 20 t ha^{-1} yr^{-1} (Lal 1989; Richter 1983), whereas Arden-Clarke and Evans (1993) state that water erosion rates in Britain vary from 1 to 20 t ha^{-1} yr^{-1}, but that the higher rates rarely occur and are localized. Boardman (1998) challenges the usefulness of an average rate of soil erosion for Europe, concluding that the rates vary too much in time and space.

Clearly, the lowest baseline is 0 t ha^{-1} year^{-1} for areas that suffer no soil erosion. An acceptable or "tolerable" baseline for areas known to experience erosion deserves more consideration, although this is certainly more contentious. In addition to soil, slope, and precipitation conditions, land use and land cover play an important role in defining any baseline greater than 0 t ha^{-1} yr^{-1}. This poses the question whether or not baselines are needed for different land uses, climatic zones, and/or soil-landscapes (and combinations of these factors). Soil, terrain, climate, and land use factors are very important for determining the amount of erosion and associated baselines. Therefore, it appears that a regional approach is needed to formulate regional baselines.

There has been much discussion in the literature about the thresholds above which soil erosion should be regarded as a serious problem. This has given rise to the concept of "tolerable" rates of soil erosion, which should be based on reliable estimates of the natural rates of soil formation. Considering the rates of soil formation derived from the results of many studies, it appears reasonable to propose a global upper limit of approximately 1 t ha^{-1} yr^{-1} for mineral soils, although under specific conditions, e.g., extremely high precipitation combined with high temperatures, actual soil formation rates can be substantially greater. However, it would be advisable to apply the precautionary principle to any policy response to counteract soil erosion; otherwise soils with particularly slow rates of formation will steadily disappear. In some cases, rates of soil erosion larger than 1 t ha^{-1} yr^{-1} are regarded as tolerable from the wider perspective of society as a whole, for example, for economic considerations. In Switzerland, the threshold tolerated for soil erosion is generally 1 t ha^{-1} yr^{-1}, although this rate is increased to 2 t ha^{-1} yr^{-1} for some soil types. In Norway, 2 t ha^{-1} yr^{-1} is adopted as the threshold for tolerable soil loss. Consequently, it may be realistic to propose different rates of soil erosion that are tolerable in different regions. Hence, the threshold values proposed for southern Europe are higher than those for northern Europe, although this aspect needs further discussion with regional experts before finalization.

Data from a recent study of continental erosion and sedimentation (Wilkinson and McElroy 2007) confirm that a precautionary approach to environmental protection should regard soil losses of more than 1 t ha^{-1} yr^{-1} as untenable in the long term (Jones et al. 2004), because this rate of loss significantly exceeds the estimated average natural rate of erosion ~0.4–0.5 t ha^{-1} yr^{-1}. In some circumstances, 1.5 t ha^{-1} yr^{-1} might be considered a tolerable rate because it does not differ greatly from the estimated maximum natural erosion rate during the Pliocene period.

19.5 Primary Indicator: Estimation of Water Erosion. A Study Case

SIAS is a pilot program led by the Italian Environmental Protection Agency that applies a new approach, which exploits the soil data and expertise that is available at the local level (see Chap. 18 for more details). All Italian regions were required to assess a soil loss indicator in order to build up a technical tool to increase knowledge about one of the main threats to European soils. The project structure requires that the most accurate and up-to-date soil data are used and analyzed directly by institutions and experts involved in soil survey at local level. Every Regional Soil Survey Service was asked first to participate in defining an exchange format, and later to fill in the format, concerning also the soil loss indicator and all related information (metadata).

To overcome harmonization problems across borders, it was decided to assess and present output data on a reference grid, built according to the INSPIRE Directive recommendations. To collect pixel data and meta-information, an exchange format was set up jointly by the working group; the format was then developed as a database with an explanatory guide in which the harmonized codes, suggested methodologies, and examples are collected. Information about soil loss and pixel coverage is stored in the so-called pixel table. Some data quality indicators were also defined and shared by the working group, both as quantitative indexes of data availability in the pixel (number of available observations, number of analyzed observations, scale of available soil maps, etc.) and as specific confidence levels for each indicator in each pixel. The special emphasis of the process lies in the exploitation of local expert judgment (the "bottom-up" approach), so that local experts can follow the assessment procedures that are most adequate in their opinion. These tables contain the process' value-added information, and any kind of input data or assessment procedure is recorded in them, through both codified items and free descriptions.

Concerning soil loss, each region was required to provide both potential and actual soil loss assessment (t ha^{-1}) for each (1 km × 1 km) pixel as final output, choosing the most suitable method. The model used by most regions was the Universal Soil Loss Equation (USLE, Wischmeier and Smith 1978), and its latest revised version RUSLE (Renard et al. 1997), which is the most commonly used model, based on the following equation:

$$A = R \cdot K \cdot L \cdot S \cdot C$$

where:

A: soil loss by water erosion (t ha^{-1} yr^{-1});
R: rainfall erosivity (MJ mm h^{-1} ha^{-1} yr^{-1});
K: soil erodibility, which means soil loss per R unit (t h MJ^{-1} mm^{-1});

L: slope length (adimensional);
S: slope angle (adimensional);
C: land cover factor (adimensional).

The model and all the input layers (land cover, climate, morphology, soil characteristics) were described in the metadata section of the exchange format; information on assessment, spatialization, and up-scaling methods was also collected.

Great effort was invested in defining a common infrastructure, suitable for recording the metadata information for each region, with different requirements and soil data availability. The regions participated in defining the exchange format that was conceived, which is codified, as far as possible, and simple to fill in, update, and query.

The activities started in 2008. However, it was not possible to involve all the regions, as some lack a regional soil service. Some regions joined the project at the beginning, and others later; at this stage of the project, 12 regions out of 20 have filled in the format, and 6 are still processing data. Some hydraulic properties of soil were determined through pedotransfer functions (Ungaro and Calzolari 2001; Ungaro et al. 2005).

With these results, it was possible to start tackling correlation and harmonization issues among regions, and to work out possible solutions and suggest them to the partners. This final stage, once the framework is completed, should lead to a national shared and harmonized tool.

The differences in soil loss assessment among regions have been highlighted and are being tackled at the harmonization stage. The two factors that seem to produce the main differences are rainfall erosivity (R) and land cover (C).

Calculating the R factor according to Wischmeier and Smith's complete formula is very complicated and requires very detailed rainfall data. This is the main reason why simplified formulas found in the literature have been often chosen by regions that do not own detailed climatic data; however, they can often lead to very different results. C factor values are linked to different land uses and conversion values that can be found in the literature or validated in regional specific situations. Large differences in the C factor are due mainly to a lack of harmonization and validation on site.

The first results (Figs. 19.1 and 19.2) highlight that only mountain and hilly areas are affected by actual soil loss. Alpine areas, which are mostly covered by forests and pastures, have no, or very low, erosion, while areas with cultivated slopes in lower mountain and hilly landscapes have more soil loss, especially in central Italy (Appennini). Concerning actual soil loss, according to the first results, average values range from 2 to 5 t ha^{-1} in the Alps, and from 6 to 23 t ha^{-1} in central Italy (Appennini).

The graph in Fig. 19.3 shows the regional mean soil loss values for the total area and for mountain and plain areas.

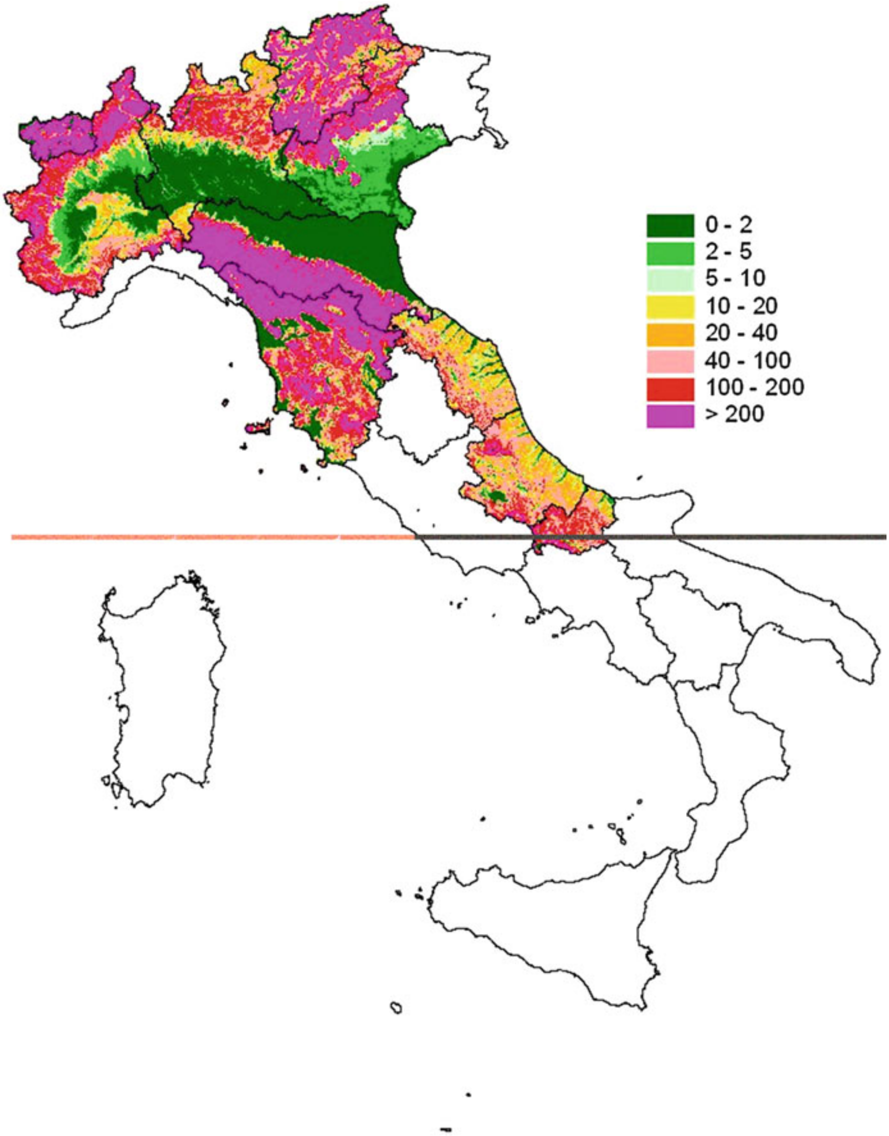

Fig. 19.1 Potential soil loss (t ha^{-1} yr)

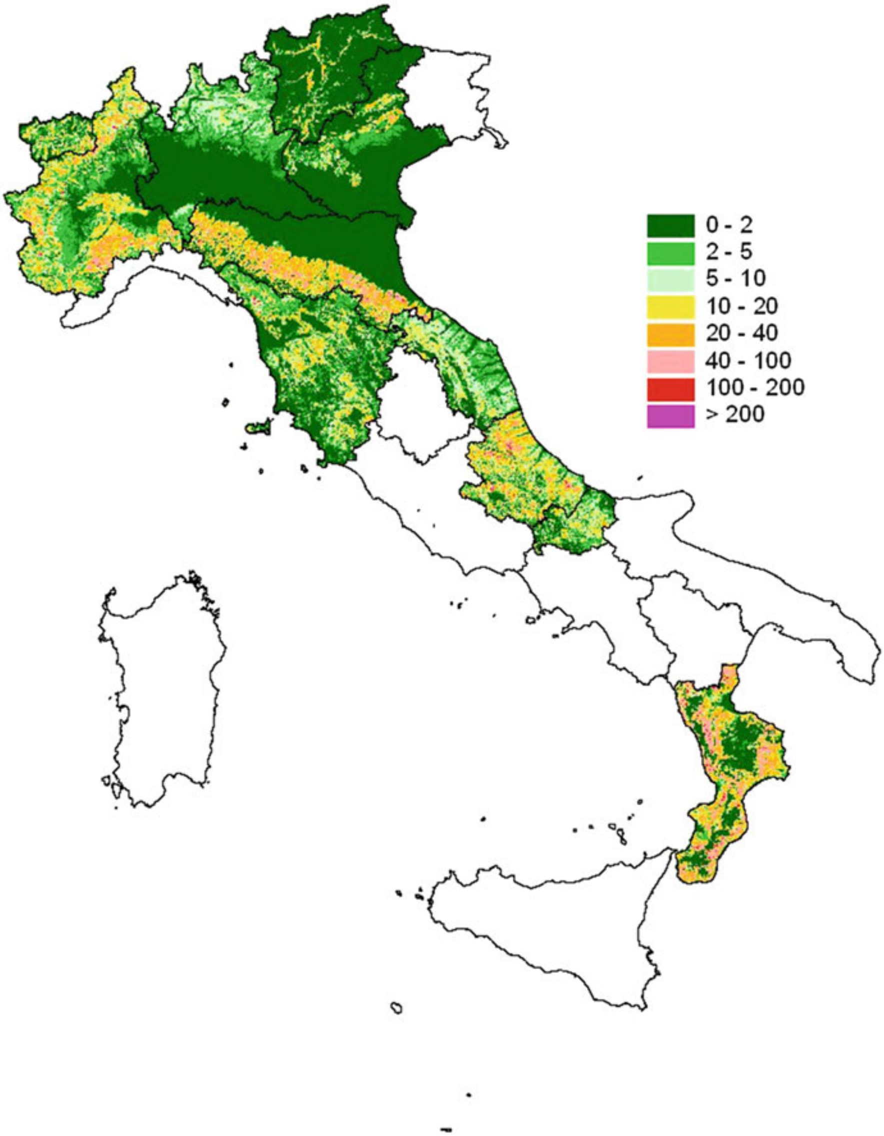

Fig. 19.2 Actual soil loss (t ha^{-1} yr)

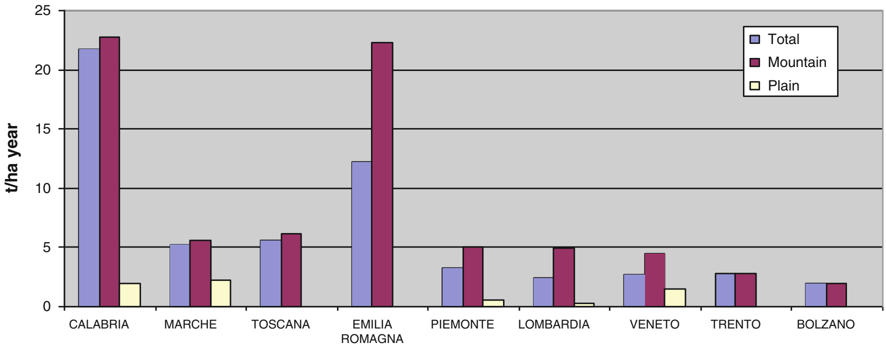

Fig. 19.3 Mean actual soil loss values (t ha^{-1} yr)

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Chapter 20
Soil Salination Indicators

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Abstract Soil salinity is one of the important soil properties that significantly affect agricultural production and environmental quality. A salinity indicator is a sign or symptom that suggests the soil is experiencing the impacts of salinity. Conventional chemical indicators of soil salinity include electrical conductivity (EC), total dissolved solids (TDS), and sodium adsorption ratio (SAR), while salt crystals and stains in surface soils are physical evidence of soil salinity. Indicator plant species have been commonly used in combination with physical and chemical indicators to determine soil salinity. The variation of environmental conditions may influence the behaviors of bioindicators. Therefore, it is important to determine the plant salt tolerance under similar environmental conditions when the tolerance range of plant species is used as an indication of soil salinity. This chapter discusses measurements of soil salinity, potential impacts of soil salinity on plant growth, and available soil salinity indicators, along with agricultural salinity management.

Keywords Soil salinity • Soil sodicity • Indicators • Phytomanagement

20.1 Soil Salinity

Salts are naturally present in soils, and many salt elements are essential nutrients for plants. The most common soluble salts in soil include major cations of sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), potassium (K^+), and anions of chloride (Cl^-), sulfate ($SO_4{}^{2-}$), bicarbonate ($HCO_3{}^-$), and carbonate ($CO_3{}^{2-}$). Soils are considered saline when soluble salt ions are elevated to high levels in soil. Soil salinity measurement indicates the salt content in soil.

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_20

Saline soils occur mainly in arid or semi-arid regions, and approximately 7 % of the world's land area is affected by high salinity. Most land salination is due to high contents of Na^+, K^+, Ca^{2+}, Mg^{2+}, and Cl^- ions in water and/or soil. Salination can arise from natural processes (i.e., primary salinity) or be induced by human activities (i.e., secondary salinity processes). Naturally-occurring salinity results from weathering of minerals (e.g., lime and gypsum) and the long-term continuous discharge of saline groundwater (Miller and Donahue 1995). In addition to mineral weathering, salts can also be added to soil from airborne salt deposition. Human activities, such as irrigation, have oftentimes altered the local water flow patterns. Soils that were previously non-saline can gradually become saline due to changes in saline groundwater discharge. Irrigation adds soluble salts to agricultural soils, particularly in arid and semi-arid environments because of high evapotranspiration along with insufficient water to leach soluble salts from the surface soil and the root zone. Poor irrigation water quality with elevated levels of soluble salts along with poor soil drainage or permeability can also result in the accumulation of salts in top soil layers. When groundwater is saline, underground water tables in dryland with shallow rooted crops can also rise and bring dissolved salts up to the root zone or the soil surface. This will happen via capillary water transport and salt precipitation in the soil after high evapotranspiration.

Soil salinity can be determined by total dissolved solids (TDS) or electrical conductivity (EC) of soil solution. TDS can be determined by a conventional procedure based on residue weight after water evaporation (mg/L). Alternatively, EC can be conveniently measured using electromagnetic (EM) sensors or metal electrodes; the unit of EC measurement is commonly expressed in dS/m (deci Siemens per meter). Both field and laboratory procedures are available for measuring soil salinity or EC (Hardie and Doyle 2012). In the field, soil salinity can be determined by the geospatial measurement (EC_a) using different devices. The field measurement of EC_a generally requires calibration to the actual salt content by conducting laboratory analyses. In the laboratory, soil salinity is usually assessed by determining either the total soluble salts (TSS) by evaporation of a soil water extract or the EC can be determined from the soil saturation extract (EC_e) of either a 1:5 soil to water (w/v) or a saturated paste. Water extraction is a commonly used procedure that simulates field conditions. EC values need to be reported with an indication of the specific extraction method used and to the nearest 0.01 dS/m. The soil extraction varies with soil texture and is related to soil-water contents under most field conditions. When using a conductivity meter, specific calibration solutions must be used to calibrate the meter system. For example, an EC value of 0.1 M KCl will be 12.9 dS/m at 25 °C. Corwin and Lesch (2013) indicated that, although the procedures for measuring soil salinity appear relatively straightforward, differences in methodology have considerable influence on the measured values and the interpretation of the results. When the soil EC measurement is not immediately performed after obtaining an extract, 0.1 % sodium hexametaphosphate [$(NaPO_3)_6$] solution can be used to prevent the precipitation of $CaCO_3$. TDS and EC values are closely correlated in soil solution. Using a conductivity factor (k), TDS can be converted into EC:

$$EC\ (dS/m) = 1/k TDS\ (mg/L)$$

The k value varies from 550 to 900, depending on soluble components, being high in chloride-rich solution but low in sulfate-rich solution.

Dryland soil salinity tends to be localized or forms "salinity hot spots." Therefore, composite soil sampling should not be used for the measurement of soil salinity in the field. Salinity is generally increasing with depth in most soils. Therefore, to assess a study area for soil salinity, soil samples need to be taken down to a >0.5 m depth at both the affected and the control areas. To determine the source of salinity, the soil profiles need to be examined for salt particles and carbonates using dilute hydrochloric acid solution. Because soluble salts are more mobile than carbonates, the soil profile observation can identify the net direction of water movement in the soil. For example, the net upward movement of water in poorly drained and groundwater discharge areas can be indicated by the highest concentrations of salts and carbonates at or near the soil surface.

Soil salinity can be categorized into the following classes based on the EC values:

Non-saline: 0–2 dS/m
Slightly saline: 2–4 dS/m
Weakly saline: 4–8 dS/m
Moderately saline: 8–15 dS/m
Strongly saline: >15 dS/m

20.2 Soil Sodicity

Soil salinity can be indicated by soil sodicity, which is generally characterized by the exchangeable sodium percentage based on sodium saturation of soil cation exchange capacity (CEC). A relatively small amount of sodium salts can negatively affect soil structure and create sodic soil, but may not necessarily have a high EC. Soil sodicity is more often expressed by the sodium adsorption ratio (SAR). SAR can be calculated from concentrations of K^+, Na^+, Ca^{2+}, and Mg^{2+} in soil solution or water extracts as follows:

$$SAR = Na^+/\left[\left(Ca^{2+} + Mg^{2+}\right)/2\right]^{0.5}$$

where Na^+, Ca^{2+} *and* Mg^{2+} are the concentrations (meq/L) of sodium, calcium, and magnesium ions in the soil extraction solution.

The SAR of a soil extract takes into consideration that the adverse effect of sodium is moderated by the presence of calcium and magnesium ions (Zhang et al. 2005).

The sodium adsorption ratio (SAR), along with soil pH, can be used to characterize salt-affected soils. For example, $pH > 8.6$, $EC > 4$, or $SAR > 13$ indicate sodic soil conditions. If the ratio of Ca to Na is <10, sodium may begin to cause soil salinity problems. When SAR is >15, soil physical structure and function will be negatively affected, and plants will have difficulty taking up water and nutrients from the soil. The soil particle-associated sodium will primarily accumulate in the surface layer of soil (van de Graaff and Patterson 2001).

The ratio of salinity (EC) to sodicity (SAR) is the dictating factor determining the effects of salts, and particularly sodium, on soils. It can be used to predict better how specific soils will be affected by the exposure to different levels of salts and sodium. For example, a severe reduction in infiltration is likely to occur in the soil with relatively low levels of EC but high levels of SAR. In general, high concentrations of sodium in soil solution would have different effects on soil physical and chemical properties, as compared with the accumulation of other salts in the soil solution. Furthermore, because of high contents of calcium and some carbonate in soils, the SAR experienced by plants in an irrigated soil environment will be 10–25 % greater than the SAR of the irrigation water itself, mainly due to the precipitation of calcium. By taking into consideration calcium and magnesium loss through precipitation, adjusted SAR values are generally made in reference to the level of bicarbonate (HCO_3^-) in irrigation water. High concentrations of anions can also increase soil salinity by affecting the exchangeable sodium and calcium ratio. When soil moisture decreases, water soluble calcium bicarbonate, $Ca(HCO_3)_2$, decomposes and becomes calcium carbonate deposits. Thus, increasing the ratio of sodium to calcium could result in sodium-dominated salinity in a calcium-dominated soil, particularly in arid and semi-arid areas of the western United States.

In sodic soils, high Na^+ contents can significantly alter some important soil physical and chemical properties, such as the dispersion of soil particles and poor soil water permeability. Soil dispersion is the primary physical process associated with high sodium concentrations (van de Graaff and Patterson 2001) because the attractive forces that bind clay particles can be disrupted by high contents of sodium ions (Falstad 2000). Dispersion of clay particles causes plugging of soil pores. Upon repeated wetting and drying and associated dispersion, soils reform and solidify into cement-like soil with little or no aggregate formation (Hanson et al. 1999), which will significantly reduce soil infiltration, hydraulic conductivity, and lead to surface crusting. All these effects will negatively impact soil quality and plant growth. For example, the cement-like soil structure will impede water flow or infiltration in the soil. As a result, there will be less plant available water, particularly at deeper depths, which will induce more surface runoff and soil erosion (Miller and Donahue 1995). Soil with well-defined aggregate structure, particularly in arid and semi-arid areas, will contain a large number of soil pores as well as many fissures. These macro-pores allow relatively rapid water flow through the soil profile (Miller and Donahue 1995). When high concentrations of sodium affect a soil, the subsequent loss of aggregate structure reduces the hydraulic conductivity (Levy et al. 1999). The subsequent soil swelling and waterlogging often leads to anaerobic conditions. This will also decrease organic matter decomposition rates, and such a decrease in decomposition leads to formation of organic matter-rich soil.

Soil surface crusting is one of the well-recognized diagnostics of sodium-affected or sodic soils in arid and semi-arid regions (Bauder and Brock 1992). The primary causes of surface crusting include physical dispersion by impact of raindrops and irrigation water, and chemical dispersion that is in relation to the soil ESP and the EC of the irrigation water (Hardy et al. 1983). McIntyre (1958) found that the formation of soil crusts includes an upper skin of approximately 0.1 mm and a washed-in layer of clay particles. Indeed, clay particles dispersion and movement in the soil further enhances crusting. Soil crust penetrating the plant root zone would negatively affect seedling emergence and water penetration (Barbour et al. 1998).

20.3 Effects of Soil Salinity on Plant Growth

High soil salinity can cause negative impacts on crop growth through the reduction in water availability to the plant or by the toxic effects of individual ions (such as chlorine, sodium, or boron) in the root zone under hyper-saline soil conditions. The presence of high levels of soluble salts in soils limits plants' absorption of water from the surrounding soil (Bauder and Brock 2001). Saline soil particles can hold water more strongly so that plant roots are not able to utilize soil capillary water. A plant will need additional or increased energy to extract water from the saline soil due to high osmotic forces (Bauder and Brock 2001). As a result, non-salt tolerant plants will exhibit symptoms of drought (such as wilting or leaf loss), even though the soil water content is still relatively high. Ayers and Westcot (1976) indicated that plants will be at their wilting point (approximately −15 bars osmotic potential) when the soil water content is 27 % and soil water EC becomes 30 dS/m. As plant uptake of water becomes progressively more difficult from the soil after irrigation, the salinity of the soil solution will increase. This process becomes particularly important in an environment with high evapotranspiration (ET). When salts accumulate in the soil profile to such an extent, plant physiological processes will be adversely affected and cause considerable disruption (Barbour et al. 1998). For example, Hadas (1965) reported that the buildup of salts in the soil resulted in the farming crop changing from wheat and barley to only barley, until the land was abandoned. Therefore, an agricultural crop's tolerance to high soil salinity needs to be well evaluated. An EC of 4 is a general salinity threshold for common traditional annual crops, such as wheat and canola.

The effects of soil salinity on plant growth or crop yield are also dependent on soil type, climate, water use, and irrigation factors. More salts, including sodium, will accumulate in clay soils as compared to sandy soils because of clay's inherently lower leaching fraction and the greater exposed soil surface. The amount of available water decreases as the salinity of irrigation water increases. Ayers and Westcot (1976) reported that, when soil water EC increased from 3 to 10 dS/m, corn forage production decreased by 50 % or was completely lost when soil water EC increased to 16 dS/m. Previous studies showed that different crop species or varieties vary significantly in salinity tolerance (Barbour et al. 1998). As sodium displaces calcium, high sodium accumulation in plant tissues might result in cell membrane damages, reduced protein synthesis, and altered hormonal activity, and subsequently, water and nutrient uptake can be negatively impacted. High concentrations of chlorine in leaf tissues can also be responsible for foliar dehydration.

A halophytic plant (or halophyte) is a plant species that grows in an environment with high salinity (Shabala 2013). Relatively few plant species are salt-tolerant halophytes, but the Chenopodiaceae are dominant (Flowers and Colmer 2008). Halophytes are naturally "salt-loving" plants. The most common halophytic species include salt marsh cordgrass (*Spartina alterniflora, S. gracilis*), saltgrass (*Distichlis spicata*), saltbush (*Atriplex lentiformis*), and pickleweed (*Salicornia bigelovii*) (Lin et al. 2002; Bañuelos and Lin 2007). *S. bigelovii* can be cultivated using original seawater for irrigation (Ayars et al. 1993; Ayala and O'Leary 1995). Salt-tolerant species have special physiological mechanisms to adapt to high saline environments, such as salt exclusion, intra-plant salt translocation (e.g., from sensitive shoots to older leaves or roots), cellular osmotic adjustment (e.g., dilution by increasing water uptake), salt intracellular compartmentation (e.g., accumulation in the spaces between cells), or salt excretion (e.g., through salt glands) that allow these halophytic species to cope with high salt concentrations in soil and water. Previous studies have primarily targeted external sequestration in salt bladders, internal Na^+ sequestration in vacuoles, stomatal aperture and density, and xylem ion loading processes. Shabala (2013) indicated that there is nothing unique that halophytic possess that is not found in other crop species. Instead, halophytes are doing everything just "a bit better" and have a set of highly complementary and well-orchestrated mechanisms in place to deal with salinity stress.

20.4 Soil Salinity Indicators

A soil salinity indicator is a sign or symptom that suggests the soil is experiencing the impacts of salinity. Physical indicators of soil salinity include salt crystals and stains (such as light gray or white colors) in surface soils. A bare patch of land might indicate high salt concentrations in the soil, which is inhibiting plant growth and making the soil take longer to dry. Because these signs are not always related to the soil salinity, the use of indicator plant species, therefore, has been commonly done in combination with physical and chemical indicators (i.e., lab/field measurements) to determine the level of soil salinity. Ideally the salinity indicator plant species should be those only growing in saline soils (Bui and Henderson 2003; McGhie and Ryan 2005), such as sea barley grass (*Hordedeum marinum*) and spiny rush (*Juncus acutus*). However, because of the variations in environmental conditions, the choice of indicator plants may also be influenced by the outcomes. It is recommended the salt tolerance be determined under similar environmental conditions when using tolerance ranges as an indication of site salinity conditions.

Different plant species vary significantly with salt tolerances. As soil salinity increases, salt-sensitive species become eliminated from the area, and vegetation becomes more dominated by salt-tolerant species (Onkware 2000). Most salt-tolerant plant species are not dependent on salt to survive, but are often only found in saline conditions. For example, *Salicornia europaea* and *Aster tripolium* can grow well in saline soils of 20 mS/cm (Piernik 2003). This is partly because, in non-saline or low salt environments, salt-sensitive species are generally more competitive than salt-tolerant species for water and nutrients. Based on soil EC_e measurements, crops can be classified into one of the following salt tolerance categories:

Salt sensitive species: 1.0–1.8 dS/m
Moderately sensitive species: 1.5–2.8 dS/m
Moderately tolerant species: 4.0–6.3 dS/m
Tolerant species: 6.8–10 dS/m

In the San Joaquin Valley of central California, irrigation with drainage waters over 6.5 dS/m would exceed the limit for most salt-tolerant agronomic crops (Jacobsen and Basinal 2004).

Plant species with distinctive responses to salts at the whole plant, tissue or cellular level can be selected as effective bioindicators of soil salinity (Ewing et al. 1995). Leaves of Buck's-horn Plantain (*Plantago coronopus*) will become red as soil salinity increases. However, few effective bioindicators or biomarkers for soil salinity have yet been developed (Ashraf and Harris 2004). Despite a wealth of published research on the salinity tolerance of plants, neither the metabolic sites at which salt stress damages plants nor the adaptive mechanisms utilized by plants to survive under saline conditions are well understood. Tejera et al. (2006) investigated the effectiveness of several nutritional and physiological indicators (such as N_2 fixation and shoot K/Na ratio) in the selection of salinity-tolerant chickpea plants (*Cicer arietinum* L.). Also, because NaCl is the predominant form of salt in most saline soils, high sodium accumulation in plants could limit the absorption of other mineral nutrients (Greenway and Munns 1980), including Ca and K, which results in a Na/K antagonism (Benlloch et al. 1994).

The field indicators of different levels of soil salinity are shown in Table 20.1. Metternicht and Zinck (2003) indicated that, because of the uses of various sensors (e.g., aerial photographs, satellite- and airborne multispectral sensors) available, remote sensing technology has been applied for remote indication, monitoring, and mapping of salt-affected lands (Fernández-Buces et al. 2006; Leone et al. 2007). Major constraints on the use of remote sensing can be related to the spectral behavior of salt types, temporal changes in salinity, and interference of vegetation (Dehaan and Taylor 2002).

Future studies need to focus on developing indices of soil salinity that incorporate soil physical, chemical, and biological properties and will be most readily adopted for their sensitivity to management-induced changes, ease of measurement, relevance across sites or over time, inexpensiveness, and close link to measurement of desired values.

Table 20.1 Diagnosis of non-saline and salt-affected soils in relation to soil salinity (EC, dS/m)

Soil salinity	Crop	Salinity measurements	Field indicators
Non-saline	Legume, vegetable crops	EC <2, SAR <13	Normal crop growth
	All other crops	EC <4, SAR <13	
Saline	Legume, vegetable crops	EC >2, SAR <13	Salt crystals at or near soil surface when dry; little or no plant growth
	All other crops	EC >4, SAR <13	
Sodic	All crops	EC <4, SAR >13	Shiny black when wet; dull grey, hard and cracked when dry; little or no plant growth; pH >8.6
Saline-sodic	All crops	EC >4, SAR >13	Any combination of the above features may be present

This table was modified from *Soil Salinity* by Manitoba Agriculture, Food and Rural Development (http://www.gov.mb.ca/agriculture/environment/soil-management/soil-management-guide/soil-salinity.html)

20.5 Management of Saline Agricultural Soils

Salinity is an important land degradation problem. Soil salinity can be reduced by leaching soluble salts out of soil with excess irrigation water. Soil salinity control involves water table control and flushing in combination with tile drainage. Soil salinity can be difficult to notice from one season to the next. In wet years, there is sufficient leaching and dissolving of salts and no significant impacts of soil salinity on crop growth; but in dry years, increasing evaporation might draw salts up to the soil surface, showing white crusts of salt. Rainwater of sufficient intensity or duration may flush salts out of the uppermost layer of soil. Proper irrigation management can prevent salt accumulation by providing adequate drainage water to leach added salts from the soil. In the San Joaquin Valley of central California, saline agricultural drainage has been managed using the concept of Integrated On-farm Drainage Management (IFDM) (Lin et al. 2002; Bañuelos and Lin 2007). For example, the IFDM system included: (1) 195 ha of salt sensitive crops, such as lettuce (*Lactuca sativa*) and tomatoes (*Lycopersicon esculentum*); (2) 52 ha of salt-tolerant crops, including cotton (*Gossypium hirsutum*), alfalfa (*Medicago sativa*), canola (*Brassica napus*), sunflower (*Helianthus anuus*), and safflower (*Carthamus tinctorius*); (3) 5 ha of salt-tolerant Eucalyptus (*eucalyptus spp*); (4) 2 ha of halophytic plants, including pickleweed (*Salicornia bigelovii* Torr.), saltgrass (*Distichlis spicata* L.), saltbush (*Atriplex lentiformis* L.), and cord grass (*Spartina gracilis* Trin.); and (5) 0.73 ha of a lined solar evaporator. The components of 3 to 5 comprised a minor portion in size for receiving the effluent produced from the irrigation of salt-tolerant crops (i.e., component 2) on the farm site. While volumes of drainage water decreased due to evapotranspiration

Table 20.2 Removal of salt and Na^+ in the aboveground harvest of selected crop and grass species

Plant species	Shoot (DM) (ton/ha)	Salt removal (kg/ha)	Sodium removal (kg/ha)
Sudan grass (*Sorghum x drummondii*)	5	72	2
Sunflower (*Helianthus annuus*)	9.2	172	4
Alfalfa (*Medicago sativa*)	11.3	178	26
Amaranth (*Amaranthus cruentus*)	5.0	182	3
Japanese millet (*Echinochloa esculenta*)	8.2	224	46
Saltbush (*Atriplex amnicola*)	2.0	500	–
Kallar grass (*Leptochloa fusca*)	10.0	800	–

Gritsenko and Gritsenko (1999), Oster et al. (1999), Barrett-Lennard (2002)

along the path of drainage water reuse, water salinity (EC) increased from 0.7 to 15.1 dS/m through the IFDM system.

Different plant species have different abilities to take up and accumulate salts in plant tissues under field conditions (Table 20.2). Halophytic plants can be used for phytomanagement of salt-affected land, because some halophytes can accumulate significant amounts of salts and Na^+ from the saline water and soil (Bañuelos and Lin 2007). For example, Atriplex species grown in salt-affected soils can accumulate 390 g salts per kg leaf ash (Malcolm et al. 1988). Qadir et al. (2007) reported that Kallar grass (*Leptochloa fusca*) grown on calcareous saline-sodic soils (about 20 dS/m) contains salt contents of 40–80 g/kg in forage. Considering an annual forage production of the grass of 25,000 kg/ha, the volume of irrigation water required to grow the grass is estimated to be 10^4 m^3/ha. If the irrigation water has a salinity level of 1.5 dS/m (typical salt concentration in irrigation water), the amount of salts in irrigation water would be equivalent to 9,600 kg/ha, as compared with 1,000–2,000 kg/ha of salt removed in shoot. The efficiency of different plant species used in phytomanagement of saline-sodic soils has been found to be highly variable. Phytomanagement of saline-sodic soils primarily occurs in the root zone, and the root depth varies among different plant species. Those species with a tap root system, such as alfalfa having a root depth of 1.2 m in soil, generally have advantages (Ilyas et al. 1993). Bañuelos et al. (2010) evaluated different clones of hybrid poplar for salt and B tolerance. Among the tested poplar clones, Parentage *trichocarpa* x *nigra* and *deltoides* x *nigra* clones showed the greatest potential salt and B tolerance, salt accumulation, and biomass production. In a different field study, Smesrud et al. (2012) indicated that also poplar trees can be used for practical land salinity management. Salt phytomanagement is much effective when used on soils with moderate levels of salinity. Plants can extract salts directly from the saline soil and accumulate salts in plant tissues. Plant roots also have the ability to increase the dissolution rate of calcite in the rhizosphere, which results in enhanced levels of Ca^{2+} in soil solution to effectively replace Na^+ on the cation exchange complex.

Conclusions

Electrical conductivity (EC) is a measure of dissolved salts in a soil extract. Generally, at EC above 2–3 dS/m, the soil salinity will reduce or prohibit plant growth at different levels depending on soil types and plant species. Many other environmental factors need to be considered when addressing the suitability of irrigation water with respect to soil salinity and sodicity. The basic relationship between EC and SAR will serve as an important baseline, with modifications such as soil texture, clay type, leaching fraction, and rainfall, for a better site-specific understanding of how plants will be affected by salts, and in particular, sodium. Environmental impacts of salts on soil quality can be devastating both to agricultural production and to local societies. Therefore, understanding how salts and sodium are likely to affect the soil ecosystem and taking great care to avoid the potential environmental damage from salinity will become one of important environmental challenges in future research.

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Chapter 21
Soil Contamination by Diffuse Inputs

Paolo Giandon

Abstract The interaction of diffuse inputs with the soil and water systems and with their uses and functions has many uncertain aspects but it is certainly a potential source of soil contamination. The two main pathways for diffuse contaminant accumulation in soil are atmospheric deposition and agricultural practices. Two key issues can be defined: diffuse contamination by heavy metals and by persistent organic pollutants. Monitoring can be a useful tool for assessing diffuse inputs and for increasing our knowledge about diffuse pollution processes. *Heavy metal content in soils* is an indicator that is relatively simple to interpret even if there is no unique methodology for defining a homogeneous map unit; many relevant data are already available throughout the world.

Keywords Contamination • Heavy metal • Anthropogenic • Soil

21.1 Definition

Soil is a central medium for food production and plant growth with strong connections to water and air and it has to be preserved from contamination processes, also if coming from diffuse sources.

There are many causes for concern about the incidence of harmful soil changes throughout urban and rural territories due to the adverse impacts on soil functions related to human activities.

The interaction of diffuse inputs with the soil and water systems and with their uses and functions has many uncertain aspects.

The following can be considered as sources of diffuse inputs to soil:

– Agricultural, horticultural, silvicultural activities, through distribution of mineral fertilizers, exogenous organic matter such as animal manure, or other soil improvers, such us sewage sludge, compost, and digestate from anaerobic digestion, and pesticides;

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_21

– Wet and dry atmospheric deposition not connected to a specific point source (vehicle exhausts, fine dust containing contaminants transported over long distances, emissions from industrial and domestic incineration).

Further, the following differentiation can be made:

– Diffuse inputs as a result of external agricultural or non-agricultural activities (atmospheric deposition, contaminants in sewage sludge or composts);
– Diffuse inputs from intentional distributions to soil (e.g., copper as a fungicide in vineyards or Cu and Zn as feed supplements for pig fattening).

Processes to be addressed when assessing the effects of pollutant inputs are:

– Bio-accumulation by plants and microorganisms on the basis of type of soil and management of specific input-output balances (e.g., metals/potential toxic elements);
– Stronger or weaker sorption/fixation to soil organic and inorganic constituents that determines the long term bioavailability of contaminants;
– Biodegradation (only for organic pollutants) by soil fauna and flora.

Soil contaminants may be components of materials that are used by farmers for plant nutrition or soil improvement or that are applied for crop protection. Copper is an example of a substance that is both an essential nutrient (and deficient in some soils), and a dangerous one, since excessive concentrations can affect soil microbiology and plant growth. A clear distinction has to be made between the beneficial functions of these elements and the potential adverse effects that can occur in particular soil conditions due to relatively high concentrations of these substances. The possibility of transfer toward compartments other than those where they are essentiality needed (e.g., ground and surface waters) must also be considered.

The two main pathways for diffuse contaminant accumulation in soil are atmospheric deposition and agricultural practices.

Two key issues can be defined that apply to a wide variety of contaminants that differ in their chemical properties and sources and pathways:

– Diffuse contamination by heavy metals and other inorganic contaminants (except nutrients),
– Diffuse contamination by persistent organic pollutants.

The first issue is probably the most important, because the process concerned is practically irreversible. It is related to heavy metals accumulation in soil not only as a result of human activities but also from natural sources (Huber et al. 2008).

21.2 Soil Diffuse Pollution Description and Monitoring

Monitoring can be a useful tool for assessing diffuse inputs and for increasing our knowledge about diffuse pollution processes. Measurements of inorganic and organic substance concentrations in soils can provide data that can be used to assess the risks of contamination. These measurements can be considered as local inventories because, in most cases, they are not repeated over time. They may also be used to draw soil maps of metal concentrations or as background values, which may be useful in local spatial planning to evaluate whether locally high values can be defined as contamination and whether they are due to natural or diffuse anthropogenic contributions.

To avoid contamination resulting from agricultural land use, it is useful to adopt a long-term balanced approach that takes into account the natural concentration of contaminants in soil. Soil contamination monitoring should be improved step-by-step in terms of the level of detail and the coverage of the collected information.

The monitoring architecture and data collection items will be updated together with the improvements in the basis of the information according to an up-scaling approach that integrates data collected for different purposes. The database design that should be implemented should have a dynamic and flexible nature and be based mainly on a number of already available and comparable indicators and parameters at the different spatial scales.

Often the soil has to be examined before organic waste, such as sewage sludge, is applied as a fertilizer. In addition, these data may be useful for scientific purposes to help us to understand better the substance flows in agricultural systems.

Monitoring of the concentrations of potential contaminants in different environmental media is the basic element that is needed to find the best national and regional intervention strategies. In general, the monitoring of heavy metals concentration in soil is based on the collection and analysis of soil samples through sampling strategies that follow a typological or a systematic approach (ISO 19258 2005). All the monitoring programs at the first level include analysis of the so-called total element through acid or alkaline digestion of a sample in order to obtain information about the quantity of metal in soil.

It should be taken into consideration that analytical methods that use stronger or weaker digestion agents seek to reflect the sorption strength or solubility of elements; if more information about the bio-available fraction of metals is needed, appropriate analysis methods have to be adopted.

Monitoring should focus on the abatement of the effects due to diffuse inputs, including also the effects of measures to reduce inputs (Van-Camp et al. 2004).

The results yielded by a monitoring program should enable the user to:

– Evaluate the impact (i.e., quantity and quality) of diffuse inputs,
– Evaluate the future state of the system, i.e., how the current land use (or changes therein) affects soil quality.

It is obvious that to control the concentration of more diffuse metals, which consist of no more than 20 elements is sustainable, while monitoring a few thousand organic substances that may enter the soil system by diffuse contamination is not feasible.

The most important substances whose monitoring for diffuse soil contamination has higher priority are briefly described below.

Cadmium can readily accumulate in crops, in particular, in acidic soils with low binding capacity. In these soils there is a high risk of leaching to the subsoil and the groundwater.

For zinc and copper, ecological risk assessment is difficult since the generic safe levels are below those necessary to sustain life in more tolerant organisms.

The amount of lead stored in the organic layers of topsoils in particular is still significant. Critical levels in soil (based on total concentrations) in terms of long-term exposure are often exceeded in urban areas, although bioavailability may be low.

Mercury is very toxic. It accumulates mainly in soils and sediments, but can be transformed into mobile fractions (e.g., methyl mercury).

Arsenic is to be considered as a priority element within the strategy for health and environment because of its high toxicity level. It is present at high natural concentrations in many soils. Arsenic accumulates in soils, in particular, in neutral to basic ones, and is linked mainly to iron oxides. The risk of leaching is usually low, as is its bioavailability. This may change, however, with soil conditions or after ingestion by humans (especially children) and grazing animal.

Nickel and chromium are less "critical," but they are often included in routine monitoring.

21.3 Indicators

The selection criteria take into account mainly:

- Data availability,
- An indicator's sensitivity and meaningfulness,
- The short and medium term feasibility of the indicator's use.

Areas where diffuse contamination already has an impact, as well as areas where the risks of future contamination require that additional protective measures be adopted, can be identified by considering the two following indicators in combination:

1. *Heavy metal content in soils* is an indicator that is relatively simple to interpret even if there is no unique methodology for defining a homogeneous map unit; many relevant data are already available throughout the world. This indicator gives basic information about the status of heavy metal contamination and its change in the long term. Changes in the indicator values are generally slow in a short term perspective (less than 5 years), and the data quality, accessibility, and harmonization need to be accurately controlled to improve information reliability.
2. *Anthropogenic/natural heavy metal content ratio* can highlight a situation of heavy metal accumulation on the soil surface as an effect of diffuse pollution processes. It can be used only in non-acid soils (from neutral to basic) in which leaching of metals along the profile does not take place.

Table 21.1 Range of median values in European topsoils of *aqua regia* extractable heavy metals contents

Heavy metal	Background contents (mg kg^{-1} dry soil)
Cadmium (Cd)	0.07–1.48
Chromium (Cr)	5–68
Copper (Cu)	2–32
Mercury (Hg)	0.02–0.29
Nickel (Ni)	3–48
Lead (Pb)	9–88
Zinc (Zn)	6–130

21.4 Baseline and Threshold Values

Usually nationally defined thresholds should be used, where they are stated, and are specific to soil parent material type and land use. Threshold values have often been defined in the context of regulations for sewage sludge application and food production, but also need to be such that they protect against the multifunctional use of soils (Kibblewhite et al. 2008).

When national thresholds are not defined, thresholds from other countries or regions with comparable parent material and land use could be used. Most countries have available data on the heavy metal content of soil, at least for some heavy metals in some areas, which could be used to identify baselines.

Background values are often used to define baselines. A brief description of background values can be found in ISO 19258 (i.e., percentiles of sample distributions).

A comprehensive study was conducted by Utermann et al. (2006) leading to an overview of the trace element content of European topsoils, differentiated according to soil parent material and land use, soil pH, and soil texture. Table 21.1 shows the ranges for the heavy metal background content of soils according to ISO 19258 (Utermann et al. 2006).

The background values differ according to the parent material, land use, and anthropogenic impacts. Depending on the objective, other stratification models are possible. Heavy metal thresholds exist in some countries and should be defined at the national, or at the larger regional scale, to allow for varying natural conditions.

21.5 Primary Indicator: Heavy Metal Background Values. A Study Case

In order to assess the contamination of soil by metals, the natural content due to the composition of the minerals in the parent material must be known. In fact, such concentrations, especially for some metals, can vary widely depending on the material from which the soil developed (Alloway 1995; Kabata Pendias 2001; Hooda 2010; Baize 1997; Baize and Tercé 2002; Adriano 2001). In Italy, rocks of very different origin and composition determine the concentration of metals in the soil, which varies widely throughout the national territory (Ottonello and Serva 2003).

During a soil field description project that was conducted to realize a regional soil map, ARPAV measured the concentration of some metals and metalloids in soil over several years, with the aim of defining a basic level of information for the regional territory.

Sampling sites were selected following the "typological approach" of ISO 19258:2005, i.e., depending on the parent material, soil types, and land use. Homogeneous areas were defined according to the parent material's composition.

For the plain, where soils were formed from alluvial deposits, areas were defined considering the origin of the sediments from which the soil originated (Ungaro et al. 2008; Amorosi and Sammartino 2007), and these areas were called "depositional units" (Fig. 21.1).

For the mountain area, where soils were formed from materials on site, areas were defined considering the prevalent rocks from which the soil was formed together with the type of pedogenetical processes, and these were called "physiographic units."

In the selection of the sampling sites, land use was also taken into account, in order to consider only sites with agricultural use, taking care to avoid contaminated areas or other sites too close to potential sources of pollutants or showing signs of human intervention.

Two sampling depths were chosen depending on the soil horizons using different strategies for plain and mountain areas: in the plain area, the first sample was taken within the upper horizon, up to a maximum depth of 40–50 cm, and the second in the subsoil within the first soil horizon below 70 cm, which usually excludes a possible anthropogenic contribution. In mountain areas, the first sample was taken within the upper horizon, whose size is variable, and the second in the subsoil within the first soil horizon or layer below 70 cm, or, if the soil was thinner, within the deeper layer.

In total, 2,393 samples were analyzed (the regional surface is about 18,000 km^2), of which 1,363 were taken from the upper layer and 1,030 from a deeper layer. In the plains, 1,119 samples were taken from the upper layer and 835 from a deeper layer, while in the mountain areas, 244 were taken from the upper and 195 from a deeper layer.

The analytical determinations, through aqua regia extraction, to measure the "pseudo-total" fraction, and ICP-AES detection, were performed at the ARPAV Laboratories of Treviso on a size fraction of less than 2 mm. The antimony, arsenic, beryllium, cadmium, cobalt, chromium, copper, mercury, nickel, lead, selenium, tin, vanadium, and zinc content were determined.

Statistical analysis of the data was performed for the whole dataset and for each depositional/physiographic unit. Some descriptive statistics were performed, keeping the values of upper horizons separate from those of deeper horizons; for each variable, many parameters were determined: mean, median, minimum,

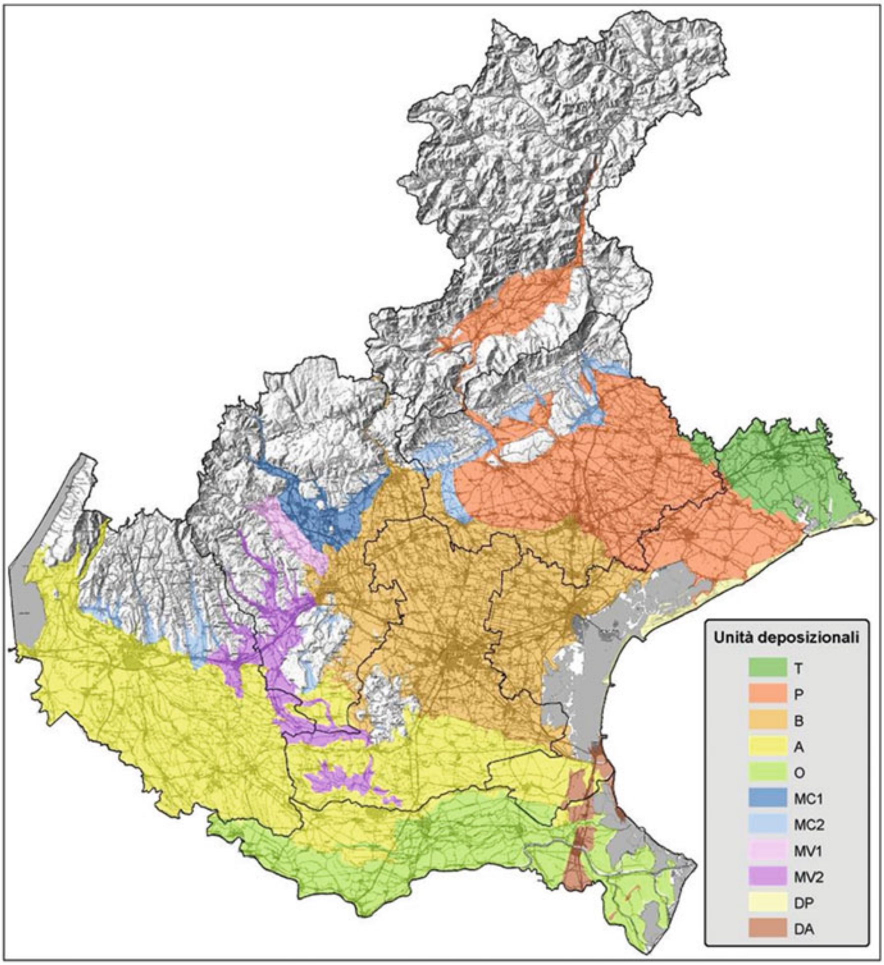

Fig. 21.1 Depositional units of the plain: *T* Tagliamento river deposit, *P* Piave river deposit, *B* Brenta river deposit, *A* Adige river deposit; O = Po river deposit; MC1 = Astico river fan; MC2 = Prealpine rivers fan; MV1 = Leogra-Timonchio rivers fan; MV2 = Agno-Guà rivers fan; DP = north-eastern coastal deposit; DA = southern coastal deposit

maximum, percentiles (5th, 25th, 75th, 90th, and 95th), standard deviation, standard error, skewness and kurtosis, and normality tests. When outliers had been removed, the background value for each metal was determined by means of the 95th percentile value within each depositional/physiographic unit. The background values were then compared to the threshold limits for residential sites stated in the Italian Environmental Act (D. Lgs. 152/2006).

In Table 21.2, the pedo-geochemical background values (deeper layers) for each metal and metalloid are reported for each depositional and physiographic unit. In Table 21.3, the background values (upper layers) are reported for the same depositional and physiographic units.

Table 21.2 Pedo-geochemical background values in depositional and physiographical units of Veneto (mg/kg). In bold, values exceeding limits for residential sites according to Italian Environmental Code

Depositional/physiographic unit	Sb	As	Be	Cd	Co	Cr	Hg	Ni	Pb	Cu	Se	Sn	V	Zn
Alps on crystalline and metamorphic basament (MA)	3.6	17	1	0.25	**20**	67	0.39	53	36	52	nd	nd	56	142
Alps on dolomite (DC)	2.4	**21**	1.3	0.71	**27**	88	0.11	87	32	79	0.29	**2.3**	64	131
Alps on silicates (DS)	1.99	17	nd	0.25	**32**	73	0.17	40	34	76	nd	nd	nd	125
Alps on Werfen Form. (DW)	1.87	**20**	nd	0.25	19	98	0.89	47	42	26	nd	nd	nd	85
Prealps on hard limestone (SA)	3.34	**27**	**3.3**	**2.99**	**39**	130	0.32	81	67	76	0.66	**4.4**	**140**	**220**
Prealps on marly limestone (SD)	1.29	**23**	**2.3**	1.58	**33**	**157**	0.27	**173**	53	89	0.58	**2.7**	95	**173**
Prealps on basalts (LB)	0.54	15	**2.4**	0.25	**79**	**260**	0.14	**190**	36	70	0.39	**3**	**220**	**160**
Hills (RC)	1.78	**20**	**3**	0.87	**26**	140	0.14	88	44	76	0.42	**3.5**	**130**	130
Tagliamento river deposit (T)	nd	12	nd	0.55	11	58	0.08	42	11	23	nd	nd	nd	65
Piave river deposit (P)	0.83	14	1.5	0.25	14	61	0.12	52	19	30	0.27	**2.7**	80	83
Brenta river deposit (B)	2.13	**45**	**2.3**	0.88	16	61	0.25	37	38	40	0.23	**6.1**	**96**	128
Adige river deposit (A)	1.37	**42**	1.4	0.83	**20**	141	0.09	**125**	36	58	1	**3.4**	88.9	114
Po river deposit (O)	1.03	**21**	1.6	0.51	20	**153**	0.06	**130**	26	46	0.9	**3.3**	80	104
Astico river fan (MC1)	2.02	**21**	2.1	0.25	**20**	59	0.08	47	38	49	0.37	**3.4**	**203**	116
Prealpine river fan (MC2)	0.79	12	1.6	0.86	15	76	0.26	48	45	114	0.4	**3.4**	81	110
Leogra-Timonchio river fan (MV1)	2.39	**25**	1.7	0.73	**32**	**153**	0.11	**120**	55	45	0.44	**2.7**	**157**	140
Agno-Guà river fan (MV2)	1.23	**35**	1.5	0.44	**51**	**190**	0.08	**160**	36	57	0.3	**2.6**	**146**	127
North-eastern coastal dep. (DA)	0.81	10	0.1	0.25	5	19	0.74	8	34	44	0.1	**1.2**	15	56
Southern coastal dep. (DS)	1.23	**23**	0.9	0.25	16	89	0.13	70	56	54	0.68	**5.8**	61	**181**

Table 21.3 Background values in depositional and physiographical units of Veneto (mg/kg). In bold, values exceeding limits for residential sites according to Italian Environmental Code

Depositional/physiographic unit	Sb	As	Be	Cd	Co	Cr	Hg	Ni	Pb	Cu	Se	Sn	V	Zn
Alps on crystalline and metamorphic basement (MA)	2.07	16	1.1	0.58	19	59	0.41	44	90	46	nd	nd	79	**153**
Alps on dolomite (DC)	2.17	**27**	1.4	1.70	**31**	77	0.22	60	96	43	0.56	**3.0**	**110**	**170**
Alps on silicates (DS)	1.85	11	nd	0.66	**27**	71	0.34	33	63	64	nd	nd	nd	110
Alps on Werfen Form. (DW)	2.54	**31**	**nd**	1.80	**22**	74	0.69	42	99	30	nd	nd	nd	**300**
Prealps on hard limestone (SA)	2.2	**26**	**2.8**	**3.40**	**30**	121	0.45	80	**130**	62	1.31	**5.6**	**210**	**245**
Prealps on marly limestone (SD)	1.83	**22**	**2.1**	1.98	**29**	**164**	0.29	101	**126**	73	0.81	**2.7**	**120**	**200**
Prealps on basalts (LB)	1.14	11	1.8	0.25	**61**	**211**	0.10	**162**	48	94	0.62	**3.0**	**180**	**165**
Hills (RC)	1.95	**22**	**2.2**	1.00	**32**	109	0.22	88	47	109	0.61	**3.4**	**130**	140
Tagliamento river deposit (T)	nd	14	nd	0.62	12	67	0.09	38	33	44	nd	nd	nd	86
Piave river deposit (P)	0.96	13	1.7	0.64	15	61	0.26	45	36	**186**	0.5	**4.0**	87	113
Brenta river deposit (B)	2.4	**36**	**2.1**	0.06	15	64	0.67	38	54	110	0.31	**7.8**	86	144
Adige river deposit (A)	1.51	**50**	1.2	1.17	19	106	0.32	92	46	83	0.7	**3.7**	63.5	**155**
Po river deposit (O)	1.35	**31**	1.5	0.60	19	143	0.08	**120**	35	63	0.9	**3.4**	78	111
Astico river fan (MC1)	1.75	18	1.6	0.66	**23**	83	0.31	64	61	103	0.4	**4.4**	**182**	137
Prealpine river fan (MC2)	0.79	12	1.6	0.86	15	76	0.26	48	45	114	0.4	**3.4**	81	110
Leogra-Timonchio river fan (MV1)	2.77	**26**	1.5	0.86	**35**	146	0.16	116	106	86	0.37	**6.4**	**140**	**200**
Agno-Guà river fan (MV2)	1.65	**41**	1.5	0.59	**49**	**180**	0.10	**161**	56	**171**	0.72	**2.9**	**146**	**164**
North-eastern coastal dep. (DA)	0.52	12	0.2	0.25	3	11	0.85	8	51	58	0.1	**5.7**	20	67
Southern coastal dep. (DS)	1.23	**23**	0.9	0.25	16	89	0.13	70	56	54	0.68	**5.8**	61	**181**

For antimony, mercury, lead, copper and selenium, no pedo-geochemical and background values exceeding the legal threshold concentrations for residential sites occur in any depositional or physiographic units. For lead and copper, 2 units exceed the limits allowed by law.

For cadmium, pedo-geochemical and background values exceeding the threshold occur only in prealpine areas on hard limestone. In addition, values close to the threshold are observed in all prealpine units in soils developed from marly limestones.

Arsenic, beryllium, cobalt, chromium, nickel, vanadium and zinc values exceed the threshold concentration in many units in both the upper and deeper layers, with a significant area within the region being involved.

In all the depositional units of the Veneto region, the situation for tin is noteworthy: in all units, the background values are above the threshold. In the Brenta river unit, the maximum values are more than seven times higher than the limit.

The units with the highest number of both pedo-geochemical and background values that exceed the threshold limits are the Prealps on basalts and Prealps on limestones units in the mountain areas and the Agno-Guà and the Leogra-Timonchio river fan units in the plain, which receive alluvial deposits from the alteration of basalts, in which the concentration of zinc, nickel, chromium, cobalt, arsenic, tin, and vanadium is significantly higher than in sedimentary rocks (Alloway 1995; Kabata Pendias 2001). Values exceeding the limit for chromium, nickel, cobalt, and vanadium often occur in the same unit.

Pedo-geochemical and background values for arsenic that exceed the limit according to the law occur in Adige, Po, and Brenta deposits. This is very significant, as the area is very wide and the toxicological characteristics of the element lead to a special warning.

In the mountain area, the unit where the values of fewer metals exceed the limits is the Alps on crystalline and metamorphic basement (MA), where only the values for zinc surpass the limit.

For many elements, no significant difference between their concentration in the upper and deeper layer was found, which is an evidence that the deposition and accumulation processes are not so diffuse in the regional territory. For some metals, such as copper, lead, mercury, and zinc, and in some units, a few cases of an upper/deeper layer concentration ratio higher than 2 occur, mainly due to diffuse pollution through deposition of traffic emissions or fertilizer and pesticide distribution by farmers.

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Chapter 22
Markers, Indicators of Soil Pollution

Monica Butnariu

Abstract As an interface between the earth's crust, atmosphere, and hydrosphere, soil is a non-renewable resource that has multiple functions: biomass production, storage, filtration, and transformation of organic and mineral matter; source of biodiversity, habitats, species, and genes; environment for humans and their activities; and source of raw materials. Impact of pollution on soil quality has increased due to population growth and extensive exploitation of natural resources. Soil pollution destroys the physical, chemical, and biological balance, which ensures soil fertility. Soil pollution can inhibit enzyme activity, reducing the diversity of fauna and flora. The degree of retention of pollutants is influenced by the presence of other pollutants and their concentration, quantity of oxygen, humidity, temperature, pH, nutrients, bioaugmentation, products of co-metabolism, and so on.

Keywords Soil • Pollution • Ecosystems • Indicators • Plants • Biological activity • Biomonitoring

22.1 Soil Quality

Soil is a dynamic system, essential for human activities and ecosystems. The term "soil quality" themselves refers mainly to the agricultural productivity (fertility). Processes that can impact soil quality are: average emissions (industry and traffic); farming techniques (use of fertilizers and pesticides organic/mineral); and ground waste deposition. In general, the rate of pollutants production and dispersion exceeds the natural processes of biodegradation. Soil is a "living organism," and therefore training and development, and its evolution take place under the action of physical, chemical and biological factors. The fertility of soil ensues from these factors; it differs from rock that was formed under the influence of pedogenetic factors.

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_22

Soil is a reservoir that accumulates pollutants from the air and water and is a natural interface between different systems (hydrosphere, biosphere, geosphere, lithosphere, and so on), and therefore constitutes an environment that can be integrated as a complex sorbent having specific properties. Soil is a component of the rural and urban environment, acting as a matrix with complex functions that constitute a two-way relationship with potential contaminants. Soil contains 93 % minerals and 7 % bio-organic substances or 85 % humus (structure), 10 % roots, and 5 % edaphon (soil organisms).

The 5 % of the total living creatures in soil are represented by 40 % fungi, 12 % earthworms, 5 % macro fauna, and 3 % micro fauna. The total living creatures in soil represent 0.35 % of the total weight of soil, but their importance for soil fertility is considerable and there are legitimate concerns about the biological balance (Postma and Lynch 2012).

Soil creatures belong to the flora and fauna and can be grouped into micro flora (algae, fungi, actinomycetes and bacteria), macro flora (plants with underground organs, roots, stems), micro fauna (protozoa: rhizopode, flagellates, ciliates), and macro fauna (flat worms and cylindrical, nematodes, enchitreide, lumbricide, insects, vertebrates). In this community, the conventional relationships are living together, prospering (metabiosis), mutual support (symbiosis), interdependence (parasitic), etc. Processes occur as a result of the activity of soil organisms' influence on fertility and hence on plant production (Sheng et al. 2012).

The complexity of biological and biochemical processes, assets, and basic soil in agrotechnical terms comprises: the formation of humus (humification), mineralization of organic matter, and release of elements used for plant nutrition (ammonification, nitrification and denitrification); enzymatic activity soil relationships between plant roots and soil microorganisms (nitrogen fixation); associations between soil microorganisms (commensalism, proto-cooperation, symbiosis, competition, amensalism, parasitism or predation); and the interactions between plant roots (favorable or antagonistic-*biochemical* inhibition /allelopathy/ exhibited) (Mavi et al. 2012).

The highlights of sustainable agricultural development schemes are: the utility planting of agroforestry belts to prevent erosion, protective effects, agrobiocenotic stability and balance, biodiversity and prevention of pollution by pesticides, etc. In open field farming system with a warming climate, the presence of pollutants and pests presents risk/disaster, stressing the importance of nurturing and the qualitative quantitative and qualitative potential of shelterbelts of the agroforestry farming system.

Under the global warming and the aridity conditions, the protective forest farm was recommended to control naturally the population of the oat leave beetle (*Oulema melanopus L.*) and limit the populations of other pests, such as aphides (*Sitobion avena Fabr*. and others) and thrips (*Haplothrips tritici* Kurd.) to levels below the economic damage threshold.

In terms of the biodiversity, the qualitative importance of the protective agroforestry farming system for biological pest limitation was highlighted as a model of sustainable and clean technology, as compared with the open field agriculture, conditions, and pest attacks in agroecoclimatic biocenoses, representing actual risk and disaster, which require treatment with insecticides.

Soil quality can be estimated by observing/measuring various properties/ processes (Butnariu and Goian 2005). Indicators can be used to determine soil quality indices.

Indicators should be easy to measure, cover the most extreme scenarios (soil types), including temporal variation, and be sensitive to environmental changes and soil management (Faria and Young 2010). Their selection should cover at least two major groups of flowering plants:

- The monocots species: *Avena sativa, Hordeum vulgare, Lolium perenne, Oryza sativa, Secale cereale, Sorghum bicolor, Triticum aestivum* and *Zea mays*.
- The dicotyledonous species: *Brassica campestris* Var. *Chinensis, Brassica napus* ssp. *napus, Brassica Rapa* ssp. *Rapa, Lactuca sativa, Lepidium sativum, Lycopersicon esculentum, Phaseolus aureus, Raphanus sativus, Sinapis alba* and *Trifolium ornithopodioides*.

Current climate changes, farm systems and technology trigger changes in agro-ecological culture. These changes include effects on soil and on crop development caused by technological mistakes, pollution, drought and heat, storms, torrents, landslides, floods and changes in the structure and abundance entomofauna pests able to destroy agricultural ecosystems. Geochemical environment is a result of living matter interaction with the local geochemical environment.

This interaction is reflected in the local route of atoms (biogenic migration).

Under the global warming and the aridity conditions, the protective forest farm was noted to control naturally the population of the oat leave beetle (*Oulema melanopus* L.) and limit the populations of other pests, such as aphides (*Sitobion avena* Fabr. and others) and thrips (*Haplothrips tritici* Kurd.) to levels below the economic damage threshold. In terms of biodiversity, qualitative importance of the protective agroforestry farming system for biological pest limitation was highlighted as a model of sustainable and clean technology, as compared with the open field agriculture, conditions, and pest attacks in agroecoclimatic biocenoses, representing actual risk and disaster, which require treatment with insecticides.

This delineation is not clear, because the accumulation of natural chemical elements is greater or less in living organisms (Butnariu 2012b). Cycles of chemical elements (geochemical cycles) have two phases: accumulation of pollutants into the structure of living systems and their release from dead organic matter. In the course of these cycles, there is a permanent exchange of pollutants between the soil, water, vegetation, and the lower troposphere. Macro elements recycling may reach high values compared to trace elements. Toxic cycles are based on the pollutants' course. There are antagonistic microorganisms, those that detoxify and others that enhance toxicity (Cytryn et al. 2012).

Metal pollution occurs in areas where large deposits are present on soil surface, but also where industrial pollution occurs continuously (Garrido et al. 2012).

The biogeochemical functions of living matter are mainly accumulation functions whose occurrence may or may not be dependent on the environment.

Living organisms accumulate pollutants when these are at large concentrations, and consequently the chemical composition of the plant reflects the mineral composition of the soil. Flora's tissues in the vicinity of metal areas has a higher metals concentration as compared to same species growing in environments with low metals concentration. These phenomena are based on the plant's ability to absorb the atoms of elements with low/null physiological importance when their concentration is high (Butnariu and Goian 2005). The plants accumulate pollutants selectively even and where they have low concentrations in biota. So, moreover to its fundamental physiological significance, a greater understanding of the stress response and the factors that modulate it may prove useful in understanding the significance for accumulates elements and in developing new approaches for biomonitoring system. (Schreck et al. 2011). The urochordates or tunicates [Ascidians (Sea Squirts)] accumulate vanadium found at low concentrations and use it in the synthesis of respiratory pigments. Diatomee *Phaeodactylum tricornutum* accumulate iron from the environment. There are circumstances where selective accumulation has no biological significance and the organisms are termed indicators of pollutant concentration.

Relationships among pollutants are based on multiple synergistic/ antagonistic interactions. The relations between abiotic and biotic factors are represented by specific composition, population density, and multiple interactions in ecosystem structure (Antiochia et al. 2007). Relationships between pollutants and abiotic factors are presented in interactions, changes in transport, transformation activities, etc., and are represented by alterations in specific composition, population density, accumulation, or reduction of pollutants.

22.2 Identifying Groups of Lichens, Mosses and Plants, Bacteria, Arthropods and Some Marker Enzymes, Considered Bio Product and Soil Quality Indicators

22.2.1 Lichens

Lichens represent an important species of bio-accumulators due to their ability to uptake pollutants from soil. Being highly sensitive to pollutants, lichens are used as bioindicators for different categories of pollutants: SO_2, NO_X, HF, Cl_2, O_3, peroxyacetic acid (PAA), metals, radioactive elements (Gupta and Igamberdiev 2010), fertilizers, pesticides and herbicides. For example, *Cladonia rangiferina* species can be used as an accumulative bioindicator of U, Fe, Pb and Ti. Other lichens, *Parmelia physodes* (L.), *Parmelia caperata* and *Evernia prunastri* (L.), are the best bioindicators species for specific monitoring of lead pollution.

Mercury is accumulated by lichens, such as *Alectoria capillaris, Alectoria tremontii, Hypogymnia physodes, Cladonia sp.* and *Collema sp*. The best known lichen bioindicator is *Hypogymnia physodes*.

22.2.2 Bryophyta (Mosses)

Mosses are also known to be high sensitive to pollutants. It is known that the number of bryophytes species has decreased significantly in urban areas and polluted industrial facilities. Some moss species have disappeared and the individuals of others have reduced in number (and biomass) in their distribution area (Dragović and Mihailović 2009).

Pleurozium schreberi, Hylocomium splendens and *Hypneum cupressiforme* were studied for pollution biomonitoring of eight metals (As, Cd, Cr, Cu, Fe, Pb, Ni, V and Zn) in Northern Europe and observed that react positively to increasing the concentration of metals. Mosses were found to accumulate radioactive elements more intensely than higher plants (Korobova et al. 2007). *Pleurozium schreberi* was used to monitor the precipitation of La, Zr, etc. as a result of nuclear tests, and species such as *Ceratodon* species, *Tortula ruralis* and *Bryum argenteum* were used to biomonitor concentrations of the radionuclide ^{137}Cs following the Chernobyl accident (Suchara et al. 2011). Testing bryophytes, an order of toxicity was established for some metals: Hg > Pb > Cu > Cd > Cr > Ni > Zn (similar to flowering plants).

Some moss species have the ability to accumulate metals up to extremely high concentrations. *Hylocomium splendens* originating from a copper mine, accumulated Pb, Cd, Cu, Zn at a concentration of 17,320 ppm (e.g., in comparison with the community of higher plants *Picea* 349.5 ppm, *Clintonia* 548.5 ppm, in the same environment) (Balabanova et al. 2010).

22.2.3 Higher Plants Bioindicator

Flowering plants and herbaceous species are known as accumulators. Species such as *Lolium perenne* L. and *Lolium multiflora* L. (plants common in parks, roadsides, and highways) are suitable as indicators of pollutants exposure. In addition to metals, these plants are indicators of sulphur and fluor. Additional grass species used as pollution bioindicators are: *Melandrium album* for Pb, *Thlaspi arvense* for Ni, Zn and *Solidago canadensis* for Pb. Species such as *Artemisia vulgaris, Calamagrostis epigeios, Chelidomium majus, Plantago major* and *Poa annua* can also be used as bioindicators of metals. *Equisetum arvense* plants were suggested as bioindicators of mercury, based on the research of the destroyed area of St. Helens volcano (USA) (Falk and Briss 2011) as well.

Achille milefolium species, *Artemisia vulgaris*, *Plantago lanceolata* and *Amaranthus retroflexus* can be used as bioindicators for V and Zn. The species *Hypericum perforatum, Urtica, Hedera helix* show high concentrations of Pb, Cu, Zn, Cd, Hg, indicating increased concentrations of these elements. Plants such as *Vaccinium vitis* and *Vaccinium myrtilus* may indicate high levels of Cd, Mn and Pb.

Plantago lanceolata, since it is common in the urban and the rural areas and its leaves are large enough for analysis purposes, is used as a bioindicator. This specie was classified as an indifferent pseudo-metallophytes, which is able to grow on contaminated soils without abundant presentation or special vitality. Plants are systems designed to give an early warning of soil changes. Plants' early and massive reaction to the presence of pollutants through visible lesions is a good indicator of pollution (Hale et al. 2001, 2010).

22.2.3.1 Deciduous Trees and Shrubs

Leaves of deciduous trees accumulate pollutants from surrounding areas (roads and nearby factories) from soil and directly from air. The more sensitive species are considered to be *Betula pendula, Fraxinus excelsior, Sorbus aucuparia, Tilia cordata,* and *Malus domestica* (Franzaring et al. 2010). Current pollution effects can be observed on their leaves in various forms such as: small scorched patches, following acid rain; pale discoloration warning of the presence of sulfur dioxide, chlorine, fluorine, ozone, lead, etc.; expanding discoloration that turns into necrosis in parallel with increased pollution; and finally underdevelopment and malformation of leaves that indicate pollutant rich toxicity thresholds.

In the case of conifers and broadleaved evergreen leaves such as *Viburnum ritidophylum* the effects of pollution are presented throughout the growing season, similarly to deciduous plants.

22.2.3.2 Accumulator Indicator-Regarded Resistant Species

The following species are regarded as resistant (through hyper accumulation): *Eleagnus angustifolia, Populus canadensis, Salix Alba,* and *Sambucus nigra* (Komárek et al. 2007).

Relatively resistant species that accumulate pollutants are *Carpinus betulus, Quercus robur, Fagus sylvatica*, *Quercus palustris, Acer saccharum* and *Platanus acerifolia*.

For example, *Platyphyllos betula* species are indicative of beryllium soil contamination (Manousaki and Kalogerakis 2009). Trees that accumulate pollutants continuously present the morphological or the biochemical alterations.

Bioindicative information from trees is persistent, as long as they live. Table 22.1 summarizes the principal indicator plants for micro and ultra-micro elements pollutants (Butnariu 2012a).

These changes reflect the progress of the pollutants' stomata penetration, expressed as magnesium separation from the chlorophyll molecule and its transformation into phaeophytin (strongly correlated to humid conditions).

The uptake rates of the ions was in the order B < Fe < Mn < La < Zn < Ga < Cu for the tops and B < Mn < Fe < Zn < La < Cu < Ga for the roots. In the roots, the uptake rates of La, Cu and Ga was exceptionally high. The toxicity of the ions tested

Table 22.1 Indicator plants for microelements and ultra-micro elements and the significant symptoms/diseases

Metal	Indicator plants for micro and ultra-micro elements	Symptoms/diseases
Ag	*Robinia pseudaccacia*	Cause injury to trees and shrubs, chlorosis.
B	*Rosa rugosa*, *Acer campestre*, *A. hippocastanus*, *Morus alba, Platanus hybrida*, *Salix alba*, *Sambuccus nigra*	Susceptible to disease and bark beetle attacks, developed chlorotic spotting.
Be	*Betula platyphylla*	Display white flecks much like freckles.
Bi	*Robinia pseudaccacia*	Genotoxicity induced by the colloidal bismuth.
Ce	*T. occidentalis, Aesculus hyppocastanus*	Translocation into newly grown leaves.
Co	*Sophora japonica*	Problems that looks similar to fungal leaf spots, particularly those of fungus Marssonina.
Cr	*Koelrenteria paniculata*	Cr(VI) is highly toxic and mobile whereas Cr(III) is less toxic. Alterations in germination process as well as in growth of roots, stems and leaves, which may affect total dry matter production.
Cs	*Rosa rugosa*	Ultrastructural malformations of cell components.
Eu	*Rosa rugosa, Thuja occidentalis*	Aberration of cell cycle, disruption of cytoskeleton, deregulation of gene expression related with programmed cell death.
Fr	*Sophora japonica*	Has no biological role and is most likely extremely toxic, but in large quantities can provoke developed chlorotic spotting.
Ga	*Rosa rugosa, Thuja occidentalis*	Leaves did not unfold completely, had a needle shape.
La	*Rosa rugosa;*	Has a low to moderate level toxicity, but in large quantities can provoke developed chlorotic spotting.
Mo	*Robinia pseudaccacia*;	Leaf blade formations (whiptail) are typical visual symptoms.
Ni	*Rosa rugoza, Sophora japonica, T. orientalis, A. hyppocastanus*	Single white bands perpendicular to leaf veins appeared on primary leaves.
Sb	*Thuja occidentalis, Aesculus hyppocastanus*	Did not develop diagnostic fully expanded true leaves, or at harvest, these leaves were dead.
Sn	*Thuja occidentalis*	Susceptible to bark beetle infestations and display needle mottling and loss.
Th	*Rosa rugosa*, *Thuja occidentalis, Abies alba*, *Picea excelsa*	Has no biological role; most likely extremely toxic; passive absorption implies diffusion uranyl ions, organically bound Th^{4+} by soils endodermis of roots, does to their imperfect selectivity, increased permeability cell membranes.

(continued)

Table 22.1 (continued)

Metal	Indicator plants for micro and ultra-micro elements	Symptoms/diseases
U	*Rosa rugosa*, *Thuja occidentalis Abies alba*, *Picea excelsa*	Depleted on growth of tree, one of species showed evidence of hormesis.
V	*Rosa rugosa*, *T. occidentalis*, *R. pseudaccacia*, *A. hyppocastanus*	Trees lose leaves prematurely and look rather sickly.
W	*Robinia pseudaccacia*	Inhibitor of molybdoenzymes, it antagonizes molybdenum for Mo-cofactor, of these enzymes.
Zn	*Robinia pseudaccacia*	Causes severe Fe-deficiency chlorosis.

was in the order $Mn < Zn < B < Fe = Ga < La < Cu$ in the tops and $Mn < Ga < Zn < Fe = La < Cu < B$ in the roots (Wheeler and Power 1994).

These changes reflect the progress of the pollutants' stomata penetration, expressed as magnesium separation from the chlorophyll molecule and its transformation into phaeophytin (strongly correlated to humid conditions). The effects of pollution on bioindicator trees are apparent at the individual level in the form of morphological alterations (discoloration and necrosis), morphological changes (smaller leaves, malformed, shorter internodes, smaller flowers or miscarriage), premature leaf fall and reductions in crown transparency and branches desiccation. The correlation between pollution and accumulation in leaves show that tree leaves accurately reflect soil pollution and its quality.

Deciduous trees are a biologically effective "filter." Above a certain threshold of pollution, forests become vulnerable either directly though disrupted metabolic processes or indirectly through ecological imbalances.

22.2.3.3 Conifers

In comparison with deciduous trees, conifers are more sensitive indicators due to their leaves' (needles) life span (3–4 years) and their exposure to pollution also in winter periods.

Sulphur dioxide (SO_2) and hydrofluoric acid (HF) pollution may be indicated by direct needles analysis (as conifers are well known accumulators). For example, *Pinus, Picea abies, Pinus banksiana, Pinus nigra, Pinus silvestris, Pinus strobus* and *Larix decidua* are sensitive to SO_2 pollution (Acquaviva et al. 2012), while *Abies alba, Picea abies, Pinus ponderosa, Pinus silvestris* and *Pinus strobus* to HF (Samecka-Cymerman et al. 2006).

When dealing with metals, *Picea abies, Pinus silvestris, Pinus nrigra, Taxus baccata* and *Thuja occidentalis* are particularly suitable as indicators of Fe, Mn, Cu, Pb. Zn, Cd, Ag and Hg pollution. *Taxus baccata* plants were used to assess metal pollution and content (Pb, Cu, Cd, Ni, Cr, Hg) indicating a pollution reduction along the trees' development (Antiochia et al. 2007). Some conifers species, *e.g., Picea abies, Pinus banksiana and Pinus strobus,* were used to indicate pollution by photochemical oxidants, (Gupta and Sinha 2007).

The concentrations of uranium in the tissues of the conifers decreases in the following order: roots >> stems > twigs > needles.

22.2.4 Microorganisms Role

Soil biological activity is largely concentrated in the topsoil (~30 cm). In the topsoil, biological components occupy a small fraction (<0.5 %) of the total volume and can reach up to 10 % of the total soil organic matter. These biological components are soil organisms, especially microorganisms. The soil contains a large and complex microbial diversity whose activity is essential for soil processes.

Direct detection of specific DNA sequences from soil bio-communities is an effective way to gather information on soil processes. However, soil activity does not depend on the number of genes present in the microbial community, but on their expression.

One approach is to extract genes directly from soil and detect the mRNA that is present (messenger RNA, the first transcription product). Soil surface heterogeneity is conveyed by colloidal matrices (mostly clay and organic matter, such as humus) able to adsorb nucleic acids, and enzyme inhibitors (mostly humic acids and ubiquitous ribonucleotids), which presents technical difficulties (Ahmad et al. 2012; Dong et al. 2012).

Heterotrophic organisms are those responsible for biosphere recycling, exploiting favorable thermodynamic chemical reactions to obtain energy and carbon from dead biomass. Their genesis lies in the oil fields as well as in microbial biodegradation of residual hydrocarbons in soil (Meynet et al. 2012). Microorganisms have ecological significance based on their ability to utilize gaseous or liquid hydrocarbons, solid aliphatic series, aromatic and asphalt, a process called bioremediation (Briones 2012).

Among the microorganisms involved in biodegradation of pollutants one can find bacteria, fungi, yeasts, and algae, bacteria and fungi being the most important groups.

22.2.5 Bacteria and Fungi ("The Benevolent Scavengers of Nature")

Among bacteria domain, aerobic bacteria such as: *Achromobacter sp., Acinetobacter sp., Actinomyces sp., Alcaligenes sp., Arthrobacter sp., Bacillus sp, Brevibacterium sp., Corynebacterium sp., Flavobacterium sp., Micrococcus sp., M. sp., Nocardia sp., Pseudomonas sp., Spirillum sp., Serratia sp., Rhodococcus sp.,* and *Vibrio sp.*, followed by anaerobic ones such as: *Geobacter metallireducens, Thauera aromatica,* *Desulfococcus multivorans, Clostridium sp.,* and *Desulfobacterium cetonicum*, are used as indicators. For example, the survival effect (toxicity) of genus *Rhizobium* under pollutant stress has been confirmed by many authors. When *Bradyrhizobium japonicum* was added (9×10^8 cells/mL) to two soils supplemented with different doses of sewage sludge, less than 1 % of the bacteria were present in both soils, after 42 days (Shentu et al. 2008). These drastic reductions were attributed to metals presence in sewage sludge.

As decomposers, fungi are often associated with woody vegetation (tolerating large amounts of tannins). Consequently, mushrooms are an organic part in the formation of soils and also playing a fundamental role in soil food chains. From the biological perspective, the parasitic species too are valuable, eliminating weak and sick individuals.

Symbiotic associations through mycorrhiza, ensure the lives of many trees, shrubs and herbaceous species. Fungi are natural indicators of pollution. Mushrooms easily accumulate metals, pesticides and radioactive substances. Chemical analysis of fungi reveals the "black box" of pollution status of a certain habitat, e.g.: mushrooms are highly sensitive to acid rain (absent when acid rain is present).

Fungi involved in hydrocarbon degradation are part of the genera: *Alternaria, Apergillus, Cephalosporium, Cladosporium, Fusarium, Graphium, Geotrichum, Mucor, Penicillium, Rhizopus* and *Trichoderma*. Genus *Achromobacter* was used in the degradation of carbazole and phenanthrene (*Achromobacter xylosoxidans*).

Of the genus *Bacillus* species *Bacillus firmus* is remarkably able to degrade completely acenaftilena, anthracene, benzo[β]fluoranthene and reduce concentrations of naphthalene, dibenzo[a,h]anthracene and indeno[123–c,d]pyrene (Schneider et al. 1996). *Bacillus licheniformis* is able to degrade completely anthracenebut only to reduce other hydrocarbon concentrations. *Bacillus subtilis* completely degrade acenaphthene, anthracene and benzo[b]fluoranthene and reduce the concentration of naphthalene, indeno[123–cd]pyrene and toluene (Magyarosy et al. 2002). *Bacillus pumilus* is effective in achieving the biodegradation of hydrocarbons degradation rate of 86.94 %. *Brevibacterium* genus isolated from soil degraded 40 % of the hydrocarbons within 12 days. *Mycobacterium* species that are able to degrade hydrocarbons are *M. lacticola, M. luteum, M. phlei* and *M. rubrum*.

The last three species degrade gasoline, oil and paraffin (Liang et al. 2011).

Of the *Pseudomonas* genus is *Pseudomonas alcaligenes* noted that degrades naphthalene, benzo[b]fluoranthene and indeno [123–cd] pyrene and reduce the quantities of anthracene, benzo[a]anthracene and benzo[ghi]perylene and *Pseudomonas putida* which has the ability to degrade organic solvents such as toluene or naphthalene (Björklöf et al. 2009) at fungi the genera *Aspergillus*, *Penicillium, Paecilomyces* and *Fusarium* are able to biodegrade hydrocarbons. *Penicillium* genus, has the ability to degrade 90 and 75 % phenanthrene (Vacca et al. 2005), and *Cladosporium resinae* species is able to degrade aliphatic hydrocarbons.

Genus *Rhizopus* (filamentous fungi, soil, fruits, vegetables and stale bread) was isolated and studied in terms of the ability of biodegradation of hydrocarbons (Chikere et al. 2011).

Biodegradation takes place in several stages and is not the result of one specific body (many strains of microorganisms acting synergistically). Between some species as *Nocardia* and *Pseudomonas*, which can degrade cyclohexane association is established phenomenon of synergism. *Nocardia* by using ciclohexanone, produce intermediate compounds, which are taken by Pseudomonas; and *Pseudomonas* produce growth factors (biotin), required *Nocardia* bacteria growth (Christ et al. 2005).

Penicillium and *Rhodococcus* have been shown to be effective in the degradation of polycyclic aromatic hydrocarbons, while *Rhodococcus* with *Aspergillus terreus* had synergistic relationships (Kılıç 2011). Microorganisms and microbial communities are an integrated measure of soil quality, an aspect which cannot be obtained by physical or chemical measurements and / or analysis of large organisms. To prevent irreversible environmental consequences, bacterial parameters were found to be sensitive to pollution, may be included in evaluation studies and monitoring strategies for contaminated soils.

22.2.6 Invertebrates

The group of invertebrate animals found in soil is made up of worms and arthropods.

The species of *Arthropoda* living in soils comprises different organisms (arachnids, myriapods, insects, etc.) that feed on plant debris or fungus mycelium. Arthropods (*Aranea, Acari* and *Insecta*) in soil, especially mites, are ubiquitous in terrestrial species.

Mites contribute indirectly to the decomposition cycle of organic matter and nutrients, regulating other populations of invertebrates. Animals in soils are key regulators of nutrients in the soil report. Most species of *Mesostigmata* are sensitive to pollution. Information obtained about arthropod species can be used to characterize almost any aspect of an ecosystem accurately (Antunes et al. 2011).

22.2.7 Metabolic Substances

There are many metabolic substances (bioproducts) that can be used as indicators of soil quality; these include sterols, antibiotics, proteins, enzymes, etc.

22.2.7.1 Ergosterol

Ergosterol (ergosta-5,7,22-thrien-3β-ol) is a vital component and the main endogenous sterol cell membrane of fungi, actinomycetes, and some microalgae (micosteroli).

Microorganisms are able to synthesize compounds isoprene residues bonds with acetic acid CoA participation. The most common micosterols are ergosterol and other sterols zimosterolul in smaller amounts. Ergosterol concentration is an indicator of increased fungal activity of organic compounds and mineralization activity.

Metals and some fungicides reduce metabolic activity by between 18 and 53 %, but do not affect ergosterol content. Other fungicides reduce the ergosterol content of biomass (Robine et al. 2005). Research conducted in grasslands and arable soils have established a link between amount of ergosterol in the hyphae of fungi and soil stability.

22.2.7.2 Glomalin

Glomalin is a glycoprotein produced by the hyphae and spores of arbuscular mycorrhiza fungi (*Glomus*) in soil and roots. Glomalin store carbon in the form of protein and carbohydrates (glucose). Glycoprotein penetrates organic substances, which are attached to particles of sand or clay. Glomalin contains about 30–40 % carbon to form associations with soil. This material aerates grained soil and fixes the carbon into it, and increases air permeability and water storage capacity in the soil. Due to glomalin, soil structure is favourably changed. Glomalin-related proteins in soil have been studied as a biochemical marker in the ground, mainly because of their stability. Glomalin is a complex substance, that is water-resistant to biodegradation, has adhesive properties (Vodnik et al. 2008), for the soil activated by photosynthetic plants (through root exudates, and in particular by root exudates of plants symbiosis producing mycorrhizal fungi). Mycorrhiza mushrooms biosynthesize phytohormones, which accelerates root development. Use of *Medicago sativa* plants inoculated with *Glomus mosseae* and *Glomus intraradices* showed a higher stability of unpolluted soil (1–2 mm) and the overall stability of soil was positively correlated with the soil and mycorrhizal root volume and low the non-mycorrhizal soil (Bedini et al. 2009). Polluted soil is poorly mycorrhizal and is low in glomalin.

22.2.7.3 Enzyme Activity

In general, the activities of soil enzymes change earlier than other parameters, thus representing early indicators of soil quality change. Methods for determining enzyme activities are more appropriate, offering indicative data in a shorter time than microbiological analyses of the soil biodegradative process.

Soil enzyme activities may be used to indicate the change in the plant-soil system, because enzymes are closely related to the nutrient cycle and soil biology and it is easy to quantify and integrate information about the status of microbial and physico-chemical properties of soil and changes in proportion to changes in the soil.

The enzyme locking mechanism is based on the reaction with amino pollutants, imino, and sulfhydryl protein, some metals competing with major elements, replacing them in metal enzymes. Other pollutants can harm cells and cause biochemical disorders, such as nitrogen and phosphorus mineralization, cellulose degradation, and nitrogen fixation. Studies of individual enzymes (with conflicting results) showed temporal and spatial variability (Garcia-Ruiz et al. 2009). Enzyme activity was associated with indicators of biogeochemical cycles, degradation of organic matter, and soil remediation processes, so that they can establish with other physical or chemical properties, soil quality. Enzymes are called indicators because they are closely related to organic matter, have physical, microbial activity and biomass of soil; they provide information on changes in quality and are evaluated quickly.

Enzymes have different origins (bacteria, fungi, plants, and macro invertebrates), different locations (intra or extracellular), different matrix association (alive or dead cells, clays or/and humic molecules), and various laboratory test conditions.

β-glucosidase (β-GLU) is an indicator of soil quality due to its importance in catalytic reactions for the degradation of cellulose, glucose being released as a source of energy to maintain microbial biomass and metabolic activity in soil. It plays a role in energy availability in the soil, which is directly related to the content of C and the ability to stabilize soil organic matter.

In general, microorganisms produce an enzyme complex where xylanases are associated with cellulases, β-GLU, etc. It protects the substrate mycelium, which lyses against other existing bacteria in the soil that could be used as a source of carbon and nitrogen, thus keeping it to air mycelium growth (Bonet et al. 2012). β-GLU activity is inhibited by the presence of metals and other pollutants.

Phosphatase (PHO). Phosphorus is essential for plant growth. Much is immobilized due to the intrinsic characteristics of the soil (pH) that affect nutrient availability, enzyme activity, and soil amendment equilibrium solid phase. PHOs are a group of enzymes that catalyze the hydrolysis of phosphoric acid esters and anhydrides, but participate in the metabolism of phosphorus compounds (nucleotides, sugar phosphates, and polyphosphates).

Because of their activity in acidic and alkaline soil conditions, phosphomonoesterases were the most studied.

PHO's role in the mineralization of soil organic phosphorus substrates. PHO activity in the soil can be influenced by soil properties (number of aerobic bacteria, ammonification level, the number of active bacteria in ammonification, nitrification degree, and the number of fungi).

PHO is a consequence of increased activity caused by the accumulation of quantities of organic matter and pollutants, representing a detoxification mechanism for microorganisms (Wang et al. 2012). Microorganisms in polluted environments are characterized by pronounced acid phosphatase synthesis, an activity that results in the formation of phosphates, used to precipitate cellular metals as metal phosphates.

Dehydrogenase (DEH) This enzyme catalyzes the release of the hydrogen ion (proton) from the molecular complex and is involved in redox processes. Its activity reflects good soil microbial activity (respiratory potential of soil microbiota). The sensitivity of DEH activity to pollution can be explained by the fact that the dehydrogenase is active inside living cells, intact, unlike other enzymes that act outside the cell. DEH activity was found to be sensitive to pollution with Cd, Pb and Zn (Wyszkowska and Wyszkowski 2010).

Intensity of the microbial metabolism in soil can be assessed by measuring dehydrogenases. Soil microflora activity is due to come, capable of multiplication and is the result of DEH's, which are components of the enzyme (indicator of biological redox systems).

Actual and potential activity due to the proliferation of living organisms and DEH interfere in H dislocation in the soil, being reductase. DEH activity is an indicator of overall soil biological activity. Determination of the activity is a global test of biological activity, DEH, reflecting the activity of microflora and anaerobic microorganisms, having the advantage that it can be applied to a number of samples.

Catalase (CAT) (the enzyme first investigated in soil) is produced by microorganisms and plants, and is characterized by high persistence. Its role is to break down toxic hydrogen peroxide, which is formed in the aerobic respiration of microorganisms being produced as a result of mitochondrial electron transport and due to various hydroxylation and oxygenation reactions. It correlates with the amount of humus, the pH, and the number of microorganisms in the soil. Accumulation, like the destruction of CATs in soil, is determined by mineral fertilization in strict interaction with the development of soil microflora. In soils deficient in nutrients and energy material, the degree of accumulation of CATs is increased as a result of mineral fertilization, the absolute level of this enzyme's accumulation in soils cannot be reached with high fertility.

DEH and CAT activities decrease with depth, due to reduced oxygenation (Cookson et al. 2007). T enzyme activities (β-GLU, PHO, DEH, and CAT) of polluted soils have values that differ from than normal.

22.3 Answer to Plant Defenses to the Soil Contamination

Phenolic compounds represent a group of secondary metabolites with antioxidant properties and are involved in plant adaptation to stress conditions.

During normal processes of growth and development, plants are subjected to various types of biotic and abiotic stress, such as drought, high salinity, mineral nutrient deficiency, ultraviolet light, extreme temperatures, hypoxia, and toxicity of metals, herbicides, fungicides, gaseous pollutants, and pathogen attack. Phenols are considered important biomarkers for phytotoxic effects of heavy metals and other pollutants. Increased production of phenolic compounds is probably a part of the defense mechanism of the plant.

Phenolic compounds are of interest because of their role in allopathic ecological processes, their role in a plant's protection against herbivores, and their involvement in the response to stress, such as competition between and/or interspecific to or pollution. Phenols are produced in the cytoplasm and form droplets in vacuoles, which later evolve into one vacuole filled with phenols.

Under these conditions of degenerating cytoplasm, organelles disappear, eventually leading to the release of cytoplasmic and/or vacuolar contents and mesophyll cell death.

Secondary metabolites are accumulated as a result of stress conditions. Impregnation of cell wall phenolic esters, suberisation of cores, and lignification defense responses appear to stabilize the cell wall architecture against degradation. Plants can synthesize and accumulate phenolic compounds, as a physiological response to soil contamination.

These compounds occur as a result of changes in various pathways of plant metabolism and not by submission in the external environment, because the epidermis (both cells and their external walls) are intact. In some regions of the leaflets, areas of necrosis are observed, cells having disintegrated after accumulation of phenolic compounds. The epidermis does not show significant changes in the general shape of epidermal cells or stomata.

In the fine sections (seen in the electronic microscope) in leaf mesophyll cells collected from unpolluted areas (witness), numerous chloroplasts with defined borders, with small dens formations, were observed. Cells have large central vacuoles (Gorshkova et al. 2010).

Sections through leaves harvested from polluted areas show varying degrees of disorganization in the mesophyll. In leaf mesophyll cells containing chloroplasts that upload large starch granules some of which are transient, cytoplasm shows signs of degeneration (Carpita et al. 2001). In some sections, there are sometimes electrono-transparent formations in the cytoplasm and vacuole. In most cells, there are electrondense deposits along the cell walls (Diotallevi et al. 2010). In many mesophyll cells of leaves collected from polluted sites, the vacuoles were larger than the control (these vacuoles push the cytoplasm to the cell wall). Therefore, the shape of the chloroplasts appears flattened (lenticular as compared to mesophyll cells from controls, harvested from unpolluted areas). In some cells, the vacuoles are filled with electrondense material, while in others they are completely transparent (Korbas et al. 2008). The tonoplastis remains intact in both cases, which suggests a continuation of various cellular components within vacuoles. Electrondense deposits, probably degenerate residues of vesicles, can be seen in intercellular spaces.

In leaves, along cell walls, compact electrondense material storage is observed, with some even being inlaid in the wall. These deposits are present in intracellular spaces and the cell periphery (Migocka et al. 2011). In a more advanced stage of degeneration, they were observed in mesophyll cells near the upper epidermis. They contain chloroplasts that the plastidial envelope tilacoid membranes degraded and system changes within the grain. Inside chloroplasts, electronodense particles are visible (Lindeboom et al. 2008).

Cellular organelles gradually degenerate as a result of cell death. At this stage of cell necrosis, no the form of organization remains, core is no longer observed, as mitochondria and vacuoles merge with the cytoplasm, leading to complete degeneration. Electrondense deposits are unevenly spread cells still adhering to the walls (McCann et al. 2007).

The presence of phenol compounds in the cell is not an unusual phenomenon for many plant species, but their precipitation in the cytoplasm and vacuole is an indication of impaired cellular metabolic pathways as a result of stress induced by various polluting substances (DalCorso et al. 2010). The presence of these deposits may be due to the fact that the properties of phenols change depending on the amount of pollutants in the environment (Simmler et al. 2010; Butnariu and Coradini 2012).

Some phenolic compounds accumulate around the chloroplast envelope and cytoplasmic vesicles, and others around the tonoplast. Sometimes, these compounds were observed even within cell walls (Yu and Jez 2008). The presence of phenolic deposits near the plasma membrane and double membranes surrounding organelles, chloroplasts, and mitochondria is consistent with subcellular sites of their biosynthesis. The appearance and accumulation of phenolic products in vacuoles and in the area apoplast (cell wall) have a role in eliminating the free radicals produced by cell metabolism (Balakrishna et al. 2009; Butnariu 2012a).

Flavonoids located near membranes prevent the lipid oxidation that affects them when subjected to the action of free radicals. Researchers have identified the role of antioxidant phenolic compounds' accumulation in leaf mesophyll cells in areas exposed to pollution, and suggest that they help reduce oxidative stress and limit the damage to the photosynthesis mechanism (Singh et al. 2012).

The accumulation of metal ions in cells stimulates the production of phenolic compounds, and therefore, the presence of metals (lead) could be one of the factors that determine the accumulation and precipitation of polyphenolic compounds in vacuoles, cytoplasm, or intercellular spaces (Bu et al. 2012; Butnariu and Giuchici 2011).

The effects of polyphenols occurring at the cellular level as a result of oxidative stress response are still unclear. While small amounts of polyphenols may be protective, their production in large quantities as a result of the sustained action of pollutants is lethal to cells, leading initially to microlesions, and subsequently to necrosis even in different areas, depending on the intensity of the action of pollutants.

Polyphenolic deposits are located near the cell wall, but inside it they appear in intercellular spaces and they adhere to the primary wall. Lead has an affinity to bind to pectin and cellulose, more easily than to hemicellulose (Rodríguez-Durán et al. 2011; Butnariu 2011). The middle lamella of the cell wall is composed of pectic substances in nature and primary cell wall contains mostly cellulose and hemicellulose (appearing as electronodense deposits in cell walls, binding reveals pollutants).

Lead acts as a pollutant, by binding to pectic substances in the middle lamella structure and the composition of the primary cell wall (Sayadi and Ellouz 1995).

Electronodense deposits in the intercellular spaces were also reported in maize (*Zea mays*). Their presence suggests the transport of lead through the cell wall apoplast, and precipitation and accumulation in these areas. The changes induced by pollutants are related to the sclerenchyma structure whose morphogenesis is visibly affected (Salgado et al. 2005). In addition to normal sclerenchyma fibers with uniform walls and moderately thickened and lignified areas, a thin-walled fiber, sometimes wavy, appears which reduces significantly the functionalities for supporting the stem (Tiveron et al. 2012). Necrotic cells within which large amounts of tannin are accumulated are observed adjacent to sclerenchyma beads.

Influence of pollutants leads to ultra-structural changes that are evident in all the analysed species. The most common changes are related to the accumulation of polyphenolic products in both leaf mesophyll cells and epidermal cells (Burk and Ye 2002). Polyphenols biosynthesis following exposure to stress can support the premise that these substances are major structural biomarkers that can be used to highlight the influence of pollutants on plants, both woody and herbaceous (Hale et al. 2001). As well as the presence of polyphenols (flavonoids), other ultrastructural changes were observed. Thus, chloroplasts are affected by the presence of pollutants, mechanisms that block starch leaching during the night (stroma accumulate, leading to the disruption of the membrane system), and other changes (Fini et al. 2011; Butnariu and Corneanu 2012). Impaired chloroplast photosynthesis efficiency decreases (as determined by blocking parallel with stomatal clogging ostioles solid deposits).

SOD analysis proves that the enzyme is present in media *Plantago media, P. lanceolata, Lotus corniculatus, Mentha sp., Potentilla anserina, Polygonum sp., Geranium sp., Linaria vulgaris* and *Cornus sanguinea*, and its level was significantly different depending on the amount of pollutant (Jozefczak et al. 2012). Pollutants induce synthesis of SOD in *Polygonum sp.*, where the level of the enzyme is over four times that in the control sample.

The species *C. sanguinea* and *Geranium sp.* that have the ability to defend themselves against the action of pollutants through increased synthesis of SOD, behave similarly, while *P. lanceolata, Mentha sp., P. anserine* and *L. vulgaris* have a different behaviour, since SOD synthesis is inhibited by pollutants. SOD can be considered as a marker of pollution, for some species, but in *Plantago, Mentha* or *Potentilla*, this indicator is not significant (Li and Hu 2005). For catalase, it is found that there is variability in terms of the constituent components. Considered as the next step in removing the reactive forms of oxygen, the catalase in different studied species is distinguished by intense catalase activity in *Polygonum sp.* and *L. vulgaris*, while the species *C. sanguinea, Plantago sp. and P. anserina* have reduced enzyme activity values.

Pollution significantly inhibits catalase activity in the species *Geranium sp. and L. vulgaris,* and stimulates it in the species *P. lanceolata, Mentha sp.* and *P. anserina*. The presence of cholinesterase indicates that in the species *Trifolium* *pratense* enzyme activity is more intense than in the species *L. corniculatus* (Keunen et al. 2011).

In conclusion, SOD may be a biomarker for species *Polygonum sp., Geranium sp.* and *C sanguinea* and catalase for *Mentha sp., P. anserina, L. vulgaris, P. lanceolata* and *C. sanguinea* (Roberts et al. 2004). For different degrees of pollution, enzyme activity (superoxide dismutase, catalase, and cholinesterase) is characteristic of each species.

22.4 Final Remarks

The management of contaminated soils using plants, microbes, and other biological systems to degrade/convert environmental pollutants under controlled conditions to a level at which they become harmless or that is lower than the limit set by regulatory authorities is an on-going challenge for researchers, industry, and regulators. Thus, the identification of indicators of soil pollution and bioremediation, applied for the rehabilitation of contaminated soil ecological reconstruction, provides an alternative that is feasible and economically and environmentally sustainable. In this context, we can use a number of biological agents that include both distributed heterogeneous microbial communities and plants with different origins. The sustainability of soil depends on the one hand on the characteristics of some physical, chemical, and biological properties that effect the soil's relative stability, and, on the other hand, how natural and anthropogenic factors act on it. Given the role of soil is actually an essential active mediator of the processes, which is the basis of life on earth, a complex biomonitoring system to identify and remove sources of pollution in order to maintain maximum ecological potential is necessary and important for soil quality.

Accurate biomonitoring is essential for anticipating risks to the environment and human health. In the future, further studies are needed to understand the genetic diversity of the microbial populations that are susceptible and tolerant to pollutants and the interactions between pollutants and soil microorganisms in natural conditions. There are several biological properties of the soil that can be used as indicators of soil quality, alone or in combination with other chemical or physical properties. However, they are far from universal and should be chosen according to the situation. From another point of view, there are many properties that are difficult to quantify and interpret, but require simpler and less costly observations, similarly, should be used and properties that are sensitive to changes in management. Appropriate strategies should be established for sampling and analysis with many variants results as essential factors to consider when using biological indicators as markers indicators of soil pollution.

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Chapter 23
Landsnail for Ecotoxicological Assessment of Chemicals and Soil Contamination – Ecotoxicological Assessment of Chemicals and Contaminated Soils Using the Terrestrial Snail, *Helix aspersa*, at Various Stage of Its Life Cycle: A Review

Annette de Vaufleury

Abstract To assess the fate and effect of pollutants in the environment, chemical measurements are efficient but not sufficient. Biological environmental indicators must also be used to provide information on environmental and toxicological or trophic bioavailability of soil contaminants. Among the biological indicators that can be affected by soil contamination, the ubiquitous landsnail species *Helix aspersa* (syn. *Cantareus aspersus*) is a primary consumer living at the soil-plant-air interface, which constitutes prey for many consumers, including humans. The rearing of *H aspersa* is possible under controlled conditions. This provides a year-round supply of eggs, juvenile, or adults for the ecotoxicological assessment of chemicals or more complex matrixes, such as sludges and contaminated soils. This chapter presents the field and laboratory methods available for using the common garden snail *H aspersa* to characterize the fate and effects of soil contaminants.

Keywords Bioindicator • Biomonitoring • Bioavailability • Bioaccumulation • Gastropod • Mollusk • *Cantareus aspersus* • Embryotoxicity • Polluted soils • Growth inhibition • Reproduction • Life cycle exposure

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_23

23.1 Introduction

Contamination is one of the threats to soil health, causing detrimental effects on the soil biota, reducing both the abundance and diversity of organisms, and disrupting soil functioning (Jeffery et al. 2010). Among the ecological indicators potentially affected by soil contamination, snails can be used to assess the fate and effects of contaminants at the soil-plant-air interface (Cortet et al. 2000). The common garden snail *Cantareus aspersus*, syn. *Helix aspersa*, is a pulmonate gastropod mollusc phytophagous, detritivorous included in various food chains and eaten by humans in some countries (Fig. 23.1). While being exposed to contaminants either by the plant they eat or the air they breathe, snails can also be contaminated by the soil through digestive (Gomot et al. 1989) and cutaneous routes (Gomot-de Vaufleury and Bispo 2000; Coeurdassier et al. 2002a). Due to their ability to accumulate some metallic trace elements (MTE), measurement of metal concentrations in snail tissues have been used for a long time to reveal field contamination (Hopkin 1989, 1993; Dallinger and Berger 1992). For such studies, wild snails sampled in the field are used in a passive biomonitoring approach.

The limitations of using wild snails include: (i) unavailability of data for their age and thus the duration of their exposure; (ii) the impossibility of comparing the bioavailability on various sites when snails of the same species are not found on these sites; (iii) possibility to perform only an *a posteriori* assessment of contaminants (i.e., when the pollutants are already in soils) and not an *a priori* assessment (i.e., before authorization of commercial use); (iv) they cannot be used to assess the toxic effects on physiological endpoints (such as hatching success, growth, or reproduction) that are needed to characterize toxicity of soil contaminants. To address such problems and extend the use of snails as environmental indicators either in the field or in the lab for the ecotoxicological assessment of chemicals and contaminated matrixes, since the 1990s we have developed a range of methods that are reviewed here.

Fig. 23.1 The garden snail *Helix aspersa* at various stages of its life cycle and some parasites or predators of its eggs, juveniles, or adults

23.2 Biological Material

Initially developed to study the endocrine regulation of the growth and reproduction of snails (Gomot and Gomot 1995; Gomot-de Vaufleury 2001), as well to promote snail farming, indoor and outdoor rearing methods (Fig. 23.2) of *Helix aspersa* and *Helix pomatia* (Gomot and Deray 1987; Gomot 1990) make available a year round supply of eggs, hatchlings, juvenile, and adult snails (Gomot-de Vaufleury 2000; Druart et al. 2010; detailed description of snail rearing can be found in Annex B of the ISO standard 15952, 2006) for ecotoxicological purposes. Snail farms that now exist in many countries make it easy also to obtain biological material for ecotoxicity testing.

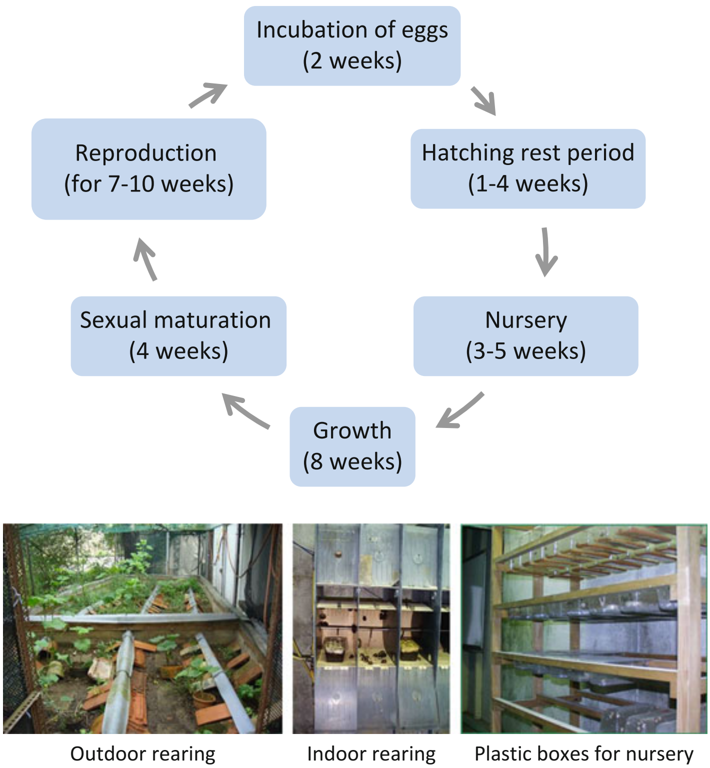

Fig. 23.2 Duration of the lifecycle under controlled conditions and simple devices for outdoor or indoor snail rearing

23.3 Field Methods

The environmental risk assessment of contaminated sites requires an accurate evaluation of the exposure to and hazard of pollutants. Exposure of organisms to pollutants depends of their bioavailability. The determination of the bioavailability of contaminants can be based on the measurement of their internal concentration in organisms exposed to contaminated soils (ISO 17402 2008; Pauget et al. 2011; de Vaufleury et al. 2013). Coupling biological assessment with the chemical measure of total or extractable trace metal elements (TME) must help avoid under- or overestimation of the exposure of organisms to pollutants. As bioavailability is organism-, contaminant-specific, it is necessary to collect of data for species that belong to various trophic levels. At the soil-plant-air interface, terrestrial snails are herbivorous, detritivorous invertebrates that also eat and move on soil (Gomot et al. 1989). Isopods present similar characteristics and can also be used as bioindicators of contamination (Gal et al. 2008); however, they occupy habitats other than those that snails do and are differently exposed to soil contaminants. Indeed, isopods are hard-bodied, soil-dwelling invertebrates, whereas the snail's soft body allows more exchange by the cutaneous route of exposure. The ability of wild autochthonous snails and especially of the ubiquitous species *Helix aspersa* (syn. *Cantareus aspersus*) to reveal the contamination of its habitat has been known for a long time (Beeby 1985). Some parameters, such as duration of exposure, populations, growth rate, and Mg in the diet, which can influence Pb bioavailability, have been described in passive biomonitoring experiments (Beeby and Richmond 2011). To deal with this variability, we developed the snail-watch method, based on caging snails of a known biological past for active biomonitoring. First, assays were performed with juvenile *H aspersa* placed for 28 days in square boxes located on an industrial waste disposal dump or by the side of a busy road (Gomot-de Vaufleury and Pihan 2000; Pihan and Gomot-de Vaufleury 2000; Viard et al. 2004a, b). After 1 month's exposure, a significant accumulation of Cu, Pb, and Zn was evidenced in snails from the roadside (Table 23.1). In an attempt to minimize the effect of environmental conditions, like humidity or autochthonous vegetation, that are able to modify growth or bioaccumulation, Viard et al. (2004b) propose to continually humidify soil throughout snails exposure and found that feeding snails with a combination clover–snail constitutes the best compromise if the objective is to combine growth and bioaccumulation assessment. However these modified devices are more complex to install and to follow for the 28 days exposure of snails. This first exposure device was then improved (e.g., to close the cage better or allow growth of plant) to be able to propose a very simple and easily reproducible system. The final device was developed by Scheifler et al. (2003a) and consists of stainless steel microcosms (diameter: 0.25 m; height: 0.25 m) covered by a stainless steel netting (mesh size: 10 mm) securely fitted over the top of the microcosm by a stainless steel picket. In the bottom of the microcosm, pieces of tile provide shelter for the snails. Snails foraged only on field soil and vegetation (Fig. 23.3a, b). Using this simple and efficient caging system, we explore metal

Table 23.1 *In situ* assessment of pollutants transfer to snail

Snails (age, total fresh mass)	Site (duration of exposure)	Tissue	Contaminants							Reference – main finding
			Cd			Cu	Pb	Zn	Ni	
			Mean concentration* mg.kg^{-1} (dry mass) except for Pauget et al in which data are median concentrations							
2 months, about 5 g	Lab	Foot	0.01			169	0.06	65		Gomot-de Vaufleury and Pihan (2000)
		Viscera	*0.25*			*88*	*5*	*120*		
	Control forest	Foot	0.02			123	0.99	90		
		Viscera	*0.42*			*138*	*12*	*253*		Snails transplanted near a busy road are more contaminated by Cu, Pb, Zn
	Busy roadside (28 days)	Foot	0.03			**189***	1.48	103		
		Viscera	*0.049*			***205****	***74****	***415****		
2 months, about 4 g	Forest: pine plantation non amended or amended with composted or liquid sludge (5–7 weeks)	Foot	0.06			18.25	0.04	6.46	0.32	Scheifler et al. (2003b)
		Viscera	0.19			17.06	1.11	65.99	0.75	
		Foot	0.06			22.78	0.03	6.98	0.21	
		Viscera	**0.25**			21.28	0.66	**81.17***	0.75	Zn transfer from soil to snail is higher on soil amended with sludge
		Foot	0.06			21.53	0.03	6.66	0.32	
		Viscera	0.2			20.07	0.77	**83.58***	0.94	
1 month, about 1 g	Cd contaminated soil from Low 0.6 to medium 15 or High 30–40 mg kg^{-1} Cd concentration at pH7 or 6 and season (kinetic study: sampling after 0, 7, 17, 25, 40 and 56 days in the field)	Whole body (soft part)	Spring		(a)					Gimbert et al. (2008b)
			7L	1.6^{a}	0.022^{a}					
			7M	12.4^{b}	0.168^{b}					Modeled assimilation flux (a; μgCd.g^{-1}snail.d^{-1}) enable to discriminate soil contamination at realistic concentrations
			7H	16.4^{b}	0.258^{c}					
			6L	2.1^{a}	0.03^{a}					
			6M	12.1^{b}	0.200^{b}					
			6H	12.2^{b}	0.242^{bc}					
			Autumn							A difference of 1 unit of pH (6/7) does not strongly modify Cd transfer
			7L	3.6^{a}	0.075^{a}					
			7M	12.2^{b}	0.314^{b}					
			7H	25.5^{c}	0.750^{c}					Season, by influencing the snail mass, may modify the Internal concentration
			6L	2.3^{a}	0.056^{a}					
			6M	11.4^{b}	0.247^{b}					
			6H	11.6^{b}	0.280^{b}					

(continued)

Table 23.1 (continued)

Snails (age, total fresh mass)	Site (duration of exposure)	Tissue	Contaminants: Cd		Cu	Pb	Zn	Ni	Reference – main finding
			Mean concentration* mg.kg^{-1} (dry mass) except for Pauget et al in which data are median concentrations						
2 months, about 6 g	Snails transplanted in a smelter-impacted area on a reference zone R or increased level of pollution P1–P2–P3	Whole body (soft part)	BE						Fritsch et al. (2011)
			R	0.7^{a}		2^{a}	197^{a}		No negative effects of TM exposure detected on snail condition (body weight, shell size, shell weight)
			P1	2.6^{a}		12.1^{a}	346^{a}		
			P2	145^{b}		187.3^{b}	4,669^{b}		
			P3	223^{c}		117.3^{c}	3,551^{b}		
	Comparison of accumulation of subadults from reproducers (F0) from the former smelter (ME) or from an unpolluted site (BE)		ME						Differences in responses to TMs between populations observed for conchological parameters, not for bioaccumulation
			R	0.7^{a}		0.9^{a}	256^{a}		
			P1	2.7^{a}		7.8^{a}	409^{a}		
			P2	166^{b}		167^{b}	5,498^{b}		
			P3	270^{b}		132^{b}	552^{b}		
2 months, about 5 g	9 field sites (cultivated sites, forests and contaminated sites)	Viscera	0.14–10.9		45–188	2.2–112	608–1,913		Pauget et al. (2013a) Determination of internal concentration of reference for 6 TME (Cd, Pb, As, Cr, Cu and Zn)
	Internal concentration of reference (CIRef)		2.27		185	12.9	1,490		Soil pH, organic carbon and iron oxides influence Cd, Cr, Cu, Pb, Zn zooavailability to snails. Proposal of the SET index

2 months, about 5 g	3 polluted sites	Viscera	1.7–10.6		2.3–112			Pauget et al. (2013b)
			(a): 0.021–0.397		(a): 0.109–4.94			Cation exchange capacity (CEC), silts and organic carbon content modulate the *in situ* bio-availability (assimilation flux (a; $\mu gCd.g^{-1} snail.d^{-1}$) of Cd and Pb)
								For As, Cd, Pb, Sb, the total concentrations in the soils were not good predictor of the bioavailability to snails
2 months, 4–7 g	Vineyard	Whole body	Glyphosate residues and its metabolite AMPA were found in snail tissues (4 and 8 mg kg^{-1} dw respectively), Residues of the fungicides tebuconazole and pyraclostrobin also, until 0.7; 0.8 mg kg^{-1} which is higher than the maximal residue level (0.05 mg kg^{-1})					Druart et al. (2011a, b)
	2 weeks after treatment by pesticides		Cu: foot 90–140					Snails can be used for risk assessment of pesticides e.g. in a vineyard agro-ecosystem under real conditions of application
			Viscera 40–80					

*Significant differences at 95 % with Control forest.
[a,b,c]Values that share similar letters within a season are not significantly different ($p > 0.05$).

Fig. 23.3 (**a**, **b**) Microcosms used to assess bioavailability of MTE on field sites (Scheifler et al. 2003a; Gimbert et al. 2008b; Fritsch et al. 2011; Pauget et al. 2013a, b). (**c**, **d**) Wired microcosms (25 × 25 × 15 cm, mesh size of grid: 1 cm) closed by a stainless steel grid of 30 × 30 cm adapted to study the fate and effects of pesticides sprayed in a vineyard (Druart et al. 2011b)

bioavailability in numerous different exposure scenarios in polluted and unpolluted field sites. Table 23.1 shows the main findings obtained as a result of static (i.e. one duration of exposure, generally for 28 days) or kinetic studies to characterize the in situ bioavailability of metal trace elements (MTE).

The mobility of MTE in soils, so called environmental availability, is often estimated using chemical extraction (ISO 17402 2008). However, these methods cannot replace biological assessment, as demonstrated, for example, by Fritsch et al. (2011) or Pauget et al. (2013a, b), who showed that total or extractable MTE concentrations are not usable to estimate the bioavailability of various MTE to snails. Indeed soil parameters that modulate speciation, mobility, and bioavailability are not similar for all the MTE, as shown for example in Table 23.2 (data presented are the result of snail exposure on 9 field sites representing 43 plots). As metal bioavailability is contaminant-, species-, duration of exposure-, route of exposure-, and source of exposure-dependent, modeling of their transfer is a complex issue that has not yet been completely solved. To deal with this complexity, biological tools that can be applied *in situ* are now available, e.g., with snails, to assess zooavailability. On the basis of field experiments conducted for several

Table 23.2 Soil properties influence on metal accumulation by snails exposed in the field

Metal	Parameter that modulate metal accumulation
As	As_{tot} ($r^2_{adj} = 0.67$)
Cd	$Cd_{tot} - C_{org}$ ($r^2_{adj} = 0.51$)
Cr	$Cr_{tot} + C_{org}$ – CEC - sands ($r^2_{adj} = 0.41$)
Cu	Cu_{tot} + clay – Al_{ox} – silts ($r^2_{adj} = 0.41$)
Pb	Pb_{tot} + pH + $Fe_{ox} - C_{org}$ ($r^2_{adj} = 0.56$)
Zn	$Zn_{tot} + Al_{ox}$ + sands – C_{org} ($r^2_{adj} = 0.42$)

Adapted from Pauget et al. (2013a)

Table 23.3 Internal concentration (Csnail) of snails exposed 28 days on various plots of a field site (reference plots (–); and increasingly contaminated plots (+ to +++)) and internal concentration of reference (CIRef) for calculation of the Sum of the Excess of Transfer (SET)

Plots	C_{snail} (mg.kg^{-1}DM)						CIRef (mg.kg^{-1} DM)						Accumulation quotient (AQ)						SET
	As	Cd	Cr	Pb	Cu	Zn	As	Cd	Cr	Pb	Cu	Zn	As	Cd	Cr	Pb	Cu	Zn	
98FA (+++)	0.24	10.9	0.03	112	168	1,181							1	4.80	1	8.67	1	1	11.47
117F (++)	0.20	6.03	0.21	34.8	136	993							1	2.66	1	2.70	1	1	3.35
117 C (++)	0.24	1.76	0.58	14.3	141	916							1	1	1	1.11	1	1	0.11
103F (+)	0.25	9.94	0.59	48.7	153	1,304	0.31	2.27	2.01	12.9	185	1490	1	4.38	1	3.78	1	1	6.15
103C (+)	0.3	5.73	0.31	61.4	161	1,599							1	2.52	1	4.76	1	1.07	5.36
TEF (-)	0.37	8.24	0.03	13.8	136	1,651							1.2	3.63	1	1.07	1	1.11	3.01
TEC (-)	0.38	2.6	0.03	9.95	106	887							1.25	1.15	1	1	1	1	0.4

Adapted from Pauget et al. (2013a). SET = Σ (AQ–1)

years (Table 23.1; Fig. 23.3a, b) and recently completed by a large panel of biological surveys on numerous French field sites, Pauget et al. (2013a) propose using the SET, Sum of the Excess of Transfer, index for an operational approach for the management of polluted sites. Table 23.3 presents an example of application of the SET index on several plots of a former smelter. It shows that the most alarming plots of the site are not the most contaminated (on the basis of total MTE concentrations) due to various parameters that modulate the bioavailability to snails. Thus, the SET index led to the recommendation that the most contaminated plot be managed first, and more surprisingly, one of the supposed reference zones. On this plot, the SET index evidenced a very high bioavailability of metals that was not expected from the measured soil concentration alone. The internal concentrations of reference (CIRef) of As, Cd, Cr, Pb, Cu, Zn have been published (Pauget et al. 2013a) and will be available for Co, Hg, Mo, Ni, Sb, Sn, Sr, and Tl in the near future. They make the interpretation quite simple and should help routine use of the snail-watch as an environmental indicator (http://ecobiosoil.univ-rennes1.fr/ADEME-Bioindicateur/english/fauna.php).

For organic contaminants, fewer data are available, in particular, because the analysis of internal concentration is more complex. However, snail-watch was successfully applied for the risk assessment of herbicides and fungicides used in a vineyard (Table 23.1, Fig. 23.3c, d; Druart et al. 2011a, b). While survival was not a sensitive endpoint, as was the case for MTE, internal residues analysis reveal surprisingly elevated capacities of snails to accumulate some of the studied active substances. These data deserve further study, e.g., through longer exposure to all the pesticides used successively in a cultural cycle. Further works are also necessary to extend the use of snail-watch to the assessment of the bioavailability of persistent organic pollutants, such as PAHs, PCB, or dioxins.

23.4 Semi-field Methods

Simplified reconstituted ecosystems have been used to assess the effect on juvenile snails of genetically modified maize (MON810 Bt-corn) (de Vaufleury et al. 2007). Bt-corn was grown in outdoor microcosms, allowing snail caging for several weeks (Fig. 23.4a). After 3 months' exposure, no effect of Bt-maize on the survival and growth of snails occurred, despite Bt protein being detected either in the Bt-corn leaves (from 22 to 42.2 $\mu g.g^{-1}$ dry wt), in the snail tissues (from 0.04 to 0.11 $\mu g.g^{-1}$ dry wt), and in their feces (from 0.034 to 5 $\mu g.g^{-1}$ dry wt). These data revealed that snail feces may constitute a source of exposure to Bt-toxin for other organisms.

The impact of various soil remediation techniques on the bioavailability of As in soil to snails has also be evaluated, thanks to microcosm exposure (Coeurdassier et al. 2010). Snails were caged for 1 month on As-contaminated soils (the concentration of the untreated contaminated soil was 121 $mg.kg^{-1}$ dw) amended with either iron grit or coal fly ash, or both (Fig. 23.4b). Lettuce was cultivated on these soils before introducing snails into the simplified ecosystem; snails were thus exposed by lettuce and soil ingestion and soil contact. The experiment was performed in summer and then in autumn. The results demonstrated the efficiency of treatments for reducing the As bioavailability to snails. Mortality was low except in summer on the untreated soil, showing that high temperatures can increase the toxic effect at similar internal concentrations of As (about 18 $mg.kg^{-1}$ dw soft tissues).

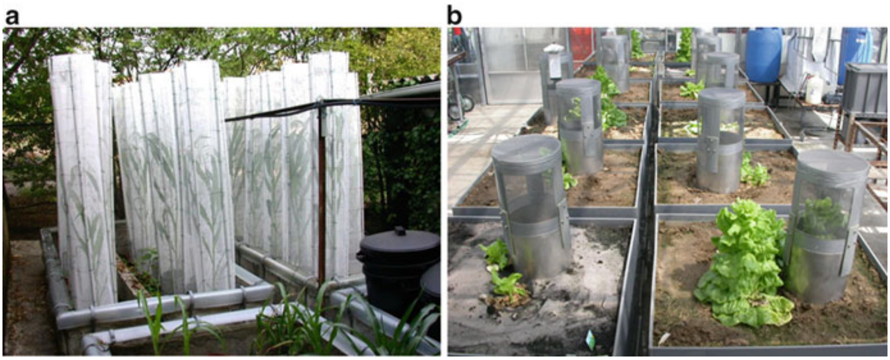

Fig. 23.4 Semi-field devices used, for example, to assess (**a**) the effect on snails of exposure to genetically modified maize (de Vaufleury et al. 2007) or (**b**) the effect of soil remediation on arsenic (As) bioavailability to snails (Coeurdassier et al. 2010)

23.5 Laboratory Methods

While field and semi-field methods are relevant for an *a posteriori* assessment of environmental and toxicological bioavailability of soil pollutants (i.e., once the pollutants are already in the soil), these methods need to be complemented by bioassays performed under controlled conditions in the lab. These *ex situ* bioassays allow an *a priori* assessment of the ecotoxicity of chemicals (i.e., before using the chemicals in the field) or an *a posteriori* assessment of contaminated matrixes, such as solid waste or polluted soils (in this case, polluted soils are sampled in the field and tested in the lab). The following paragraphs present the methods we developed to assess the ecotoxicity of chemicals or contaminated soils or sludges at various stages of the lifecycle of *H aspersa*, from embryotoxicity to partial or full lifecycle testing.

23.5.1 Embryotoxicity

Hatching success is a key parameter in population maintenance. While many publications deal with this important endpoint for aquatic mollusk species (such as, for example, *Lymnaea stagnalis*, e.g., Gomot 1998a; Bandow and Weltje 2012), much fewer data are available on the embryotoxicity of chemicals or contaminated soils to terrestrial invertebrates such as snails. As the incubation of snail eggs takes place in soil (Figs. 23.1 and 23.5), this phase of the lifecycle is relevant to proposing

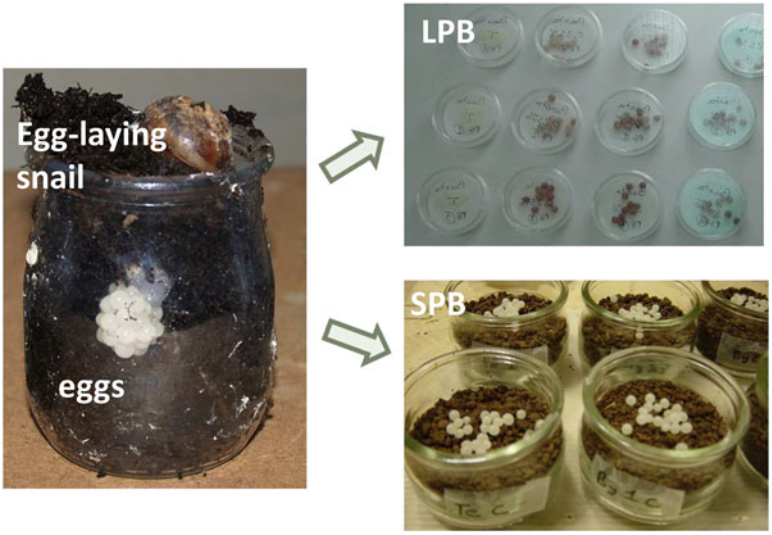

Fig. 23.5 Liquid phase bioassay (LPB) and solid phase bioassay (SPB) for embryotoxicity testing (Druart et al. 2010, 2012; Baurand et al. 2014)

Table 23.4 Embryotoxicity to snail eggs of the fungicide Corail (active ingredient a.i.: tebuconazole) in an artificial OECD soil or in a natural field soil sampled in vineyard (Druart et al. 2012)

Soil	OM (%)	pH	EC50 (mg a.i./kg)
Vineyard	2.9	6	0.8
Artificial	10	8.4	7.8

OM organic matter, *EC50* effect concentration that reduce hatchability by 50 %

a soil quality bioassay. For this purpose, Druart et al. (2010, 2012) developed three exposure methods: a solid phase bioassay (SPB) to expose eggs to soils or solid matrixes; a liquid bioassay (LPB) to mimic exposure of eggs to contaminated soil leachates; and a gaseous phase bioassay (GPB), where eggs are exposed to the toxic compounds that can be emitted by soils. The SPB (Fig. 23.5) was used to assess the ecotoxicity of various pesticides sprayed in vineyards, such as the herbicide glyphosate or the fungicide tebuconazole (Druart et al. 2012). SPB also allows it to be demonstrated that the characteristics of soils, such as pH and organic matter content, dramatically influence the toxicity of chemicals to snail eggs development (Table 23.4), and thus, the importance of the choice of the substrate used for the hazard assessment of pesticides, which is generally artificial OECD soil. SPB has been used study the effect on the hatchability of snails' eggs of the activated Cry1Ab toxin from *Escherichia coli* as a surrogate of the Bt protein produced by the MON810-Bt corn (Kramarz et al. 2007a). It was found that neither time to hatch (18.4–18.9 days) nor percentage of hatching (85–95 %) was reduced when incubation took place in soil spiked with 0–88 mg.kg^{-1} Bt-toxin. As Bt-protein residues were detected at concentrations between 0.9 and 2.2 μg.kg^{-1} soil dw (Andersen et al. 2007), it was concluded that the cultivation of Bt-corn does not constitute a threat for snail egg development. The LBP was used by Baurand et al. (2013) to analyze the Cd effect at the molecular level. On the basis of random amplified polymorphic DNA profiles analysis (RAPD) coupled to high resolution capillary electrophoresis system analysis, Baurand et al. (2013) demonstrated that the RAPD profiles of Cd exposed embryos of *H aspersa* were modified. The available snail-embryotoxicity bioassays open the door not only to obtain toxicity data of chemicals or of contaminated soils or sludges for snails embryos, but also to study the mechanisms involved in the toxic responses of embryos at various biological levels of organization (Baurand et al. 2014).

23.5.2 Growth Inhibition and/or Bioaccumulation Assessment- Source of Exposure

Various studies have demonstrated that the growth inhibition of juvenile *H aspersa* is a sensitive endpoint for studying the toxic effect of a chemical (Table 23.5). On the basis of these data, a standardized bioassay was published (ISO 15952 2006), allowing the assessment of the effect of chemicals or polluted matrixes on the

Table 23.5 Effect of chemicals on the growth of juvenile snails (1 month, 1 g fresh mass) by food or soil exposure and bioaccumulation in soft tissues after 28 days exposure

Chemical/ contaminated matrix	Source of exposure	EC50-growth 28 days (μg/g or %)	Internal concentration (μg/g dw)	Reference
Cd	Food	68–140	Until 2,200 in viscera	Gomot (1997) and de Vaufleury et al. (2006)
			$IC50^a$ = 720 viscera	
	Soil	534–877	Until 626 in viscera	
Cd spiked artificial ISO soil (0–1,000 μg/g)	Soil by cutaneous and/or digestive exposure	Between 500 and 1,000	Growth inhibition (%) = 0.15[Cd in whole body] + 3.88	Coeurdassier et al. (2002a) (evidenced cutaneous transfer of Cd)
Cd sprayed on colza leaves	Food	Growth inhibition of 43 % for snails exposed to 177 μgCd/g food (leaves)	180 and 680 respectively in foot and viscera of snails exposed to the highest Cd concentration (177 μg/g)	Scheifler et al. (2002a, b)
Cr	Food	300–350	Until 3,000 in viscera	Coeurdassier et al. (2000)
Cu	Food	1,200	nd	Gomot-de vaufleury (2000)
Pb		>30,000		
Zn		5,800		
Pentachlorophenol		1,980		
Dimethoate	Food	665	$<6.10^{-3}$	Coeurdassier et al. (2001, 2002b)
	Soil	150	nd	
Sewage sludge (S)	Food	55 % of S in food	Cu, Zn measured but not related with growth inhibition	de Vaufleury et al. (2006)
	Soil	10 % of S in soil		
Bt toxin, Cry1Ab	Food	No growth inhibition observed at concentration from 0 to 88 μg Bt/g^1 dw	nd	Kramarz et al. (2007b)
Soil spiked with metals (M: Cr, Cu, Pb, Zn) or with organic compounds (OC: phenanthrene, TCP, PCP)	Food (mixture soil + food)	M: 80 %	Cd, Cr, Pb, Zn respectively: until 101, 412, 154 and 5,000	Gomot-de Vaufleury and Bispo (2000);
		OC: 75–85 %	OC: nd	
	Leachate (sprayed on snails)	M: no effect	Cd, Cr, Pb, Zn respectively: 2-56-1.5-205	Gomot-de Vaufleury and Pihan (2002)
		OC: 100 %	OC: nd	

(continued)

Table 23.5 (continued)

Chemical/ contaminated matrix	Source of exposure	EC50-growth 28 days (µg/g or %)	Internal concentration (µg/g dw)	Reference
Soil spiked with polycyclic aromatic compounds (DI-S) and acridine	Soil	> 2,800: pyrene, fluoranthene, phenanthrene, fluorene, carbazole	6.9: carbazole	Sverdrup et al. (2006)
		1,600 dibenzothiophene	31: dibenzothiophene	
		> 4,000 (acridine)	1.4: acridine	

[a]IC50= internal concentration corresponding to EC50-growth – nd: not determinated

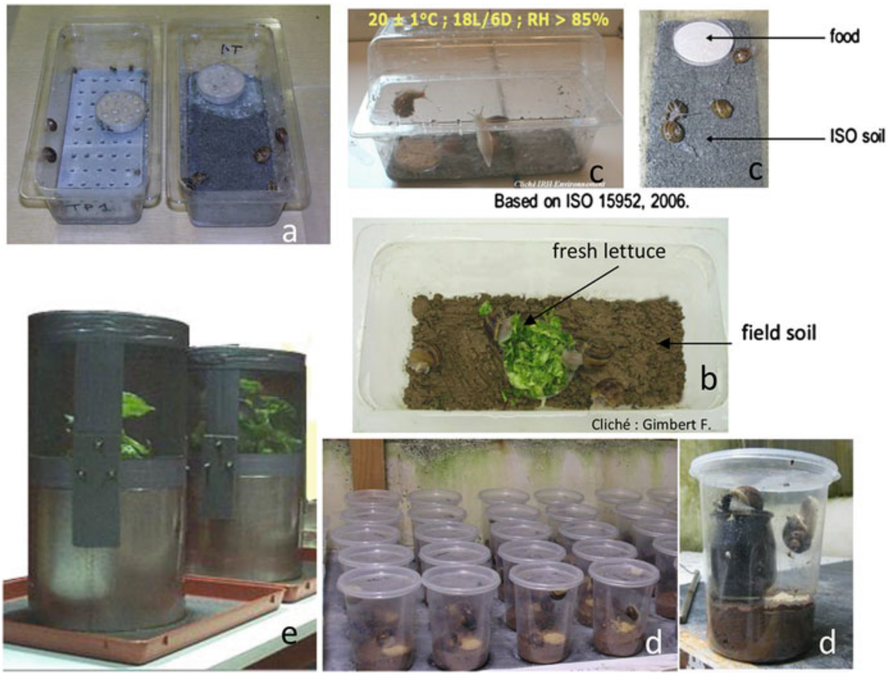

Fig. 23.6 Laboratory devices used to assess the transfer and effect of MTE (**a**) by various routes of exposure (digestive or cutaneous and digestive) in a 28-day assay (Coeurdassier et al. 2002a) or (**b**) effect of soil and/or plant exposure in a 28- (Pauget et al. 2012) or (**c**) 28 or 56- day experiment (ISO 15952 2006; Gimbert et al. 2008a, c), or (**d**) long-term effects of pesticides from hatching to reproduction (Druart 2011) or (**e**) in a simplified soil-lettuce-snail food chain (Scheifler et al. 2006)

survival and growth of juvenile *H aspersa* (Fig. 23.6a–c). This bioassay allows the toxicity to juvenile snails of chemicals present in the soil or in the food to be measured. Separation of the two sources of exposure for toxicity assessment was necessary to provide an ECx value for each source. Indeed, when occurring simultaneously, it is not possible to distinguish the participation of each source in the toxicity or bioaccumulation observed. In the field, both sources are involved in snail exposure; thus, other exposure methods were developed to allow an integrated evaluation of the fate and effect of chemicals in a simplified food chain in lab microcosms (Scheifler et al. 2006; see below).

Tests of the effect of chemicals separately by food or soil exposure demonstrated that their effect can be very different depending on the source of exposure. For example, we found that dimethoate (an organophosphorus pesticide) was much more toxic when present in the soil (i.e., causing cutaneous and digestive exposure) than in the food (i.e., digestive exposure mainly). A similar result was obtained with urban sewage sludge, whereas the opposite was observed with Cd, which is six times more toxic in the food than in the soil (Table 23.5). For the higher toxicity of dimethoate and sludge in the soil (Coeurdassier et al. 2002b; de Vaufleury et al. 2006; Fig. 23.6a), one hypothesis was that an efficient epithelial uptake of chemicals could occur, allowing a different toxicokinetic pattern than that allowed by digestive exposure (in the latter case, chemicals could be subjected more rapidly to metabolisation in the hepatopancreas). Further studies are needed to understand the mechanisms of toxicity involved at the molecular or enzymatic levels (EROP, ECOD, PROD, glutathione-dependent activities) as done for example by Ismert et al. (2002) in tissues of *H. aspersa* exposed 3 days to a naphthalene-saturated atmosphere.

The ability of wild snails to accumulate some metals, such as Cu, Cd, Pb, or Zn, is known (Hopkin 1989, 1993; Dallinger and Wieser 1984a, b; Dallinger and Berger 1992). In edible reared snails, it was found that genetic and environmental factors could be responsible for differences in Cu and Zn concentrations in the snail's tissues (Gomot 1998b). Among environmental factors, we demonstrated that the quality of the food (e.g., in terms of Cu and Zn concentration and speciation) dramatically influences the concentration of metals in the soft body of snails (Gomot and Pihan 1997). The internal distribution of some metals has been studied in *Helix aspersa*, and as demonstrated by Dallinger et al. (1997, 2001) for other species, Cd was found mainly in the cytosolic fraction associated with metallothioneins (Hispard et al. 2008a; Höckner et al. 2009, 2011; Palacios et al. 2011). Pb was found mainly in the granular fraction associated with granules, whereas Zn showed affinities for both cytosolic and granular fractions, leading to intermediate uptake and excretion patterns (Gimbert et al. 2008a).

In some cases, the bioaccumulation of metals was accompanied by growth inhibition and/or mortality (Table 23.6), allowing, for example, determination of Cd critical body concentration (IC50). The fate of chemicals was studied by static (analysis of residues in tissue after 28 days of exposure) and dynamic exposure (analysis after various durations of exposure); in the latter case, it was shown that the way the metals enter the body (i.e., "speed" of uptake) conditions their toxicity (Gimbert et al. 2006). Table 23.6 summarizes the main findings obtained from kinetic studies.

Results obtained on the basis of laboratory and field exposure to polluted soils make it possible to use snails very efficiently to assess the bioavailability of metals

Table 23.6 Toxicokinetic and toxicodynamic of metals in snails

Source of contamination	Snails	Internal concentration (μg Cd/g^{-1} dry mass) *Or body burden (BB: $\mu g/snail$)*	K_1: uptake rate (mgsoil/ mgsnail/day) (a): assimilation flux (mg metal/ kgsnail/d)	Reference (*additional conclusion)
Field soil contaminated by Cd, Pb, Zn (ME4) or ISO soil spiked with Cd, 20, 100 µg/g	1 g 3 months exposure	Equilibrium concentration of 0.7 (±0.1), 11.3 (±2.4), 73.3 (±4.8) and 6.3 (±1.3) for ISO 0, ISO 20, ISO 100 and ME4	K_1 of 0.118 – 0.171 and 0.102 for ISO 20, 100 and Me4 respectively	Gimbert et al. (2006, 2008a) *52 % Cd accumulated removed during depuration
	3 months depuration	Viscera 0.7 (ISO-0)	(a) viscera 2.6 (ISO-20)	Gimbert et al. (2008c)
		11.2 (ISO-20)	18 (ISO-100)	*Growth inhibition of 5 and 10 % after 70 and 84 days for ISO20 and ISO100 and 4 weeks delay for reproduction
		73 (ISO-100)	2 (ME4)	
		6.3 (ME4)		
Field soil contaminated by Cd (20), Pb (1900), Zn(1300) (ME4)		Cd: 6.3 | *BB-Cd 8.8*	(a) Cd: 2.1 | *(a) BB-Cd: 0.059*	Gimbert and de Vaufleury (2009)
		Pb: 27 | *BB-Pb 29*	Pb: 133 | *BB-Pb: 1.273*	
		Zn: 291 | *BB-Zn 290*	Zn: 153 | *BB-Zn: 7.079*	
Soil at various pH and organic matter content spiked with Cd, Pb	5 g	Cd: From 33 to 127	(a) 0.8–10.9 for Cd depending on pH, OM and clay content	Pauget et al. (2011)
		Pb: from 671 to 900 (increase with decreased pH or organic matter content)	39–178 for Pb	
17 soils from a polluted site	5 g	Depend on metal bioavailability in soils, modulated by total metal concentration in soil, pH, CEC, Alox and feox	(a) 0.2–1.3 for Cd	Pauget et al. (2012)
	28 d		1.38–171 for Pb	*EDTA and the total soil concentration usable to assess Cd and Pb environmental bioavailability to snails
			9.1–273 for Zn	

in soils (Pauget et al. 2011, 2012, 2013a, b). As this parameter is essential to characterize the transfer of metals in soils, the presented results allow the terrestrial snail *H aspersa* to be included in the battery of methods available for soil risk assessment. Snails are exposed differently to soils than other soil bioindicators, such as earthworms, nematods, or isopods. Furthermore they were shown to be able to access the nonlabile soil Cd pool (that contributed 16 % to the total Cd accumulated by snails), which in general is considered nonbioavailable (Scheifler et al. 2003b). Thus, their place at the soil-plant-air interface, the various sources and routes of exposure they integrate, their role as food item in many food webs, make them relevant as an environmental bioindicator of contaminated soils.

Bioaccumulation assessment can be performed using 1 g juvenile *Helix aspersa* if the aim is to investigate the relation between growth and the evolution of internal concentration. However, one difficulty with using juveniles is that growth makes the interpretation of internal concentration more complex than in adult or subadults, as growth causes dilution of accumulated metals (Gimbert and de Vaufleury 2009). For this reason, we propose also using subadult (fresh mass about 5 g, just after the end of the exponential growth, Table 23.6) to assess the environmental bioavailability of metals to snails. With these subadults, the comparison of the risk (exposure, hazard for snails) posed by several soil samples is possible, with negligible impact of growth dilution. The choice of the life stage (juvenile, subadult, or adult) is very important, as we demonstrated that juveniles were able to reach higher Cd concentrations when exposed to 20 or 100 $mg.kg^{-1}$ in the food than adults (de Vaufleury and Gimbert 2007) (Fig. 23.7). The growth of juveniles over the experiment, reduced at 100 μg $Cd.g^{-1}$ DW food, and the related growth dilution prevented the interchangeable use of concentrations and body burdens. However, when body burdens were used (i.e., $\mu g.snail^{-1}$ instead of $\mu g.g^{-1}$ snail), accumulation patterns led to similar conclusions being drawn for the two life stages exposed to Cd. Yet, it is important to consider the physiological state that influences the metabolic needs of tested organisms when assessing the effect of chemicals and the accumulation/elimination processes.

23.5.3 Life Cycle Assessment: From Hatching to Reproduction

Accurate assessment of the ecotoxicity of chemicals or contaminated soils should ideally be based on long-term exposure through full lifecycle tests. Due to higher cost, such chronic bioassays are rarely performed, at least in a toxicity screening approach. However, they must be available to collect chronic relevant data allowing a relevant calculation of the PEC/PNEC (predicted environmental concentration/predicted no effect concentration) ratio used for the risk assessment of chemicals. Such experiments were realised with *H aspersa* to evaluate the effect of chronic exposure to soil contaminated by Cd (Gimbert et al. 2006, 2008a, c; Table 23.5) or by common herbicides (Druart 2011; Druart et al. 2011c). Results showed that such

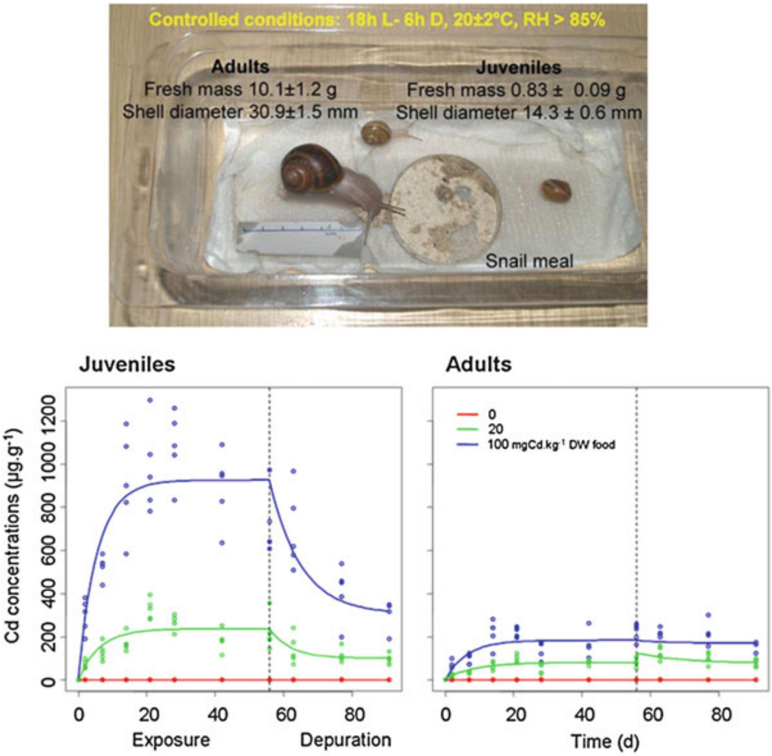

Fig. 23.7 Influence of the age of snails on their internal concentration of Cd after exposure to Cd contaminated food (de Vaufleury and Gimbert 2007)

long exposure duration was necessary to reveal that Cd inhibited growth by 5 % and 10 % after 84 days of exposure when present in artificial soil at 20 and 100 mg Cd kg^{-1}, respectively. Furthermore, at the end of this 6-month experiment, for the two Cd concentrations tested, a reduced number of clutches and a 4-week delay in the egg-laying cycle occurred (Gimbert et al. 2008c). Reprotoxicity of Cd has also been described at high exposure concentrations through food (Gomot- de Vaufleury and Kerhoas 2000) for 7 weeks. The data obtained for soil exposure at environmentally relevant Cd concentrations (Gimbert et al. 2008c) demonstrated that the reproduction disruption of *H aspersa* is also sensitive to soil contamination.

For herbicides, Druart et al. (2011c) demonstrated that long-term exposure to glyphosate and glufosinate does not cause either growth inhibition or sexual maturation disruption (only the mass of the albumen gland was reduced by 40 %, but, due to high variability, this difference was not significant; Fig. 23.8). Yet, a low environmental risk of glyphosate and glufosinate was estimated. However, residues of glyphosate (6 mg kg^{-1}) have been detected in snails exposed continuously to food, suggesting that snails can represent a source of exposure to predators. Full life cycle exposure of *H aspersa* to Bt-maize Mon810 has been performed: from the age of 4–88 weeks, snails were fed either powdered Bt-maize or non-Bt-maize and exposed

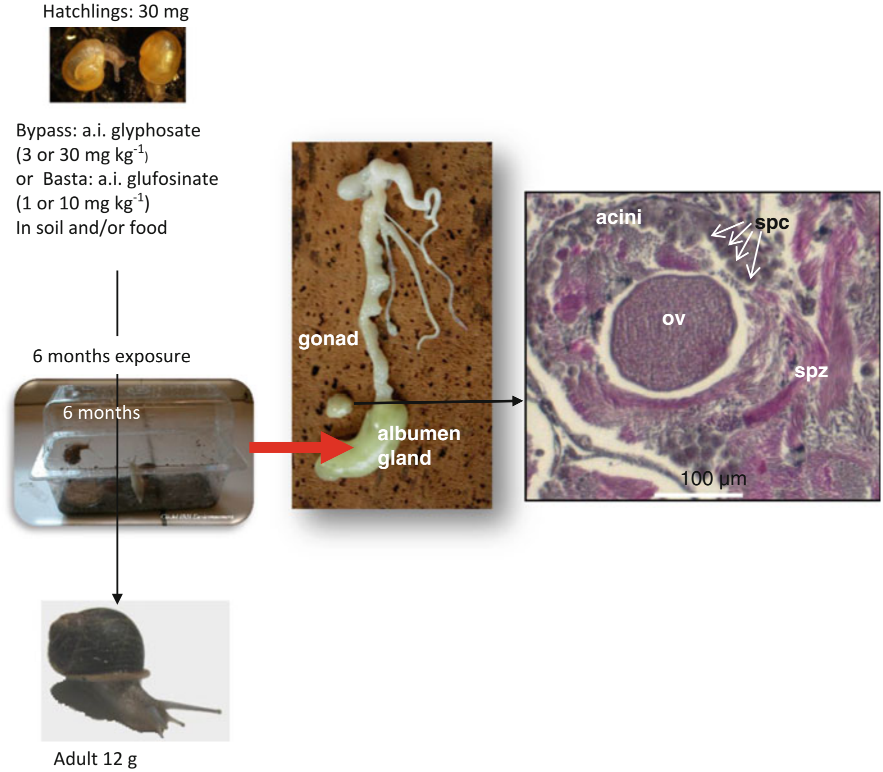

Fig. 23.8 Long term exposure of *Helix aspersa* to herbicides: from hatching to sexual maturation (Adapted from Druart et al. 2011c). a.i.: active ingredient of the commercial formulation; *ov* ovocyte, *spc* spermatocyte, *spz* spermatozoid

to soil samples collected after harvesting either the Bt-maize or non-Bt-maize. Survival was good; differences of body mass were observed after the end of the growing period (47 weeks) but were not more significant after 88 weeks, may be in relation with variation in fertility between exposed and non exposed groups but number of replicates were not sufficient to conclude (Kramarz et al. 2009).

23.5.4 Food Web Transfer

As stated in 23.5.2., snails can be used to assess the bioavailability of metals in soils (i.e., environmental bioavailability) and to assess the toxicological effects that polluted soils may cause to snails (i.e., toxicological bioavailability). They can also provide useful information to characterize the more complex transfer of contaminants, such as from soil and plant to snails or from snail to consumers. Such data are needed, for example, to determine the exposure of predators in environmental risk assessment procedures or models (like Eco-SSl; http://www.epa.gov/ecotox/ecossl/).

23.5.4.1 Soil- Plant- Snail – Interaction with Other Invertebrates

Using in-the-lab microcosms (Fig. 23.6e), Scheifler et al. (2006) evaluated the transfer of Cd, Cu, Ni, Pb, and Zn in a soil–plant (lettuce, *Lactuca sativa*)–invertebrate (snail, *Helix aspersa*) food chain for 2 months. In these conditions, the soil contribution to snail contamination was higher than 80 % for Pb, from 30 to 60 % for Zn, and from 2 to 40 % for Cd. The experimental device of Scheifler et al. (2006) is relevant for mimicking what happens in the field, where snails are exposed to both soil and plant.

Transfer of ^{137}Cs was studied in microcosms to determine the contribution of soil and lettuce in the accumulation of ^{137}Cs in snails (Fritsch et al. 2008). The contribution of lettuce and soil was estimated at 80 and 20 %, respectively. In the reconstituted soil–earthworm–plant–snail food web, soil-to-plant transfer was high, with a transfer factor (TF) of 0.8, and was not significantly modified by the presence of earthworms. Soil-to-snail transfer was lower (TF, 0.1) and was significantly increased in the presence of earthworms. The influence of earthworms on the bioavailability of soil pollutants to snails was also observed by Coeurdassier et al. (2007), with snails showing higher concentrations of Cd, Cu, and Zn when they were exposed with earthworms, while no difference was detected for Pb. When associated with a complementary device allowing the measurement of transfer only from the plant, lab-microcosms can help determine the contribution of soil and plant to snail exposure (Scheifler et al. 2006).

The devices used in the ISO 15952 standard (Fig. 23.6b, c, e) to assess the effect of pollutants on snail survival and growth are also relevant for exploring interactions between soil invertebrates. They were used, for example, by Fritsch et al. (2008) to study the bioavailability of ^{137}Cs in a 5-week exposure to contaminated soil with or without earthworms. It was found that transfer factors (TFs) were lower than $3.7.\ 10^{-2}$ and that the presence of earthworms caused a two- to threefold increase in ^{137}Cs concentrations in snails.

23.5.4.2 Snail- Invertebrate or Vertebrate Consumer

Snails are prey for many consumers (including humans in some countries) and their role in food web transfer of contaminants has been cited (Laskowski and Hopkin 1996). When we investigated the trophic bioavailability of Cd, a metal for which snails show a particularly elevated ability of bioaccumulation, we found that Cd transfer from snail to consumer depends on the considered consumer: carabid larvae show a lower Cd uptake than rats fed with contaminated snails, but the effect of Cd transfer was much higher in invertebrate larvae (Fig. 23.9). These results confirm that the uptake rate of contaminants cannot be extrapolated from one species to another and are not always predictive of toxic effects in the consumer of contaminated prey. Furthermore, Hispard et al. (2008b, c) demonstrated that Cd accumulation in rats depends on the form of ingested Cd: for example, $CdCl_2$ added to the food of rats does not cause similar Cd distribution in rat tissues as ingestion of the Cd

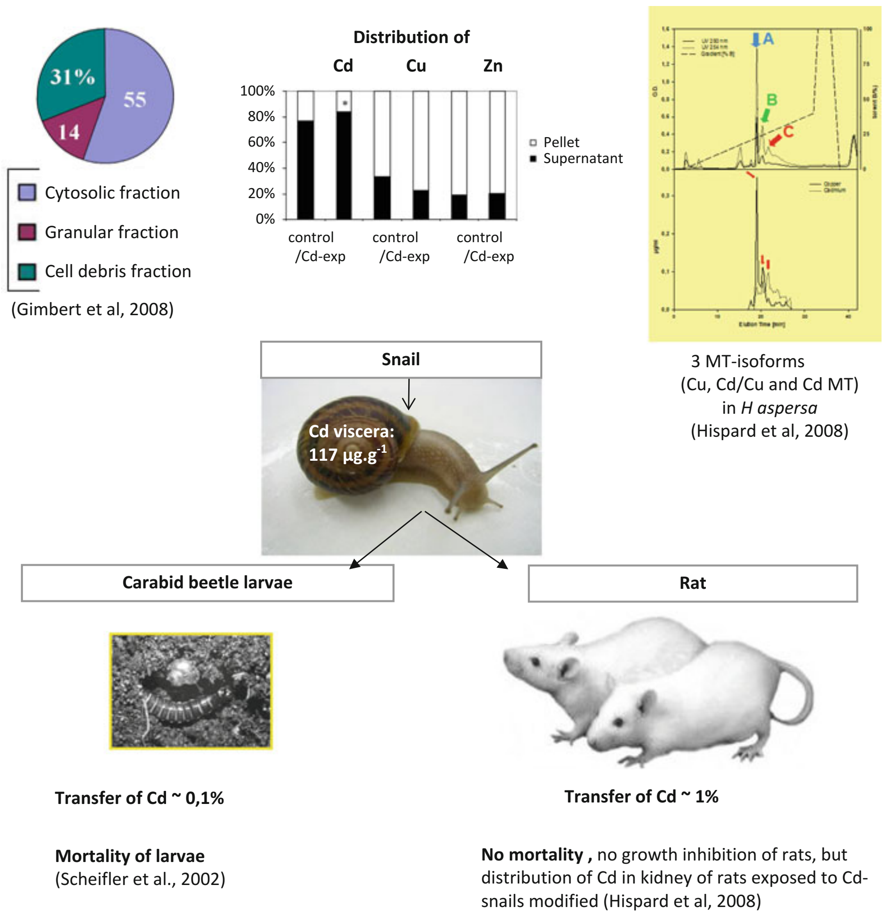

Fig. 23.9 Trophic bioavailability of Cd (Adapted from Scheifler et al. 2002b; Gimbert et al. 2008a; Hispard et al. 2008a, b, c). Cd in snail is mainly present in the cytosolic fraction, associated to metallothionein (MT) in the supernatant of centrifuged extracts

accumulated in snail tissues. These experiments provide an accurate way of evaluating the trophic and toxicological bioavailability of chemicals that is more relevant than by gavage or injection of the pure chemical in the consumer.

Conclusion – Perspectives

Snails have been the subject of numerous research studies in ecotoxicology (Dallinger et al. 2001), but their use in the routine assessment of contaminated soils or chemicals is still limited. The methods presented here allow the ubiquitous species *Helix aspersa* to be used either in bioassays to assess ecotoxicity of polluted soils or of chemicals, or in an embryotoxicity test, or

(continued)

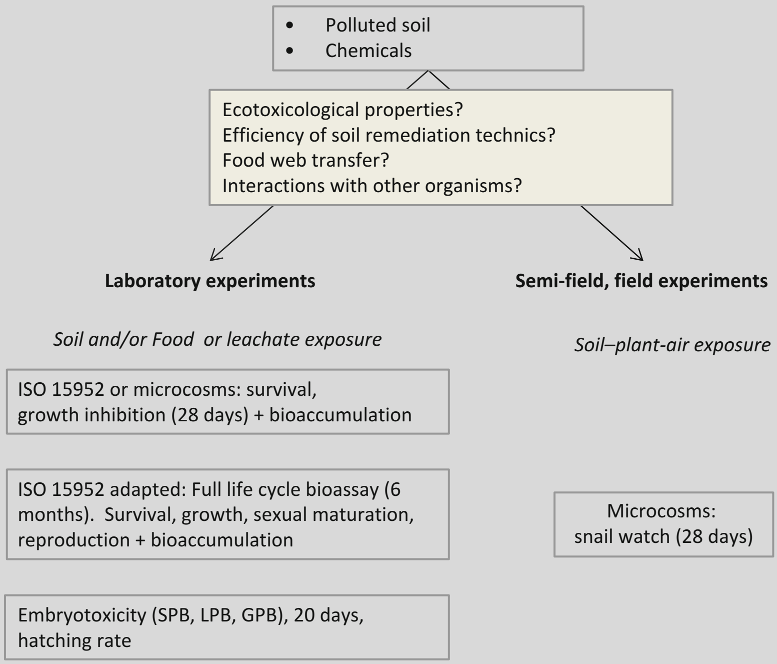

Fig. 23.10 Synthesis of snail methods and example of application as environmental indicators

in a full lifecycle bioassay. All these methods could be coupled with bioaccumulation assessment, making possible the analysis of the environmental, toxicological, and trophic bioavailability of contaminants present in soils.

Snail-watch enables *in situ* biomonitoring of soil contamination. This method is also adaptable to air pollution assessment (Ismert et al. 2002; Regoli et al. 2006). As data on organic contaminants are scarce, we hope the data and methods presented here will promote the development of studies dealing with the fate and effects of such pollutants, and also a similar development using other snail species, as recommended in the annex of ISO 15952. Associated with the measurement in various snail species when laboratory rearing is possible, and performed at various biological levels, from the molecular (Itziou and Dimitriadis 2011; Ianistcki et al. 2009; Leffa et al. 2010; Baurand et al. 2013) to cellular (Snyman et al. 2000) or enzymatic levels (Coeurdassier et al. 2001, 2002b; Mazzia et al. 2011) and to bioaccumulation assessment when relevant, it is hoped that the presented results using the terrestrial snail, *Helix aspersa* at various stages of its lifecycle will promote ecotoxicological assessment of chemicals and contaminated soils to preserve the quality of our environment (Fig. 23.10).

Acknowledgments The author warmly thanks all the students and colleagues that participated to the research presented here and particularly Renaud Scheifler, Michael Coeurdassier, Frédéric Gimbert, Florian Hispard, Clémentine Fritsch, Coline Druart, Benjamin Pauget, Pierre-Emmanuel Baurand for their implication during and after their PhD and Dominique Rieffel, Anne-Claude Goydadin, Nadia Crini, Jean-Claude Lambert, Marlène Gruet, Brigitte Jolibois for their technical assistance. The author also gratefully thank Cécile Grand, Antonio Bispo, Isabelle feix from the Agence De l'Environnement et de la Maîtrise de l'Energie (ADEME) for fruitful scientific discussion for the development of relevant bioindicators. ADEME, Agence Nationale de la Recherche (ANR, contract n°ANR-05-ECCO-004) and the Regional Council of Franche-Comté, the Ministry of Research, financially supported the presented works and are also thanked.

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Part IX
Land Use

Chapter 24
Land Use Changes and Landscape Degradation in Central and Eastern Europe in the Last Decades: Epigeic Invertebrates as Bioindicators of Landscape Changes

Jaroslav Boháč and Zuzana Jahnova

Abstract The division of communities of epigeic beetles (Coleoptera: Carabidae, Staphylinidae) based on indicative taxonomical groups and the index of epigeic beetles used for evaluation of human impact on communities are presented in this paper. In the Czech Republic, the indicative classification of the main epigeic taxonomical groups was made according to ecological characteristics and sensitivity to human influence. This paper also presents long-term monitoring of epigeic beetles from 1869 to 2003 in Prague, the capital city of the Czech Republic, and information about invasive species. A brief comment on land use changes and landscape degradation is also included.

Keywords Epigeic invertebrates • Bioindicators • Methods • Land use • Landscape degradation • Central and eastern Europe

24.1 Introduction

The increasing demand to identify biological indicators corresponds to the need for efficient, cheap, and quick means to formulate judgements and evaluation scales regarding the state of environmental health. This method was first applied to check the environmental quality of ground water, rivers, and other water bodies (e.g., Blandin 1986; Burger 2006; Woodiwiss 1978), and then, in more recent years, of soil (Curry 1987; Foissner 1999; Paoletti 1988; Paoletti et al. 1991).

Epigeic invertebrates live on the surface of the soil and in the upper layer of soil, namely, litter. The most numerous groups of epigeic invertebrates are beetles, especially ground beetles and rove beetles, and arachnids and ants (Zillioux et al. 2006). Carabids and staphylinids are groups of epigeic beetles that are very

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_24

sensitive to a number of environmental factors, including global climate changes, landscape structure change, deforestation, unsuitable management in landscape, fragmentation in landscape, urbanization, and overdrainage and the consequential desiccation of landscape, as well as unsuitable fertilizers and pesticide application (Zillioux et al. 2006). They demonstrate a flexible set of responses to these abiotic and biotic factors through changes in numbers, species composition, morphology, and chemical body burdens (Boháč and Fuchs 1991; Boháč 1999; Chobot et al. 2005; Avgin and Luff 2010). Carabids and staphylinids are relatively well known taxonomically in central and eastern Europe. In general, ground beetles and staphylinid beetles show good dispersal capabilities, and as a result, are found in a variety of landscapes. These groups are relatively easy to sample quantitatively, especially by using pitfall traps (see Sect. 24.2). The ecology of the central Europeans species is relatively well known (e.g., Koch 1989).

Carabids and staphylinids are a key group of organisms in ecosystems and their occurrence in the landscape or ecosystem can indicate the value of a landscape's or ecosystem's biodiversity (Boháč and Fuchs 1991). For these reasons, the interpretation of results from field studies is relatively easy as compared to those for other groups of insects where less is known about their ecology (Zillioux et al. 2006). The next sections demonstrate the method based on the indicative classification and data processing. The historical changes of the epigeic beetle communities in the last 100 years and the recent tendencies are presented.

24.2 Methods of Sampling

Collection methods for surveying carabid assemblages are pitfall traps, sticky traps, sweep netting, Malaise traps, window traps, hand picking, litter washing, and beating (Raino and Niemala 2003). Staphylinids can also be collected by pitfall trapping or by taking soil quadrate samples. The material should be collected during a 1-year period and the same method should be used to compare various biotopes (Boháč 1999). The most common method used for catching carabids is pitfall trapping, which is widely discussed. The method is easy and cheap, but the catch indicates species-specific activity density rather than relative abundance (Greenslade 1964). Pitfall traps can be modified according to the study objective. Trap losses can occur at any time during the activity period and have traditionally been dealt with by standardising the catch duration to 100 trapping days, without taking into account variability in activity across the season (Kotze et al. 2011).

24.3 The Naturalness of Habitats

Bioindicators are a widely-used method of assessing habitat degradation or various types of environmental conditions. Indicative classification of appropriate taxonomical groups is an important part of this process. To choose a feasible bioindicator is a fundamental and often discussed problem related to environmental assessment (Duelli and Obrist 2003; Hilty and Merenlender 2000). Epigeic invertebrates are often considered to have bioindicative value (Chobot et al. 2005). Limits to its practical use are linked to our limited knowledge of these small living creatures. There is a need to increase knowledge of the undervalued epigeic invertebrates in order to appreciate better the many benefits that human derive from their existence.

The naturalness of biota can be regarded as an indicator of a well-preserved biotope. To asses the naturalness of biota, a comparison must be drawn between the biota of a given biotope and the biota of a biotope that is considered characteristic and well-preserved. In view of the fact that there is almost unlimited variability in natural biotopes, it would be difficult to interpret the result of this type of research. Variability resulting from different statuses of naturalness could not be set apart from variability resulting from geographic variation (Boháč and Fuchs 1991).

The elementary idea of indicative classification is that organisms that are captured in a certain type of biotope can be used to evaluate this biotope (Chobot et al. 2005). Indicative classification is based on long-term studies of a taxon's bionomics, and its accuracy increases with the increase in the amount of investigated data. The presence of the indicator defined above reflects certain environmental conditions at a locality. The occurrence of phytophagous species depends primarily on the occurrence of their host plant, which is limited by site factors.

However, simultaneously, if some abiotic or biotic factors of investigated localities correlate, it cannot be concluded which site factor is the limited one. It is documented that some species considered as relict species have unpredictably occurred at secondary sites (spoil tip, etc.). These species are limited by a different site characteristic that is common to both sites (Boháč 2005; Boháč et al. 2005).

Another obstacle is that species living at different sites are limited by different environmental conditions. It can be concluded that bioindicators in the sense defined above can be used only in the area where the observation was held and where the classification was done. The validity of indicative classification decreases with the increase in the amount of dissimilarities between sites (e.g., geographical distance, climatic variability, soil conditions variability). The practical use is hence restricted to the same biogeographical regions (central and eastern Europe), or more practically to the area of a state (e.g.. the Czech Republic).

24.4 Classification of Habitat Factors

Dispersal ability, habitat requirements, abiotic factors (climate factors, soil type, subsoil, humidity) and biotic factors (e.g., vegetation) are the main factors influencing the occurrence of epigeic invertebrates in habitat (Chobot et al. 2005).

The dispersal ability of epigeic invertebrates is better than that of other soil organisms (Boháč 2005; Boháč et al. 2005). We can always find some habitats that are possibly appropriate for certain species, but for some reason they do not live there. No characteristic of the habitat can be concluded from the absence of this species in that habitat. The occurrence of species in a habitat depends on the dispersal ability of species. This does not mean that species with good dispersal ability are relatively better at colonizing habitats than species with low dispersal ability. The stability of habitat also plays an important role in this process. E.g., river banks are less stable habitats, and members of species that want to live there must have better dispersal ability than the members of the same species that would like to colonize stable habitats such as forests.

Other factors that influence the epigeic species are abiotic factors. For climatic factors, not only mean values are important but also day-to-day and year-to-year fluctuations. Microclimatic conditions are considered to be the most important climatic factors. Soil type and subsoil are also important because species are in close contact with the soil surface. Soil surface is used as a shelter and it is the place where species try to find food. Vegetation influences the microclimatic conditions of habitat, and also the occurrence of potential food.

It can be concluded that the presence of particular species in a habitat is influenced by a combination of the unique characteristics of habitat and of the unique characteristics of species.

One task of biomonitoring is to find species that indicate the naturalness of habitats (Boháč and Fuchs 1991; Růžička and Boháč 1993). Natural biotopes are often regarded as valuable or of good quality. This term was created by man and it is subjective. A natural habitat, in the sense of a habitat that has never been affected by man, probably does not exist in the world. Natural habitats should be defined as stable habitats able to exist without human intervention where K-strategists dominate. The dispersal ability of species living there is lower. Natural habitats formed at the initial succession stage depend on disturbance. R-strategists dominate in these habitats because they have good dispersal ability.

Rare species are species having a low population density and narrow ecological niche, and living in a specific area of disturbance. Sometimes rare species can occur in secondary habitats, e.g., the rare ground beetle *Cicindela arenaria viennensis* lives on mine reclamations (Boháč 2005).

The relative proportion of rare and generalist species in a habitat can serve as an indicator of the naturalness of the habitat. Change in the proportion of rare and generalist species indicates the beginning of habitat change (Růžička 1985).

24.5 The Selection of Proper Indicative Taxonomic Groups

There are a number of reasons for using bioindicators. Prerequisites for being a good indicator include vast knowledge on its taxonomy and ecology, ease and standardization of sampling methods, and wide distribution and knowledge about basic life-history. For projects in large areas with a high number of localities, the knowledge of taxonomy is the limiting factor (Koivula 2011; Raino and Niemala 2003).

Recent analyses of various insect groups as potential bioindicators were summarized in a special issue of *Agriculture, Ecosystems and Environment* (Paoletti 1999). In this issue, it was concluded that as bioindicators in agricultural ecosystems we can use: bacterial diversity, mycorrhizal fungi, soil Protozoa, soil Nematoda, earthworms, woodlice (Isopoda), soil dwelling Diptera, ground beetles (Carabidae), rove beetles (Staphylinidae), spiders (Araneae), true bugs (Heteroptera), net-winged insects (Neuroptera), lady bugs (Coccinelidae), hover flies (Syrphidae), ants (Formicoidea), and certain groups of Acari (Oribatida, Gamasida).

Several papers also describe the use of other groups: springtails (Collembola) (Nelson et al. 2011), potworms (Enchytraeidae) (Wilson and Kakouli-Duarte 2009), coprophagous beetles (Scarabaeidae) (Hanski and Cambefort 1991), snout beetles (Curculionidae), leaf beetles (Chrysomelidae), and butterflies (Lepidoptera) (Brereton et al. 2011). To evaluate forest communities, saproxylic insects are used (e.g., Coleoptera: Elateridae, Lucanidae, Scarabaeidae, Cucujidae, Bostrychidae, Cerambycidae) (Schlaghamerský 2000).

It can be suggested that as a bioindicator we can use almost any group of invertebrates that is represented by the following characteristics: sufficient number of species, good knowledge of bionomics, heterogeneous life-history strategies, quick response to abiotic and biotic factors, cost-effectiveness, and easy collecting methods. The above-mentioned considerations constitute a guideline for the choice of the best type of bioindicator for the various monitoring objectives (Chobot et al. 2005).

Brustel (2004) compared the suitability of different groups of epigeic invertebrates for monitoring the ecological quality of forest communities in France. This model was modified and is represented in Table 24.1.

Duelli, Obrist (2003) provide more detailed information of suitable indicators based on a satisfactory amount of data.

There are numerous standardized methods for collecting almost all kinds of insects, e.g., pitfall traps, flight traps, and soil quadrate samples, but not all taxonomic groups are suited as bioindicators because of identification. Making the identification of biota easier and subsidizing it more is an important goal that must be reached. The question is: how can we improve our knowledge of millions of invertebrate species, which historically and psychologically have been ignored because of their status as human parasites or pests? Between 600 and 3,000 species of invertebrates inhabit most mixed landscapes in temperate countries, and some of these have a different larval stage or vary in colour patterns (Paoletti 1999).

Our knowledge about popular and well-known groups (*Carabidae, Lepidoptera, Arachnida*) is based on the knowledge of amateur collectors. In general, the interest in taxonomy is in decline because of non-existent public subsidies. To learn taxonomy is a difficult and long-term task. In the Czech Republic, there are only a few scientists able to identify *Isopoda, Chilopoda, Diploda*, and *Collembola*, which limits their potential use as bioindicators (Rusek 2005).

Table 24.1 Indication criteria of selected groups of epigeic invertebrate species

	Indication criteria		Biotope demands			Practicability	
Group of invertebrate species	Diversity of group	Diversity of habitat requirements	Functional groups	Time continuity	Diversity of environment	Participation of non-specialists	Ease of sampling
Formica rufa	–	–	+	+	–	+	+
Carabidae	+	+	–	+	+	+	+
Staphylinidae	+	+	+	+	+	–	+
Isopoda	–	+	–	–	–	–	+
Chilopoda	–	+	+	+	+	–	+
Diplopoda	+	+	+	+	+	–	+
Collembola	+	+	+	+	+	–	–
Mollusca	+	+	–	++	+	–	+

Brustel (2004), Chobot et al. (2005), Rusek (2005), Tuf and Tufová (2008, edited)

24.6 Indicative Classification and Data Processing

Various characteristics (e.g., frequency of species with summer and winter activity of imagos, proportion of winged species, various body size groups, thermo- and hygropreference and geographical distribution and habitat preferences) are used in broad classification systems (Thiele 1977; Turin et al. 1991).

In the Czech Republic, the indicative classification of main epigeic taxonomical groups was done according to its ecological characteristics and sensitivity to human influence. This classification was done for spiders (Buchar and Růžička 2002), ground beetles (Hůrka et al. 1996), ants (Bezděčka 2004), and rove beetles (Boháč et al. 2007).

Ground beetles, ants, and rove beetles were divided into three analogous groups:

- Group R (R1) – includes species remaining from communities of a past period, e.g., species with arcto-alpine, boreomontane, and boreo-alpine occurrence, inhabiting mainly mountains and peatbogs, or occurring only in the remains of forests stands, which because of their high species diversity resemble recent climax forests.
- Group A (R2) – encompasses species of both natural and managed forests.
- Group E – comprises eurytopic species that successfully occupy deforested sites and are also found in areas strongly affected by man.

The classification of spider species was done with respect to their ability to inhabit sites disturbed by man to various degrees. Spiders are divided into four groups: (1) species living in climax habitats, (2) species living in semi-natural habitats, (3) species living in regularly disturbed habitats, and (4) species living in man-built habitats.

Well known ecological indices, such as Simpson's dominance index or the Shannon index of biodiversity, describe biodiversity in terms of simple compositional parameters such as number of species, groups of species or habitats, evenness. Indicators of structure and function are even more rarely associated to the measurement of biodiversity. The meaning attributed to the richness measure is the more, the better (Moonen and Barberi 2008). The following index of epigeic beetles deals with the frequency of species of ecological groups. This index was proposed by Boháč (1999) as the index of staphylinid communities, but it can be used for ground beetles too (Nenadál 1998).

The index of epigeic beetles (IEB) is a simple mathematical expression covering all three ecological groups (R1, R2, E). It is defined as

$$\mathrm{IEB} = 100 - (\mathrm{E} + 0.5\,\mathrm{R2}),$$

where the first right-hand sum comprises the percentage abundance of individuals of eurytopic species (Group E), and the second the half of abundance of individuals of species of natural and managed forests (Group R2). The value of this index ranges from 0 (only eurytopic species are present and the community is highly affected by man) to 100 (only species of group R1 are present and the community is virtually unaffected by man). Upon establishing the index values for different biotopes, it is possible to characterize the degree of man's influence in the examined communities by a single figure, thus avoiding dubious comparison with sparse control. In addition, the relationship between the index values for a given biotope and the species abundance within the communities can be employed as an index of the sensitivity of various species to human-induced stress, and can also serve as a refinement of the classification (Boháč 1990).

Ecological analysis for the evaluation of community structure was employed in a study of beetle communities in biotopes with different degrees of anthropogenic affects (Boháč and Fuchs 1991). Various characteristics (frequency of ecological groups according to their relation to the naturalness of biotopes, frequency of species with summer and winter activity of imagos, proportion of winged species, various body size groups, thermo- and hygropreference and geographical distribution) were used during this analysis. Increased influence of man was found to bring about an increase in the frequency of eurytopic species, an increase in the frequency of species with summer activity of imagos, and decrease in the proportion of species with winter activity of imagos. One peak in the seasonal activity of staphylinids was found in biotopes with increased influence of man in contrast to two peaks in seasonal activity in semi-natural habitats. Furthermore, an increase was also seen in the proportions of winged species and individuals possessing a higher migrating ability, large body size (size Groups IV and V after Boháč and Růžička 1990; Růžička and Boháč 1993), species with higher temperature and lower moisture preferences, and species with an area of occurrence wider than Europe. A decrease in the number of life forms was accompanied by a decrease in the beetle community index. More extensive human activity was also shown to bring about an alternation of the sex ratio. The ecological analysis of staphylinid communities was used for evaluation not only of the author's data but also of data collected by other authors (Boháč 1999) and was able to identify the critical stage of communities, when staphylinid communities are unstable and their structure is changing year by year, in response mainly to various management practices (Table 24.2) (Boháč 1999). Multivariate analysis has recently been applied to compare staphylinid communities of various biotopes (Boháč 1999, 2003).

Table 24.2 Parameters indicating the critical stage of staphylinid communities

Parameters	
Frequency of ubiquitous specimens	More than 90 %
Index of community	Less than 35
Number of life forms	Less than 4
Frequency of large individuals (IV and V size groups)	More than 20 %
Frequency of individuals with summer activity	More than 40 %
Non flying species	Absence
Frequency of species with higher temperature requirements	More than 70 %
Frequency of species with lower temperature requirements	More than 70 %
Value of sex ratio index	More than 10 % from 1 : 1

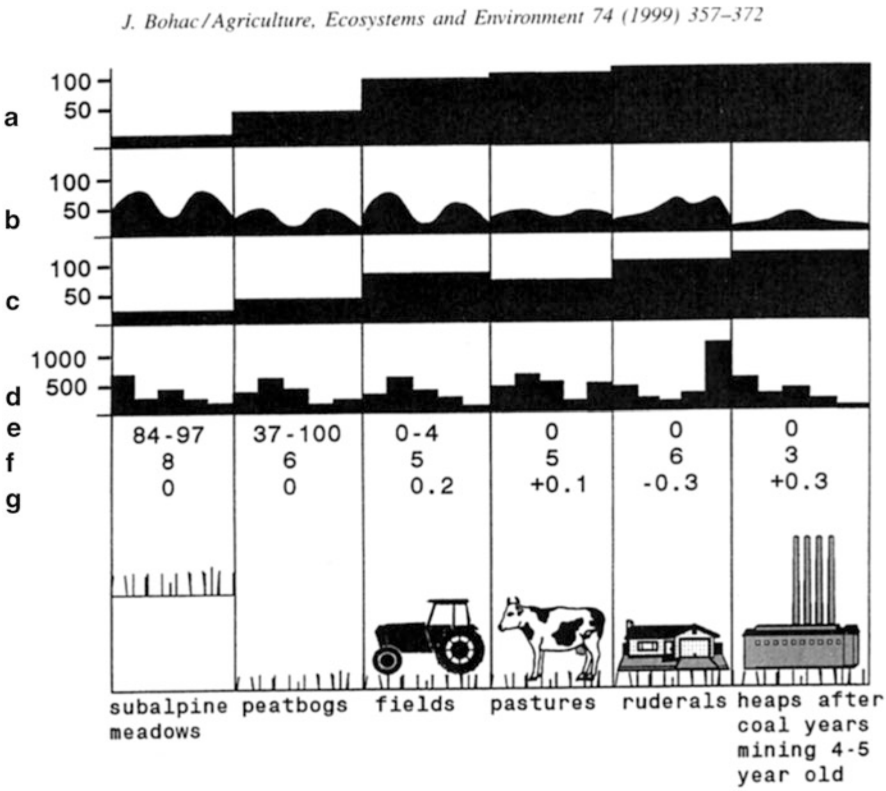

Fig. 24.1 The influence of man on communities of staphylinid beetles in non-forest landscapes: (*a*) percentage of eurytopic species, (*b*): seasonal dynamics (spec./m^2), (*c*): percentage of species with good migrating ability, (*d*): distribution of individuals in relation to body size (spec.), (*e*): index of community, (*f*): number of life forms, (*g*): sex ratio (female-male/N). Bars in panel D represent body size Groups I–V (from *left* to *right*) ranging from smallest to largest, respectively (Boháč 1999)

The relationship between the value of the index of epigeic beetles and the frequencies of species occurrence in the community is demonstrated in Fig. 24.1. The species can be divided into several groups:

- Species living in habitats of low index value, subgroup with high frequencies in the community (Fig. 24.2a)
- Species living in habitats of low index value, subgroup with low frequencies in the community (Fig. 24.2b)
- Species living in habitats of middle index value, subgroup with high frequencies in the community (Fig. 24.2c, e)
- Species living in habitats of middle index value, subgroup with low frequencies in the community (Fig. 24.2d)
- Species living in habitats of high index value, subgroup with high frequencies in the community (Fig. 24.2f)
- Species living in habitats of high index value, subgroup with low frequencies in the community (Fig. 24.2g).

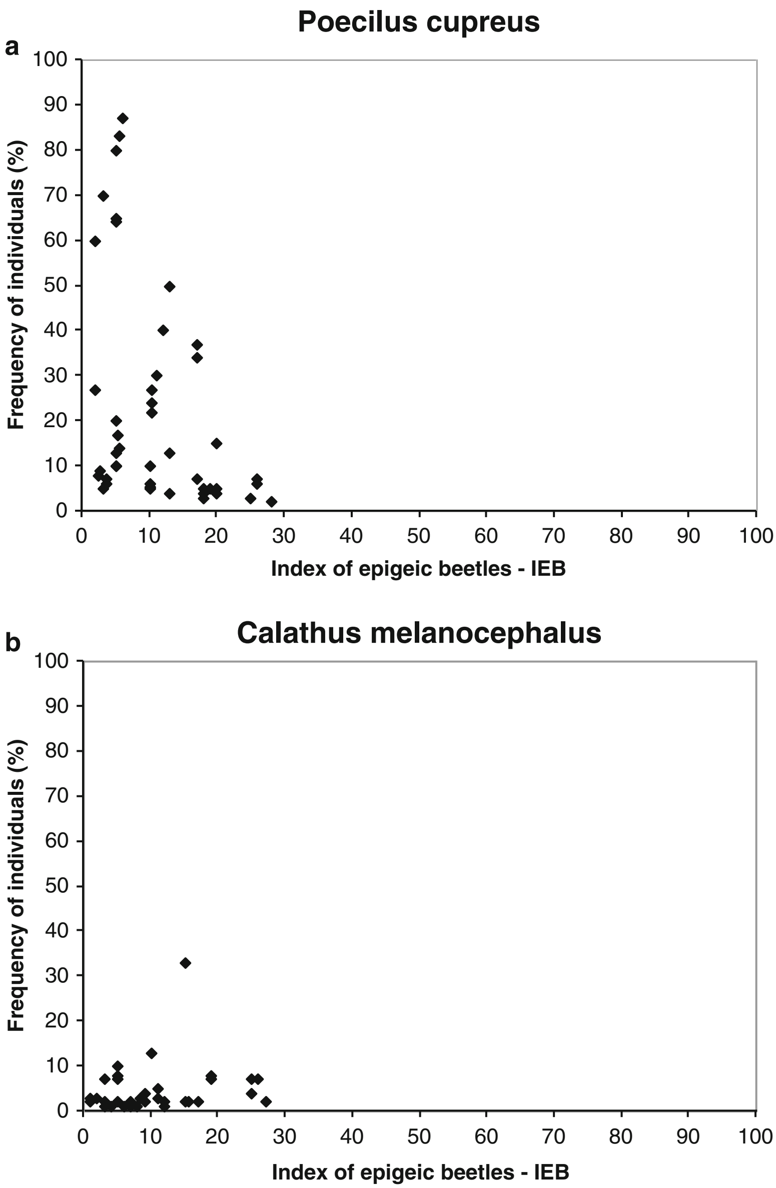

Fig. 24.2 Relationship of the index of epigeic beetles and frequencies of species occurrence in the community for carabid beetles

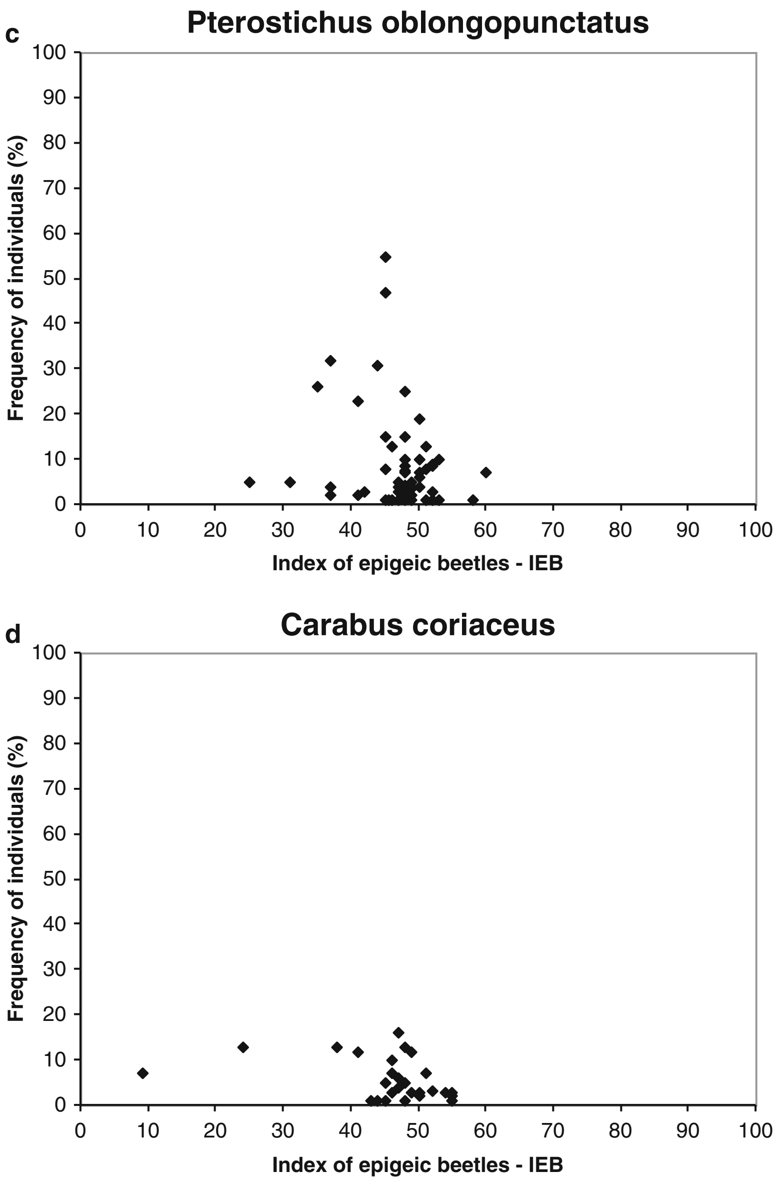

Fig. 24.2 (continued)

This scheme can be used to verify whether the species was classified into the appropriate indicative group.

The relation between frequency of individuals and frequency of number of species is described by the logistic sigmoid curve (Růžička and Boháč 1993).

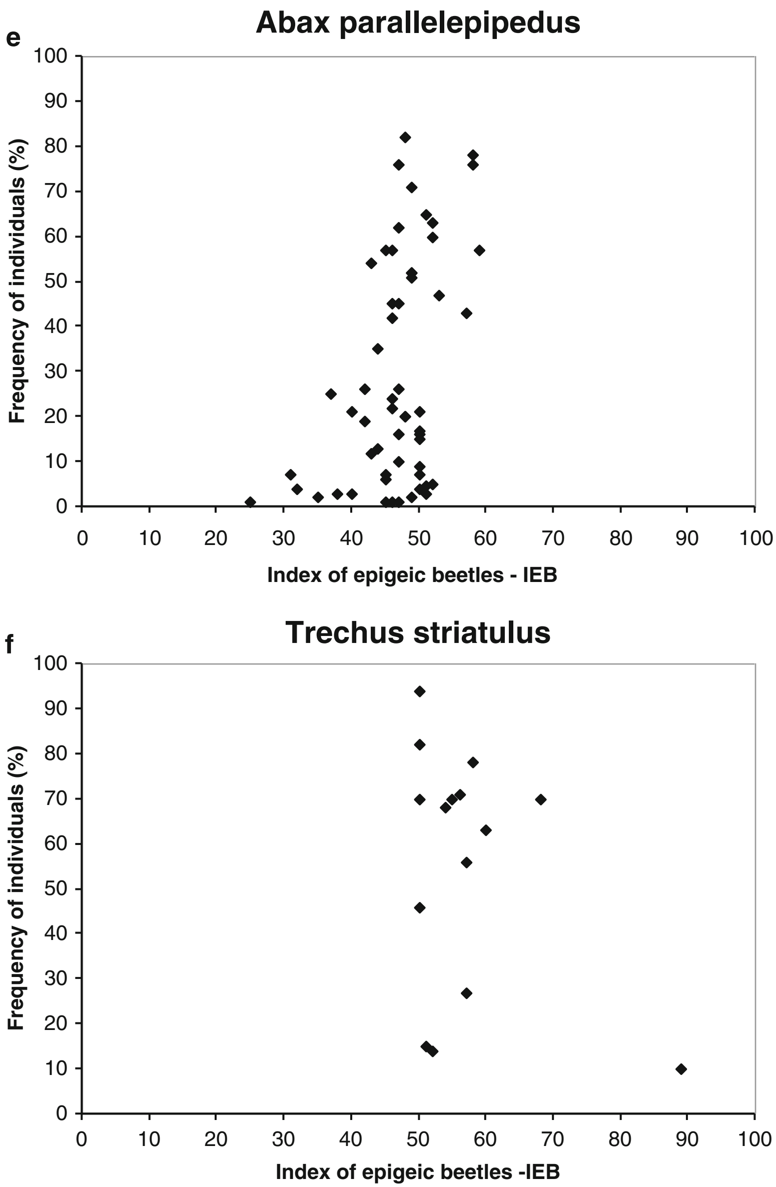

Fig. 24.2 (continued)

The initial stage of growth is approximately exponential; then, as saturation begins, the growth slows, and at maturity, growth stops. If observed values are outside this relation, it can be concluded that the state of habitats is changing.

This approach has a use in the evaluation of habitats. Virgin or natural habitats host several species of group R, a majority of species of group A, and a minimum of species

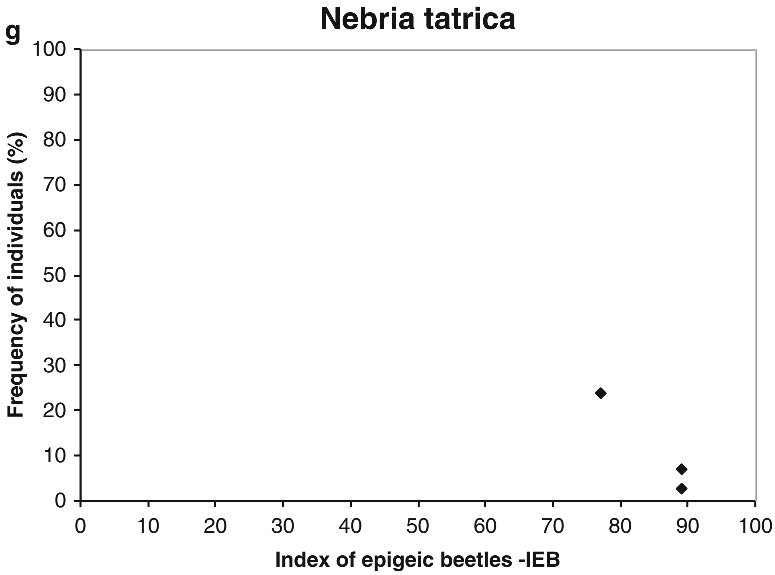

Fig. 24.2 (continued)

Table 24.3 Division of habitats according to Index of epigeic beetles

IEB	Human impact on habitat	Type of habitats
0–15	Very strong human impact	Large areas of arable land without ecotones; ruderal areas, landfills, etc.
10–35	Strong human impact	Small-areas of arable land with ecotones (hedgerows, forest edges), meadows, pastures, orchards
30–50	Impacted habitats	Production forests, forest parks, natural meadows, banks of backwaters
45–65	Less impacted habitats	Semi-natural forests in protected areas, virgin forests, subalpine meadows, banks of highland streams, peat bogs
50–100	Non impacted habitats	Climax forests, alpine meadows, screes, edge of snow fields, shore of montane lakes and streams

Boháč (1990), Nenadál (1998)

of group E. The more species of group R are present in a community, the better the natural state of the habitat is. A change in the proportion of indicative groups reflects changes in anthropogenic pressure on habitats and beetle communities.

Boháč (1990) and Nenadál (1998) proposed the division of habitats according to index of epigeic beetles (Table 24.3).

24.7 Communities of Epigeic Beetles as Indicator of Biodiversity in the Czech Republic

The present communities of epigeic beetles are deprived of species in almost the whole area of the Czech Republic. We can also find places where it is possible to say that communities of epigeic beetles are becoming extinct. The decline is not uniform throughout the area; it is connected to specific habitat decline (Boháč 2005; Boháč et al. 2005).

Forest epigeic beetles form the most important and initially most abundant part of epigeic beetles (Boháč 2005; Boháč et al. 2005). The highest species diversity and the lowest amount of ubiquitous species are present. Bioindicator species in these habitats in the Czech Republic are as follows: species of the tribes *Cychrini, Patrobiini, Trechini, Pterostichini (Carabidae)* and species of subfamilies *Omaliinae, Tachyporinae, Aleocharinae (Staphylinidae*). We can classify indicators of original virgin forests: species of tribe *Rhysodini* (*Carabidae*), some species of subfamily *Olistheriinae* and *Omaliinae* (e.g., species of genera *Phyllodrepoidea, Phloeonomus*), *Tachyporinae* (e.g., species of the genus *Lordithon*), *Aleocharinae* (e.g., species of genera *Phymatura*, *Phymaturosilus*) (*Staphylinidae*).

Communities of floodplains and wetlands are characterised by carabid species of tribes *Bembidiini, Platynini* (species of the genus *Agonum*, especially) and *Oodini* and *Odacanthini* (Boháč 2005) and staphylinid species of genera *Bledius, Carpelimus, Ancyropho*rus, *Gymnusa, Deinopsis, Myllaena, Ischnopoda, Calodera, Stenus, Quedius*, etc.) (Boháč et al. 2005).

Communities living in rock steppe remained well preserved, because rock steppe is difficult to cultivate. Despite this fact, several localities were damaged by the introduction of *Robinia pseudoacacia* and *Pinus nigra*, or by limestone mining. The highest species diversity is found on rock steppe formed by limestone, e.g., carabids *Notiophilus rufipes, Harpalus cordatus, Harpalus tenebrosus centralis a Harpalus winkleri* (Boháč 2005), and staphylinids *Ocypus winkleri, Ocypus ophthalmicus* (Boháč et al. 2005) are specific for those habitats.

Dry grasslands were formed in the pleistocene and holocene periods and remained in existence as refugia in agricultural landscape; they are always affected by man. *Carabus hungaricus, Cymindis, Parazuphium*, some species of genus *Harpalus* (Boháč 2005) and *Ocypus compressus* (Boháč et al. 2005) are indicative species of these habitats. During the second half of the twentieth century, these communities were affected by excessive utilization of biocides and chemical fertilizers. Up to the present, some species of genus *Cymindis* and *Calosoma* are nearly extinct and some species of genus *Amara* are on the decrease (Boháč 2005).

24.8 Invasive and Expansive Epigeic Beetles

The problem of invasive species is less serious, favouring epigeic invertebrates (Table 24.4). Other invertebrates, e.g., phytophagous insects, are connected with their host plants. If an invasive host plant spreads into new localities, phytophagous insects spread too.

Table 24.4 Non-native species of epigeic invertebrates in the Czech Republic

Epigeic invertebrates (non-native)	Number of species	Origin of species
Arachnida	2	Tropics and subtropics, the Far East
Diplopoda	4	Atlantic, Western Europe, the Mediterranean
Chilopoda	1	The Mediterranean
Carabidae	13	Western Asia, Eastern Asia, South Europe
Staphylinidae	8	Southeast Asia, North America

Mlíkovský and Stýblo (2006), Veselý (2002), Boháč and Matějíček (2003)

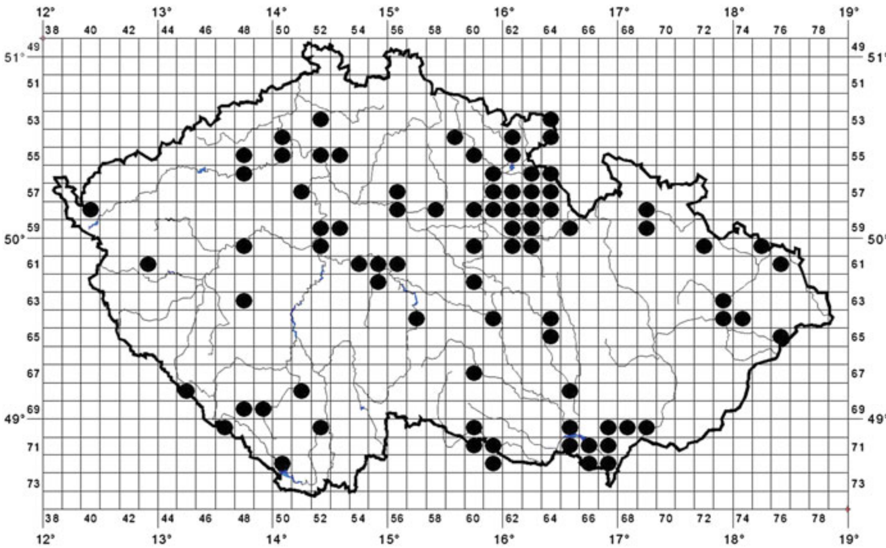

Fig. 24.3 Distribution of invasive species *Philonthus rectangulus* in Czech Republic

Mapping of invasive and non-native species must be carried out in collaboration with amateurs and must be recorded on faunistic grid maps.

Examples of invasive epigeic beetles are the ground beetle *Philonthus rectangulus* (Fig. 24.3) and rove beetle *Oxytelus migrator*. It is difficult to catch *Oxytelus migrator* by classic methods of sampling and therefore it is supposed that it spreads to a larger area. Its present distribution is illustrated in Fig. 24.4.

Since 1990, the halophilic ground beetle *Pterostichus leonisi* has been spreading into Prague. Its occurrence is probably caused by winter chemical road treatment (Veselý 2002)

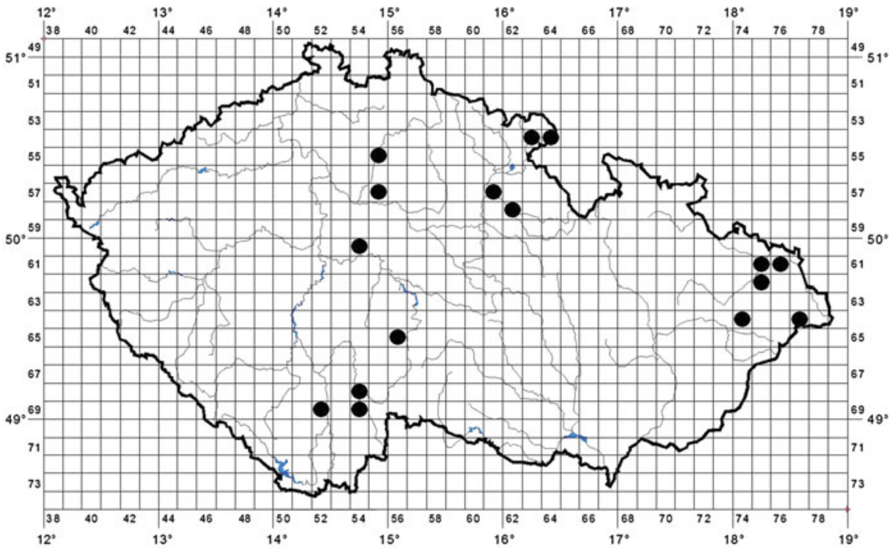

Fig. 24.4 Distribution of invasive species *Oxytelus migrator* in Czech Republic

24.9 Case Study. Long Term Monitoring of Epigeic Beetles: A Comparison of Ground Beetle and Rove Beetle Fauna During Last 100 Years

There are hundreds of scientific works in the Czech and Slovakian literature (for more information, see references of Veselý 2002; Boháč and Matějíček 2003) containing historical data and quantitative evaluation of assemblages of epigeic invertebrates, especially beetles, from 1869 to the present. Heterogeneous data are available in these papers. Communities of wet lands or communities of forests are well described, whereas communities of biotopes strongly affected by man (ruderal biotopes, agricultural ecosystems, etc.) have only recently (since the end of the 1930s) been given adequate attention by several authors (e.g., Roubal 1942). Critical evaluation of these datasets is still required.

Of the long-term monitorings of communities of epigeic beetles, it is necessary to mention the monitoring of epigeic beetles in Prague (capital town of the Czech Republic) (Veselý 2002; Boháč and Matějíček 2003). Concerning rove beetles, the unique monitoring of species was carried out from 1869 to 2000 and the results were published in the Catalogue of the beetles (Coleoptera) of Prague (Veselý 2002; Boháč and Matějíček 2003).

In the period of interest from 1869 to 2003, the area of Prague hosted 358 carabid species and 730 staphylinid species. This means 80 % (for carabids) and 5 % (for staphylinids) of all species reported so far in the Czech Republic.

Bioindication groups are represented as follows:

- Carabids – 62 (17 %) species of Group I, 209 species (58 %) of Group 2 and 87 eurytopic species (24 %).
- Staphylinids – 154 species of Group R1 (21.1 %), 376 species of Group 2 (51.5 %) and 200 eurytopic species (29.8 %). In the area of Prague, there were found 154 species included in the Red Book, i.e., about 10.1 % of the total number of staphylinid species. Considering staphylinid fauna of the whole Czech Republic, the Red Book includes 556 species (40 % of fauna).

During the period between the first list made by Lokay (1869) and the year 2003, the extinction of 74 carabid species and 80 staphylinid species was recorded.

A comparison of the fauna from the initial period, i.e., at the time when the first list of the staphylinids of Prague was published (Lokay 1869), with the present state is complicated. In the initial period, according to this systematic survey of the carabids and staphylinids of Prague,

- 111 carabids species were recorded – now we recorded 284 species.
- 198 staphylinid species were recorded – now we recorded 730 species.

The species taxonomy in a large number of carabid and staphylinid groups improved: many species were not differentiated in the past and thus a single species comprised a complex of related species. The species showing a decrease in the number of localities during the period of the survey are very difficult to detect due to the lack of data.

Staphylinid beetles are a typical group, our knowledge about which has developed quickly in the last decades. Twenty staphylinid species – newly differentiated or newly described after 1936 – were gradually recorded. Their occurrence in the previous periods is, of course, highly probable. The immigrant staphylinid species (invasion) spread due to migration during the last 30 years from other zoogeographical areas. The species concerned are as follows: *Lithocharis nigriceps* (Kr.), *Sunius debilicornis* (Wollaston), *Philonthus spinipes* Sharp, *Thecturota marchii* (Dodero) and *Bohemiellina flavipennis* (Cameron). They all occur mainly in compost or in ruderal biotopes.

24.10 Survey of the Causes of Fauna Changes

A survey of the changes in fauna composition formed a basis for detecting the causes that lead to them. The most important ones were the regulation of the banks of the rivers Vltava and Berounka or other smaller watercourses, disturbances and gradual disappearance of water regime and related changes in the Vltava flood plain, liquidation of sandy sections and sandpits outside river banks, devastation of xerothermic pastures, overgrowing of grass biotopes and thus extinction of some species of ants (classic localities of myrmecophils – Závist, Břežany), changes in forest and agricultural management, eutrophication of biotopes and intervention of invasive plants, acidification, drying of the wetlands, and disappearance of tiny ponds (Malvazinky, Radotín). In some cases, the influence of these factors was manifold. The characterization of technical changes is based on the publication by Kohout and Vančura (1986). The following changes, according to the number of extinct species, are presented, starting with those that influenced the staphylinids most seriously, up to those where the impact was less serious:

(a) **Regulation of river bank**s
Due to river banks regulation, 26 carabid species (e.g., *Agonum viridicupreum, Asaphidion caraboides, Bembidion argenteolum, B. ascendens, B. atrocoeruleum, B. monticola, Dyschirius agnatus, D. angustatus, Elaphrus aureus, Nebria livida, Thalassophilus longicornis*, etc.) and 30 staphylinid species (e.g., *Amauronyx maerkeli, Brachygluta xanthoptera xanthoptera, Pselaphaulax dresdensis dresdensis, Anthobium unicolor, Geodromicus nigrita, Thinodromus dilatatus, Thinobius longipennis, Bledius crassicollis, Stenus formicetorum, S. guttula, S. scutator, Paederidus ruficollis, Paederus caligatus, Lobrathium bicolor, Lathrobium scutellare, Dolicaon biguttulus, Philonthus punctus, Rabigus pullus, Gymnusa brevicollis, G. variegata, Myllaena gracilis, Pronomaea rostrata, Tachyusa balteata, Hydrosmecta subtilissima, Aloconota languida, Atheta malleus, Calodera protensa, Parocyusa protensa, P. rubicunda, Aleochara laticornis*) disappeared (35 % and 38 % of the extinct species) (Veselý 2002; Boháč and Matějíček 2003). This problem was related mainly to the regulation of the banks of the large rivers Vltava and Berounka, as well as liquidation of the natural stands (sandy, loamy and gravel banks, riparian growths etc.).

(b) **Changes in forest management**
The changes in forest management are responsible for the extinction of 7 carabid species (e.g., *Calosoma sycophanta, Carabus problematicus, Cymindis vaporariorum, Harpalus solitaris, Pterostichus aethiops, Sericoda quadripunctata, Trechus pilisensis sudeticus*) (9.5 % of the total number of extinct species) and 16 staphylinid species (e.g., *Plectophloeus erichsoni, P. rhenanus, Trichonyx sulcicollis, Amauronyx maerkeli, Saulcyella schmidti, Batrisodes vesustus, Claviger longicornis, Phyllodrepa translucida, Rugilus mixtus, Ocypus macrocephalus, O. tenebricosus, Phymatura brevicollis, Zyras similis, Lomechusa emarginata, L. pubicollis, Aleochara moerens*) (20 % of the total number of extinct species) (Veselý 2002; Boháč and Matějíček 2003). The most important changes regarding these species are the liquidation of old trees, removal of dead wood, and chemical treatment of growths.

(c) **Changes in agricultural management**
The changes in agricultural management are responsible for the extinction of 5 carabid species (e.g., *Acupalpus interstitialis, Amara crenata, Calosoma auropunctatum, Harpalus zabroides, Ophonus stictus*) (7 % of the total number of extinct species) and 13 staphylinid species (20 % of the total number of extinct species) (e.g., *Bythinus securiger securiger, Claviger testaceus,*

Eusphalerum torquatum, Carpelimus punctatellus, Anotylus fairmairi, Ocypus ophthalmicus, Zyras similis, Lomechusa paradoxa, Lomechusoides strumosus, Lamprinodes saginatus, Lamprinus erythropus, Calodera protensa, Aleochara breiti) (Veselý 2002; Boháč and Matějíček 2003).

Here, the most important factors are the liquidation of balks and preserves; also, chemical treatment of fields could influence the extinction of some carabid and staphylinid species; however, direct evidence is missing. After 1990, agricultural production became less intensive (the decrease in the application of fertilizers and pesticides), and some fields turned into fallow land or were built up.

(d) **Overgrowth, changes in water regime, no mowing**
Overgrown vegetation and changes in water regime probably caused the extinction of 8 staphylinid species (10 % of the total number of the extinct species). The main decline is due to myrmecophilous staphylinid species, such as *Chennium bituberculatum, Centrotoma lucifuga, Ctenistes palpalis, Claviger testaceus, Borboropora kraatzi, Zyras fulgidus, Myrmoecia plicata* and *Oxypoda depresipennis*. Overgrowing and microclimatic changes negatively affected the hosts of these, mainly myrmecophilous, species (Boháč and Matějíček 2003).

(e) **Disappearance of pastures**
The disappearance of pastures and free grazing is responsible for the extinction of 10 carabid species (13.5 % of the total number of extinct species) (e.g., *Amara lucida, Cicindela germanica, Cymindis scapularis, C. variolosa, Lebia cyanocephala, Licinus cassideus, Poecilus kugelanni, P. punctulatus, P. sericeus, Polistichus connexus*) and 6 staphylinid species (7.5 % of the total number of the extinct species) (e.g., *Philonthus intermedius, P. corruscus, P. cruentatus, Emus hirtus, Dinothenarus pubescens* and *Ocypus ophthalmicus*). The disappearance of pastures was manifested directly by the extinction of coprophilous predator species depending on the larvae and imagoes of other invertebrates. In addition, there was also the indirect influence manifested by overgrowing (see also the changes in agricultural management and the changes in water regime) (Veselý 2002; Boháč and Matějíček 2003).

(f) **Disappearance of sandy sections and sandpits**
The disappearance of sandy sections and sandpits influenced 11 carabid species (15 % of the total number of the extinct species) (e.g., *Amara praetermissa, A. spreta, A. tricuspidata, Carabus arvensis, C. nitens, Cryptophonus melancholicus, Harpalus autumnalis, H. flavescens, Olisthopus rotundatus*) and 6 staphylinid species (7.5 % of the total number of the extinct species) (e.g., *Bledius subterraneus, Paederidus ruficollis, Tachyusa balteata, Hydrosmecta subtilissima, Parocyusa protensa* and *P. rubicunda*). The liquidation of sandy sections and sandpits is responsible for the disappearance of the only biotope suitable for psammophilous carabid and staphylinid species (Veselý 2002; Boháč and Matějíček 2003).

(g) **Disappearance of natural water regime**
The disappearance of the natural water regime in flood plains (the absence of regular spring floods and the transport in the alluvium) apparently affected 13 carabid species (17.6 % of the total number of the extinct species) (e.g., *Agonum dolens, A. lugens, Badister unipustulatus*, *Bembidion tenellum, Blethisa multipunctata, Diachromus germanus, Elaphrus fuliginosus, Harpalus progrediens, Chlaenius sulcicollis, Ch. tristis, Pterostichus gracilis*) and three species (4 % of the total number of the extinct species) (*Eusphalerum longipenne longipenne, Stenus asphaltinus* and *Parocyusa longitarsis*). These and further species were perhaps regularly floated down from the more elevated localities during spring floods (Veselý 2002; Boháč and Matějíček 2003).

(h) **Changes in the use of farm buildings, stables, and cellars**
It seems probable that one carabid species (*Sphodrus* leucophthalmus) and three staphylinid species became extinct due to the changes in the use of farm buildings, stables, and cellars (4 % of the total number of the extinct species) (*Phyllodrepa puberula, Tasgius ater* and *Aleochara discipennis*). These species were probably synanthropic, and the destruction of minor farming in the vicinity of towns and its traditional ways (breeding small animals, manure disposal, etc.) caused their extinction.

(i) **Direct liquidation of localities due to built-up areas**
The direct destruction of biotopes was definitely one of the most important causes of the extinction of many species. Unfortunately, we mostly lack data on these changes. E.g., according to some data (Boháč and Matějíček 2003), the biotopes of the following staphylinid species were destroyed: *Stenus ater* – due to the construction of a swimming pool in the place of a former brick-yard in Břevnov, *Trichonyx sulcicollis* – due to the construction of a sports complex in Cibulka, and *Bledius denticollis* – the sand pit was built up with family houses in Řepy.

Currently, we can often witness intensive construction activities in places of natural biotopes in the suburb of Prague: big stores, supermarkets, new highways, residences, etc., Staphylinids occurrence as an indication of the impact on the environment (EIA process) is used rather exceptionally (Veselý 2002; Boháč and Matějíček 2003), and our data on species disappearance are insufficient.

Apart from the stated causes of species extinction, there are other negative influences affecting carabid and staphylinid beetles (Veselý 2002; Boháč and Matějíček 2003). However, these impacts are difficult to prove: changes in ruderal area and character, large-scale exploitation in quarries and clay pits, afforestation of abandoned pastures and other areas, disappearance of vineyards, changes in maintenance of urban parks and lawns, high numbers of visitors in localities, salting, and climate change.

The data for the influence of floods in 2002 on carabids and staphylinids are insufficient. This influence can be both negative (damage and destruction of riparian growths, uprooted trees, damaged historical parks, e.g., Stromovka, and other damaged localities – Císařský isle, Krňák and Malá Řeka pools, etc.) and positive (formation of new biotopes by deposits of gravel and sand).

There are hundreds of scientific works in the Czech and Slovakian literature containing historical observations and quantitative evaluation of assemblages of epigeic invertebrates, especially beetles, from 1869 to the present. Heterogeneous data are available in these papers. Communities of wet lands or communities of forests are well described, whereas communities of biotopes strongly affected by man, e.g., ruderal habitats, agricultural ecosystems, etc., have only recently (since the end of the 1930s) been given adequate attention by several authors (e.g., Roubal 1942). Critical evaluation of these observations still needs to be done.

Of the long-term monitoring of communities of epigeic beetles, it is necessary to mention the monitoring of carabid beetles in Prague (capital city of the Czech Republic) (Veselý 2002). Concerning rove beetles, the unique monitoring of species was carried out from 1869 to 2000 and the results were published in the Catalogue of the beetles (Coleoptera) of Prague (Boháč and Matějíček 2003) (Table 24.5).

24.11 Land Use Changes and Landscape Degradation in Central and Eastern Europe in the Last Decades

The Czech rural landscape, like the cultural landscape of the Central Europe, has undergone a long historical development under a dominant anthropogenic influence. The traditional character of the Czech landscape with tiny patches of fields, thick web of country roads lined with fruit trees, so admired by painters and photographers, survived till the latter half of the twentieth century. Since that time, during the transition to large-scale socialist production, the agricultural landscape has been considered a productive area. According to official government instructions, parcels of arable land were unified so as not to be interrupted by meadows, pastures, shrubs, or other elements hampering efficient cultivation. The result of this recent development has been the origin of the large-scale landscape formed by large collective open fields, regardless of the fine natural structure of the landscape. It has been accompanied by many ecologically negative consequences. Characteristic features and specific regional differences between landscapes were wiped out, and specific regional small-scale landscape types vanished. A striking decrease in the length of landscape boundaries (ecotones) corresponds to a strong decrease in landscape diversity and stability. Small strips of meadows and pastures along forests, pathways, water streams, grassy balks, and old orchards on slopes have been abandoned (Lipský 2000).

The development of landscape heterogeneity between 1988–1989 shows a slow positive trend of changes in relation to the previous period (1958–1978), when the dramatic social changes and a very intensive agriculture and industrialization of agriculture was described (Sklenička 2002). These positive trends are expressed by

Table 24.5 Number of extinct species of ground beetles of Prague (Czech Republic) and its surroundings during different time periods

Period	Number of extinct species: Rove beetles/ ground beetles	Indicative group	The cause of extinction
1790–1899	13/15	R – 9/12, A – 4/3	Change in agricultural management, change in forest management, disappearance of sandy sections and sandpits, disappearance of pastures
1900–1909	12/12	R – 8/9, A – 4/3	Disappearance of natural water regime, disappearance of pastures, disappearance of sandy sections and sandpits, regulation of river banks, change in forest management, disappearance of natural water regime
1910–1919	6/8	R – 3/3, A – 3/5	Regulation of river banks
1920–1929	1/3	R 1/2, A – 0/1	Disappearance of natural water regime
1930–1949	14/18	R – 6/10, A – 8/8	Regulation of river banks, change in forest management, disappearance of sandy sections and sandpits, disappearance of pastures, disappearance of natural water regime
1950–1959	12/15	R – 6/8, A – 6/7	Change in agricultural management, change in forest management, disappearance of pastures, disappearance of natural water regime, disappearance of sandy sections and sandpits
1960–1969	4/3	R – 1/1, A – 3/2	Change in forest management, disappearance of natural water regime, disappearance of sandy sections and sandpits, disappearance of pastures
1970–1979	6/5	R – 3/2, A – 3/3	Change in forest management, disappearance of natural water regime, disappearance of sandy sections and sandpits, disappearance of pastures
1980–1989	5/3	R – 3/1, A – 2/2	Change in agricultural management, change in forest management, disappearance of natural water regime, disappearance of pastures
1990–1999	1/0	R – 1/0	Regulation of river banks
2000–2010	? data are still evaluated	?	?

Veselý (2002), Boháč and Matějíček (2003, edited)

increasing the percentage of grassland in agricultural landscape. Recently, non-productive functions of agriculture and cultural landscape, such as recreation and tourism, landscape and nature conservation, or drinking water accumulation and supply, have gained more and more importance. The present development of the Czech landscape corresponds to the European trend of decrease in arable and agricultural land and increase in forestland (Lipský 2000)

An increasing proportion of ruderal habitats and brownfields causes the expansion of ubiquitous and expansive species (e.g., carabid species *Pterostichus caspius* and staphylinid species *Oxytelus migrator, Lithocharis nigriceps, Lithocharis ochracea, Sunius debilicornis, Philonthus rectangulus, Philonthus spinipes*, *Thecturota marchii* and *Bohemiellina flavipennis*). Currently, we can often witness intensive construction activities in places of natural biotopes in the suburb of big towns: big stores, supermarkets, new highways, residences, etc. Staphylinids occurrence as an indication of the impact on the environment (EIA process) is used rather exceptionally and our data on species disappearance are insufficient (Boháč and Matějíček 2003). The data on the influence of floods in 2002 on carabids and staphylinids are also insufficient. This influence can be both negative (damage and destruction of riparian growths, uprooted trees, damaged historical parks, e.g., Stromovka, and other damaged localities – Císařský isle, Krňák and Malá Řeka pools, etc.) and positive (formation of new biotopes by deposits of gravel and sand).

There are other negative influences affecting rove and ground beetles (Veselý 2002; Boháč and Matějíček 2003). However, these impacts are difficult to prove: changes in ruderal area and character, large-scale exploitation in quarries and clay pits, afforestation of abandoned pastures and other areas, disappearance of vineyards, changes in maintenance of urban parks and lawns, high numbers of visitors in localities, salting, the change of climate.

Conclusion

Communities of invertebrates undergo continuous evolution. The abundance of assemblages as well as the state of our knowledge on biogeography and bionomics of species, are changing. The proposal of indicative classification must therefore be considered as a proposal connected to the current state of knowledge. The observations should be updated permanently. Nevertheless, the potential of these models is of great importance in nature conservation. It can be used for complex monitoring of communities living in agricultural landscape or in Natura 2,000 habitats (Natura 2,000 is an ecological network of protected areas in the territory of the European Union). This paper also presented the results long-term monitoring of epigeic beetles from 1869 to 2003 in Prague, the capital city of the Czech Republic and information about invasive species.

Acknowledgement This work was supported by the Grant Agency of the University of the South Bohemia České Budějovice, Czech Republic (GAJU 063/2013/Z).

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Chapter 25
Environmental Indicators of Biological Urbanization

Anders Pape Møller

Abstract The objectives of this chapter on biological urbanization (the biological process resulting in exploitation by living beings of urban habitats and the successful establishment of populations of such organisms in urban habitats from ancestral populations living in natural or rural man-made habitats) were to (1) identify environmental indicators of urbanization; (2) rank these indicators in terms of indicator ability; and (3) test for spatial and temporal consistency in indicator ability. Four different measures of urbanization have been proposed: (1) year when a rural population became urbanized, as judged by direct observations of the first reproducing individuals in the urban habitat; (2) the difference in population density between urban and rural habitats with higher density in urban habitats reflecting more ancient and hence more advanced urbanization; (3) at least one urban population having higher population density in urban than in nearby rural populations of the same species; and (4) records of reproduction in city centers. The three largest mean effect sizes (Pearson's product-moment correlation coefficient) reflecting likelihood of urbanization of birds were 0.47 for predation-related factors, 0.46 for geographic range and population density, and 0.29 for body size. The year of urbanization for different populations of the same bird species had a repeatability of 0.44 among sites. The difference in population density between nearby urban and rural habitats had a repeatability of 0.26 among the same sites. Selection for adaptation to the novel urban environment included (1) a reduction in dispersal propensity and hence a reduction in morphology associated with efficient flight or movement; (2) changes in vocalizations of birds and other organisms to cope with altered urban noise; (3) changes in songs and positions in the vegetation used for song related to changes in a predator community between rural and urban habitats; (4) changes in flight distance due to change in predator community; and (5) a change in flight behavior in response to the proximity of humans toward perpendicular flights away from the walking direction of humans to avoid human disturbance.

Keywords Dispersal • Flight initiation distance • Heat island effect • Indicator ability • Selection • Spatial scale • Temporal scale • Urbanization

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_25

25.1 Introduction

One of the most pronounced changes in natural habitats is caused by the conversion of rural habitats into urban areas, resulting in urbanization. This conversion now happens at a rate that implies a doubling of urban habitats every few years. Many countries now have more than 10 % of the land surface covered with urban areas with the maximum for the Netherlands now being more than 15 % of the entire land surface covered with urban habitats (European Commission 2006; Schneider et al. 2009). Movement of humans has caused conversion of land from rural to urban areas, and by 2008 more than half of all humans were living in urban areas (Handwerk 2008). Importantly, this trend is predicted to increase in the coming years as the total human population grows further and migrates to urban habitats predicted to reach more than 70 % by 2050 (United Nations 2007).

Urbanization is usually defined as change in land-use due to conversion of rural habitats into urban ones, which is a geographical term. However, urbanization is also a biological term referring to the biological process resulting in exploitation by living beings of urban habitats and the successful establishment of populations of such organisms in urban habitats from ancestral populations living in natural or rural man-made habitats.

The history of urbanization is on a biological time scale recent and brief. The first urban centers arose in China, India and the Middle East ca. 10,000 years ago when humans settled together in close proximity (Diamond 1997). This occurred as a consequence of surplus production of agricultural products that allowed many humans to live together. Probably many different kinds of organisms ranging from bacteria and other microorganisms to insects, birds and mammals were attracted to this super-abundance of resources. Hence populations of many different organisms became established in urban areas. Not surprisingly, the mechanisms associated with domestication (e.g. Darwin 1868; Kohane and Parsons 1988) are very similar to those being associated with urbanization (Møller 2012). Some of the first organisms associated with human cities were domestic flies *Musca domestica*, house mice *Mus musculus*, brown rats *Rattus norvegicus* and house sparrows *Passer domesticus*. A recent genetic analysis of the house sparrow showed clearly that there was only a single colonization event of urban areas in the Middle East ca. 10,000 ago (Summers-Smith 1963; Sætre et al. 2012). Urbanization of organisms accelerated as the human population increased, and many species of birds were already tolerant of human proximity during the Middle Ages (Gesner 1669) and more recently during the industrialization (Bonaparte 1828).

Urban areas often differ in climate from nearby rural areas, with important consequences for urban species. Temperatures are typically one or two degrees higher in urban than in nearby rural areas, especially in winter at higher latitudes, the so-called heat island effect (Gilbert 1989). Rainfall patterns also differ between urban and rural habitats because pollution causes rain to be concentrated on days late in the week in urban areas, while being distributed evenly in rural habitats, and urban areas often have increased rainfall downwind of the urban center (e.g. Shepherd et al. 2002). Because of higher temperatures and thresholds for accumulated spring temperatures (so-called degree days) being reached earlier in spring, urban areas have longer growing seasons with spring starting earlier and fall extending for longer than nearby rural areas. Therefore, the duration of the breeding season for many species of birds is up to 3 weeks longer in urban than in nearby rural areas (Klausnitzer 1989; Chamberlain et al. 2009). This change in timing of reproduction is also reflected in the annual reproductive cycles of urban birds that show earlier onset in spring and later regression in summer for reproductive hormones and size of reproductive organs compared to rural birds (Partecke et al. 2004). Furthermore, population density is often considerably higher in urban than in rural habitats due to higher primary productivity and a surplus of food (Evans et al. 2010a, b; Møller et al. 2012). Urban areas also have higher levels of noise and light than nearby rural areas (Gilbert 1989; Klausnitzer 1989).

The study of biological aspects of urbanization was partly covered by Darwin (1868) in his book on domestication. There is a more recent long history of studies of urbanization in Eastern Europe (Tomialojc 1970; Klausnitzer 1989; Marzluff et al. 2001). The main findings of this literature were fewer, but more abundant species in cities. Thus some species could make the transition from rural to urban habitats, but not others. Why? Species that eventually successfully colonized urban habitats and hence achieved high population densities there, sometimes even greater densities than anywhere else, were already abundant in rural habitats. This gave rise to the conclusion that such urban species had particular characteristics, and the identification of these characteristics has since then been an active area of research. Likewise, research on the underlying mechanisms allowing some species to make the transition from rural to urban habitats, including stress tolerance and tolerance of human proximity, has been an active area of research.

The objectives of this chapter were to (1) identify environmental indicators of urbanization; (2) rank these indicators in terms of indicator ability; and (3) test for spatial and temporal consistency in indicator ability. Surprisingly there have only been modest attempts to analyze the extent to which different indicators of biological urbanization reflect the degree and the timing of urbanization. This is surprising given that rigorous indicators of urbanization and their indicator ability are a crucial first step for understanding the underlying biological processes.

25.2 Environmental Indicators of Urbanization

25.2.1 Testing for Consistency in Indicator Ability Among Indicators

At least four general indicators of urbanization have previously been reported in the literature (Table 25.1): (1) Year when a rural population became urbanized as judged by direct observations of the first reproducing individuals in the urban

Table 25.1 Environmental indicators of urbanization, aspects of urbanization, their advantages and disadvantages and references

Indicator	Aspects of urbanization	Advantages	Disadvantages	Reference
Year when urbanized	Timing of immigration	Reflects history of urbanization Continuous variable	Difficult or impossible to assess	Møller (2008)
Difference in population density between urban and rural habitats	Subsequent expansion	Easy to assess Continuous variable	Other factors than urbanization may affect difference in density	Evans et al. (2010a, b), Møller et al. (2012)
At least one urban population having higher population density in urban than in rural populations	Subsequent expansion	Relatively easy to assess	Relies on extensive knowledge from many areas to be meaningful Discrete variable	Møller (2009)
Recorded reproduction in city centers	Adaptation to high rise buildings, perhaps linked to habitat preference of mountainous areas	Easy to assess	Other factors than reproduction in city centers are important Discrete variable	Croci et al. (2008)

habitat (Møller 2008); (2) the difference in population density between urban and rural habitats with higher density in urban habitats reflecting more ancient and hence more advanced urbanization (Evans et al. 2010a, b; Møller et al. 2012). Evans et al. (2010a, b) list several similar indices; (3) at least one urban population having higher population density in urban than in nearby rural populations of the same species (Møller 2009); and (4) records of reproduction in city centers (Croci et al. 2008). I have previously investigated these indicators of urbanization for birds in the Western Palearctic and found generally strong Pearson correlations exceeding 0.50 (Fig. 25.1) with one exception (this exception was the correlation between difference in density and whether a species breeds in the city center; Møller 2014). The relatively small correlations show that different indicators reflect slightly different phenomena. While these correlations may be considered modest, they are actually high for biological phenomena (Cohen 1988; Møller and Jennions 2002). A principal component analysis on the four indicators listed above revealed a single component accounting for 57 % of the variance with loadings greater than 0.43 for all four indicators, implying an improved indicator ability of this component compared to the four separate indicators (Møller 2014). For many taxa and locations it will be virtually impossible to obtain estimates of year of urbanization, leaving the three remaining indicators as possible tools. Importantly, all three can readily be recorded in a single year even with a modest involvement of fieldwork.

Adaptation to proximity of humans is a key feature of urbanization with reduced fear responses, corticosterone levels and flight distances (Cooke 1980; Partecke

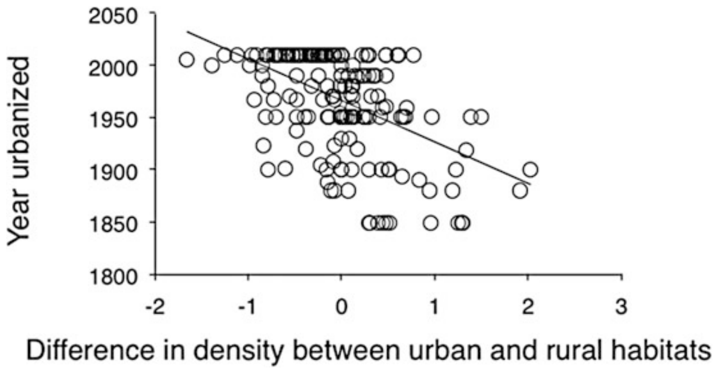

Fig. 25.1 Difference in population density between urban and rural populations and estimated year of urbanization in European birds (Adapted from Møller et al. 2012)

et al. 2006; Bonier et al. 2007; Møller 2008). Flight initiation distance, estimated as the distance at which individuals take flight when approached by a potential predator (including humans), is a behavioral indicator of urbanization (Cooke 1980; Møller 2008). A possible indicator of urbanization is the difference in mean flight distance between urban and rural habitats with more urbanized populations having much shorter flight distances than rural populations (Møller 2008). Likewise, the difference in variance in flight distance between urban and rural habitats is an independent indicator of urbanization with urbanized species having greater variance in flight distance than non-urbanized species (Møller 2010a; Carrete and Tella 2011). The difference in flight distance between nearby urban and rural populations was indeed positively correlated with the difference in breeding population density and with the year of urbanization (Møller 2008), as predicted if the variables reflected the same underlying phenomenon.

25.2.2 Ranking of Indicators in Terms of Their Indicator Ability

Superior indicators of urbanization should show large differences between urbanized species and species from the same neighborhood that did not become urbanized. Møller (2014) provided a meta-analysis of the factors associated with urbanization of birds, relying on numerical values of Pearson's correlation coefficient ranging from 0 to 1 as a measure of effect size. A total of 99 effect sizes for 13 different categories of effects were evaluated (Fig. 25.2). The three largest mean effect sizes were 0.47 for predation-related factors (hence accounting for $0.47 \times 0.47 = 22\ \%$ of the variance in urbanization), 0.46 for geographic range and population density and 0.29 for body size. The high effect size for predation is mainly linked to a change in predator community in particular an increased

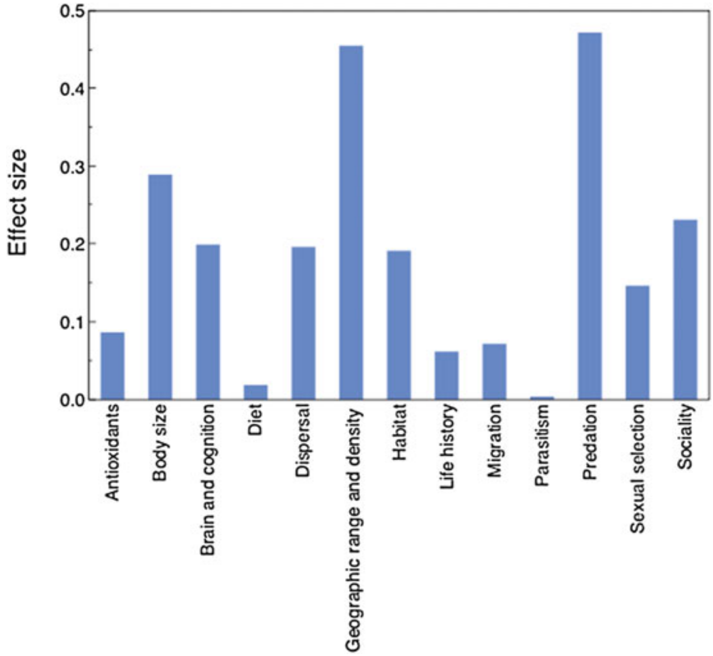

Fig. 25.2 Mean effect size for different categories of factors affecting urbanization of birds. Effect size is Pearson's product-moment correlation coefficient (Adapted from Møller 2014)

abundance of cats *Felis catus domesticus* in urban compared to rural habitats (Baker et al. 2008; Møller et al. 2010; Møller 2011). In contrast, the three smallest mean effect sizes were 0.06 for life history, 0.02 for diet and 0.00 for parasitism. These latter effects were small and accounted for less than 1 % of the variance. Other factors such as brain size and cognitive ability (e.g. Maklakov et al. 2011) fall in between these extremes. Thus indicators of predation and anti-predator behavior, geographic range, population density and body size are likely to be superior in their indicator ability.

25.2.3 Testing for Consistency in Indicator Ability Across Spatial Scales

We would predict that indicators of urbanization would tend to be similar across spatial scales if the process of urbanization has been independent for different cites, as in the case of the European blackbird *Turdus merula* (Evans et al. 2009a, b). Even if urbanization of different cities by the same species was not statistically independent, there could still be significant repeatability of indicators of urbanization because different cities were colonized by a given species at approximately the same time. For example, European blackbirds have colonized most of Europe several decades ago (Evans et al. 2010a, b), while the closely related song thrush *Turdus philomelos* has so far only colonized cities in U. K., Ireland and some parts of North-western Europe. Møller et al. (2012) showed that the year of urbanization for different populations of the same species had a repeatability of 0.44 among sites ranging from populations in Rovaniemi in Northern Finland to populations of the same species breeding in Granada in Southern Spain. Likewise, the difference in population density between nearby urban and rural habitats had a repeatability of 0.26 among the same sites. This implies that there is significant consistency in indicator ability of both year of urbanization and difference in population density, although these repeatabilities are modest by any yardstick.

25.2.4 Testing for Consistency in Indicator Ability Over Time

There are no explicit tests of change in indicator ability over long time scales. However, difference in population density among years for the same species and locality are highly consistent (Møller et al. 2012). We could expect a temporal change in indicator ability if modern urban environments have facilitated a recent increase in urbanization of organisms. While some species like the house sparrow have been urbanized since long, most other species have only been urbanized recently. The year of urbanization of 55 different species of birds in Europe was on average 1975, SE = 4.84 years, skewness = −1.84, indicating a preponderance of cases of relatively recent urbanization. Møller et al. (2012) tested whether the repeatability of two indicators of urbanization differed between species that have been urbanized since long and species that only have become urbanized recently. They reported no significant difference in repeatability for difference in density between anciently and recently urbanized species (ancient: $F = 2.02$, df = 7,32, $r^2 = 0.31$, $P = 0.08$, $R = 0.17$ (SE = 0.10); recent: $F = 2.47$, df = 51,158, $r^2 = 0.44$, $P < 0.0001$, $R = 0.27$ (SE = 0.05)). Likewise Møller et al. (2012) reported no significant difference in repeatability for year of urbanization between anciently and recently urbanized species (ancient: $F = 3.80$, df = 7,20, $r^2 = 0.57$, $P = 0.009$, $R = 0.44$ (SE = 0.15); recent: $F = 1.82$, df = 51,102, $r^2 = 0.47$, $P = 0.005$, $R = 0.21$ (SE = 0.07)). These limited analyses do not suggest any clear difference in repeatability over time.

25.3 Biological Consequences of Change in Selective Regime Due to Urbanization

Differences in phenotype between ancestral rural and current urban habitats may arise as a consequence of phenotypic plasticity, phenotypic sorting or evolutionary adaptation. The first mechanism implies that single individuals differ in phenotype between habitats. Phenotypic sorting implies that migration by specific kinds of individuals to urban or rural habitats is responsible for differences between habitats. The final mechanism represents micro-evolutionary change whereby differences in phenotype are due to differences in genetic constitution. Given that the urban environment differs qualitatively and quantitatively from the ancestral rural habitat we can expect selection for adaptation to this novel environment and even adaptation to urban habitats. For example (1) we would expect a reduction in dispersal propensity and hence a reduction in morphology associated with efficient flight or movement (Cheptou et al. 2008; Evans et al. 2012). Thus seeds of plants growing in cities are likely to have lost appendages that allow transport by wind as in more rural habitats. Likewise resident birds are favored over migrants of the same species (Pulliainen 1963; Evans et al. 2012). Likewise, (2) we would expect changes in vocalizations of birds and other organisms to cope with altered urban noise (Slabbekorn 2013). (3) We would also expect changes in songs and positions in the vegetation used for song being related to change in predator community between rural and urban habitats (Møller 2011). Thus birds singing from positions higher in the vegetation in urban habitats dominated by cats as potential predators. (4) We would expect changes in flight distance due to change in predator community (Cooke 1980; Møller 2008, 2009; Díaz et al. 2013). (5) We would expect change in flight distance in response to proximity of humans towards perpendicular flights away from the walking direction of humans to avoid human disturbance. Likewise we would expect urban birds (and other organisms) to more closely assess whether humans are walking towards them or just passing them at close range (Rodríguez-Prieto et al. 2009; A. P. Møller and P. Tryjanowski, submitted). Many other such changes are likely to occur in animals, but for some of these changes also in plants and other organisms.

25.4 General Discussion

Some species are better able to colonize and live in urban habitats than others (Tomialojc 1970; Klausnitzer 1989; Gliwicz et al. 1994; Stephan 1990; Anderies et al. 2007; Kark et al. 2007; Møller 2009, 2010a, b). The reason why that is the case remains an active area of research. Differences in phenotype between rural and urban habitats can be attributed to phenotypic plasticity, sorting of phenotypes between habitats and evolutionary change. A first example of adaptation in the blackbird to urban habitats through genetic changes has recently been linked to a gene related to avoidance of harm (Müller et al. 2013).

Here I have provided the first assessment of different indicators of biological urbanization. I have also tested for spatial and temporal patterns of consistency in indicator ability showing significant albeit moderate effects. The reasons why effects are only moderate are either true moderate effects, lack of precision in estimates, or different indicators of urbanization reflecting different aspects of urbanization. I consider the latter explanation to be most likely (see also Møller 2014).

Biological urbanization has parallels in invasion biology by consisting of immigration, which may be followed by subsequent establishment and eventually population expansion (see Sol et al. 2013; Møller 2014). Urbanization also has parallels in domestication and other human-induced biological changes (Møller 2014). Future progress in the study of biological indicators of urbanization will rely of integration of these different approaches.

25.5 Future Prospects

Future studies of indicators of urbanization will benefit from identification of biological correlates of these indicators. Furthermore, identification of species that have increased in abundance in urban habitats and those that have not will help in this endeavor. That will particularly be the case when multiple indicators are adopted in the same setting and their biological correlates identified (see Møller et al. 2012; Møller 2014 for this approach).

Which are the underlying mechanisms generating biological urbanization? Urbanization may rely on changes in stress resistance, changes in coping strategies and ultimately changes in underlying physiological responses (Bonier et al. 2007; Partecke et al. 2006; Zhang et al. 2011). These mechanisms may either be based on phenotypic plasticity, non-random migration of different phenotypes (sorting) or evolution.

Which are the conservation consequences? Specialist species are increasingly threatened by urban habitats (e.g. Dickman and Doncaster 1987) and in particular urban sprawl encroaching on natural habitats, and that is the case in particular in the tropics where dramatic population growth feeds the expansion of urban habitats. However, new biodiversity is also generated in urban habitats due to founder effects of small populations and lack of dispersal between rural and urban populations and among urban populations. Thus there is significant genetic divergence between urban and rural populations and among urban populations (Fulgione et al. 2000; Rutkowski et al. 2005; Baratti et al. 2009; Björklund et al. 2010). This divergence results in different phenotypes in rural and urban habitats such as different coloration of birds, differences in songs and differences in flight morphology and hence most likely flight behavior (Hõrak et al. 2001; Isaksson et al. 2005; Evans et al. 2012; Møller 2014; Slabbekorn 2013). There is no consensus on how such novel biodiversity is valued.

Which are the consequences of biological urbanization for humans and human relationships with nature? As the area of urban habitats increases, and the fraction of humans living in cities increases, humans become increasingly alienated from nature (Turner et al. 2004). Even this claim may seem about to change as citizen science and nature protection become an integral part of modern urban life in many developed countries. The British Trust for Ornithology has even managed to convince citizens with bird feeders to pay for reporting birds in their own gardens to internet-based databases that are then used for research purposes.

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Part X
Environmental Pollution

Chapter 26
Environmental Impact of the Coal Industry and Resource Equivalency Method for Environmental Damage with Ecological Indicators

Jaroslav Boháč and Josh Lipton

Abstract Historical coal mining in northwestern Czech Republic has caused substantial environmental damage. The ecological effects of coal mining include adverse impacts at the species, habitat, and landscape levels. Ecological functions of landscapes also have been disrupted. We used information regarding the ecological consequences of coal mining to describe an illustrative case study of how resource equivalency analysis methods could be used to calculate environmental liabilities.

In performing our equivalency analysis, we described damages to resources, habitats, and services using several different metrics: vegetative cover, biodiversity, and temperature amplitude. Vegetative cover was found to be an insensitive indicator of service loss for this hypothetical case study, with changes in biodiversity proving to be a better metric. However, we emphasise several important caveats in assessing biodiversity data. Observations of species numbers at mining-impacted sites does not consider: (1) species abundance or biomass; (2) whether species are pollution-tolerant; (3) whether damaged habitats fully support the needs of species, or whether observations of organisms are indicative of only transient individuals; and (4) the increased probability of observing individuals in vegetatively sparse habitats relative to natural forests. Despite these important caveats, biodiversity information was a useful metric of habitat- and species-level damage in our equivalency calculations.

Changes in temperature amplitudes represent a novel approach to integrating landscape-level changes in ecological services, although research questions remain

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_26

regarding the appropriate functional relationship between temperature amplitude and other ecological metrics.

We calculated environmental liabilities using available data for terrestrial remediation projects. Liabilities were sensitive to the selection of the metric used to describe service losses.

Keywords Chronic coal mining • Resource equivalency method for environmental damage measurement • Ecological indicators • Central and eastern Europe

26.1 Introduction

This study addresses the effects of mining, particularly coal mining, on terrestrial habitats in northwestern Czech Republic (Bohemia). The study focuses on the use of alternative metrics to describe environmental damage and recovery. We also consider the extent to which primary remediation results in recovery of damaged ecosystems and ecological functions. The study analysis is based on quantitative modeling of a hypothetical scenario. However, the hypothetical scenario is illustrative of a large number of historically damaged locations in northwestern Czech Republic and is based on extensive data that have been collected over the past 15 years by various researchers.

The case study generally is organized according to the outline presented in the *Toolkit for Resource Equivalency Analysis for Environmental Damage in the European Union* (Remede Deliverable 10, 2008, (www.envliability.eu). Although all equivalency methods used in this case study conform to those described in Lipton et al. (2007), we have deviated slightly from some of the individual steps in that document, where appropriate, to reflect the specifics of this case study.

26.2 Initial Evaluation

26.2.1 Introduction and Overview: Historical Background of Case Study Region

Mining began in the northwestern Czech Republic in the Middle Ages. Silver mining started in the eleventh and twelfth centuries. Large-scale coal mining began in the eighteenth century, with construction of large, open-pit mines in locations where coal was found at ground level. With the introduction of the steam engine in the second half of the nineteenth century, large open-pit coal mines were expanded. Steam engines were used both for mining and for pumping underground water in order to prevent mine flooding. Following World War II, small mining companies were nationalised into large, state-owned concerns, and the size of open-pit mines increased substantially leading to the development of mines covering several square kilometers.

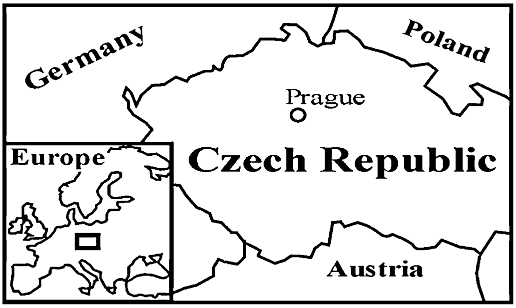


Fig. 26.1 The geographical position of study area – The Great Podkrušnohorská spoil heap

Table 26.1 Estimated extent of landscape-level impacts from open-pit mining in mining districts in northwestern Czech Republic

Damage of landscape deterioration	District	District area (km^2)
Extreme deterioration	Chomutov	935
	Most	467
	Teplice	469
	Ústí nad Labem	405
Strong deterioration	Karlovy Vary	1,628
	Sokolov	754

Source: Anonymous (1998)

Table 26.2 Annual coal extraction and overburden removed (millions metric tonnes, MMT) by individual coal companies

Coal company	Annual coal extraction (MMT)	Overburden (MMT)
SU a.s.	10	38
MU a.s.	22	60
SD a.s	21	82

Source: Burian (1997)

Large scale open-pit mining developed mainly in northwestern Czech Republic along the border with Germany in a region close to the Krušné Mountains known as "Podkrušnohorská brázda" (Fig. 26.1). Mining and associated activities have dramatically changed the landscape. Table 26.1 illustrates the degree of landscape deterioration in individual mining districts that are named for nearby towns. As shown in Table 26.1, landscape-level damages have been observed over thousands of square kilometers in northwestern Czech Republic.

The primary open-pit mining companies in the region are *Mostecká uhelná* (MU, or Most Coal Company) (Burian 1997), *Sokolovská uhelná* (SU, or Sokolov Coal Company), and *Severočeské uhelné doly Chomutov* (SD, or North Bohemian Mines Chomutov). Table 26.2 provides estimates of the capacity of these coal companies, expressed in terms of annual amount of coal mined and overburden removed.

26.2.2 Data Availability

Data have been collected for the mining region over the past decades. These data include information on water quality, biodiversity data, remediation studies, and information regarding the costs and efficacy of remediation. More limited data are available to enable quantitative evaluation of changes in abundance of biota. Data are contained in the literature cited section of this case study report.

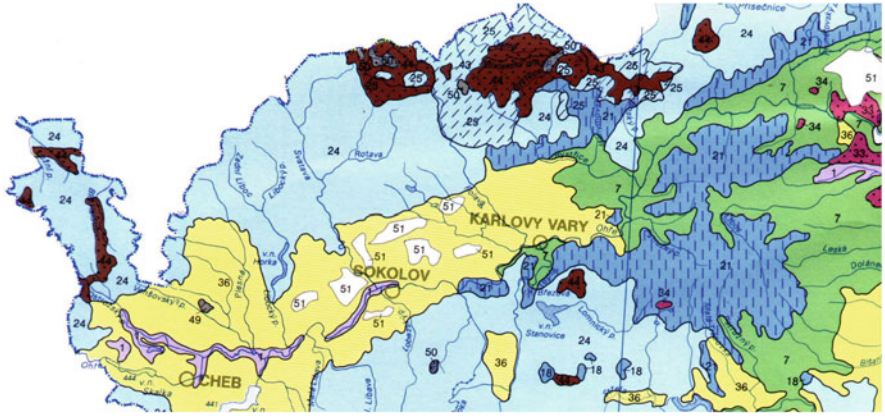
26.2.3 Illustrative Description of Affected Environment

Although there is considerable variation in ecological and mining features of the case study area, we selected the overburden waste site known as *Podkrušnohorská výsypka* (PV) to illustrate conditions in mining-impacted regions. The PV mine site is located northeast of the mining district town of Sokolov [Long. 12° 30′ (East), Lat. 50° 15′ (North)]. Elevations range from 400 to 600 m above sea level, with an average elevation of approximately 450 m. Annual average temperature is 7.3 °C, with an average annual precipitation of 611 mm. The greatest precipitation is in July (78 mm); the lowest precipitation is in February and March (30 mm and 34 mm, respectively). The average number of days with precipitation over 1 and 10 mm is 96 and 14, respectively, and average snow cover lasts over 40 days (Bejšovec and Milič 1994). Since 1960, approximately 3×10^9 m^3 of material have been transported to the overburden heap.

Figure 26.2 shows prevailing terrestrial habitats in the study region. Prior to mining, acidofilic oak forests were prevalent in this area. Oak-hornbeam forests were characteristic along the Ohře river. Xerothermic oak forests occurred in warmer locations. Pine-oak forests were dominant in areas with shallow soils. Swamp alder meadows were found in wet areas (Culek 1996; Neuhauslová 1998). Wet meadows were characterized by *Molinion* and *Calthion* and *Caricion fuscae* and dry meadows by *Violion caninae* and *Arnoseridion*. Willows (*Salia cinerea*) typify shrub vegetation. *Carex elatus and C. gracilis* are dominant along water basins (Culek 1996).

Based on this information, predominant habitat types for the case study were assumed to consist of upland forests (primarily oak and mixed-oak forests), and wetlands. Although open water exists in the case study area, our analysis focuses on the terrestrial habitat types.

Typical biota of the forest habitat types include *Miliaria calandra, Erinaceus europaeus, Apodemus microps, Salamandra salamandra*, etc. Representative biota of the wetland habitat type include *Larus canus, Sterna hirundo, Locustella luscinioides, Remiz pendulina*, *Bufo calamita,* etc.



01 alluvial woodland forests (bird cherry-ash woodland, partly in complex with alder carrs)

07 oak-hornbeam and lime-oak woodland with *Melampyrum nemorosum*

21 herb-rich beech woodland (beech woodland with Cephalanthera species)
24 acidophilous beech and silver fir woodland (woodrush-beech woodland)

33 subacidophilous Central-European thermophilous oak woodland (oak woodland with *Potentilla alba*)

36 acidophilous woodrush-, silver-, birch-, and pine-oak woodland (woodrush-oak and/or silver fir-oak woodland)

49 mires (complex of submontane *Pino rotundatae-Sphagnetum, Eriophoro vaginati-Pinetum sylvestris*)
50 mires (complex of montane raised bogs, partly with *Pinus mugo* agg. and/or *Sphagnum*-rich spruce woodland)
51 complex of successional stages on anthropogenic sites (open-cast coal mines)

Fig. 26.2 Predominant vegetation types in case study region (Neuhauslová 1998)

26.2.4 Preliminary Identification of the Nature of Damages: Environmental Impacts of Coal Mining

Open-pit mining in North and West Bohemia devastated hundreds of km^2 of landscape, resulting in total removal of vegetation cover and in the breakdown of hydrological cycles. Vegetation has been lost as a result of excavation and placement of overburden. Natural water courses were routed into pipes, straightened, or diverted. Wetlands were drained and large areas were excavated into open-pit mines or used for deposition of overburden.

Overburden heaps typically consist of a mixture of clay, low quality coal, and pyrites (Bejšovec and Milič 1994). Clay contains high amounts of Ca, Mg, Na and carbonates; S^{2-} from pyrites is oxidized on exposure to air, forming sulfate. Associated decreases in pH (also through oxidation of pyrite) results in releases

Table 26.3 Chemical composition of water from PV overburden compared with range of typical surface waters in the Czech Republic

Parameter	Unit	PV Site	Typical surface waters in the Czech Republic
pH		6.5–8.4	6.5–8.5
Alkalinity	mmol L^{-1}	7.0–25	0.5–3.0
Conductivity	Scm^{-1}	0.05–20	0.05–0.5
NH_4-N	mg L^{-1}	0.05–1.0	0–5.0
TP	mg L^{-1}	0.01–0.1	0.05–0.4
Na^+	mg L^{-1}	400–5,000	2–50
K^+	mg L^{-1}	3–25	1–35
Ca^{2+}	mg L^{-1}	400–1,500	10–200
Mg^{2+}	mg L^{-1}	50–400	5–50
Cl^-	mg L^{-1}	5–30	5–30
SO_4^{2-}	mg L^{-1}	1,000–15,000	20–200
HCO_3^-	mg L^{-1}	700–1,400	50–200
Fe	mg L^{-1}	0.01–50	0.01–0.5
Mn	mg L^{-1}	0.05–8.0	0–0.2

Source: Frouz (1999), Přikryl and Vlasák (2001), Přikryl et al. (2002)

of Fe, Mn, and other metals. The water discharged from overburden heaps generally has a high concentration of base cations (Na^+, Ca^{2+}, Mg^{2+}), as well as sulfate. Table 26.3 shows the results of water samples collected from the PV overburden heap in comparison to typical surface waters of the Czech Republic. The concentration of soluble ions is more than an order of magnitude higher in the water from the overburden heap than in typical surface waters. Aerial releases of materials from coal mining has affected the water quality of local precipitation. Local rainfall is characterized by relatively high conductivity associated with elevated concentrations of Mg, Ca, bicarbonate, and sulfate. Table 26.4 shows the chemical composition of rain water from PV samples compared with two other locations in the Krušné Mountains: Carlsfeld (Germany), and Slavkovský Forest (Czech Republic).

26.2.5 Preliminary Identification of Affected Services

As noted above, affected services include: habitat services; loss of floral and faunal biodiversity; and ecological services such as hydrological cycling, decomposition, and thermal regimes. Potentially affected collateral human services include: agriculture and silviculture; aesthetic values; and recreational, commercial, and subsistence hunting and fishing. These human services are not evaluated explicitly in this case study.

Table 26.4 Chemical composition of rain water from PV overburden heap compared with two other locations in the Krušné Hory mountains: Carlsfeld (Germany) and Lysina in Slavkovský Forest (Czech Republic)

Parameter	Unit	Carlsfeld	Lysina	Lomnice
pH		4.53	4.67	5.50
Conductivity	Scm^{-1}	19.14	24.31	96.50
Na^{+}	mg L^{-1}	0.27	0.27	2.10
K^{+}	mg L^{-1}	0.04	0.19	1.70
Ca^{2+}	mg L^{-1}	0.16	0.27	5.00
Mg^{2+}	mg L^{-1}	0.04	0.07	1.10
NH_4	mg L^{-1}	0.86	1.31	1.70
NO_3	mg L^{-1}	2.05	2.76	4.70
Cl^{-}	mg L^{-1}	0.41	0.45	1.20
SO_4^{2-}	mg L^{-1}	1.92	2.83	22.70
Fe	mg L^{-1}	–	0.04	0.94
Al	mg L^{-1}	–	0.05	0.90

Sources: Frouz (1999), Přikryl and Vlasák (2001), Přikryl et al. (2002)
Note: Values for the burden heap estimated from weekly bulk sampling of rain water

26.2.6 Social, Economic, or Transboundary Issues

No unique social, economic, or transboundary issues were identified in our initial evaluation.

26.2.7 Preliminary Remediation Planning: Primary Remediation of Mine-Impacted Areas

According to Czech law, coal companies must remediate mined areas after mining is completed. Table 26.5 presents the types of remediation and the areas which have been remediated by individual mining companies. Both forest and agriculture remediation have been undertaken. Agricultural remediation prevailed until 1989. Since that time, forest remediation has been more common. Other types of actions completed include: construction of roads and paths; water management in lakes, streams, and wetlands; and infrastructure support.

As illustrated by the "water management" data in Table 26.5, less than 2 % of remediated areas were wetlands. The low percentage of wetland remediation is a function of the feasibility (and cost) of draining large overburden heaps prior to removal and excavation of wetland areas. As described in greater detail below, primary remediation activities have not fully returned habitats to baseline conditions.

Table 26.5 Types and areas (ha) of remediation actions undertaken by individual coal companies

Type of restoration	Restoration projects complete (ha)		
	MU	SU	SD
Agriculture	1,190	789	1,129
Forest	1,594	1,470	1,090
Water management[a]	29	13	95
Other	183	29	109
Total	2,996	2,301	2,323

Source: Burian (1997)
[a]lake, stream, and wetland remediation

26.2.8 Determining the Scale of the Assessment

As shown in Table 26.1, the overall scope of environmental damages in the north-western Czech mining district is substantial, including areas with virtually complete loss of terrestrial vegetation, wetland loss, and alteration of ecological cycles. However, for the purposes of this case study, we apply the equivalency methods described in Lipton et al. (2007) to a hypothetical, but representative, case study involving environmental damage to 10 ha of terrestrial oak forest and 10 ha of wetland. This illustrative analysis could be extended, by analogy, throughout the affected region. However, we note that any such landscape-level extrapolation of our hypothetical illustration would involve a substantial amount of uncertainty.

26.3 Determining and Quantifying the Damage

In this section, we discuss available information that enables a description of the environmental damages observed in the case study area. This information, which is drawn from a number of studies, is then used to develop the hypothetical scenario used to illustrate the application of the habitat equivalency method. First, we discuss pre-mining baseline conditions, relying on information from early mapping studies and from nearby reference locations. We then describe damages to resources, habitats, and services using several different metrics: vegetative cover, biodiversity, and temperature amplitude. This latter metric represents a novel approach to integrating landscape-level changes in ecological services. Finally, we describe the hypothetical scenario used to illustrate the implementation of the above metrics in a resource equivalency framework.

26.3.1 Pre-mining Baseline Conditions

Although the onset of mining in many areas was too early to enable quantitative descriptions of pre-mining baseline conditions, maps from the middle of the nineteenth century depict floodplains that consisted of meandering streams, fish ponds, wet meadows with natural springs, and wetlands covering at least 15 % of the region (Trpák et al. 2006). Data from nearby reference locations (discussed below) provide a more recent depiction of baseline conditions.

Historical maps from 1841 to 1842 indicate that lands consisted of forested areas, alluvial plains, pastures, and meadows. Vegetative cover occupied more than two thirds of the area. Data from Bičík and Jeleček (2001) indicate that permanent greenery comprised some 65–70 % of the case study area. Open water covered approximately 2–3 % of the landscape.

Based on analysis of historical maps and nearby reference areas (see, for example, Fig. 26.2), baseline vegetative habitats of the case study area were determined to be wet (swamp) alder forests, acidophilic oak forests, and xerothermic oak forests (Pecharová et al. 2001). The water, spring and swamp plant communities are represented by growth of *Phragmites* and *Carex* in wet depressions and along water courses and reservoirs.

26.3.2 Biodiversity Damages: Species-Level Evaluation

Biodiversity damages were evaluated through evaluation of historical data, as well as comparisons of observed biodiversity on spoil heaps and nearby reference locations. We emphasize several important caveats in assessing biodiversity data. First, observations of species numbers does not consider: (1) species abundance or biomass; (2) whether species are pollution-tolerant; (3) whether damaged habitats fully support the needs of species, or whether observations of organisms are indicative only of transient individuals; and (4) the increased probability of observing individuals in vegetatively sparse habitats relative to natural forests. Despite these important caveats, biodiversity information can provide a useful metric of habitat- and species-level damage.

Table 26.6 presents data from Fouz (1999) on species numbers at overburden piles and in adjacent reference areas. Biodiversity reductions were observed for all taxonomic groups studied, with percent reductions from baseline conditions ranging from 45 to 90 %. The relatively high number of species on the mine heaps is likely to be a function of the high biodiversity in the nearby landscape, which provides a source of immigrants. In addition, a number of spoil areas are in different successional stages, thereby providing a somewhat artificially enhanced diversity of habitats. Interestingly, however, the composition of species types differs somewhat in the mine spoil areas. For example, a number of species of organisms that are common in the surrounding reference areas (e.g., amphibians or reptiles such as *Hyla arborea, Rana arvalis, R. ridibunda, Anguis fragilis, Coronella austriaca, Vipera berus*) are absent in the mine-damaged locations. Certain other species occur mainly on the mine soil heaps (e.g., *Bufo calamita* or *B. viridis*) and are more abundant than in the surrounding areas. This indicates that some species substitution has occurred in the mine-affected areas. This substitution likely has resulted in the replacement of less tolerant organisms, such as frogs, with more pollution-tolerant forms, such as toads.

Table 26.6 Number of species observed at coal mine spoil heaps and surrounding reference landscapes

Organism group	Number of species: surrounding reference landscapes	Number of species: coal mine spoil heaps	% of reference condition
Vascular plants	332	302	90
Zooplankton	98	70	71
Trichoptera	40	18	45
Butterflies	257	165	64
Critical endangered species (based on Czech law)	7	6	86
Strong endangered species	19	15	79
Endangered species	23	18	78

Source**:** Based on Růžička and Boháč (1990), Zavadil (1997, 1998), Frouz (1999), Boháč (1999), Přikryl and Vlasák (2001)

The avifauna of mine heap areas has also been damaged. Table 26.7 provides data collected pre- and post-deposition of mine spoil materials. In the pre-deposition baseline, a total of 27 endangered bird species were observed. Post-deposition, this number was reduced to 12 species (44 % of reference). As with the biodiversity data discussed above, both a reduction in total species and a change in the species mixture were observed in the mine-damaged area.

26.3.3 Landscape Damages

A comparison of the current landscape-level vegetative cover with pre-mining conditions can be accomplished by comparing recent satellite images of landscape cover with historical maps. The original habitats and habitats of cultural landscape from the period 1841–1842 were largely destroyed in mined areas. These ecosystems played an important role in local water and temperature cycles, as well as providing habitat for many organisms. Figure 26.3 presents recent satellite imagery from the case study area. Pre-mining landscapes, consisting of approximately 65–70 % permanent vegetative cover (forests, meadows, wetlands), have largely been replaced by mining heaps, bare areas, and other altered landscapes.

26.3.4 Soil Structure Damage

Replacement of native soils with mine spoil materials has caused damage to soil structure and function. The overburden substrate emplaced on waste heaps is variable throughout the case study area, but includes substrates with pH values as

Table 26.7 Endangered bird species observed in pre- and post- deposition of mine spoils

Species	Pre-deposition	Post-deposition
Ixobrychus minutus	+	–
Platalaea leucorodia	+	–
Nycticorax nycticorax	+	–
Anser anser	+	–
Porzana porzana	+	–
Porzana pusilla	+	–
Lanius collurio	+	–
Anas crecca	+	–
Anas strepera	+	–
Carpodaccus erythrinus	+	–
Circus aeruginosus	+	–
Muscicapa striata	+	–
Accipiter nisus	+	–
Oriolus oriolus	+	–
Sylvia nisoria	+	–
Alcedo atthis	+	–
Pernis apivorus	+	–
Tringa hypoleuca		
Falco vespertinus	?	+
Gallinago gallinago	+	+
Oenanthe oenanthe	+	+
Rallus aquaticus	+	+
Cyrcus cyaneus	+	+
Lullula arborea	+	+
Luscinia svecica cyanecula	+	+
Saxicola rubetra	+	+
Corvus corax	–	+
Remiz pendulinus	+	+
Podiceps cristatus	+	+
Hirundo rustica	+	+

Source: Based on Zavadil (1997), Přikryl and Vlasák (2001)
Note: Presence of species denoted by (+); species absence denoted by (–)

low as 2.7. The prevailing substrate material is clayey and unfavorable for further soil development. Mine spoil areas typically have reduced abundance of the soil organisms that are required to assist in the decomposition of litter and facilitate the formation of soil organic matter. The diversity and biomass of soil invertebrates is strongly reduced on new spoils after coal mining. It needs about 20–30 years for the sanitation of soil fauna in plots remediated by forest (alder) (Boháč 1999; Frouz 1999). The soil fauna has great importance in enhancing the C removal from the litter layer and its accumulation in the mineral layer. The accumulation of C in the mineral layer of the heap resulted in long term enhancement of microbial biomass and respiration (Frouz 2002).

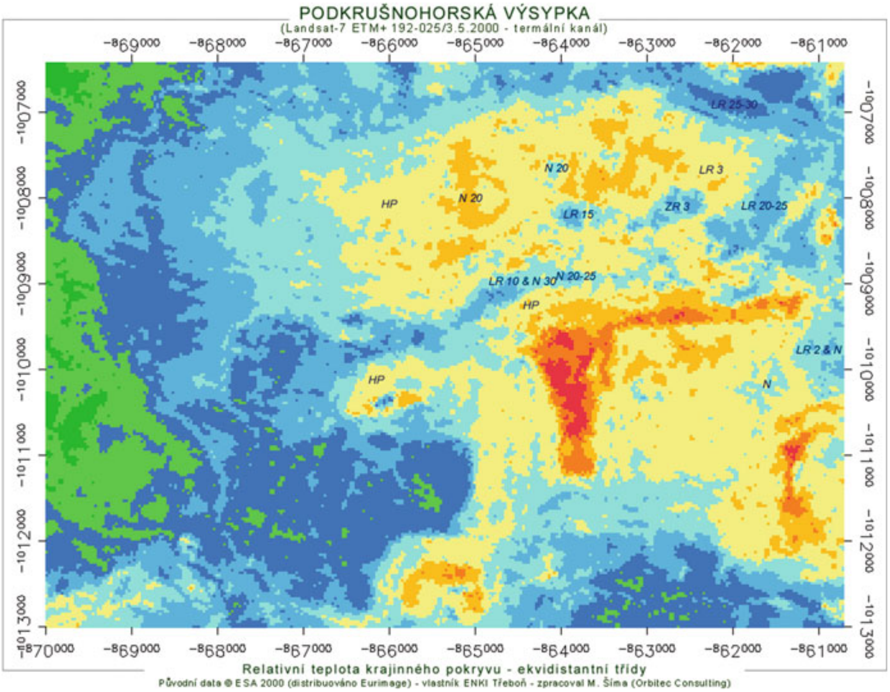


Fig. 26.3 Satellite imagery of the PV case study area. Temperature data was used to classify surficial habitats. Pre-mining landscapes, consisting of approximately 65–70 % permanent vegetative cover (forests, meadows, wetlands) have largely been replaced by mining heaps, bare areas, and other altered landscapes. D – deposits of coal, HP – bare plots of heaps and quarries, L – forest, LR – forest remediation, N – sweep of shrub, PP – ash from power station, VN – water plots, ZR – agricultural remediation (with the permission of Martin Šíma, Orbitec Consulting)

26.3.5 Damage to Ecological Functions: Water Regime Disturbance and Changes in Landscape Temperature Characteristics

Water and vegetation play a critical role in maintaining the thermal characteristics of a landscape. Specifically, the regulation of incident solar energy is maintained by available water, vegetation, and soil functions (e.g., soil organic matter and water-holding capacity). This temperature regulation contributes to local climate and is associated with biodiversity. Coal mining has altered this natural thermal regime by draining areas and removing vegetation. Draining large areas negatively influences local thermal regimes: when water evaporates, solar energy does not enter the latent heat of water vapor; it only warms the landscape. Under normal hydrological conditions, solar radiation is consumed by open water and water

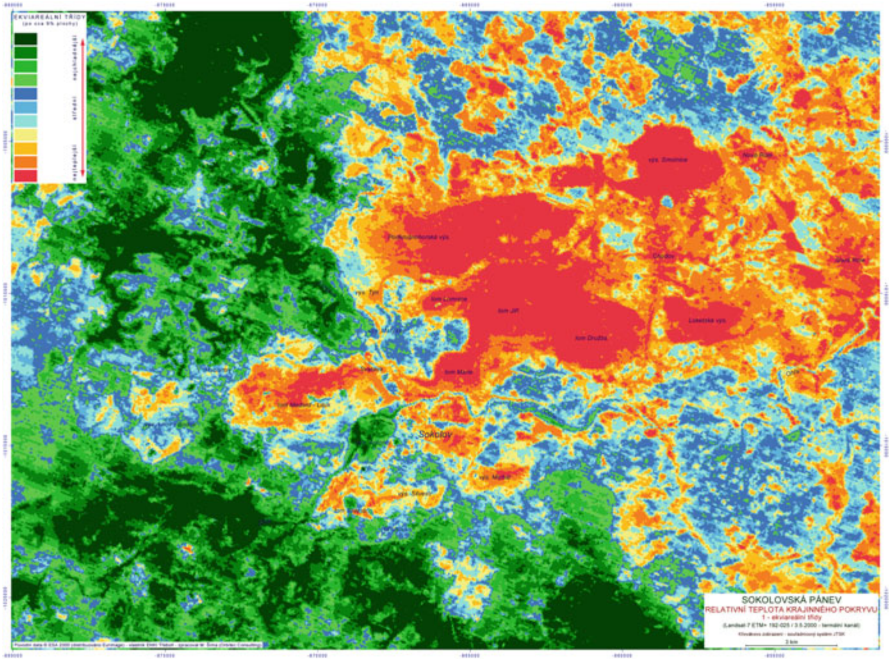


Fig. 26.4 Map of surface temperatures created from the thermal channel of the Teplotní Landsat ETM+. Warmer areas, shown in *red*, are characterized by mining alterations

vapor. Then, during the condensation of water vapor to liquid water, heat is released, warming colder areas. Similarly, vegetation plays a mediating influence on incident solar radiation. (Procházka et al. 2001; Pokorný et al. 2007). Changes to local microclimates can be seen in Fig. 26.4, which illustrates radiative heating of mine-affected areas.

Localised measurements also confirm this warming pattern. The greatest degree of warming was observed in a bare mine dump without vegetation, whereas the lowest values were found in older birch stands (approximately 8 years of tree growth) and in sedge stands in a floodplain (approximately 7 years of growth).

In addition to surficial warming, alteration of water regimes and loss of vegetative cover result in increased daily temperature fluctuations, similar to those observed in desert ecosystems. This occurs because water, water vapor, plants, and soil organic material are required to store solar radiation during nighttime. Barren areas, therefore, are characterised by rapid heat gain during daylight hours, followed by rapid heat loss at night. These temperature fluctuations can be used as a metric of landscape level disturbances that integrate across a number of distinct ecological functions.

Table 26.8 Summary of information regarding environmental damage in coal mine case study area

Damage metric	Nature of damage
Vegetative cover – Landscape	Reduction of permanent vegetation from 65 to 70 % to approximately 20 %. Localized variation ranges from wholly devegetated areas to well-vegetated sites
Biodiversity	Reduction in biodiversity of plants and fauna. Biodiversity in damaged areas 45–90 % of reference conditions, depending on taxonomic group studied
Thermal Regime: Increased Temperature	Devegetated mine spoil areas demonstrate two-fold increase in average daily temperature relative to vegetated reference sites
Thermal Regime: Increase in Daily Temperature Amplitude	Devegetated mine spoil areas demonstrate six-fold increase in daily temperature fluctuations through increase rates of warming and cooling

26.3.6 Determination of Damages: Summary

Environmental damages associated with coal mine development include losses of vegetative cover, reduced biodiversity, and alterations of thermal regimes. Table 26.8 summarises information regarding these damage metrics.

26.4 Determining and Quantifying Gains from Remediation

26.4.1 Identification of Remediation Alternatives

Several types of remediation alternatives have been utilised in the case study area (as noted previously, Czech law requires post-mining remediation to be conducted by the coal companies). The primary remediation alternatives that have been implemented in the case study area are:

- *Natural recovery*. Under this alternative, no actions are taken and landscapes are assumed to revegetate naturally.
- *Dry land remediation to agricultural uses*. Under this alternative, dry (i.e., non-hydric) lands are converted to agricultural areas through soil management and limited planting. Primary agricultural uses include meadows.
- *Dry land remediation to forest*. Under this alternative, affected lands are replanted with natural tree species in an attempt to restore healthy forests.
- *Wetland remediation to agriculture*. Under this alternative, historical wetlands that had been damaged by water diversions and mine spoils are converted to dry land agriculture.
- *Wetland remediation to functional wetlands*. Under this alternative, historical wetlands that had been damaged by mine spoils and water diversions are returned to natural wetlands through a combination of excavation and replanting with wetland plant species.

26.4.2 Effectiveness of Remediation Alternatives

As described above, both biodiversity, ecological functions and ecological services of the affected landscapes have been substantially degraded by mining operations. Remediation of ecological functions is therefore considered a precondition for successful recovery of other ecosystem services.

In studies of *dryland/agricultural remediation*, in which the waste heap surface is covered by topsoil containing a clover-grass seed mix, total vegetative cover reached 80 % 4 years after planting. Twenty-nine species of vascular plants were recorded, with grass and clover species prevailing. Maximum temperature amplitude measured on treated soil surfaces was about 20 °C. Humidity on surface soil horizon reached approximately 98 % early in the morning (Přikryl and Vlasák 2001).

Dryland/forest remediation uses only the heap surface where terrain has been modified; the spacing for planting the bare-rooted seedlings is usually 1 per meter. The seedlings are structured as required by the target stand composition, with minimum introductory species (spruce, including blue spruce, European black pine, Scotch pine, white pine or other exotic pine species, larch, mountain oak, forest oak, swamp oak). Only rarely does such forest remediation result in a healthy and functioning forest stand. Frequently the stand does not survive or function. For example, the stand situated on the Big Heap in the Ore Mts. foothills displayed gaps with the remains of withered seedlings after 4 years despite repeated plantings. The stand provides the same ecological functions as landscapes with no or limited vegetative cover. The total vegetation cover in the Big Heap remediation area (including woody plants) was only about 3 %, and it did not exceed 10 % within the entire Panské povodí basin. Plant species are represented by approximately 6 taxa whose cover did not exceed 2 %. The stand displays diurnal temperature amplitudes of up to 50 °C, humidity in the surface soil layer did not exceed 82 %.

Wetland remediation typically consists of reed (*Phragmites communis*) or cattail (*Typha latifolia, Typha angustifolia*) stands. Reed stands are of great importance for newly forming wetland ecosystem and are considered to be the “condensation cores” of the emerging water cycle in anthropogenically modified landscapes. The coverage rate of these remediated stands usually reaches 80–90 %. Remediated wetlands display diurnal temperature amplitudes up to 15 °C, humidity was not monitored as the soil profile is permanently soaked with water.

The above data indicate relatively rapid recovery of remediated wetlands. Similarly, remediation to dryland agriculture shows success, although it must be understood that the remediated habitat does not provide natural (baseline) habitat functions. However, standard methods of forestry remediation do not appear to be effective as measured by plant cover, thermal amplitude, and soil moisture.

Table 26.9 presents daily temperature fluctuations at remediated sites. In soils, the lowest temperature amplitudes were measured in wetland remediation sites (alder trees and sedges/reed stands - 1.7 and 2.8 °C, respectively). The highest temperature amplitude was recorded in dryland/agriculture remediation sites and in a young spruce plantation (7.0 and 6.1 °C, respectively). The highest daily temperature amplitudes were measured at the soil surface of a reforested spruce plantation

Table 26.9 Daily temperature amplitude in various restored sites

	Air (2 m)	Air (0.1 m)	Soil surface (0 m)	Soil (−0.1 m)
Forest (spruce)	22.0	26.3	34.2	6.1
Agriculture	21.7	25.4	17.3	7.0
Alder *(alnus glutinosa) Carex nigra*	22.6	22.9	17.7	1.7
Phragmites australis	24.9	23.6	12.9	2.8

Source: Procházka et al. (2001)

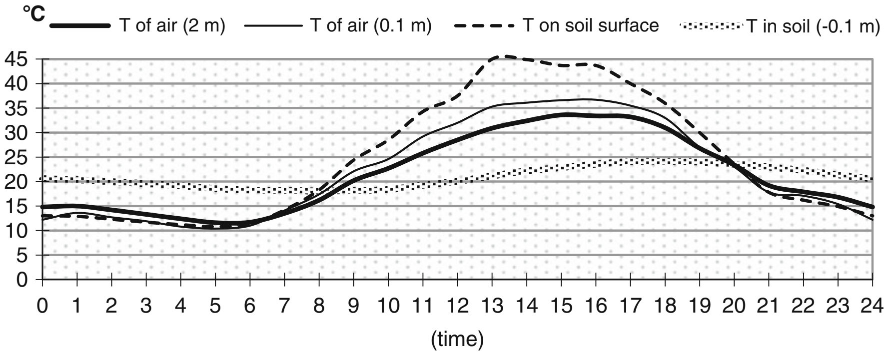


Fig. 26.5 Measured daily temperature (T) amplitudes; dryland/forest remediation (first year after plantation of spruce and pine)

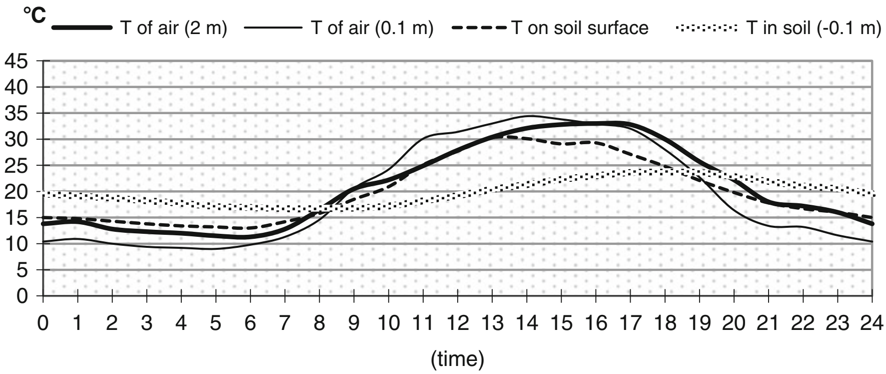


Fig. 26.6 Measured daily temperature (T) amplitude; dryland/agriculture remediation after the first year of remediation

(34.2 °C), whereas in agriculture crop and in alder stand the daily amplitudes on soil surface were lower (17.3 and 17.7 °C, respectively). The smallest amplitude was measured in a reed/sedge stand (12.9 °C). Figures 26.5, 26.6, 26.7, 26.8, 26.9, 26.10 present data on measured daily temperature amplitudes in various terrestrial

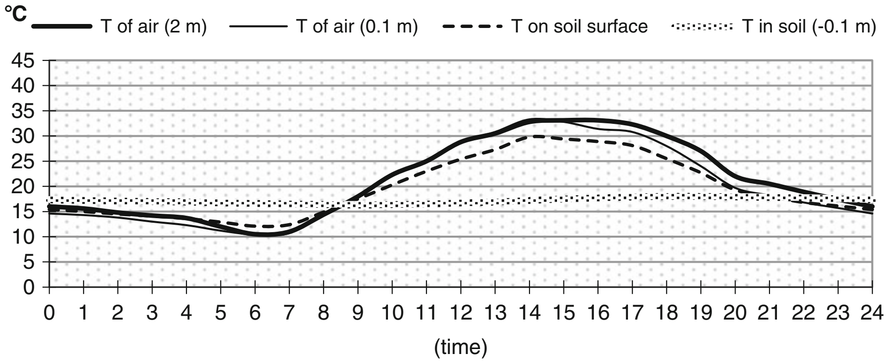


Fig. 26.7 Measured daily temperature (T) amplitude; wetland (*Phragmites* and *Carex*) remediation during the first year after remediation

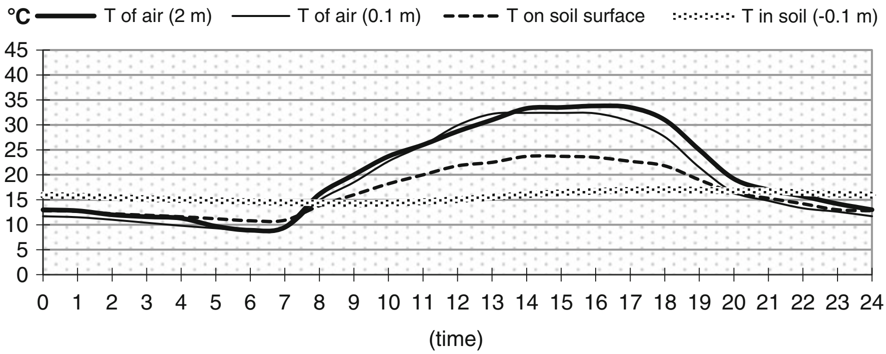


Fig. 26.8 Measured daily temperature (T) amplitude; remediation of alder (*Alnus*) wetland during the first year after remediation

remediation projects (Procházka et al. 2001). These data demonstrate the relative effectiveness of wetland remediation at controlling temperature amplitude damages. Forest remediation, however, has been relatively unsuccessful at managing such temperature variation.

The above data suggest another remediation alternative for dryland systems. Instead of proceeding directly to forest remediation, repeated sowing with classical clover-grass seed mixtures could be used to stabilise affected areas. After approximately 5 years, forestry remediation can proceed in this revegetated plots. We anticipate that the likelihood of success of the dryland/agriculture + forest alternative would be substantially greater than for the traditional dryland/forestry alternative.

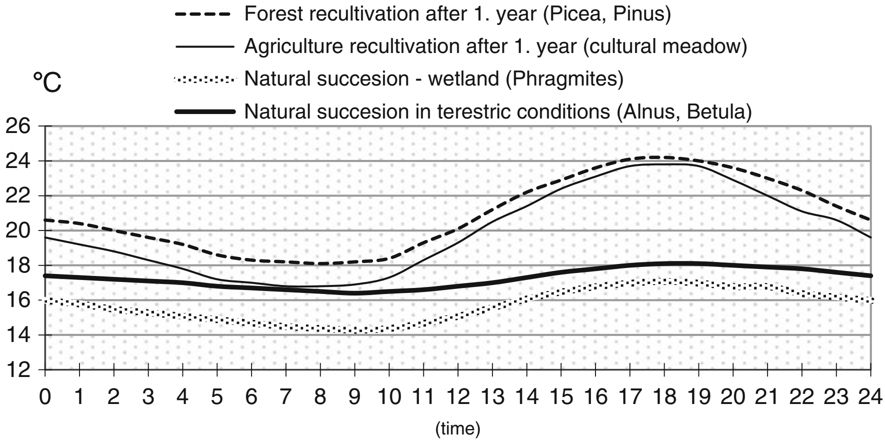


Fig. 26.9 Comparison of daily temperature amplitudes measured in soil surfaces in various remediation treatments of the Burden heap

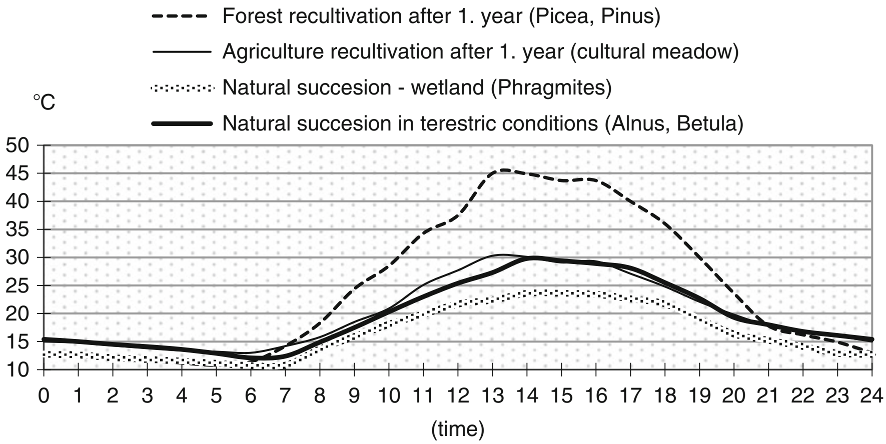


Fig. 26.10 Comparison of daily temperature amplitudes measured in soils (0.1 m depth) in various remediation treatments of the Burden heap

26.5 Quantifying Damages and Scaling Remediation – Illustrative Case Study Scenario

26.5.1 Calculating Debits Caused by Damage

To illustrate the application of the resource equivalency method, we developed a case study scenario of damages based on the information presented above. The case study scenario assumes that mining operations have damaged 10 ha of forest habitat and 10 ha of wetland habitat. We assume that impacts to the forest habitat consisted of

Table 26.10 Illustrative scenario used in case study

Habitat type	Forest	Wetland
Damaged area (ha)	10	10
Year damages start	2007	2007
Primary remediation start	2012	2012
Primary remediation alternative/ areas	Natural recovery: 5 ha	Natural recovery: 5 ha
	Dryland/agriculture: 2.5 ha	Dryland/agriculture: 2.5 ha
	Dryland/forest: 2.5 ha	Wetland: 2.5 ha

The presented data is just for illustration

creation of an upland waste spoil deposit with subsequent biodiversity impacts to natural forest. For the wetland habitat, we assume draining and subsequent emplacement of waste spoils. We assume that damage began in 2007, and that 50 % of each habitat type were remediated in the year 2012 (primary remediation). For the forest habitat type, we assume 2.5 ha of dryland/agriculture remediation, and 2.5 of dryland/forest remediation, with the remaining 5 ha left to natural recovery. For the wetland habitat type, we assume 2.5 ha dryland/agriculture remediation, and 2.5 ha wetland remediation. Again, the remaining 5 ha are assumed to be left to natural recovery. Table 26.10 summarises this basic case study scenario.

We used several different metrics to describe service losses relative to baseline:

- Percent vegetative cover;
- Biodiversity, expressed as relative numbers of vegetation, avian, amphibian, and invertebrate taxa;
- Ecological functions, expressed as daily temperature amplitude and average soil temperature.

Use of these metrics considers damages at the species, habitat, and functional levels of organisation. Table 26.11 presents the percent of baseline services assigned to each metric for the two habitat types. It is emphasised that these service levels are illustrative based on our review of generalised data; conditions at actual sites would be expected to differ from these illustrative values.

As can be seen in the table, use of the different metrics provides highly variable estimates of baseline services. Vegetative cover was the least sensitive metric in this example; whereas bird, amphibian, and invertebrate diversities were the most sensitive metric measured in the referenced literature. For the purposes of this illustrative case study, we scaled the daily average soil surface temperatures using a linear function, i.e., 35 % increase in soil surface temperature equals = 35 % service loss. However, we think it unlikely that this response function is linear. It is more likely that the relationship is non-linear, with a 35 % increase in soil surface temperatures being associated with greater than 35 % service loss. This non-linearity appears to be supported by the generally higher service losses observed for the other metrics. Therefore, as an alternative, we also adopted a non-linear assumption that 35 % increase in soil surface temperature equated to a 70 % service loss.

Table 26.11 Percent of baseline services assigned to different damage metrics in case study

Damage metric	Habitat type	
	Forest (%)	Wetland (%)
Percent vegetation cover	100	95
Vegetation diversity (number of species of vascular plants)	50	66
Avian diversity (number of species)	25	30
Invertebrate diversity (number of species of epigeic beetles)	13	17
Amphibian diversity	25	75
Number of protected species	71	80
Ecological function (daily average soil surface temperature) – linear model	65	100
Ecological function (daily average soil surface temperature) – nonlinear model	30	100

Source: Based on Růžička and Boháč (1990), Zavadil (1997, 1998), Boháč (1999), Frouz (1999), Hájek (2001, 2002), Procházka et al. (2001), Pecharová et al. (2004), Přikryl and Vlasák (2001), Krampl (2004), Pokorný et al. (2007)

To evaluate the beneficial influence of primary remediation, we assumed the following recovery rates and degrees of improvement. For the forest habitat type, natural recovery was assumed to provide a linear 30-year recovery trajectory, with a maximum of 10 % improvement of the initial damage (e.g., if the initial degree of damage is 50 % of baseline, natural recovery was assumed to be at 55 % of baseline). For dryland/agriculture, we assumed a linear 5-year recovery, with a service gain of 55 % of the damage (e.g., if the initial degree of damage is 40 % of baseline, the remediated condition was assumed to be at 55 % of baseline). For dryland/forest, we assumed a 30-year recovery period (linear), with a service gain of 10 % of the damage (illustrating the poor recovery of the forest planting alternative). For the agriculture + forest alternative, we assumed a 35-year recovery period, with full recovery to 100 % of baseline. It should be noted that the two-phased agriculture + forest restoration alternative may provide additional benefits that are not quantified in this case study. For example, grassland planting in the initial phase of remediation may provide carbon sequestration benefits (albeit, relatively small) that could accrue to the Czech Republic. Alternatively, harvesting of planted grasslands prior to conversion to forest ecosystems could potentially be used to support innovative biofuel technologies.

For the wetland habitat type, natural recovery was not assumed to occur because of the hypothesized hydrologic modifications. For dryland/agriculture, we assumed a linear 5-year recovery period, with a service gain of 25 % of the initial damage amount. For wetland remediation, we assumed a linear 5-year recovery period, with a service gain of 75 % of the initial damage amount. Table 26.12 summarises the recovery estimates used in our calculations.

Table 26.12 Recovery estimates used to calculate benefits of primary remediation actions

Remediation alternative	Recovery period (years)	Degree of recovery
Forest Habitat		
Natural recovery	30	10 % of damage
Dryland/agriculture	5	25 % of damage
Dryland/forest	30	10 % of damage
Dryland/agriculture + forest	35	100 % of damage
Wetland		
Natural recovery	None	None
Dryland/agriculture	5	25 % of damage
Wetland	5	75 % of damage

Note: All recovery paths were assumed to be linear

Table 26.13 Total discounted service hectare years (DSHaYs) of debit calculated for the different damage metrics used to assess service loss

	Habitat type	
Damage metric	Forest	Wetland
Percent vegetation cover	0 (0)	28 (21)
Vegetation diversity (number of species of vascular plants)	275 (250)	187 (144)
Avian diversity (number of species)	413 (374)	385 (296)
Invertebrate diversity (number of species of epigeic beetles)	479 (434)	457 (351)
Amphibian diversity	413 (374)	138 (106)
Number of protected species	160 (145)	110 (85)
Ecological function (daily average soil surface temperature) – linear model	193 (175)	0 (0)
Ecological function (daily average soil surface temperature) – nonlinear model	385 (349)	0 (0)

Note: DSHaYs are presented for the initial damage condition and, in forest remediation (30 years), wetland (5 years), the residual damage following primary remediation. Calculations assume 10 ha of initial damage to each habitat type, the service reductions shown in Table 26.11, and the primary remediation assumptions shown in Tables 26.10 and 26.12

Using the above information, we calculated the total amount of debit in terms of (discounted)-service-hectare-years (DSHaYs) for the different damage metrics (over 30 years' time interval for forest remediation and 5 years for wetland) (Table 26.13).

Table 26.13 illustrates how selection of the scaling metric influences the degree of service loss and, consequently, the total DSHaYs of damage, with metrics associated with greater service loss causing more DSHaYs of harm. Table 26.13 also illustrates how implementation of primary remediation actions has reduced the total DSHaYs of damage. The DSHaYs following primary remediation represent the amount of residual damage for which complementary and compensatory remediation is required.

26.5.2 Scaling Complementary/Compensatory Remediation

Complementary/compensatory remediation actions are needed to offset the residual debits shown in Table 26.13. To calculate the scale of necessary actions, we first determined the preferred remediation alternatives. For both habitat types, we selected our preferred alternative based on the relative effectiveness of the different alternatives. For the forest habitat, agriculture followed by forest remediation was assumed to be the most effective alternative. As noted above, in addition to remediating lost ecological services, this alternative may provide additional unquantified benefits in terms of carbon sequestration and source materials for innovative biofuels production. For the wetland habitat, wetland remediation (creation) was assumed to be the most effective alternative.

We adopted different recovery assumptions to calculate the credits associated with complementary/compensatory remediation, because we assumed that projects would be implemented at locations that were not damaged by coal mining. For wetland habitat remediation, we assumed that the project would involve restoring historical wetlands at locations that had been drained for agricultural or domestic uses. For these projects, we assumed a net service gain of 50 % above current conditions. For the agriculture + forest remediation alternative, we assumed that these projects would be implemented at cleared sites that could be restored to functional forests. We assumed a net service gain of 75 % for such projects. We employed the same linear recovery periods shown in Table 26.12 for the remediation alternatives.

Using the above recovery, we calculated that each hectare of forest remediation (agriculture + forest rehabilitation) generates 15 DSHaYs of benefit. Each ha of wetland remediation provides 15.2 DSHaYs of benefit. Diving the per unit benefits of these remediation alternatives into the residual DSHaYs shown in Table 26.13 yields the total ha of required remediation (Table 26.14).

Table 26.14 Total required complementary/compensatory remediation (ha) needed to compensate for residual damage

	Habitat type	
Damage metric	Forest	Wetland
Percent vegetation cover	0	1.4 (21/15.2)
Vegetation diversity (number of species of vascular plants)	16.6 (250/15)	9.4 (144/15.2)
Avian diversity (number of species)	24.8 (374/15)	19.4 (296/15.2)
Invertebrate diversity (number of species of epigeic beetles)	28.8 (434/15)	23.1 (351/15.2)
Amphibian diversity	24.8 (374/15)	6.9 (106/15.2)
Number of protected species	9.6 (145/15)	5.6 (985/15.2)
Ecological function (daily average soil surface temperature) – linear model	11.6 (175/15)	0
Ecological function (daily average soil surface temperature) – nonlinear model	23.2 (349/15)	0

Note: Values are provided for the different damage metrics used to assess service loss. For forest remediation, the preferred alternative was agriculture + forest rehabilitation. For wetland remediation, the preferred alternative was wetland remediation (creation)

Table 26.14 again demonstrates the sensitivity of calculations of required remediation to input assumptions regarding the degree of service loss, as well as the variability in service losses according to the selection of metric. To address this variability, one approach that might be implemented is to develop a weighted index of alternative metrics. For example, an index of the metrics for the forest habitat might be to average the values for the individual biodiversity measurements:

- Vegetation diversity (number of species of vascular plants);
- Avian diversity (number of species);
- Invertebrate diversity (number of species of epigeic beetles);
- Amphibian diversity. This would yield a total required amount of remediation of 24 ha (interestingly, this is virtually the same value as was generated for the nonlinear model of soil surface temperatures). Alternatively, weights could be assigned unequally across the metrics (e.g., 0.66 × biodiversity + 0.33 % cover). Ultimately, the Competent Authority must make this determination based on consultations with knowledgeable local ecologists.

26.5.3 Remediation Costs

To determine the total environmental liability associated with the necessary complementary/compensatory remediation, the costs of the remediation alternatives were determined from unpublished industry sources (Leitgeb and Růžička 1999). Costs were calculated using Czech labor rates. It should be noted that labor costs in the Czech Republic are relatively low compared to many parts of the European Union (particularly Western European countries). Costs of the wetland remediation alternative were calculated to be approximately 7,000 Euro/ha. Costs of the forest agriculture + reforestry alternative were found to be approximately 45,000 Euro/ha. Table 26.15 shows the total cost of the required complementary/compensatory

Table 26.15 Total costs (Euro) of required complementary/compensatory remediation (ha)

	Habitat type	
Damage metric	Forest	Wetland
Percent vegetation cover	–	9,723
Vegetation diversity (number of species of vascular plants)	745,290	66,118
Avian diversity (number of species)	1,117,934	136,124
Invertebrate diversity (number of species of epigeic beetles)	1,296,804	161,405
Amphibian diversity	1,117,934	48,616
Number of protected species	432,268	38,893
Ecological function (daily average soil surface temperature) – linear model	521,703	–
Ecological function (daily average soil surface temperature) – nonlinear model	1,043,405	–

Note: Remediation areas based on values provided in Table 26.14. Costs of wetland remediation are approximately 7,000 Euro/ha. Costs of forest remediation are approximately 45,000 Euro/ha remediation using the areas provided in Table 26.14. Depending on the service loss metric used, remediation costs range (excluding those metrics that yielded no service loss and which were deemed to be insensitive indicators of environmental damage for this case study) from about 432,000–1.3 million Euro for forest remediation, and from about 10,000–160,000 Euro for wetland remediation. Using the average of the biodiversity metrics, remediation costs were approximately 1.1 million Euro for forest remediation, and 103,000 Euro for wetland habitat remediation.

Conclusion

Historical coal mining in northwestern Czech Republic has caused substantial environmental damage. The ecological effects of coal mining include adverse impacts at the species, habitat, and landscape levels. Ecological functions of landscapes also have been disrupted. We used information regarding the ecological consequences of coal mining to present an illustrative case study of how resource equivalency analysis methods could be used to calculate environmental liabilities. In performing our equivalency analysis, we described damages to resources, habitats, and services using several different metrics: vegetative cover, biodiversity, and temperature amplitude. Vegetative cover was found to be an insensitive indicator of service loss for this hypothetical case study, with changes in biodiversity proving to be a better metric of service loss. However, we emphasize several important caveats in assessing biodiversity data. Observations of species numbers at mining-impacted sites does not consider: (1) species abundance or biomass; (2) whether species are pollution-tolerant; (3) whether damaged habitats fully support the needs of species, or whether observations of organisms are only indicative of transient individuals; and (4) the increased probability of observing individuals in vegetatively sparse habitats relative to natural forests. Despite these important caveats, biodiversity information was a useful metric of habitat- and species-level damage in our equivalency calculations. Change in temperature amplitudes represents a novel approach to integrating landscape-level changes in ecological services, although research questions remain regarding the appropriate functional relationship between temperature amplitude and other ecological metrics. We calculated environmental liabilities using available data for terrestrial remediation projects. Liabilities were sensitive to the selection of the metric used to describe service losses.

Acknowledgement This work was supported by the Grant Agency of the University of the South Bohemia České Budějovice, Czech Republic (GAJU 063/2013/Z)

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Chapter 27
Environmental Quality Assessment: Geoenvironmental Indices

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Abstract The present chapter considers various parameters describing the state, distribution and dynamics of pollutants in specific geosystems as geoenvironmental indices of chemical environmental pollution. It compromises methods of geoenvironmental indices calculation related to marine environmental pollution, such as: background concentration, activity and mobility of pollutants, etc. Calculation examples of geoenvironmental pollution indices are presented for some areas of the North Caspian sea.

Keywords Marine pollution • Geoenvironmental indices • Background concentration • Activity • Mobility of pollutants

27.1 Introduction

Long-term struggle with chemical environmental pollution has lead to reduction of pollution level. However it's not enough for us to feel completely safe. This struggle is still to go on, but the adopted common approaches have failed to succeed. As a result we have to change the tactics and make it more adjustable to environmental changes in time and space.

Currently we are using chemical and biological indices for assessment and standard-setting in the field of environmental pollution (Khenari et al. 2009). The drawbacks of these indices are well-known. Chemical indices are incomplete, as they can't cover all the range of substances produced by chemical industry, and biological indices are non-specific, as they can't directly point to the nature of chemical pollution.

However this is not the main problem, which is that the chemical signal and the biological response (let us refer to them as to basic toxicometric indices, BTI) do not always correspond to each other. Alongside with this, the dependence between them ("exposure- effect" curve) established in laboratory conditions (in vitro), may not occur in reality (in situ) or may be distorted, as the pollutant and the

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_27

organism do not interact directly in real conditions, both of them have their own environment.

Geoecology focuses on interaction of man and society at the landscape level, so the parameters describing state, distribution and dynamics of pollutants in specific ecosystems should be referred to as geoenvironmental parameters of environmental pollution. We have also considered the terms "ecochemical indices" and "ecogeochemical indices", but they are not associated with the landscape approach, so we have rejected them.

Special attention has also been paid to the pair "pollution – biota", and we offer to refer to the parameters of specific ecosystems determining their response to chemical pollution as to the parameters of ecosystems' responsiveness to pollution. The indices of environmental pollution and the response of the biota to it can be called geoecotoxicometric indices (GETI). In our opinion the GETI can partly compete with or partly complete the BTI and make the struggle against environmental pollution more efficient.

The present review describes the methods used to determine and apply geoenvironmental indices of marine pollution. Some of them can be directly applied to other water bodies, and in some cases the common approach can be helpful. It should be noted that in some of our previous papers the methods used to determine geoenvironmental indices were referred to as the methods of sea pollution diagnosis. The indices themselves were referred to as diagnostic features.

Sea as the object of study was selected unintentionally, because we have been studying the pollution of the Caspian Sea for 15 years. The materials used in the paper mainly describe the pollution of the North Caspian, the shallow sea part, which can be considered as the Volga estuary (Fig. 27.1). Regular observations of

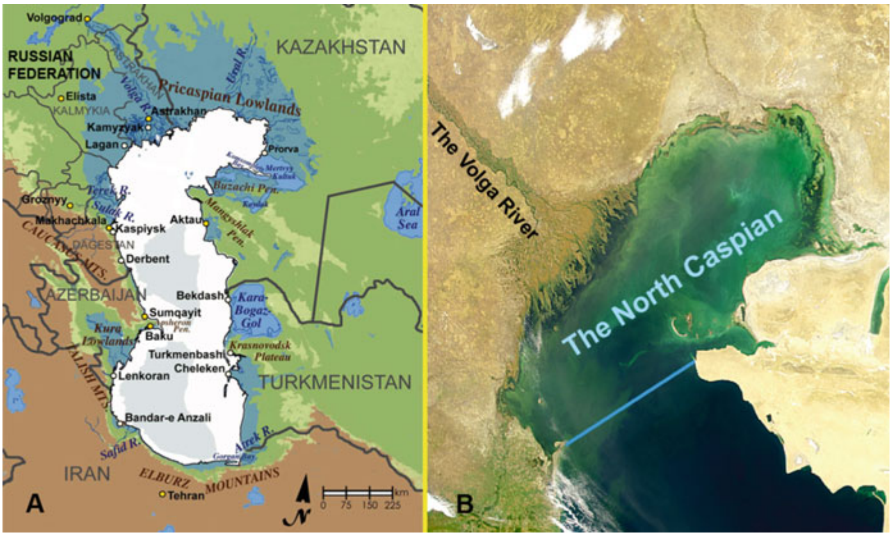

Fig. 27.1 Physical and geographical map of the Caspian Sea (**a**) and a satellite image of the North Caspian (**b**)

marine environmental pollution in the North Caspian have been held within the framework of state monitoring of: (a) state and pollution of the marine environment; (b) water biological resources as far as their habitat is concerned. However most of the data used were obtained through engineering and environmental survey and industrial environmental monitoring in the areas of search, prospecting and development of hydrocarbon resources.

27.2 Background Marine Environmental Pollution

One of the main geoenvironmental indices of marine environmental pollution is the background pollutant concentration (Bastami et al. 2014). This is true only for one of the meanings of "background concentration" term, which can have numerous meanings. So, the background can serve as the temporal or spatial category of different scale (Table 27.1). As a local phenomenon background concentration can be considered either as normative or actual background concentration.

Standard background concentration is the concentration of a pollutant substance (PS) near a "passive" pollution source calculated by a special technique and having specific designation. Standard background concentration is used in setting maximum permissible emissions (discharges) of a pollutant for an active pollution source under the condition that disseminated PS concentration in total with the background concentration must not exceed maximum permissible concentration adopted in accordance with sanitary and/or other requirements.

Standard background concentration in the surface waters of the RF inland water bodies is calculated in accordance with RD 52.24.622-2001 "Calculating background concentration of chemical substances in water streams". According to these guidelines, background concentration is the statistically valid (with probability

Table 27.1 Background concentration as a phenomenon of different scale and category

Scale	Category of	
	Time	Space
Global	Pollutants concentration before Homo Sapiens[a] appeared	Pollutants concentration in ecosystems which are less exposed to anthropogenic impact[b]
Local	Concentration of the pollutant substances in the environment before new pollutant source emerged	Concentration of pollutant substances in the specific location conditioned by pollutants entry from external sources.

Notes

[a]Many of the pollutants, such as hydrocarbons and heavy metals existed before Homo Sapiens appeared, though after that the entry of these pollutants to the environment greatly increased. The pre-historic global background can be estimated by the concentration of pollutant substances in conservative objects (sedimentary rock, etc.), and the clarke (mean concentration of chemical elements in the Earth's crust and other Earth mantles (hydrosphere, atmosphere)) is often used for heavy metals

[b]In Russia, state biosphere reserves carry out monitoring of background environmental pollution

p = 0.95) upper confidence contour of the mean arithmetic concentration of a PS calculated for the least favourable hydrological conditions as far as water quality is concerned.

The guidelines for estimation of background PS concentration in sea water have not been developed yet. In accordance with the sanitary and epidemiological requirements to the protection of coastal sea water adopted in the RF in 2010 (SanPiN 2.1.5282-10), background concentration of standardized substances is the mean arithmetic value of substance concentration for the least favourable period. Currently the State Oceanographic Institute (SOI), an RF methodical centre in the field of marine pollution monitoring– recommends using the upper confidence contour of the pollutant concentration instead of its mean arithmetic value upon the analogy with RD 52.24.622-2001. Alongside with this, SOI recommends taking into account the requirements of the official "Technique for development of standards on permissible discharges of substances and micro-organisms in the water bodies by water consumers" (adopted by Order of Ministry of Natural Resources No. 333 from 17/12/2007) while estimating the background concentration. In particular, according to this technique background concentration must be estimated with help of observation data collected at the stations located in the distance of more than 5 km from waste water discharge spots.

It follows, that the concept of standard background pollution complies two subjective aspects, conditioned by its purpose, i.e. its reference to a certain pollution source (background values are calculated only for its impact area) and to least favourable conditions of PS distribution.

The concept of background concentration is not affected by such subjective aspects, as it is the concentration of pollutants formed within a certain natural object (or part of it) by external pollution sources. This background concentration free from subjectivism should be referred to as the actual background. It is often referred to as natural background, which we consider incorrect, as pollution is inherently of anthropogenic nature (though it can have natural analogies).

As a compromise, one can use the term "geochemical background concentration" (geochemical background) to denote the actual background, as the distribution of pollutants in the environment is mainly determined by geochemical processes. Although this term is also not very precise, as it suits more to describe global pollution in contrast to local background pollution, we will use it further on.

It is obvious that only geochemical background concentration can serve as a geoenvironmental pollution index, as only it describes its state under specific conditions (at a given time and place). The latter circumstance is reflected in the offered term "landscape background"; still we have decided to select the best existing term instead of offering something new.

The term "geochemical background" is used in classical geochemistry (studying the distribution and behaviour of chemical elements in the Earth's geospheres) and in environmental geochemistry (which does the same, but for technophile elements) in almost the same meaning, which means the mean concentration typical of the specific object under specific conditions. Classical geochemistry considers normal conditions as the lack of mineral deposits within the area, while environmental geochemistry regards them as the absence of local pollution, when the level of pollutants content in environmental components is determined exclusively by their entry from outside.

The indicated property makes it possible to estimate geochemical background of pollutants with help of methods already used to estimate geochemical background of chemical elements. In case of normal distribution background is assumed as mode (the most commonly encountered concentration value) or mean arithmetic value. In case of asymmetric distribution (e.g. lognormal) background is assumed as a geometric mean. Before carrying out calculations, series should be freed from anomalous values, which can be determined by mean square deviation (sigma) multiplied by 1, 2 or 3.

Discreetness of measurements of any substance concentration in space is very important to determine the background. If sampling points are located far from each other, one may not trace the anomaly. If all these points are flocked up, the background can get distorted. If sampling is properly organized and the measured data series are properly ranged, the anomalies occupy “extreme points”, making all the distribution asymmetric. So, background can be best expressed by a statistical parameter. (a) summarizing all the data; (b) lying in the distribution centre; (c) independent of extreme values.

Mathematical statistics shows that structural mean values (mode and median) are less dependent on extreme values than exponential mean values (arithmetic, geometric, square, cubic and harmonic means). If we assume this and take into account that the data obtained through geochemical surveys are asymmetrically distributed, then the median should serve as the geochemical background as a centre of the ranged series. We should also take into consideration that mode, median and arithmetic mean are equal in case of normal distribution.

Intuition as well as calculations prompts that the median is least dependent on extreme values. In this regard, we recommend using it to determine the background concentration of pollutants in sea water and bottom sediments. In this case we refer to background as to local-scale spatial category (see Table 27.1).

However we have held a special research to prove the correctness of our choice. We have used data series of copper concentration at two polygons in the Caspian Sea as source data. The first polygon was described by positive asymmetry, while the second one – by negative asymmetry.

Data series were ranged in ascending order. In the first scheme of the numerical experiment maximum (in the first case) or minimum (in the second case) values were consequently excluded from data series one by one. In the second scheme of the experiment maximum and minimum values were alternately excluded from the ranged data series: first maximum value, then minimum, then maximum etc.

Median, arithmetic mean, geometric mean and asymmetry coefficient were estimated for the shortened data series after every step. The experiment results are presented in Fig. 27.2. They show that the median is less dependent on the impact of events occurring at the edges of data series than mean values.

So, geochemical background concentration (F), serving as a geoenvironmental index of environmental pollution, is considered as a spatial category denoting

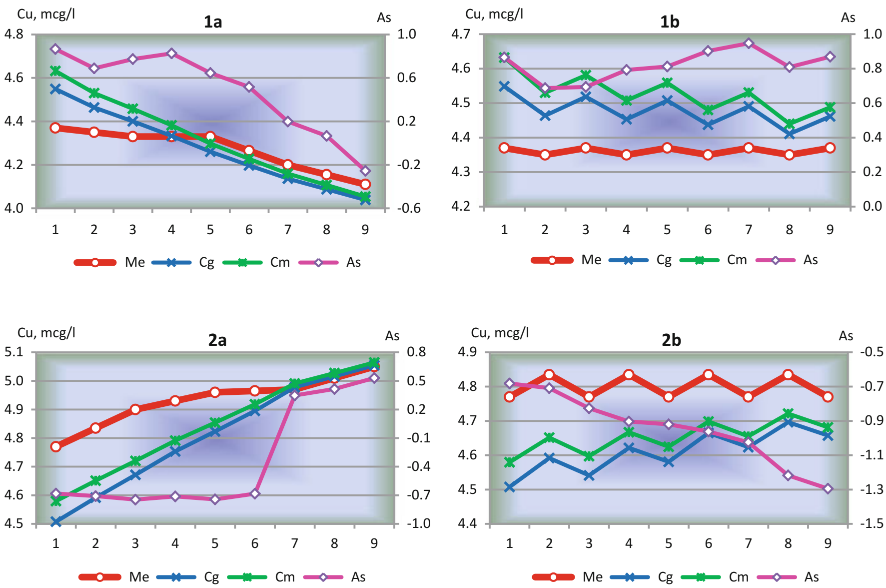

Fig. 27.2 The results of the numerical experiment on assessment of the impact of events at the edges of data series on distribution parameters. *Me* median, C_m arithmetic mean, C_g geometric mean, *As* asymmetry coefficient: **1** – source data series with positive asymmetry; **2** – source data series with negative asymmetry; **a** – first scheme; **b** – second scheme. Step numbers are marked on the horizontal axis

pollutants concentration within the area which is conditioned by pollutants entry from external sources. It follows that F is to be subject to temporal variability, as the pollutants entry varies in time. F temporal changes in the North Caspian usually follow the changes of average concentration (Fig. 27.3) either deviating from or getting closer to it.

We suggest using the following parameters to describe F temporal variability:

– instant background concentration (F value at a given moment of time);
– interval background concentration (mean F value for any interval of F temporal series);
– persistent background concentration (value of F temporal series having 90 % exceedance probability);
– current background concentration (last F value in a temporal series).

F series shown in Fig. 27.3 shows that instant background concentration of oil products in the shallow Volga estuarine area is subject to seasonal and inter-annual fluctuations. Persistent background concentration for the period under consideration made 1 mcg/l, and the current background concentration made 60 mcg/l. The second half of this period in contrast to the first one was poor in water content, and the spatial and temporal variability of concentration reduced (Fig. 27.3). Mean concentration fell, but interval background concentration of oil products in coastal waters increased (Table 27.2).

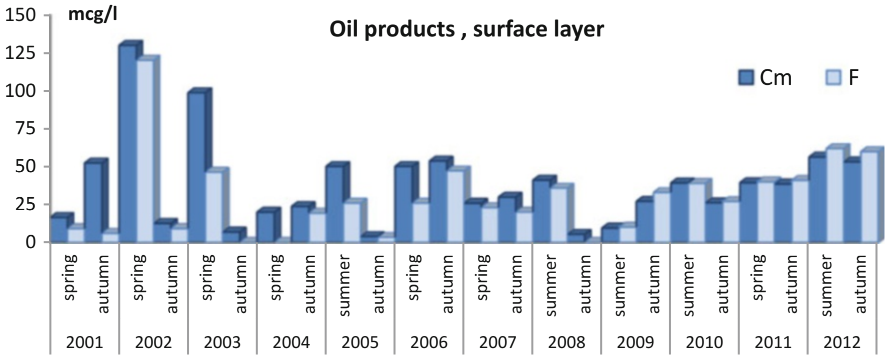

Fig. 27.3 Changes of mean (Cm) and background (F) concentration of oil products (mcg/l) in the surface layer of the shallow area of the Volga estuary in 2001–2012

Table 27.2 Background concentration as a phenomenon of different scale and category

Period, years	Mean volume of annual discharge of the Volga River, km^3	Concentration of oil products in water, mcg/L	
		Mean	Interval background
2001–2006	251.6	43.2	26.1
2007–2012	225.2	32.7	32.6

To determine F value it is necessary to carry out the so-called survey of – quasi-synchronous observations within the network of stations evenly distributed across the water area. Such surveys can be held on a regular basis. Time interval between two surveys should be at least by one order more than the time interval (in days), commonly required for holding each of the surveys. In case the surveys are held regularly and stations location is constant with the exception of F series (and other parameters describing the dynamics of spatial fields), data series can be formed which describe temporal changes of concentration at every station – P_j, where j – is the number and/or character of the station (concentration at a specified point or point concentration).

To describe P_j temporal variability we suggest using the following parameters;

– instant point concentration (P_j value at a given moment of time);
– interval point concentration (mean Pj value for any interval of F temporal series);
– central point concentration (median of temporal P_j series);
– persistent point concentration (value of Pj temporal series having 90 % exceedance probability);
– current point concentration (last Pj value in a temporal series).

Figure 27.4 presents diagrams describing the changes of interval and central point concentration of oil products in water at different points of the Volga estuary according to the data of 2001–2012. The diagrams clearly show that point

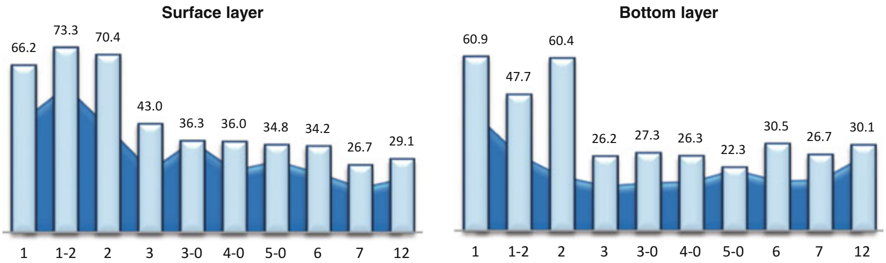

Fig. 27.4 Changes of interval (*bar graph*) and central (*area chart*) point concentration of oil products in water (mcg/l) at different points of the Volga estuary according to data of 2001–2012. Station numbers are indicated on horizontal axis in ascending order, which corresponds to their direction from the west to the east

concentration (both interval and central) is decreasing in the direction from the west to the east. It is conditioned by the fact the main discharge of water and pollutants is concentrated in western branches of the Volga delta.

As a result of spatial and temporal isomorphism typical of environmental processes and phenomena, P_j variability can reflect the changes of background pollution of the water area conditioned by the entry of pollutants from external sources. However it is obvious that F does this better than P_j (though in some our previous papers we didn't differentiate between them). Here we can draw an analogy with a football team, which level can be usually compared with the level of individual players of this team, but the example with a Russian football club "Anji" shows,[1] that this is not always necessary.

Not all of the above mentioned parameters describing background pollution will be used in this paper, but we suppose it's necessary to list them (not all of them, though) to show that there are a lot of parameters which can be used as normative background, which is currently represented by some parameters selected with good intentions but on a subjective basis.

27.3 Contribution of Local Processes to Marine Environmental Pollution

Let us assume that a pollution source appeared in the sea water area evenly covered with a network of stations, and its impact is restricted to several stations only. The spatial series of pollutant concentration values received through the survey in this water area will be characterized by positive asymmetry. Average concentration value will drift far from the median and shift to larger values.

[1] Russian football club "Anji" received sufficient funds from a generous sponsor and bought several world class players, but that didn't help the club to come to the fore.

Assume that within the same water area an artificial reef has been installed instead of the pollution source. The reef absorbs the pollutants from water and its impact area is also restricted to several stations. The spatial series of pollutant concentration values received through the survey in this water area will also be characterized by asymmetry, but negative one. Average concentration value will also drift far from the median and shift to smaller values.

These two theoretical experiments which can easily be reproduced in nature show that the quantitative merit of impact of local anomalies to marine environmental pollution can be represented by both the asymmetry coefficient and the difference between the mean value and median of the spatial data series. Asymmetry coefficient is convenient because it does not depend on concentration measurement units. But the difference between the mean value and the median has more meaning if we consider median as background concentration.

It is difficult to explain why, but the deviations of mean value from background make more sense than asymmetry coefficient, that is why it (deviation) can be regarded as another geoenvironmental coefficient of marine environmental pollution. Moreover, it is more easily converted to non-dimensional form. To do it, one should correlate it with mean concentration (C_m) and express it in per cent. To estimate the impact of local anomalies (E_s) in marine environmental pollution a simple formula can be used:

$$E_s = 100(C_m - F)/C_m \tag{27.1}$$

Now let us assume that regular observations of pollutants content in sea water had been held before the station was affected by a new pollution source. Then the temporal concentration series completed with new data will also be characterized by positive asymmetry and mean concentration value will drift from the median and shift to larger values. We are not going to describe the changes in statistical characteristics of the temporal data series after the stations become affected by the artificial reef, as the reader has already guessed what's going to happen.

So, the temporal data series reacts to short-term anomalies in the same way as the spatial series reacts to local anomalies. We won't delve deeply into the meaning of this ontological statement. It follows (it's more important from practical viewpoint) that formula (27.1) can be used to estimate the impact of short-term anomalies to marine environmental pollution (E_l) after P is replaced with F – central point concentration:

$$E_l = 100(C_m - P)/C_m \tag{27.2}$$

Let us pay attention to the fact that C_m in formula (27.1) refers to the mean concentration of the spatial series, and in formula (27.2) – to the mean concentration of the temporal series. Besides it is easy to note that both the impact of local anomalies (E_s), and the impact of short-term anomalies (E_l) to marine environmental pollution can take either positive or negative values, the former corresponds to pollution (enrichment), and the latter corresponds to purification (depletion of the environment with pollutant substances).

Table 27.3 The unified scale used to estimate the contribution of local processes to marine environmental pollution

Verbal contribution assessment	$\|E_s\|$ or $\|E_l\|$, %
Very low	$0 < E \leq 5$
Low	$5 < E \leq 10$
Middle	$10 < E \leq 25$
High	$25 < E \leq 50$
Very high	> 50

Zinc, E_s, %	Water layer	
	surface	bottom
Mean	10.14	9.64
Maximum	28.98	24.23
Minimum	0.48	0.65
Median	8.31	6.24
Quartile 0.25	3.42	2.62
Quartile 0.75	15.21	15.40

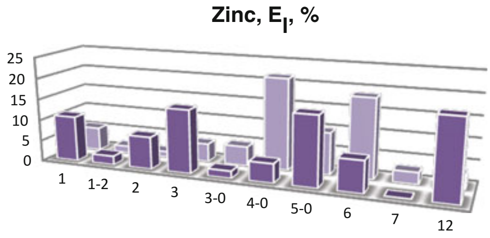

Fig. 27.5 The contribution of local processes to zinc pollution in the shallow area of the Volga estuary in 2001–2012. The table shows the contribution of local anomalies (E_s,%); the diagram shows the contribution of short-term anomalies (E_l,%) at different points of water area (see note to Fig. 27.4). The closer row of the diagram shows surface layer, and the farther row shows the bottom layer

The aggregate local (limited by their distribution) and short-term (limited by their duration) anomalies are hereinafter referred to as to local processes. By this moment we have had enough experience to determine E_s and E_l, which has formed the basis for the development of the unified scale used to estimate the contribution of local processes to marine environmental pollution which is presented in Table 27.3. It should be noted that only absolute values of E_s и E_l are used for this estimation.

We have estimated the impact of local processes to marine environmental pollution while analysing the data of regular observations of marine environmental pollution in the areas of exploratory well construction or stationary oil platform location for the several past years. It gives more ground to assess their impact on the marine environment or to detect the absence of any impact. We also account for the fact that local processes are not necessarily of anthropogenic origin, and they are quite typical of the North Caspian with active dynamics of water masses and bed silts.

Figures 27.5 and 27.6 show the results of the analysis of local processes contribution to zinc pollution of the shallow Volga estuarine area in 2001–2012. The impact of local anomalies (E_s) is subject to temporal (seasonal and inter-annual) variability and in most cases is estimated as low, thow its maximum impact is estimated as high. The contribution of short-term anomalies (E_l,%) is subject to spatial variability. In most cases it is estimated as very low, though in its maximum – as average.

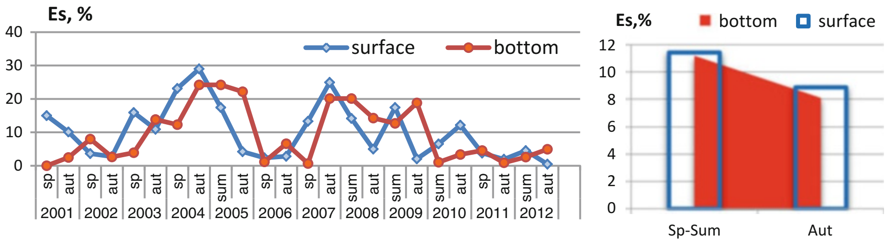

Fig. 27.6 Inter-annual and seasonal changes in contribution of local anomalies (E_s, %) to zinc pollution of the shallow Volga estuary in the license area "North – Caspian Field" in 2001–2012

27.4 The Distribution of Pollutants in Physical and Parametric Spaces

The analysis of pollutants distribution in the four-dimensional physical space (X, Y, Z are spatial coordinates and T is time) made it possible to establish two geoenvironmental pollution indices (background concentration and the contribution of local processes), which have been discussed above. However the list of the indices of the same kind is not restricted to them. The analysis of pollutants distribution in n-dimensional parametric space gives more opportunities to search for geoenvironmental pollution indices, as it helps trace the connection of their transformation in natural ecosystem with the changes of its state.

Sometimes the joint analysis of pollutants distribution in physical and parametric spaces can be helpful. Due to it the list of geoenvironmental pollution indices has been completed with the gradient index, or, as we more often refer to it, the index of pollution origin.

Gradient is the increase (decrease) of a substance concentration along the specially selected direction of physical space. Gradient points to the source of the substance entry and distribution. For instance, the decrease in concentration of oil products in the direction from the river to the sea points to their entry with the river runoff.

However the water dynamics in the estuarine area (especially if alongshore currents are present) does not always make it possible to identify the specific pollution source and the ways of pollutant distribution using the map only. This task can be solved with help of the analysis of the pollutant distribution in a salinity field, which minimum value is the property of riverine water, and maximum – to sea water.

The salinity space is not an ideal environment to determine pollutants origin, which behaviour is non-linear as they disappear in one salinity "windows" and re-appear in others. But the joint analysis of pollutants behaviour in physical and parametric spaces makes it possible to judge with more certainty about the pollutants origin than the analysis of their behaviour in any of these spaces.

The interrelation of water salinity and the pollutants content can be traced by means of correlation and regression analysis, but it's not always possible because of the non-linear behaviour of pollutants. In this connection we have offered a method for the diagnosis of pollutant gradient in a salinity space with help of K index, further referred to as the index of pollutants origin.

K estimation is quite simple. The data series describing the pollutant content in mixed riverine and sea waters is ranged by salinity and smoothed by a moving average. Then the extreme mean value located at the "marine" edge of the modified series is divided by the extreme mean value located at the "riverine" edge. This ratio is K index.

In the North Caspian which can be considered as the Volga estuary K value exceeding 1.1 points to the marine pollutant origin. If K is less than 0.9 the origin of pollutants is more likely to be riverine. If K value ranges from 0.9 to 1.1 the pollutant origin can not be identified.

Let us set a specific example. The origin index was calculated for 18 surveys carried out in the shallow area of the Volga estuarine zone in 2001–2009 for a group of priority pollutants (i). Temporal K_i series were statistically analysed, and the results were represented by means of diagrams which are commonly called box-and-whiskers diagrams. Figure 27.7 shows that mean K value calculated for the whole observation period points either to riverine or identified origin of pollutants. The exception is lead which is obviously of marine origin.

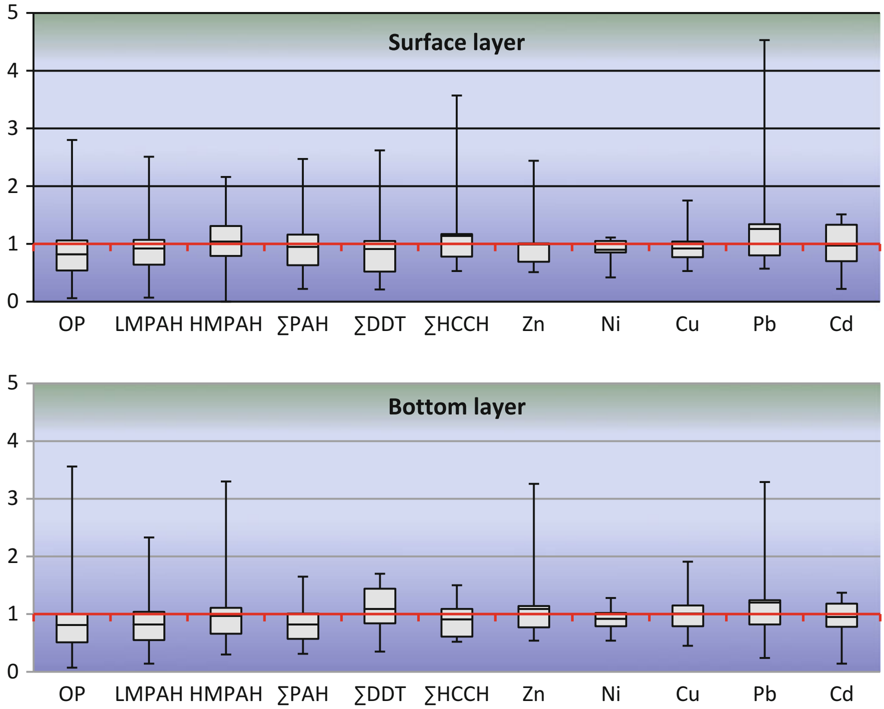

Fig. 27.7 The dynamics of K coefficient describing the origin of pollutants in the shallow water of the Volga estuary in 2001–2009. *OP* oil products, *PAH* polycyclic aromatic hydrocarbons, *DDT*, *HCCH* organochlorine pesticides

However big peak-to-peak value and a wide space between the “top” (quartile ¾) and the “bottom” (quartile ¼) of the “boxes” displayed in Fig. 27.7 show that at any specific moment of time (year, season), pollutants as a rule have a certain – marine or riverine – origin.

We have used the index of pollutants gradient (origin) for several years to describe the environmental conditions in the North Caspian. The results of pollutants origin diagnosis are used to determine the direction of trans-boundary transfer of pollutants in the water areas crossed by delimitation lines.

27.5 Deviation from Background: Inter-phase and External Mass Exchange

Speculations on what has caused the deviation of point concentration from background concentration have brought forward some other geoenvironmental indices of marine environmental pollution. One might guess that one of these indices is the deviation itself, which we denote as D (earlier we referred to it as to lability and denoted it by L symbol).

In accordance with the suggested definition, deviation can be calculated by a simple formula:

$$\mathrm{Df_j} = \mathrm{P_j} - \mathrm{F} \tag{27.3}$$

where $\mathrm{Df_j}$ – is the actual deviation at a given point of the water area; $\mathrm{P_j}$ – is the instant point concentration of the pollutant (see above); F –is the instant background concentration of this substance within the specified water area (see above).

The numerical expression of $\mathrm{Df_j}$ depends on concentration measurement units. To avoid this dependence where it is an obstacle (e.g. if we compare the deviation of different substances, which concentration is expressed in different units) we suggest using normal deviation ($\mathrm{Dn_j}$), calculated by formula:

$$\mathrm{Dn_j} = \mathrm{Df_j}/\mathrm{C_m} \tag{27.4}$$

where $\mathrm{Dn_j}$ – is the normal deviation at a given point of the water area; $\mathrm{C_m}$ – mean concentration of the pollutant within the specified water area.

For this purpose we can use standard deviation ($\mathrm{Ds_j}$) instead of normal deviation. It is calculated by formula:

$$\mathrm{Ds_j} = \mathrm{Df_j}/\mathrm{s} \tag{27.5}$$

where $\mathrm{Ds_j}$ – is the standard deviation at a given point of the water area; s – standard deviation of the pollutant concentration within the specified water area.

In our opinion the deviations of point concentration from background are mainly caused by inter-phase and external mass exchange.

The inter-phase exchange is the exchange of pollutants between different components of the marine environment: water and plankton, water and suspended matter, suspended matter and bottom sediments etc. A typical example of the inter-phase mass exchange is the adsorption and desorption of pollutants by suspended matter. We offer to refer to the ability of pollutants for inter-phase exchange as to biogeochemical activity and to denote it with A character (in previous publications other symbols were used).

The external mass exchange includes the processes of pollutants' entry to the specific water area and their outflow beyond its borders, including decomposition and irreversible disposal of pollutants We offer to refer to the pollutants' involvement into the external mass exchange as to mobility and denote it with M symbol.

In accordance with the statement presented above, deviation should be considered as the sum of activity and mobility:

$$\mathrm{Df_j} = \mathrm{Af_j} + \mathrm{Mf_j} \tag{27.6}$$

where $\mathrm{Af_j}$ – is the actual activity of the pollutant at a given point of the water area; $\mathrm{Mf_j}$ – is the actual mobility of the pollutant at a given point of the water area.

To solve Eq. (27.6) in terms of numbers one must know the values of at least its two members. Taking into account the fact that $\mathrm{Df_j}$ can be calculated by formula (27.3), only one equation member must be known. Activity is more suitable for this, as it can be considered as an opposite of conservative behaviour of pollutants, when their concentration is determined by homogeneous processes exclusively. The example is the mechanical water mixing.

It follows that a pollutant activity is expressed in deviation from its conservative behaviour. This deviation can be determined by the comparison of the pollutant dynamics with the dynamics of the conservative substance within the considered water area.

We go on to describe the procedure (calculation) we use to solve this task. The procedure involves introduction of some new parameters and symbols. Concentration of the pollutant (active) substance at the specified station at a given moment of time is denoted as $\mathrm{P_j}$, and the concentration of the conservative substance measured at the same time and at the same station is denoted as $\mathrm{C_j}$.

At the first calculation stage $\mathrm{P_j}$ values are ranged by $\mathrm{C_j}$ in the direction of $\mathrm{C_j}$ values increasing. The results of simultaneous measurements of $\mathrm{P_j}$, and $\mathrm{C_j}$ at the same stations during the quasi-synchronous survey of the water area are used as source data.

At the second stage the expected values ($\mathrm{P_{jw}}$) are calculated for every point of the ranged $\mathrm{P_j}$ series (with the exception of two extreme points) on the basis of the assumption, that the pollutant behaviour is of conservative nature. The calculation is carried out by the following formula:

$$\mathrm{P_{jw}} = \mathrm{P_{j-1}} + \left[\left(\mathrm{C_j} - \mathrm{C_{j-1}}\right)/\left(\mathrm{C_{j+1}} - \mathrm{C_{j-1}}\right)\right] \times \left(\mathrm{P_{j+1}} - \mathrm{P_{j-1}}\right) \tag{27.7}$$

where $\mathrm{P_{j-1}}$ – is the actual concentration of the active substance at a previous point of the ranged series; $\mathrm{P_{j+1}}$ – is the actual concentration of the active substance at a following point of the ranged series; C_j – is the actual concentration of the conservative substance at a given point of the ranged series; C_{j-1} – is the actual concentration of the conservative substance at a previous point of the ranged series C_{j+1} – is the actual concentration of the conservative substance at a following point of the ranged series.

At the third stage the actual activity of pollutants (Af_j) is calculated for every point of the ranged series (it corresponds to the specified station within the water area). It is calculated by formula:

$$Af_j = P_j - P_{jw} \tag{27.8}$$

where P_{jw} – is the expected pollutant concentration at the specified station (water area point); P_j – is the actual concentration of the pollutant at this station.

In its numerical expression Af_j (as well as Df_j) depends on the concentration dimension. To avoid this dependence, we suggest using normal activity (An_j), calculated by formula

$$An_j = Af_j / C_m \tag{27.9}$$

where An_j – is the normal activity at a given point of the water area; C_m – mean concentration of the pollutant within the specified water area.

Standard activity (As_j) can also be used instead of normal activity. It is calculated bu formula:

$$As_j = Af_j / s \tag{27.10}$$

where As_j – is the standard activity at a given point of the water area; s – is the standard deviation of pollutant concentration within the specified water area.

In principle, the activity of the pollutant can be identified in any component of the marine environment, but if we want to identify it with the method suggested above we require simultaneous measurements of concentration of the conservative substance. For water this substance is definitely the content of dissolved salts which is expressed in water salinity (mineralization). It is not so simple to choose the conservative substance for other components (suspended matter, plankton and bottom sediments). So at the moment we restrict our activities to determining the activity of pollutants in water. We also gain experience in determining the activity of pollutants in bottom sediments, using the chemical elements widely spread in the lithosphere (iron, aluminium, calcium) as conservative substances.

Having the numerical value of deviation calculated by formula (27.3) and numerical value of activity calculated by formula (27.8) we can easily calculate the numerical value of actual mobility at a given point of the water area, converting formula (27.6) as follows:

$$Mf_j = Df_j - Af_j \tag{27.11}$$

In its numerical expression Mf_j (as well as Df_j and Af_j) depends on the concentration dimension. To avoid this dependence, we suggest using normal mobility (Mn_j), calculated by formula:

$$Mn_j = Mf_j/C_m \tag{27.12}$$

where Mnj– is the normal mobility at a given point of the water area; C_m – is the mean concentration of the pollutant within the specified water area.

Standard mobility (Ms_j) can also be used instead of normal mobility. It is calculated by formula:

$$Ms_j = Mf_j/s \tag{27.13}$$

where Ms_j – is the standard mobility at a given point of the water area; s – is the standard deviation of pollutant concentration within the specified water area.

We regard concentration, activity and mobility of pollutants as basic geoenvironmental indices of environmental pollution for two reasons: First, these indices characterize the state of pollutants for every point of the water area and not for its area as a whole. Due to this fact activity and mobility can be dealt with as concentration itself –one can make maps of spatial distribution, seasonal graphs, calculate mean value, etc. This is illustrated by graphs presented in Fig. 27.8, which show that the standard activity of oil products in the shallow area of the Volga estuary is lower than their standard mobility. Consequently, inter-phase mass exchange dominated over external exchange.

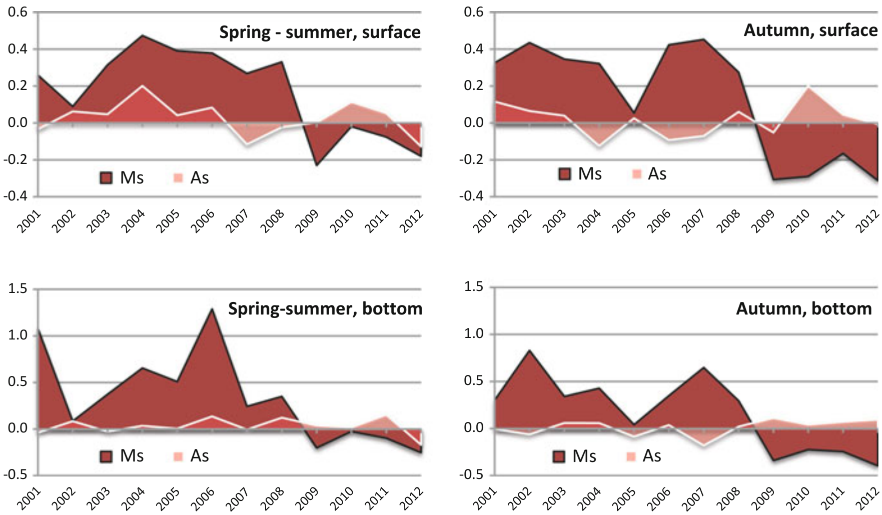

Fig. 27.8 Changes of mean standard mobility (M_s) and standard activity (A_s) of oil products in the shallow area of the Volga estuary in 2001–2012

The second reason is that, these geoenvironmental indices can be used not only to assess the state of pollutants and their movements in the environment, but also to assess and standardize the pollution impact on biological systems (see below).

In conclusion of the first chapter it's time to discuss philosophical issues. The understatement is that all the suggested geoenvironmental indices of marine environmental pollution and/or methods of their identification are based on the analysis of pollutants distribution in space (physical and parametric). Therefore two questions arise: (1) what is the correlation of actual differences and measurement errors in this distribution? (2) what is the correspondence between sampling and general distribution? We suppose that geoenvironmental indices of marine environmental pollution are objective enough, as we are trying to reduce subjectivity by increasing sampling series and eliminating obvious measurement errors.

This is the reason why we start the assessment of marine environmental pollution with the analysis of variability of concentration, activity and mobility of pollutants using a wide range of statistical parameters. Table 27.4 shows the results of the analysis of variability of concentration, activity and mobility of pollutants in

Table 27.4 The results of the analysis of variability of concentration, activity and mobility of oil products in the shallow area of the Volga estuary

Statistical parameters, symbols and calculation formulae[a]	Concentration, mcg/l		Activity, mcg/l		Mobility, mcg/l	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
Mean value X_m	50.2	15.0	4.5	2.2	20.5	3.8
Median, Me	26.0	9.0	−12.1	−2.0	10.7	2.4
Asymmetry coefficient, As	1.83	1.97	0.86	1.44	1.17	1.39
Maximum, Max	230.0	62.0	190.7	53.6	117.2	26.4
Minimum, Min	0.0	0.0	−85.2	−30.1	−15.5	−7.8
Quartile 0.25; q1	12.5	5.5	−48.9	−9.4	−8.0	−3.0
Quartile 0.75; q3	88.0	21.0	66.0	6.0	32.9	7.1
Absolute peak-to-peak value, $R = Max - Min$	230.0	62.0	275.9	83.8	132.8	34.2
Quartile peak-to-peak value, $Rq = q3 - q1$	75.5	15.5	114.9	15.4	40.9	10.1
Standard linear deviation, d	41.9	11.3	53.8	12.5	26.0	6.0
Standard deviation, σ	54.1	15.9	73.5	19.6	35.7	9.1
Oscillation coefficient, $Vr = R/Xcp$	4.6	4.1	60.9	38.7	6.5	9.0
Standard linear deviation, $Vd = d/Xcp$	0.8	0.7	11.9	5.8	1.3	1.6
Variation coefficient, $V\sigma = \sigma/Xcp$	1.1	1.1	16.2	9.0	1.7	2.4
Relative quartile deviation, $Vq = Rq/Xcp$	1.5	1.0	25.4	7.1	2.0	2.7

Note
[a]Calculation formulae are given only for the parameters which are relatively seldom used in descriptive statistics

the shallow area of the Volga estuary in the spring of 2006. The assessment variability is important not only to answer “philosophical” questions. Variability also reflects the energy and intensity of processes occurring with the pollutants in the environment.

At this point we complete the first part of our overview, devoted to the methods of calculation of geoenvironmental indices of marine environmental pollution and shift to the second part (see Chap. 28) where we’ll describe their practical application.

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Chapter 28
Nonpoint Source Pollution: Assessment and Management of Environmental Quality According to Geoenvironmental Indices

Sergey Monakhov, Olga Esina, Galina Monakhova, and Vitaly Tatarnikov

Abstract Specific examples are presented to describe geoenvironmental indices application in marine environmental pollution in order to assess and control local pollution, to determine local quality standards, to calculate maximum permissible load of pollutants on the water areas and to manage marine environmental quality at local level.

Keywords Marine pollution • Geoenvironmental indices • Pollution assessment • Marine environmental quality management at local level

28.1 Ensemble Assessment of Marine Environmental Pollution

The endeavour to reduce environmental pollution means that regular environmental assessment must be carried out to lay the basis for the planned activities and to assess the efficiency of the implemented activities (Sierra et al. 2012; Nasrabadi et al. 2010).

To assess marine environmental pollution by chemical parameters, one of the following criteria is normally used: maximum permissible concentration (C_l); background concentration (F); or maximum permissible load (Cp). The following formula is applied to calculate the maximum permissible load:

$$Cp = C_l - F \tag{28.1}$$

The list of the pollutants used to assess marine environmental pollution is normally restricted to several parameters (Agusa et al. 2004). For instance, the official method of sea water pollution assessment adopted in Russia uses C_l as a

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_28

criterion, and the list of chemical parameters comprises four substances, including dissolved oxygen.

The suggested method of the integrated assessment of marine environmental pollution is multi-criterial (all the mentioned criteria are used) and multi-parametric (all the identified pollutants, for which the maximum permissible concentration is standardized, serve as the parameters).

We suggest referring to the multi-criterial and multi-parametric pollution assessment as the ensemble assessment, which is a complex (ensemble) of three estimates: quality estimate (C_l criterion); accumulation estimate (F criterion); and load estimate (Cp criterion).

The ensemble assessment (E) technique comprises several stages. In the first stage, the numerical estimate for every point of the spatial series resulting from quasi-synchronous survey is calculated. The numerical value of quality estimate (E_l), the criterion of which is the maximum permissible concentration (C_l), is calculated by

$$E_{li} = P_i / C_l \tag{28.2}$$

where P_i is the concentration of pollutant i at a specified point of the spatial series.

The numerical value of accumulation estimate (E_f), the criterion of which is background concentration (F), is calculated as

$$E_{li} = P_i / F \tag{28.3}$$

The numerical value of load estimate (E_p), the criterion of which is the maximum permissible load (C_p), is calculated by

$$E_{li} = P_i - F / Cp \tag{28.4}$$

The mean estimate for every pollutant i is calculated at the following stage for the whole water area (spatial series). The pollution estimate is calculated as an arithmetic mean of E_{li} series, the accumulation estimate as an arithmetic mean of E_{fi} series, and the load estimate as an arithmetic mean of E_{pi} series.

To make the estimates (E_{ji}) obtained through different criteria comparable, they are converted into scores using the unified scale presented in Table 28.1 and Fig. 28.1.

Table 28.1 Unified scale for the conversion of mean numerical values of single-criterion estimates (E_{ji}) into scores

Score estimate	Quality estimate, E_{li}	Accumulation estimate E_f	Load estimate E_{pi}	
			If $C_l > F$	If $C_l < F$
0	$E_{li} \leq 1.0$	$E_{fi} \leq 2.0$	$E_{pi} \leq 0$	$E_{pi} \geq 1.0$
1	$1.0 < E_{li} \leq 2.0$	$2.0 < E_{fi} \leq 3.0$	$0 < E_{pi} \leq 1.0$	$0 \leq E_{pi} < 1.0$
2	$2.0 < E_{li} \leq 3.0$	$3.0 < E_{fi} \leq 4.0$	$1.0 < E_{pi} \leq 2.0$	$-1.0 \leq E_{pi} < 0$
3	$3.0 < E_{li} \leq 5.0$	$4.0 < E_{fi} \leq 5.0$	$2.0 < E_{pi} \leq 3.0$	$-2.0 \leq E_{pi} < -1.0$
4	$E_{li} > 5.0$	$E_{fi} > 5.0$	$E_{pi} < 3.0$	$E_{pi} < -2.0$

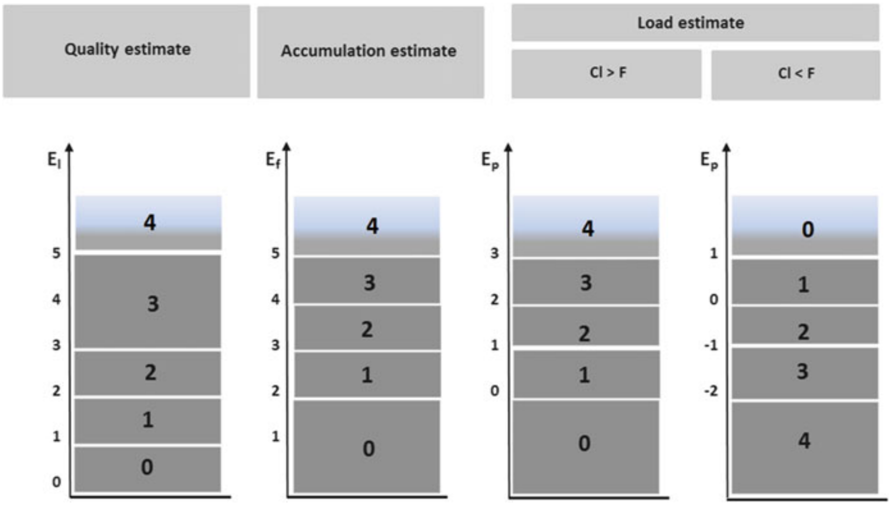

Fig. 28.1 Illustration of the unified scale for the conversion of mean numerical values of single-criterion estimates (E_{ji}) into scores. The latter are denoted with figures located to the right of the concentration axes, split into segments depending on the estimate criterion

Table 28.2 Classification of marine water area pollution in accordance with the ensemble assessment

Class of pollution	Verbal assessment	Numerical estimation
First	Clean	Less than or equal to 0.50
Second	Moderately polluted	Ranging from 0.51 to 1.50
Third	Polluted	Ranging from 1.51 to 2.50
Fourth	Dirty	Ranging from 2.51 to 3.50
Fifth	Very dirty	More than or equal to 3.51

The operation for calculating the single-parametric estimate of the water area pollution with every pollutant I, in particular (E_{ki}), is as follows. Different estimates (of quality, accumulation and load) expressed in scores are summed and divided by the number of the criteria used. In the final stage, single parametric and multi-criteria estimates E_{ki} are averaged into the multi-parametric and multi-criteria (or ensemble) estimate. The calculation results are used to classify and describe marine pollution in accordance with Table 28.2.

The ensemble assessment technique is completed with the construction of a matrix, the columns of which are the estimation criteria and the rows are the pollution parameters (Table 28.3). It helps combine the integral and differential approaches to the assessment of marine environmental pollution. The integral approach is reflected in the final ensemble estimate (w), and the differential approach in the analysis of the final matrix by columns (y) and rows (z).

Table 28.3 Matrix representation of the ensemble pollution estimation

Index	Pollution estimate, E			
	Estimate of quality, E_l	Accumulation estimate, E_f	Load estimate, E_p	Multi-criterial estimate, E_k
i_1	x	x	x	z
i_2	x	x	x	z
i_3	x	x	x	z
i_n	x	x	x	Z
$\mathbf{E_1}$	$\boldsymbol{y}$	$\boldsymbol{y}$	$\boldsymbol{y}$	$\boldsymbol{w}$
$\mathbf{E_2}$	$\boldsymbol{y}$	$\boldsymbol{y}$	$\boldsymbol{y}$	$\boldsymbol{w}$
$\mathbf{E_3}$	$\boldsymbol{y}$	$\boldsymbol{y}$	$\boldsymbol{y}$	$\boldsymbol{w}$

Note: i – pollutant, x – single-parametric and single-criterion estimate; y – multi-parametric and single-criterion estimate; z – single-parametric and multi-criterial estimate; w – multi-criterial and multi-parametric (ensemble) estimate

Table 28.4 Results of the ensemble assessment of marine water pollution in area "X" in the autumn of 2012

Index	Quality estimate E_l	Accumulation estimate E_f	Load estimate E_{pi}	Ensemble estimate E_k
BOD_5	0	0	0	0
N-NH_4	0	0	0	0
OP	1	0	1	0.67
Iron	2	0	1	1
Zinc	0	0	0	0
Nickel	3	0	1	1.33
Copper	1	0	1	0.67
Lead	0	0	0	0
Cadmium	0	0	0	0
$\boldsymbol{E_1}$	**0.8**	**0.0**	**0.4**	**0.41**
$\boldsymbol{E_2}$	**1.8**	**–**	**1.0**	**0.92**
$\boldsymbol{E_3}$	**3.0**	**0.0**	**1.0**	**1.33**

We recommend presenting the multi-parametric estimation, including the ensemble estimate (i.e., each of the matrix columns, see Table 28.3), as follows: (1) as a *generalized* estimate ($E_1 = E/n$); (2) as a *priority* estimate ($E_2 = E/N$); and (3) as an *extreme estimate* ($E_3 = E_{max}$). Here, n is the total number of pollution parameters, N is the number of parameters where $E > 0$, and E_{max} is the maximum E value.

Data obtained in the course of surveys in different parts of the Caspian Sea were used to test this method. The ensemble assessment of marine water pollution in area "X" in the autumn of 2012 is presented in Table 28.4.

According to the data presented in Table 28.4, sea water in area "X" in the autumn of 2012 was assessed as "clean" ($E_{k1} = 0.41$) in accordance with the generalized ensemble estimate (by the complex of parameters comprising nine pollutants). The content of four pollutants did not correspond to the criteria set for pollution assessment. According to ensemble priority estimation, the water was also assessed as moderately polluted ($E_{k2} = 0.92$). Nickel showed the highest pollution level ($E_{k3} = 1.33$), but, in accordance with the extreme ensemble estimation, the water was assessed as moderately polluted.

In accordance with the generalized load estimation, sea water in area "X" in the autumn of 2012 was assessed as clean ($E_{p1} = 0.4$). The content of four pollutants did not meet the criteria set for pollution assessment. According to priority and extreme load estimates, the sea water was assessed as moderately polluted ($E_{p2} = E_{p3} = 1.0$).

In accordance with the generalized accumulation estimate, sea water in area "X" in the autumn of 2012 was assessed as clean ($E_{f1} = 0$). According to the extreme accumulation estimate, sea water was also characterized as clean ($E_{f3} = 0$).

In accordance with the generalized quality estimate, sea water in area "X" in the autumn of 2012 was assessed as moderately polluted ($E_{l1} = 0.8$). The content of four pollutants did not meet the criteria set for pollution assessment. According to the *priority quality estimate*, the water was assessed as polluted ($E_{k2} = 1.8$). Nickel showed the maximum concentration in water among all the pollutants ($E_{l3} = 3.0$). Thus, in accordance with the *extreme quality estimate*, the water was assessed as dirty.

The comparison of generalized estimates of quality and accumulation shows that the main contributors to the pollution of the water area were sources located outside its borders, as $E_{11} > E_{f1}$. The same fact becomes obvious when we compare the extreme estimates of quality and accumulation ($E_{13} > E_{f3}$).

Presently, we have sufficient experience in using the ensemble method to assess marine environmental pollution. This experience shows that the benefit of this method is in the combination of the integral and differential approaches to the assessment of marine environmental pollution, where the first approach describes total pollution and the second approach describes the contribution of separate factors, including local and external sources, different pollutants, etc. Virtually, the generalized ensemble assessment can be expressed in one figure or verbal expression. Alongside this, matrix representation of the ensemble assessment results makes it possible to differentiate it not only by separate parameters and criteria, but also by different types.

In the description presented above, the ensemble method is used to assess the pollution of the water area on the basis of the results of a single quasi-synchronous survey. Consequently, F in formulae (28.1), (28.3), and (28.4) is the instant background concentration. To analyse the dynamics of marine environmental pollution according to the data of a number of surveys separated by certain time periods, we recommend using the interval and/or stable background concentration instead of the instant one.

The ensemble assessment usually completes the analysis of water pollution, which also comprises variability assessment and the diagnosis of marine environmental pollution by geoenvironmental indices. These analysis results give complete coverage of both general and specific features of the water area pollution. Therefore we refer to it as the "image of pollution."

28.2 Identification and Assessment of Local Pollution

The control of environmental pollution sources can be implemented in two ways. The first case implies monitoring of the sources directly, which is not always efficient. The second case implies monitoring of the pollution-affected area. This type of control is focused on the identification and assessment of local pollution.

We normally start solving this problem with the assessment of the contribution of local processes to marine environmental pollution, which is performed using the method described above. Then, we turn to mathematical, statistical, and graphic-analytical methods, the application of which is described below.

If the source data are limited to spatial series only, then we recommend using standard deviation (quadratic mean deviation) of the whole data series as a criterion to identify and assess anthropogenic changes.

This method can have two modifications depending on the location of the stations, which can be either radial (inside a radius in the impact area, and outside a radius beyond the borders of the impact area) or non-radial (some of the points are to be located within the impact area, and others outside its borders).

To identify and assess the anthropogenic changes, the H index is used. If it is used to denote the standard deviation criterion, it will be referred to as HS. In the case of radial location, two methods are used to calculate the HS value. In the first case, the following formula is used:

$$H_{S1} = |\mathrm{X}_{RN} - \mathrm{X}_{RD}|/S \tag{28.5}$$

where X_{RN} is the arithmetic mean of the X parameter at the short range points, X_{RD} is the arithmetic mean of the X parameter at the long range points, and S is the standard deviation of X series.

Instead of X_{RD} in formula (28.5), one can use the background value (F) of X series, denoted as F_X. In this case:

$$H_{S2} = |\mathrm{X}_{RN} - F_X|/S \tag{28.6}$$

If the points are located non-radially, the spatial data series is ranged by the distance between the stations, and then smoothed by the moving average (with the window width normally equal to 3). In this case,

$$H_{S3} = |\mathrm{X}_F - \mathrm{X}_L|/S \tag{28.7a}$$

where X_F is the first value of the ranged and smoothed series, X_L is the last value of the ranged and smoothed series, and S is the standard deviation of X series.

Instead of X_L in formula (28.7a), one can use the background value (F) of X series, denoted as F_X. In this case,

$$H_{S4} = |\mathrm{X}_F - F_X|/S \tag{28.7b}$$

The K_S value points to the presence and the nature of anthropogenic changes. $K_S > 1$ points to the presence of anthropogenic changes in the marine environment. *If* $1 < K_S < 2$, the changes are assessed as slight, *if* $2 < K_S < 3$, then the changes are moderate, if $3 < K_S < 5$ they are big, and if $K_S > 5$ the changes are very big.

Our experience shows that H_{S2} и H_{S4} indices, which are calculated using the background concentration (instant background concentration), react better to anthropogenic changes than H_{S1} и H_{S3} indices. Thus, in the course of the drilling of an exploratory well in the North Caspian, the H_{S4} index helped identify the slight impact of drilling operations on the content of coarse sand in the bottom sediments, the concentration of phenols in the water, synthetic surfactants and lead in the bottom sediments, and the moderate impact on barium content in the near-bottom water layer.

To illustrate anthropogenic changes in the case of radial location of the stations around the impact source, we recommend using pie charts (Fig. 28.2). If the stations are not located radially, we should use the data curve ranged by the distance from the impact source (Fig. 28.3). For better visualization, these graphs can be approximated by a linear trend.

To identify and assess local pollution from a known source, the balance method should be used together with the methods described above. This method applies the

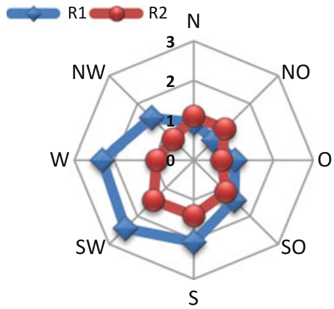

Fig. 28.2 Spatial distribution of synthetic surfactants in the bottom sediments (mg/kg) within the short (RN) and long (RD) ranges from the drilling point

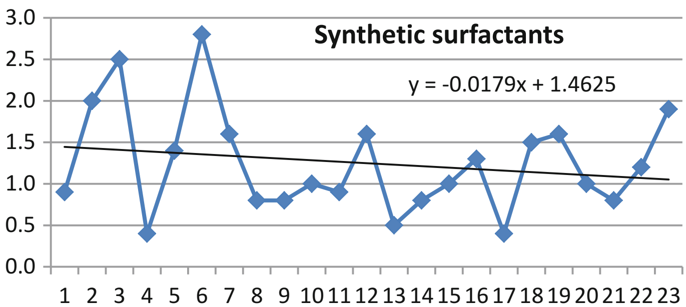

Fig. 28.3 Series, ranged and approximated by a linear trend, of synthetic surfactants concentration values in the bottom sediments (mg/kg) in the area X well construction after the drilling operations

comparison of the pollutant mass dynamics in the impact area with the dynamics of its entry to the environment (both actual and probable discharges of pollutants should be taken into account).

28.3 Elaboration of the Local Standards of the Marine Environmental Quality

Man and wildlife pose a threat to each other, although they try not to cross the borderline, as they also need each other. For environmental protection, this borderline is the maximum permissible concentration of pollutants (MPC).

MPC can be set to protect human health (sanitary MPC), natural resources (economic MPC), or natural ecosystems (environmental MPC). When there is no environmental MPC, it is *de facto* substituted by a sanitary and/or economic MPC (which can sometimes completely cope with this task).

It is the state that is responsible for setting MPCs, and the standard, as a rule, covers the whole area without taking account of ecosystem biodiversity. This rule refers to sanitary and economic MPCs only. In the setting of the MPCs, the diversity must be accounted for, as different ecosystems respond to pollution in different ways, and the aggressiveness of pollutants depends on their environment.

Three approaches can be used to develop environmental MPCs. We should note that an environmental MPC becomes essential when sanitary and/or economic standards can no longer protect natural ecosystems.

The first approach consists of the identification of the biological species that is most sensitive to pollution (among those playing an important role in the functional organization of the population), determination of the MPC for the species, and its application to the whole ecosystem.

The second approach presupposes the study and identification of the “dose-effect” dependence at the supra-organism level, which is more correct from the theoretical viewpoint, but can be implemented practically in exceptional cases, as every such case requires the mobilization of all the available resources.

In the third approach, the environmental mission is passed to the sanitary or economic MPC, which is to be modified by means of amendments that take into account the characteristic features of pollution of a specific area and the ecosystem responsiveness to pollutants. The pollution peculiarities are characterized by geoenvironmental indices, and the responsiveness by structural and functional ecosystem parameters, which determine its response and resilience to pollution.

It should be noted that any of the above mentioned approaches can result in the value of the environmental MPC being not only lower, but also sufficiently higher than the value of the sanitary and/or economic MPC. As a rule, if there is a discrepancy between the values of MPCs having different designations, the one that has the lowest value is applied.

Sea water areas are used both for cultural and fishery purposes, and therefore, fishery MPCs can be set for marine pollutants alongside the sanitary MPC. As a rule, the values of the fishery MPC (MPC_{fish}) are lower than those of sanitary ones. For this reason and for the reason that fish are constant marine inhabitants, MPC_{fish} formed the basis for the elaboration of environmental MPCs. As environmentally modified MPCs (hereinafter referred to as MPC_{em}) can be applied to a limited water area, they are also called local standards of marine water quality.

If the pollution of a certain water area could be described by means of geoenvironmental pollution indices, then the correction factor for the environmental modification of the MPC should be identified among them or their combinations.

As follows from the theoretical background, we can suppose that the inter-phase exchange ability of pollutants, including the exchange with the "living matter," is directly linked to their toxic impact on the biota. Thus, the higher is the absolute activity value, the lower must be the MPC. On the other hand, one can suppose that the mobility, which is the external exchange ability of pollutants, is directly linked to the decrease in pollutants' impact on the biota. Thus, the higher is the absolute mobility value, the higher should be the MPC. Therefore, the activity and mobility are opposite to each other: the activity of pollutants is hazardous for the biota, while their mobility is beneficial.

Thus, we offer the following formula to modify fishery MPCs taking into account geoenvironmental indices of marine environmental pollution.

$$MPC_{EM} = MPC_{fish}(m/a)^{a/m} \tag{28.8}$$

In formula (28.8), a is the mean standard activity of the pollutant for the whole water area calculated by

$$a = \sum A' s_j / n - 2 \tag{28.9}$$

where $A's_j$ is the absolute value of the standard activity at every point of the water area calculated by formula (27.10), and n is the number of points (stations) where samples were taken throughout the survey.

In formula (28.8), m is the mean standard mobility of the pollutant for the whole water area calculated by

$$m = \sum M' s_j / n - 2 \tag{28.10}$$

where $M's_j$ is the absolute value of the standard mobility at every point of the water area calculated by formula (27.13), and n is the number of points (stations) where samples were taken throughout the survey.

The mobility and activity of pollutants in sea water varies over time (Fig. 28.4). This means that the environmental MPCs calculated by means of the data of geoenvironmental indices will be subject also to temporal variability. This can be clearly seen in the graphs presented in Fig. 28.4, where MPC_{em}, calculated by formula (28.8), is smoothed by moving 3-year periods.

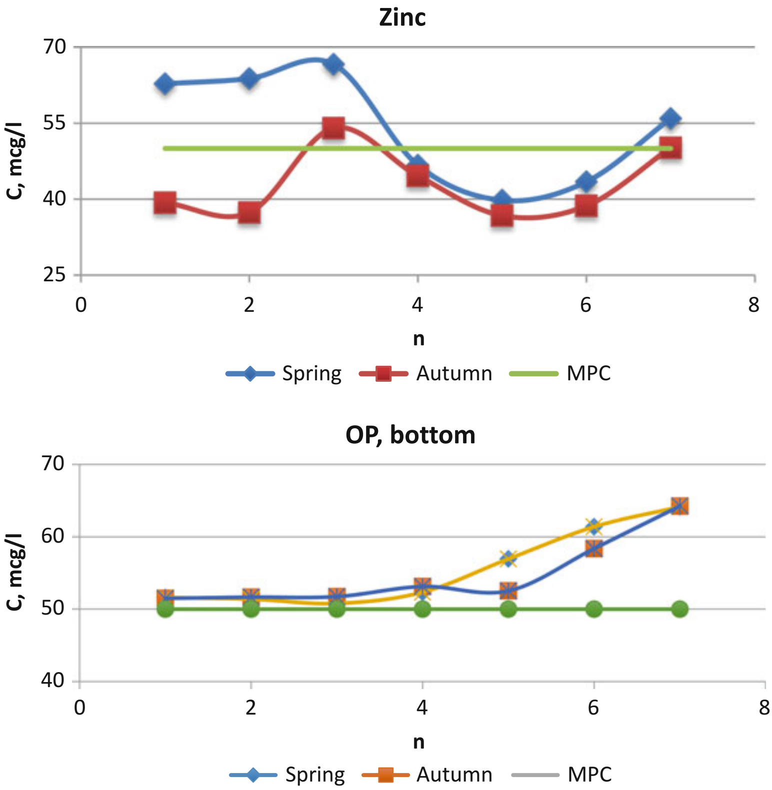

Fig. 28.4 Series of MPC_{em}, smoothed by moving average, of zinc and oil products (OP) in the sea water of the deep Volga estuarine zone, calculated using data of 1998–2010. The *green horizontal line* is the MPC_{fish} of zinc and oil products in the sea water (which equals 50 mcg/l for both substances); *n* –smoothing

Thus, the environmental MPC calculated by geoenvironmental pollution indices is a "floating" value. However, this does not prevent us from using it to assess the pollution ("quality") of the marine environment, including the use of the ensemble method presented above.

MPC is a basic parameter for calculating the maximum permissible discharges (MPD) of pollutants to water and the maximum permissible impact (MPI) on water bodies. MPCs are set for pollution sources, and MPIs for water bodies as a whole and/or for separate sectors of the water area. It is not always convenient to use the "floating" MPCs to solve these tasks, although it is possible. The application of these standards is facilitated by the fact that both MPCs and MPIs have a limited validity term and must be regularly revised.

It should be noted that the use of the "maximum permissible impact" term as applied to water bodies in general, as defined by the existing regulatory documents in Russia, has introduced some confusion into the accepted range of terms. In accordance with it, nature protection standards were subdivided into quality standards (set for separate environmental components), impact standards (set for separate pollution sources), and load standards (set for certain areas and natural sites).

Of all the three types of nature protection standards, quality standards are the basic ones, and the other standards ensure compliance with these standards throughout the period of environmental impact. When this impact is pollution, we can speak about a unified standard, expressed in units of mass (quality standard) or units of flow (load and impact standards). Thus, the task of impact and load standard-setting can be presented as the task of transition from units of mass to units of flow. The methods for solving this task will be described in the following section of our review.

28.4 The Assessment of the Assimilation Capacity

The concept of maximum permissible load almost completely corresponds to the concept of assimilation capacity (A_m), which refers to the maximum speed of pollutants flow, which passes through the marine ecosystem without damaging its integrity, which is calculated for the unit of the sea area.

A_m estimation always starts with the estimation of the actual speed of the pollutants flow passing through the ecosystem. The available data on marine water pollution as a rule are measured in units of mass (concentration) in contrast to flow. A balance method is usually used to shift from units of mass to units of flow (the change of mass in a unit of time). A pre-requisite for the use of this method is the availability of long-term regular observations.

The assessment of the assimilation capacity of the water area consists of several stages. The first stage implies the preparation of the source data of observations of the pollutants concentration in sea water. This stage includes data grouping by the date of observation, taking into account the natural cyclicity of the processes ongoing in the marine environment. For instance, we chose observation data for April (the end of the winter low-water period, the start of the spring flood), June (the end of the flooding period, the start of the summer low-water period), August (the end of the summer and the beginning of the autumn low-water period) and September (the end of the autumn and the beginning of the winter low-water period) for the Volga estuary.

In the second stage, we estimate the instant load of the pollutant i on the water area under study. Changes in the water volumes conditioned by seasonal and long-term fluctuations of the sea level were accounted for in the course of the estimation of the pollutants mass in the shallow-water North Caspian. The instant load of the pollutant substance (L_{it}) is calculated by

$$L_i = \frac{V}{S} C_i \tag{28.11}$$

where S is the area of the water area under consideration, V is the volume of the underlying water column, and C_i is the mean concentration of pollutant i in the water column at a certain moment of time.

The speed of load change (R_i) is calculated in the third stage by

$$R_i = \frac{L_{it} - L_{i(t-1)}}{T} \tag{28.12}$$

where L_{it} is the instant load at a certain moment of time, $L_{i(t\text{-}1)}$ is the instant load at a previous moment of time, and T is the time interval between these two moments in days.

Later, the maximum and minimum values are selected from the obtained R_i series for every season. The former is the water pollution potential (P_{pi}), and the latter (its absolute value) corresponds to water purification potential (P_{mi}).

In the fourth stage, the assimilation capacity of the water area (A_{mi}) is calculated for substance i by

$$A_{mi} = q_i P_{mi} \tag{28.13}$$

where P_{mi} is the water purification potential, and q_i is the assurance factor.

The assurance factor q_i in turn is calculated by

$$q_i = \frac{L_{li}}{L_{\max i}} \tag{28.14}$$

where L_{li} is the maximum permissible load, and $L_{max\ i}$ is the maximum load.

The L_{maxi} value is selected from L_{it} series for the month at the beginning of the seasons, and for which A_{mi} is calculated. For instance, to estimate the assimilation capacity of the Volga estuary in the flood season the L_{maxi} value was selected from the L_{it} April series. The maximum permissible load L_{li} is calculated using formula (28.11), which uses the environmentally modified MPC value instead of C_i (MPC_{em}).

MPC_{fish}, or background concentration (either interval or stable), or another target water quality index can be used to calculate the maximum permissible load instead of $\mathrm{MPC_{em}}$.

In the section devoted to the ensemble assessment, we used the term "maximum permissible concentration" to denote the difference between the MPC and background concentration denoted as Cp in formula (28.1). In this respect, it should be noted that, in contrast to L_{li}, expressed in units of flow, Cp is expressed in units of mass (concentration), and, as follows from formula (28.1), it describes the load from local sources only.

Consequently, Cp as well as MPC_{em} can be used to calculate L_{li} using formula (28.11). The outcome of this calculation is the maximum permissible load from local sources expressed in units of flow. The analogous calculation using MPC_{em} will result in obtaining the maximum permissible load from all the sources (local and external).

The accuracy of the balance method depends on the length of the observation data series. It is advisable that these data cover the years with the highest pollution level. Such data series can be encountered quite rarely. In most cases, we have the data of one or several surveys for one water area, separated by a large time period. The balance method cannot be applied for this type of data.

In these cases, we suggest using the synoptic method, which is based on the assumption that uneven distribution of a pollutant in the water mass homogeneous in its physical parameters results from the ongoing self-purification processes, the reference point of which is the last storm in the water area (that is why the method is called a synoptic method).

In this method, the flow of pollutants i passing through a unit of water volume (denoted by U) is calculated by

$$U = (C_{max} - C_{min})/T \tag{28.15}$$

where C_{max} is the maximum, and C_{min} is the minimum concentration of the pollutant i within the water area under consideration, and T is the time in days that passed from the last storm in the water area.

As has previously been established, to determine the speed of pollutants flow that does not cause harm to the ecosystem (this value is the assimilation capacity), the U value must be multiplied by MPC_{em}/C_{max}, and calculated per units of area. Correspondingly, to calculate the assimilation capacity (A_{mi}), the following formula should be used:

$$A_{mi} = U\frac{\text{ПДК}}{C_{max}}1000h \tag{28.16}$$

where h is the thickness of the water layer in metres, for which the assimilation capacity is calculated, or the sea depth if this layer covers the water column from the bottom to the surface. MPC_{em} and C_{max} must be expressed in mg/m^3. Any other target water quality index can be used instead of MPC_{em}.

The main challenge in the application of the synoptic method is to identify a hydrologically homogeneous water body. This is especially challenging in the areas where water masses interact. Such an area is the North Caspian Sea. We first tested the synoptic method for the license area of "Caspian Oil Company" Ltd., where relevantly homogeneous water masses were identified according to the data of two surveys (in the autumn of 2005 and in the spring of 2006). The results of calculating the assimilation capacity for oil products by means of the synoptic method revealed that it amounted to 20–25 mg/m^2 a day.

The assimilation capacity for hydrocarbons had previously been calculated using the means of the balance method for the western part of the North Caspian according to the long-term observational data. The license area of the "Caspian Oil Company" Ltd. is located in the northern sector of this water area, the assimilation capacity of which is 0.5–5.0 mg/m^2 per day, depending on the season.

Thus, the estimate of the assimilation capacity obtained using the synoptic method exceeds the estimate obtained using the balance method, which we consider more valid. The higher estimates of the synoptic method can be explained by the fact that no homogeneous water mass could be identified during the research study.

If we could subdivide the maximum permissible pollution of marine ecosystems into two categories, maximum permissible *mean* load (MPML) and maximum permissible *one-time* load (MPOL), we could use the estimate of the assimilation capacity obtained by the balance method to establish MPML, and a similar estimate obtained using the synoptic method to establish MPOL. The benefit of the latter is a sufficient reduction in time and costs for standardizing of the anthropogenic load on the sea water areas, while drawbacks can be avoided through careful planning of the research.

Conclusions

"Think globally, and act locally" is a principle that sounds good but fails to work, as the global level lacks consensus, and the local level lacks the required tools.

All the existing environmental protection institutions are like balloons hanging somewhere between the "floor" and the "ceiling," while most of them should be in one place or the other.

When we started the elaboration of geoenvironmental indices of the marine pollution, we had no idea that as a result we would acquire a complete set of tools to manage the quality of the marine environment at the local level.

Environmental feasibility studies for offshore projects can be expanded through the diagnosis and assessment of marine environmental pollution by means of geoenvironmental indices.

The planning stage should require the development of local standards of marine environmental quality and the calculation of the maximum permissible load of pollutants on external and local pollution sources.

The implementation stage will involve the methods of identification and assessment of the local pollution, and the ensemble assessment using the specified values of background pollution and local quality standards, which will require local monitoring of the marine environment.

Throughout the whole project, and in the case of the project's extension (reconstruction), the local standards of marine environmental quality and the standards of maximum permissible load of pollutants on the water area must be revised and updated taking into account the monitoring data.

Thus, geoenvironmental pollution indices can launch the process of marine environmental quality management at the local level. Once launched, this process can continue on its own and can easily be managed with the help of target quality indices.

An attentive reader might have noticed that there is one thing lacking in the process: the indices of the marine ecosystem responsiveness to pollution, which should be used to determine the local quality standards alongside the geoenvironmental indices.

(continued)

We hope to fill this gap in the nearest future, but the experience of the application of geoenvironmental indices for the protection of the North Caspian Sea ecosystem proves that they can cope with this task on their own and can be applied for other seas.

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Chapter 29
Point Source Pollution Indicators

Robert H. Armon and Janetta Starosvetsky

Abstract Point source is a pollution input that can be related to a single outlet, such as untreated, or inadequately treated, sewage disposal (domestic/industrial). Sewage is most likely the major point source of the pollution of the world's waters, while other point sources include mines and industrial effluents. Point sources are confined and characterized by a relatively constant discharge over time of certain pollutants that can be used as indicators. In the case of human sewage, several microbial indicators have been suggested for freshwater sources, while for marine waters used as recreational sites several marine organisms (mussels or shrimps) have also been suggested as such.

Keywords Point source pollution • Non-point/diffuse pollution • Stream • Marine coast • Industry • Sewage treatment plant

29.1 Background

According to US Environmental Protection Agency (EPA) point source pollution is defined as: "any single identifiable source of pollution from which pollutants are discharged, such as a pipe, ditch, ship or factory smokestack." Perhaps the most common types of point source are those that treat/manufacture pollutants, such as sewage treatment plants and factories. Currently, under a variety of laws and guidelines, point source pollution is regulated and, if neglected, different fines are applicable, including final closure of the source. The situation is much better in developed countries; however, in developing ones because of continuous economic growth, there is much to be desired.

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_29

29.2 Sources of Point Pollution

There are at least seven point source pollution sources: (1) Leaking septic-tanks systems, in remote areas where a sewer is not available (small and farm communities); (2) leaking storage lagoons for polluted waste, mostly from giant livestock farms (called Concentrated Animal Feeding Operations or CAFOs) producing astounding volumes of animal waste that have an intense effect on human health and the environment (Burkholder et al. 2007); (3) unlined landfills generating highly toxic leachate that, via soil migration, contaminate the water table, especially in areas with shallow water tables (Hoehn et al. 2000; Al Yaqout and Hamoda 2005); (4) leaking underground storage tanks that contain chemicals or fuels such as gasoline, mostly located underground in soil rather than bedrock causing shrink-swell and corrosion reactions that finally result in leakage and soil contamination (Hudak et al. 1999); (5) polluted water from abandoned and active mines (acid mine drainage the most prevalent, alkaline mine drainage in the presence of calcite and dolomite, and metal mine drainage from abandoned mines) (Anonymous 2000); (6) water discharged by industries, mainly those with high water output (food, textiles, etc.), e.g., China's textile industry, which revealed an increasing trend from 2001 to 2010, surpassing the peak value of 1.09 Gm^3/yr (giga cubic meter a year) in 2007 (Wang et al. 2013); and (7) public and industrial wastewater treatment plants containing certain traceable pollutants (Gruttner 1997; Sharma et al. 2012; Sánchez-Pérez et al. 2009) (Fig. 29.1).

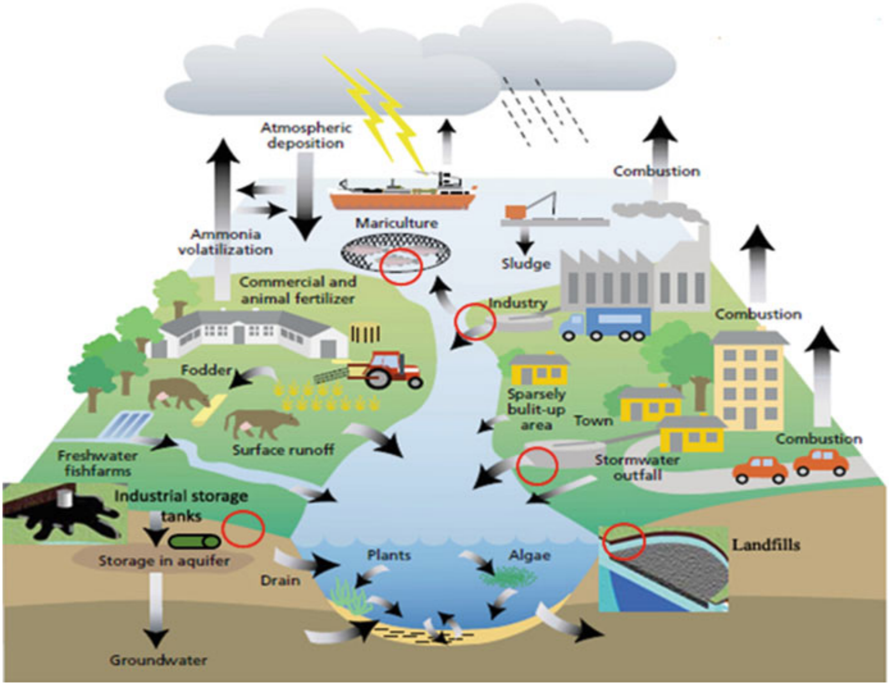

Fig. 29.1 Point sources pollution (*red circles*) and non-point sources of pollution in a populated area (Adapted from Ærtebjerg et al. 2003)

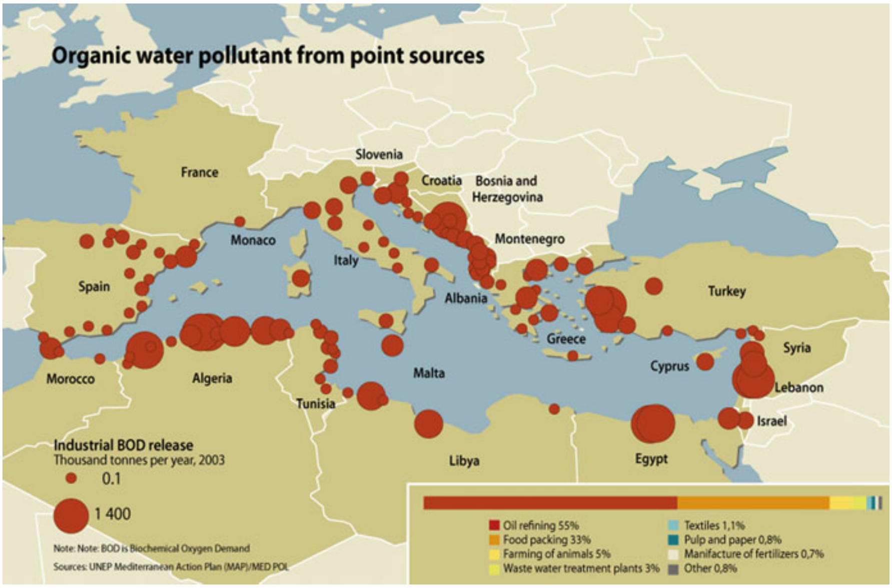

Fig. 29.2 Point sources pollution along Mediterranean shores (Source: UNEP Mediterranean Action Plan-MAP/MEd POL)

From the industrial point of view, the following industries are the main contributors: refinery, sugar, fertilizer, cement, distillery, thermal power plant, tannery, dye, pesticide, foundry, mining, pharmaceuticals, and marine transport (Fig. 29.2). The waste of these industries owns certain characteristics that are relatively easy to detect as indicators of pollution, such as disease causing agents, oxygen demanding wastes, organic pollutants, inorganics, plant nutrients, oil, sediments, radioactive substances, and heat.

29.3 Potential Indicators of Point Source Pollution

Lewis and Foss (2000) presented the grass shrimp (*Palaemonetes pugio* -Holthius), an estuarine benthic organism widely distributed along the Atlantic coast and the Gulf of Mexico as useful in the detection of sediment toxicity originating from both point and non-point pollution. Using the early-life stage of this caridean grass shrimp, the authors showed acute toxicity in 28 % of pore water, which suggested a limited sediment contamination. However, these authors were not able to differentiate between point and non-point pollution.

Another marine organism has been also suggested as a sentinel (indicator) of marine pollution by metals. The common blue mussel (*Mytilus edulis*) has been suggested as an indicator of trace metal concentrations, including Pb, Cu, and Zn (Popham et al. 1980). These authors showed that, "since trace metal concentrations in mussels decrease rapidly with distance from a point source, mussels can be used to locate precisely (within 30 m) a point source discharge of trace metals such as lead, copper and zinc".

Sorensen et al. (1989), screening various small streams in the states of New Mexico, Idaho/Utah, and California, suggested *Clostridium perfringens* anaerobic bacteria (a commensal of our guts) as a potential indicator of point pollution. Previous studies have shown that chlorinated STP effluents or untreated wastewater do contain high concentrations of *C. perfringens* spores in comparison to non-point pollution sources. Non-point pollution sources, such as cow, horse and sheep feces, farmlot runoff, oxbow lakes that receive fecal material from animal feeding facilities, and animal grazing area soil, revealed low *C. perfringens* spores concentrations, but contained high concentrations of other fecal indictor bacteria. As the common bacterial indicators of water pollution (e.g., coliforms and fecal coliforms) are much less resistant to environmental stresses and water treatment, it seems that *C. perfringens* spores can be used as an indicator of the influence of point sources in streams receiving a considerable input of fecal indicators. The authors emphasized that "*C. perfringens* spores appear to be a sensitive indicator for microorganisms entering streams with municipal wastewater, even when agricultural non-point sources of fecal indicator bacteria are important in the receiving stream."

In connection with bacterial indicators, it is obvious that fecal indicator bacteria (FIB) are a useful sentinel for fecal pollution in surface waters impacted by point sources, such as outfalls of untreated or partially treated sewage (Bartram and Rees 2000). However, as already mentioned, these indicators are relatively fragile and sometimes they do represent also non-point diffuse pollution, i.e., sewage from septic tank leach fields located near the river bank (Walsh and Kunapo 2009).

Among other enteric bacteria, *Bifidobacterium* spp. have also been suggested as the best bioindicator able to identify four characteristic groups of point pollution sources in the Nanshih river, by applying a two-dimensional principal component analysis (PCA) of four approaches: ten water parameters, the median river pollution index parameters, bacterial numbers, and specific fluorescence in situ hybridization indicators (Chang and Chang 2014). According to their results, the point source pollution was identified as a hot spring resort; however, their approach has to be studied worldwide before its adoption as an accurate indicator of point source pollution!

In summary, point source pollution is much easier to detect owing to its definite contribution (can be used as indicators) to any stream in comparison to diffuse pollution, which is much more problematic to detect based on specific indicators because of its multi-component nature.

The most important indicator of a point source is its specific contaminant that can be traced to only one source, for example, the pharmaceutical industry!

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Chapter 30
Noise Pollution Indicators

Arnaud Can

Abstract Noise is a major environmental issue, which gave birth in the last decades to extensive research and consecutively to the development of many estimation and mitigation engineering methods. The specificity of this pollution, which lies in its high spatiotemporal variations, its rich spectral component, its variety of sources, and the complexity of human hearing, explains the abundance of the existing noise indicators. Many energetic, statistical, noise event or emergence general indices have been developed. Complementing these, indicators have been produced to describe specific noise sources (road traffic, railway, aircraft. . .) and their resulting effects on human well-being, which makes the development of indicators directly influenced by the progress in modeling. This review shows the difficulty in finding a set of indicators able to capture both the physical characteristics of noise environments and its effects.

Keywords Noise indicators • Noise fluctuations • Noise spectrum • Noise perception • Noise annoyance • DPSEEA model • Noise exposure • Dynamics road traffic noise models • Global environmental indicators • Communicative tool • Energetic indicators • Statistical indicators

30.1 Introduction

Noise is a major environmental issue, with acknowledged and quantified adverse health effects: hearing impairment, sleep disturbance, cardiovascular and physiological effects, etc., which concerns both developed and developing countries (WHO 1997, 1999). In Europe alone, more than 210 million citizens are exposed to harmful noise levels, leading to a dramatic cost to the community, evaluated at more than 40 billion €/year (Den Boer and Schroten 2007). Thus, it is not surprising that noise is the source of annoyance most frequently cited by European city dwellers.

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_30

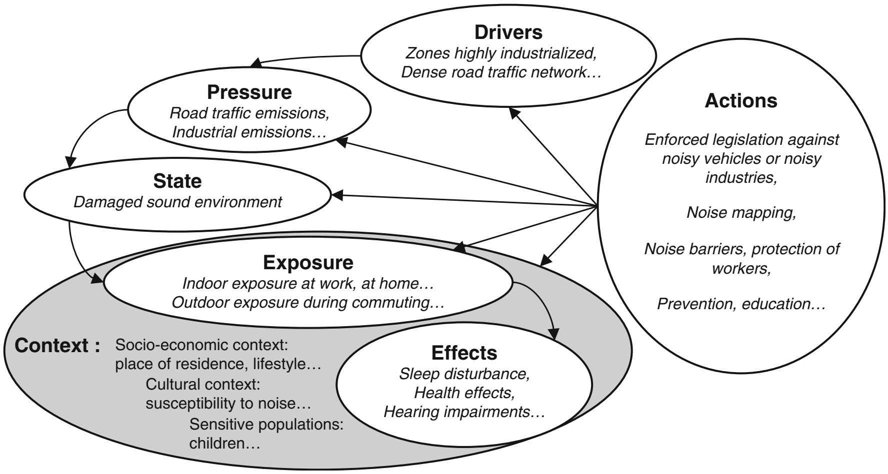

Fig. 30.1 DPSEEA model in the noise pollution context

Fortunately, solutions to mitigate noise exist. Noise emissions can be reduced for example with enforced legislations (prohibiting noisy vehicles, taxing noisy industrial sources, etc.) or optimized transportation plans. Noise can also be reduced between the source and the receivers, for example, by erecting noise barriers, improving building insulation, or designing headphone protectors for workers. Finally, the publication of noise maps is a communicative tool that has gained interest, since the European Directive 2002/49/CE imposed it on cities of more than 100,000 inhabitants.

Indicators suitable for the evaluation of noise mitigation strategies are required. The DPSEEA Model has been proposed for designing a system of environmental health indicators within the decision-making context (WHO 2004). The causal chain involved in noise pollution is illustrated in Fig. 30.1 with some examples. This advocates noise indicators able to: (i) Underline the characteristics of noise environment (Pressure and State in Fig. 30.1); (ii) capture the Exposures (spatial and temporal distribution of noise); and (iii) quantify the Effects. The following section highlights that these three points lead to very different indicators according to the scope of the study and the noise source considered.

30.2 Requirements for Noise Indicators

Noise pollution has the specificity of carrying a large amount of information, since various noise sources superimpose on each other to form complex noise environments. The human ear is capable of detecting a large part of this information (Fastl and Zwicker 2006), possibly leading to annoyance or adverse health effects after a given duration of exposure.

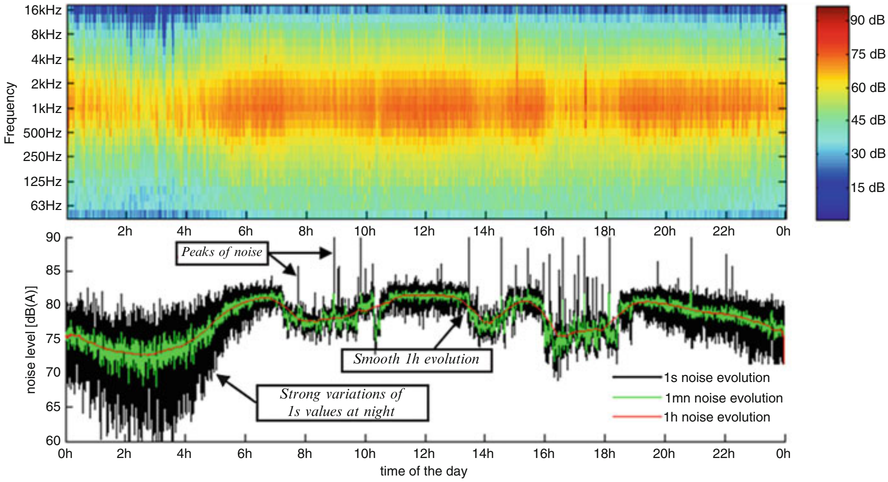

Fig. 30.2 Noise environment measured continuously over one day in front of a Belgium busy ring road; up: 1/3 octave bands spectrogram; down: noise levels evolution (The figure is the result of the analysis of data collected during the IDEA project: http://www.Idea-project.be/)

Figure 30.2 illustrates an example of noise environment characterized in detail. This amount of information has to be captured by physical indices, which can then be use directly or be combined as indicators. Noise characteristics impose the following requirements for noise indicators:

- ***Large noise amplitudes***: The acoustic pressure p has a large domain of variation, of about 10^7. The logarithmic scale has been generalized in the acoustic community to reduce this domain. As a result, noise pressure levels L_p are defined (in decibels dB) as: $L_p = 20\log(p/p_0)$, with the acoustic reference pressure $p_0 = 20*10^{-6}$ Pa. Hence the noise levels encountered range from 0 dB (the human hearing threshold at a frequency of 1,000 Hz) to about 140 dB, between which characteristic noise levels often cited are about 30 dB for a quiet park, 75 dB for a noisy street, or 110 dB for a concert;
- ***Large spectrum variations***: Noise environments are generally formed of many frequency components, which vary with time (see Fig. 30.2). The human ear is sensitive to frequencies between 20 Hz and 20 kHz, although less sensitive to low and high tones (Fastl and Zwicker 2006). It is crucial not to neglect this dimension of noise, which distinguishes this pollution from any other, when defining indicators. Standards reduce the spectral component of noise into octave or 1/3 octave bandwidths, defined by AFNOR EN61260. An octave bandwidth ranges between f_{inf} and $f_{sup} = 2*f_{inf}$. Eight octave bandwidths are generalized in environmental noise, from 63 Hz to 8 kHz (ISO 266:1997). Frequency weighting functions have been introduced to reduce the frequency content to one value. The most common function is the A-weighting, which reproduces the response of the ear at 40 dB (Beranek 1988). Although recommended by the legislation, it is often criticized for being based on noise

levels much lower than those encountered in environmental acoustics, hence underestimating the impact of the low frequencies (Fastl 1997), which generate increased annoyance (Berglund et al. 1996).

- ***Large temporal variations***: The durations of exposure to noise that lead to adverse health effects can be very brief (i.e., less than 100 ms for gunfire). Therefore, it is crucial to define carefully the integration time τ over which noise is evaluated. Environmental noise indices are usually calculated from the $L_{eq,\tau}$ or ($L_{Aeq,\tau}$ if A-weighted) values. Common periods of integration are $\tau = 1$ s (S (slow) weighting) or $\tau = 125$ ms (F (fast) weighting) (NF EN 61672–1:2003);
- ***Large spatial variations***: Some noise sources can affect inhabitants up to a distance of some kilometers. These spatial fluctuations are shown by noise maps (European Commission 2006), but indicators able to quantify the populations exposed to predefined thresholds are required.

This large quantity of information must be reduced for decision-making. Ancient measurement devices imposed this reduction *de facto* as they were unable to capture short term levels and spectra variations and were limited in storage capacities. These limitations disappear with modern measurement devices (Aflalo and Luquet 2005), allowing complex noise indices calculations. This reduction of information can be guided by the recommendations of the European Commission (2000), which states that the following criteria should be addressed when selecting noise indicators for decision making:

- ***Validity***: *Indicators should be related to health effects: annoyance, sleep disturbance, etc.*
- ***Practical applicability***: *Indicators should be easy to measure or calculate from available data, and should offer a reliable base to decision making.*
- ***Transparency***: *Indicators should be easy to explain and intuitive.*
- ***Enforceability***: *Indicators should allow a comparison with defined thresholds and the evaluation of mitigation strategies.*
- ***Consistency***: *Indicators should offer as little difference as possible with current practice.*

This makes clear that the quest for a single indicator that solves all these questions is in vain in the noise context, especially as these criteria suggest emphasizing different characteristics of noise according to the nature of the source observed. Unsurprisingly, many noise indices have been proposed to characterize physically specific noise sources identified as annoying. A critical review of the most common indicators is given in the next section.

30.3 A Critical Review of the Main Noise Indicators

A large number of indicators have been proposed over the last decades to measure noise pollution; this review is limited to outdoor environmental noise indicators. The reader can refer to Bradley (2011) or ISO 3382-1 for details about indoor indicators, developed with more qualitative criteria (speech intelligibility, etc.). A review of indicators dedicated to building insulation can be found in ISO-717-2.

30.3.1 General Environmental Noise Indices

The most common general noise indices are:

- The equivalent sound pressure level $L_{eq,T}$, defined in ISO 1996–1, expresses the level of a continuous noise that would have the same total acoustic energy as a fluctuating noise measured for the same specific period T: $L_{eq,T} = 10\log_{10}\left(\frac{1}{T}\int_0^T \frac{p^2(t)}{p_0^2}dt\right)$ $[dB]$. One speaks about $L_{Aeq,T}$ when the A-weighted function is applied. This index has been widely used and supported by studies that showed its rather good correlation with long term effects or annoyance (Schultz 1978; Miedema and Vos 1998).
- General environmental noise indices have been proposed to focus on the different periods of the day:
  - The "Night Level" L_{night}, represents the equivalent sound pressure level during the night period;
  - The "Day-Night equivalent level" L_{DN} fixes a 10 dB(A) penalty for noise at night;
  - The "Day-Evening-Night equivalent level" L_{den} fixes penalties of 5 dB(A) for the evening period (usually [18–22 h]) and 10 dB(A) for the night period (usually [22–06 h]) (Directive 2002/49/CE).
- The Sound Exposure Level SEL (ISO 1996–1) is often used to rate impulse or aircraft noise and estimate associated sleep disturbance effects (Fidell et al. 2000). It is expressed as SEL $= L_{eq} + 10\log(T)$, where T is usually the duration of the event.
- The maximum sound pressure level L_{max}, which can be calculated with $\tau = 1$ s or $\tau = 125$ ms.
- The "statistical level L_X" represents the noise level (usually $\tau = 1$ s) exceeded X % of the observation period (ISO 1996/1). The most commonly used statistical indices are L_{10}, L_{50}, and L_{90}. L_{10} and L_{50} are commonly used to rate road traffic noise (Schultz 1972), while L_{90} is often used to describe background noise. However, some studies recommend the use of L_{50} to rate background noise (Beaumont and Petitjean 2003), with short periods of observation T. Finally L_1 is often used to describe emergent noises.
- The "Number of Noise Event" NNE, is often used to describe emergences. It is simply defined as the number of events that exceed an agreed threshold, which can be a fixed value (i.e., 70 dB) or a statistical level (i.e., L_{10}).

Some limitations of the energetic indices for characterizing noise environments have been pointed out. Alberola et al. (2005) underlined the lack of representativeness of these indices when calculated over periods less than 1 h. Can et al. (2008) proved that these indices are not sufficient to discriminate road traffic noise environments and highlight their main physical characteristics. Finally, Schomer (2005) pointed out the limitation of energetic indices for evaluating perceptively fluctuating sounds.

30.3.2 Contextual Noise Indices

Noise indices have been proposed to adapt to the characteristics of specific noise sources, supported by studies on noise perception, which showed in particular that: (i) Noise fluctuations negatively impact noise annoyance (Fujii et al. 2002); (ii) low frequencies increase annoyance (Berglund et al. 1996); (iii) noise indicators should be more sensitive to tonal components (Beaumont and Petitjean 2003); and (iv) noise assessment of urban environments would benefit from more qualitative approaches (Notbohm et al. 2004; Raimbault et al. 2003; Nilsson and Botteldooren 2007). The aim of contextual indices is to fulfill these requirements.

30.3.2.1 Road Traffic Noise Indices

Classical Road Traffic Indices

Road traffic noise is characterized by strong fluctuations, especially in urban area, which can be slow (day and night alternation) or fast (traffic cycle phases) (Nelson 1987). A specific Traffic Noise Index (TNI) has been proposed by Griffiths and Langdon (1968) to account for the increase of annoyance due to these fluctuations: $\mathrm{TNI} = 4(\mathrm{L}_{10} - \mathrm{L}_{90}) + \mathrm{L}_{90} - 30$. Robinson (1971) proposed to account for the whole noise distribution through the standard deviation σ, with the "noise pollution level" $L_{\mathrm{NP}} = L_{\mathrm{eq}} + 2.56\sigma$. However, these indices are based on assumed Gaussian noise distributions, which are not suitable for urban traffic noise (Don and Rees 1985), and are now in disuse; nevertheless they are good examples of the wish to account for fluctuations when assessing noise environment. Interestingly, the UK CRTN (Calculation Road Traffic Noise) method proposes instead of L_{den} the use of the $L_{10,18\mathrm{h}}$, which also relies on statistical levels as the arithmetic average of 18 $L_{\mathrm{Aeq,1h}}$ values from 6:00 to midnight, to present road traffic noise exposures (UK Department of Transport 1988). Relations have been established by O'Malley et al. (2009) to link $L_{\mathrm{A10,18h}}$ to L_{n} and L_{den} values.

Dynamic Road Traffic Indices

The indices revealing road traffic noise fluctuations were neglected in the past because models were anyway unable to estimate them, making them useless for decision-making. The recent modeling advances inverse this tendency and allow more qualitative approaches to be implemented. New propagation models allow the adaptation of indices usually dedicated to room acoustics (such as the reverberation time) to noise assessment within canyon streets (Guillaume et al. 2012). This allows more qualitative analysis, for example in shielded urban areas (Forssén and Hornikx 2007).

The evaluation of road traffic noise fluctuations is made possible by new integrated modeling approaches. They outperform the classical approaches, which consider road traffic as a constant line source, and model noise emitted at each time step (usually 1 s) by each vehicle on the road network. To do so, they rely on microscopic traffic models that represent the motion of vehicles on the network: SYMUVIA in Leclercq and Lelong (2001) and Can et al. (2009); HUTSIM in Heltimo et al. (2003); PARAMICS in De Coensel et al. (2005); DRONE in Bhaskar et al. (2007); AVENUE in Oshino and Tsukui (2006). Consequently, indices have been proposed to reflect urban traffic noise dynamics:

- Indices highlighting the spreading and the homogeneity of the distribution of $L_{Aeq,1s}$ values have been proposed in Leclercq et al. 2008. Defrance et al. (2010) proposed indices that underline the roughness of noise, by calculating statistics (average, spreading) on the noise differences $\delta L_{eq,1s}$ between consecutive noise levels. Indices that underline quiet or noisy periods, such as the NI70 (percentage of time when $L_{eq,1s}$ is greater than 70 dB for at least 4 s) or the TI60 (percentage of time when $L_{eq,1s}$ is less than 60 dB for at least 4 s) are used in Defrance et al. (2010).
- Can et al. (2008) proposed a set of indices that describes noise fluctuations at the traffic cycle scale. These indices highlight the two modes of the noise distribution observed in the vicinity of traffic signals, corresponding to red and green traffic light phases. Complementing these, indices such as the $N_{L95>65}$ (percentage of traffic cycles *tc* when $L_{95,tc}$ exceeds 65 dB(A)) are proposed to underline the periodic rarefaction of calm periods. Finally, indices such as the $N_{Lmax>80}$ (percentage of traffic cycles when $L_{max,tc}$ exceeds 80 dB(A)) are proposed to underline periodic peaks of noise. These indices have been estimated successfully in Can et al. (2009), using the microscopic traffic model SYMUVIA. Finally, indices adapted from the building acoustics have been estimated in Can et al. (2010a), such as the Noise Rating curves, which underline the emergent frequencies.
- De Coensel et al. (2003) and Botteldoren et al. (2006) proposed the use of the slope of the Fast Fourier Transform of the $L_{Aeq,1s}$ evolution to underline the rhythm of road traffic noise, adapted from works in the musical context that proved that regular spectra are associated with more pleasant sound environments (Voss and Clark 1978). This index has been estimated in De Coensel et al. 2005, using the microscopic traffic model PARAMICS.

However, although this new modeling progress clearly opens possibilities for more qualitative noise mitigation strategies in urban areas, the correlation of these new indicators with pleasantness or annoyance is not yet clearly established.

30.3.2.2 Railway Noise Indices

Although the legislation recommends the use of $L_{Aeq,[6–22h]}$ and $L_{Aeq,[22–6h]}$ to rate railway noise, it is also sometimes assessed with the SEL or the Transit Exposure

Level TEL (ISO 3095:2005), which account for the duration of a train passing by. The use of these indices is supported by studies that proved the increase of annoyance due to train peaks of noise (Lambert et al. 1996).

30.3.2.3 Aircraft Noise Indices

The L_{den} is the noise index recommended by the European legislation to rate noise levels in the vicinity of airports. Specific indices have been proposed that complement the L_{den} and the SEL (ISO 3891) to capture the specificities of aircraft noise, and rate the resulting annoyance or sleep disturbance. The first is the Perceived Noise Level PNL, which accounts for the annoyance relative to aircraft noise at different frequencies (Kryter 1959), but is used to describe the noise emitted by a single event. Several indices based on it have been developed since, with different formula:

- The "Effective Perceived Noise Level" EPNL introduces a correction for the duration when $\mathrm{EPN} > \mathrm{EPN}_{\mathrm{max}} - 10$, and a correction for discrete frequency components.
- The "Noise Exposure Forecast" (NEF), the "Weighted Noise Exposure Forecast" (WECPNL) and the Noise Number Index (NNI) (HMSO 1963), include parameters for the number of flights per day and per night.
- The Psophic Index (IP) is similar to the TNI, but adds a penalty for noise at night.

30.3.2.4 Wind Turbines Noise Indices

Wind turbines are a good example of a new anthropogenic noise source that generates complaints and whose effects need therefore to be evaluated. This requires developing indices able to capture its main physical characteristics (regular fluctuations due to the blades, specific spectra…) and that correlate annoyance (Siponen 2011). Recent approaches tend to capture these characteristics through a so-called "fluctuation indicator", based upon a Fourier spectrum of the 1/3-octave band 1/8-s time (Bockstael et al. 2012).

30.3.3 Indicators for Exposure and Effects Assessments

30.3.3.1 Qualitative Indicators

The indices presented above describe noise environments physically, which is not necessarily sufficient to form relevant indicators. There is a trend of thought that advocates a more qualitative description of noise when assessing its effects. This resulted in the development of psycho-acoustical indicators, which describe noise sources more precisely, by accounting for fluctuations, roughness of sound, etc. (Fastl 1997). Finally, more holistic approaches also try to take the nature of the noise source into consideration when evaluating annoyance; see Marquis-Favre (2005a; b) for a review of the resulting indicators. However, their calculation often remains complex and their estimation through modeling is as yet impossible, complicating their use for decision-making.

30.3.3.2 Indicators for Exposure Assessment

All the indicators described above are limited to noise assessment at a given location. However, the evaluation of some noise mitigation strategies, such as an urban displacement plan, requires considering noise impacts over a defined spatial zone. Spatial indicators have been produced to enable these analyses, such as:

- km^2 of territory where $L_{\mathrm{den}} > L_{\mathrm{den,limit}}$;
- percentage of people exposed to $L_{\mathrm{den}} > L_{\mathrm{den,limit}}$;
- $L_{\mathrm{den,\,population}} = 10\log\left(\sum_i n * p * 10^{L_{den,i}/10}\right)$, where n is the number of dwellings exposed to the noise level $L_{\mathrm{den,i}}$ and p the number of inhabitants per dwelling (EEA 2010; Mediema 2004).

The calculation of these indicators requires geographic knowledge of the territory, and can advantageously integrate Geographic Information Systems. Finally, spatial indicators can also be adapted in the dynamic traffic noise modeling context to compare traffic scenarios, resulting in indicators such as "km^2 of territory where $L_{1,\mathrm{scenario\ A}} > L_{1,\mathrm{scenario\ B}} + x$ dB(A)" (Can et al. 2010b).

30.3.3.3 Indicators for Annoyance Assessment

Relating noise characteristics to annoyance is a crucial but tedious task. As shown in Fig. 30.1, there is no direct link between Action and Effects, and Exposure and Effects are impacted by non-acoustical parameters and socio-demographic factors. This makes it difficult to correlate physical indicators to perceived annoyance. In general, the annoyance is estimated through dose/effect relations, which evaluate the number of people annoyed or very annoyed for given thresholds of noise levels. Examples of dose–response relationships have been proposed for L_{den} by the European Commission (2002). Complementing these, different indicators have been produced to describe the resulting annoyance of combined noise sources. They suggest that the global annoyance is either the sum of the contribution of each source (Taylor 1982) or that the most annoying source dominates (Rice 1986). The models proposed by Vos (1992) and Mediema (2004) combine these approaches, and propose an indicator that sums the annoyances, but previously corrects the single contributions according to the nature of the noise sources.

30.3.3.4 Aggregated Indicators

The complexity of the existing noise indicators makes them sometimes inefficient as a communication tool. Aggregating complex noise indicators into a single dimensionless indicator (that varies for example from 0 to 10), which combines this set of indicators could solve this issue (Harmonica 2013). Finally, noise indicators can be combined with other environmental indicators (greenhouse effect, air pollutants. . .) to form composite indicators, which can summarise multi-environmental dimensions with a view to supporting decision-makers, and the public often find easier to interpret. Their pro and cons are discussed in Nardo et al. (2005). In particular, statistical analysis and weightings should be handled with care to avoid misleading policy messages or disguising serious failings in some dimensions. Another complementary approach consists of including noise indicators in a global evaluation system in which they cohabit with environmental and socio-economic indicators, within multi-criteria decision analysis or economic approaches (Joumard and Gudmunsson 2010).

Conclusion

This review showed that the development of indicators in the domain of outdoor noise pollution has been oriented mainly by the need to capture the main characteristics of noise, which substantially differ from one source to another. Yet, the quest of indicators that in the mean time are able to capture these characteristics, discriminate noise environments, and correlate annoyance, is not ended.

The risk is not null that research leads to more and more specified indicators, relevant to describing physically noise environments, but deficient in terms of *transparency* or *enforceability*. Moreover, this “indicator approach” will in the future be for decision-making complemented by (or competing with) the technique of auralization, whose recent progress allows us to listen directly to the noise environment resulting from a mitigation strategy.

Therefore, this will be the goal of the research in environmental acoustics in the next years, to work on the development of noise indicators closely related to sound environments, but still easy to manipulate and understand as communicative tools. This harmonization work has already started (European Commission 2000); now it will be important that the set of indicators currently defined in environmental acoustics will be progressively enriched by the ongoing progresses on noise source and noise propagation modeling.

Acknowledgements The author would like to thank Michel Bérengier for his kind and precious review of this paper.

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Chapter 31
Snow Samples as Markers of Air Pollution in Mass Spectrometry Analysis

Albert T. Lebedev, Dmitry M. Mazur, Olga V. Polyakova, and Osmo Hänninen

Abstract Snow can store with minimal further modifications the air born pollutants carried by winds over long distances. The "Cold Finger" phenomenon carries the pollutants from warmer zones toward cold ones i.e., to Polar Regions and high mountains. This automatic natural sample storage keeps them in fall out layers. Mass spectrometry provides information not only on the structures of the pollutants but also on their relations and sources. This issue helps in the analysis of even distant sources of pollution, as well as the problems of transboundary transfer. Both targeted and non-targeted analyses are applicable. Examples are given to illustrate the values of these technologies in the identification of distant pollution sources in Antarctica, Canada, Greenland, Finland, Russia, etc.

Keywords Air pollution • Snow samples • Environmental mass spectrometry • Gas chromatography/mass spectrometry • Priority pollutants • Targeted/non targeted analysis • Organochlorines • Polycyclic aromatic hydrocarbons

31.1 Introduction

Human health, along with lifespan and mortality, is often treated as a statistical indicator of the standard of living in a country, city, or certain region. That is a superposition of various factors affecting the health of each person. One of the most important issues involves the state of the environment (air, soil, and water quality). Agricultural development is directly linked to the state of the soil, which affects its suitability for growing crops. Another important characteristic of the soil deals with water filtering. As water passes through the various layers of soil, it washes away

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_31

with it certain compounds. Having contaminated soil, one finally gets contaminated ground water and, as a consequence, contaminated drinking water sources.

The need for water for human consumption is regular. A person can live without water only a few days. The water can be subjected to several degrees of purification, while nowadays some people prefer to drink only bottled water. Without air, a man can survive only few minutes. Therefore, air quality is one of the most important parameters that affect the population health. Improving the air quality may be treated as a priority international task.

Contaminants in the atmosphere can be divided into three main types: gaseous, vaporous (chemical substances having boiling points below 250 °C), and sprays. The latter, in turn, can be divided into liquid aerosol particles (mist) and particulate matter (smoke, dust). Air can be very contaminated not only with nitrogen and sulfur oxides, but also with heavy metals, organics, such as polychlorinated biphenyls (PCBs), pesticides, and even microorganisms. Air purification is applied primarily only at industrial facilities, that function with constant emissions. Unfortunately, not all facilities have treated this problem responsibly. Sometimes, a company has an inefficient air filtration system, or spontaneous emissions occur. In addition, the sources of air pollution are not limited to emissions from industrial facilities. Traffic, power plants, landfills, leaks, spills, etc. are important pollution sources. Since the air is more susceptible to contamination, it is very important to monitor the state of the atmosphere, in particular, in densely populated areas. One of the most efficient approaches (especially for the cold regions of the globe and mountain territories) is to collect the data on air pollution. This involves the analysis of snow samples in spring, before the active period of melting. Snow is an excellent matrix that allows the vast majority of pollutants to be retained, including the not very stable ones. As a result, a researcher obtains a sample containing all the chemical compounds deposited from the atmosphere during the whole winter period.

31.2 Mass Spectrometry in Snow Analysis and Cold Finger Effect

Mass spectrometry has shown its sensitiveness, being an informative and reliable analytical tool for dealing with any types of pollutant (from chemical elements to the most complex organic compounds and microorganisms). The benefits of this technique for the environmental problems have recently been covered (Lebedev 2012, 2013). The reported applications of mass spectrometry in the analysis of snow (atmospheric) pollution can be divided into two main groups:

A – Targeted analysis to obtain exact information concerning the preliminary selected compounds.

B – Non-targeted analysis to identify as many pollutants in the sample as possible.

Quite often, a study requires both approaches. The tasks may involve the estimation of environmental situation in certain regions, studies of transboundary atmospheric transfers, including the "cold finger" effect, attempts to create priority pollutants list for particular industrial plants, water reservoirs or regions, etc.

A certain problem deals with the fact that the safe levels for the regulated compounds are usually developed for air, water, and soil. Therefore, direct application of the obtained results for snow pollution to derive conclusions on the population health or ecosystem safety should be done carefully. Anyway, as qualitative data are very reliable, they allow making certain decisions and planning alternative experiments to confirm the obtained results.

The first reports on the application of mass spectrometry to the analysis of snow samples appeared in the late 1980s. This is a typical example of targeted approach. A large number of samples of precipitation (rain and snow) were analyzed in Hannover, Germany in 1988–1990 (Levsen et al. 1991). n-Alkanes, fatty acids, aldehydes, phenols, and PAHs were chosen as target compounds. Various analytical tools were used, while fatty acids were methylated and analyzed by GC/MS. Phenols were also analyzed by GC/MS and HPLC with photodiode array detector. The authors identified alkanes from $C_{17}H_{36}$ to $C_{40}H_{82}$. Fatty acids from $C_6H_{13}COOH$ to $C_{25}H_{51}COOH$ were identified in 8 samples of rainwater and snow in 1988 and in 22 samples in 1989. The predominance of palmitic and stearic acids in the samples was quite predictable. The results showed that the acids with even number of carbon atoms were present at higher levels than the acids with odd numbers. This pattern is typical for acids of biogenic origin. Palmitic acid concentration varied from 2.6 mg/L to 18.4 mg/L, while the total concentration of fatty acids, from 9.1 to 64.1 mg/L. The levels of aldehydes in snow samples reached 4.9 μg/L for formaldehyde, 5 μg/L for acetaldehyde, and 0.1 μg/L for propionaldehyde. Phenol, three isomeric cresols, and isomeric dimethylphenols were also detected. Among these, phenol was the predominant component (1.3–15.4 μg/L). The total concentration of 3- and 4-methylphenols was 0.49–9.9 μg/L, while that of 2-methylphenol was much lower. In 1989, only 2- and 4-nitrophenols were identified. Moreover, 4-nitrophenol prevailed in all the samples; its concentration was 0.3–19.5 μg/L. Relatively high concentrations were found for 2,4-dinitrophenol (0.1–4.6 mg/L) and 3-methyl-4-nitrophenol (0.04–1.2 mg/L). Eleven PAHs from fluoranthene to indeno[1,2,3-cd]pyrene were identified in 28 samples. Among PAHs fluoranthene prevailed (23–457 ng/L), while the carcinogenic benzo[a]pyrene levels were in the range 1.1–187 ng/L. An increase in the average concentration of PAHs during the cold period was predictable, since it is related to fuel combustion and lower photochemical degradation in winter. However, despite the expected increase in the total concentration of PAHs in winter, their levels decreased in winter 1989/1990 due to the exceptionally warm weather. This fact explains the low levels of PAHs in the snow sample in March 1990 (119 ng/L).

Alber et al., focused their research on nitrophenols (Alber et al. 1989). Nitrophenol, and in particular dinitrophenols, are toxic substances that inhibit oxidative phosphorylation in organisms (McLeese et al. 1979). 2-Nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, and 4,6-dinitro-2-methylphenol are included into the list of priority pollutants of the US Environmental Protection Agency (US EPA). Snow and rain samples were collected in Western Germany (Alber et al. 1989). All the samples were analyzed by two methods: GC and HPLC. Classic liquid-liquid extraction with dichloromethane was used for GC. Several detectors were used with GC: electron capture detector (ECD), nitrogen-phosphorous detector (NPD), chemiluminescence detector (TEA), and MS detector with electron ionization (EI) and negative ion chemical ionization (NICI). Due to their high electron affinity, nitrophenols are readily ionizable in NICI conditions. This fact enhances the sensitivity and selectivity in comparison to EI. Dichloromethane extracts were also used for HPLC analysis with a photodiode array detector. However, dichloromethane was replaced with methanol in this case. Although HPLC resolution is lower than that of GC, analysis of nitrophenols in the environment is easier by HPLC, because all nitrophenols have an absorption maximum between 200 and 500 nm. The HPLC method is also useful for the analysis of polar dinitrophenols, which could not be analyzed by GC without derivatization. Quantitative analysis revealed that 4-nitrophenol was the major component. Concentrations of 2- and 4-nitrophenols in snow samples varied from 0.5 to 5.7 μg/L (mean 1.2 μg/L) and from 0.5 to 16.1 μg/L (average concentration of 3.7 μg/L), respectively.

The presence of methyl-*tert*-butyl ether (MTBE) in 43 snow samples in the urban area of Frankfurt (Germany) and 12 rural and remote areas in winter 2001–2002 and 2002–2003 was studied in (Kolb and Püttmann 2006). MTBE is characterized by relatively high water solubility and a low rate of biodegradation. It can be expected that the concentration of MTBE in snowmelt water will be significant. Evaporation of fuel and car exhausts are major sources of MTBE in the environment, as it is added to gasoline to increase the octane number and reduce emissions of carbon monoxide and hydrocarbons leading to a decrease in the level of ozone in the air. In summer, solar activity is high, and therefore, the content of MTBE in the environment is reduced due to its photochemical transformation into *tert*-butyl formate.

The snow samples were collected during snowfall or just by swiping the top layer of snow. Melted snow (4 g) was analyzed with headspace GC/MS. The detection limit for MTBE was 10 ng/L. MTBE was detected only in 28 of 43 samples; its concentration ranged from 11 to 631 ng/L. In 17 samples, the concentration exceeded 100 ng/L, and in four fresh snow samples from Frankfurt concentration was below 54 ng/L. These values were comparable to the concentrations of MTBE detected in rain water in the same region in winter 2000–2001 (Achten et al. 2001). The levels of MTBE in urban and rural areas were similar due to air transport. However, in summer the picture changes because of active photochemical degradation.

Chinese scientists carried out a targeted analysis of snow samples in Beijing for nine aromatic compounds (benzene, toluene, chlorobenzene, ethylbenzene, p-xylene, styrene, isopropylbenzene, n-propylbenzene and 1,2-dichlorobenzene) (Zhou et al. 2005). Three samplings of snow were conducted in four districts of the city. Analyses of melt water (10 mL) were performed by solid-phase microextraction followed by GC/MS and GC/FID. The highest concentrations were determined for benzene and toluene (37.4 and 621 ng/mL). p-Xylene, cumene and styrene were present in the samples at several ng/mL, while chlorobenzene, ethylbenzene, and n-propylbenzene were not detected. Benzene and toluene were the main aromatic pollutants, and their principal sources involved vehicle exhausts and industrial emissions. The highest levels of benzene and toluene were recorded in South Beijing due to the proximity to the Third Belt Road. Furthermore, since a chemical plant is situated nearby, the concentration of 1,2-dichlorobenzene (16.5 ng/mL) in Southern and Eastern parts of the city was more than twofold that in other areas.

In (Sieg et al. 2008), investigators analyzed samples of freshly fallen snow, collected in the village Jungfraujoch in the Swiss Alps, for the presence of volatile organic compounds (VOCs): benzene, toluene, ethylbenzene, o-, m- and p-xylene (BTEX), and n-aldehydes (C_6–C_{10}). Analysis was carried out using headspace solid phase dynamic extraction followed by gas chromatography – mass spectrometry (HS-SPDE-GC/MS). The analytes were extracted from the vapor phase onto the immobilized coating on the inner wall of the cooled needle (-15 °C), and then desorbed directly into the GC/MS injector. Among the substances of BTEX, toluene dominated (0.23 μg/L), while among aldehydes the maximal concentrations belonged to n-hexanal (1.58 μg/L) and n-nonanal (1.89 μg/L). Comparing these data with the results of (Kos and Ariya 2006a), when the content of toluene (316 ± 47 μg/L) was determined in old snow, the authors concluded that BTEX and n-aldehydes precipitated into the snow matrix during the whole winter period.

Dicarboxylic acids were the object of targeted analysis in (Kippenberger et al. 2008). Concentration of carboxylic acids in the atmosphere depends on various sources. Direct sources are fossil fuel combustion, biomass burning, and cooking. Secondary sources include photo oxidation of unsaturated fatty acids and cyclic alkenes. The authors developed a method for determining homologous aliphatic α-, ω-dicarboxylic acids from C_5 to C_{13}, as well as pinonic, pinic, and phthalic acids in snow samples using solid phase extraction and subsequent analysis by HPLC/MS with electrospray ionization in the negative ion mode. The detection limit of the method was in the range between 0.9 nmol/L for dodecanedioic acid and 29.5 nmol/L for pinonic acid. The exception involved pinic acid with a detection limit of 103.9 nmol/L. This technique was applied to the analysis of 60 snow samples taken at various altitudes from 3,056 to 3,580 m on the glacier Fee (Switzerland) in December 2006 and January 2007. Volume of samples in the form of melt water ranged from 200 to 500 mL. Only dicarboxylic acids C_5–C_{12} and phthalic acid were quantified. The levels of tridecanedioic, pinonic, and pinic acids were below the limit of quantitation. Concentrations of glutaric (3.9 nmol/L), adipic (3.35 nmol/L) and phthalic acids (3.04 nmol/L) were maximal.

A paper (Prieto et al. 2010) describes a method developed for the analysis of different classes of organic pollutants (PAHs, PCBs, phthalates, nonylphenol, bisphenol A (BPA), and certain steroid hormones). Microextraction by packed sorbent (MEPS) and simple solid-phase extraction (SPE) followed by GC/MS analysis were used. Both methods allow for accurate determination of 41 target organic contaminants in water. Detection limits for substances using classic SPE for 100 mL sample volume range from 0.2 to 736 ng/L, whereas MEPS provides detection limits ranging from 0.2 to 266 ng/L for 800 μL sample. The developed methods were applied to samples of wastewater and snow taken in Leipzig (Germany) in 2010. Snow samples taken near a busy street and Institute parking lot contained the highest levels of acenaphthylene and acenaphthene (>1,000 ng/L), indicating the accumulation of products of combustion of diesel fuel. Concentrations of other PAHs have been quite similar in all samples (ng/L levels). Phthalates in the snow samples were detected at μg/L levels. Concentration of diethyl, dibutyl, and bis(2-ethylhexyl) phthalate in the samples ranged from 985 to 9,973 ng/L. BPA, being a component of various technical products, was detected in concentrations up to 2,000 ng/L (snow sample near the parking lot). In this case BPA might be released into the environment from plastic automobile parts, varnish, and tires.

31.2.1 Antarctic Snow

Despite its remoteness from any direct sources of air pollution, Antarctica undergoes noticeable contamination due to transboundary transfer and "cold finger" effect, which involves the long range air transport and settling of contaminants in regions with colder climates. A number of researchers analyzed samples collected in various regions of Antarctica. Zoccolillo et al. (2007) reported the identification of the most common volatile chlorinated hydrocarbons (VCHC) in the surface snow. The snow was collected during two Italian expeditions to Antarctica. The aim of the work involved monitoring of VCHC along the continent to understand how VCHC reached remote areas and was deposited into the snow. Snow samples were analyzed by purge-and-trap followed by GC/MS. Sample volume was 10 mL. The samples collected in the first expedition in 1998/1999 (T1) were analyzed primarily for carbon tetrachloride, 1,1,2-trichlorethylene, and tetrachlorethylene. In the snow samples of the second expedition in 2000/2001 (T2) the authors again identified chloroform and 1,1,1-trichloroethane. The distribution of VCHC in the samples T1 was quite uniform, and the concentrations were around 50 ng/kg. The authors noted that earlier (Zoccolillo et al. 2004) VCHC were detected in the sea waters around Antarctica. Therefore, marine aerosols were considered as potential sources of VCHC. However, since the route of the expedition went inland from the coastal zone, the authors concluded that the uniform concentration of VCHC in various points along the route excluded marine aerosols as one of the main sources of VCHC in this area.

The appearance of VCHC was caused by the long range atmospheric transport and "cold finger" effect. The VCHC concentrations in T2 samples were higher than in T1. In particular, the chloroform level was significantly higher than that of all other VCHC considered, as it is released into the atmosphere by many industrial sources. The authors tried to use their results to correlate the levels of VCHC with

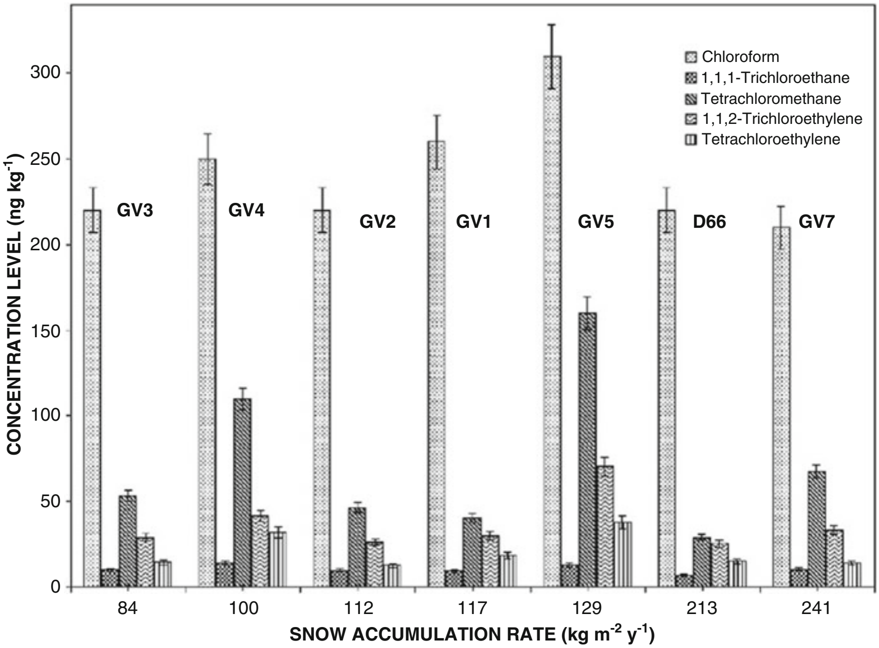

Fig. 31.1 VCHC levels in the traverse T2 versus snow accumulation rates *in Antarctica* (Zoccolillo et al. 2007)

the overall mass of snow at the definite periods of time. Figure 31.1 shows the concentration of VCHC, depending on the amount of snow accumulated over the year. According to the observed pattern, the authors concluded that the concentration of VCHC did not correlate with the annual accumulation of snow. In other words, the amount of fallen snow over the year does not affect the concentration of the VCHC in the snow, meaning that the dry deposition mechanism is negligible.

To understand the sedimentation processes of pollutants with snow, the authors compared the results of the analysis of fresh and old snow. Six samples of fresh snow were collected during two snowfalls near the Italian station "Mario Zucchelli" during the expedition of 2001/2002. The average VCHC concentrations in fresh snow were 237 ng/kg for $CHCl_3$, 9.7 ng/kg for $C_2H_3Cl_3$, 52 ng/kg for CCl_4, 58 ng/kg for C_2HCl_3, and 9.5 ng/kg for C_2Cl_4. The values for VCHC in the fresh and aged snow were quite similar, that is, old snow did not show any significant increase or decrease in the levels due to dry deposition or evaporation, respectively. Therefore, the authors concluded that the main mechanism for the accumulation of VCHC involved deposition on the surface from the atmosphere along with the snowfall. Weather conditions play a special role for deposition and accumulation of contaminants in the Antarctic, namely the lowest temperatures in the Antarctic are quite close to the melting point of some VCHC (e.g. 1,1,2-trichlorethylene and chloroform) and higher than the melting points of 1,1,1-trichloroethane, tetrachloromethane, and tetrachloroethylene. Therefore, the authors believe that the investigated substances are not only accumulated from the gas phase, but are also adsorbed on the snow as solid aerosols.

One of the objectives of the international expedition ITASE involved the collection and analysis of 35 samples of surface snow to determine the levels of more than 20 organochlorine pesticides (Kang et al. 2012). Water volume of about 100 mL was extracted with dichloromethane, concentrated, and analyzed by gas chromatography coupled with high resolution mass spectrometry, (GC/HRMS). In the samples collected along the route of the expedition, only three target toxicants were found: α-hexachlorocyclohexane (α-HCH), γ-hexachlorocyclohexane (γ-HCH), and hexachlorobenzene (HCB). The major pollutant appeared to be γ-HCH (33–137 pg/L), followed by α-HCH (18–83 μg/L). The concentration of HCB ranged from the detection limit up to 182 pg/L. The total concentration of the analytes in the samples was 65–326 pg/L. The authors compared their results with those obtained two decades earlier for the Antarctic samples (Tanabe et al. 1983) and noted that the total concentration of HCH dropped by more than an order of magnitude. The levels of γ-HCH in the case of the Antarctic samples were higher (1,150–1,500 pg/L), while the concentration of HCB was comparable in both cases. Average concentrations of α-HCH and γ-HCH in the snow collected during the second expedition in winter of 2001 on the Western Antarctic Peninsula, were 1.76 and 4.28 pg/L, respectively. The difference in concentrations was caused by the sampling time, and sampling and analysis procedures. It should be noted that low resolution GC/MS or GC/ECD (electron capture detector) were used earlier, whereas the use of isotope dilution GC/HRMS provided more reliable results.

The most well known ecotoxicants are polycyclic aromatic hydrocarbons (PAHs). Na et al. (2011) analyzed snow samples to study the distribution and extent of PAHs contamination in Antarctica. The samples were collected at seven points on the Fildes Peninsula of the Island of Waterloo in December 2009. To check the reliability, 10 L of snow were taken from each sampling point. Solid phase extraction disks were used for sample preparation, and the analysis was performed by GC/MS. All 16 PAHs controlled by US EPA were identified, except benzo[a]pyrene. The total concentration of PAHs in the samples ranged from 52 to 272 ng/L. The main components were the compounds with 2 or 3 aromatic rings. The reason for such a high concentration of PAHs is that there are several research stations around the island. The main source of energy for these stations is often the burning of fossil fuels and wood. The results of principal component analysis confirmed that the sources of PAHs could be air transport and combustion of fuel in the Fildes Peninsula. Comparison of concentrations and types of PAHs between the fresh fallen snow and aged snow showed that the concentrations of the major components were higher in the old snow. This fact supports the concept of possible dry deposition of pollutants from the atmosphere and somehow contradicts that proposed by (Zoccolillo et al. 2007). The difference may involve different volatility of the target compounds in the studies.

31.2.2 PCNs

Polychlorinated naphthalenes (PCNs) represent a group of persistent organic pollutants. Their presence in the environment attracts increasing attention due to dioxin-like toxicity and accumulation in biota. PCNs – are industrial chemicals that are used similarly to PCBs, due to their high chemical and thermal stability, good dielectric properties, and low flammability. An important source of PCNs in the environment is the use of technical mixtures (e.g., Halowax 1001, 1014, 1099). Simultaneous sampling of air and snow was conducted in two separate areas of the Norwegian Arctic (Herbert et al. 2005). The first study was carried out in Ny-Alesund (Svalbard, Spitsbergen) during April 2001, and the second, in the mountains near Tromso (Norway) during February-April 2003. An activated phase cartridge Florisilk was used to get organic compounds from melted snow from the metal containers. The cartridge was then eluted with dichloromethane. Water was filtered and subjected to solid phase extraction on the discs. Filters were extracted with dichloromethane in a Soxhlet apparatus. All the extracts were combined and concentrated. Analysis of PCNs was performed by GC/MS. Since organochlorine pesticides were not separated from the PCN fraction in the final extract, some of the pentachloronaphthalenes (penta-CNs) coeluted with components of chlordane with the same molecular weight. Average concentrations of total PCNs were similar in both areas (~300 pg/L of melt water), reflecting the similarity of the concentrations of PCN in the air of these areas. However, some differences were noted. The range of concentration was much wider (59–1,100 pg/L) in the samples from Spitsbergen than in those from Tromso (100–440 pg/L). PCBs and organochlorine pesticides were detected in a wide range of concentrations, demonstrating that it was not the result of an error in snow sampling (Fig. 31.2).

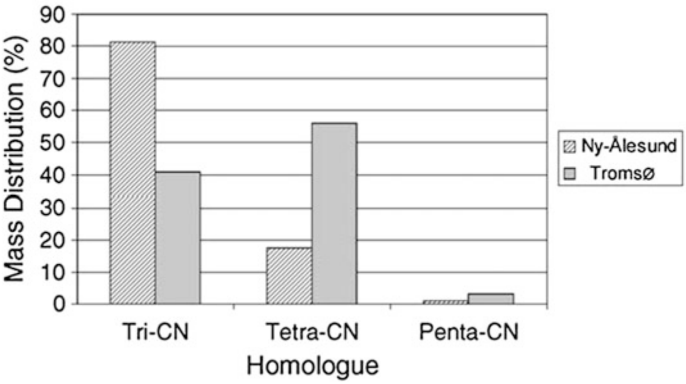

Fig. 31.2 The average levels of PCNs observed in surface snow at Ny-Olessune and Tromso (Herbert et al. 2005)

The authors (Herbert et al. 2005) mentioned that the distribution differences reflected the difference between the types of snow and the time it spent on the ground before the sampling. The lower is the density of the fresh snow, the higher is the concentration of PCNs. Aged snow of higher density may contain considerably lower quantities of more volatile trichloronaphthalene.

31.2.3 Mountain Ecosystems

Mountain ecosystems may well absorb various persistent organic pollutants representing another case of the “cold finger” effect. Quiroz et al. (2009) analyzed snow samples from the mountains of Aconcagua in the Southern Andes in January 2003 to determine PCBs. Sampling was carried out at 3,500, 4,300, 5,000, 5,800, and 6,200 m above sea level. PCBs were removed from the melt water on a magnetic stirrer coated with PDMS-absorbing film and injected into a GC/MS system using thermal desorbers. As a result, 25 PCBs were detected. The total concentration of PCB changed from 0.01 (detection limit) to 0.43 ng/L. The most frequently detectable were PCBs 138 and 180, whose concentrations reached 0.08 and 0.06 ng/L, correspondingly. It was found that the major source of PCBs in this area was due to commercial product Aroclor 1260, which had previously been extensively used in the Southern hemisphere. When comparing the data with those for other parts of the Andes, the authors concluded that PCBs got into the Andes mountain system due to air transport and deposition processes.

31.2.4 Possibility of Re-evaporation from Snow

In (Finizio et al. 2006), the authors investigated the mechanism of adsorption of persistent organic pollutants and their re-evaporation from the surface of freshly fallen snow. Snow samples were collected in the Monte Rosa massif in the Italian Alps at a height of 4,250 m at various time intervals after a snow storm in July 2003. 5 cm of the upper layer of fresh snow was collected every 12 h during 3 days. As a result, 6 snow samples were collected. Melt water was extracted three times with 200 mL of dichloromethane, concentrated, and dissolved in n-dodecane for subsequent determination of PCBs and pesticides. The target compounds were isomers of DDT (p, p′-and o, p′-isomers) and its metabolites (DDE and DDD,), α-, β-, γ-, and δ-hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), and some PCB congeners. Analysis was performed by GC/MS. The detection limits were 1 pg/mL for DDT isomers and 0.5 pg/mL for PCBs and other substances.

Figure 31.3 represents diagrams of the levels of persistent organic pollutants, depending on the time of snow collection after a snowfall. Up to 44 h after snowfall, relative homogeneity is observed, while the major components were γ-HCH and tetrachlorobiphenyls (50–70 % and 15–30 % of contamination, respectively).

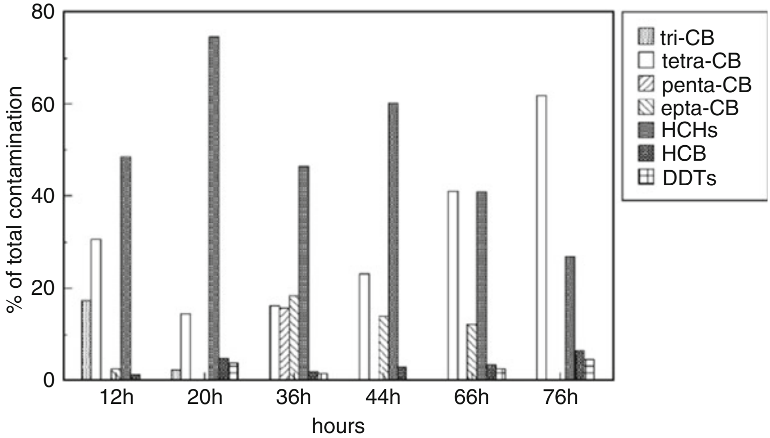

Fig. 31.3 Distribution diagrams for tri-CB, tetra-CB, penta-CB, hepta-CB, HCH, HCB and DDT, depending on the time of sampling *in the Italian Alps* (Finizio et al. 2006)

Trichlorobiphenyls were detected in the first three samples, whereas the presence of PCBs with a higher degree of chlorination and DDT derivatives was of a random nature. In the range from 66 to 76 h, tetrachlorobiphenyls prevailed. At the end, γ-HCH covered approximately 30 % of the total amount of pollutants, while the rest was mainly tetra-CB. Significant contribution of heptachlorobiphenyls to the total pollution is associated with a rapid rate of extinction of other toxicants. Thus, the authors (Finizio et al. 2006) proposed that the concentration of analytes in snow decreased over time, depending on the physico-chemical properties of each compound. This conclusion definitely requires further study, as some contradicting results were also published (Sieg et al. 2008; Kos and Ariya 2006a; Na et al. 2011). Besides, the authors did not mention temperature and the level of Sun irradiation during the sampling, while the marked decrease mainly involved the most volatile species among the studied analytes.

31.3 Non Targeted Analyses

A non-targeted approach has been applied in several studies conducted by A.T. Lebedev's group. GC/MS with electron ionization to study snow samples was used in (Lebedev et al. 2000a, b). Ten samples of snow were collected at the beginning of March in several parts of Finland (Central and Eastern Lapland), and in various regions of Russia (several districts of Moscow, Shchuchye and the Baikal). Triple liquid-liquid extraction with dichloromethane at pH 2 and 11 was used for sample preparation. The task involved mainly non-targeted analysis with the idea of identifying as many organic compounds as possible. Quite unexpectedly, organophosphate pesticides were found in snow samples, with the highest concentrations being observed in the samples from the Baikal ($\Sigma = 1.64$ μg/kg), although this region is considered clean. Taking into account that diazinon and pirimifos methyl were not used in Russia, while their use is widespread in Chinese agriculture, it was possible to conclude that transboundary transfer was responsible for this sort of contamination of the Baikal region. The situation was similar in the case of three organochlorine ecotoxicants (DDD, DDE, and eldrin aldehyde, 0.4 μg/kg). PCBs, di- and trichlorobenzene were found in trace quantities. However, in the Finnish snow samples they were not detected. Forty-seven petroleum hydrocarbons (C_9–C_{36}) were found, while Finnish samples were more contaminated by this group of ecotoxicants. The Russian maximal allowable concentration (MAC) for fishery watersheds for petroleum hydrocarbons was exceeded by three times (Anonymous 1999). Among phthalates, the most common were dibutyl- and bis(2-ethylhexyl). The MAC for dibutylphthalate was exceeded in all the samples (Anonymous 1999). PAHs levels were generally low in all the samples with the exception of the Moscow sample, which was very contaminated with these pollutants. In the case of phenols, the observed situation was similar to that of PAHs; the highest concentration exceeding MAC was observed only in the sample from Moscow (Lebedev et al. 2000a, b).

An important and significant contribution to the environmental pollution involves the “cold finger” effect. This phenomenon was confirmed in (Lebedev et al. 2000a, b), as the highest concentrations of petroleum hydrocarbons were found in the most northern Finnish sample, although there were no major sources of these pollutants in the area.

In (Lebedev et al. 2003) the authors used snow samples to estimate the environmental impact of a metallurgical plant in Kostomuksha, Karelia, near the Russian-Finnish border. The raw material for the plant is iron ore with a high iron content, whereas the main atmospheric emissions consisted of sulfur dioxide and dust. In March 2001, six samples of snow were collected in Karelia and Finland in the vicinity of the factory. GC/MS was used to identify and quantify the most various organic pollutants, while mass spectrometry with inductively coupled plasma (ICP/MS) was applied to quantify the levels of the environmentally relevant chemical elements. Sample preparation and analysis were performed according to US EPA 8270 and 6020 methods, respectively. As a result, more than 200 individual organic compounds were identified. These compounds belong to the classes of petroleum hydrocarbons, alcohols and organic acids, PAHs, phenols, phthalates, and antioxidants. The measured levels were compared with the existing standard safe values (MAC) for fishery watersheds (Anonymous 1999) and for drinking water. For petroleum hydrocarbons, safe values were exceeded in all the samples. PAHs’ concentrations in the samples were quite different, indicating the inhomogeneity of the distribution of these toxicants in the area, which was likely caused by the presence of other sources of pollution (emissions of cars, trains, and thermoelectric plants). The highest concentration of phenols exceeding MAC (1 μg/L) was found in the samples collected near the factory, while in other samples the MAC value was not exceeded. The highest concentrations of phthalates were 200 and 174 μg/L. Despite this, the plant cannot be considered as the main source of phthalates in the environment. Concentrations of dibutylphthalate and bis (2-ethylhexyl) phthalate exceeded MAC in all the samples. Low-toxic antioxidants based on 2,6-di-*tert*-butyl-4-methylphenol (ionol), posing little danger to the environment, were found in all samples. Analysis of inorganic pollutants showed high levels of Li, B, Mn, Fe, Co, Ni, Cu, Zn, Mo, Sn, Hg, and Pb. As a result, analysis of the snow samples allowed proposing a list of priority pollutants for the Kostomuksha plant (Lebedev et al. 2003).

31.3.1 Overall Air Pollution

The identification of the overall pollution of the atmosphere by various classes of organic compounds by a screening non targeted analysis was reported in (Kos and Ariya 2006b). Snow samples were collected in several urban and remote areas in Quebec and Nunavut, Canada in order to determine a wide range of toxicants. Sampling was carried out using a 500 mL Teflon container or 10 mL vials in the second half of February 2004 at various depths of snow cover. Analysis was performed by SPME-GC/MS. Oxygen-containing compounds (ethyl acetate, benzaldehyde, nonanal, acetophenone, etc.), organochlorines (chloroform, dibromomethane, diiodomethane, chlorobenzene, etc.), as well as aromatic compounds (benzene, toluene, m- and p-xylenes, etc.), were identified in the samples. Organochlorines generally have anthropogenic origin with a small contribution from ocean sources (e.g., dibromomethane). The widest assortment of substances was found in the most remote sample “Resolute.” Long range air transport was the main source of pollution in this case. The high stability of some compounds and high degree of degradation of others indicated that the snow was already old, and it was a long-term accumulation. Only aromatic compounds were quantitatively determined, while toluene dominated (23–316 μg/L). The concentration of other compounds (benzene, ethylbenzene, styrene, xylenes, 1,2,4-trimethylbenzene, chlorobenzene, 1,2-dichlorobenzene, benzaldehyde, acetophenone) was below 40 μg/L, often about 10 μg/L.

31.3.2 Greenland Glacier Layers

In (Schneidemesser et al. 2008), the authors estimated atmospheric pollution over Greenland for several years and tried to identify the source of contamination by analyzing the snow for the presence of molecular markers. Snow samples were collected in the Greenland glacier near the settlement at the summit (altitude 3,200 m) in the summer of 2005. Three meter thick snow was split into 10 cm layers, which were analyzed for ionic composition, trace metals, and $\delta^{18}O$, while 20 cm layers were analyzed for the presence of organic compounds. In addition, in the spring of 2006 samples of freshly fallen snow (48 h) were collected at the forest reserve of the Highlands, near Wisconsin. Samples of melted water were acidified with concentrated sulfuric acid to pH 2.5 and then triply extracted with dichloromethane. The extracts were dried over sodium sulfate, redistributed in 5 mL of methanol, concentrated, and analyzed by GC/MS. Measurements of the total concentration of organic carbon revealed that the average burden was about 64 mg/kg. The levels of alkanes were in the range 4–13,000 ng/kg, PAHs – 0.3–1.1 ng/kg, hopanes – 0.14–0.53 ng/kg, saturated fatty acids – 12–2,200 ng/kg, unsaturated fatty acids – 49–330 ng/kg. Among the detected PAHs phenanthrene, fluoranthene and retene were mentioned in particular. The main sources of PAHs involve the burning of fossil fuels. Phenanthrene and fluoranthene were released into the environment with engines' emissions and retene due to the burning of wood. Thus, the authors proposed a method to monitor forest fires in Canada and Siberia using retene as a biomarker in remote areas such as Greenland.

Among detected n-alkanes from C_{18} to $C_{40,}$ hexatriacontane (C_{36}) was the most frequently encountered. Hopanes are a class of natural organic substances belonging to triterpanes. They are regularly detected during the identification of air pollution due to their use in lubricating oils for engines. Hydrocarbons and their degradation products are the major source of carboxylic acids in the atmosphere. The process involves the gas phase peroxyacyl radical reactions and olefin ozonolysis reaction. However, the formation of acids may also take place as a result of photochemical reactions in gas phase above the snow. Two main acids in the samples were hexadecanoic and octadecanoic.

31.4 Flame Retardants in Snow

Along with PCB, environmental samples often contain polybrominated diphenyl ethers (PBDE), which are used extensively, primarily as flame retardants in polymeric materials from textiles to electronic devices. Like PCB, PBDE are resistant to chemical and biological degradation. Relatively recently, commercially available Penta-BDE and Octa-BDE have been added to the list of substances controlled by the Stockholm Convention on persistent organic pollutants and prohibited in the markets of the European Union (2003/11/EU). Quiroz et al. (2008) analyzed snow collected in the remote mountainous areas of Europe, for the identification of PBDEs in the atmosphere. SPME discs with deposited C18 stationary phase were used for sample preparation. Samples were analyzed by GC/MS in NICI mode. Analysis of the samples showed the presence of some members of PBDEs with concentrations from 5 to 45 pg/L. The rainwater was rich in lighter and more volatile tri- and tetrabromodiphenyl ethers, while PBDEs with a high content of bromine were present in the snow. The results were rationalized by different mechanisms of accumulation of air pollutants in the two forms of precipitation. This issue was earlier reported in (Franz and Eisenreich 1998). The authors mentioned that due to their high porosity, snowflakes are more efficient in the accumulation of atmospheric particles than rain. Therefore, snow absorbs more brominated derivatives mainly linked with suspended particles.

31.5 Creation of the Lists of Priority Pollutants

In a recent study led by Lebedev (Lebedev et al. 2012, 2013a, b; Polyakova et al. 2012a, b), GC/MS was applied to estimate the atmospheric pollution of Moscow during the winter period. As far as there is no list of priority pollutants for Moscow, the principal aim of the study involved the creation of a list of priority pollutants specific for Moscow. Eight–twelve snow samples every year were collected at the end of March during 2011–2013. This sampling time allowed estimating the pollution of Moscow air during 4 months (December–March). The sampling was performed along the perimeter of Moscow belt road and in several sites in the city. The US EPA 8270 method was applied. GC/MS with EI was used as an analytical tool to identify and quantify organic pollutants. Both targeted and non targeted approaches were realized. Furthermore, GC/HRMS with EI and glow discharge (GD) ionization as well as GC × GC/MS with EI was applied for more precise identification of organic pollutants (Lebedev et al. 2013a).

Mass-chromatography was used for targeted xenobiotics. It allows the detection and reliable quantification of trace components usually camouflaged by the main ingredients on the total ion chromatogram (Lebedev 2009, 2012). The effectiveness of this approach is shown in Fig. 31.4. Peaks of targeted α- and

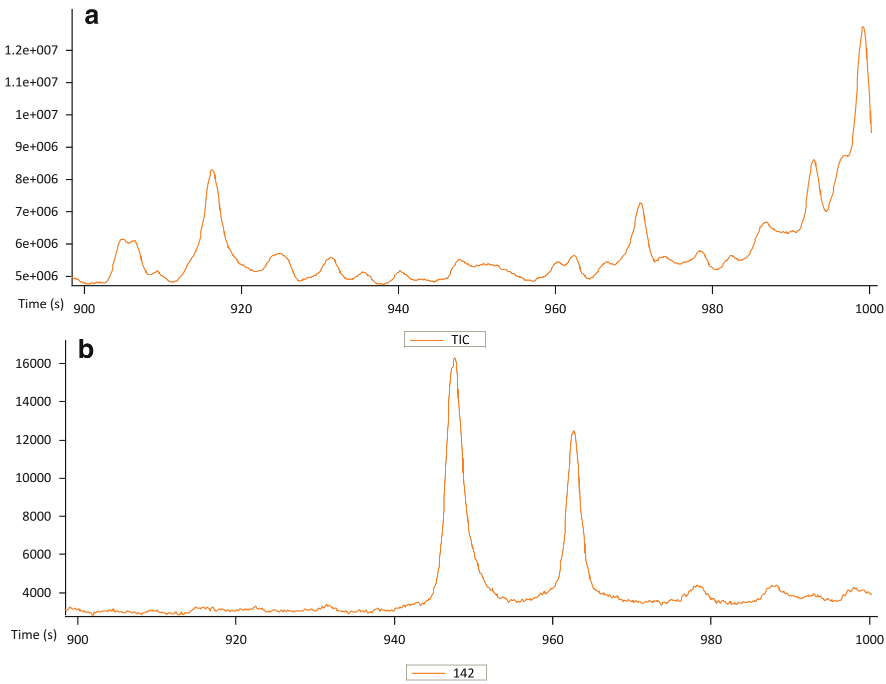

Fig. 31.4 Fragment of total ion current chromatogram (900–1,000 s) of a snow sample (**a**) and mass-chromatogram for the characteristic ion (m/z 142) in the same range revealing methylnaphthalenes (**b**) (Lebedev et al. 2013a)

β-methylnaphthalenes are absent in the total ion chromatogram, but are represented with distinct peaks at 947 s and 962 s in the mass-chromatogram reconstructed on the basis of the current of characteristic ions of these compounds (m/z 142). This approach was successfully used for targeted analysis to check for the presence of important toxicants belonging to PAHs and their alkyl derivatives, organochlorines, including pesticides, PCBs, phenols, and phthalates, and other compounds on the US EPA list of priority pollutants.

The composition of pollutants in all the samples was quite similar. The most common contaminants in environmental samples in general are petroleum hydrocarbons, consisting of alkanes, naphthenes, alkylbenzenes, PAHs and their derivatives, therpenes, and others. Among these, PAHs were considered separately. Besides 16 PAHs listed in US EPA list of priority pollutants, alkylated PAHs were also identified in the snow samples. Their concentration ranged from several ng/kg up to 1 μg/kg for phenanthrene. If unsubstituted PAHs are considered mostly as the products of incomplete combustion, their alkylated homologues are the components of diesel fuels. The most polluted areas were in the East and South of Moscow, while the purest samples were collected in the West of Moscow. Since national safe values have been developed only for naphthalene and benzo[a]pyrene, the estimation of the hazard could be done only for these regulated compounds (Anonymous 1999). Nevertheless, the obtained data demonstrated that the level of benzo[a]pyrene exceeded its safe level (MAC 5 ng/L) at all the sites. In one sample, the concentration was almost 100 times higher than the MAC value. The integral level of petroleum hydrocarbons is also regulated in Russia (MAC 50 μg/L). As integral concentrations of hydrocarbons in snow samples were between 31 and 64 μg/L, it was proposed that this class of pollutants (as well as benzo[a]pyrene) be included in the list of priority pollutants for Moscow air.

Despite the fact that the use of PCBs was prohibited long ago, due to their high stability they are still found in a wide variety of environmental objects, including the Polar Regions. Moscow snow samples were not an exception. Concentrations of PCBs were within a range from 0.01 (detection limit) to 0.1 μg/L. It is hard enough to identify the sources of PCBs. Since the safe value for these compounds is zero (Anonymous 1999), they should be on the list of priority pollutants for the Moscow atmosphere.

Phthalates are the most common class of anthropogenic toxicants worldwide. Nowadays, it is difficult to find an environmental sample that does not contain at least traces of phthalates. This is due to the high stability of these substances and their broadest use as plasticizers in polymers. Twenty four compounds of this class were detected in the Moscow snow samples (Lebedev et al. 2012). Most of them are technological impurities of the main representatives of this group and are present in small quantities. The most serious attention should be paid to dibutyl phthalate, which is the most popular plasticizer. Taking into account its properties, the European Union Directive 76/768/EEC banned it as an ingredient of cosmetics, including nail polish in 1976. In 1999 it was banned for the production of toys. In November 2006, dibutyl phthalate was added to the list of potential teratogens in the USA, that is, substances that cause malfunctions in embryonic development.

The maximal concentration of this compound (more than 200 μg/L) was detected in the most polluted samples in the East of Moscow. This is a very high level from the environmental point of view, particularly when taking into consideration that concentrations of the related di(*iso*-butyl) phthalate and di(*sec*-butyl) phthalate were also very high. Fishery MAC for this phthalate is 1 μg/L (Anonymous 1999), making this compound an obvious priority toxicant for Moscow region.

Phenols are included in the lists of priority toxicants worldwide. Despite the fact that targeted analysis was conducted to detect all 11 phenols on the US EPA list, only unsubstituted phenol was found, at a level of about 0.5 MAC (MAC 1 μg/L (Anonymous 1999)). Since all the samples contain practically the same concentration of phenol, it can be concluded that there are no significant point sources. Phenylphenol detected in all the samples is not yet regulated. It is used as an antiseptic substance for leather, textiles, wood, and paper products, for the synthesis of non-ionic surfactants. Considering that the maximal concentration of the compound was found in the Western samples, and taking into account the wind rose, it was suggested that phenylphenol was transferred from Moscow region or comes from building and automobile markets along the Moscow belt road. Due to hazardness of phenol and its levels being close to the MAC value, the authors (Lebedev et al. 2012) proposed including it in the priority pollutants list.

Widespread of polymeric materials results in the detection of various stabilizers, antioxidants, and flame retardants in the environment. The most frequently occurring in the territory of Russia antioxidants are compounds based on di-*tert*-butyl phenol. The main one is 2,6-di (*tert*-butyl)-4-methylphenol (ionol), but it should be noted that the snow samples in 2011–2013 contained 4-ethyl- and 4-nitro derivatives at almost the same levels (0.05–0.6 μg/L). The toxicity of these compounds is not high, and therefore, despite the prevalence, they cannot yet be included in the list of priority toxicants.

Another pollutant worth mentioning is 1,1,2,2-tetrachloroethane. It is a volatile compound, which is not supposed to be quantified using EPA 8270 method. Nevertheless, in all the snow samples, relatively high concentrations of tetrachloroethane were found (up to 160 μg/L in the North sample). Since the MAC value is 50 μg/L (Anonymous 1999), while real levels of 1,1,2,2-tetrachloroethane in the samples were probably much higher, it was considered a candidate for the list of priority pollutants for Moscow.

Unexpectedly high levels of organophosphates (OPs) were discovered in the majority of the collected samples (Lebedev et al. 2012). These compounds are used as multipurpose additives, mainly flame retardants and plasticizers. As compared to polybrominated diphenyl ethers, organophosphates are less dangerous. It was shown that transport is a major source of this class of toxicants (Marklund et al. 2005). Since the levels of these compounds were increasing from 2011 to 2013 (Lebedev et al. 2013a), the authors mentioned that these compounds required certain attention.

The appearance of isomeric dibenzothiophenes could be related to transport. These compounds are components of diesel fuels. Their uniform distribution around the perimeter of the belt road indicated the absence of other point sources. Similar conclusions were drawn for alkylpyridines.

Among nitrogen-containing compounds quinoline, isoquinoline, N,N-dimethyl- and N,N-dibutilformamids were identified. These compounds are used in the chemical industry. The maximal concentration of these substances was found in the East samples (Lebedev et al. 2012).

Besides the compounds mentioned above, 65 fatty acids and esters, 35 aldehydes and ketones, 20 fatty alcohols, and more than 100 compounds of other classes were identified in the snow samples (Polyakova et al. 2012a, b). The results obtained allowed the authors to propose the following list of priority pollutants for the atmosphere of Moscow:

- Petroleum hydrocarbons
- Benzo[a]pyrene
- Dibutylphthalate
- Polychlorinated Biphenyls
- 1,1,2,2-Tetrachloroethane
- Phenol

31.6 Further Method Developments

Mass-chromatography is very useful in the case of two-dimensional chromatography, which provides important information about the composition of multi-component mixtures (Lebedev 2012). The primary long capillary column with a non-polar phase is usually used to separate substances according to their boiling points, while the secondary short polar column separates them by polarity. In GC × GC mode, all classes of organic compounds occupy certain segments of the two-dimensional map, and therefore, by reconstructing mass-chromatograms for characteristic ions of each class of substances, they could be directly identified. For example, the ion of m/z 73 is characteristic for the components of column phase and for fatty acids (Fig. 31.5). GC × GC differentiated these compounds quite easily (Polyakova et al. 2012a, b).

Another example involves differentiation between naphthenes and alcohols. Both classes are widely represented among the modern contaminants (Lebedev et al. 2012, 2013a; Polyakova et al. 2012b). The difference in the mass-spectra of the compounds of these two classes is negligible. Molecular ions of alcohols are unstable in EI conditions and are usually not registered (Lebedev 2003). They easily lose water molecules, converting into molecular ions of isomeric alkenes or naphthenes. Therefore, it is often impossible to distinguish them by mass spectra, even when using a modern library search. When reconstructing mass chromatograms for the characteristic ions of naphthenes and alcohols (m/z 55, 69) working in GC × GC mode, two series of peaks appear on the two-dimensional mass chromatogram: the front row, containing less polar substances, corresponds to naphthenes, the second row, to alcohols (Fig. 31.6).

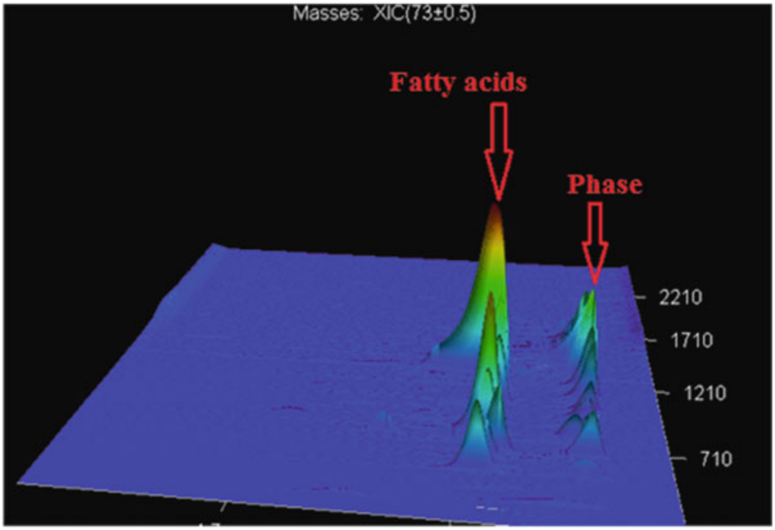

Fig. 31.5 Two-dimensional mass chromatogram for ions with m/z 73, typical for fatty acids and silicon components of chromatographic phase (Polyakova et al. 2012a)

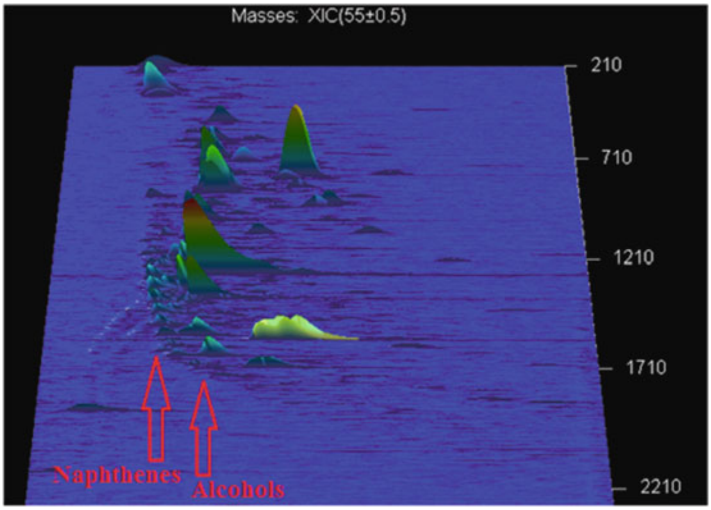

Fig. 31.6 Two-dimensional mass chromatogram based on the current of the characteristic ions (m/z 55) of naphthenes and alcohols (Polyakova et al. 2012a)

Continuing their research on the contamination of atmosphere of Moscow using snow samples, Lebedev et al. (2013a) reported the successful use of high resolution mass spectrometry with EI and glow discharge (GD) ionization. It is worth mentioning that dichloronitromethane ($CHCl_2NO_2$) was found in all the samples in 2012 and 2013 (Lebedev et al. 2013a). The low resolution mass spectrum did not

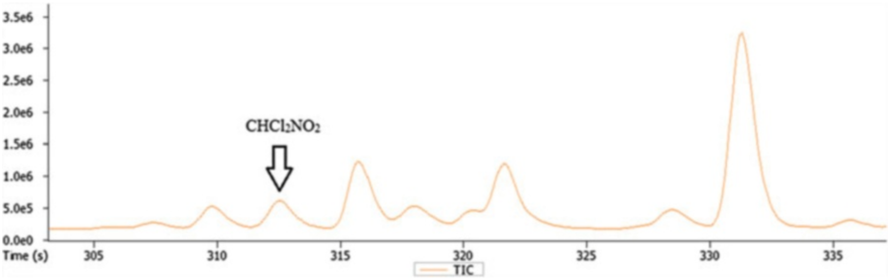

Fig. 31.7 A fragment of total ion current chromatogram (305–335 s) of a snow sample from Moscow (Lebedev et al. 2013a)

allow reliable identification of this compound, as molecular ion was barely noticeable, while the main peak in the mass spectrum corresponded to the $CHCl_2$ fragment typical for the fragmentation of haloalkanes. Since a standard for this substance was lacking, the retention time was also not helpful for the identification (Fig. 31.7).

High-resolution mass spectrometry allowed determination of the elemental composition of all the ions (Fig. 31.8), including the molecular one (Fig. 31.9).

Earlier, this compound was identified only once in precipitations in Sweden and Poland (Laniewski et al. 1998a). The most probable source of this compound in the atmosphere involves waste incinerators (Laniewski et al. 1998b). Unfortunately, the toxicological characteristics of dichloronitromethane have not yet been studied. Anyway, it was considered by the authors (Lebedev et al. 2013a) as a possible candidate for the list of priority pollutants for Moscow.

It is well known (Lebedev 2003; Samokhin and Revelsky 2012) that in electron ionization mode a molecular ion peak is not always present in the spectrum. Identification cannot be considered reliable, if there is no information about the molecular ion. In addition, deconvolution in difficult cases or a small intensity of the minor peaks in the spectrum results in a low score and in low reliability of the use of spectral databases. It is therefore important to use additional ionization methods that allow the molecular ion to be registered. The most popular are chemical ionization, photoionization, field ionization, atmospheric pressure chemical ionization, electrospray, MALDI, and others (Lebedev 2012). The authors (Lebedev et al. 2013a) applied GD ionization, which is rather rare for organic pollutants, leading to odd electron molecular ions $[M]^{+\bullet}$ and protonated molecules $[M+H]^+$, depending on the nature of each compound and its concentration in the source. Since the ionization method is "soft," fragmentation is not pronounced, and quite often only the peak of the molecular ion is present in the spectrum.

Combining the data obtained with EI and GD coupled to accurate mass measurements the identification could be much more reliable. For example, Fig. 31.10 represents the experimental and library mass spectra for snow component with RT 823.2 s, which is tris-(1-chloro-2-propyl) phosphate.

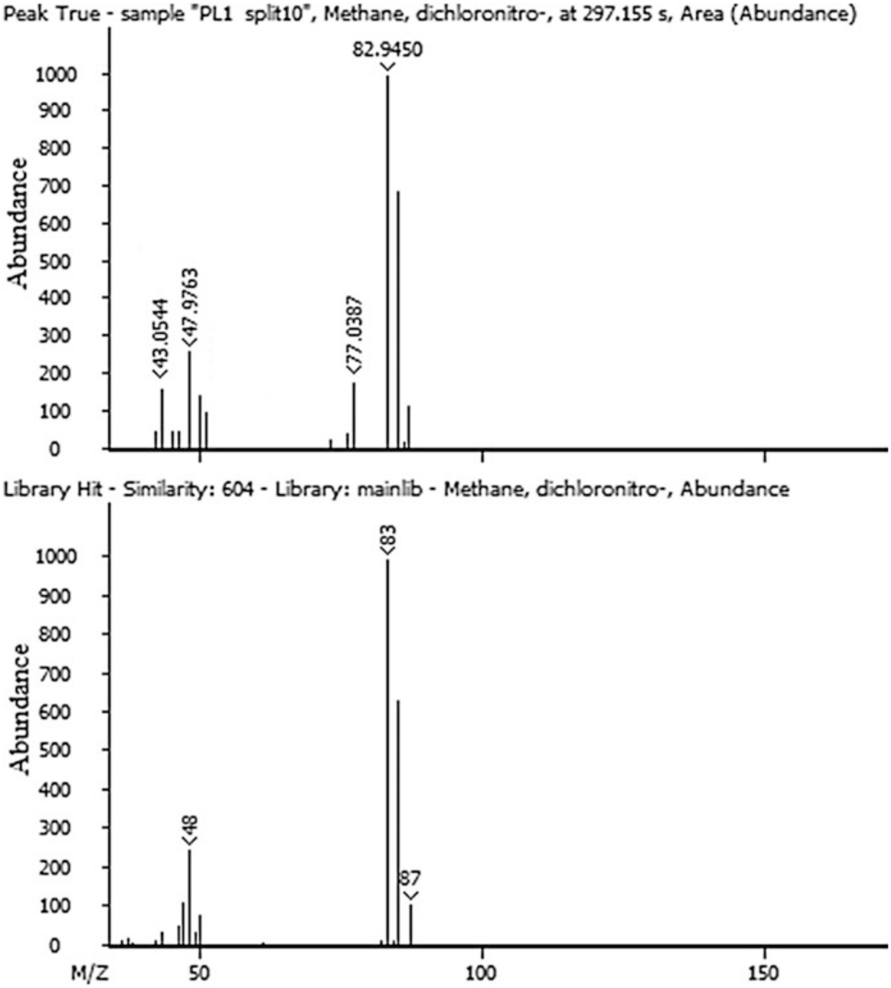

Fig. 31.8 Experimental and library mass spectra of dichloronitromethane (Lebedev et al. 2013a)

Neither spectra do contain a molecular ion. The library search program provides the result with a score of 589, which leaves doubt about the correctness of the identification. In GD mode, a spectrum with a single peak of protonated molecule is obtained (Fig. 31.11) $[M+H]^{+\bullet}$ ($C_9H_{19}Cl_3PO_4$). Together with the EI information on fragmentation patterns, it leaves no doubt that the substance is really tris-(1-chloro-2-propyl) phosphate (Lebedev et al. 2013a).

The peaks of molecular ions of lower carboxylic acids are quite intensive in the EI spectra. However, with increasing length of the alkyl radical, as well as the number of branches in the carbon chain, molecular ions become less stable, and their peaks may not be registered (Lebedev 2003). Many fatty acids were found in

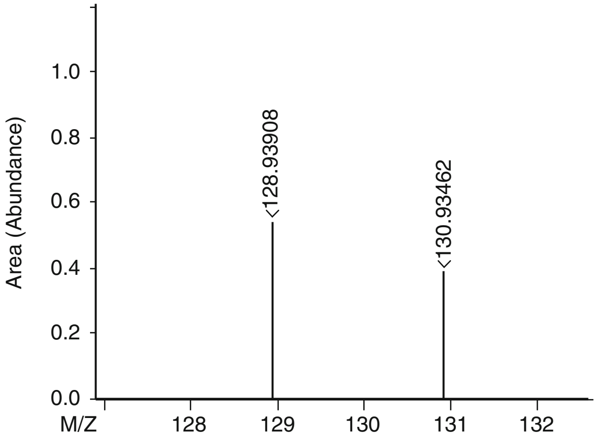

Fig. 31.9 Fragment of mass spectrum of dichloronitromethane containing molecular ion (Lebedev et al. 2013a)

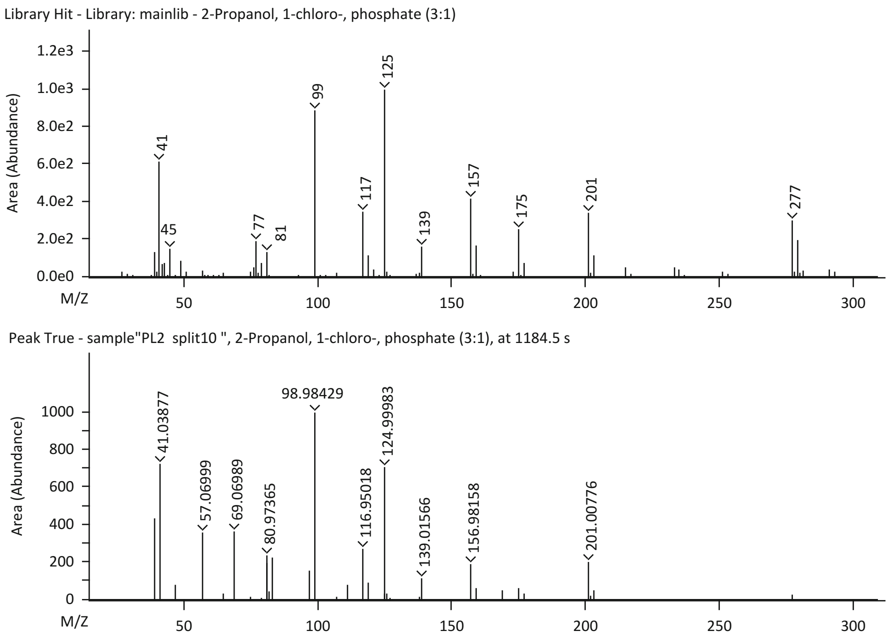

Fig. 31.10 Library and experimental EI mass spectra of tris-(1-chloro-2-propyl) phosphate in snow sample collected in Moscow in March 2012 (Lebedev et al. 2013a)

the Moscow snow samples. Determination of some of them using EI spectra was sometimes not obvious, and therefore, information about the molecular ion in the GD spectra was rather useful. For example, the EI spectrum of decanoic acid (Fig. 31.12) did not contain a molecular ion, and fragment ions might correspond to acids with longer carbon chain. The GD mass spectrum presented in Fig. 31.13

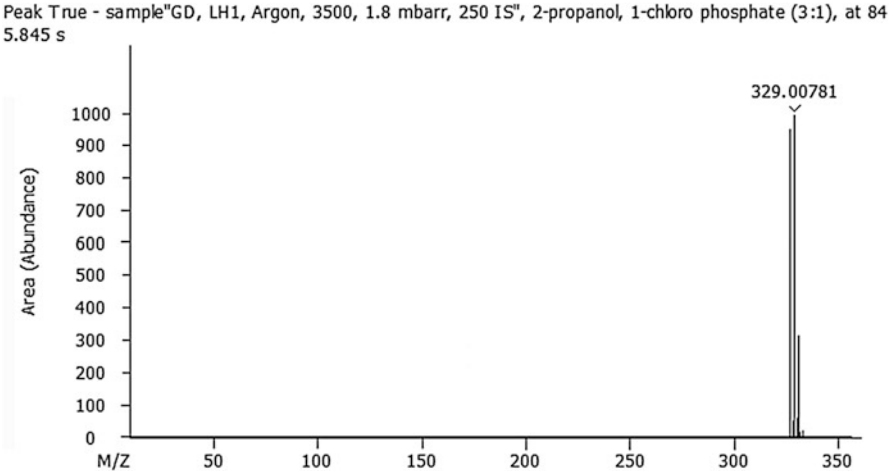

Fig. 31.11 GD mass spectrum of tris-(1-chloro-2-propyl) phosphate (Lebedev et al. 2013a)

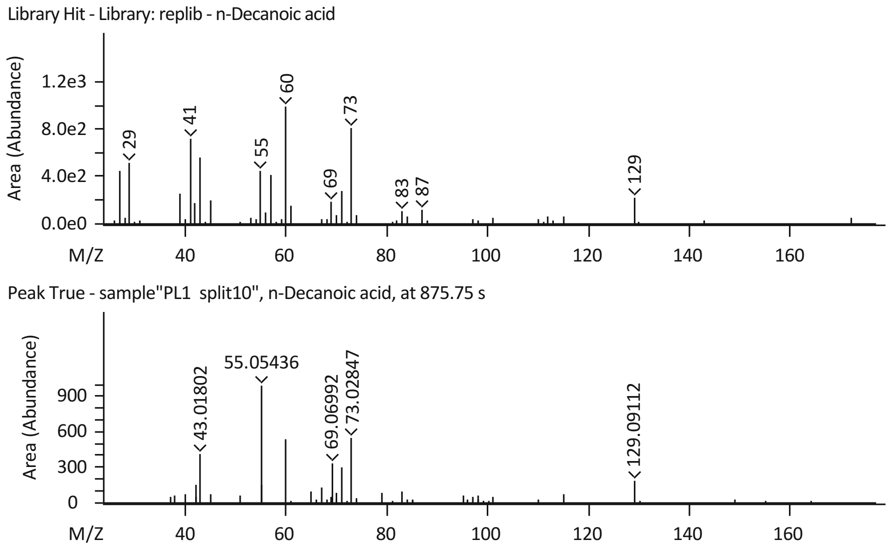

Fig. 31.12 Library and experimental EI mass spectra of decanoic acid. (Lebedev et al. 2013a)

allowed correct determination of the composition of the protonated molecule ($C_{10}H_{21}O_2$).

Unfortunately, reports on the application of LC/MS approaches for the analysis of snow samples are almost absent. It is possible to mention preliminary results of a joint Russian-German study of the polar pollutants in the Moscow snow (Polyakova

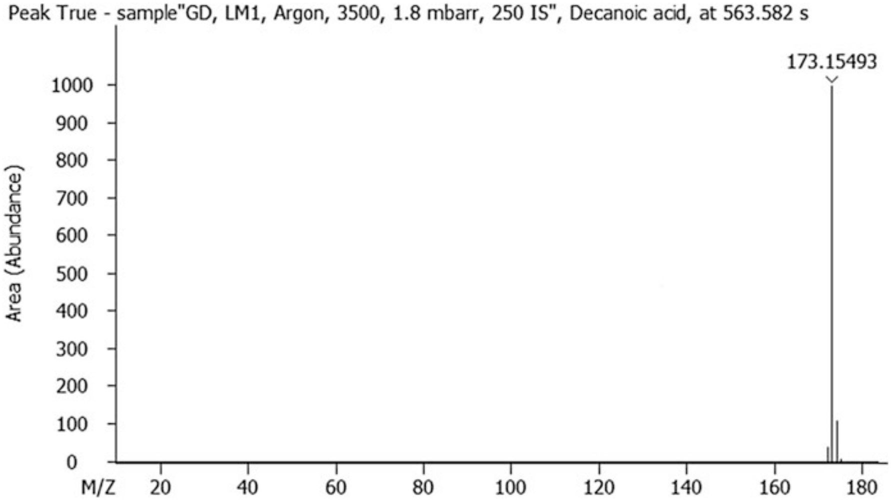

Fig. 31.13 GD mass spectrum of decanoic acid (Lebedev et al. 2013a)

et al. 2012a). Application of Fourier transform mass spectrometry to the snow samples subjected to electrospray ionization allowed the number of identified compounds (elemental composition) to be increased from hundreds (with GC/MS) to several thousands. A number of oxidized sulphur-containing compounds were detected as the principal contaminants. In addition, more complicated routes of atmospheric pollutant spread were discovered.

Conclusions

In summary, the results obtained so far (Fig. 31.14) for the use of mass spectrometry methods to study air pollution by analyzing snow samples, allow us to mention the benefits of this approach, including the possibility of obtaining information about various compounds of interest in a single injection, sensitivity, and reliability. The method may provide an answer for different environmental questions and allow correct decisions to be made. A wider application of LC/MS for the analysis of snow will definitely increase significantly the scope of chemicals that are amenable to the analysis and important from the environmental point of view. There are pending questions on the mechanisms of deposition of toxicants (only with snow, or dry) and on the further possibility of re-evaporation of the deposited chemicals. Fundamental studies are required to answer these questions.

(continued)

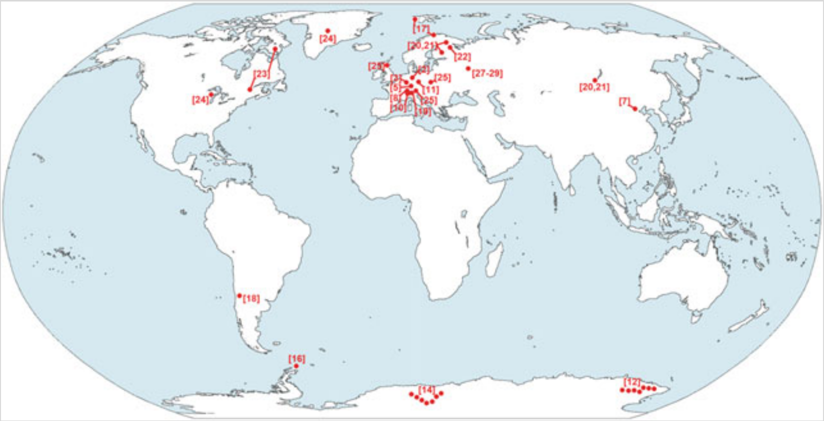

Fig. 31.14 World map with the marks at the sites where snow samples were collected. A number in the brackets corresponds to the publication in the reference

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Part XI
Water Pollution

Chapter 32
Marine Pollution-Environmental Indicators in Marine Meiofauna from Brazil

Patrícia Pinheiro Beck Eichler, Beatriz Beck Eichler, and Helenice Vital

Abstract To assess the primary stresses that affect environmental quality, recent benthic foraminiferal distribution in Brazilian domestic outfalls of Baixada Santista, São Paulo State (Santos Bay, Long Beach, Guraujá Cove), close to oil refineries in Todos Santos Bay (BA), Guanabara Bay (RJ), and Sao Sebastião Channel, and from environments polluted by pesticides in Laguna (SC) were compared through foraminifera species in 250 sediment samples.

In Santos Bay, living species of *Buliminella elegantissima* and *Bolivina* spp. reflect the large amount of organic substances exiting the sewers, however, the occurrence of large amounts of aerobic and anaerobic species seems to indicate that, while the eastern portion of the Santos Bay and the region near the outfall are probably subject to contamination, these environments are relatively well oxygenated due to high dynamic circulation in the Bay. Brackish rivers and mangroves in Santos Bay are populated by *Arenoparrella mexicana, Haplophragmoides wilberti, Ammotium salsum, Gaudryina exillis, Miliammina fusca, Paratrochammina* sp.*, P. clossi, Polysaccammina ipohalina, Siphotrochammina lobata, Warrenita palustris, Glomospira gordialis, Ammobaculites* ssp.*, Trochammina inflata.*

Aerobic species in Long Beach are more abundant in the northern portion with higher densities being correlated with the distance to the outfall. In the Guaruja Cove, species of anaerobic environments are comparatively more abundant near the outfall output, and the occurrence of large concentrations of anaerobic and aerobic species in the western portion of the Guaruja Cove seems to reflect the North Eastern current system, which penetrates this portion of the Bay. Apparently, although there is evidence of contamination in this area, the system presents current conditions of relatively well-oxygenated environments. In Todos Santos Bay*, Ammonia* spp.*, Bolivina* spp.*, Fursenkoina pontoni* tolerate sediment

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_32

with aliphatics, whereas *Elphidium* spp. decreases under the influence of petroleum-derived pollutants. In Guanabara Bay*, Buliminella elegantissima*, *Bolivina striatula, Bulimmina elongata* flourish under conditions of poorly oxygenated waters in organic enriched sediments. On the other hand, *Quinqueloculina seminulum* shows intolerance to poorly oxygenated bottom water, and *Cassidulina subglobosa* and *Discorbis williamsoni* are governed by lower temperature and higher salinities in the Bay's entrance, showing marine influence capable of renewing waters. In São Sebastião Channel, most anaerobic species were alive, indicating that the density of organic matter is not yet affecting the fauna of foraminifera. The São Sebastião channel and Laguna estuarine system presented *Buccella peruviana* as a coldwater species showing the influence of Malvinas currents. In relation to the petroleum pollutant outfall in São Sebastião, fauna are distributed along a remarkable gradient related to the distance from the outfall. The dominance of *Ammonia* spp., *Bolivina* spp., *Buliminella elegantisssima*, *and Fursenkoina pontoni* in high organic sediments shows slight contamination. *Miliamina fusca* denotes the presence of freshwater, as well as its tolerance to polluted sediments. On the other hand, *Hanzawaia boueana, Pseudononion atlanticum, Discorbis williamsoni, D. floridana, Quinqueloculina* spp.*, Pararotalia cananeiaensis, Cassidulina subglobosa, Elphidium* spp.*, Poreoponides lateralis,* and *Pyrgo* sp. reflect high intensity marine currents. In Laguna, the presence of *Buccella peruviana, Bolivia striatula, Cassidulina subglobosa, Pseudononion atlanticum, Saccamina sphaera, Quinqueloculina miletti, Q. patagonica, Ammonia tepida,* and *Elphidium poeyanum* is an indicator of marine water intrusion. As fresh water indicators, *Ammobaculites exigus, Gaudryina exillis, Ammotium salsum,* and *Miliammina fusca,* together with the thecamoebians, inhabit environments with the highest freshwater input. It was also noted that *M. fusca* is the only species that tolerates pesticides contamination.

Keywords Foraminifera • Thecamoebians • Anthropogenic impacts • Freshwater • Pollution • Contamination

32.1 Introduction

As the number of people inhabiting the world's coastlines continues to rise, coastal ecosystems are increasingly threatened by anthropogenic impacts. The population of Brazil has grown and the necessity of studying its consequences in the water and sediment of coastal environments has grown as well. The study of foraminifera behavior in polluted coastal environments and its use as "indicator organisms" to monitor human pollution in coastal regions is increasing at a rapid pace and the results are very encouraging (Alve 1991, 1995; Yanko et al. 1994, 1998, 1999; Yanko 1997; Eichler et al. 2012). The importance of determining the species of foraminifera occurring in a particular region lies in the fact they constitute a proxy that can be easily handled, is inexpensive, and can summarize the general characteristics of the environment. Studies seek to define proxies that best adapt to the environmental conditions related to pollution and contamination. In this sense, Foraminifera enables a rapid assessment of the impact of pollutants and the ecotoxicological risk. Because they are very sensitive, foraminifers respond rapidly to any change, through deformation of the shells, no chambers, reduction in the number and size of chambers, or community mortality. Conversely, there may be species that rather benefit from pollution.

The horizontal extent and effects of pollution caused by organic enrichment depends on the hydrodynamic conditions prevailing in the coastal regions, and therefore, the assessment of environmental change also depends on the correlation between biological indicators and hydrographic properties. With this in mind, studies have correlated the distribution of foraminifera and water masses in the region of the São Sebastião Channel (Cardoso 2000; Eichler et al. 2009), the Cape of Santa Marta (Eichler et al. 2008), using foraminifera to understand the movement of water in Flamengo Bay, Ubatuba, SP (Duleba et al. 1999), establish foraminifera indicators of the influence of fresh water, pollution, and contamination in Bertioga channel, a subtropical, mixohaline, estuarine channel (Rodrigues et al. 2003; Eichler et al. 2004a, 2007) to understand the marine influence on Brazilian bays, estuaries and lagoons (Eichler-Coelho et al. 1996, 1997; Bonetti 2000; Debenay et al. 1997, 1998, 2001a, b; Duleba and Debenay 2003; Eichler et al. 2004a, b, 2006, 2010), and to observe the response of foraminiferal fauna to the marine pollution on the inner continental shelf of southern Brazil (Eichler et al. 2012). In the assessment of ecosystems, Eichler-Coelho et al. (1996, 1997) describe the importance of the associations of foraminifera in determining the ecological impact of Valo Grande (System Estuary Cananéia-Iguape, SP), and the search for bio indicators of pollution in the Guanabara Bay and its integrations of ecologic patterns has been described by Vilela (2003), Vilela et al. (2007), Eichler et al (2001, 2003) and Pereira et al (2004).

The present paper deals with the ecology of foraminifera and environmental parameters in the evaluation of bays and estuarine systems contaminated and polluted by domestic sewage and industrial waste. Our aim is to describe the indicator species that provides proxy information on hydrodynamic energy, circulation patterns, and pollution in some of the estuarine environments of Brazil.

Data from more than 250 samples were compared in terms of absolute and relative frequency of foraminiferal species from domestic outfalls of Baixada Santista, São Paulo state (Santos Bay, Long Beach, Guraujá Cove, Sao Sebastiao), nearby oil refineries in Todos Santos Bay (Bahia), Guanabara Bay (Rio de Janeiro), and in Sao Sebastiao Channel, and from agriculture pesticides in Laguna (Santa Catarina) (Fig. 32.1).

32.2 Methods

Samples were collected with a Van Veen grab sampler and were sub-sampled with a spatula, and about 10 cm^3 of sediment was removed, preferentially from the top layer (2 cm). The material collected was stained with Rose bengal diluted in

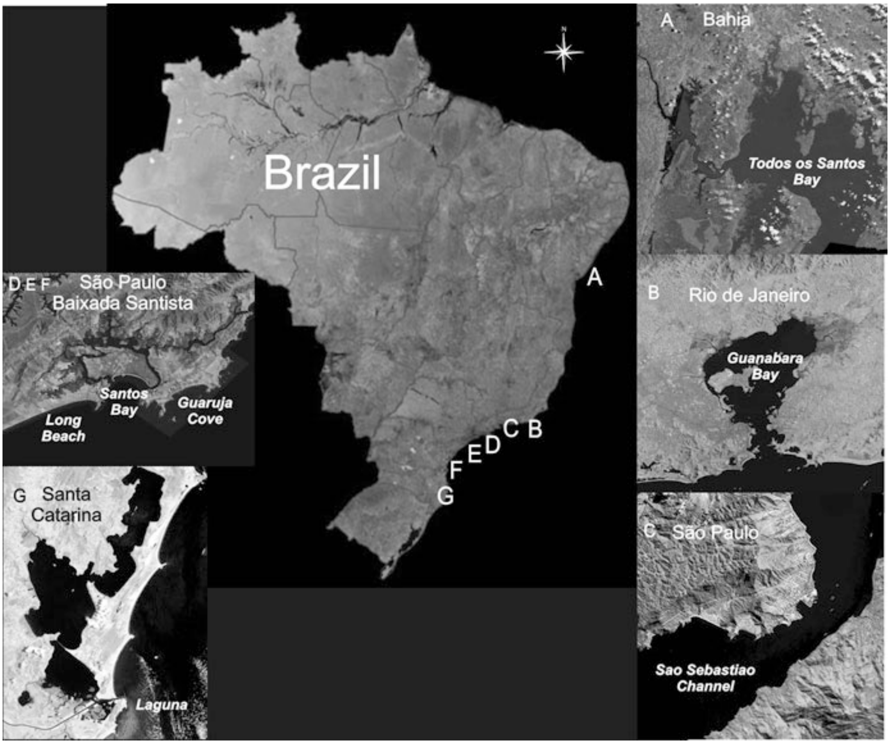

Fig. 32.1 Brazil map in the center showing locations of sampling sites (A, B, C, D, E, F and G). *A*. Todos Santos Bay (BA), *B*. Guanabara Bay (RJ), *C*. Sao Sebastiao Channel (SP), *D*. Long Beach (SP), *E*. Santos Bay (SP), *F*. Guraujá Cove (SP), *G*. Laguna (SC)

alcohol, so as to stain the cytoplasm of the specimens that were alive at the time of sampling. Sampling time, number of samples, and sampling year in the different environments are described in Table 32.1.

32.3 Results and Discussion

32.3.1 Santos Bay

The highest frequency of anaerobic species was found in the eastern portion of the Bay, just off the Canal do Porto. Some parts present many living species of *Buliminella elegantissima* and *Bolivina* spp., reflecting the large amount of organic substances exiting the sewers. The highest occurrences of aerobic species (*Discorbis* spp. and *Hanzawaia boueana, Quinqueloculina* spp.) were found at the entrance of Canal do Porto, and also near the outfall. This distribution pattern seems to reflect the circulation pattern of the North Eastern currents of Santos Bay, on

Table 32.1 Number of samples and kind of pollution from investigated environments

Investigated Environments	Kind of Pollution	Number of Samples (Winter)	Sampling year	Number of samples (Summer)	Sampling year
Santos Bay	Domestic waste	12	1997	12	1998
Long Beach	Domestic waste	20	1997	20	1998
Guraujá Cove	Domestic waste	13	1997	13	1998
Sao Sebastiao	Domestic waste	19	1997	19	1998
Todos os Santos Bay	Industrial waste	20	2003	20	2003
		25	2005	25	2005
Guanabara Bay	Industrial waste	25	2000	25	2001
Sao Sebastiao Channel	Industrial waste	9	1998	9	1998
		9	1999	9	1999
		9	2000	9	2000
		9	2001	9	2001
		9	2002	9	
Laguna estuarine system	Pesticides	25	2002	25	2002

which current systems to the south, generated by cold fronts, are sometimes superimposed, in addition to its own Canal do Porto currents. The occurrence of large amounts of aerobic and anaerobic species seems to indicate that, while the eastern portion of the Santos Bay and the region near the outfall are probably subject to contamination, these environments are relatively well oxygenated due to the existing pattern of circulation in the Bay, allowing a good relationship between foraminifera and organic matter found in the sediment.

Based on foraminiferal assemblages, Santos Bay was divided in two subenvironments (Fig. 32.2). The first is the Canal do Porto, where marine normal salinity water is characterized by high population densities and diversities of *Pararotalia cananeiaensis*, *Ammonia tepida*, *Elphidium* spp., *Brizalina striatula*, *Pseudononion atlanticum*, and *Discorbis floridana*, indicating that this environment is more efficient in terms of water renovation. The second subenvironment comprises the channels formed by the estuary of São Vincente, where agglutinated foraminifera dominates, represented by associations of *Arenoparella Mexicana*, *Haplophragmoides wilberti*, *Ammotium salsum*, and *Gaudryna exilis*. These species, indicative of continental input, are characteristic of environments where the renewal of marine waters is less efficient.

Long Beach has a great number of anaerobic species in the northern portion of the beach, close to the outfall, in the southern portion of the beach, and near the mouth of the river. Aerobic species are more abundant in the northern portion of the beach with higher densities of aerobic species being correlated with the distance

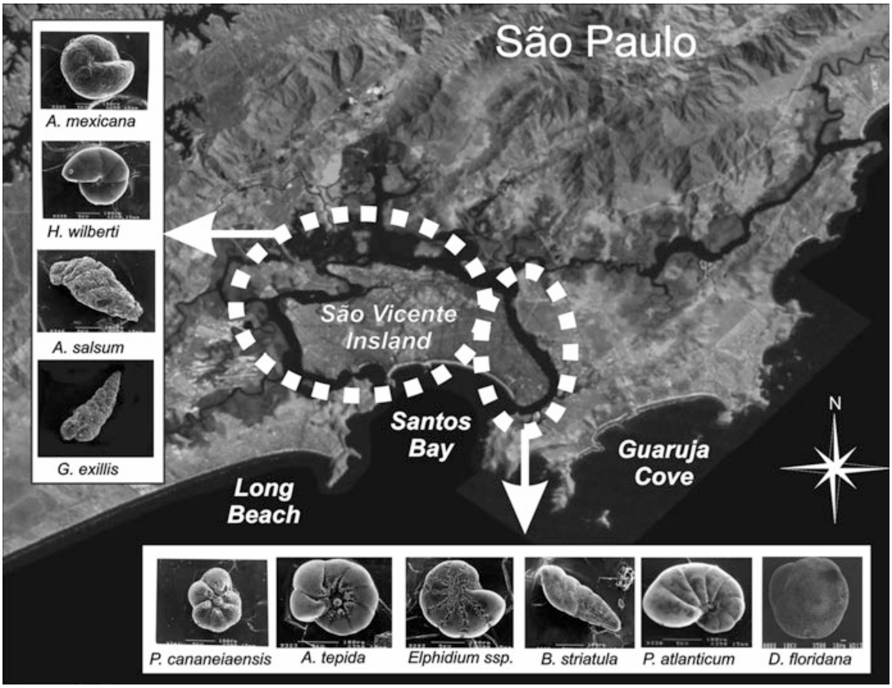

Fig. 32.2 Two assemblages of foraminifera species in Santos Bay (SP). One assemblage inhabits regular marine salinity water and is characterized by high population densities and diversities of *Pararotalia cananeiaensis, Ammonia tepida, Elphidium* spp.*, Brizalina striatula, Pseudononion atlanticum,* and *Discorbis floridana*. The second subenvironment comprises channels formed by the estuary of São Vincente, where the assemblage is formed by agglutinated foraminifera, such as *Arenoparella mexicana, Haplophragmoides wilberti, Ammotium salsum*, and *Gaudryna exilis*

to the outfall. In the Guaruja Cove, indicator species of anaerobic environments are comparatively more abundant near the outfall output. The highest concentrations of aerobic species also occur in the same locations where the highest concentrations were observed for anaerobic species. As in the Santos Bay, the occurrence of large concentrations of anaerobic and aerobic species in the western portion of the Guaruja Cove seems to reflect the North Eastern current system, which penetrate this portion of the Bay. Apparently, although there is evidence of contamination in this area, the system presents current conditions of relatively well-oxygenated environments.

32.3.2 São Sebastião Channel

São Sebastião Channel presents a well differentiated microfauna where the highest density of aerobic species occurs over the entire region, with large concentrations near the Araçá Cove and the Ferry Terminal Most anaerobic species were alive, indicating that the density of organic matter is not yet affecting the fauna of foraminifera. Lots of deformed and fragmented specimens are found in the region of the São Sebastião Channel, and it is attributed to the intense dynamics of currents in the Channel. The occurrence of large specimens from oxygenated environments, such as *Hanzawaia boueana, Pseudononion atlanticum, Discorbis williamsoni, Discorbis floridana, Quinqueloculina* spp.*, Pararotalia cananeiaensis, Cassidulina* spp.*, Elphidium* spp.*, Poroeponides lateralis,* and *Pyrgo* sp., reflects strong currents mainly in the northern part. According to Debenay et al. (2001), the dominance of *P. cananeiaensis* occurs in high hydrodynamic environments with strong currents.

Another important assemblage found in the study area was *Cassidulina minuta*, *Globigerina bulloides*, *Bucella frigida*, and *Angulogerina angulosa*, situated in the southwest channel stations. Such species are cold water ones and their occurrence in this part suggests that the South Atlantic Central Water is playing a role as water mass. In addition, the presence of large epifaunal species, most broken or fragmented, also reflects the high hydrodynamics of the area. The species *Elphidium excavatum*, *Elphidium articulatum, Ammonia rolshauseni, Fursenkoina pontoni, Bolivina striatula* and *Buliminella elegantissima* in the northern area are characteristics of coastal water mass (Fig. 32.3). External shelf typical species were not observed, suggesting that foraminifera transport in the region is quite low. In addition, most of the species found are infaunal (live inside the sediment), which reinforces the low hydrodynamic level in this part of the São Sebastião channel.

The São Sebastião channel shows variations in the patterns of benthic foraminifera diversity and dominance related mainly to the distance to the TEBAR outfall. Figure 32.4 shows the results of MDS analysis of Foraminiferal fauna. TEBAR outfall is at station 7. Stations 5 and 9 located 500 m from TEBAR present a similar fauna pattern. Stations 11, 12, and 13, which were sampled the farthest away from Tebar toward the northern part of the São Sebastião channel present a peculiar fauna. The fauna response is directly associated to the distance from the outfall. Through MDS analysis, we have also observed that the fauna is distributed along a gradient related to the distance of the outfall.

Regarding the distribution pattern of environmental variables observed in the PCA, two sites are locations of deposition of total aliphatic, PAHs, organic matter percentage, percentage of CIT, N, and N t, P, T, Arsenic, Chromium, Copper, Zinc and clay, while another site is a deposit of sand. It has been observed that deposition occurs for almost all pollutants mainly at two sites. This demonstrates that there are at least two sites that constitute depositional environments and are subject to the contribution of TEBAR. It was also noted that the deposition sites are in the south. On the other hand, three sites are located in a high hydrodynamic environment and are less prone to the accumulation of pollutants.

32.3.3 Todos os Santos Bay

Ammonia tepida, Elphidium spp.*, Bolivina* spp.*, Pseudononion atlanticum,* and *Quinqueloculina* spp. dominate marine environments with a small influence of

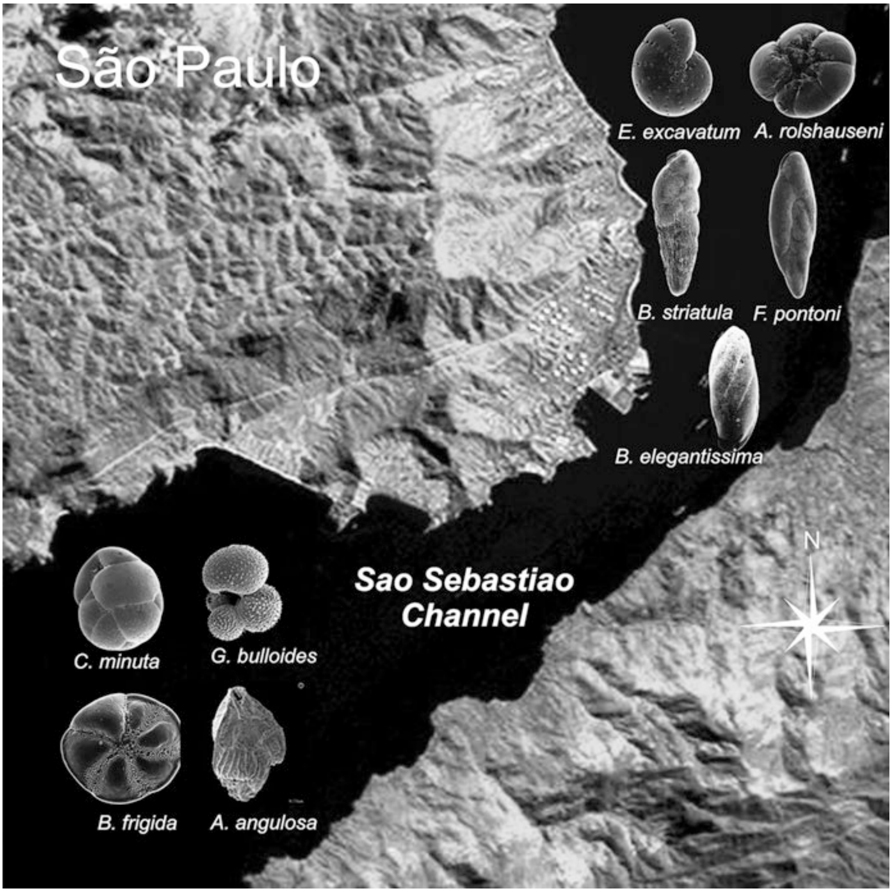

Fig. 32.3 In the southwest channel stations the most important assemblages found in the study area are coldwater species (*Cassidulina minuta*, *Globigerina bulloides*, *Buccella peruviana*, and *Angulogerina* angulosa), suggesting the presence of South Atlantic Central Water. The coastal species *Elphidium excavatum*, *Elphidium articulatum, Ammonia rolshauseni, Fursenkoina pontoni, Bolivina striatula,* and *Buliminella elegantissima* dominate in the central and northern parts of the channel

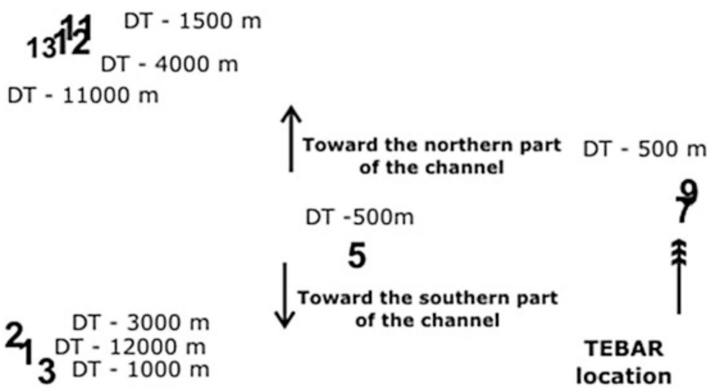

Fig. 32.4 MDS data showing the differentiation of foraminifera fauna from São Sebastião channel. (Stations are numbered and DT is distance from TEBAR)

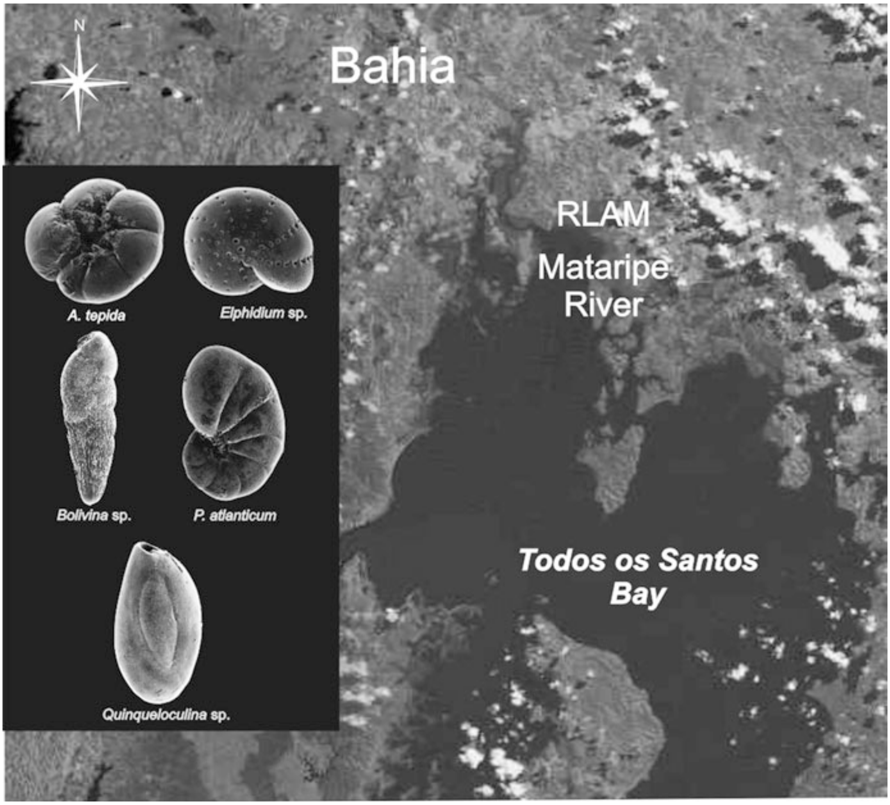

Fig. 32.5 Dominant species found in Todos os Santos Bay: *Ammonia tepida, Elphidium* spp., *Bolivina* spp., *Pseudononion atlanticum* and *Quinqueloculina* spp.

the river of Todos os Santos Bay (Fig. 32.5). A decrease in evenness indicates less stability close to Mataripe River and RLAM area. We observed high diversity in central and east parts of TSB and low diversity values in Mataripe River and RLAM area. Some areas present alifatics accumulation, and silt and clay accumulation. *Ammonia tepida, Bolivina* spp., and *Fursenkoina pontoni* tolerate sediment with alifatics and an unresolved complex mixture, while *Elphidium* spp. is decreased in areas under the influence of pollutants. *Ammonia* spp., *Bolivina* spp., and *Fursenkoina pontoni* are known organic matter and low oxygen-tolerant foraminifers, and in the TSB they are also tolerant to petroleum derived pollutants.

32.3.4 Guanabara Bay

Temperature, salinity, dissolved oxygen, and organic carbon content control recent benthic foraminiferal distribution patterns in Guanabara Bay. Patterns of foraminiferal fauna differ between the entrance of the bay and inner parts. The distribution of *Cassidulina subglobosa* and *Discorbis williamsoni* are governed by the lower temperature and higher salinities found in the entrance of the bay. According to dissolved oxygen content, we observed that *Quinqueloculina seminulum* occurs when values are higher than 2 mg/l, being intolerant to low-oxygen bottom water conditions. On the other hand, *Buliminella elegantissima, Bolivina striatula*, and *Bulimmina elongata* flourish in low oxygen waters and in sediment where the organic matter accumulation is high, being found mainly in the central parts of the bay (Fig. 32.6). In general, the distribution of foraminifera found in Guanabara Bay in winter and summer is similar, consisting mainly of opportunistic species that are tolerant and of low diversity, with a strong dominance of few species. The species of benthic foraminifera, being highly controlled by environmental factors, present micro-geographical features and can be established in different environments. In Guanabara Bay, in spite of the major factors controlling the establishment of species being changes in salinity and temperature (Eichler et al 2001, 2003), in the present study, the change in pH and oxygen levels also showed a significant role in controlling the establishment of foraminiferal species.

We emphasize that Guanabara Bay is highly impacted, reflecting a low diversity fauna, dominated by few species. The number of species per sample increases when environmental conditions are more typically saline. Therefore, one would expect that the Guanabara Bay would present more species per sample than other lagoons and estuaries in the Brazilian southeast states that have been studied to date: in estuarine Lagoon System Cananéia-Iguape, SP (Eichler-Coelho et al. 1996, 1997), mangrove of Cardoso Island in Cananéia-Iguape estuarine system, SP, (Semensatto et al. 2009), Bertioga Channel, SP (Rodrigues 2000; Eichler 2001; Eichler et al 2007), the estuaries of Estação Ecológica Juréia-Itatins, SP (Duleba and Debenay 2003), Lagoa da Conceição, SC (Debenay, et al 1997), Rodrigo de Freitas Lagoon, RJ (Vilela et al. 2011). This finding suggests that the pollution or contamination of an environment overlaps the natural environmental factors, and is thus able to limit the establishment of species that are not opportunistic. In Guanabara Bay, benthic foraminifera have been looked as bioindicators in ecological studies by Vilela (2003), Vilela et al. (2004, 2007), including the determination of human impact in coastal and paralic environments.

32.3.5 Laguna Estuarine System

The area is a choked coastal lagoon connected to the ocean via a single narrow channel. Sediment samples for foraminifera and thecamoebian analysis were collected at 25 stations in summer time, as well as hydrographical data on the fixed station. Sampling started in the entrance, close to the ocean, and extended inward to the inner parts of the system. In the fixed station, the surface and bottom temperature varies between 24 and 26 °C, surface salinity varies between 0 and

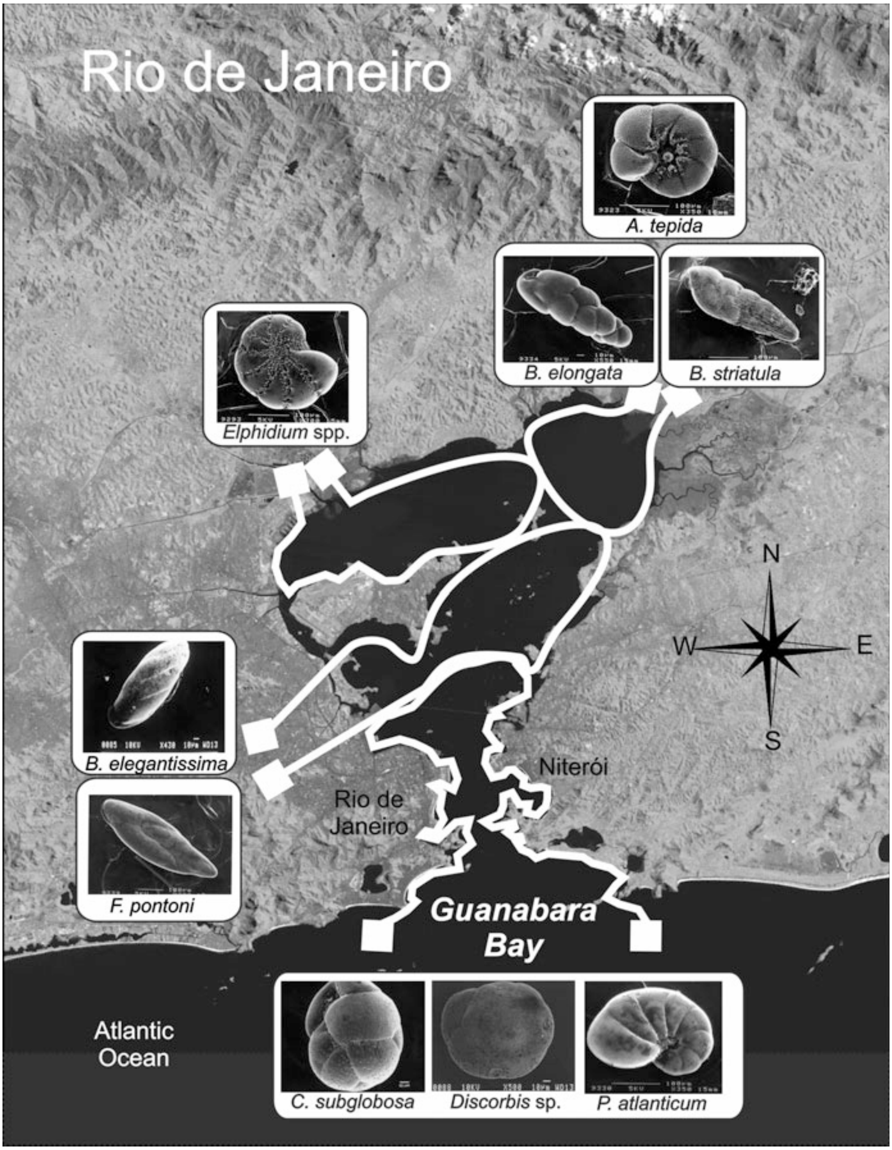

Fig. 32.6 Foraminifera distribution of *Cassidulina subglobosa, Discorbis williamsoni,* and *P. atlanticum* appear to be governed by the lower temperature and higher salinities found in the entrance of the Guanabara Bay. *Ammonia tepida*, *Bolivina striatula*, and *Bulimmina elongata* dominate the northeastern part. *Elphidium* spp. dominates the northwestern part and *Buliminella elegantissima* and *Fursenkoina pontoni* dominate the central part

30, while the bottom values are between 30 and 35. In relation to the fauna distribution, the entrance of the lagoon presents a higher number of species, followed by the central part. Toward the inner parts, the diversity value reaches its minimum. Cluster analysis revealed two different assemblages in Laguna. The fresh water influenced group is composed of *Ammobaculites exigus, Gaudryina exillis*, and *Ammotium salsum, Miliamina fusca* and thecamoebians species. The second group is related to higher diversity of species with *Buccella peruviana, Bolivina striatula, Cassidulina subglobosa, Pseudononion atlanticum, Saccamina sphaera, Quinqueloculina miletti, Q. patagonica, Ammonia tepida*, and *Elphidium poeyanum* as indicators of marine water intrusion (Fig. 32.7).

32.4 Discussion

The distribution of foraminifera in the central São Sebastiao channel near the TEBAR is characterized by the presence of foraminiferal species characteristic of sediments with high organic matter content (*Ammonia* spp., *Bolivina* spp., *Buliminella elegantisssima*, *Fursenkoina Ponton*). According to Culver and Buzas (1995), the occurrence of *B. elegantissima* is a reflection of organic contamination. Corroborating these data, the absence of *Cibicides* spp., *Uvigerina* spp., *P. cananeiaensis*, and *Robulus* spp., characteristic species of marine environments, close to TEBAR, indicates the strong presence of continental input in this region. On the other hand, the occurrence of specimens of robust features oxygenated environments, such as *Hanzawaia boueana*, *Pseudononion atlanticum*, *Discorbis williamsoni, D. floridana*, *Quinqueloculina* spp., *Pararotalia cananeiaensis*, *Cassidulina* spp., *Elphidium* spp., *Poroeponides lateralis*, and *Pyrgo* sp. reflect the action of currents of high intensity particularly in the north. According to Debenay et al. (2001a), the significant occurrence of *Pararotalia cananeiaensis* (a marine species of the coastal region) can also be attributed to the penetration of sea currents in the channel, indicating high hydrodynamics. With respect to those pollutants, the presence of *Miliamina fusca* and *Textularia* spp. is indicative of the freshwater stations 5, 7 and 9 still exhibiting the characteristic tolerance of these species in relation to the high concentration of pollutants in this region.

In general, the results of the analysis of benthic foraminifera associations, occurring in the outfalls of São Paulo coast (Long Beach, Santos Bay, Guarujá Cove, São Sebastião Channel), indicate that, at stations near the outlets of the outfall and entrances of river and estuaries, where there is the greatest amount of organic matter, there is also the largest number of anaerobic species. It was observed that precisely at these places where the aerobic foraminifera species lives the water circulation pattern for dispersion of the pollutants plays a major role.

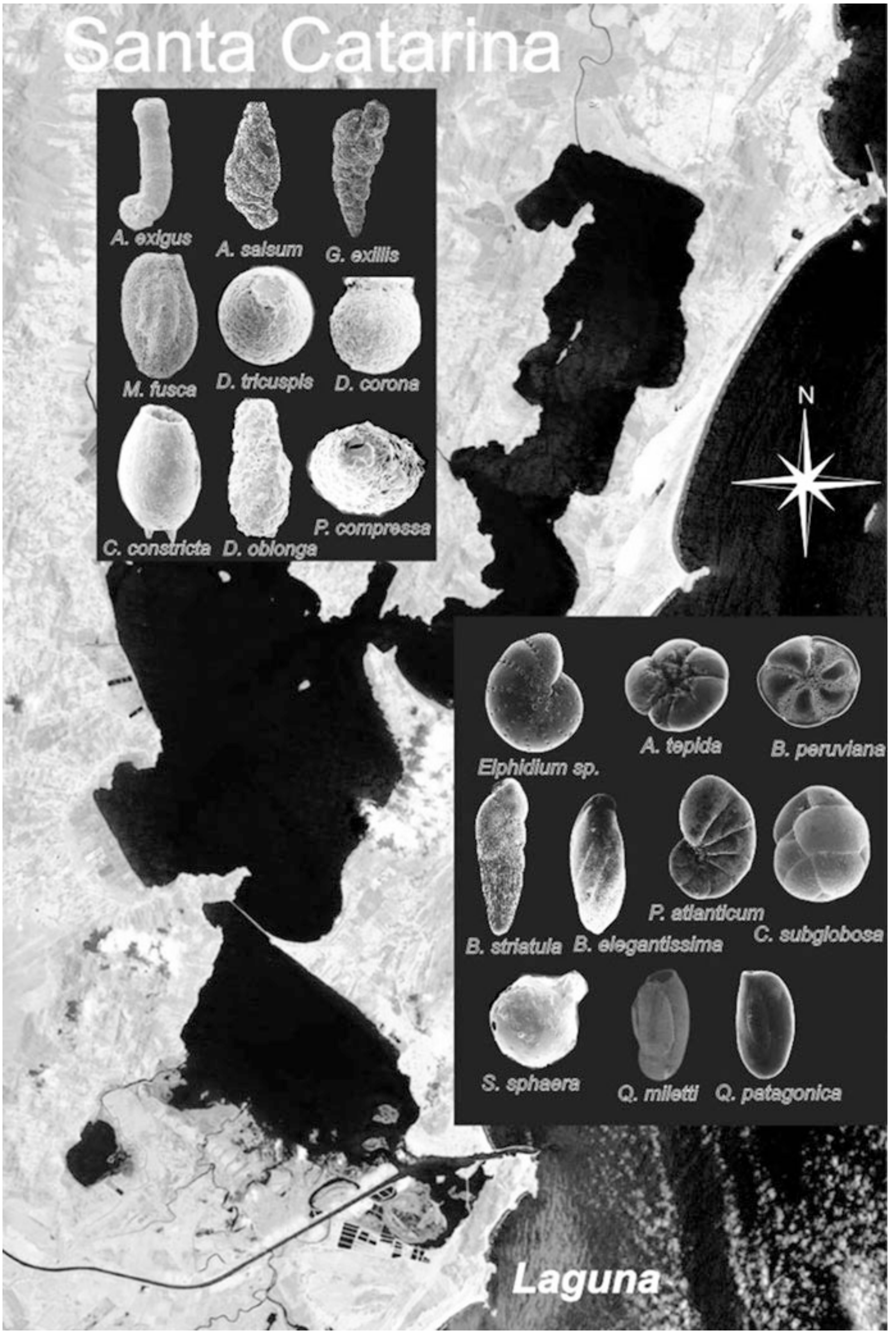

Fig. 32.7 Two different assemblages found in Laguna. The fresh water influenced group is composed of *Ammobaculites exigus, Gaudryina exillis*, and *Ammotium salsum, Miliamina fusca* and thecamoebians species. The second group is related to higher diversity of species with *Buccella peruviana, Bolivina striatula, Cassidulina subglobosa, Pseudononion atlanticum, Saccamina sphaera, Quinqueloculina miletti, Q. patagonica, Ammonia tepida*, and *Elphidium poeyanum* as indicators of marine water intrusion

Conclusions

Our findings show that the population dynamics of foraminifera respond to different environmental parameters as follows:

Influence of fresh water is indicated by the presence of species of foraminifera *Miliammina fusca*, *Ammobaculites exiguus*, *Gaudryina exillis*, *Ammotium salsum*, *Siphotrochamina lobata*, *Ammobaculites* ssp., *Arenopaarrella mexicana*, *Haplophragmoides wilberti*, *Trochmmina inflata*, and the thecamoebians, *Difflugia pyriformis*, *D. capreolata*, *and Centropyxis. marsupiformis*.

Intrusion of sea water is recorded by the presence of *Hanzawaia boueana*, *Pseudononion atlanticum*, *Discorbis williamsoni*, *Pararotalia cananeiaensis*, *Cassidulina subglobosa*, *Poreoponides lateralis, Pyrgo* sp. Hypersaline lagoons have *Ammonia tepida* species, *Triloculina oblonga*, *Elphidium excavatum*, *Poreoponideslateralis*, *Pseudononion atlanticum*, *Quinqueloculina lamarckiana*, and *Pararotalia* spp. as dominant species

Buccella peruviana is indicative of cold sub-Antarctic waters, at least in the subtropical part of Brazil.

Organically enriched sediments and waters with low oxygen under the influence of pollutants and contaminants include *Ammonia* spp., *Buliminella elegantisssima*, *Bolivina striatula, Bulimina elongata*, and *Fursenkoina pontoni*, while *Elphidium* spp. decreases its population. *Quinqueloculina seminulum*, in turn, shows intolerance to oxygen poor water.

Acknowledgments We thank the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) through the Edital Ciências do Mar (207/2010) for the Post Doc Fellowship at the Laboratório de Geologia e Geofísica Marinha e Monitoramento Ambiental da Universidade Federal do Rio Grande do Norte (GGEMMA-UFRN-Brazil).

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Chapter 33
Environmental Impacts of Reservoirs

Gordana Dević

Abstract The construction of reservoirs is one of the most important practices for the development and management of water resources. Many large reservoirs were built without a thorough or systematic evaluation of the long-term environmental, social, and economic interactions of different alternatives.

Up to the last quarter of the twentieth century, those responsible for the construction of dams and creation of reservoirs – entrepreneurs, decision makers, engineers, investors – were praised for the acknowledged benefits of their works: water supply, irrigated agriculture, flood control, improved navigation and firm hydroelectric generation (considered clean and unequivocally renewable energy). However, on the other hand, alarmist, especially environmental groups and organizations, have been exaggeratedly stating that infrastructure works, in general, and dams and reservoirs, in particular, cause serious and intolerable environmental impacts. Reservoir construction leads to a number of environmental issues, both during building and following completion. The physical, chemical character and water quality of rivers draining into lakes and reservoirs are governed in part by the velocity and the volume of river water. In these last decades of industrialization and rapid population increase, human intervention on the balance of nature has never been so various and so extensive as it is today.

This chapter reviews a large range of potential impacts linked to the exploitation of reservoirs and dams, such as: (1) Climate-changing greenhouse gases emissions; (2) Changes in the Temperature Regime (3) Reservoir sedimentation; (4) Water pollution; (5) Destruction of Eco-systems, and (6) Planning and reservoir management.

Keywords Reservoirs • Water resources • Environmental impacts

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_33

33.1 Introduction

Reservoirs are found primarily in areas with relatively few natural lakes, or where the lakes are not suitable for human water requirements. They are much younger than lakes, with life spans expressed in historical terms rather than geological time. Although lakes are used for many of the same purposes as reservoirs, a distinct feature of reservoirs is that they are usually built by humans to address one or more specific water needs. These needs include municipal and drinking water supplies, agricultural irrigation, industrial and cooling water supplies, power generation, flood control, sport or commercial fisheries, recreation, aesthetics and/or navigation (UNEP 2000). The reasons for constructing reservoirs are ancient in origin, and initially focused on the need of humans to protect themselves during periods of drought or floods. Small reservoirs were first constructed some 4,000 years ago in China, Egypt, and Mesopotamia, primarily to supply drinking water and for irrigation purposes (Sumi and Hirose 2009). Simple small dams were constructed by blocking a stream with soil and brush, in much the same manner as beavers dam a stream. Larger reservoirs were constructed by damming a natural depression, or by forming a depression along a river and digging a channel to divert water to it from the river. Dams have made important contributions to human development, and the benefits derived from them have been considerable (WCD 2000). It has been estimated that the volume of water in impoundments increased by an order of magnitude between the 1950s and the present (Downing et al. 2006). The volume of fresh surface water on the earth is only 0.0075 % of the total global water: 104,620 km^3, distributed in lakes (90,990 km^3), swamps (11,510 km^3) and rivers (2,120 km^3). According to the International Committee on Large Dams – ICOLD, the total water storage in man-made lakes is around 6,620 km^3 (White 2010).

Most reservoirs are concentrated in the temperate and sub-tropical zones of the northern and southern hemisphere. Nearly all major river systems in the world have reservoirs in their drainage basins, and a number of river systems also have cascades of reservoirs within their basins. It has been estimated that approximately 25 % of all the water that previously flowed to the oceans is now impounded in reservoirs. Reservoirs exist on all continents and in all countries, except Antarctica (Fig. 33.1), although their distribution within specific countries and regions is irregular.

Man-made reservoirs constitute an intermediate type of water-body between rivers and natural lakes (Fig. 33.2a). Like lakes, reservoirs range in size from pond-like to very large water-bodies. The variations in type and shape, however, are much greater than for lakes. Reservoirs formed by a dam across the course of a river, with subsequent inundation of the upstream land surface are often called impoundments. Water bodies not constructed within the course of a river and formed by partially or completely enclosed water-proof banks are often referred to as off-river, or bunded, reservoirs (Morley 2007). Reservoirs created by dams serially along a river course form a cascade (Fig. 33.2b).

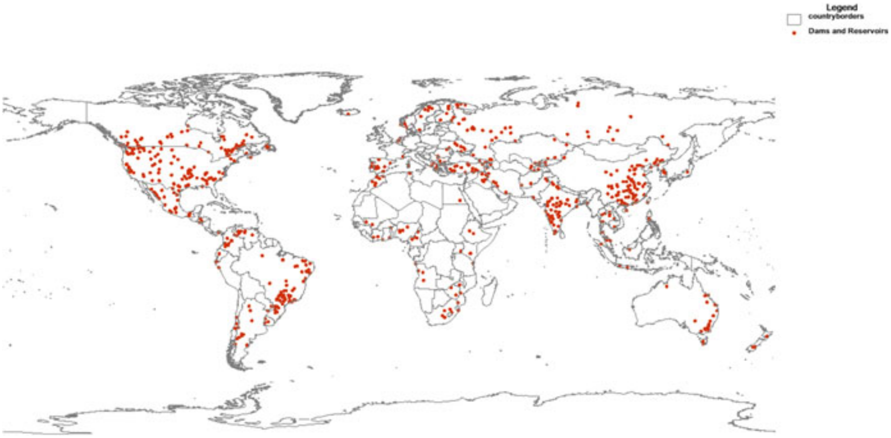

Fig. 33.1 Distribution of dams and reservoirs that have been digitally georeferenced as part of an ongoing collaborative development of a comprehensive global database on dams and reservoirs (Lehner et al. 2011 (unpublished data))

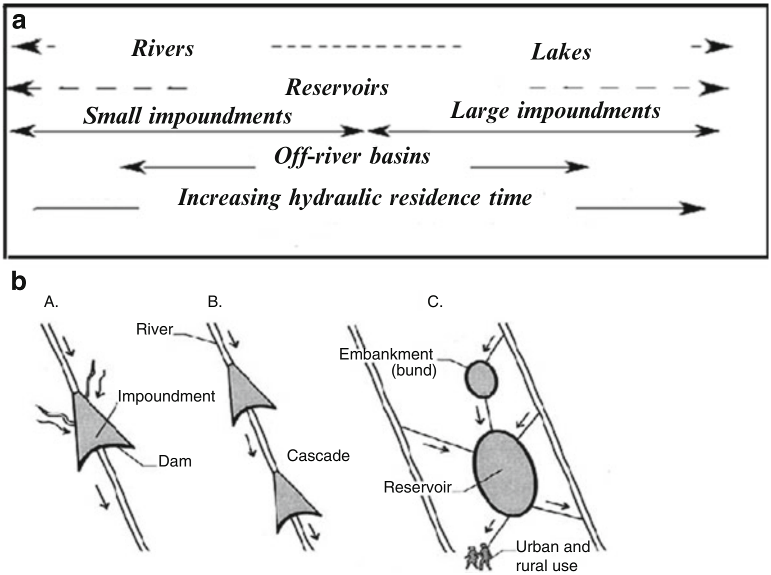

Fig. 33.2 (**a**) The intermediate position of reservoirs between rivers and natural lakes, (**b**) Different types of reservoirs systems

Depending on their use, the water level of reservoirs may be either more or less stable, or it may fluctuate according to a periodicity linked to the water cycle and its exploitation – from full to empty in the extreme case (Wildi 2010).

Reservoirs typically receive larger inputs of water, as well as soil and other materials carried in rivers, than do lakes. As a result, reservoirs usually receive larger pollutant loads than lakes. However, because of greater water inflows flushing rates are more rapid than in lakes. Thus, although reservoirs may receive greater pollutant loads than lakes, they have the potential to flush the pollutants more rapidly than lakes do. Reservoirs may therefore exhibit fewer or less severe negative water quality or biological impacts than lakes for the same pollutant load.

In these last decades of industrialization and rapid population increase, human intervention in the balance of nature has never been so varied and extensive as it is today. Reservoir construction leads to a number of environmental issues.

This chapter reviews a large range of potential impacts linked to the exploitation of reservoirs and dams, such as: Climate-change, greenhouse gases emissions, Changes in the Temperature Regime, Reservoir sedimentation, Water pollution, and Destruction of Eco-systems.

33.2 Environmental Impacts of Reservoirs

For thousands of years, reservoirs and dams have been important tools for the management of extreme hydrological events. Water-related disasters, such as floods and droughts, have been successfully mitigated by the intelligent use of the storage provided by reservoirs. Up to the last quarter of the twentieth century, those responsible for the construction of dams and the creation of reservoirs – entrepreneurs, decision makers, engineers, investors – were praised for the acknowledged benefits of their work: water supply, irrigated agriculture, flood control, improved navigation, and reliable hydroelectric generation (considered clean and unequivocally renewable energy). However, on the other hand, alarmists, especially environmental groups and organizations, have been exaggeratedly stating that infrastructure works, in general, and dams and reservoirs, in particular, cause serious and intolerable environmental impacts (Palau 2006; Gomide 2012). Reservoir construction leads to a number of environmental issues, both during building and following completion (Table 33.1). The construction of a dam results in post-impoundment phenomena that are specific to reservoirs and do not occur in natural lakes. One difference is that during the first reservoir filling terrestrial habitats are submerged and destroyed. Thus, dams and the creation of reservoirs require the relocation of potentially large human populations if they are constructed close to residential areas. The record for the largest population relocation is held by the Three Gorges Dam built in China. Its reservoir submerged a large area of land, forcing the displacement of over a million people (Tan and Yao 2006). Another difference is that level fluctuations may be much larger than those normally found in a natural lake. Non-earth storage dams often have a bottom outlet. This may enable both sediment flushing and water release from deep below the surface. Major changes in the river system occur both upstream and downstream.

Table 33.1 Environmental changes associated with reservoirs and dams

Cause of Impact	Possible direct effects	Possible indirect effects
Creation of dam	Creation of a major obstacle in the river	Barrier to migration for certain aquatic vertebrates (fish)
	Associated construction work	Disruption of habitat
		Increased sediment erosion and temporary effects on river water quality
	Population displacement	Population reduction in the vicinity of the reservoir
	Modification of landscape	Presence of new water body in landscape
		Presence of newly-built associated structures (turbine plants, treatment plants)
		Change in slope gradient
		Creation of a tourist attraction (recreation-seasonal population influx)
Reservoir impoundment	Flooding of land	Habitat destruction
		Destruction of archaeological and historical features
		Decomposition of organic material
		Splitting of continuous forested areas in two belts
		Possible migration barrier for terrestrial fauna
Presence of a permanent still water body	Creation of a still water habitat	Change from riverine to lacustrine ecosystem
		Stratification of the water body with associated changes to the ecosystem
	Creation of a micro-climate	Increased humidity and attenuated temperature changes upstream of the reservoir
	Rice in groundwater levels upstream of the reservoir	Possible flooding of land and increased salinization
		Changes in groundwater flow regime
	Effect on bedrock	Possible induced seismic activity (in the largest impoundments)
	Water use	Change in downstream land use due to the availability of a new water resource
Accumulation in the reservoir	Sediment trapping	Sedimentation of the reservoir with associated water volume reduction
		Leaching of nutrients and other substance
	Nutrient enrichment-causing eutrophication	Evolution of ecosystem. Appearance of water detrimental to recreation uses-toxic algae
	Atmospheric acidic deposition	Acidification of reservoir, low pH and effects on ecosystem
	Chemical pollution	Accumulation of heavy metals, pesticides and other micro-pollutants
	Biological pollution	Possible presence of pathogens

Modified data: European Environment Agency 1999

33.2.1 Climate-Changing Greenhouse Gases Emissions

The construction of a reservoir results in the total inundation of all areas upstream of the dam. These regions are often rich in trees and forests. The process of deforestation actually emits carbon dioxide into the atmosphere, and is responsible for 20 % of the world's greenhouse gas emissions. There is growing interest and concern regarding greenhouse gas emissions from lakes and reservoirs (St. Louis et al. 2000; Huttunen et al. 2002; Tremblay et al. 2005). The fact that CH_4 has a global warming potential up to 25 times stronger that of carbon dioxide on a 100-y scale has made the monitoring of this greenhouse gas of particular importance. Atmospheric CH_4 concentrations are currently at the highest levels observed in the last 650 ky and have an ever-growing list of natural and anthropogenic sources (Forster et al. 2007).

Greenhouse gases, primarily methane (CH_4) and carbon dioxide (CO_2), are emitted from all of the dozens of reservoirs where measurements have been made (Bastviken et al. 2011). A first estimate indicated that for global large dams, area of $1.5 \cdot 106\ km^2$, about 69.3 Tg CH_4 (1 Tg = 1,012 g) could be released annually by bubbling and diffusion processes (Lima et al. 2008).

Despite the uncertainties about upstream emissions, the growing consensus is that emissions downstream from dams might be responsible for a substantial release of CH_4 into the atmosphere (Abril et al. 2006; Lima 2005; Lima et al. 2008).

The current state of knowledge shows that N_2O emissions from the great majority of freshwater reservoirs are negligible (Guérin et al. 2008). N_2O has the potential (over a period of 100 years) to contribute 298 times more than CO_2 to global warming.

Gases are emitted from the surface reservoirs, at turbines and spillways, and for tens of kilometres downstream. Emissions are the highest in hot climates. Hydro plants in the tropics with large reservoirs relative to their generating capacity can have a much greater impact on global warming than fossil fuel plants generating equivalent amounts of electricity. Emission levels vary widely between different reservoirs depending on the area and type of ecosystems flooded, reservoir depth and shape, the local climate, and the way in which the dam is operated. For instance, China's reservoirs are often deep but sludge-filled, while Brazil's reservoirs are shallow and in a tropical zone. Both cases lead to high gas emissions (International Rivers 2007).

33.2.2 Changes in the Temperature Regime

Temperature affects a number of physical, chemical, and biological processes in natural aquatic systems. The temperature regime of a lake is a function of seasonal/diurnal ambient air temperatures and the morphology and setting of the reservoir. One of the most important effects of temperature is the decrease in oxygen solubility with increasing temperature. Increasing temperature can also increase the oxygen demand of biological organisms, such as aquatic plants and fish. The rate of chemical reactions generally increases at higher temperatures. Some compounds are also more toxic to aquatic life at higher temperatures. Reservoirs act as thermal regulators that may fundamentally alter the seasonal and short-term fluctuations in temperature that are characteristic of many natural rivers. Depending on the geographical location, water retained in deep reservoirs has a tendency to become thermally stratified (Hutchinson 1957). Reservoirs closest to the equator are the least likely to become stratified. Many deep reservoirs, particularly at mid and high latitudes, do become thermally stratified, as do natural lakes under similar climatic and morphological conditions. However, the release of cold water into the receiving river from the hypolimnion of a reservoir is the greatest non-natural consequence of stratification.

An example of thermal stratification is shown in Fig. 33.3, which compares the annual temperature pattern at monitoring sites on the South Fork McKenzie River upstream and downstream of the Cougar Dam. The Cougar Dam on the South Fork McKenzie River, Oregon., USA, is a multi-purpose dam and reservoir impounding 270 million m^3 of water. The Cougar Dam controls the flow of and greatly influences the temperature in the South Fork McKenzie River downstream of the dam. The Cougar Reservoir becomes thermally stratified in summer, with warmer, less dense water near the surface and colder, denser water at the bottom. The warm and sunny summer weather of Western Oregon's adds additional heat to the surface of the reservoir, stabilizing its stratification throughout the summer. As the dam was built with its major release point at a relatively low elevation, the dam historically released relatively cold water from near the bottom of the reservoir in mid-summer. As the reservoir was drawn down in autumn to make room for flood-control storage, the heat that was captured in the upper layer of the reservoir's during the summer was released downstream. As a result, the seasonal temperature pattern downstream of the Cougar Dam through 2001 was quite different from the pattern upstream of the Cougar Reservoir (Fig. 33.3a), (Rounds 2007).

The McKenzie River supports the largest remaining wild population of Chinook salmon in the upper Willamette River Basin, and the South Fork McKenzie River provides good spawning habitat. The altered temperature pattern downstream of the Cougar Dam, however, can create problems with regard to the timing of migration, spawning, and egg hatching (Caissie 2006). To restore the suitability of this reach for salmon spawning, the U.S. Army Corps of Engineers added a sliding gate assembly to the intake structure of the Cougar Dam. To allow for construction, the reservoir was drawn down from 2002 to 2005; the construction was completed in early 2005. The new selective withdrawal tower allows dam operators to blend warm water from the top of the reservoir with cooler water at the other levels, or simply to select a depth from which to withdraw water, in an attempt to match a downstream temperature target (Rounds 2007). The selective withdrawal tower was employed successfully in 2005 and 2006 to restore a more-natural seasonal temperature pattern to the South Fork McKenzie River downstream of the Cougar dam (Fig. 33.3b).

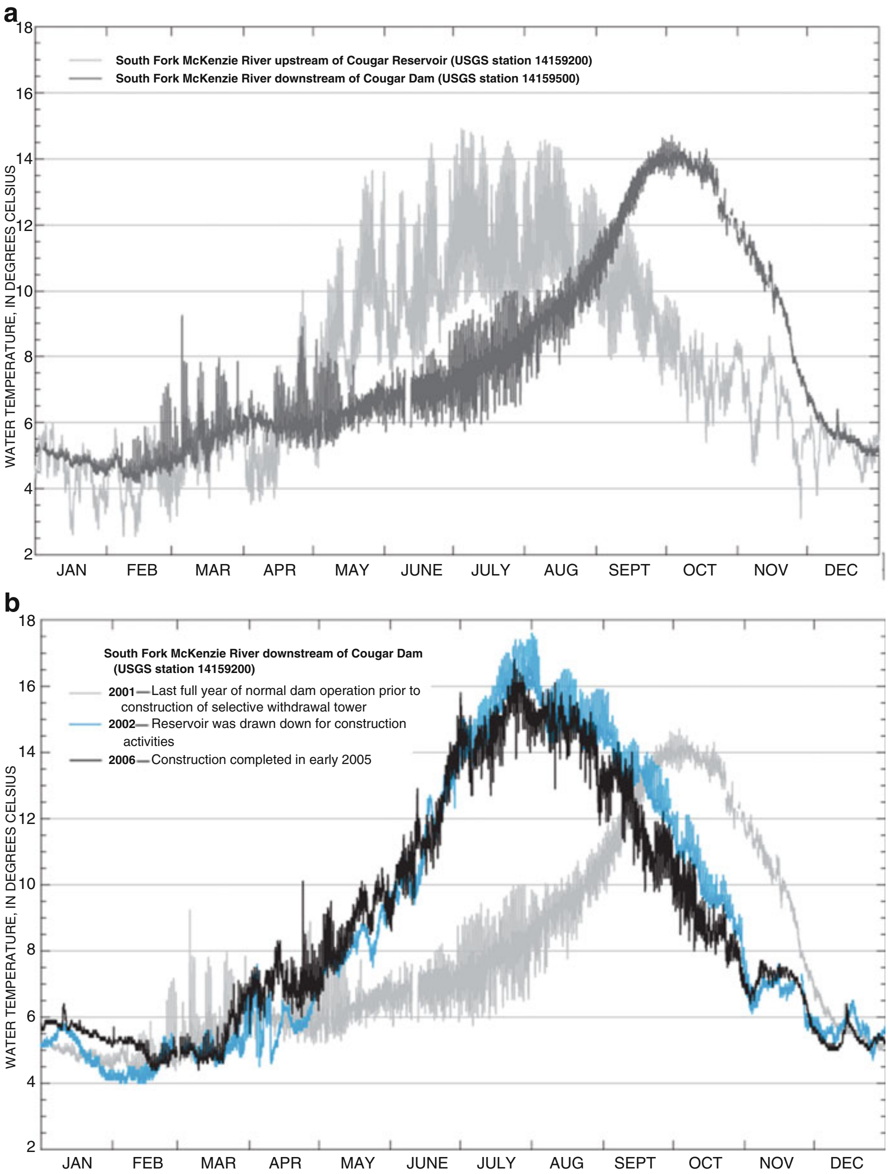

Fig. 33.3 (**a**) Seasonal water temperature patterns in the South Fork McKenzie River upstream and downstream of Cougar Reservoir, Oregon. The *light grey line* shows, for the upstream site, a pattern as you might expect – temperatures heating up in late spring and rising during the summer with the fall bringing lower temperatures. It shows a normal bell-curve type of pattern that closely follows seasonal air temperature patterns. Fish living in this reach of the river would be adapted for these normal temperature patterns. Cougar Reservoir becomes thermally stratified in summer, with warmer, less-dense water near the surface and colder, denser water at the bottom. Western Oregon's warm and sunny summer weather adds additional heat to the reservoir's surface, stabilizing its stratification throughout the summer. Because the dam was built with its major release point at a relatively low elevation, the dam historically released relatively cold water from near the bottom of the reservoir in mid-summer. As the reservoir was drawn down in autumn to

33.3 Reservoir Sedimentation

The construction of >800,000 dams over the past century has reduced sediment loads to the oceans by ≈50 % (Vörösmarty et al. 2003). About 1,100 km^3 of sediment has accumulated in the world's reservoirs, taking up almost 20 % of the global storage capacity (WCD 2000). In China, 8 billion m^3 of storage capacity of 20 large reservoirs have been lost due to sedimentation, which is 66 % of the total reservoir capacity of these reservoirs (Wang and Chunhong 2009). The storage capacity of reservoirs is being lost at an annual rate of 2.3 % in China and 1 % worldwide (White 2001). A wide range of sedimentation-related problems occurs upstream from dams as a result of sediment trapping. Sediment can enter and obstruct intakes and greatly accelerate abrasion of hydraulic machinery, thereby decreasing its efficiency and increasing maintenance costs. Dam construction is the largest single factor influencing sediment delivery to the downstream reaches. The cut-off of sediment transport by dams can cause stream bed degradation, accelerate the rates of bank failure, and increase scouring at structures such as bridge pillars. Stream morphology downstream of dams can be dramatically impacted by reduction in the supply of sediment. Clear water in the river channel, downstream of the dam tends to scour the stream bed causing it to coarsen, degrade, and become armoured. Channel degradation can raise bank heights, increase bank erosion rates, increase the severity of scouring at downstream bridges, lower water levels at intakes, reduce navigational depth in critical locations, and lower groundwater tables in riparian areas (Wang and Chunhong 2009).

Sedimentation reduces reservoir storage worldwide, causing serious problems not only for water and electricity supply, and flood control, but also for ecosystem development up-and down-stream of large dams. The consequences are especially precarious in (semi-) arid environments, where many reservoirs have been built for irrigation, water supply, flood control, and production of electricity. However, also in other areas sediment storage behind dams can have large implications for ecosystem and coastal development downstream of large river systems (Vörösmarty et al. 2003). Furthermore, storage of possibly contaminated sediments in a reservoir and subsequent chemical reactions occurring within the sediments due to long term storage cause serious problems for water quality and the possibilities for using the sediments further after dredging or flushing operations (de Vente et al. 2005). Therefore, it is of utmost importance to be aware of sediment yield on the basin scale and the composition of the sediments, and to understand which factors determine the sedimentation rate of reservoirs. This knowledge will enable

Fig. 33.3 (continued) make room for flood-control storage, the heat that was captured in the reservoir's upper layer during the summer was released downstream. As a result, the seasonal temperature pattern (*darker line* on chart) downstream of Cougar Dam through 2001 was quite different from the pattern upstream of Cougar Reservoir. (**b**) Seasonal water temperature patterns in the South Fork McKenzie River downstream of Cougar Dam in 2001, 2002, and 2006 (Data from Rounds 2007) the probable lifespan of a reservoir to be estimated and moreover, allow proper measures against reservoir sedimentation, water shortage, and river bank and coastal erosion to be undertaken (de Vente et al. 2005).

33.4 Water Pollution

Water storage in reservoirs induces physical, chemical, and biological changes in the stored water. As a result, the water discharged from a reservoir could have a different composition to that flowing into the reservoir. Temperature changes relate to the thermal mass and surface area of the reservoir for radiant exchange, retention time, thermocline development, and whether the released water originates from the surface or a depth (Quinn, et al. 2004) (see Sect. 33.2.2). Chemical changes include altered nutrient levels and dynamics, modified water-column and sediment oxygen regimes, nitrogen supersaturation in downstream waters, and increased mobilization of certain metals and organic contaminants. Nutrients (phosphorous and nitrogen) are released biologically or leached from flooded vegetation and soil. Eutrophication of reservoirs may occur as a consequence of large influxes of organic loading and/or nutrients (Camargo et al. 2005; Perkins and Underwood 2000; Huang et al. 2012). In many cases, these are a consequence of anthropogenic influences in the catchments rather than a direct consequence of the presence of the reservoir. Nutrient pulses in conjunction with specific environmental conditions can cause oxygen depletion and increased concentrations of iron and manganese in the bottom layer and increased pH and oxygen in the upper layers of stratified reservoirs. Although the oxygen demand and nutrient levels generally decrease over time as the organic matter decreases, some reservoirs require a period of more than 20 years for the development of stable water-quality regimes. After maturation, reservoirs, like natural lakes, can act as nutrient sinks particularly for nutrients associated with sediments.

Heavy metal contamination has recently been highlighted as a major reservoir problem in some countries (Müller et al. 2000; Audry et al. 2004; Akoto et al. 2008; Feng and Qiu 2008; Larssen et al. 2010). Among environmental pollutants, metals are of particular concern, due to their potential toxic effects and ability to bioaccumulate in aquatic ecosystems (Censi et al. 2006). These metals may be introduced into a fluvial environment as a result of natural weathering, erosion, and transport processes, as well as from a range of anthropogenic activities (Audry et al. 2004). The release of heavy metals can occur both in dissolved and particulate form. When released in particulate form or adsorbed to particles, heavy metals can settle down and be deposited in the river bottom sediments under the favourable hydraulic conditions provided by natural and reservoir lakes. Reservoir sediments usually accumulate at high rates (typically > 2 cma^{-1}), compared to lacustrine sediments (often <3 cm a^{-1}; Audry et al. 2004). Due to these rapid sedimentation rates, reservoir sediments are considered to be little affected by early diagenesis processes and to provide preserved historical heavy metal inputs. A special problem is the contamination of newly formed reservoirs with mercury. When the terrestrial landscape is flooded to create a reservoir, the organic carbon within the soil and vegetation begins to decompose. Under the anoxic conditions prevalent in new reservoirs, sulphur-reducing bacteria thrive causing microbial methylation of inorganic mercury, naturally accumulated through long-term wet and dry atmospheric deposition, into the highly toxic form, methyl mercury (MeHg) (Mailman et al. 2006). Elevated production of MeHg in new reservoirs may last for more than 13 years and be rapidly transferred through the food web, causing increased metal levels in fish, which may persist for up to 30 years after flooding (Mailman et al. 2006).

A major impact on the surface water quality may stem from biological processes, such as bacterial contamination. Water turbidity could be increased by high plankton concentrations and there may be a proliferation of mosquitoes and other insects, as well as rats and other nuisances. In the surrounding area and downstream of the reservoir, groundwater levels generally rise due to damming, increased infiltration, and rise in the hydraulic base level (Wildi 2010).

For many reservoirs that are found in arid or semi-arid areas where the surface water is naturally scarce, the problem of salinization could be severe. The salinisation of water below dams in arid climates is particularly problematic and is exacerbated in areas of marine sediments and where saline drainage water from irrigation schemes is returned to the rivers downstream of dams. Salinisation has also proved to be a problem on floodplain wetlands in the absence of periodic flushing and dilution by flood water. If sufficiently high and prolonged, elevated salinity will affect aquatic organisms (Akindele et al. 2013). The South African Department of Water Affairs (DWA 1986) gives a range of median total dissolved solids (TDS) concentrations, for 13 major reservoirs throughout the country, of between 137 and 955 mg l^{-1}. The extreme values of TDS measured in these reservoirs ranged from 99 to 2,220 mg l^{-1}. Salinity in this range limits the possible employment of the water because all but a few salt-tolerant crops, and most industrial and other uses, of the water are seriously affected by high salinity.

33.5 Destruction of Eco-systems

Changes in the physical and chemical characteristics of water from impoundment inevitably affect the distribution and abundance of aquatic biota and the resulting community structure (Morita et al. 2000; Dudgeon 2000; Tullos 2008). Within new reservoirs, fish populations are often quite large during the first few years, largely because of increased nutrients leached from flooded soils and vegetation, enhanced productivity throughout the food chain, and provision of secure sites for spawning and predator protection. Once established, the new physical/chemical characteristics of a reservoir could pose challenges to biota, primarily because they are not in synchrony with natural cycles. Disturbance to spawning results from the drawdown/raising of water levels, changes in seasonal temperature cycles, and blocked migration for fish (Walks et al. 2000; Quinn, et al. 2004).

Some reservoirs also provide habitats for birds and other fauna, but this often does not outweigh the loss of habitat downstream.

Eutrophication can lead to algal blooms in reservoirs that may have numerous adverse consequences for both the operational efficiency and the wildlife of the reservoir (Baxter 1977). In particular, toxic products produced by algae can cause mass fish and invertebrate mortality. The role of harmful algal blooms in animal mortality and disease events has only recently begun to be understood (Landsberg 2002). Mercury and other heavy metals can have a dramatic effect on parasite transmission and host–parasite relations in aquatic habitats (Morley 2007).

33.6 Planning and Reservoir Management

Proper water management is of vital importance to human society in a world where increasing demands are being placed on a relatively finite but potentially renewable resource. Moreover, effective water management demands transboundary coordination in the context of the fact that a total of 276 international river basins cover almost half the earth's surface (WWAP 2012).

Reservoirs represent an important component of the social and economic structure of both developed and developing countries. Many large reservoirs were built without a thorough or systematic evaluation of the long-term environmental, social, and economic interactions of different alternatives. The "dead storage" concept has been used in the planning and design of reservoirs to store sediment for a predetermined useful life, say 50–100 years. However, many existing reservoirs have reached, or may soon reach, their designed useful life. For instance a significant amount of sediment storage capacity at the Japanese reservoirs, which were designed for a life span of 100 years, has already been lost because sedimentation has occurred faster than expected (Sumi et al. 2004). Reservoir sedimentation is one of the most crucial issues to be solved this century to realize sustainable water resources management. The reservoir sedimentation problem has been a challenging issue for many countries worldwide; however, only a limited number of countries have been actively playing roles in reservoir sedimentation management. In the present situation, for those countries which have progressively developed various techniques and possess example cases, key issues are not to put off dealing with this problem but to make a continuous effort toward developing techniques further and putting them into practice, and to share the resulting information and knowledge widely with every country in need of them (Kantoush and Sumi 2010).

In addition, environmental, social, economic, and political considerations, and the fact that suitable dam sites are now scarce, necessitate new and innovative approaches for the development and management of water resources. To cope with population increases and the increasing demands of higher standards of living, more reservoirs will be built, especially in developing countries (Yang 2006). Reservoir construction has been largely completed in North America and Europe, but continues in the developing world, and most new reservoirs in the future will be located in Asia, Africa, and Latin America (White 2005).

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Part XII
Water Biological Pollution

Chapter 34
Bacteriological Indications of Human Activities in the Ecosystems

Elias Hakalehto

Abstract The central role of microbes in the material cycles in Nature is worth studying for understanding the basis of healthy living on this planet. Human actions have been interfering with the balances in the ecosystems. The microbes compensate these effects by establishing new equilibria. The human impacts on the environment can be monitored by researching the microbial communities in soil, water and air. Wetlands as well as forest ecosystems are important sites for transitions in the natural cycles. Some microbiological follow up via satellite technology, or with climatological point of view, as well as with a focus on species distribution have been included. Any waste outlets from municipal, agricultural or industrial sources contain micro-organisms, whose environmental emission has ecological and health effects. Monitoring these effects is important for improving health, promoting the versatility in Nature, and for all efforts to maintain the functionability of the ecosystems. In environmental microbiology, it is not enough to solely track the intestinal indicator organisms. More holistic views on microbiological phenomena are required. The PMEU (Portable Microbe Enrichment Unit) has been included in this chapter as an example of an approach for implementing fast recovery methods, metabolic monitoring, and automated screening of environmental microbes. These techniques are essential for rooting out many devastating bacteriological diseases, such as cholerae, tuberculosis and salmonellosis. The applications with indicator bacteria could also be broadened into the source tracking of the origins of the pollution.

Keywords Indicator bacteria • Microbial degradation • Water hygiene • *Escherichia coli* • *Salmonella* • Mycobacteria • *Campylobacter* • *Klebsiella* • *Vibrio cholerae* • Air-borne micro-organisms • Rural development • PMEU • Municipal raw water • Forest ecosystem • Water circulation

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_34

34.1 Introduction

The discipline of microbiology has been underestimated, or at least its use has been restricted, in the simulation and approximation of human impacts on the environment. In the global cycles, water returns to earth in rainfalls. It is not unaffected by what it meets on the way and when it comes down onto the earth and meets the soil, where it flushes away organic and inorganic matter incorporated with myriads of micro-organisms.

To follow these universal phenomena, we require microbiological tools and understanding. In the Nordic climates or in high mountain areas, water in the annual rainfalls collects as snow during a period of roughly half a year before the springtime. This means that when it melts the water masses flowing toward the seas and oceans increase, flooding and flushing away inorganic and organic matter with micro-organisms. The composition of the microflora in this water can be an indicator of the status of the air, soil, and fresh water on its route. Besides the actual polluting microbes from human sources or from domestic animals, anthropological effects in the Nature can be reflected in the composition of the microflora.

Consequently, in this chapter we further widen the concept of microbial indicator organisms from solely the fecal strains to other signals of human activities at the ecosystem level in the environment. Besides the water cycle, various elements circulate in nature, particularly in the biosphere. Carbon is the skeleton of organic molecules, and is the fundamental element in this cycle of life (Fig. 34.1). Together with the circulating water it shapes the biosphere.

It is important to pay attention also to the airborne organisms. In the atmosphere, particles less than 10 μm in diameter do not fall down as a consequence of gravity. Their ultimate fate is to wander around with the winds, or to be caught in pouring rain. On earth, they meet either water or land ecosystems, the latter of which can absorb them more or less effectively. In the tropical forests, the soil may accumulate onto the vegetation whose roots partially hang in the air, resulting in a forest ecosystem where the ground is a continuous "melting point" of gaseous, liquid, and solid substances. This kind of habitat makes the enhanced exchange of energy, materials, and information between the three phases possible. There, micro-organisms play a central role in this circulation, where the flow is most intense at the borderlines.

In the different climates from the arctic to the tropical hemispheres, from mountains to the oceans, micro-organisms constitute ecosystems. Unlike plant or animal species, the distribution of a microbial species is often global. Our inner ecosystem is a reflection of the universal microflora, with which we become connected by the microbial communities of our alimentary tract (Hakalehto 2012a). In order to investigate the above-mentioned phenomena in a closed system of scientific observation, we used the PMEU (Portable Microbe Enrichment Unit) as a tool. Through this equipment, fast recovery and enhanced enrichment of environmental microbes have become simultaneously achievable (Hakalehto and Heitto 2012). Moreover, various

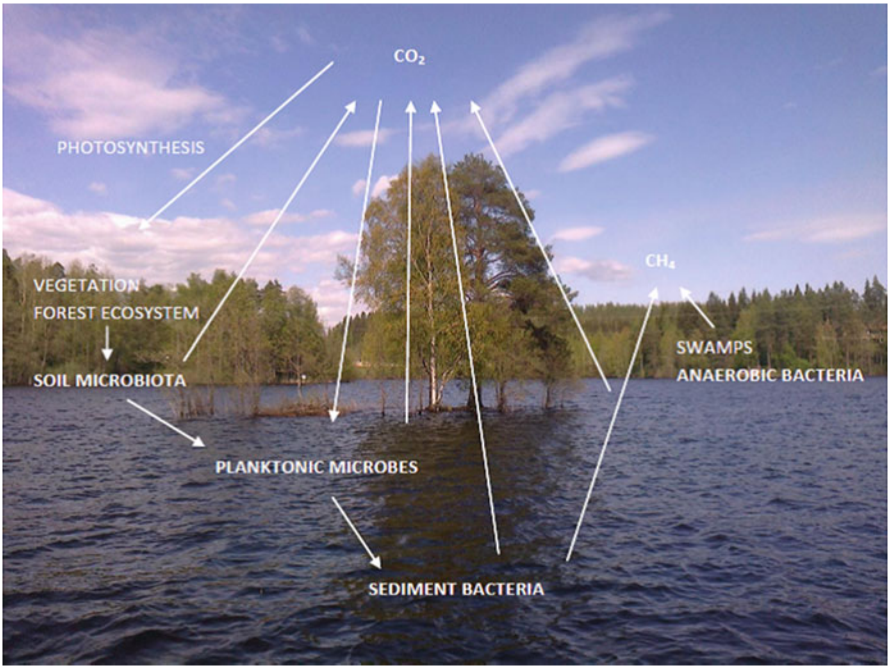

Fig. 34.1 Microbial carbon circulation in Finnish Nature. Micro-organisms liberate carbon into the air mostly as CO_2 in respiration and fermentation, and CH_4 in symbiotic fermentation (by acid-producing eubacteria and methane-producing archae). Any anthropogenic impact on any of the parts of these sequences will eventually affect all the parts, and consequently disturb the balance (Photo taken by Lauri Heitto during springtime floods)

interactions between the strains have been simulated (Hakalehto et al. 2008, 2010). In particular, the intestinal ecosystems have been studied using this technique (Hakalehto 2012a; Pesola and Hakalehto 2011; Hakalehto and Jaakkola 2013). Microbial contamination of retail milk has been studied by the gas emissions using the PMEU Scentrion® (Hakalehto et al. 2013a). The microscopic reactions in the bioprocesses have also been investigated with respect to biorefineries development using the PMEU technology (Hakalehto et al. 2013b). The fecal emissions from the municipal effluents can be monitored with an automated PMEU version (Hakalehto et al. 2013c). Results from polluted water can be compared with those from unspoiled water. The hygiene indicators have been screened in the water distribution network using this method (Hakalehto et al. 2011). It is increasingly important to improve the methodology, as risks of epidemic tuberculosis, enteric diseases, multi-drug resistant bacteria, HIV, dengue, leishmaniosis, filariasis, and schistosomiasis emerge in a global perspective (Fong 2013).

Water raining on earth collects substances and particles, together with microbes, from vegetation and from forests and fields and marshlands, as well as from our cities. From these areas, we get our living, and our industries obtain a major part of raw materials. Therefore, it is of high importance that we are able to maintain the balance of Nature in these “humanized ecosystems.” In monitoring this development, we need microbiological means.

34.2 Air-Borne Dissemination of Micro-organisms

In trials, a jet plane (Hawk training jet, BAE Systems, UK) was equipped with samplers under its wings, and collected air specimens at heights between 300 and 1,000 m. The microbes from the air flow were collected onto a filter. Then bacterial counts were relatively low, partially due to the dehydrating circumstances in the air and during sampling, and also as a result of the high levels of disinfecting UV radiation. In contrast, the average mold concentrations of the *Cladosporium* type of colonies dissolved from small pieces of filters cultivated on Petrifilm™ medium varied between 0.50 and 13.38 above cities, and between 0.25 and 1.00 above countryside. The number of the blue or turquoise *Penicillium* type of colonies varied between 1.62 and 1.74 above city, and between 0.42 and 0.75 above countryside locations. The collection was carried out on a cool autumn day. During warmer seasons, the *Penicillium* was observed to be clearly typical for urban areas. It is probably derived mostly from the ventilation systems of buildings in towns. Molds belonging to such genera as *Aspergillus, Arternaria* and *Fusarium* were more present in the air above rural areas. These latter molds originated from vegetation, and analyzing them could also give an indication of microfungi concentrations in the atmosphere, as well as an early warning of spreading plant diseases, even across national borders. The average content of mold spores above Finland at an altitude of 1 km was found to be about 50–100 cfu (colony forming units) per cubic meter of air. In our search for novel bioindicators, the use of bacterial or mould spore counts from the atmosphere could give some indication of the human impact on air microbiology and the environment as a whole. It relates also to the actual problems of moist buildings, which have various health implications.

In principle, particles less than 10 μm in diameter move freely in the atmosphere independently of the gravitational forces. A recent study, “Dust and Biological Aerosols from the Sahara and Asia Influence Precipitation in the Western US,” appeared on Feb. 28, 2013 in the online version of Science (Creamean et al. 2013). In this and other related investigations, it was found that winds can carry aerosols such as dust at altitudes above 5,000 m from continent to continent. A specific dust could even make a complete circuit around the planet several times. Furthermore, the dust particles act as ice nuclei within clouds at elevated temperatures. They initiate the freezing of water vapour and droplets, and then precipitate as rain. Bacteria, viruses, pollen, and plants, of both terrestrial and marine origin, also add to the mix of aerosols making the transcontinental voyage. In an analysis of winter storms in 2011, it was found that dust and biological aerosols tend to enhance precipitation-forming processes in Asian or African Sierra Nevada.

34.3 Carbon Cycles in the Finnish Forests and Beyond

In modern times, the cleanliness of the global natural water is dependent on the levels of waste water purification in different countries. Moreover, it is also a consequence of our ways of treating our solid wastes, and recollecting the chemical energies accumulated in them (Hakalehto 2015). Direct combustion often increases various climatological and environmental health effects, but more advanced biotechnological methods can avert these consequences. The circulation of matter, and the carbon in it, into air and further to land and water ecosystems is partially a consequence of our industries, housing, agriculture, traffic, etc. The contribution of the natural microbiological background needs to be understood in this context in different ecosystems.

In Finnish nature, there is a huge carbon content bound to the vegetation, and to the soils (Fig. 34.2). The most substantial carbon reservoir is in the marshlands. Nowadays, 23 million m^3 of peat is combusted annually. In Nature, this vegetation no longer binds water. As the micro-organisms carry out the cycles of elements, they become more and more rapidly flushed into the water, and increasingly so in floods.

In Finland, the forests have always provided the means for survival for humans. In earlier times, they were used for slash and burn and for seasonal cultivation (-Lindqvist 2013). Nowadays, they are the raw material source for paper and timber industries, and bioenergy production. For example, 50 % of the logs are made into sawn timber, 10 % becomes sawdust, and 30 % wood chips, and 10 % is separated as bark (Lagus 2011). A big portion of the "latter half" of the wood is burnt either as such or in the form of pellets. This practice, together with peat production, is the means for Finland to achieve its goal of generating an adequate portion of her

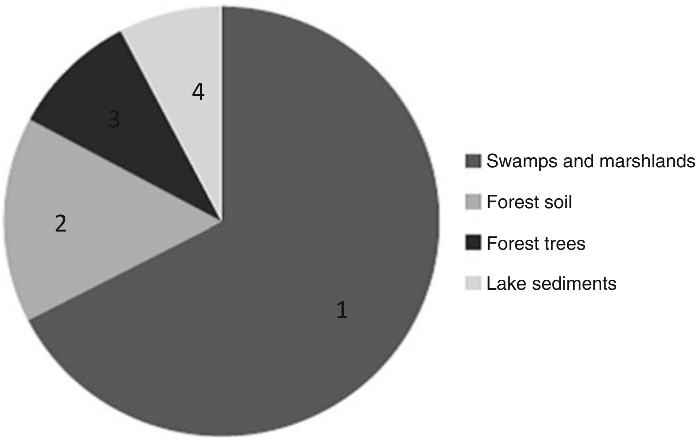

Fig. 34.2 Carbon storage in Finnish Nature. The total amount of about 8.5 M tons of carbon is distributed into swamps and marshlands, forests, and lake sediments. Direct combustion of peat or wood materials can thus severely diminish the carbon storages in Nature (Source: Wikipedia Commons, Jorma Laurila, Matti Nieminen)

Table 34.1 Saproxyles in the Finnish forest. The numbers of species indicate the versatility of northern forest ecosystem (according to Mehtola 2010)

Group of saproxyles in Finnish forest ecosystem	Number of species
Birds	24
Butterflies	30
Beetles	800
Hymenopterans	500–1,000
Flies	500–1,000
Other insects	50
Other arthropods	300
Other invertebrates	100
Hepatics	20
Agarics and gasteroid fungi	300
Dacrymycetes	65
Mushrooms of the artificial order	600
Ascomycetes	600
Myxomycota	150
Lichens	50
Total	4,089–5,089

energy from biological sources. This industrial activity, however, is being built "on the shoulders" of a vast forest and lake ecosystem. The micro-organisms decay the organic matter, which influences directly the lives of thousands of species (Table 34.1). The composition of the forest soil microflora reflects the changes in this ecosystem. Its reestablishment after reforestation can take decades.

In a Finnish forest, there are about 4,000–5,000 species dependent on degrading wood material. These saproxyles are divided into several taxonomic entities (Mehtola 2010). Their versatility illustrates the multitudes of living forms directly associated with the circulation of organic matter by the saprophytic bacteria. These "higher" organisms also compete with the heterotrophic microbes for the energetically rich chemical compounds. They also belong to the cycles as important links. This statistics demonstrates the importance of maintaining the versatility of natural ecosystems while their energies are transformed into industrial usage. If the forest is removed, simultaneously this elaborate cycling mechanism is abolished and the soil microbes largely flushed away. The micro-organisms on the vegetation and on animals also need to be taken into account.

Many of the species in the saprophytic community are macroscopic fungi. They are involved in continuous interactions with microbes, such as bacteria, microfungi, and algae. In fact, lichens represent a highly developed form of symbiosis between fungal and algal species. The saproxyles together with micro-organisms degrade wood in four phases. Some wood starts to disintegrate when the trees are still alive, during "the zero phase" (Mehtola 2010). The first phase of actual degradation includes the breaking down of the phloem layer beneath the bark for a couple of years. After that, the holes made by insects and birds open up the inner parts of the wood for degradation. This second phase takes 5–10 years. The most time consuming third phase of wood degradation follows then, having a duration of about 50 years. Finally, the completion of the degradation process takes about 20 years. During these many decades, the carbon in the wood is assimilated, and a big part of it is liberated into the atmosphere as carbon dioxide. The microbial strains participating in the soil degradation processes include globally approximately 30,000 strains of bacteria, 1,500,000 fungi, 60,000 algae, 10,000 protozoa, 500,000 nematodes, and 3,000 earthworms (Pankhurst 1997). Many of the microorganisms have also been isolated and developed for industrial uses. However, alongside the industrial bioprocess development, waste recycling should be combined with this development by reusing the organic materials and returning them to the site of harvesting, in this case into the forest soil. In fact, the bioprocess industries should be operating like natural ecosystems (Hakalehto et al. 2013b; Hakalehto 2015).

In tropical forest soil in its natural "original" constitution, some ecological parameters of the microbial communities have been investigated in order to study the interactions in an undisturbed area (Vasconcellos et al. 2013). In this undisturbed soil, lower soil densities with higher macroporosity were detected. Total carbon and nitrogen contents in this soil were twice as high as that in soil recovering from human influence. Nitrate rates were also higher, being elevated three-fold in summertime, indicating the accelerated seasonal speed of microbial metabolism. Macroporosity had a positive effect on CO_2–carbon evolution, microbial nitrogen biomass, and acid phosphatase activity. All these had positive sustainable impacts on the forest growth. This porous structure of natural forest soil can enhance soil respiration, as well as nitrogen fixation. It should be kept in mind that plant root symbiotic microbes play an important role in the circulation of nitrogen. Such activity is associated with e.g. the leguminous trees in the tropics (Haukka 1997).

Some of the tropical forests have been specifically called as "rainforests." There water, in the forms of rainfall and humidity, plays an essential role in the constitution of the forest soil. Water flows and relatively high temperatures also keep the organic matter and nutrients cycling in an incredibly thin layer of humus and fertile organic soil. The speed of the cycles makes it possible for this thin layer to sustain dense vegetation. The epiphytes climb on the trees, and debris is often accumulated onto the trunks and branches, as well as loosely onto the network of the roots. The rain forest structure is a layered one for effective assimilation of light energy. In fact, corresponding layers can be found in Finnish forests:

1. Trees
2. Bushes
3. Twigs and grasses
4. Mosses and lichens (bottom layer)
5. Small algae
6. Fungi and bacteria.

All these layers of vegetation are flushed by the rains and ventilated by the winds, which provokes diffusion, evaporation, and movements of soil and its particles. Air microbiology is, therefore, related to the water cycles.

The status of the African rainforests between 1990 and 2000, as well as between 2000 and 2010 in West Africa, Central Africa and Madagascar has been studied by such methods as Landsat satellite imaging (Mayaux et al. 2013). According to these surveys, the net deforestation rate is estimated to be at 0.28 % $year^{-1}$ for the period 1990–2000 and 0.14 % $year^{-1}$ for the period 2000–2010. Even though West Africa and Madagascar exhibit a much higher deforestation rate than the Congo Basin, the expanding agriculture and fuelwood demand in the latter region are real threats to the ecosystem, whereas the timber exploitation is more in control. In the tropical rainforest, the principal carbon storage location is the vegetation. In Finland, it is stored in peat and soil, as well as in lake sediments. The borderline between woods and marshland is often blurred. Besides microbial indicator species, also the use of different microbial groups has been proposed as a future basis for establishing criteria for the evaluation of forest ecological condition, soil, or water ecosystems.

The Muir Woods redwood (*Sequoia sempervirens*) forest near San Francisco, California, USA has been maintaining an ecological balance throughout centuries. The wood trunks have accumulated atmospheric carbon bound to the macromolecular cellulose (Fig. 34.3). Other minerals and trace elements have been

Fig. 34.3 Redwoods (*Sequoia sempervirens*) in Muir Woods, California, USA (Photo: Elias Hakalehto)

circulated in a seasonal cycle of degrading organic materials of coniferous origin. This unchanging ecological balance in the redwood forest is based on balanced microbial ecosystems in the soil. When the woods were exploited, this “destroyed ground cover plants and compacted the soil so severely that in places vegetation has not returned to this day” (Morley 1991). This is an indication of the close association and interdependence of forest plants with soil microbes. Correspondingly, in a Finnish forest the reoccurrence of *Basidiomycetes* macrofungi is a long process during the reforestation of agricultural lands. This observation reflects the relatively slow build up and completion (or sophistication) of the balanced microbiological ecosystem in the forest. At present, the delicate and fragile understory vegetation and soil qualities are preserved in the Muir Woods redwood forest by restricting touristic movements to the main trails in the protected area.

It has been stated about the coast redwood: “Possessing a regenerative life force probably greater than that of any other tree, the coast redwood (*Sequoia sempervirens*, evergreen sequoia) is indeed a wonder of the plant kingdom. Its longevity, size, method of reproduction and resistance to decay are remarkable.” (Morley 1991). Natural, restricted fires “open new areas to the sun, convert ground litter into fertilizing ash, and kill insect infestations.” Otherwise, in the Autumn, redwoods shed a few needles in a random pattern. Each discarded branch contains several years’ growth. “Other tree species such as maple and alder leaves begin to drift downstream and collect behind fragile dams of redwood needles.” This annual return of minerals and trace elements, as well as organic debris, maintains the microbiological balance of the forest soil, which is a prerequisite for redwood growth and binding of CO_2 into organic matter. Consequently, the regenerative force behind the redwood trees is actually their long-lasting association and cooperation with microbial communities, where the balance is highly sophisticated and vulnerable to human disturbances. As a result, it can be deduced that detailed analysis of the soil microbes can be used for evaluating the status of the ecosystems, as well as their recovery from human impacts (or adaptation to them). This kind of research has been carried out (Vasconcellos et al. 2013).

34.4 Microbes in Ecosystems

At borderlines, the distinction between forest soil, air, and water is sometimes hardly possible. There all three phases, solid, liquid, and gaseous, meet without clear distinction. The microbiological activity is often the highest, which becomes evident in the case of flooding waterways (Fig. 34.4).

In contrast with earlier beliefs, the mycorrhizas do not actually fix atmospheric nitrogen (Mikola 1986). It has been concluded that the fixation of atmospheric nitrogen detected in numerous experimentations is carried out by some root or soil bacteria (Van Dijk et al. 1988; Pawlowski et al. 2000). These strains can then be found also in the pulp and paper making process and its effluents (Knowles et al. 1974; Gauthier and Archibald 2000; Niemelä and Väätänen 1982;

Fig. 34.4 Spring flood in River Lampaanjoki, Eastern Finland (Photo: Lauri Heitto)

Gauthier et al. 2000). In particular, such species as *Klebsiella* sp. have been associated with the fixing activity in the nitrogen-poor environment (Roberts et al. 1978; Temme et al. 2012). One third of 132 industrial or environmental *Klebsiella* isolates possessed the nitrogen fixing capability (Knowles et al. 1974). The strains from the paper and pulp industries are spread into the waterways, where they may accumulate, as well as the chemical loads. In turn, the chemical pollution accumulated during decades in the form of halogens and heavy metals has been demonstrated to influence the bacterial and diatom composition of different sediment layers (Suominen et al. 1999).

Klebsiellas have a dual role in human pathophysiology, because even though some strains could become pathogenic, members of this genus are also a commensal, or beneficial, members of the intestinal flora (Hakalehto 2013a). It participates in the Bacteriological Intestinal Balance (BIB) initiated by the small intestinal microbiota (Hakalehto 2011a, 2012a, 2013a). The klebsiellas, besides balancing the duodenal pH around 6 together with such mixed acid producers as *E. coli*, also compensate the osmotic pressures caused by excess glucose concentration (Hakalehto et al. 2015). As for fungal mycorrhiza, whether endo- or exomycorrhiza, their role in soil is related to the increase of the uptake of immobile nutrients, in particular, phosphorus (P) (Bolan 1991). Moreover, the fungi and microfungi have a vast number of enzymatic reactions in the soil and in the proximity of the plant roots. It could be postulated that zones of enhanced hydrolytic activity are formed around the hairy roots of many plants. It is also possible to determine the nature of the interactions between the plants, fungi, and bacterial strains, such as *Klebsiella* sp. An important part of the biological fixation of atmospheric nitrogen occurs in the root nodules of specific plants (Triplett 2000).

A considerable amount of N_2 is cycled in this way by some trees (Werner and Müller 1990). The nitrogen-fixing bacteria fix the atmospheric nitrogen, which balances the C/N ratio in soil or in water, and the carbohydrates produced or modified there, either:

1. By photosynthesis of the plants by their surfacing parts, which produces easily exploitable sugars also for the root cells and the associated micro-organisms,
2. As a result of the activities of fungal and bacterial degrading enzymes in the rhizosphere, or
3. By enhanced microbial metabolism around the roots, and symbiotically in the root nodules.

In this chapter, we wish to raise the curtain in front of the microbial action in the water polluted by increasing mining industries, as well as in the dark sediments of the lakes. For illustrations of the Finnish microbial ecosystems, see Fig. 34.2. This contribution of micro-organisms in the huge cycling of water and elements ultimately reflects onto our health. If the soil is healthy, it grows healthy food. If water is pure, it cleans the earth and our body system (with the aid of microbes). If air is clear, it is safe for respiration. In turn, if the ecosystem is diseased, it emits diseases.

The macro- and microscopic structure of soils receiving the circulating water as rainfall maintains a specific kind of microflora. In order to be preserved in these conditions, microbes need to establish biofilms. These biofilms are often well structured layers with versatile biological activity and interspecies biochemical regulation of the metabolic action. For example, cometabolism occurs as a result of the joint activity of different microbes (Dalton and Stirling 1982). This kind of joint action makes it possible to achieve degradation of substances, which would not otherwise be decomposed or utilized by any single microbial strain alone. Thus, even the most robust recalcitrants are decayed by the microbes and their elements returned to the cycles.

In the case of bioremediation of soil contaminated with hydrocarbons, the potentially active microbe strains have been listed on the basis of earlier reviews by Chikere et al. (2011). These bacterial genera include:

Achromobacter, *Acinetobacter, Alcaligenes, Arthrobacter*, *Bacillus*, *Burkholderia*, *Collimonas*, *Corynebacterium*, *Dietzia, Flavobacterium, Gordonia, Micrococcus, Mycobacterium Nocardia*, *Nocardioides*, *Pseudomonas*, *Ralstonia*, *Rhodococcus*, *Sphingomonas*, and *Variovorax*,

whereas the hydrocarbon-degrading fungal flora consists of:

Aspergillus, *Candida*, *Cunninghamella*, *Fusarium*, *Mucor, Penicillium*, *Phanerochaete, Rhodotorula*, *Sporobolomyces* and *Trichoderma*.

The bioremediation is a good example of the stabilizing influence of micro-organisms in the ecosystems. The environmental effects of the oil drilling accident in the Gulf of Mexico in 2010 have been demonstrated on the level of microbial communities (Kostka et al. 2011). During a recent geochemist conference in Florida at the end of August 2013, Professor Joel Kostka, a microbiologist from Georgia Institute of Technology in Atlanta, concluded with some more recent research evidence: “Oil is a natural product, made of decayed plants and animals, and so is similar to the normal food sources for these bacteria. But because oil is low in nutrients such as nitrogen, this can limit how fast the bacteria grow and how quickly they are able to break down the oil. Our analysis showed that some bacteria are able to solve this problem themselves – by getting their own nitrogen from the air.” He also stressed the possibilities for supporting the natural microbial clean-up processes.

34.5 Microbes Take Part in the Cycles of Elements

The global status of forest soil, and equally the agricultural or arable soil, influences both global food production and biomass yields for other purposes (Dalhqvist 2013). A matter of such relative importance would give reasons enough for developing methods for assessing soil nutritional and ecological qualities on the basis of its microflora status and composition. In different climates, the importance of that information relates to the objectives of producing biomass for energy and biochemicals (Dalhqvist et al. 2013; Hakalehto 2015).

Natural carbon and nitrogen circulations involve similar conversions of various redox states on the organism level (Capone et al. 2006). Only 0.05 % of the carbon is circulating in biological cycles, water, or the atmosphere. The majority of global carbon is bound into the lithosphere. In contrast, a major part of nitrogen is stored in the atmosphere as molecular nitrogen, N_2. Microbial enzyme systems are largely responsible for returning this nitrogen into circulation (Ferguson 1998; Einsle 2011). The role of different elements in the living cells and their circulation in nature is a background for studying the ecosystems and understanding the broad concept of bacterial and microbial indicators in them.

In Nature, a vast majority of sulphur resides in inorganic form. In addition, sulphur is a biochemically important element in many proteins, influencing their structure and function. Microbes reduce sulphate to sulfide for their energy production. This is carried out in anaerobiosis by many bacteria. Sulphur deposits are also concentrated into the lake sediments, where it increases eutrophication in certain circumstances (Hasler and Einsele 1948). This kind of eutrophication has been reported, e.g., in a Finnish lake ecosystem (Saarijärvi et al. 2013). The potential of lake sediment to release phosphorus under various sulphate concentrations has been studied with the PMEU (Portable Microbe Enrichment Unit), which is illustrated in Fig. 34.5.

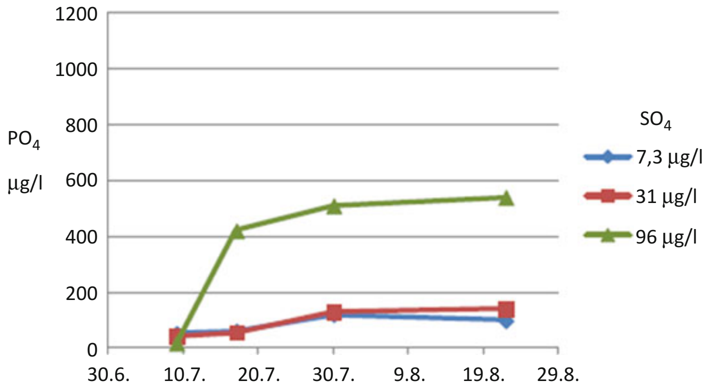

Fig. 34.5 The effect of sulphate concentration originating from an active mining site in Finland on the liberation of phosphorus from the river or lake sediment

34.6 Microbial Structure and Metabolism as a Tool for Survival and Transmission

The fungal hyphal structures and their larger surface areas give them a "competitive edge" when compared with bacterial flora. However, the bacteria transfer genetic elements between strains and species, which allow them to achieve novel degradation or metabolic activities. This originally environmentally important capability can influence even human pathobiology. Since the seventh pandemia of cholera caused by *Vibrio cholerae* El Tor variant in 1961, the pathogenic strains of cholera bacteria have been using the 2,3-butanediol (butylene glycol) route of fermentation instead of the mixed acid fermentation associated with the earlier pathogenic strains (Yoon and Mekalanos 2006). The explanation for this switch of the main metabolic reaction sequence could be related to the better survival of the strains inside the human body by improved ability to utilize sugars without acid production. This capability could offer the strains also protection against osmotic pressure caused by high sugar concentrations (Hakalehto et al. 2015). In the case of *Vibrio* sp., *V. cholerae* MSHA (Watnick et al. 1999), together with such species as *V. parahaemolyticus* (Shime-Hattori et al. 2006), was shown to possess a biofilm forming type IV fimbriae. In fact, the production of 2,3-butanediol could assist the *V. cholerae* El Tor strain to grow and metabolize in the intestinal chyme, and onto the biofilms formed there on food particles (Hakalehto and Jaakkola 2013). In this study, the active role of the crushed seed particles in the intestinal chyme as platforms for the attenuating activity of minor lactic acid bacterial toward otherwise dominating intestinal enterobacterial and other flora was demonstrated by experimentation using the PMEU Spectrion®.

In the distribution and dissemination of pathogenic bacteria in the intestines, fimbriation plays a central role (Hakalehto et al. 2007). The SSY01 mutant of *V. cholerae* failed to develop biofilms when utilizing *N*-acetyl-d-glucosamine as a carbon source (Yoon and Mekalanos 2006). This reflects the disability of this strain to grow on chitin in certain aquatic environments, and it was concluded that the strains of classical biotype would be similarly defective as compared to those of El Tor in growth in any environmental niche that is rich in chitin or other metabolizable carbohydrates.

34.7 Microbes in Water and Soil

The microbes in the soil are eventually flushed away and become water-borne microorganisms. In waterways they continue to fulfill their role in the circulation of matter. Hence, many aquatic microbial ecosystems possess features of the terrestrial ones. These communities are found in water plants and animals, in sediments, and in particles transported with the water. Human wastes bring another category of contamination into water, as agriculture, municipalities, and industries leak their effluents, treated or untreated, into the waterways. In some cases, technological exploitation of water and the natural hydrological flow pattern has been combined, as in the Niagara Falls between the US and Canada, where one half of the water in channeled through turbines in order to produce electricity (Fig. 34.6). Whatever the human contribution, the microflora has to adapt to it, and in Nature it also buffers, or attenuates, the human interference.

Fig. 34.6 Niagara Falls transfer water, energy and flow of microbes downstream (Photo: Elias Hakalehto)

In fact, it is highly likely that in the human digestive tract the principles of microbial action could resemble the activities occurring in larger environmental ecosystems. In trials with facultative *Escherichia coli* and *Klebsiella* strains, the high efficiency of these strains in removing toxic cadmium from industrial effluents was detected (Haq et al. 1999). Since these facultatives are active members in the duodenal flora taking part, e.g., in the pH adjustment (Hakalehto et al. 2008), as well establishing the foundation for the BIB (Bacteriological Intestinal Balance) (Hakalehto 2011a, 2012a, 2013a), it can be assumed that their role in the human alimentary tract could extend to the elimination of such toxic substances as heavy metals. This link demonstrates the extent to which we are connected with our environment via the microbes. Correspondingly, the microbes protect our health and the environment in a similar fashion.

In microbiological studies on minerals in alpine glaciers, a novel species belonging to the genus *Pedobacter* was described (Margesin et al. 2003). A facultatively psychrophilic, Gram-negative, aerobic, rod-shaped strain, with temperature optimum of 15 °C for hydrocarbon degradation and protease activity, was isolated, having the temperature range of 1–25 °C. This strain also possessed activities of oxidase, catalase, DNAse, protease (gelatin, casein), amylase, beta-glucosidase, beta-galactosidase, and beta-lactamase. This metabolic repertoire indicated that a wide variety of organic matter recycling activities can occur in cold climate conditions. In fact, the ability of the environment to function normally, and to recover such imbalances as those caused by oil accidents, for example, is highly dependent on the versatility and capabilities of the natural microbial flora. This species was designated as *Pedobacter cryocognitis*.

Another species of this genus, namely *Pedobacter roseus*, was isolated from the more mesophilic conditions of a freshwater pond (Hwang et al. 2006). Its temperature range was 5–33 °C, with an optimum between 25 and 30 °C, and the pH range for growth was 6–8. The latter shows clear preference for natural water as such. The isolation of another species, *Pedobacter jeongneungensis*, with rather similar requirements, from Korean forest soil (Jung and Park 2012) indicates the relationship between the forest soil and the water leaching or flushing it and finally ending up in the waterways. In general, the determination of species as a taxon is more complicated in the bacterial world than in case of the eukaryotes. However, it is possible to characterize the microflora and its composition as an indicator of the status of both the water and soil ecosystems.

34.8 Indication of Microbial Behavior in the Wetlands

As indicators of wetland integrity, microbial communities have several beneficial characteristics as biological indicators (Adamus and Brandt 1990):

- Microbial communities are involved in many fundamental processes (e.g., decomposition, denitrification, respiration)
- Microbial samples are easily collected and transported, but also the decreasing quality due to inactivation of strains has to be taken into account

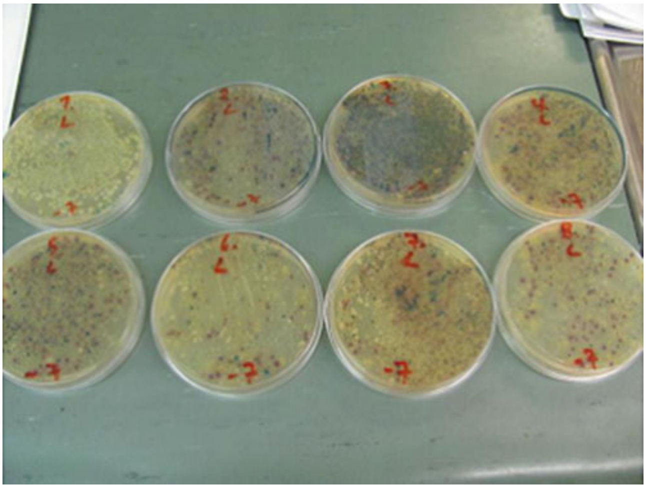

Fig. 34.7 Samples of PMEU broth cultures inoculated on ChromagarTM plates after 8 h of cultivation of rumen content in TYG (tryptone, yeast extract, glucose) plates. Pink colonies are likely to be *E. coli* growth, and a part of the blue ones of *Klebsiella* origin used for inoculating the pre-enrichment broth. The variation in the different types of the indicator bacteria in samples originating from the same source can be seen (See also text; Photo: Kevin King)

- Microbial communities are sensitive and give an immediate response to human influences
- Microbes are measurable in wetlands year-round (in northern climates even under ice), and in wetlands that lack surface water
- Microbes are sensitive to the presence of some chemical contaminants, and assay protocols are available (e.g., Ames test, Microtox test)
- There is sufficient published scientific information to identify a few "indicator taxa" associated with particular stresses.

When any microbiological sample is pretreated with distinctive methods, the results of the analysis vary accordingly. In Fig. 34.7, various samples with *Klebsiella mobilis* as the "internal control" were inoculated into the rumen contents and in the cow house waste water in the PMEU. After a brief 8 h enrichment at 37 °C, further samples were plated on Petri dishes. Regardless of the equal inoculation with full grown *Klebsiella* inocula (approximately 100,000 bacterial cells each), the final counts differed. The klebsiellas were diluted out in some cases, whereas they became dominant in some others. The natural background level of *E. coli* both in the rumen contents and in the cow house waste water was about 30 million cells per ml. Different pretreatments were: (1) Rumen content hydrolyzed overnight with cellulolytic enzymes at 50 °C, *Klebsiella* inoculation, diluted 1:3 with sterile water before PMEU cultivation; (2) as No. 1, but with cow house waste water; (3) Rumen content hydrolyzed 2 h with cellulolytic enzymes at 50 °C, *Klebsiella* inoculation, diluted 1:3 with sterile water before PMEU cultivation; (4) as No. 3, but with cow house waste water; (5) Rumen content hydrolyzed overnight with cellulolytic enzymes at room temperature, *Klebsiella* inoculation, diluted 1:3 with sterile water before PMEU cultivation; (6) as No. 5, but with cow house waste water; (7) Rumen content hydrolyzed overnight with cellulolytic enzymes at room temperature, without *Klebsiella* inoculation, diluted 1:3 with sterile water before PMEU cultivation; (8) as No. 7, but with cow house waste water.

In this experiment, the dependence of hygiene indicator numbers on the conditions in the waste material in the different environments is demonstrated (Fig. 34.7). It seems that replacing the waste water with sterile water somewhat diminished the enterobacterial count in all other sample pairs, but not in the case of enzymatic pre-treatment overnight at elevated temperature (Sample 1). This could be an indication of the attenuation of these members of *Enterobacteriaceae* growth in the presence of certain lactic acid bacterial strains as observed recently (Hakalehto and Jaakkola 2013). In the case of Sample 1, the bacterial growth when diluted in sterile water was mostly caused by strains other than the enterobacterial ones. These strains originate from rumen, and the mechanism of their distribution in most hydrolysed sample material reflects the other strains outgrowing *E. coli* and *Klebsiella*. The PMEU studies with the latter have been recently summarized by Hakalehto (2013a). The *E. coli* research with the PMEU was summed up first 2 years earlier (Hakalehto 2011a). The interactions of these two coliformic groups is the basis for the intestinal (duodenal) pH regulation, and the entire gut microflora composition and functions (Hakalehto et al. 2008). These groups are, as universal symbionts of intestinal tracts, also important hygienic indicators, and they have been automatically monitored in water departments (Hakalehto et al. 2013c).

When studying the aquatic ecosystem during winter in Lake Sysmäjärvi in Eastern Finland, it was detected that under the icy landscape at temperatures down to −30 °C some mud layers remained unfrozen (Fig. 34.8). The reason for this higher temperature, and pH values of one magnitude higher than in the nearby lake, was the bacteriological activity occurring in the mud. Such organic compounds as acetate, propionate, and butyrate, as well as ethanol, were produced in the mud in proportional concentrations resembling those in the cow house and slaughterhouse waste, although the concentrations in the latter biomass were approximately 10,000 fold when compared to the unfrozen mud at 1.8 °C under the winter snow belt (Hakalehto et al. 2015). This indicates the common mode of action of the environmental microbiota and the waste microbe population.

34.9 Floods and Other Climatological Influences on and Deriving from the Microbes

The microbial content of natural water is changeable. It is influenced by internal factors related to, e.g., the movements of water masses, reactions inside the sediments and between the sediment and free water, and activities of higher

Fig. 34.8 Lake Sysmäjärvi in Eastern Finland (Photo: Elias Hakalehto)

organisms as the water plants (and also microbial algae) bind carbon and energy into biomasses and produce oxygen in the photosynthesis. Various flowing substrates and microbial loads are derived from human sources, such as agriculture and forestry, industries, and municipalities. Microbiological streaming of water (or air) does not recognize state borders. To evaluate the human factor, we need to consider some of the sources of the inputs. Many plant pathogens of bacterial origin are airborne. For example, various *Streptomyces* strains cause potato common scab (Hiltunen et al. 2009; Hiltunen 2010). This plant disease is associated with humid weather conditions and increased rainfalls. In the case of barley kernel microbiological load by molds, the amount of rains (snowfall) in March had the highest positive correlation with the contamination level in autumn time (preliminary studies of the author as a research trainee at the State Research Centre of Finland. VTT, during 1982–1983). This implies long-term consequences of the weather conditions on microbial populations.

Variations in weather are interdependent of the anthropological influences. We stare at the skies to foresee the weather. However, even in natural conditions the weather results from climatological factors, which could be influenced by microbial action. This is illustrated by the global impacts of the giant viruses, giruses, in the oceans (van Etten 2011). They regulate the amount of phytoplankton by destroying its cells. This action liberates organic matter into the sea water, which is then evaporated as organic sulphur compound, DMS, whose increasing atmospheric concentration provokes rains. For illustration, see Hakalehto and Heitto (2012) where the consequences of microscopic events in a larger scale are underlined. Besides the climatological effect, the giruses have an influence also on the biological systems in the oceans, as well as on geological formations, since the breakage of the plankton cells liberates calcium carbonate, which accumulates onto the rocks (e.g., the famous white cliffs of Dover) (van Etten 2011). Consequently, how our activities manipulate the microbial ecosystems and their relations with the circulation water, and of carbon and other elements, is not meaningless.

Concentrations of various micro-organisms are dependent also on the dilution with water in natural ecosystems. On the other hand, floods detach soil and its microbes, thereby changing the composition of water microbiota. In addition, the risks of increasing emission of pathogens into flood water are existential (Baig et al. 2012). In rural Pakistani villages, *E. coli*, *Salmonella*, *Shigella*, and *Staphylococcus aureus* were liberated into the streaming water due to the damaged water and environmental sanitation infrastructure. Therefore, continued water quality monitoring, boiling of the raw water, application of household based disinfectants, as well as healthy domestic hygiene practices are advisable precautions in corresponding circumstances. The simultaneous monitoring of indicator species and pathogens is also recommendable (Hakalehto and Heitto 2012).

34.10 Effect of Mining Industries on the Microbiological Balance of the Waterways

Intensive mining industries are threatening vulnerable ecosystems, e.g., by changing the natural cycles of minerals. These effects are often caused by changed microbiological activities and balance in the water environment. In mineral deposits, Natural microbial populations occur and also get flushed into the water flow. In PMEU Spectrion® experiments with mineral calcium carbonate sludge, aerobic bacterial growth was recorded in about 10 h after the onset of cultivation (Hakalehto 2015). The bacterial strains were identified as *Bacillus* sp. Corresponding strains are often found also in the paper and pulp industries, where they are inoculated from the soil-derived minerals used in the processes (Mentu et al. 2009). In an environmental study with water and sediment, using samples taken downstream from a mine in Finland, the behaviour of the ecosystem was simulated in a PMEU during several months (Fig. 34.9). It was found out that increased sulphate concentration in polluted natural water liberated phosphorus from the sediment (Fig. 34.5)

34.11 Industrial and Municipal Microbiological Pollution

In the case of several water users, issues regarding the origin of pollution often arise. These are often public and even legal matters, which underlines the requirement for prudent, reliable methodology for source-tracking microbiological contamination.

Fig. 34.9 Different work phases in the experimentation for simulating the sediment microbial activity using the PMEU cultivation (Photos: Anneli Heitto)

A realistic picture of the magnitude of the environmental stresses is often urgently needed for finding the right and effective countermeasures for eliminating the risks of spoiling the waterways in the course of several years of accumulating loads of effluents. In an economic consideration, it was concluded that monitoring the microbiological situation is usually cheaper in the long run than remedying the results of negligence (Jääskeläinen 2007). Thus, all the impacts of pollution on public health, industries, fisheries, tourism, etc. were taken into account. For example, factories disseminate the strains into natural waters (Fig. 34.10).

As a consequence of the water crisis in 2007 in the town of Nokia in Western Finland, a nationwide Polaris Project was initiated for developing means for preventing such accidents. Then, the municipal wastewater tubes were unintentionally connected to the clean water distribution system. As a result, there were outbreaks of bacterial, viral, and protozoan diseases, and more than 10,000 people became ill, some of them chronically. Many food industries, as well as hotels, were temporarily closed, and local inhabitants and institutions were subjected to water use restrictions during the cleaning up of the damages. In the above-mentioned Polaris Project, the Coliline PMEU™ (Berner Oy, Helsinki, Finland) with ASCS

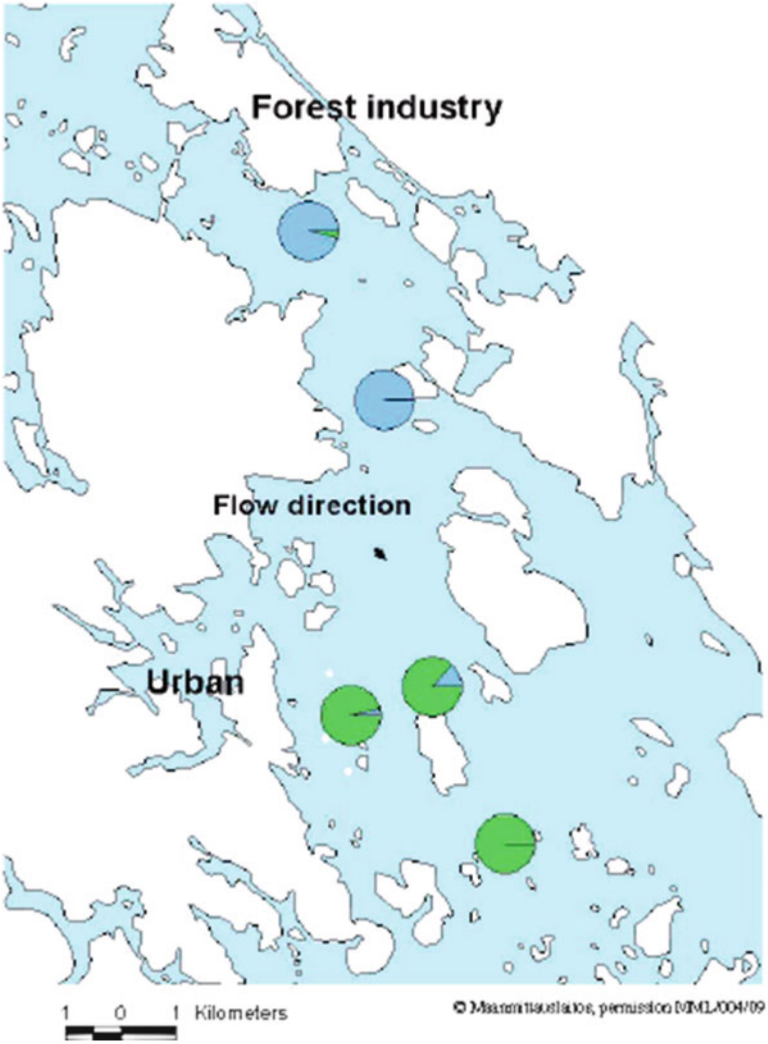

Fig. 34.10 Proportion of enterococci cgf-group (*blue*) and *E. faecalis*/*E. faecium* (*green*) in Lake Kallavesi near forest industry and urban sewage treatment plants (Heitto et al. 2009)

(Automated Sample Collection System) was tested as an early-warning system for microbial contamination at the water department (Heitto et al. 2012; Hakalehto and Heitto 2012). This system was validated for water hygiene monitoring based on the detection of *E. coli* and other coliforms by the State Research Centre of Finland (Wirtanen and Salo 2010). The Colilert™ medium (IDEXX Laboratories Inc., Westbrook, Maine, USA), which is based on the same principle, has also been used for fast and automated monitoring of coliforms in different PMEU versions (Hakalehto et al. 2013c).

In order to source-track the contaminations in natural waterways, a PMEU method was developed for field use for separating fecal and industrial enterococcal strains in Lake Kallavesi in Central Finland (Heitto et al. 2009). The distribution of fecal species of municipal origin and the cgf-strains from the pulp factory was mostly confined to the proximities of sources of the corresponding effluents (Fig. 34.9).

34.12 Verification of Indicator Bacteria and Pathogens

All phases in the environmental air, water, and soil form vector matrices for the dissemination of the microbial diseases. Besides that, communicable diseases are spread from man to man, or between animals and man (the zoonoses) (Armon and Cheruti 2012). Besides human agricultural, other food and industrial products can serve as vehicles for transmission.

In water microbiology, some microbes or groups of microbes have become the standard indicators of microbiological water quality. Some of the most common microbial indicators of fecal contamination are:

– *Escherichia coli*
– Fecal enterococci
– *Clostridium perfringens*
– F-specific bacteriophages (see Chap. 35)

Some other important groups of microbes indicating the hygienic quality of water are:

– Heterotrophic micro-organisms
– Coliformic bacteria
– Somatic coliphages
– *Pseudomonas aeruginosa*

These various indicators have somewhat different uses as indicators. For example, *Pseudomonas aeruginosa* can indicate the microbe load of chemically contaminated, hospital or recreational, or industrial water, since this particular bacterium is rather resistant to chemical stresses (Mena and Gerba 2009). However, it is not anaerobic, and in the sediments, the pollution could be monitored better by screening the presence of *Clostridium perfringens* (Sterne and Warrack 1964). Sediments play an important role in the river basin and offer a variety of habitats to many aquatic microorganisms, among which clostridia are indispensable for many symbiotic and pathogenic relationships with higher organisms (Mancini et al. 2008). Therefore, the clostridial communities have proven to be the most suitable microbiological indicators for characterizing the ecological quality of sediments. Therefore, the European Water Frame Directive 2000/60/CE requests the creation of a net for holistic sediment studies (SedNet) (European Parliament and the Council).

The most widely used standard hygienic indicators are perhaps fecal coliforms, especially *E. coli* (Heitto et al. 2012). Automated monitoring experiments of this bacterial group have been carried out in the Finnish water departments before and during the national Polaris project using the PMEU (Hakalehto et al. 2011, 2013c). The presence of a single *E. coli* cell in water was documented by the PMEU Spectrion® in 10 h in a validation study carried out by the Finnish State Research Centre (VTT) (Wirtanen and Salo 2010). Its presence in water samples should be estimated taking into account the risk of lost information as a consequence of inactivated bacterial cells. Therefore, more advanced methods for sampling and recovery are warranted. In the case of isolating enterobacterial strains from fecal samples, it was found out that PMEU enrichment produced 2.6 times more individual strains than direct plate culturing (Pesola and Hakalehto 2011). In the case of monitoring urinary tract infection by *E. coli*, the contamination was verified in 3–4 h by PMEU Scentrion® detecting the volatiles liberated from the bacterial metabolism (Pesola et al. 2012). This device documented the growth caused by a single *Salmonella* sp. cell from a tap water sample in about ten hours, even with the selective medium (RVS broth) (Hakalehto et al. 2011).

In large sample volumes and in continuous monitoring, the importance of automated systems is emphasized. A Coliline PMEU™ system with ASCS (Automated Sample Collection System) has been used with Colilert® for monitoring municipal raw water before pumping into the tube network (Heitto et al. 2012; Hakalehto and Heitto 2012; Hakalehto et al. 2013c). In principle, the microbial load of the sample was detected in about 4–5 h, and the water was automatically disinfected by a dispenser before it was pumped into the distribution network in test conditions.

Besides the Coliline PMEU™, other devices and systems have been developed for the fast detection and monitoring of coliformic water contaminations (Tryland et al. 2002; Zuckerman et al. 2009). The PMEU technology offers means for monitoring heterogeneous bacterial contaminations (Hakalehto et al. 2011, 2013c; Heitto et al. 2012; Hakalehto and Heitto 2012). In the case of the water distribution system of the city of Kuopio in Eastern Finland, almost 30 preliminary alarms were obtained from a weekly surveillance during a one-month period with the PMEU, whereas by the routine method, only a couple of early warnings were given (Hakalehto et al. 2011). In waterways, methods based on the measurements of such parameters as antibiotics or caffeine in water have been successfully developed to indicate fecal contamination (Sauvé et al. 2012). The relationship between the rate of β-D-glucuronidase hydrolysis (GLUase-HR) and the *E. coli* concentration may provide a rapid alternative technique for estimating *E. coli* concentrations in fresh water (Farnleitner et al. 2001).

The indicators are often considered as signs of the potential presence of more pathogenic bacterial or other microbial species. In the course of developing methodology, it is inevitable that efforts will be made to survey various pathogens themselves. For example, by combining the enrichment of campylobacteria in the PMEU with realtime PCR, it was possible to achieve the detection of water contamination by these pathogens in about 5 h only (Pitkänen et al. 2009; Pitkänen

2010). In the case of artificially contaminated tap water, single cells of *Salmonella* were verified in about 10 h by PMEU Scentrion® detecting the emission of microbial volatile organic compounds (voc's) (Hakalehto et al. 2011). In a more recent study, the detection of environmental mycobacteria by enrichment in the PMEU was reduced to 1–4 days (Hakalehto 2013b).

For the case of developing a biotype-based indication of emerging strains, we can use *V. cholerae* as an example. The novel pandemic strain El Tor can be identified on the basis of PCR results, as the biotype-specific DNA sequence differences in the gene encoding TcpA, a structural component of toxin-coregulated pilus (fimbriae), have been used to differentiate El Tor strains and classical strains by simply comparing the sizes of the PCR products (Taylor et al. 1988; Keasler and Hall 1993). Besides the O1 serotype of *V. cholerae*, where the classic and El Tor subtypes originally were found, also the O139 serotype was responsible for later epidemics and also detected by its genetic traits related to transmittable elements in a filamentous bacteriophage CTXΦ encoding the cholera toxin (Waldor and Mekalanos 1994). This movable genetic marker, together with a capability to produced toxin-regulated pili (fimbriae), is then required for full virulence. The strain O139 possesses the same neutral end products-producing capability as the earlier El Tor isolates (Yoon and Mekalanos 2006). Also, spherical FK and type IV phages have been suggested for typing these pandemic strains (Takeya et al. 1981). The case where the cholera-causing agent was classified and characterized illustrates the power of molecular biology in studying the epidemics and distribution of pathogenic bacterial strains.

Besides *Campylobacter* ps. and *Salmonella* sp., other pathogens, such as members of the genus *Mycobacterium*, isolated from water, have been verified using the PMEU technology (Hakalehto 2013b). The *Mycobacterium* sp. strain isolated from river water by the Finnish Institute of Health and Welfare gave a clear indication of growth on a liquid medium in the PMEU Spectrion® in 2 days (Fig. 34.11), *M. marinum* in 2–4 days, and the faster growing *M. fortuitum* strain in 10–11 h only. The effective gas exchange in the PMEU cultivation units produced the vigorous growth of these normally slow-growing organisms. Many of these mycobacterial strains are water-borne pathogens.

In microscopic examinations, capsular structures were observed, e.g. around the *M. marinum* cells, protecting them from host immunoresponses and other defenses (Fig. 34.12). This molecular shield is especially important for many mycobacterial pathogens because of their slow growth pattern. Multiresistant strains constitute 5 % of all *M. tuberculosis* infections in India, and 20 % of the renewed cases (Mahr 2013). Their eradication is one of the big challenges for environmental health and clinical specialists globally. In the case of the clinical investigations for revealing *M. tuberculosis* from sputum specimens, a semiautomated laboratory robot system (BACTEC-460® by Becton Dickinson Microbiology Systems, Sparks, MD, USA) was compared with two liquid medium systems, namely, MB Redox tube (Biotest AG, Dreieich, Germany, or Biotest Diagnostics Corporation, Danville, NJ, USA) and MGIT® (Mycobacteria Growth Indicator Tube) (Becton Dickinson). The recovery of strains when using these methods was 92.2 %, 80.5 %, and 63.6 %, respectively, in comparison with a plate culture method (Heifets et al. 2000).

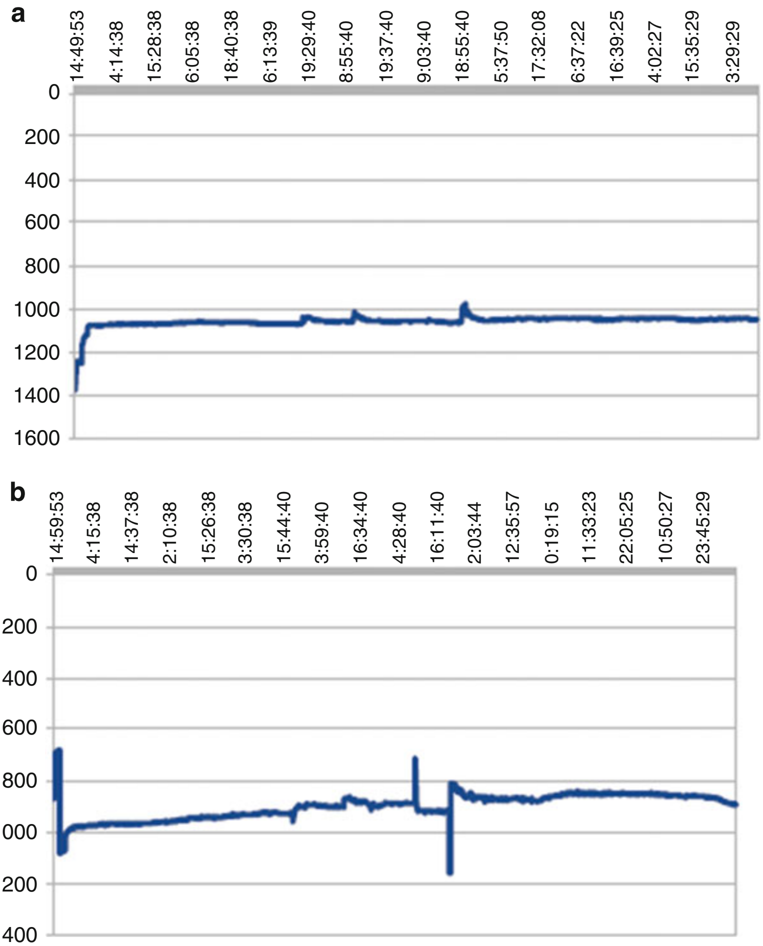

Fig. 34.11 (**a**) The stagnant culture of *Mycobacterium marinum* did not demonstrate any growth, whereas the (**b**) enhanced cultivation in the PMEU Spectrion® produced a clear indication of *M. marinum* in about 2–3 days

In addition, other *Mycobacterium* species besides *M. tuberculosis*, such as *M. avium paratuberculosis*, have been causing severe human infections (Eltholth et al. 2009). Many of these strains are isolated from drinking or natural water or food, where they constitute a significant health hazard (Collins et al. 1984; Kvaeska and Hruska 2010). They are often particularly persistent under various purification methods (Best et al. 1990). In preventive clinical and environmental microbiology, it is of essential importance to speed up the verification of the multi-resistant *Mycobacterium* sp., the analysis of which presently requires a couple of weeks (Åjders-Koskela and Katila 2003). Their fast detection with the PMEU equipment seems to be possible on the basis of the above-mentioned enhanced enrichment and detection results (Hakalehto 2011b, 2013b).

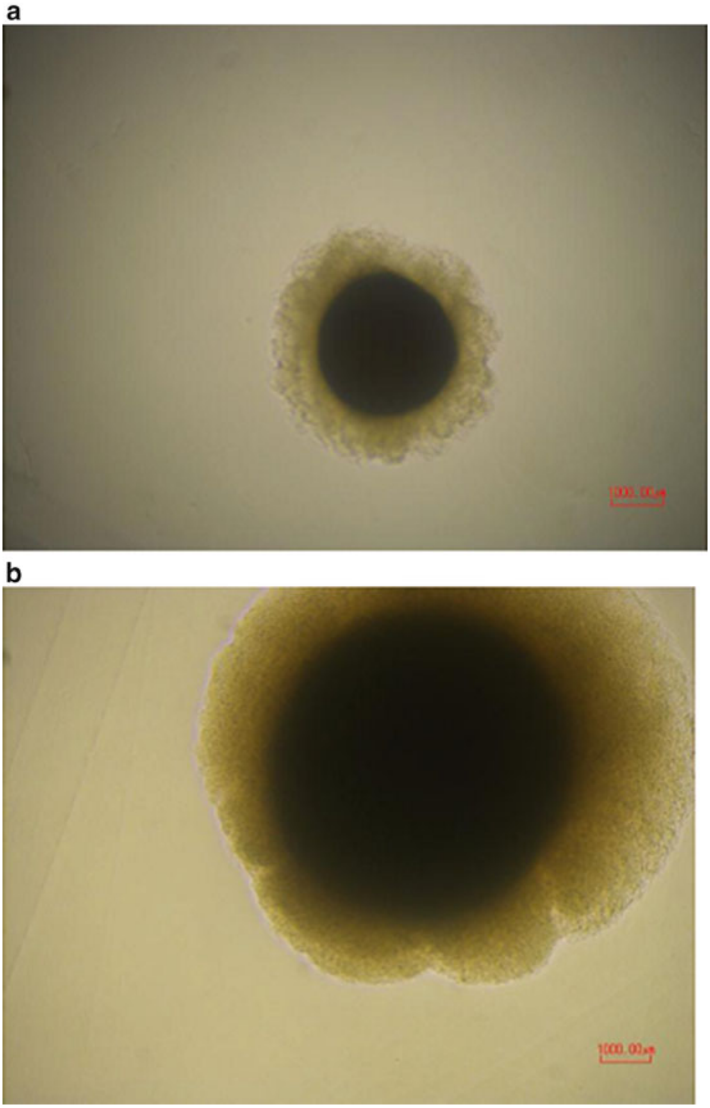

Fig. 34.12 (**a**) *Mycobacterium marinum* and (**b**) *Mycobacterium* sp. (a river isolate) plate cultures after inoculation by pre-enrichment broth from the PMEU. The colonies are surrounded with capsular material (Photos: Anneli Heitto)

Essential improvements are needed for the detection of the antibiotic-resistant strains among the bacterial isolates. These markers have been successfully screened in *Enterobacter cloaceae* septic strain originating from hospital equipment using the PMEU Spectrion ® (Hakalehto 2011b). In 2012, the first *Klebsiella pneumoniae* strain coproducing NDM-1, VIM-1 and OXA-48 carbapenemases was isolated in Morocco (Abouddihaj et al. 2013). In Finland, the occurrence of ESBL strains, a group consisting of facultative coliformic strains with multi-resistance, has been increasing, even though the prevalence of MRSA has decreased in the healthcare system (Hakalehto 2011b).

34.13 We Want to Solve the Equation with the Microbes

In order to understand the essential role which the microbes play in every ecosystem, we need methods to:

1. Detect them
2. Enumerate them
3. Characterize the strains
4. Follow up the trends
5. Simulate the natural interactions and man-made interferences.

Besides returning the organic matter into Nature or into biological fertilization of agricultural land, it will be increasingly important to cultivate the right kinds of microbial cultures for supporting or recreating its fruitful productivity. In this type of activity, the follow up of the microflora development is the primary focus. The soil microflora is

– buffering
– detoxifying
– degrading
– immobilizing

incoming organic and inorganic materials. Its interactions with these water soluble loads can be surprising, e.g., the importance of toxic aluminium for the Austrian forest soil microbial activities (Illmer et al. 2008).

Microbial bioindicators have usually been associated with the detection mainly of fecal pollution (Heitto et al. 2012). By differentiating and typing the contaminating strains, it is possible to carry out source-tracking, as well as to determine the routes of contamination. However, the emissions of microbes into the air and back to earth or water due to climatological phenomena can be strongly affected by man. Moreover, besides more common indicators of specific types of contamination, also more hazardous microbes can be directly screened out by more advanced methodology (Hakalehto and Heitto 2012). For example, the presence of single *Salmonella* cells in artificially contaminated tap water can be verified in 10 h with volatiles measuring PMEU Scentrion® (Hakalehto et al. 2011). This result somewhat equaled the speed of detecting single *E. coli* cells by the PMEU Spectrion®, where the measurement is based on the IR, visible light, or UV fluorescence (Wirtanen and Salo 2010). This study was conducted by the State Research Centre of Finland in order to validate the PMEU method. The automated version, Coliline PMEU™, was used for continuous monitoring of water flow in distribution pipelines (Hakalehto et al. 2013c). This method can be further speeded up by using the gas bubble flow to enhance growth, as in the other PMEU versions. In fact, it was documented that a bubbling CO_2 flow in the PMEU provoked the onset of the growth of many bacteria, such as *E. coli* (Hakalehto 2011a), clostridia (Hakalehto and Hänninen 2012), and the klebsiellas (Hakalehto 2013a).

Some of the facilitators of nearly online monitoring of water microbiological contaminations to be targeted are the following:

– Fast recovery of bacterial and other microbial indicators regardless of possible environmental stress (some of the techniques to facilitate the recovery are indicated in Hakalehto (2012b) for improved online follow up and enrichment)
– Selective growth of the desired organism, whether an indicator or pathogenic species
– Homogenous growth of desired sample micro-organisms
– A sensible and reliable sensor system.

When using PMEU technology, it has been documented that about 2.5 times more enterobacterial cells become viable than with the standard cultivation method (Pesola and Hakalehto 2011). It is possible to type the indicator bacteria, e.g., according to phenotypic (Kühn 1985) or genotypic differences (Farnleitner et al. 2000).

34.14 Microbes, Soil Fertility, and Food Safety

In debates on the "green revolution," the microbiological dimension is often forgotten. The microbes are liberating and upgrading minerals from soils. Agriculture and forestry are based on this quality of the soil. It is not enough to provide all nutrients for plant growth, but for healthy food, all micronutrients should also be adequately included to avoid many important human diseases (Braganza et al. 1993; Bonnefont-Rousselot 2004; Drain et al. 2007; Ylivainio 2009). Inside the arable soil, microbes form ecosystems, whose type is more or less "scattered" (Hakalehto 2012a). In microscale, this means that after consuming the nutrients in its close proximity, a microbial cell turns on the secondary metabolism, or the resting mode. The cycles of elements can be monitored from the surveys of specific types of microbes in earth, OR in the water leaked out of the areas. If the irrigation water contains human or animal wastes, it may cause hygienic problems and lead to the dissemination of pathogenic species. This was observed in Burkina Faso, West Africa, in a joint study of the Finnish National Institute of Health and Welfare with local researchers, and our PMEU developing research group. The contaminated irrigation water could cause the occurrence of epidemics caused by *Campylobacter* sp. and *Yersinia* sp. These pathogens could be isolated from the water, and from the vegetables in the nearby market using the PMEU (unpublished results). The availability of pure water is of utmost importance for societies. It is essential also for healthy animal feed production, which improves general human health (Klintenberg and Verlinden 2008).

Conclusions

We as humans are linked with our environment in many ways. One major "ecological ligament" is our normal flora, which contains species also abundant in many natural ecosystems. Traditionally, the strains that typically represent fecal contamination are considered to be the most useful indicators. This is truly the most direct measure of organic harmful pollution with a risk of disseminating human diseases. Therefore, methods for surveying these indicators, such as fecal coliforms, need to be continuously developed. Besides these environmental health aspects, also human, animal, and plant pathogens need to be monitored using environmental samples. These include such groups as *Mycobacterium* sp., salmonellas, and campylobacteria. However, the systematic anthropogenic effects on the global ecosystem are a still wider issue. Any manmade impacts on water, soil, air, or climate should be investigated also microbiologically, and novel concepts and tools have to be developed for this purpose. Microbial communities sensitively reflect the status of the ecosystem. Besides, they have a central role in its biogeochemical cycles and recovery from pollution.

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Chapter 35
Indicators of Waterborne Viruses

Robert H. Armon

Abstract Enteric viruses excreted by humans and animals may reach water resources and cause large outbreaks. Drinking water is one of the essential global life elements for humanity. However, some of our resources are contaminated with viruses and indicators for continuous monitoring have been developed. The classical ones are coliforms and fecal coliforms that are still the iron standard for water indicator monitoring (see Chap. 34). In the last decades, bacteriophages have been suggested as potential indicators of enteric viruses and many studies showed their potential as such mainly due to their comparable resistance to water processes such as disinfection. In this chapter, the indicator role of bacteriophages in water is critically reviewed and discussed.

Keywords Enteric viruses • Water pollution • Human origin sewage • Fecal-oral transmission • Eneterobacteriacea • *E. coli* • Coliforms • Bacteriophages • F-male specific phages • Somatic phages

35.1 Background

Human enteric viruses, which by definition are transmitted via the fecal-oral route, are the main waterborne group of viruses that pose a real public health hazard (Estes et al. 2006). Thus far, enteric viruses have been divided into eight families (Table 35.1). The most relevant ones are hepatitis A and E, enteroviruses, rotaviruses, caliciviruses, astroviruses, and enteric adenoviruses, which may cause the respective severe diseases: hepatitis, paralysis, meningitis, myocarditis and heart anomalies, fever, gastroenteritis, conjunctivitis, and respiratory disease (Fig. 35.1).

Enteric viruses are excreted in the feces of infected patients (10 % of the population can shed ~ 1×10^6 particles/g of feces, at any given time) and due to contamination of different water sources, i.e., rivers, lakes, effluents, land runoff, estuaries, and groundwater, may infect people via faulty septic systems, sewage outfall, urban and agricultural runoff, wastewater discharge from vessels, and in

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DOI 10.1007/978-94-017-9499-2_35

Table 35.1 Properties and clinical characteristics of major human waterborne and food enteric viruses

Family (genus)	Common name	Size (genome)	Envelope	Incubation/illness duration (days)	Contaminated source	Season	Symptoms
Picornaviridae (enterovirus)	Polio, Coxsachie A & B, echo, human enterovirus (types 68 to 71)	28 nm (ssRNA)	No	4–35/7–14	Water and shellfish	Mostly winter	Cardiomyopathy, meningitis, CNS motor paralysis, gastroenteritis
Picornaviridae (kobuviris)	Aichivirus	28 nm (ssRNA)	No	39 h/2–4	Shellfish	All seasons	Gastroenteritis
Picornaviridae (hepatovirus)	Hepatitis A virus	28 nm (ssRNA)	No	15–50/7–14 (to several months in serious cases)	Food-borne	Late spring to early summer (in Hong-Kong)	Hepatitis
Hepeviridae (hepevirus)[a]	Hepatitis E virus (formerly non- A non-B hepatitis)	34 nm (ssRNA)	No	21–56/7–28	Mainly water	Winter	Hepatitis
Rotaviridae	Rotavirus	70 nm (dsRNA)	No	2–6/5–7	Mainly water		Gastroenteritis (diarrhea)
Adenoviridae (mastadenovirus)	Adenovirus group F, types 40 and 41	100 nm (dsDNA)	No	8–10/5–12	Water and fecal-oral route	No certain seasonality	Mild diarrhea
Caliciviridae (saprovirus)	Saprovirus	34 nm (ssRNA)	No	1–4/6	Shellfish	Mostly winter	Gastroenteritis
Caliciviridae (norovirus)	Norovirus (Norwalk-like viruses)	34 nm (ssRNA)	No	1–3/4	Water and food-borne	Mostly winter	Explosive projectile vomiting
Astroviridae (mamastovirus)	Human astrovirus	28 nm (ssRNA)	No	1.5–2/1–4	Water and shellfish	Mostly winter	Mild gastroenteritis
Parvoviridae	Wollan, ditchling, Paramatta and cockle agents	25 nm (ssDNA)	No	4–14/7	Food-borne (shellfish)	Late summer to late spring	Gastroenteritis
Coronaviridae	Coronavirus and Torovirus	spherical, 120–160 nm diameter (ssRNA)	Yes	2–5/7	Fecal-oral route or by aerosols of respiratory secretions	Winter and early spring	Severe acute respiratory syndrome (SARS) in humans

[a]Emerson (2005)

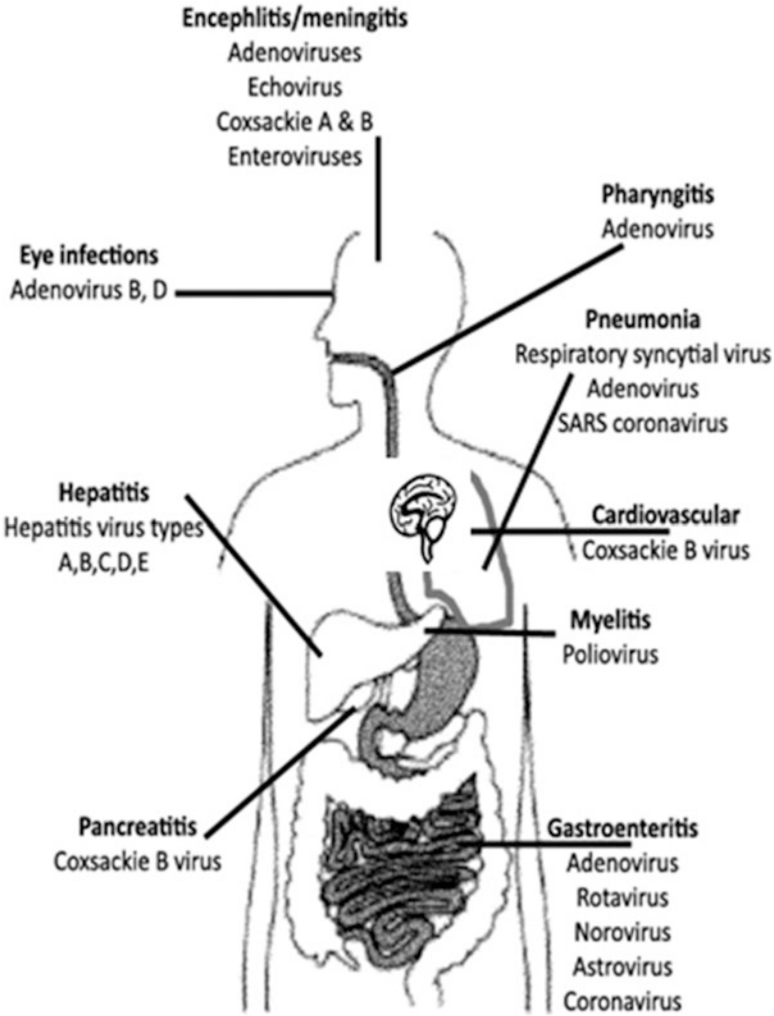


Fig. 35.1 Schematic viral infections in humans and their target organ

most cases, through the use of untreated wastewater for irrigation, typically in less developed countries (Okoh et al. 2010).

Enteric viruses may be transferred in the environment by attachment to particulates present in groundwater, estuarine and seawater, rivers, shellfish grown in contaminated waters, and aerosols emitted by sewage activated sludge processes. Direct human exposure to enteric viruses occurs through various routes, such as irrigation of crops with sewage (intended for water and fertilizers), seafood (shellfish grown in sewage polluted areas), contaminated recreational areas (by means of water sports), and finally, via contaminated potable water. Categorically, studies have shown that waterborne viral disease outbreaks occurred when the following elements were involved: (a) consumption of untreated surface water; (b) consumption of untreated groundwater; (c) insufficient or sporadic water treatment; (d) faulty public distribution network; and (e) miscellaneous (sewage irrigation, contaminated food, aerosols, etc.). Faulty water treatment and distribution systems contributed to > 80 % of global viral outbreaks.

35.2 Viral Indicators

The best way to monitor viral contamination is through direct detection of the pathogens themselves without using indicators as a proxy. However, this task is strenuous as enteric virus detection and growth methods, where infectivity/viability potential may require cultivation and direct manipulation of pathogenic organisms, are still cumbersome, requiring the processing of large volumes of sample-pathogens where frequently they are present in low concentrations, expensive (tissue culture and molecular methods), and finally time consuming (days). On the one hand, the current molecular methods available in different variations are accurate, relatively fast, and continuously evolving; on the other hand, they are still expensive, require specialized equipment, and do not discriminate between live and dead viral particles (at least, thus far).

Consequently, the indicator system is still the method of choice in virus detection in water sources, essentially due to the procedural simplicity. According to Mossel (1982), when categorizing food marker organisms, there are two imminent definitions that ought to be discriminated: "amongst marker organisms two groups should be distinguished....the first one provides information on the risk of occurrence of given pathogens or toxin-formers (not the case of viruses, R.A.)... suggesting the name of index organisms for this group" and "a second group of marker organisms used for the purpose of assessing the risk of inadequate bacteriological quality of a general nature that should be called indicator organisms." As indicated by Mossel (1982), a marker organism "may serve both as an indicator and as an index and even in the same food." Since the present chapter is dedicated to water viral pollution, it will be useful to unify the two definitions, as viruses fulfil both classifications without losing the main denotation. An indicator must meet several prerequisites to fulfil its task, but only a meronym is essential as such (the most essential ones are indicated by bold letters). It should be:

(a) **Stable in the environment and under various treatments (survives as long as, or longer, than the pathogens).**
(b) **Not able multiply outside its host.**
(c) **Ubiquitous (available in fresh and saline waters).**
(d) **Exclusively fecal (present at densities related to the severity of fecal contamination or, in other words, it should be associated with the source of the pathogen and be absent in unpolluted areas).**
(e) **Greater in number/frequency than pathogens.**

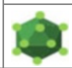
(f) Highly prevalent throughout the year.
(g) Removed by WWT (wastewater treatment plant) close to pathogens.
(h) **Simple and inexpensive to count accurately and reproducibly, that is, its analysis procedure should be easy.**
(i) **Of human or animal origin.**
(j) A "surrogate" for many diverse pathogens.
(k) **Not be pathogenic to humans.**

Historically, the conventional indicators of water microbial and viral pollution, some of which are still valid at present, are *Escherichia coli* (total, fecal, and thermotolerant coliforms), *Enterococcus* spp. (fecal streptococci), and *Clostridium perfringens* (sulphite reducing clostridia or spores of sulphite reducing clostridia). However, questions have been raised about the capability of the above indicators to measure water biological quality and predict waterborne viral diseases, primarily because there is a lack of correlation between these indicators and viruses in water samples (Wyer et al. 1995; Borchardt et al. 2003, 2004), and secondly because enteric viruses are more resistant to natural stressors and disinfection processes than are conventional bacterial indicators (Scott et al. 2003). Briefly, some indicators are sensitive to disinfectants and environmental stresses (*Aeromonas*, *Escherichia coli*), while others are too sturdy (*C. perfringens* spores), some present at low numbers in sewage, some are excreted by both humans and animals, some are also pathogens (*E. coli*, *P. aeruginosa*), some are obligatory anaerobes (*Bifidobacterium*), and some do multiply in sewage (most of heterotrophic bacteria). Since the late 1980s, bacteriophages have been regarded as reliable indicators of viral pollution of drinking water via contact with feces or sewage (Hoffmann-Berling and Mazé 1964; Armon 1993; Armon and Kott 1993; Havelaar et al. 1993; Havelaar 1993). However, to be precise, several researchers already suggested the idea of using various bacteriophages as indicators of fecal pollution of water in the 1940s–1950s of the last century (Abdoelrachman 1943; Guelin 1950; Cornelson et al. 1956, etc.). The grounds for this idea are that bacteriophages are also viruses, infecting specifically only bacteria, and the only organism group that closely resembles human viruses, and hence, are worthy candidates as indicators based on their morphology, genomics, and their presence in human or animal feces, and because they are highly resistant to environmental stresses and present in adequate amounts to be enumerated directly without further concentration (Armon et al. 1997; Schaper et al. 2002). Prospective new indicators from this group are somatic coliphages (Kott et al. 1974; IAWPRC Study Group 1991; Armon 1993; Armon and Kott 1996), F^+-male specific bacteriophages (named also F^+ RNA coliphages) (Havelaar and Hogeboom 1983; Durán et al. 2002, 2003), and phages specifically infecting *Bacteroides fragilis* bacteria (IAWPRC Study Group 1991; Jofre et al. 1995). Consequently, according to the discrepancies previously described and major indicator prerequisites, bacteriophages have been shown to fit best as viral pollution indicators.

35.2.1 Somatic Coliphages (Potential Indicators of Enteric Viruses)

Frequently, somatic coliphages have been selected from a heterogeneous group of different families' morphology such as *Myoviridae* (i.e., phage T4), *Siphoviridae* (i.e., λ phage), *Podoviridae* (i.e., phage T7), or *Microviridae* (i.e., phage ΦX174) (Table 35.2). Somatic coliphages contain a double-stranded or a single-stranded DNA (ds/ss DNA), encapsulated in a proteinaceous isometric or elongated capsid. One of their major features is the tail (contractile or not), except for *Microviridae* (lacking a tail), that help in infection by attachment to a certain receptor (typically part of a protein, a lipopolysaccharide, the peptidoglycan, teichoic acid, or an exopolysaccharide) on their *E. coli* host's outer membrane, *E. coli* C being the most commonly used as the host (Armon et al. 1988). Other additional hosts have been also reported, such as *E. coli* B, C, C-3000, F-amp, and K-12 derivatives, such as WG21 and W3110, plus several undesignated strains of *E. coli*. However, most of these hosts have restriction enzymes capable of inactivating the invading phages, except *E. coli* C, which does not own a DNA-modifying or restricting system, explaining the high efficiency of plating with somatic phages. Attachment and infection via a receptor located on the *E. coli* cell's outer surface imparted their collective group name "somatic coliphages." Somatic coliphages are regularly found in human sewage and are more prevalent than F^+ RNA coliphages in marine water and warm waters (Mocé-Llivina et al. 2005; Lovelace et al. 2005; Burbano-Rosero et al. 2011). These bacteriophages show frequent occurrence in human and animal feces (10^2–10^8/g) and wastewater (10^3–10^4/ml), and good environmental persistence, although they are readily inactivated by water treatment processes, with the exception of a few types (Hot et al. 2003; Mocé-Llivina et al. 2005). Kott et al. (1974) found that somatic coliphages were present in wastewater and other fecally-contaminated waters in numbers at least equal to human enteric viruses. Coliphages have been used as water quality indicators for estuarine, sea, fresh, potable, and waste waters, and biosolids (Mocé-Llivina et al. 2003; Sinton et al. 1999), and as indicators of enteric viruses in aerosols from activated sludge, sewage effluents, shellfish, and shellfish-growing water (Fannin et al. 1977; Vaughn and Metcalf 1975), and found to have several limitations. Among these limitations are: their potential multiplication in the environment, as pointed out by many authors (Vaughn and Metcalf 1975; Seeley and Primrose 1980; Parry et al. 1981; Borrego et al. 1990; Grabow 2001); poor correlation of coliphage and enterovirus densities (Nieuwstadt et al. 1991; Wommack et al. 1996); the inability of several coliphages to indicate the presence of solid-associated infective viruses (Moore et al. 1975); the inverse correlation of coliphages and enteric viruses with temperature (Geldenhuys and Pretorius 1989); presence of autochthonous bacteriophages in unpolluted waters (Seeley and Primrose 1980), and finally, host strain variability (Havelaar et al. 1986). Justification for the use of somatic coliphages as sentinels of enteric viruses in wastewater suffers from another potentially important but critical limitation. From the infectivity point of view, this phage group is not

Table 35.2 Bacteriophage families with phage types of particular interest in water quality assessment (as enteric virus indicators)

Group (family)	Characteristics	Representative phages (host)
Myoviridae	dsDNA long contractile tail. isometric or elongated capsids up to 100 nm	T2, T4 (*Enterobacteria, e.g., E. coli, Bacillus,* and *Halobacterium*) 
Siphoviridae	dsDNA long non contractile tails ~ 150 × 10 nm isometric capsids up to 60 nm	λ (*Enterobacteria, e.g., E. coli*), *Bacteroides fragilis* B40-8, *Mycobacterium* and *Lactococcus*) 
Podoviridae	dsDNA short tails isometric capsids up to 65 nm	T7, P22 (*Enterobacteria, e.g., E. coli* and *Bacillus*) 
Microviridae	ssDNA without tail isometric capsids ~ 25–30 nm	ΦX174 (*Enterobacteria, e.g., E. coli, Bdellovibrio, Chlamydia*, and *Siroplasma* 
Leviviridae	ssRNA tailless isometric capsids ~25 nm	f2, MS2, GA, Qβ, F1 (F-plasmid bearing bacteria) (*Enterobacteria, Caulobacter, Pseudomonas*, and *Acinetobacter*) 
Inoviridae	dsDNA capsids ~800 × 6 nm long and flexible rods	fd, M13 (F-plasmid bearing bacteria) (Bacteria) 
Tectiviridae	dsDNA tailless isometric capsids up to 60 nm lipid membrane below capsid	PRD1, PR722 (Gram-negative bacteria, e.g., Enterobacteria) 

Adapted from Ackermann (2009), Lee (2009)

specific only to *E. coli* species. There is evidence that somatic coliphages may multiply in other species of the family Enterobacteriaceae that comprise the total coliform group (*Citrobacter, Enterobacter, Hafnia, Klebsiella*, and *Escherichia* spp.) often found associated with vegetation and biofilms and not restricted to fecal sources. Of these bacteria, the two most common species are *Klebsiella pneuomoniae* and *Enterobacter cloacae* (Souza et al. 1972). Therefore, it is possible that somatic coliphages may be produced/present while being unrelated to fecal contamination, and therefore, unrelated to any health risk. Consequently, the use of somatic coliphages as indicators of fecal pollution and enteric virus presence has serious shortcomings and should be considered as such. Muniesa et al. (2003) studied the factors affecting somatic phage replication using *E. coli* strain WG5. They concluded that there is little chance of somatic coliphages replicating in environmental waters, although it cannot be ruled out completely. The host bacteria and phage threshold densities used by these authors were greater than the highest densities of somatic coliphages and host bacteria reported in most human and animal raw wastewaters. Therefore, they concluded that there are few natural environments in which the densities of non-replicating host bacteria and their physiological status could support somatic coliphage replication. They also concluded that the ratio of phages to bacteria will not be affected by replication in water, and consequently, the likelihood of somatic coliphage replication is very low outside the animal gut. This potential replication could be affected by several factors, such as the densities of host bacteria and phages, the physiological condition of host bacteria, the dissolved and suspended solids in water, ambient temperature, other bacteria present in water, and additional factors. The replication potential of somatic coliphages in water environments has been considered as a weakness of using somatic coliphages as appropriate viral indicators in water.

35.2.2 F$^+$RNA Phages (Synonyms F$^+$-Male/F$^+$-Specific Phages; F$^+$-Specific RNA/DNA Bacteriophages) (Potential Indicators of Enteric Viruses)

F$^+$-male specific phages comprise two major groups of bacteriophages (group E and F), according to their genomic composition (RNA or DNA, respectively) and are characterized by attachment and infection of their bacterial host through the pilus (Fig. 35.2) (Singleton and Sainsbury 1993). The pilus is an appendage type, present on the surface of bacterium male strains, encoded by an episomal F-factor. The F-factor is a DNA sequence or plasmid that confers on certain bacteria the ability to produce a sex pilus for conjugation with other bacteria. The F-factor can consequently occur as an independent plasmid. However, it can also integrate into the bacterial genome or chromosome. Hence, bacteria may be classified in relation to the F-factor as HFr (*high frequency of recombination*) when the F-factor is DNA-integrated or F$^+$ when separate, both states conferring on a bacterium the so-called "male property."

F$^+$ male phages are a homogenous group (group E) of the family *Leviviridae* with physical properties resembling those of enteroviruses, and group F comprises F$^+$ DNA phages of the *Inoviridae* family (Table 35.2). The F$^+$ RNA phages (group E) are comprised of non-enveloped, spherical particles with icosahedral symmetry (~26 nm in diameter) containing single-stranded RNA (ssRNA) and divided in four main groups, based on serological and physicochemical properties: group I (phages MS2, f2, BO1 and JP501), group II (phages GA, BZ13, TH1, KU1 and JP34), group

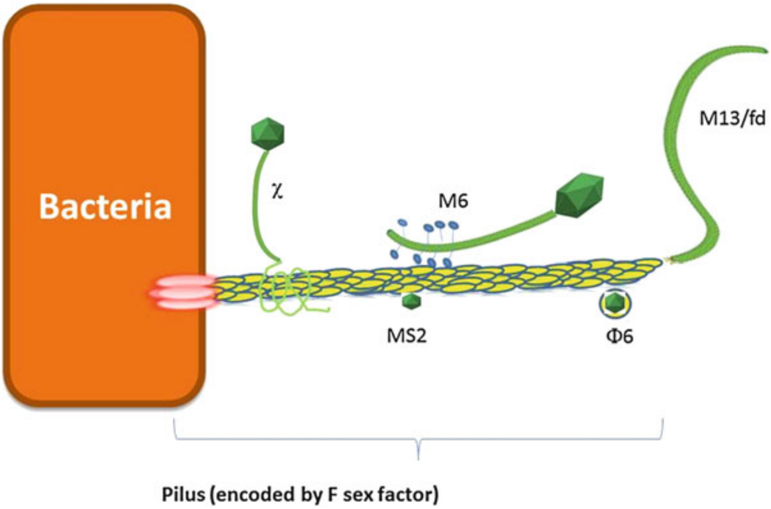


Fig. 35.2 F^+ pilus as attachment and infection site of various F^+-male specific phages (see the different attachment positions of F^+-male specific phages on the same pilus)

III (phages Qβ, VK, ST and TW18), and group IV (phages SP, FI, TW19, TW28, MX1, and ID2) (Osawa et al. 1981). The F^+ DNA phages (Group F) are comprised of a non-enveloped, rod of filaments with a helical capsid with adsorption proteins, on the one hand (7 nm in diameter and 700 to 2,000 nm in length), and a DNA genome, e.g., phage SJ2 (host *Salmonella*), phage fd (host *E. coli*), phage AE2 (host *E. coli*), phage M13 (host *Enterobacter*), phage L51 (host *Acholeplasma*), and phage Pf1 (host *Pseudomonas*), on the other.

The common hosts used to detect F-male specific phages are: *S. typhimurium* phage type 3 Nalr (F = 42 lac::Tn5) (using a male *Salmonella* strain, constructed by the introduction of the plasmid F'42 lac::Tn5 into *Salmonella typhimurium* phage type 3) (Havelaar and Hogeboom 1984), *E. coli* K-12 HFr or other F^+ types, and perhaps the best one, *E. coli* HS[pFamp]R (harboring antibiotic resistance markers, ampicillin on the F_{amp} plasmid, which codes for pilus production, and streptomycin and nalidixic acid on the chromosome) (Debartolomeis and Cabelli 1991). The strain *E. coli* HS[pFamp]R is resistant to coliphages T2 to T7 and ΦX174 and more than 95 % of the phages from environmental samples that plaqued on this strain were F-male specific.

F^+ RNA phages are intermittently excreted in human and animal feces (up to 10^3 PFU/g), but found repeatedly in wastewater (10^3–10^4 PFU/ml). One of the main features of these phages is their environmental multiplication only at temperatures > 30 °C, which is attributable to bacterial pilli formation (male hosts) that occurs only at > 30 °C. These phages also have a relatively high resistance to environmental stresses, such as disinfectants, sunlight, salinity, heat treatment, and water and sewage-treatment processes (Havelaar and Hogeboom 1984; Havelaar and Nieuwstad 1985; Armon et al. 2007). However, according to their indicator role they have several drawbacks, such as: (1) serotypes may be related to the human/animal origin of fecal pollution; (2) their excretion is not always in sufficiently large numbers to be easily enumerated; and (3) the F^{+}RNA coliphages are infectious to bacteria that possess the F-plasmid, and this F plasmid is transferable to a wide range of Gram-negative bacteria, a transferability that raises concern over the lack of *E. coli* specificity (Sobsey et al. 1995).

35.2.3 **Bacteroides fragilis** ***Phages (Potential Indicators of Enteric Viruses)***

Relative new comers in the area of indicator bacteriophages are lytic bacteriophages that are specifically infectious for the anaerobic gut bacterium: *Bacteroides fragilis* (Tartera and Jofre 1987). *Bacteroides fragilis* is one of the most abundant colonic bacterium living and excreted in human feces (up to 10^8/g). Bacteriophages infecting strains of *Bacteroides fragilis, Bacteroides tethaiaotaomicron, Bacteroides ruminicola*, and *Bacteroides ovatus* have been detected in feces and wastewater (Booth et al. 1979; Tartera and Jofre 1987; Klieve et al. 1991; Payán et al. 2005). Bacteriophages infecting *B. fragilis* have been reported to be incapable of replicating outside the gut, merely because of their host strain's requirements, such as anaerobiosis and nutrients, whose absence prevents their replication (Tartera and Jofre 1987). The bacteriophages that infect different *Bacteroides* species have a tail, resembling the morphology of the *Siphoviridae* family: an icosahedric head and a flexible tail (non-contractile, filamentous with fibers) (Table 35.2) (Booth et al. 1979; Klieve et al. 1991; Queralt et al. 2003; Payán 2006). The bacteroides phages' genome consists of double stranded DNA (dsDNA), similar to that of other members of the *Siphoviridae* family (Puig and Gironés 1999; Hawkins et al. 2008). *B. fragilis* phages (grown on *B. fragilis* HSP40 as host) occur only in human feces and do not multiply in the environment, are a relatively homogeneous group, and are relatively highly resistant to environmental stresses, which are qualities of great merit for an indicator; however, they have also some disadvantages, such as: (a) the host strain may not be applicable worldwide (e.g., based on collaborative studies, host *B. fragilis* HSP40 resulted in high phage counts in Southern Europe, Israel, and South Africa, but much lower counts in the USA, UK, and Scandinavia (Armon and Kott 1995; Kator and Rhodes 1992; Puig et al. 1999); host *B. tethaioataomicron* GA17 resulted in high counts in Southern Europe but lower counts in the UK (Payán et al. 2005); *B. ovatus* GB124 resulted in high counts in UK but lower counts in Spain (Payán et al. 2005); *B. fragilis* HB13 resulted in high counts in Spain but lower counts in Colombia (Payán et al. 2005); and the host *Bacteroides* spp. HB73 was good only in Hawaii and *Bacteroides* ssp. ARABA 84 only in Switzerland (Vijayavel et al. 2010; Wicki et al. 2011; Ebdon et al. 2007)); (b) there numbers are relatively low in wastewater (<1–10^4/ml); and

(c) only 10 % of the population excrete these phages in their feces (albeit large numbers in excretors, ~10^8 PFU/g) (Tartera and Jofre 1987; Tartera et al. 1989).

In terms of resistance, somatic coliphages, which outnumber phages infecting *B. fragilis* by more than two orders of magnitude, died off faster. Therefore, it can be concluded that *B. fragilis* phages are much more persistent than somatic coliphages and approximately as resistant as F^+-male specific coliphages (Armon et al. 1997). Lucena et al. (1996) reported high resistance of *B. fragilis* phages as compared to F^+-male specific coliphages to natural inactivation processes and water treatment (in this case even higher than *Clostridium* spores) (Lucena et al. 1996; Jofre et al. 1995).

Conclusions

It should be emphasized that up to the present time, the only universally accepted indicator of enteric viruses presence in water are still *E. coli* bacteria or, as most laboratories call them, fecal coliforms. As previously presented, *E. coli* is a universal inhabitant of the human gut, excreted in large numbers in feces reaching our sewage. Indeed, the numbers are high enough to be detected easily, but they have a prominent disadvantage: the fecal coliform does not survive well in the environment (e.g., in seawater) and sewage treatment processes (including disinfection), and therefore, as compared with enteric viruses, the *E. coli* indicator is a very fragile one and will decline first. This major problem that tormented environmental virologists for decades has been ameliorated since the 1970s and even earlier, when bacteriophages of different bacteria present in human feces were suggested as better viral indicators (Kott et al. 1974; Armon and Kott 1996). Indeed, bacteriophages seem to fulfil the major prerequisites of viral indicators due to their viral resemblance, fecal excretion, and survival capability characteristics. Table 35.3 summarizes the numbers and/or presence/absence frequency of the three bacteriophage groups isolated from various water sources. From our personal experience and based on others' research, it can be stated that certain bacteriophages can be useful as viral indicators under certain conditions. For instance, the bacteriophage host should be selected from a certain human population, i.e., gut flora can differ between different populations and countries, as previously revealed for the *B. fragilis* host, which is suitable mostly in Europe but not in North America. In the USA, *Bacteroides fragilis* phages were not detected in large numbers in sewage when the Spanish *B. fragilis* HSP40 bacterial host was used for phage detection (Sobsey and Kator, personal communication, 1997). It may be possible that, for bacteriophage detection in a certain geographical area, it will be necessary to isolate primarily a well-defined bacterial host. Furthermore, for each type of water contamination, we should look at one or several

(continued)

Table 35.3 Comparison of the three bacteriophage groups (coliphages, F+-male specific coliphages, and *B. fragilis* phages) their presence/isolation frequency/reduction in various water sources

Source	Coliphages	F+-male specific phages	Bacteroides *fragilis* phages	Reference
Surface water (river, lakes, ponds, etc.)	34–100 % positive samples	31.8–100 % positive samples	36.4–100 % positive samples	Jofre et al. (1995)
	Enteric viruses 0–55 %	Enteric viruses 0–55 %	Enteric viruses 0–55 %	Chung and Sobsey (1993), Tartera et al. (1988)
			B. fragilis HSP40 (host) Detected in 72 % of water and sediment samples while enteroviruses were detected in only 56 % of those samples	
Ground water	Low concentration	Low concentration	Low concentration	Leclerc et al. (2000)
Water treatment plant reduction[a] (prechlorination-flocculation-sedimentation)	Log 2.6–5.6	Log 2.3–5.2	Log 2.2–2.9	Jofre et al. (1995), Bradley et al. (1999), Kott et al. (1974)
	Enteric viruses: >2.9–>3.4	Enteric viruses: >2.9–> 3.4	Enteric viruses: >2.9–> 3.4	
		High resistance		
Brackish Water Salinity (0.1 1–30 ppt) and Marine water >30 ppt	3 PFU/ml 6.0 MPN/100 ml <1 to 3.4×10^3 PFU/100 ml (in seawater)	0.050–682 MPN/100 ml	> 10 PFU/ml	Madhusudana and Surendran (2000), Love et al. (2010)
Feces	4.3×10^3 PFU/g	<1–6.25 PFU/g, 1–10^5 PFU/g (<1 year old infants)	7×10^1–PFU/g	Leclerc et al. (2000)
			$24–2.4 \times 10^8$/g $0–2.4 \times 10^8$/g	Gino et al. (2007)
	Found in humans and animals	Found in humans and animals	Frequency : present in 10–11 % of fecal samples (only humans)	Gantzer et al. (2002) Tartera and Jofre (1987)

(continued)

Table 35.3 (continued)

Source	Coliphages	F+-male specific phages	Bacteroides *fragilis* phages	Reference
Urban Sewage or STP	3.6×10^1–1.59×10^4/ml	10^2–10^4 plaque-forming units (pfu) ml^{-1}.	5.3×10^3/100 ml	Dhillon et al. (1970), Gino et al. (2007)
		~10^5 PFU/100 ml		
Effluents	1.4×10^3 PFU/l	10^3 to 10^4 PFU/100 ml	0.8 to 13 PFU/l	Gantzer et al. (1998), Debartolomeis and Cabelli (1991)
Oxidation ponds	$2–3 \times 10^3$ PFU/ml	$300–10^4$ PFU/ml	?	Gino et al. (2007)
	Poor correlation with enteroviruses			
Sediments	$>10^6$–$> 10^7$ PFU/100 ml	$>10^5$–$> 10^7$ PFU/ml	$>10^4$–$> 10^5$ PFU/100 ml	Chung and Sobsey (1993), Tartera et al. (1988), Araujo et al. (1997)
			B. fragilis HSP40 (host). Detected in 72 % of sediment samples, while enteroviruses were detected in only 56 %	
Shellfish	Weak correlation	Significantly related to Norwalk-like viruses, less to HAV, adenovirus, enterovirus	*B. fragilis* RYC2056 (host)	Formiga-Cruz et al. (2003)
			Less frequently detected	Chung et al. (1998)

[a]Decimal reduction, decrease in logarithms. Numbers indicate the decimal reduction calculating the value of phages present in finished water using Thomas' equation for the calculation of the most probable number (MPN) for long series of data (De Man 1975). MPN is the number that makes the observed organisms concentration (λ) most probable, expressed by Thomas' equation:

$$\sum_{j-1}^{k} \frac{g_{j\,m_j}}{1-\exp\left(-\lambda m_j\right)} = \sum_{j-1}^{k} t_{jm_j}$$

where exp is e^x, K is the dilutions number, g_j is the test positive numbers in the jth dilution, m_j is the amount (volume or weight) of the original sample in each test volume in the jth dilution, and t_j is the number of tubes in the jth dilution (if tubes used). The equation is generally solved by iteration.

(continued)

groups of bacteriophage types in order to define a certain correlation with sewage or fecal pollution.

Bacteriophages have been intensively studied for almost 60 years as indicators of viral pollution. Nevertheless, governmental regulations rarely specify their use as such and again there is not yet a consensus in the scientific community on their merit. Reviewing the literature, we gradually came to the conclusion that there is no one indicator or index microorganism that can fulfil perfectly the definition previously described. It is our opinion that, similar to the case of the coliform/fecal coliform indicator, in the case of which it was decided to include certain bacterial families as well as to apply a highly defined group, such as fecal coliforms (usually referred to as thermotolerant *E. coli*), as a more specific indicator, bacteriophages will require similar fine-tuning in order to fulfill their real role as indicators.

The use of bacteriophages as indicators started with the broad-spectrum group of bacteriophages infecting *E. coli* host strains (erroneously termed coliphages, as some of them infect other Enterobacteriaceae as well), which resulted in confused conclusions about their indicative potential. Furthermore, there has been no one universally accepted bacterial host, and each laboratory uses its own selected strain. It is clear that this inconsistency prevented an objective comparison of the experimental results among the various laboratories and led to doubts about bacteriophages as potential indicators of water pollution by sewage or fecal material (Gerba 1987).

For the last 30 years, scientists have examined various specific bacteriophages groups, i.e., *Serratia marscens* phages, cyanophages, F^+-male specific RNA phages, and *B. fragilis* phages (Stanley and Cannon 1977; Smedberg and Cannon 1976), that might fit the indicator role for specific types of pollution. Havelaar et al. (1993) emphasized this idea by showing that F^+-male specific RNA phages are an adequate model for enteric viruses in fresh water. However, even this publication excluded raw and biologically treated sewage, due to lack of correlation between the presence of these phages and enteric viruses. Kamiko and Ohgaki (1993) substantiated the results of Havelaar et al. (1993) by showing that Qβ, an F^+-male specific RNA phage, does not multiply in water below 25 °C, but excluded the host in the exponential growth phase. It might be that in raw and biologically treated sewage these indicators do multiply and consequently alter the expected correlation between the levels of the phages and enteric viruses.

Unquestionably, improvement in bacteriophage detection and host specificity will result in a better correlation between their levels and those of various pathogens present in polluted water. However, despite our recent and future progress, we should narrow the definitions of indicators according to the degree of pollution and its presence. In brief, the bacteriophage groups that have been related to a certain pollution criteria and found to correlate

(continued)

with the presence of human pathogens do not need to correlate with the same pathogen in a different pollution environment or in a different geographical area. The ubiquity that we seek so intensively in order to adapt it for guidelines is perhaps the main pitfall in reaching the right conclusions. An excellent example for the above assumptions is the *B. fragilis* bacteriophage group: the bacterial hosts used in Spain for their specific phages is *B. fragilis* HSP-40, resulting in good phage detection from human fecal wastes, while *B. fragilis* RYC2056 detects phages in both human and animal fecal wastes (Puig et al. 1999). For example, on the global scale, the *B. fragilis* RYC2056 host showed good results, while *B.fragilis* HSP40 showed geographic variability, as mentioned earlier (high counts for Southern Europe, Israel, South Africa versus low counts for the USA, Sweden, and the UK). Chung et al. (1998) showed that *B. fragilis* VPI3625 used in USA was similar in its plaquing efficiency to *B. fragilis* RYC2056.

In summary, there are several critical issues that still need clarification before the introduction of bacteriophages as routine indicators of viral pollution of water resources. These are: (1) detection methodology, that is choosing the host and phage choice according to water source, geographical site, and past experience (Furuse et al. 1983); (2) validation methods based on inter- and intra-laboratory reproducibility (mainly at the country level); (3) establishment of specificity; (4) sensitivity increase through selection; (5) epidemiological support by combined studies including enteric viruses; and (6) low cost and simplicity of routine tests performed by water laboratories. Finally, a recent publication theoretically suggested the use of the Torque teno virus transmitted primarily via the fecal-oral route in humans (based on the presumption that this enteric virus is "ubiquitous in humans, elicits seemingly innocuous infections, and does not exhibit seasonal fluctuations or epidemic spikes") as an appropriate indicator of viral contamination of drinking water (Griffin et al. 2008). Still, this theoretical proposition preeminently emphasizes the major indicator challenge: (1) it needs to be tested, including in terms of densities and occurrences, including spatial and temporal stability; (2) a viral assay and infectivity test has yet to be developed; and (3) determination and correlation along real enteric pathogenes!

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Chapter 36
Algal Bloom Indicators

Robert H. Armon and Janetta Starosvetsky

Abstract Algae (so called phytoplankton) are an important food resource for many marine organisms, however as a result of our water resources pollution, sometimes they overgrow and cause a variety of negative artifacts: increased toxin production, hypoxia, increase in bacterial population (mainly the one able to decompose dead algae) and decrease in the sunlight penetrating water bodies. It is the common belief that eutrophication (natural or anthropogenic) combined with water mixing (upward advection) are the major factors in algal bloom; however, some recent results do raise some questions about the model's simplicity and its variation according to geographical distribution. In this chapter, potential indicators of this phenomenon is discussed.

Keywords Phytoplankton • Algal bloom • Eutrophication • Harmful algal bloom-HAB • Toxin • Hypoxia • Fish • Climate change

36.1 Background

The classical definition of algal bloom is "the rapid increase and accumulation of algal population (mostly microscopic) in aquatic systems (fresh and marine environments)". Aquatic algae are called phytoplankton and their rapid growth in large numbers colors the source owing to their high photosynthetic pigment concentration. The first indication of algal bloom is the coloration of the water source with green, yellow-brown, or red pigments according to the species of algae. For example, bright green color is mainly attributed to cyanobacteria, i.e., *Microcystis*; red or brown hue is formed with the bloom of dinoflagellates, i.e., *Alexandrium* and *Karenia* genus or *Heterosigma akashiwo* (Raphidophyceae). Beside the aesthetic problem, there are four main reasons for preventing algal bloom:

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_36

1. Some algae are capable of neurotoxins production resulting in mass mortalities of fish, sea turtles, marine mammals, and seabirds (Scholin et al. 2000; Spitzer 1995; Khan et al. 1997; Bourdelais et al. 2002)
2. Human disorders by means of ingestion of seafood contaminated by toxic algae (Ferrante et al. 2013; Backer et al. 2008)
3. Increased bacterial biomass degradation of dead algal cells resulting in hypoxia of the water source (Conley et al. 2011)
4. Water equipment and fish gill epithelial tissues become clogged leading to consequent malfunction and fish asphyxiation (Shen et al. 2011)

Toxic algae are the most important due to their highly potent toxins excreted in water bodies. Table 36.1 shows a general view of harmful algal bloom (HABs) reported in the literature and their specific toxins (Anonymous 2010).

Table 36.1 Characteristic toxic algae, their toxins and humans/animals effects

Algae examples	Toxin types	Toxin examples	Effects
Alexandrium minutum, Karenia brevisulcata (Chang) Anabaena, Aphanizomenon, Oscillatoria (Planktothrix) Cylindrospermopsis, Lyngbya	Neurotoxins	Anatoxin-a, anatoxin-a(s), saxitoxin, neosaxitoxin	Central nervous system: causes seizures, paralysis, respiratory failure, and death
Microcystis aeruginosa, Cylindrospermopsis raciborskii, Aphanizomenon, Cylindrospermopsis, Raphidiopsis, Umezakia, Anabaena, Aphanocapsa, Hapalosiphon, Microcystis, Nostoc, Oscillatoria, Planktothrix Nodularia (brackish water)	Hepatotoxins	Microcystins, nodularins, cylindrospermopsin	Liver: causes hemorrhaging, tissue damage, tumors, liver cancer, and death
Gracilaria coronopifolia, Lyngbya majuscule	Dermatotoxins and Gastrointestinal toxins	Aplysiatoxins, lyngbyatoxin-a, lipopolysaccharide endotoxins	Skin and mucous membranes: causes rashes, respiratory illness, headache, and stomach upset
Lyngbya (marine)			
Schizothrix (marine)			
Aphanizomenon ovalisporum, Cylindrospermopsis raciborskii	Cytotoxins	Cylindrospermopsin	Liver and other organs: causes chromosome loss, DNA strand breakage, and organ damage

36.2 Cyanobacteria and Cyanobacterial Toxins Exposure

Algal bloom of toxin-producing algae (so called **harmful algal bloom-HAB**) are of major importance because of their large amounts and the wide exposure of animals and plants. Humans and animals are continuously exposed to algae and their potential toxins depending on environmental conditions. Exposure to algae or to their toxins can occur through: (a) drinking untreated water or treated water containing harmful algal bloom cells; (b) recreational activities (swimming, surfing, etc.) in water source contaminated with algal bloom through aerosols inhalation or swallowing; (c) use of contaminated water (with algal bloom) for lawn and golf course irrigation; (d) through foods or supplements contaminated with microcystins and medically through dialysis (Jochimsen et al. 1998).

It is not clear yet how and why algal blooms spread globally, forming new spots of bloom along a period of almost 30 years (Fig. 36.1). However it is obvious, that continental peripheral beaches contaminated with PSP-producing algae had increased considerably. There are several potential explanations for this significant shift: (1) better and more sophisticated equipment for PSP detection; (2) climate change, including *El Niño* and *La Niña*, etc., favoring the development of phytoplankton in new geographical areas; (3) considerable pollutants accumulation along time connected to algal proliferation; and (4) possible increase in maritime traffic unwillingly transporting phytoplankton from one continent to another.

The effects of HAB phenomenon displaying a worldwide distribution is presented in Table 36.2.

It is the common belief that eutrophication (natural or anthropogenic) combined with water mixing (upward advection) are the major factors in algal bloom; however, some recent results do raise some questions about the model's simplicity and its variation according to geographical distribution (He et al. 2011). The relation between nutrients abundance/scarcity and their impact on algal bloom was reported by Gobler and Sunda (2012), covering a 20-year time interval in shallow estuaries of the United States and South Africa. These authors described an interesting ecosystem where brown tides are promoted by positive feedback mechanisms involving the ability of these brown algae to grow competitively at low nutrient and reduced light levels, their low rates of grazing mortality, and the associated low grazing-mediated recycling of nutrients as described in Fig. 36.2.

36.3 Potential Indicators of Algal Bloom

McGillicuddy et al. (2011) reported abundant levels (30 % more than the 2005 historic red tide bloom count) of dormant seed-like cysts of *Alexandrium fundyense* in seafloor sediments and possible bloom initiated from cyst accumulations in major seedbeds in the region (Anderson et al. 2012; Sagert et al. 2008). The behavior of *Alexandrium* cells was affected by ocean currents (eddies), water

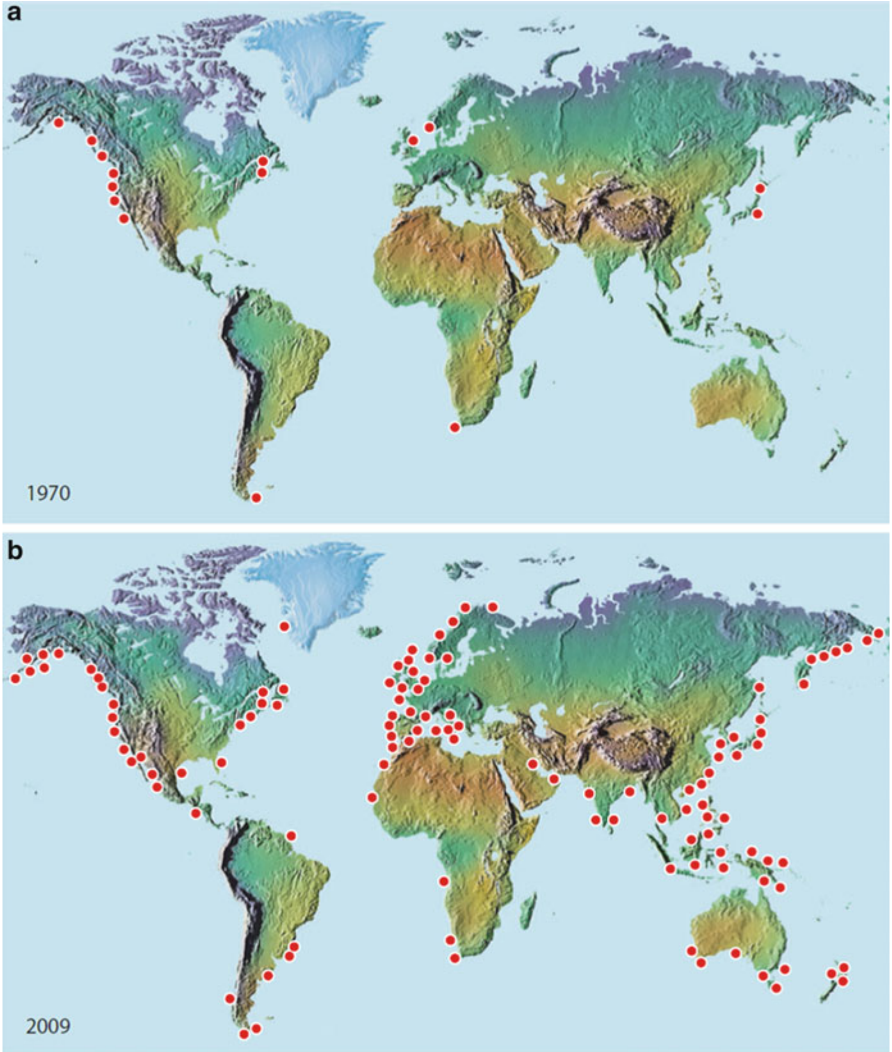

Fig. 36.1 Global paralytic shellfish poisoning (PSP) toxins detected in shellfish or fish in 1970 (**a**) and 2009 (**b**) (Source: U.S. National Office for Harmful Algal Blooms)

temperature, and salinity, river runoff, winds, and tides (McGillicuddy et al. 2007). It should be mentioned that *Alexandrium* algae are notorious for their toxin that accumulates in shellfish, causing paralytic shellfish poisoning (PSP). In the above case, authorities issued warnings and closed shellfish areas from Canada to Massachusetts (Keafer et al. 2005).

Fish kills have long been an indicator of the presence of toxic phytoplankton species. Thronson and Quigg (2008) reviewed 55 years of fish death in the Gulf of Mexico. Biotoxins originating from algal bloom accounted for 7 % of fish death,

Table 36.2 Global notable occurrences of algal blooms and their effects

Site	Year	Algae	Causes/Effects	Ref.
New England (USA)	1972	*Alexandrium (Gonyaulax) tamarense*	~30 cases of PSP[a] were reported, with no fatalities	Coleman et al. (1986)
Maine and Massachusetts (USA)	2005	*Alexandrium spp.*	New England spring weather of 2005 produced higher than usual amounts of rain and snowmelt in addition to two nor'easters in May. These conditions coupled with constant northerly and easterly wind patterns may have pushed the abundance of Alexandrium cells south into Massachusetts Bay and Cape Cod Bay	Anderson et al. (2005) and Keafer et al. (2005)
Brittany (France)	2009		High amount of fertilizer discharge into the sea due to intensive pig farming	Chrisafis (2009)
North Atlantic	2010		Ash containing iron from Eyjafjallajökull volcano	Langmann et al. (2010, 2012)
Salton Sea, California (USA)	1992	Cyanobacteria	Associated with deaths of Eared Grebes	Carmichael (2001)
Denmark and USA	1993–1995	Cyanobacteria blue-green algae, *Anabaena flos-aquae*	Death of Crested Grebe, Black-necked Grebe, Coot, domestic ducks and geese	Henriksen et al. (1997) Cook et al. (1989)
British Columbia Canada and Washington USA	1992–1993	*Microcystis aeruginosa*	Net-Pen liver disease of Mari-cultured Atlantic Salmon	Andersen et al. (1993)
England and Australia.	1992; 1993–1994	Cyanobacterial (blue-green algal), *Microcystis aeruginosa*	Acute non-lethal toxicity in natural populations of trout and carp	Rodger et al. (1994) and Carbis et al. (1997)
Pernambuco, Brazil	1996	Cyanobacteria	At least 52 human fatalities from use of contaminated municipal water in a hemodialysis clinic	Jochimsen et al. (1998) Carmichael et al. (2001)

[a]Paralytic shellfish poisoning

while the major killing (57 %) was attributed to low dissolved oxygen. Low dissolved oxygen can be linked also to high organic load and intense microbial activity as well to decomposition of large algal mass in a water body!

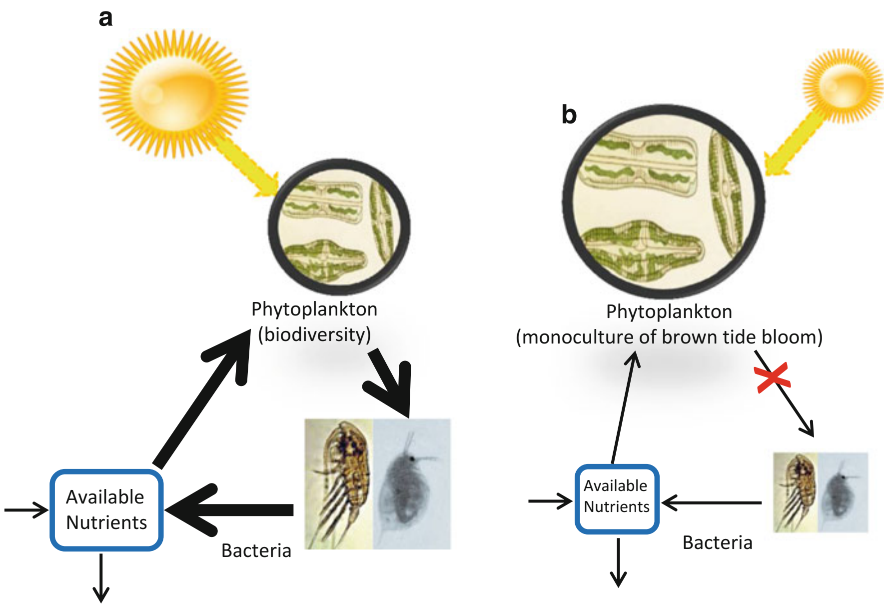

Fig. 36.2 (**a**) Normal recycled and grazed ecosystem where phytoplankton is diverse with many species in shallow lagoons (the internal nutrient cycle is phytoplankton-grazers-bacteria is the significant cycle as compared to external contribution/loss indicated by *heavy* and *light arrows*); (**b**) the ecosystem "dominated" by brown algae bloom as a result of grazing inhibition, reduced available nutrients and light (Adapted from Gobler and Sunda 2012)

CSIR scientists have developed a method that uses a water plant and insects as indicators of the toxicity of blue-green algae in rural drinking water (Oberholster et al. 2009). The authors reported the duckweed *Spirodela punctate* to be the most sensitive bioassay, showing "reduction of root growth and fronds weight as well as changes in the chlorophyll *a* and *b* ratio content" within the first 12 h after exposure to a low concentration of cyanobacterial synthetic microcystin-LR (0.1 μg/L).

Hypoxic conditions (water dissolved oxygen levels < 2 mg/L) may occur by decomposition of large algal blooms, as seen in the Finnish Archipelago Sea. Conley et al. (2011) found within the Baltic Sea that hypoxia commonly occurred in the estuaries of the Danish Straits ("through decomposition of algal blooms that have been fed by large nutrient loads and the strong stratification in the area"). Consequently hypoxia can be used as an indicator of algal bloom.

Since 1990, blooms of the benthic dinoflagellates *Ostreopsis* spp. occasionally cause benthonic biocenosis suffering and human distress. This dinoflagellate type produces palytoxin-like compounds (highly potent toxins type). Pistocchi et al. (2011) reported that the highest abundances of *Ostreopsis* spp. were recorded during warmer periods (characterized by high temperature, salinity, and water column stability) displaying different optima with increased toxin levels associated with best growth conditions. These authors also reported an Adriatic strain whose growth is positively correlated with increasing salinity, though its toxicity is lowest at the highest salinity value (i.e., 40 psu).

Li et al. (2008) developed an ecological dynamic model for the simulation of two pelagic phytoplankton groups (diatoms and dinoflagellates) in the East China Sea (ECS) along a time interval of 20 years. Model simulations' results suggest that diatoms favor greater irradiance, less dissolved inorganic nitrogen (DIN)/PO_4–P ratios, higher SiO_4–Si/DIN ratios, and higher nutrient concentrations in comparison to the dinoflagellates group. These results support the speculation that the increase in the DIN/PO_4-P ratio and the decrease in the SiO_4–Si/DIN ratio in the East China Sea may be accountable for the configuration conversion in the functional Harmful Algal Bloom (HAB) groups from diatom to dinoflagellate communities over the last 20 years.

Schmincke (2004) described in his comprehensive volcanology book that volcanos are one of the leading factors in "surface ocean iron-fertilization and phytoplankton increase by volcanic ash" as demonstrated in Kasatochi example, although the volcanic ash flux from Kasatochi was relatively small in comparison to that of other major historical volcanic eruptions.

A more advanced concept has been presented by Barlaan et al. (2007), which used electronic microarrays to detect bacteria associated with harmful algal bloom from coastal and microcosm environments. The developed methodology facilitated the presence or absence detection and relative abundance of the HAB-related ribotypes in coastal and microcosm blooms. These bacterial indicators need additional verification before being established as such. Another study, which also needs further verification, tried to link bakterioplankton to spring phytoplankton bloom, through their outer surface hydrophilicity/hydrophobicity ratio. The authors reported that the highest increase in this ratio's value was obtained shortly before peaks in observed bacterioplankton abundance, showing a direct and rapid response of bacterial surface properties (particularly hydrophilicity) to changing environmental conditions (Stoderegger and Herndl 2005).

An interesting finding has been reported concerning *Didymosphenia geminata* (commonly known as rock snot), an obnoxious (invasive species) colonial diatom blooming in streams worldwide, from Canada to China to New Zealand to England and in many USA states from Maine to New Mexico to Arkansas. Conditions most favorable to Didymo colonization and bloom are: (1) high N/P ratio, low phosphorus (<2 μg/L) in the water; (2) bright sunlight; (3) low TSS (total suspended solids); (4) pH (7–9); (5) generally cold waters, but found in waters from 4 to 27 °C; and (6) stable water flow: "mean flow regime is associated with bloom development, based on a significant negative relationship detected between *D. geminata* biomass and mean discharge." In a study on the negative effects of Didymo, undertaken by Dr. Erica Shelby of the Akansas Department of Environmental Quality, a significant decrease in the biodiversity of invertebrates associated with populations of Didymo (Shelby 2006) was found. This biodiversity reduction may be also related to as an indicator of phytoplankton bloom for freshwater areas.

An additional advanced method has been described by Campbell et al. (2013), which used a continuous automated imaging-in-flow by the Imaging FlowCytobot

(IFCB) device to provide early warnings of HAB events. The automated method was developed in order to substitute the time-consuming manual methods for identification and enumeration of phytoplankton with an automated one. The authors described six HAB events that they were able to provide early warning of *Karenia brevis* bloom at Port Aransas, Texas, USA.

Finally, Liu et al. (2008) showed chlorophyll a to be an excellent indicator of algal bloom in Lake Taihu, which provides drinking water to millions of people in Wuxi city (China). The authors established a linear ratio between band 1 (Reflectance at 620–670 nm) and band 2 (Reflectance at 841–876 nm) data provided by Terra Moderate Resolutions Imaging Spectroradiometer (MODIS) reflectance images, which made it possible to identify water color changes related to chlorophyll a concentrations. Their study demonstrated that the moderately high resolution of MODIS/Terra 250-m data was useful for monitoring the chlorophyll a distribution in a small inland water body, such as Taihu Lake.

In summary, to date there are numerous available and potential indicators to warn of algal bloom occurrence in various environments, which may save large sums of money and protect humans and their environments from hazardous algae (Table 36.3).

Table 36.3 Summary of potential/available indicators of algal bloom

Indicator	Magnitude (↑↓)	Water source	Practicability
Nutrients ratio (N:P)	↑	All	Easy
Cysts accumulation in sediments	↑	Seawater	Easy
Temperature	↑↓	All	Easy
Salinity	↑↓	Seawater	Easy
River runoff	↑	Seawater	Easy
Eddies	↑	Seawater	Moderate
Fish death	↑	All	Easy
Duckweed	↓	Freshwater	Easy
Hypoxic	↓	All	Easy
DIN/PO_4-P ratio	↑	Mainly seawater	Moderate
SiO_4–Si/DIN ratio	↓	Mainly seawater	Moderate
Iron-fertilization	↑	Seawater	Easy
Hydrophilicity/hydrophobicity ratio of bakterioplankton	↑	Seawater	Complex
Biodiversity reduction	↓	Freshwater	Complex
Chlorophyll a	↑	Freshwater	Moderate
Bacteria associated with harmful algal bloom	↓↑ **HAB-related ribotypes**	All	Complex (electronic microarrays)
Biotoxins or grazing inhibitors	↑	All	Complex

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Chapter 37
Biological Indicators of Water Quality: The Role of Fish and Macroinvertebrates as Indicators of Water Quality

Eugenia López-López and Jacinto Elías Sedeño-Díaz

Abstract Freshwater systems contain about 10 % of the fauna species on earth and offer environmental services; however, human activities affect freshwater resources structurally and functionally, reducing the possibilities of using it. Thus, freshwater ecosystems are recognized as the most threatened worldwide, and therefore, aquatic organisms require attention for their conservation. Biological methods have proved to be suitable for the surveillance of aquatic ecosystems. In this sense, given their biological and ecological features, freshwater fish and macroinvertebrates, from the suborganismal to community level, exhibit excellent response signals to stressors. In this contribution, we review the main approaches for assessing freshwater ecosystems using fish and macroinvertebrates. At low organization levels, biomarkers are excellent early warning indicators making evident that organisms have been in contact with contaminants and the effects can be reversible, while the high organization levels reflect an overview of the global impact on aquatic resources; both organization levels show spatial (locally and regionally), and temporal (past and present) effects of water quality conditions of the aquatic ecosystems.

Keywords Stressors • Fish sentinel • Macroinvertebrates • Bioassessment

37.1 Introduction

Human activities, undoubtedly, affect the water resources in structural and functional dimensions in ways that compromise its value as a habitat for organisms. Structurally, water resources are affected by habitat modification (channelization,

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_37

sedimentation increases, damming, etc.), and functionally by water quality detriment (waste water discharges of urban, agricultural, and industrial origin, nutrient enrichment, decreased light penetration, etc.) and changes in flow regime (water diversion, water extraction, damming, etc.). In this sense, freshwater ecosystems are considered as the most endangered and threatened worldwide (Dudgeon et al. 2006), specifically those in developing countries since they feature an extremely high population growth, strong industrialization and urbanization processes, and constant changes in land uses (Thorne and Williams 1997; Mustow 2002). Because freshwater systems have been estimated to contain about 10 % of all animal species on earth (Balian et al. 2008), freshwater organisms require more attention for their conservation. This condition indicates an urgent need for developing the most comprehensive methods possible for assessing the aquatic ecosystems health, and maintaining the goods and services of these ecosystems.

Water quality has usually been assessed using physical and chemical techniques (Sedeño-Díaz and López-López 2007; Espinal-Carreon et al. 2013); however, biomonitoring has been proven to be a necessary supplement to these monitoring techniques (Li et al. 2010; Springer 2010). In certain developed countries, such as Australia, United States of America, and members of the European Community, the biological evaluation is a government obligation (Couceiro et al. 2012). In addition, countries such as Colombia and Costa Rica have implemented biological assessment in their legislation.

Biomonitoring implies the use of biological variables to survey the environment (Gerhardt 1996), and requires the selection of one organism or a group of organisms (the bioindicators) and the use of its biological responses to identify and monitor changes in the environment. Bioindicators can be used to monitor changes in water quality, changes in the stream habitat, or even changes to surrounding watersheds (Reece and Richardson 2000). Moreover, biomonitoring provides additional and factual information concerning the present state and the past trends in environmental behavior (Oertel and Salánki 2003). Aquatic organisms, such as diatoms (John 2003), benthic macroinvertebrates (Flores and Zafaralla 2012; Cerniawska-Kusza 2005; Ferreira et al. 2011), and fish (Tejeda-Vera et al. 2007; Trujillo Jiménez et al. 2011), can serve as bioindicators and are the organisms more frequently used. The aim of this review is to highlight the role of two groups of important aquatic organisms, fish and macroinvertebrates, as ecological indicators in freshwater ecosystems. First, we analyze the various levels of organization in which fish and macroinvertebrates are used as biomonitors, and then, the advantages and more conventional approaches for biomonitoring are presented.

37.2 Levels of Organization

Measurements (endpoints) used for biomonitoring may be selected from any level of biological organization (suborganismal, organismal, population, community, and ecosystem) (Li et al. 2010). Specifically, bioindicators have been used to identify

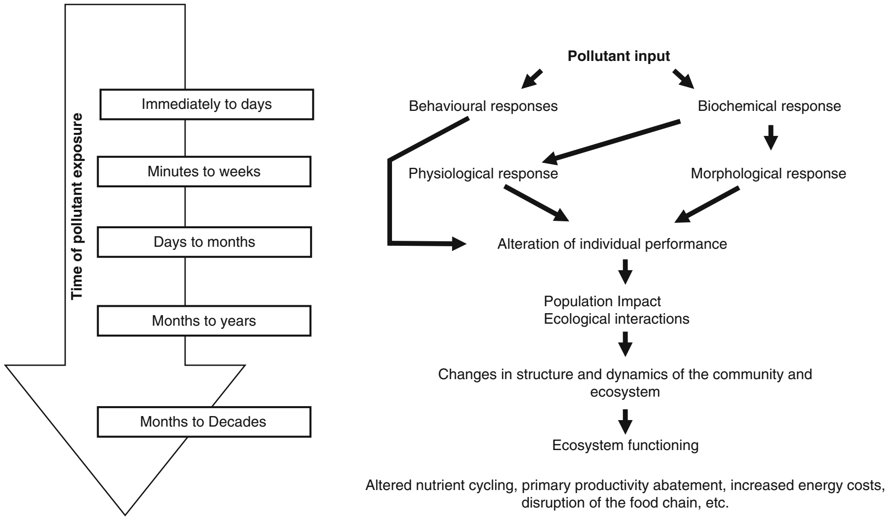

Fig. 37.1 Sequential order of development of biological responses to contaminants through different organization levels (modified of Adams and Greeley 2000)

structures or processes indicating exposure or effects measured at higher levels of organization (e.g., organism, population, community, ecosystems) (Adams and Greeley 2000; Bartell 2006). Biological communities reflect overall ecological features (e.g., chemical, physical, and biological), integrating effects from different stressors, and therefore providing a broad measure of the combined impacts (Cota et al. 2002).

Biological responses to contaminants have a sequential order of development, but also evolve over time. First, contaminants make contact with the organisms and are uptaken in different ways, such as oral, epidermal, through absorption by tissues such as gills, etc. These processes occur in a matter of seconds, minutes, or hours (maybe days) and organisms can be affected at molecular, cellular, physiological, and morphological levels, frequently accompanied by behavioral changes (Fig. 37.1). Thus, damages in these suborganismal levels can be detected through early warning methods. Second, while more time elapses, the damages occur at other levels. Exposure for days, weeks and months, spreads damage individually with an alteration in individual performance. The long-term damages are evident at the population, community, and even ecosystem level, and become irreversible. Disturbances in these levels range from alteration in nutrient cycling, decreases in primary productivity to increases in energy costs, disruption of food chain, alteration of intra and inter-specific interactions, etc. (Fig. 37.1).

The study of biological signal responses at low levels of organization is mainly through early warning biomarkers, which have been defined by several authors, all of them, effectively, in reference to biological responses to contaminants exposure (Sedeño-Díaz and López-López 2012). Shugart et al. (1992) defined a biomarker as a xenobiotically induced variation in cellular or biochemical components or processes, structures, or functions that is measurable in a biological system or samples.

Biomarkers must meet certain requirements to give reliable information about the aquatic condition. Van der Oost et al. (2003) proposed some of these requirements: (a) biomarkers must be reliable, relatively cheap and easy to perform; (b) a biomarker's response should be sensitive to pollutant exposure and/or effects in order to serve as an early warning parameter; (c) the baseline data of the biomarker should be well defined in order to distinguish between natural variability and contaminant-induced stress (signal); (d) the impacts of confounding factors on the biomarker response should be well established; (e) the underlying mechanism of the relationships between biomarker response and pollutant exposure (dosage and time) should be established; and (f) the toxicological significance of the biomarker, i.e. the relationships between its response and the (long-term) impact to the organism, should be established. Likewise, is advisable that biomarkers should preferentially be non-invasive or non-destructive, to allow or facilitate environmental monitoring of pollution effects in protected or endangered species (Fossi and Marsili 1997).

Therefore, biomonitoring can be addressed at least at two main levels of organization: suborganismal (biomarkers), and bioindicators (organism, population, community, and ecosystems) (Adams and Greeley 2000). Van der Oost et al. (2003) mentioned that suborganismal level measures are potentially much more diagnostic and sensitive to pollutants, but the ecological relevance is poor. Organism-level measures are intermediate in relevance, sensitivity, and diagnostic utility; likewise, Adams and Greeley (2000) indicates that bioindicators in general have high ecological relevance.

37.3 Freshwater Fish as Biomonitors

The taxonomic group of fishes, with an estimated number of 28,000–40,000 species (Nelson 2006), probably accounts for nearly 50 % of all vertebrate diversity. Fishes have colonized virtually every aquatic habitat (Wootton 1992). This condition allows this group to be elected as an indicator of the environmental conditions of the aquatic ecosystems. Researchers have focused on fish as biomonitors of water pollution due to their special biological characters and advantages as indicators of the health of freshwater ecosystems. Among these features can be mentioned the following: fish live in the water all their life, unlike many invertebrates (Hogan and Vallance 2005), and therefore, they continually inhabit the receiving water and integrate the chemical, physical and biological histories of the aquatic ecosystems; they are sensitive to several kinds of disturbance, such as hydrologic alteration, as well as to the impact of pollutants; fish living in aquatic environments impacted by several disturbances are excellent models in which to analyze responses to several stressors; most fish species have a long lifespan (about 2–10 years) and can reflect both long-term and current water quality; fish have great diversity in their feeding habits, and therefore, are able to integrate ecosystem health over larger spatial and temporal scales. In this sense, fish are less affected by natural microhabitat differences than smaller organisms, making them extremely useful for assessing regional and macrohabitat differences (Hogan and Vallance 2005). Furthermore, the taxonomy of fishes is well established. Additionally, fish is one of the most studied groups in aquatic environments in terms of their biological and physiological responses. Fish provide ecosystems "goods and services" such as the produce of fisheries. More importantly, various fish species are at the top position in the aquatic food chain and may directly affect the health of humans, which is of much significance to biomonitoring using fish (Zhou et al. 2008).

37.4 Biomonitoring with Fish at Different Levels of Organization

37.4.1 Fish as Indicators at Lower Levels of Organization

Conventional tools for environmental monitoring and assessing contaminant levels do not reveal interactions between pollutants. The occurrence of a particular chemical in the environment, as revealed by chemical analyses, does not necessarily mean that it is bioavailable, nor can any conclusion be drawn with regard to any resultant harmful effects, or indeed any measurable effects on biological systems (Lam 2009); likewise, in aquatic ecosystems, pollution appears as a complex mixture of xenobiotics (van der Oost et al. 2003). In this sense, biomarkers can respond to toxic stress with various levels of specificity, and can also unveil the global effects of a mixture of contaminants in organisms. That is, some biomarkers are highly specific, as they respond to only one chemical or group of chemicals; however, perhaps the majority of biomarkers are less specific and respond to environmental stress in general (Lam 2009).

The most general effect of xenobiotics on fish is oxidative stress (disturbance of the pro-oxidant–antioxidant balance in favor of the former), which includes a variety of oxidative reactions that impair the health conditions of fish (van der Oost et al. 2003). Several contaminants can give rise to an increased generation of free radicals, particularly oxygen free radicals, also known as reactive oxygen species (ROS).

The ROS or their intermediates include superoxide anion (O^{2-}), hydrogen peroxide (H_2O_2), and the hydroxyl radical ($^{\cdot}OH$). Increased ROS production with exposure to pollution can occur by several mechanisms, which include the uptake of redox cycling metals and organic xenobiotics, the metabolism of xenobiotics to redox cycling derivates, such as quinones, and the induction of oxyradical generating enzymes (Livingstone 2003).

Recently, the production of contaminant-stimulated ROS and the resultant oxidative stress have been indicated as a mechanism of toxicity in aquatic organisms exposed to pollution (Livingstone 2003), and are known to play a large role in the pathology of several diseases and longevity in a number of species, thereby establishing ecological relevance.

ROS can cause severe damage to cellular macromolecules through the oxidation of DNA, membrane lipids, and proteins. However, cells possess efficient antioxidant enzymes to detoxify ROS (superoxide dismutase, catalase, and glutathione peroxidase, mainly), and the extent of damage to cellular macromolecules will depend on the balance between ROS production and antioxidant defense (known as primary defenses). Higher level consequences of ROS induced oxidative damage may include tumor formation and other oxyradical-mediated diseases, which depend on the species, organ, or cell type considered.

Lipid peroxidation is the oxidative deterioration of polyunsaturated lipids. The occurrence of lipid peroxidation in biological membranes causes impaired membrane functioning, decreased membrane fluidity, and inactivation of membrane bound receptors and enzymes. ROS can also cause the inactivation of numerous enzymes directly or through the indirect action of lipid peroxidation products. Biomarkers of oxidative stress include the lipid peroxidation level and activity of antioxidant enzymes, and have been applied in various fish species by several authors for assessing the health of aquatic ecosystems and environmental risk studies (Tejeda-Vera et al. 2007; Mahabub-Uz-Zaman et al. 2008; Trujillo Jiménez et al. 2011; López-López et al. 2011). Biomarkers of oxidative stress, although not specific biomarkers, are good indicators of stress exerted by a wide range of pollutants in aquatic ecosystems (van der Oost et al. 2003).

Other biomarkers also have been applied in fish to assess the impact of different chemicals released into environment whose ultimate destination is aquatic systems. Inhibition of cholinesterases has been widely used as a biomarker for organophosphate and carbamate pesticides (García et al. 2000), among which, inhibition of acetylcholinesterase (AchE) is one of the most commonly used biomarkers of neurotoxicity. Jebali et al. (2006) assessed the inhibition of AchE in fish *Seriola dumerilli* exposed to different concentrations of malathion, observing that AchE was significantly inhibited after 2 and 7 days of exposure in a dose-response manner, but no inhibition was observed after 13 days of exposure. López-López et al. (2006) carried out bioassays of exposure of fish *Girardinichthys viviparus* to water from different zones of the lake system of Xochimilco, Mexico, and found an inhibition of AChE activity of 5–20 % in the liver and gill, while brain values were less than 5 %. Authors conclude that neurotoxic compounds are present in the Xochimilco ecosystem.

Among other biomarkers can be mentioned the metallothionein levels, which have been used as biomarkers of exposure to heavy metals (Jebali et al. 2006; Linde-Arias et al. 2008).

In concordance with Lam (2009), biomarkers in fish can be used to devise rapid, effective screening assays, which can have a major role to play in programs of environmental monitoring and protection. Moreover, a battery of biomarkers used to assess the effects of pollution in an aquatic ecosystem allows the integration of a larger number of biological responses (Tejeda-Vera et al. 2007; Linde-Arias et al.

2008); some indices have been developed to integrate biomarker values into a single value, and serve as a tool in studies of environmental risk assessment; such is the case of the Integrated Biomarker Response (Beliaeff and Burgeot 2002), which was developed to assess several biomarker responses through computing the area of star plots, taking into account the spatial and temporal variations of biomarkers.

37.4.2 Fish as Indicators at Higher Levels of Organization

Several authors have used bioindicators at higher levels of organization (Ortiz-Ordoñez et al. 2011; Nath Singh and Srivastava 2010; Oertel and Salánki 2003; Tejeda-Vera et al. 2007; Trujillo Jiménez et al. 2011). Morphological alterations are individual level parameters that are measured to identify damage in sentinel organisms. Individual metrics include condition indices, such as the condition factor, the liver-somatic index, spleno-somatic index, and visceral-somatic index. All of these are indicators of overall organism health Others are several measures of reproductive integrity, including the gonado-somatic index (GSI), fecundity, and the incidence of atretic oocytes (Barton et al. 2002; Tejeda-Vera et al. 2007). At the population level, the metrics that can be used are size at age (growth indicator), sex ratio, and size-frequency distribution (mortality and reproductive indicators). These indicators show the structure of the population.

Several ecologically relevant responses at the community level have been used to assess fish community health. Environmental stress or degradation generally results in changes in the number of species (richness), their identity (similarity), and the relative abundance of the species that are components of the community. It is of major relevance to use the number of native species to assess species richness, which typically decreases with increased environmental degradation. Diversity indexes are useful for comparing communities. Odum (1985) gave the features that may be expected in a stressed ecosystem, including changes at community level: the proportion of "*r*" strategists increases; size of organisms decreases; lifespan of organisms decreases; food chains shorten because of reduced energy flow at higher trophic levels and /or greater sensitivity of predators to stress; and species diversity decreases and dominance increases.

Biotic indices for fish communities have been developed to measure relative ecosystem health. Karr and Dudley (1981) defined Biological Integrity as "the capability of supporting and maintaining a balanced, integrated, adaptive, community of organisms having species composition, diversity, and functional organization comparable to that of natural habitat of the region", and proposed the first biotic index for fish called the index of biotic integrity (IBI), noting that different factors may affect this biotic integrity (physical and chemical factors of the aquatic ecosystem, and biotic factors). The IBI is assessed based on metrics or fish assemblage attributes. The metrics should describe features, such as the taxonomy (species richness and composition), trophic (trophic position of species), reproductive (oviparous, viviparous), and tolerance features of the assemblage.

37.5 Benthic Macroinvertebrates as Biomonitors

Macroinvertebrates are all of those invertebrates that can be seen without the aid of a microscope or magnifying glass. Aquatic macroinvertebrates spend all or part of their life cycles in water and include many insects, crustaceans, mites, mollusks, and worms (Chessman 2003). Macroinvertebrate assemblages include a broad range of trophic guilds, which have been described according to adaptations for food acquisition rather than food eaten and are therefore called functional feeding groups (FFG) (Cummins and Klug 1979). They play a significant ecological role since they are an important link between energy inputs and their transfer to other trophic levels through the food web (Hanson et al. 2010), and participate in the balance between heterotrophs (depending of organic matter from terrestrial origin) at the head of rivers, and autotrophy that depends on primary production of the periphyton and macrophytes at downstream reaches of rivers. In this sense, also they are in contact with contaminants entering the system, accumulating them and transferring them to other levels. FFG are the basis of the river continuum concept developed by Vannote et al. (1980), which describes the structure and function of biological communities along a river system, and where the tendency of these biological communities moves toward a very efficient use of energy inputs through resource partitioning.

In addition, macroinvertebrates have an impressive diversity of respiratory adaptations (Chapman et al. 2004) ranging from aerial (v.g. Coleoptera, Hymenoptera), to branchial (v.g. Trichoptera, Plecoptera), cutaneous (v.g. Turbelaria, Nematoda, Diptera), and pulmonary (v.g. Gastropoda: pulmonata), and in special cases, to a combination, branchial-aerial respiration (v.g. Odonata Anisoptera) or branchial-cutaneous respiration (Simulidae). The presence of accessory respiratory pigments may also vary, being red in Chironomidae and some Oligochaeta (Jesus 2008). These strategies have associated costs and benefits that vary with ecological context and they limit the ability of some groups of invertebrates to use hypoxic waters (Chapman et al. 2004). Because there are different tolerances to concentrations of dissolved oxygen among taxa, the respiratory modes of macroinvertebrates are excellent traits to use as bioindicators of environmental conditions.

Macroinvertebrates are ubiquitous and abundant in most streams, occupy different habitats, and are present even in small streams where only a limited fish fauna is supported. Likewise, macroinvertebrates have limited movement or their lifestyle is sedentary. Most species of macroinvertebrates have long life cycles (approximately 1 year or more), which allow them to integrate environmental conditions over long periods of time (Mathuriau et al. 2011), and therefore, it is possible to monitor the contaminant effects along time. In this sense, macroinvertebrates assemblages are a good picture of local environmental conditions.

Macroinvertebrates exhibit a wide tolerance spectrum to contaminants, ranging from especially sensitive groups to those that tolerate highly polluted conditions.

Thus, the structure of the macroinvertebrate assemblages changes in response to environmental disturbances in predictable ways. Species richness and abundance (diversity) of the macroinvertebrate assemblages undergo a strong reduction in impacted areas, and more tolerant species predominate, whereas sensitive species only are present in environments with least or un-impaired conditions. Thus, the gradient of stream conditions from least-impaired to highly impacted zones is reflected in the diversity and structure of macroinvertebrates assemblages. These characteristics are the basis for biomonitoring using macroinvertebrates.

Sampling is relatively easy, and requires few human resources and inexpensive equipment. In addition, macroinvertebrates are relatively easy to identify at the family level, which is representative of their tolerance to contamination.

In the ecological context of biomonitoring, it is possible that some components of macroinvertebrate assemblages are not present during any time of year in the monitoring site. This will depend on the seasonality, life stages, and the effects of natural and induced drift. Another factor to take into account is the nature of the substratum, because macroinvertebrates have different preferences for substrate type. These variations do not necessarily depend on the effects induced by human activities and may cause bias in the biomonitoring because of the absence of some groups of macroinvertebrates, affecting those evaluation methods that are based mainly on scores by taxonomic group.

37.6 Approaches Using Macroinvertebrates for Assessing Aquatic Ecosystems Health

Several different assessing approaches are currently employed to evaluate river ecosystems. Some authors suggest the existence of at least 50 or more methods (Mandaville 2002). All of these methods are based on the characteristics mentioned above, through different mathematical tools, and may include diversity indices, biotic indices, integrated biological indices, multimetric, multivariate, and functional approaches; recently early warning biomarkers have become important in biomonitoring. Likewise, bioassays protocols using macroinvertebrates are an important tool for testing the acute and chronic toxicity effects of xenobiotics presents in water or sediments, as well as for testing toxicity from specific contaminants. In concordance with Karr (1991), a perfect index should be sensitive to all stressors from human activities exerted on biological systems; however, they also must discriminate those stresses from natural variation. Obviously, there are few indices that can fulfill this premise, but there are some indices with multimetric or biological integrity focus that consider more factors than those based on a few variables. No index is actually perfect. Below we attempt to describe some of these methods, from the simplest to the integrative.

37.6.1 Diversity Indices

Diversity indices reflect species richness and abundance of each species. There are different diversity indices that are sensitive to both the number of species and relative abundances of the species, such as the Shannon-Wiener and Simpson indices (Krebs 2009), as well as indices that estimate the homogeneity of distribution of abundances among species (evenness). Krebs (2009) points out that there are six factors that cause diversity gradients, one of which is disturbance. If we consider that the disturbance acts locally and can be represented by the environmental impacts, then diversity indices may reflect changes resulting from these impacts, and then, diversity indices allow us to assess easily the state of aquatic ecosystems. Communities with high scores of diversity indices show good environmental conditions, whereas those with low scores show environmental impacted conditions.

Flores and Zafaralla (2012) assessed the water quality status of the Mananga River in the Philippines using selected physicochemical factors in combination with the composition of macroinvertebrates and diversity indices. They found that taxa richness and diversity scores decreased significantly downstream, with better water quality and more favorable conditions for macroinvertebrate communities in the upper reaches of the river. Obolewski (2011) investigated the relationships between macrozoobenthos communities and the level of hydrological connectivity and hydrological similarities in a group of oxbow lakes using the Shannon diversity index, and found that benthofauna is strongly influenced by hydrological connectivity between the main river and oxbow-lakes. In both cases, taxa richness and diversity indices were excellent indicators of certain disturbances or environmental conditions.

37.6.2 Biotic Indices

Biotic indices have been developed to evaluate aquatic ecosystems through numerical scores for specific bioindicators at a particular taxonomic level; they are based on the fact that the healthiest streams have the greatest number of different types of pollution-sensitive organisms (Perry 2005). Score systems using macroinvertebrates have been developed to detect changes in communities; the results take the form of lists of taxa with or without abundances, which are analyzed to produce a score, class, or index (Armitage et al. 1983). Biological Monitoring Working Party (BMWP) was set up in 1976 (Hawkes 1997) to assess the biological condition of a river, which was suitable for presenting a broad picture of the biological condition of rivers in the UK. BMWP works with the taxonomic level of family, and the final score is obtained by summing the individual scores of all families present in a study site. Score values for individual families reflect their tolerance to contamination. Families intolerant to contamination have high scores, while families tolerant to pollution have low scores (Hawkes 1997; Armitage et al. 1983). BMWP index is one of the most widely used and has been adapted to the fauna of other countries in Europe and even adapted for use on other continents. The Average Score Per Taxon (ASPT) represents the ratio of BMWP score and the total number of taxa, and has been promoted as yielding results that are less sensitive to sampling effort and seasonal changes. Wyzga et al. (2013) carried out a study to evaluate the ecological state of the river Biala in Poland, using the BMWP index adapted to Poland (BMWP-PL), as well as ASPT values. They found that the macroinvertebrate community is sensitive to hydromorphological degradation. Likewise, Roche et al. (2010) used the original BMWP and some adaptations from other countries, and ASPT indices to identify environmental quality at different sites and seasons of a neotropical stream. They concluded that an adaptation of the BMWP for use in Brazil is the most appropriate for application in neotropical streams. This highlights the importance that biotic indices should have been adapted and calibrated for specific regions.

Kalyoncu and Zeybek (2011) used several biotic and diversity indices to determine water quality changes in the streams of Dariören and Isparta (Turkey). They found that diversity indices and the EPT (Ephemeroptera-Plecoptera-Trichoptera) biotic index reflect the water quality conditions much better, and in cases of high polluted study sites biotic indices proved to be good indicators.

37.6.3 Multimetric Approaches

Multimetric indices represent a means to integrate a set of variables or metrics that represent various structural and functional attributes of an ecosystem (Li et al. 2010); they have evolved into highly quantitative measures used to assess ecological conditions at different scales (from regional to continental) (Stoddard et al. 2008); also, metrics can include biotic indices. Metrics such as taxa richness (total number of taxa, number and ratios of Ephemeroptera, Trichoptera and Plecoptera taxa), diversity, tolerance measures (BMWP, ASPT, EPT/Chironomidae), composition measures (percentage of different taxa) and functional measures (composition of functional feeding groups), have been taken into account by several authors to develop multimetric indices (Ferreira et al. 2011; Thorne and Williams 1997).

37.6.4 Multivariate Approaches

Multivariate methods are basically statistical tools for determining relationships between bioindicators and environmental characteristics with respect to a reference site (Abbasi and Abbasi 2012). Among multivariate approaches for bioassessment may be included ordination analyses, such as principal components analysis, detrended correspondence analysis, canonical correspondence analysis, discriminant function analysis, etc., and clustering analysis such as similarity measures, hierarchical and nonhierarchical clustering, multidimensional scaling, among others. In addition, with reference to the condition approach, multivariate approaches have given way to predictive models, such as the River Invertebrate Prediction and Classification System (RIVPACS), and some derivative models, such as the Australian Rivers Assessment System (AusRivAS) and Benthic Assessment Sediment (BEAST) (Li et al. 2010).

37.6.5 Indices of Biological Integrity

Although initially developed for use with fish communities, the ecological establishments of IBI can be used to develop similar indices that apply to other taxa, such as algae, macroinvertebrates and macrophytes, or even to combine taxa into a more comprehensive assessment of biotic integrity. In any case, the value for each metric is based on comparison with a regional reference site (pristine site) characterized by little or no influence from human activities (Karr 1991). The IBI uses a combination of univariate and biotic indices in an attempt to capture with greater sensitivity the impacts of anthropogenic disturbances on aquatic ecosystems (Abbasi and Abbasi 2012); several attributes can be used for the development of an IBI, but they must be within one of the three groups types of metrics: (a) species richness and composition, (b) trophic composition, and (c) abundance and condition (Karr 1991). An IBI requires a comparison of the index scores of test sites with the scores achieved by the natural habitat of the region. Thus, the aim of an IBI is to convey a more integrated picture of ecosystem health (Abbasi and Abbasi 2012). Weigel et al. (2002) developed an IBI based on macroinvertebrates using attributes such as taxa richness and composition, feeding morphology, and tolerance to organic pollution, and could discern that effluents of the sugar cane industry and municipal wastewater discharges are the main factors that affect the environmental condition in rivers of the Mexican Pacific Slope.

RIVPACS is a special case of IBI and multivariate approaches, and is a predictive method for identifying deviations of an ideal macroinvertebrate community as a result of human impact.

37.6.6 Functional Approaches

Cummins et al. (2005), state that macroinvertebrates may be used to conduct biological assessments of streams and rivers through two approaches. The first and the most usually applied is the taxonomic approach, as we have seen above. The second is the functional approach, which is more appropriate for assessing the ecosystem condition. In fact, researchers have promoted the functional classification of species into groups with similar biological and ecological traits that are expected to respond consistently along specific environmental gradients (Poff et al. 2006). Menezes et al. (2010) indicate that a trait is defined as a characteristic that reflects a species adaptation to its environment, and traits are divided in two categories: biological traits, such as life cycle and physiological and behavioral characteristics, feeding and reproductive strategies, etc., and ecological traits, which include habitat preferences, biogeographic distribution, and tolerance to organic pollution, among others. Culp et al. (2010) found that among the advantages of using traits in biomonitoring are: (a) the ability to provide mechanistic linkages of biotic responses to environmental condition and improve sensitivity, (b) consistent descriptors or metrics across broad spatial scales, (c) more seasonal and inter-annual stability as compared with taxonomic measures, (d) the ability to integrate traits-based analysis seamlessly into current assessment programs, and (e) greater utility of biomonitoring outputs in ecological risk assessment.

To date, functional approaches based on the biological traits of macroinvertebrates are used for assessing aquatic ecosystems health. Mainly, traits such as FFG (Bonada et al. 2006), respiratory strategies (Chapman et al. 2004; Jesus 2008), and a combination of several traits (Gerhardt 1996; Ippolito et al. 2012) are being considered.

37.6.7 Early Warning Biomarkers

Despite the fact that the population, community, and ecosystem are key levels for monitoring deleterious effects from adverse environmental impact in aquatic ecosystems, toxic effects are manifested at the molecular, subcellular, biochemical, physiological, morphological and behavioral levels that alter biological functions that harm individual organisms (Hyne and Maher 2003), and it is at these levels that abnormalities can be detected whose amelioration could prevent damage at the population, community, and ecosystem levels (Sherry 2003). Therefore, studying the biochemical effects of pollutants on organisms is a reliable approach to diagnose early damage in organisms (Barata et al. 2005). Biochemical approaches based on biomarkers offer the possibility of rapidly detecting the initial stages of damage in the suborganismal level. Bonada et al. (2006) indicate that biomarkers have been increasingly used as a diagnostic tool in aquatic invertebrates for assessing the ecological status of aquatic ecosystems, including biomarkers such as mixed-function oxidases, acetylcholinesterase, cellulose/carbohydrase, genotoxicity, ion regulation, stress proteins, and oxidative stress. Studies of the temporal response of contaminant levels and biochemical effects in sentinel macroinvertebrates can be a reliable and essential method if they are used to diagnose ecological impairment due to contaminants (Hyne and Maher 2003; Barata et al. 2005).

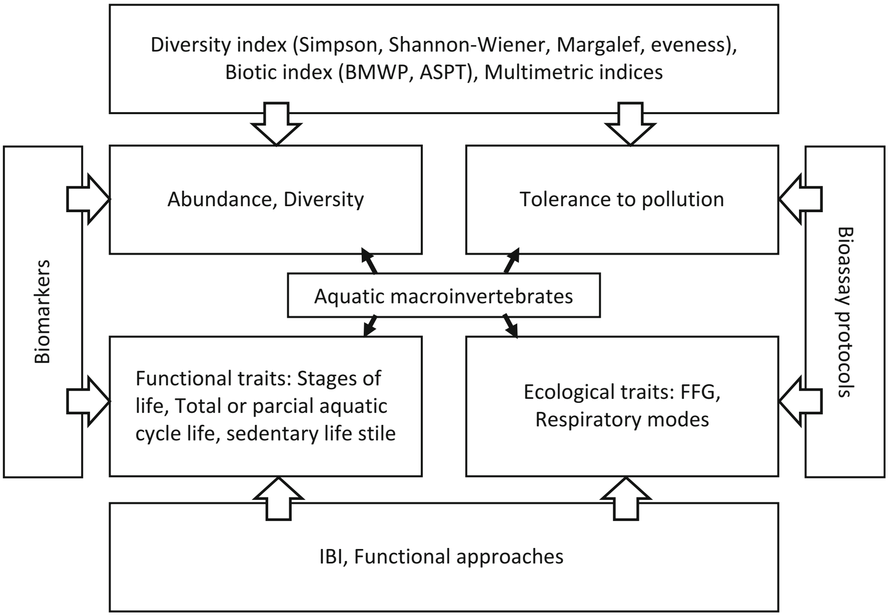

Fig. 37.2 Aquatic macroinvertebrates features as biomonitors and its relationships with approaches used for assessing aquatic ecosystems health

37.6.8 Bioassays Protocols

Macroinvertebrates have an important role in aquatic ecosystems, mainly as components of the food web, and they are able to accumulate contaminants from sediments or water column; therefore, they are especially useful as test organisms for identifying the acute and chronic effects of specific pollutants. Tests are performed through exposure bioassays. There are several bioassay protocols with specific purposes. The Environmental Protection Agency has developed several procedures for testing freshwater organisms, such as *Hyalella azteca* and *Chironomus tentans*, where the end point for *H. azteca* is survival, and for *C. tentans,* survival and growth. Borgmann and Munawar (1989) proposed a new standardized bioassay procedure for testing the chronic toxicity of sediments to *H. azteca*. This new standardized bioassay is being applied for the assessment of sediments from areas of concern in the Great Lakes and St. Lawrence River. Gerhardt (1996) performed a bioassay using two macroinvertebrates species as sentinels to test the effects of wastewater from a factory.

As we have seen, the main approaches to assessing the aquatic ecosystems health based on macroinvertebrates depend on the features that distinguish the macroinvertebrates as biomonitors. Figure 37.2 shows the main features of macroinvertebrates as biomonitors and their relationship to different assessment approaches. Richness, evenness, diversity indices, biotic indices, and multimetric indices are based primarily on characteristics such as diversity, abundance, and tolerance to contaminants. These features have proven to be excellent indicators of aquatic ecosystem health, but could also reflect the aspect of human impacts.

IBI and functional approaches, in addition to diversity and tolerance to contaminants, have a narrow relationship with functional and ecological traits (Fig. 37.2) because the biological and ecological functions of the organisms involved allow us to have a clearer picture about what is happening in aquatic ecosystems. These approaches are more integrative to higher levels of organization.

Biomarkers approaches are an eminent test as to whether toxicants have entered the organisms and have effected critical targets. Different results can be yielded, depending on the stage of life analyzed, as well as on the type of organism studied. Therefore, these approaches are closely related to measures in sentinel species in which the effects of exposure to xenobiotics are evident. In this sense, a sentinel species with sedentary habits is eligible; also, the measurements must be made in the sensitive stages of the life cycle. Juvenile stages of invertebrates are far more sensitive to a large variety of pollutants (Lagadic and Caquet 1998). It is desirable that sentinel species are abundant and ubiquitous (Fig. 37.2).

Bioassays protocols are extremely useful for testing the isolated effects of individual pollutants and evaluating their toxic effects, but also for assessing the effects of a mixture of pollutants in the test organisms. The bioassays are based primarily on pollution tolerance of sentinel species and ecological characteristics, such as feeding habits, respiratory modes, and their place in the food web (Fig. 37.2).

Concluding Remarks

Aquatic organisms provide direct and indirect evidence of affectations occurring in the aquatic ecosystems. Fish and macroinvertebrates, from the suborganismal level to community level, exhibit excellent response signals to stressors, making them two of the most suitable groups for the assessment of aquatic ecosystems.

Differences in macroinvertebrates' tolerance to contaminants is the basis of biomonitoring; therefore, they reflect, both the spatial (locally and regionally) and temporal (past and present) effects of the water quality conditions of water bodies.

The assessment of physicochemical water quality provides results according to individual parameters, while biological responses integrate a multitude of stressors that may be present in aquatic ecosystems. Biological and ecological responses of aquatic organisms reveal the real effect-causing contaminants and their mixtures, and integrate effects with measurable responses from suborganismal to community levels.

The role of biomonitoring is, finally, the development of a diagnosis to identify the causes and effects of the different impacts on water resources and

(continued)

assist in the decision making regarding the actions to be taken to protect, restore, and conserve of aquatic resources. Since there are different approaches to assessing the aquatic ecosystem health, the selection of one of them depends on the objectives, infrastructure, and resources available.

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Chapter 38
Histopathological Indicators in Fish for Assessing Environmental Stress

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Abstract We present the usefulness of histological and histopathological techniques as tools for evaluation of fish health. Stress at the individual level is frequently presented in the form of tissue damage and we are interested in the study of this level as a health indicator, since it is intermediate between the biochemical and reproductive levels. In addition, we analyzed two case studies conducted using the viviparous fish *Goodea atripinnis,* the first about the health status by size class of the fish species in the Yuriria Lake, which is affected by a complex mixture of xenobiotics from agriculture, industry, and wastewater, and the second about chronic exposure to a herbicide based on glyphosate. In both cases, various anomalies were found in the liver (fibrosis, cellular disorganization, hemorrhages and vacuoles, pyknosis, and cell lysis), and gills (lamellar fusion, sloughing, hypertrophy, hyperplasia, and leukocyte infiltration). Both studies demonstrated the utility of fish as sentinel organisms and histopathological analysis as a useful tool in environmental biomonitoring to detect early warning signals in aquatic environments.

Keywords Tissue damage • Histopathological analyses • Gill and liver damages • Target tissues • Chronic exposure

38.1 Introduction

Water bodies are systems that are constantly altered by a variety of pollutants from various sources. The increase in the synthesis of chemicals for domestic, industrial, and agricultural use has generated a continuous discharge of these chemicals, which

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_38

are known as xenobiotics, into aquatic ecosystems. The input of the xenobiotics to water bodies is the result of several factors: its proximity to the site in which the compounds are used, chemical spills after an aerial application, or various hydrological and atmospheric processes (Stegeman and Hahn 1994). Lakes and reservoirs have a different configuration and dynamic than other aquatic ecosystems (*i.e.*, streams and rivers), and are therefore more likely to receive and accumulate contaminants from drains, household waste, and agricultural runoff (Ahmad et al. 2006), giving rise to the generation of complex mixtures of xenobiotics that are unstable over time and space.

Thus, organisms that inhabit these water bodies are faced with continuous exposure to mixtures of xenobiotics, which can cause disruption in the health of the biota (van der Oost et al. 2003). However, in most aquatic systems it is difficult to establish a clear link between environmental pollutants and the health of organisms due to the wide variety of environmental and ecological factors that influence the response of aquatic biota (Adams et al. 1999). Moreover, the responses of the aquatic biota to stress are dissimilar at different levels of organization, since the responses can occur at the cellular, tissue, organism, population, community, and ecosystem level (Adams et al. 2001).

Therefore, it is necessary to use tools that allow the identification and quantification of the damage exerted by the mixtures of xenobiotics on aquatic biota in their natural environment, particularly when the exact composition of the agents that are in the water and the antagonistic or synergistic reactions triggered by the interaction of these compounds are unknown. Furthermore, it is necessary to use the most appropriate test organism according to the objectives of each investigation, as well as the appropriate level of organization. In the aquatic environment, fish are an important component of the ecosystem: fish are distributed in virtually all aquatic systems, are involved in the flow of energy through different trophic levels, have varied habits, relatively long life cycles, different reproductive and feeding strategies, a relatively high mobility in the water column (van der Oost et al. 2003; Linde-Arias et al. 2008), and are relatively easy to capture, manage and identify; in addition, they are able to show biological responses to contaminants exposure at different organization levels (suborganismal, individual, population, and community); hence, they are commonly chosen as sentinel organisms. At the individual level, histopathological alterations are presented that may occur as a result of environmental stressors other than contaminants and that are known to occur as a consequence of adverse environmental conditions. The histopathological research seeks to find differences between organ lesions induced by diseases and other environmental factors and those due to pollutant exposure (Schwaiger et al. 1997). The use of histopathological biomarkers is relatively recent. Moreover, there are few studies of histopathology in fish, and even fewer of organisms obtained *in situ* or in field studies, most studies being focused on the microscopic description of cells and tissues (histological technique) and occasionally being used to complement bioassays. Some of these are the studies of Schwaiger et al. (1997), Au (2004), Ajani et al. (2011), Ortiz-Ordoñez et al. (2011). The aim of this contribution is to review the utility of histopathology as an indicator of fish health through the results of two cases of study.

38.2 The Use of Histology in Biomonitoring with Fish

Biochemical markers have the advantage of a rapid response time, but the limitation that their ecological relevance is unclear; on the other hand, growth and reproductive responses have the advantage of high biological and ecological significance, but the limitation of relatively low sensitivity to stress. The individual organism, and particularly the manifestations of stress at tissue level, represents an intermediate level between biochemical and reproductive levels (Teh et al. 1997). Histological changes are more sensitive and occur earlier, are manifestations of alterations produced in the molecular and biochemical levels and presented before reproductive damage (for example, the mechanism of action of several xenobiotics could initiate the activation of a specific enzyme that causes changes in metabolism, further leading to cellular intoxication and death, at a cellular level, whereas this manifests as necrosis in tissue level), and are more sensitive than growth or reproductive parameters, providing a better assessment of fish health, as well as the effects of pollution, than a single biochemical parameter (Segner and Braunbeck 1988; Velkova-Jordanoska and Kostoski 2005; Valon et al. 2013). Histopathological biomarkers are a viable tool for detecting the effects of xenobiotics on aquatic biota, including fish, because the adverse changes manifested in the tissues of organisms allow those organs that are more prone to damage caused by xenobiotics to be identified as target organs. Schwaiger et al. (1997) reveal that histopathological investigations appear to be valuable tools for detecting the effects of various aetiologies and contribute to the understanding of the nature of stress responses at lower levels of biological organization; however, a standardized working protocol that allows the use of histopathology as a tool in biomonitoring programs is lacking.

38.2.1 Target Organs

The mode in which the various organs respond to xenobiotic exposure has proven their useful as a tool in determining the health condition of fish, since histopathological biomarkers are considered the primary indicators of exposure to pollutants and show little temporal variation (Au 2004). These indicators also integrate the effects of environmental factors (Auró and Ocampo 1999 and Gernhofer et al. 2001), and adaptation and fitness events that the organisms may have suffered along their life history, such as budgets in energy, biochemical, and physiological processes, better known as "trade-offs" (Jones and Reynolds 1997; Iwama et al. 2004; Fonseca et al. 2009; Johansen et al. 2005; Pörtner et al. 2005). Sometimes, it is difficult to determine the appropriate tissue for histological study, and hence, the first criterion to be taken into account is the type of study to be conducted. Fortunately, in fish some "target organs" there have been detected, such as the gills and liver, which are frequently employed in toxicological analyses and recently for environmental biomonitoring (INECC 2009; Ruiz-Picos and López-López 2012).

The gills of fish are a multifunctional organ responsible for respiration, osmoregulation, acid-base balance, and excretion of nitrogen compounds. This organ is sensitive to the presence of chemicals in the water, since the filaments and lamellae provide a wide surface of contact with water contaminants (Au 2004).

In turn, the liver is the largest and most important organ of the body, having several physiological functions, including the biotransformation of organic xenobiotics, excretion of harmful metal traces, storing of energy sources (such as glycogen), and protein synthesis; and this organ has high enzymatic activity. Additionally, the liver of fish is sensitive to environmental contaminants because some contaminants tend to be accumulated in this organ, causing bioaccumulation. Therefore, the responses observed in the liver are indicative of the overall health of the fish upon exposure to toxic xenobiotics, carcinogenic materials, and urban pollution in general, although this organ has no direct contact with pollutants dissolved in water as gills (Au 2004; Fernandes et al. 2008; Gül et al. 2004; Wolf and Wolfe 2005; Zhu et al. 2008; Valon et al. 2013).

Some authors have used these organs as target organs to identify histopathological damage. Fernandes et al. (2008) and Rondón-Barragán et al. (2007), who worked with *Liza saliens* and *Piaractus brachipomus*, respectively, all found gills with hypertrophy, hyperplasia, and lamellar fusion. In addition, there are records of parasitic infections in the gills of various species, such as *Piaractus mesopotamicus*, *Colossoma macropomum*, *Xiphophorus maculatus*, and *Oncorhynchus mykiss*, as described by Laterca and García (1996), Mitchell et al. (2005), Omrani et al. (2010) and Olson and Pierce (1997), respectively. Other authors, such as Wolf and Wolfe (2005) and Gül et al. (2004), recorded several types of liver damage in fish including liver fibrosis, the presence of vacuoles, and cell lysis. In the following paragraphs, we will highlight two study cases where histopathology was used as an indicator of fish health.

38.3 Case Studies

The first case study shows the performance of the fish *Goodea atripinnis* as a sentinel organism in assessing a reservoir located in the central plateau of Mexico using a histological biomarker in different size classes. *Goodea atripinis* is a viviparous fish endemic to the Central Plateau of Mexico and is characterized as an omnivorous species, with sexual dimorphism, attributes which were taken into account when choosing this species as sentinel.

These organisms inhabit the Yuriria Lake, an artificial reservoir built in 1548, located in the Lerma River basin, known as the Lerma-Chapala system (Guanajuato state, Mexico). This water body receives wastewater from industrial and urban origin through their tributaries with consequent input of various xenobiotics forming a complex mixture. Furthermore, the land use around the lake is basically agricultural and livestock, which adds products such as fertilizers, pesticides, and organic matter. Additionally, recreational fishing activities are carried out in the lake, and the water hyacinth covers a considerable portion of the surface of the lake. All these activities produce complex mixtures of pollutants that once incorporated in the lake exert a direct impact on several fish species inhabiting this water body.

The methods employed include the collection of a group of fish at two study sites in the lake: "Cahuageo" and "Isla." The first study site is impacted by domestic wastewater and fishing, while at the second study site, the main activities include agriculture. Domestic wastewater is also an issue but its impact is less evident. A total of 70 fish per study site were collected, which were sacrificed by decapitation. Their standard length was measured and fish were dissected to obtain liver and gills of each organism. These tissues were fixed in 10 % formalin with phosphate buffer and transported to the laboratory, where the histological technique was conducted in paraffin to obtain ten slides per tissue, which were subsequently stained using the hematoxylin-eosin and Masson Trichrome techniques. A photomicroscope was used for observing the slides observation and capturing images. The analysis of the results involved the assessment of the percentage of the incidence of each morphological damage identified. A group of control organisms was simultaneously processed using this technique; organisms were obtained from a culture free of contaminants to observe the condition of the tissues without xenobiotic exposure.

Results showed that over 90 % of the specimens at both study sites had some sort of affliction in the liver, while about 50 % of the organisms had some damage in the gills (Fig. 38.1). The identification of pathologies in both tissues was conducted to observe the type of damage and the conditions in which tissues were found.

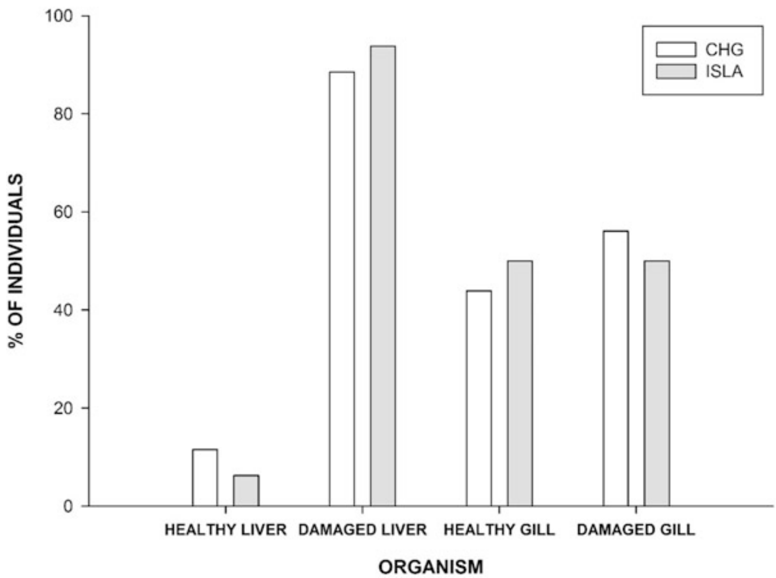

Fig. 38.1 Proportions of *Goodea atripinnis* organisms with affections in the liver and gills of organisms of Cahuageo (CHG) and the Isla

Damage detected in the liver of the organisms include thickening of fibers, cell disorganization (loss of typical arrangement of hepatic cords), cell lysis, hemorrhages, and the development of vacuoles (Fig. 38.2a–d). The highest percentage of affected organisms in terms of this tissue was found at the Isla site: mainly cell disorganization, bleeding, and cell lyses (Fig. 38.3).

In the gills, the damage detected was, hypertrophy and hyperplasia, epithelial sloughing, cysts of parasites and lamellar fusion (Fig. 38.4a–d). In this case, organisms from Cahuageo showed the highest percentage of all types of damage (Fig. 38.5).

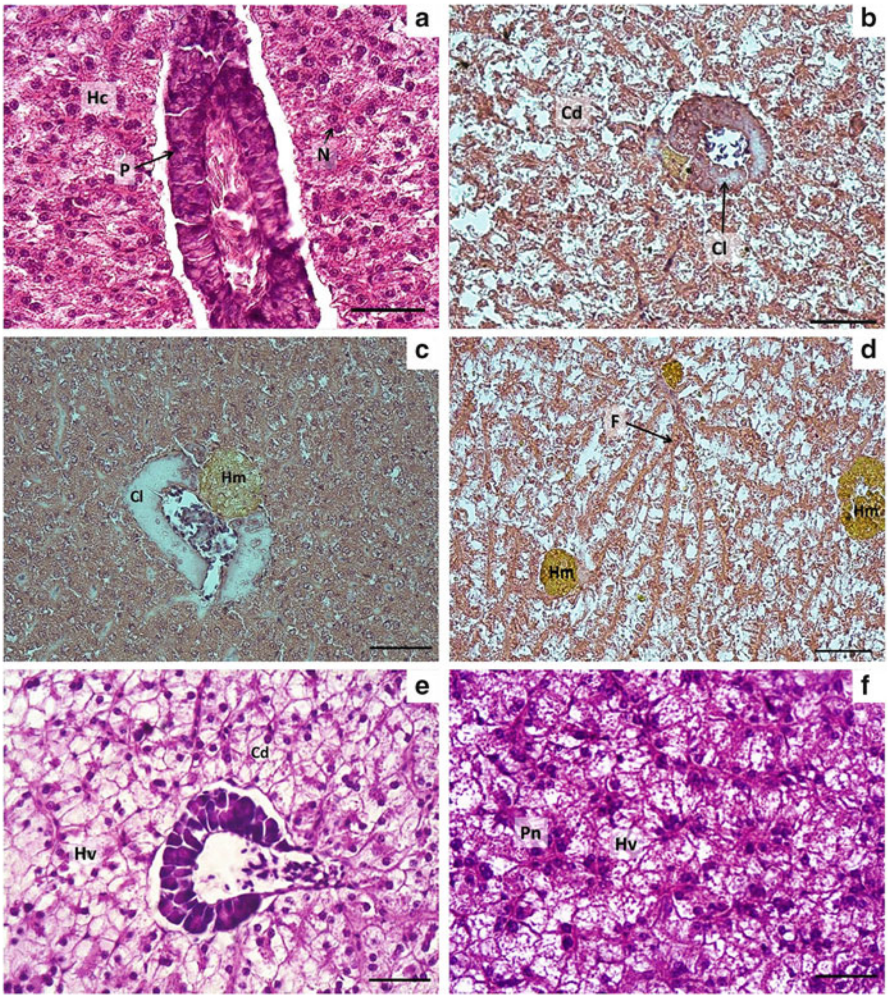

Fig. 38.2 Structures and liver pathologies in *Goodea atripinnis*: (**a**) hepatic cords (*Hc*), pancreas (*P*) and nuclei (*N*); (**b**) cell disruption (*Cd*) and cell lysis (*Cl*); (**c**) hemorrhage (*Hm*) and cell lysis (*Cl*); (**d**) fibrosis (*F*) and hemorrhage (*Hm*); (**e**) vacuole (*Hv*) and cell disruption (*Cd*); (**f**) nuclei pyknosis (*Pn*) and vacuole (*Hv*). Technique Hematoxiline-Eosin, 40×, bar = 20 μm

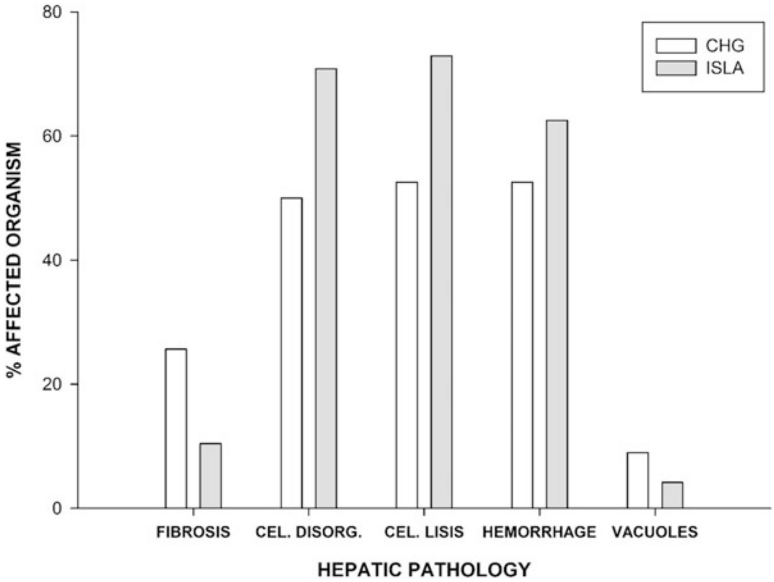

Fig. 38.3 Proportion of individuals affected by the pathologies identified in the liver of *Goodea atripinnis* in Cahuageo (CHG) and the Isla

Size classes of organisms were determined using Battacharia method (Sparre and Venema 1998) in order to determine the differences between juvenile and long-lived organisms. Three size classes were found: Class I comprising smaller organisms less than 39 mm standard length, Class II comprising organisms between 40 and 59 mm, and Class III comprising organisms of more than 60 mm in standard length.

The results for the liver by size class indicated that the presence of fibers increases with the fish length in both locations, the bleeding is enhanced significantly in the organisms of the Class III, cell disorganization is more common in individuals of the Class I and II, and the presence of vacuoles occurs primarily in Class III, although there are some cases in organisms from the study site 2 that belong to Class II (Fig. 38.6).

In contrast to data observed in the liver, in the gills hypertrophy, hyperplasia, and epithelial sloughing cysts appear to affect the smaller size classes more, and hence the highest percentage of individuals affected corresponds to Classes I and II, showing a greater effect at the Cahuageo site, except for lamellar fusion that was observed only in Class III in this site (Fig. 38.7).

The second case of study corresponds to that described in Ortiz-Ordoñez et al. (2011), and also was performed using *Goodea atripinnis* as a test organism. The experiment consisted of exposing a batch of 50 organisms to a single sublethal dose corresponding to 1/49 of the LC_{50} for *G. atripinnis* of a commercial herbicide formulation containing glyphosate, for a period of 75 days. At the same time, a control group was cultured free of xenobiotics. Every 15 days, nine organisms were drawn at random and were sacrificed and dissected to obtain the gills and liver, which were

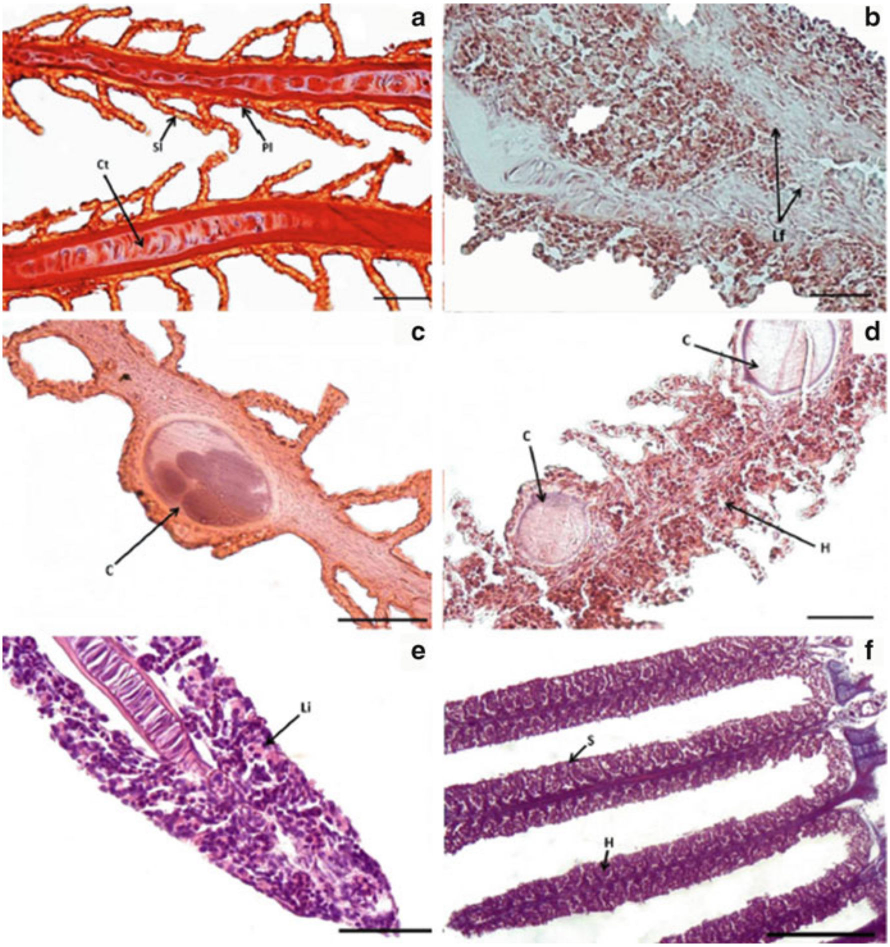

Fig. 38.4 Structures and gill pathologies in *Goodea atripinnis*: (**a**) cartilage (*Ct*), primary lamella (*Pl*) and secondary lamellae (*SL*); (**b**) lamellar fusion (*Lf*); (**c**) cysts (*C*); (**d**) hypertrophy and hyperplasia (*H*) and cysts (*C*); (**e**) leukocyte infiltration (*Li*); (**f**) epithelial sloughing (*S*), hypertrophy and hyperplasia (*H*). Masson trichrome technique (**a**) and hematoxylin-eosin, 40× and 10× (**f**) bar = 20 μm

fixed and stored in 10 % formalin in phosphate buffer. Subsequently, histological technique was performed as described above for obtaining the corresponding slides.

The liver of specimens exposed to the herbicide showed changes in structure after 30 days of treatment. Alterations included the presence of vacuoles that increased in number and size over time, the displacement of the nuclei to the periphery, pyknosis of the nuclei, and the development of fibers (fibrosis) whose length and thickness increased to become completely conspicuous (Fig. 38.2e, f).

After 30 days of exposure, gill cell hypertrophy was evident, with vascular congestion and disruption of capillaries, demonstrating the presence of blood

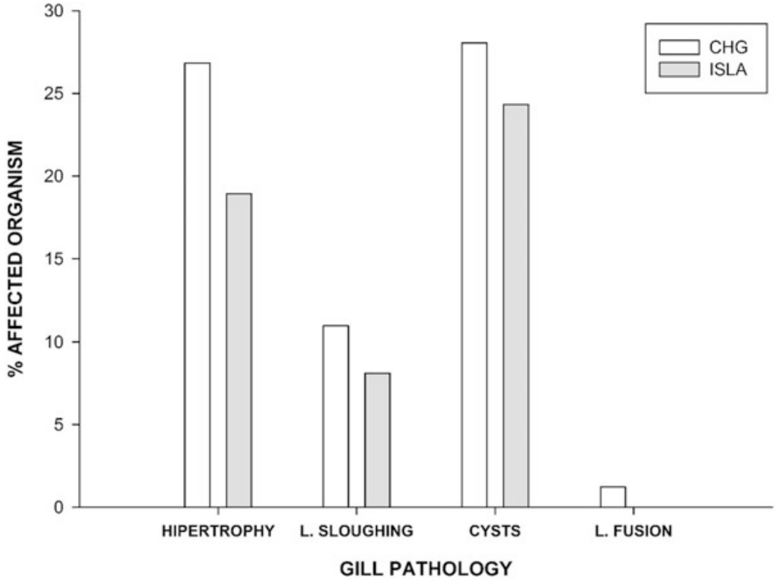

Fig. 38.5 Proportion of individuals affected by the pathologies identified in the gills of *Goodea atripinnis* in Cahuageo (CHG) and the Isla

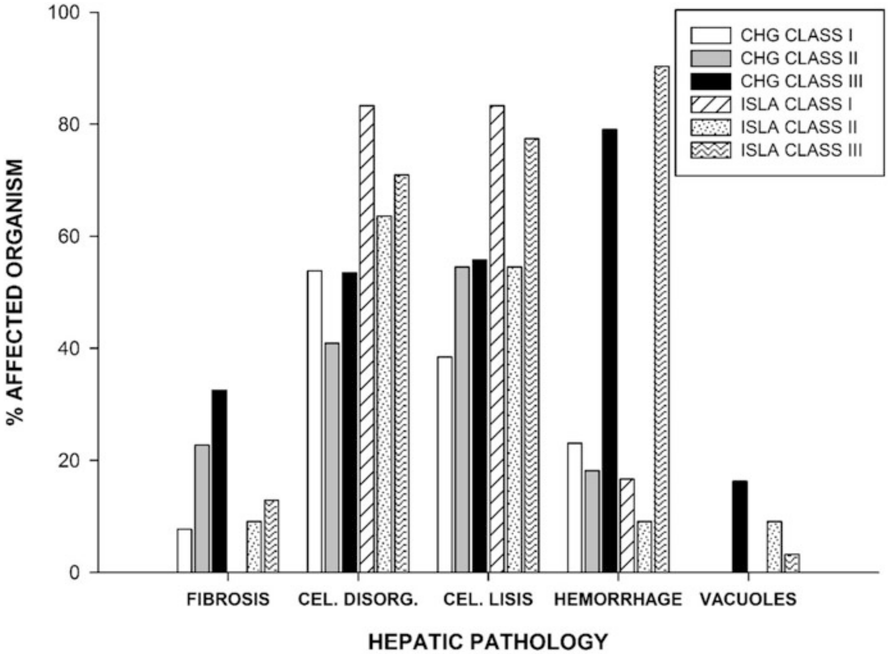

Fig. 38.6 Proportion of individuals affected by the pathologies identified by size class in the liver of *Goodea atripinnis* in Cahuageo (CHG) and the Isla

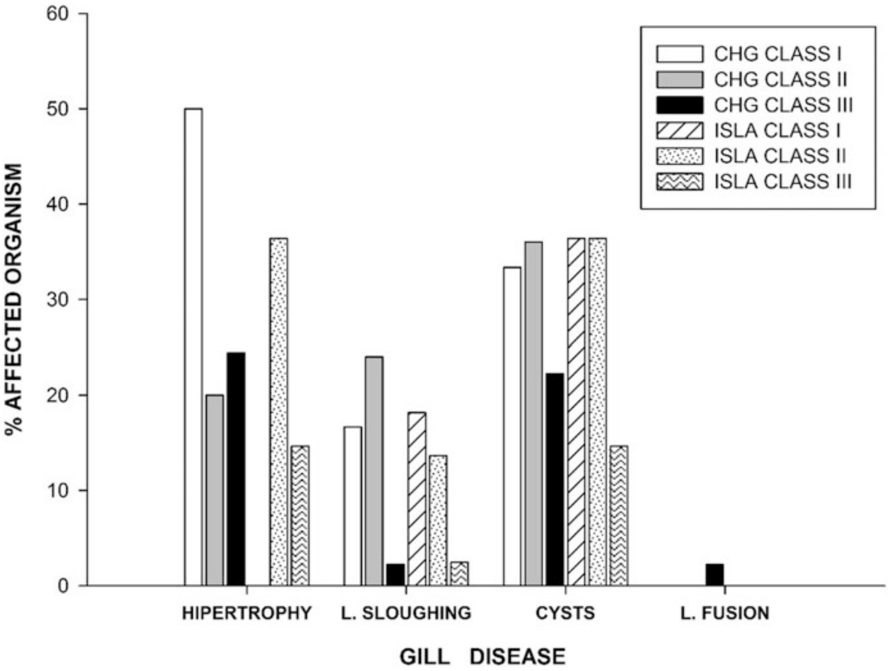

Fig. 38.7 Proportion of individuals affected by the pathologies identified by size class in the gills of *Goodea atripinnis* in Cahuageo (CHG) and the Isla

cellular components involved in this tissue. In addition, sphacelation (detachment of the epithelium in tissue) was evident after 45 days of exposure (Fig. 38.4e, f). In this study, it was possible to detect a histological damage cause-effect, in both liver and gills as a consequence of a specific xenobiotic exposure.

38.4 Scope of Histological Analysis

The amount and quality of information obtained from histological studies depends on several factors, including the efficiency in performing the histological technique, the detailed analysis of the samples, and the complementary tools to be added to the study. In the case studies, the usefulness of histopathology was exemplified. In the first case, enough information was obtained to provide a general assessment of the effects of water quality on fish health, showing the proportion of affected individuals for each tissue and each size class. In addition, it was possible to detect the most affected target organ in each locality: in the study site "Isla," the liver was the most damaged organ, while in "Cahuageo," the gills were apparently more susceptible to the effects of contaminants present in water.

Finally, by determining the size classes of organisms, it was possible to observe the proportion of individuals affected, their pathologies, the potential target organ in each locality and, furthermore, that size class more susceptible to a certain pathology caused by the effects of contaminants at each study site. This approach allows us to identify that chronic exposure of organisms to the conditions of the Lake Yuriria causes severe damage to the population structure per size class and in turn affects important events, such as the growth and reproduction of the organisms, jeopardizing their survival in the lake.

In the second case study, evidence was found that chronic exposure to a particular contaminant, in this case an herbicide, has adverse effects on the tissues of *G. atripinnis*, and also that the damage can be accentuated over time until some of the damage becomes irreversible.

38.5 Advantages and Disadvantages

Valon et al. (2013) mentioned that fish liver histopathology is a good bioindicator and can be used to detect chemical pollution in fish. Through histopathological analysis, these authors concluded that the Sitnica River (Kosovo) is chemically contaminated. Ruiz-Picos and López-López (2012), using histopathological techniques in combination with a battery of oxidative stress biomarkers in Lake Yuriria (Mexico), found a gradient of histological damage from juvenile to longer-lived organisms, which can reduce the fitness of fish by reducing their lifespan and reproductive capacity. Thus, histological analysis can be a highly effective tool in the biomonitoring of water if used properly; however, as in most cases, it has advantages and disadvantages, some of which are listed in Table 38.1.

Table 38.1 Advantages and disadvantages of histopathological analysis

Advantages	Disadvantages
The effects of exposure of fish in laboratory to specific pollutants show that histopathological analyzes are excellent indicators of damage by the exposure to xenobiotics	No clear cause-effect relationship for studies *in situ* The histological technique is laborious and time consuming
The effects are manifested in the short and long term	
The results show scarce seasonal variation effect in organs such as liver and gills	
Morphological damage responses combine antagonistic and synergistic effects of pollutants	
Histopathology can be used in toxicological acute and/or chronic studies, and *in situ* studies	
Histopathology allow the identification of target organs	
Consider the seasonal adjustment and possible genetic adaptations	
Can be combined with other complementary approaches such as early warning biomarkers, scanning electron microscopy and histochemical techniques used to highlight specific molecules or their activity	
Relatively inexpensive	

Conclusions

Fish are versatile organisms for biomonitoring studies in water bodies. They truly act as sentinel organisms through integrating the effects of xenobiotics and environmental factors in responses that can be detected by several techniques, including histological, to assessing their health condition. Histological and histopathological techniques have proved to be a suitable tool for fish health condition studies, since the results obtained indicate not only the current condition of the organism studied, but also allow long-term projections of the effects that can be expected in the future. Furthermore, the consequences at higher levels of organization, such as population, community, and ecosystem, can be predicted. Thus, we conclude that the histological technique can effectively assist in assessments as an indicator of fish health.

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Chapter 39
Risk Management During Effluent Application for Irrigation

Gideon Oron, Laura Alcalde-Sanz, Leonid Gillerman, Yossi Manor, Amos Bick, and Miquel Salgot

Abstract Reuse of treated wastewater is a favourable direction for solving water shortage problems and meeting environmental quality criteria. Domestic wastewater in isolated communities in arid regions can be treated efficiently in a stabilization pond system. The effluent quality can be further improved when stored in a series of stabilization reservoirs. However the salinity of the wastes in the ponds will increase due to evaporation. There is a series of parameters that characterize the effluent quality for agricultural reuse. The conventional biological parameters include faecal coliforms as a microbial indicator. The use of faecal coliforms does not reflect the viral pollution of the effluent due to the poor correlation with virus occurrence. Therefore, phages are proposed as enteric virus pollution indicators. Phages exhibit similar behaviour and survival in an aquatic environment, and their quantitative assessment is easy and a reliable enteric virus measure. Field results from the treatment plant of the City of Arad (Israel) reveal the possibility of characterizing the effluent quality in stabilization ponds and additional reservoir systems. The field data also allows the type of reactor of which the system consists to be defined, and the kinetic expressions for further forecasting of the treatment system behaviour and removal rate of the pathogens.

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_39

Health risks to consumers due to the consumption of agricultural products irrigated with reclaimed wastewater were assessed by numerical simulation. The analysis is based on defining of an Exposure Model (EM), which takes into account several parameters: (i) the quality of the applied effluent; (ii) the irrigation method used; (iii) the elapsed times between irrigation, harvest, and product consumption, and; (iv) the consumers' habits of consuming these agricultural products. The exposure model is used for numerical simulation of human consumers' risks by running the Monte Carlo simulation method. Although some deviations in the numerical simulation, which are probably due to uncertainty (impreciseness in quality of input data) and variability due to diversity among populations, reasonable results were obtained. Accordingly, there is a several orders of magnitude difference in the risk of infection between the different exposure scenarios with the same water quality. Extra data are required to decrease uncertainty in the risk assessment. Future research needs to include definite acceptable risk criteria, more accurate dose-response modeling, information regarding pathogen survival in treated wastewater, additional data related to the passage of pathogens into and in the plants during irrigation, and information referring to the consuming habits of the human community.

Keywords Risks • Pathogens • Stabilization ponds • Effluent • Reclamation • Reuse

39.1 Introduction

Fast population growth along with intensified groundwater pumping, primarily in arid and semi-arid regions, related to the demand for high quality water along with natural shortage and continuous restrictions in supply, are stimulating the search for alternative sources. These additional sources include high quality fresh water obtained from sea-water desalination, run-off water, saline water, and treated wastewater. Treated wastewater, primarily domestic wastewater, can be used for agriculture, industry, recreation, and aquifer recharge. Reuse of treated wastewater, mainly for agricultural irrigation, simultaneously promotes solutions for water scarcity, and improved environmental pollution control (Alves et al. 2007; Hafez et al. 2007; Oron et al. 2006; Palacios et al. 2007). Microbial quality and dissolved solids content are the most contentious issues linked to wastewater disposal and reuse. The risk of pathogens, disease- causing bacteria, viruses, and other microorganisms in the effluent released by wastewater treatment plants into receiving bodies of water can cause considerable threats to public health (Feachem et al. 1983). It is common that "the most widespread contamination of water is from disease bearing human wastes" (World Bank 1992). Adequate processes, based primarily on disinfection or membrane ultrafiltration, are essential for avoiding problems of waterborne diseases in human beings and to maintain safe agriculture production and a clean environment (World Health Organization 1989; Bourgeous et al. 2001; Asatekin et al. 2007).

Most of the agricultural areas around the world are still irrigated by open-surface methods in which large portions of the plants' foliage are in contact with the applied water. The tendency to use water more efficiently for irrigation has enhanced the development and implementation of advanced application methods. Sprinklers and spray are methods that are advantageous in terms of water use; however, their high demand for energy and investment in equipment. The above foliage irrigation methods are subject to wind effects and water quality that might damage the plants' leaves and increase health risks due to pathogen accumulation (e.g., in corn cobs). Onsurface Drip Irrigation (ODI), although very efficient in terms of effluent use, still poses some health risks due to the contact between the upper soil layer and the plants' foliage that is spread out on it. Subsurface Drip Irrigation (SDI), in which the drip laterals are installed approximately 35 cm below the soil surface, is a promising application technology for minimizing health risks during effluent application. The purpose of this work is to show, using a dose-response model, that under SDI the risk of applying secondary effluent, even of low quality, can be minimized (Kosma et al. 2014).

The approach to water resources use includes advanced irrigation technologies along with improved treatment of domestic, industrial and agricultural wastes. The advanced treatment methods are based on combined biological, chemical and mechanical processes, including methods using membrane technology and disinfection processes with minimal by-products (Oron et al. 2007).

Waste Stabilization Ponds (WSP) is one of the most common extensive wastewater treatment methods for reducing pathogens. However, there is still a risk of contamination of crops and soil irrigated with this kind of effluent. The purpose of this work was to examine the fate of microorganisms (faecal coliforms, coliphages F^+ and CN_{13}) in a combined system of WSP and Waste Stabilization Reservoirs (WSR) (Liran et al. 1994) and the implications for agriculture irrigation. The obtained effluent is used for irrigation of a variety of crops, such as almond trees, wheat, barely, sunflower, and alfalfa under onsurface and subsurface drip systems.

39.2 Pathogens in the Wastewater Treatment System

Pathogen microorganisms can survive for extended periods on agricultural plants and in soil, subject to the treatment method and environmental conditions. Pathogens decay processes are enhanced under extended retention time and high solar radiation in the treatment plant. Besides the application technology, the bacterial quality of the applied effluent is therefore important. Consequently, in the case of food crop irrigation with reclaimed water, there are at least three barriers to minimize the risk of disease transmission: (i) eliminate pathogens from wastewater prior to irrigation; (ii) prevent direct contact between the reclaimed water and the edible portion of the crop, or (iii) process the crop to destroy pathogens before sale to the public or others.

39.3 Pathogens Removal Processes in a System of Stabilization Ponds and Reservoirs

Inactivation and/or removal of pathogens in oxidation ponds is controlled by a number of factors, including temperature, sunlight, pH, infection by bacteriophages, predatory processes by other microorganisms, and adsorption to or entrapment in settleable solids. Indicator bacteria and pathogenic bacteria may be reduced by 90–99 % or more depending upon retention times (Forslund et al. 2010; APHA 1992).

Residence time is considered to be amongst the most important parameters that influences pond performance with respect to the removal and elimination of pathogenic and parasitic microorganisms. It follows that additional physical parameters, particularly wind speed and direction, bottom of ponds, dead zones, inlet and outlet arrangements, and baffles can all affect mixing.

Pond performance for pathogen removal is substantially depending on retention time and the system layout. A WSP system exists adjacent to the City of Arad (Israel) (Fig. 39.1 and Table 39.1). If 1 % of sewage enters and leaves a pond in less than 24 h, the performance of the system can hardly exceed 99 % removal efficiency. Similarly if 10 % of wastewater short-circuits and leaves the pond within 24 h, then performance is unlikely to exceed 90 % removal (Huertas et al. 2008).

The purpose of this paper is to review the pond system's performance, using phages as the wastewater quality indicators, and to assess the risk to the health of the community associated with treated wastewater reuse. The content of the phages in the system components also allows the kinetic coefficients and the order of the reactions within the ponds to be assessed. The present study focuses on the risk to consumers of using agricultural products irrigated with reclaimed domestic wastewater. The work is limited to comparing conventional ODI and SDI. Risks to farmers and workers are not in the scope of this work. The risks associated with microbial aerosol dispersion and the related impact on adjacent living communities have been reported elsewhere and are not included in current analysis (Baggett et al. 2006; Gillerman et al. 2006; Kamizoulis 2008; Muñoz et al. 2009; Manickum and John 2014).

39.3.1 The Treatment Site

The treatment plant, consisting of a series of stabilization ponds, three stabilization reservoirs, and a large operational storage, is located several km west of the City of Arad, Israel (Fig. 39.1). The rocky pond actually performs as a horizontal trickling filter for improved pathogens removal. Daily flow rate varies in the range of 5,000 m^3/day upto 5,500 m^3/day. The typical quality of the raw domestic

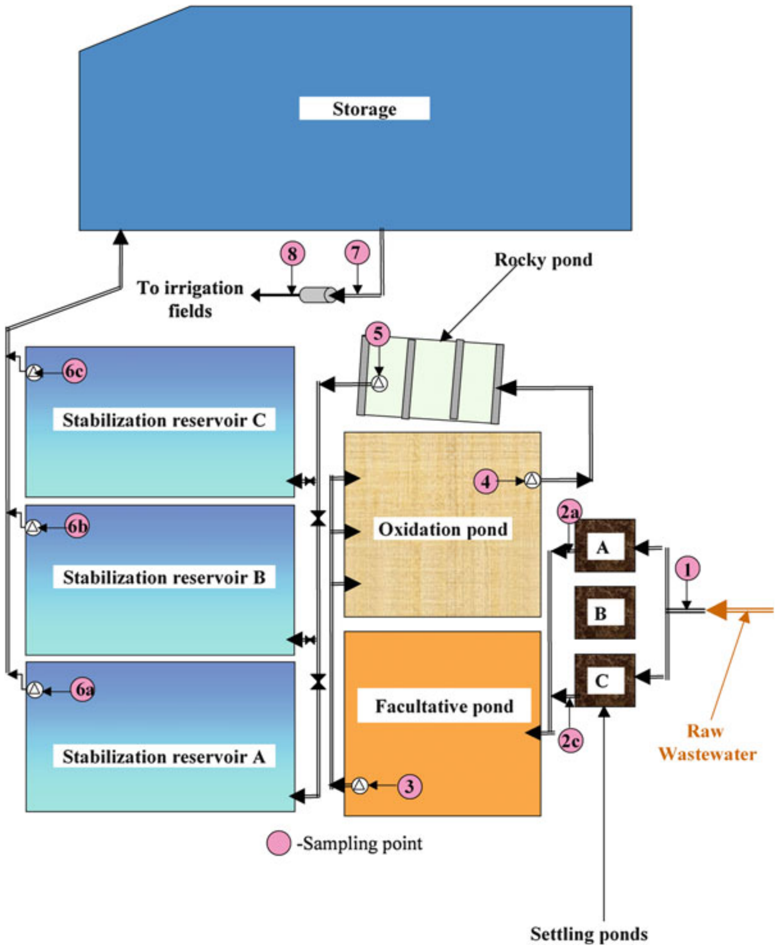

Fig. 39.1 The layout of Arad wastewater treatment system and sampling points

Table 39.1 Functioning and design parameters of Arad treatment system[a]

Designation in the system	Function of the component	Volume, $m^3 \times 10^3$	Surface area, $m^2 \times 10^3$	Depth, m
1a	Settling	5	2.3	5
1b	Settling	5	2.3	5
1c	Settling	5	2.3	5
2a	Facultative	42.5	29	2.5
2b	Oxidation	37.5	25.5	1.5
3	Rock pond	13	7.7	2
4a	Stabilization reservoir	100	26.3	5
4b	Stabilization reservoir	100	26.3	5
4c	Stabilization reservoir	100	26.3	5
5	Large storage	650	50	13

[a]Data presented for maximal effluent depth in the related pond/reservoir

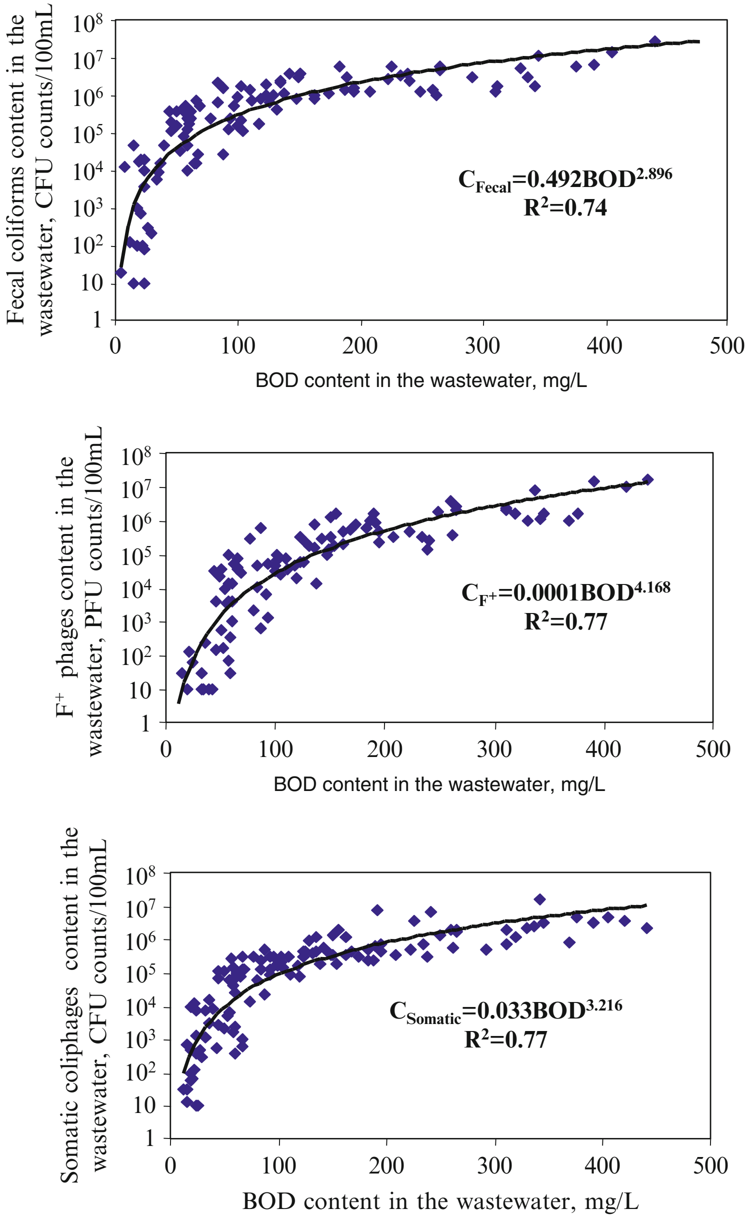

Fig. 39.2 The different phages content in the waste stabilization ponds of the City of Arad (Israel)

wastewater and obtained effluent is described in Fig. 39.2. All treated wastewater is used for irrigation in the adjacent agricultural areas. Sampling was conducted with a view of avoiding any deviations from real quality.

39.3.2 Monitoring and Laboratory Assays

Wastewater and effluent quality samples were collected (grab samples) three to four times per month. Conventional methods were employed for the constituent's content and conventional biological indicators (APHA 1992).

Fecal Coliforms Assays Fecal coliforms were quantified using the membrane filtration technique after various dilutions in peptone water (1 g/L peptone, pH 7.2), as described in the Difco manual (Jiang et al. 2007; Zimbro et al. 2009). Wastewater or soil suspension was filtered through a membrane with 0.45 μm pores. The filters were placed on mFC agar and incubated for 24 h at 44 °C, after which the number of specific colonies for each dilution was determined.

Bacteriophages Assays Somatic coliphages and F-specific RNA phages were quantified by standard procedures using *E. coli* CN (ATCC 700078) and *E. coli* HS (pFamp) R respectively as host strains. The double layer agar technique was used for both types of bacteriophages.

Pathogens Survival in the Pond System – A Kinetic Description The accumulated data were used to assess the kinetic coefficients for the decay processes in the ponds and reservoir system. Prior to determination of the kinetic expression, it is required to determine the type of flow, namely, completely mixed flow, plug flow, or an intermittent type reactor. The general expression for the pathogens decay processes is given by

$$dC/dt = -KC^n \tag{39.1}$$

where C is the pathogen concentration (#/100 ml) in the pond, n designates the order of the reaction and K is the kinetic coefficient [day^{-1} (for first order)] depending on "n." One of the problems tackled in this study is assessing the order of the pathogen decay reaction (namely value of "n") for the specific pathogens considered. According to the analysis, a first order reaction can adequately describe the decay process. K gives the related reaction constant

$$K = K_0\theta^T \tag{39.2}$$

where K_0 is the kinetic constant at 0 °C. The value of K_0 at this temperature was used because frequently the wastewater temperature is below 20 °C. θ is the constant assessed at 1.16 for the system under examination, and T is the wastewater temperature, °C (Fig. 39.3).

A very poor correlation was found between the content and the removal of the fecal coliforms, F + phages, and the somatic coliphages contained in the waste stabilization ponds. However, a relatively good correlation was found for the stabilization ponds for the natural decay and the temperature of the wastewater ponds (Fig. 39.4). The decay coefficient depends on the temperature, namely, winter *vs.* summer. Some of the values are given in Table 39.2.

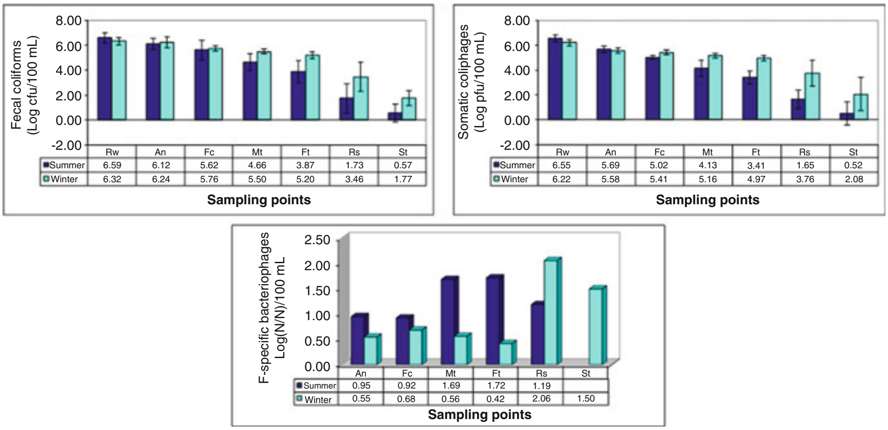

Fig. 39.3 Mean and standard deviation of fecal coliform, somatic coliphage and F-specific bacteriophage content in raw wastewater and the effluent of each component of the treatment system for summer and winter periods (*Rw* Raw wastewater, *An* Anaerobic ponds effluent, *Fc* Facultative pond effluent, *Mt* Maturation pond effluent, *Ft* Rock filter effluent, *Rs* Stabilization reservoirs effluent, *St* Seasonal storage reservoir effluent)

39.4 The Risks Associated with Effluent Application

Health risk assessment is a process in which toxicological data are combined with information concerning the degree of exposure to external risks. It is performed in order to predict quantitatively the likelihood that a particular adverse response will arise in a specific human community (Paustenbach 1997). Quantitative microbial risk assessment has recently been applied to estimate the risk of infection and illness from enteric pathogens in water and food. Several studies focus on health risk assessment of wastewater reuse in agriculture (Asano et al. 1992; Rose et al. 1996; Salgot 2008). Two major risks can be considered: (i) those related to microbial pollutants that pose health hazards, and include bacteria, viruses, helminthes, nematodes, protozoa, fungi, and algal toxins (Toze 2006; Salgot 2008), and; (ii) chemical risks, which are subject to the concentration levels of the main chemicals in the applied effluent, and actual reuse standards (Asano et al. 1992). Endocrine Disrupting Chemical (EDC) and pharmaceutical active compounds pose additional health risks (Wagner and Strube 2005; Weber et al. 2006; Verlicchi and Zambello 2014). Limited attention has been focused on exposure assessment and health risk due to the consumption of agricultural products irrigated with reclaimed wastewater. The exposure of consumers to contaminants due to wastewater irrigation depends on a series of factors: (i) the quality of the applied wastewater; (ii) the irrigation method; (iii) the elapse time between irrigation, harvest, and subsequent products consumption, and; (iv) consumers' habits. Previous works deal roughly with the effect of the irrigation method, which is, in practice, one of the key issues for their exposure estimate (Zhuo et al. 2012).

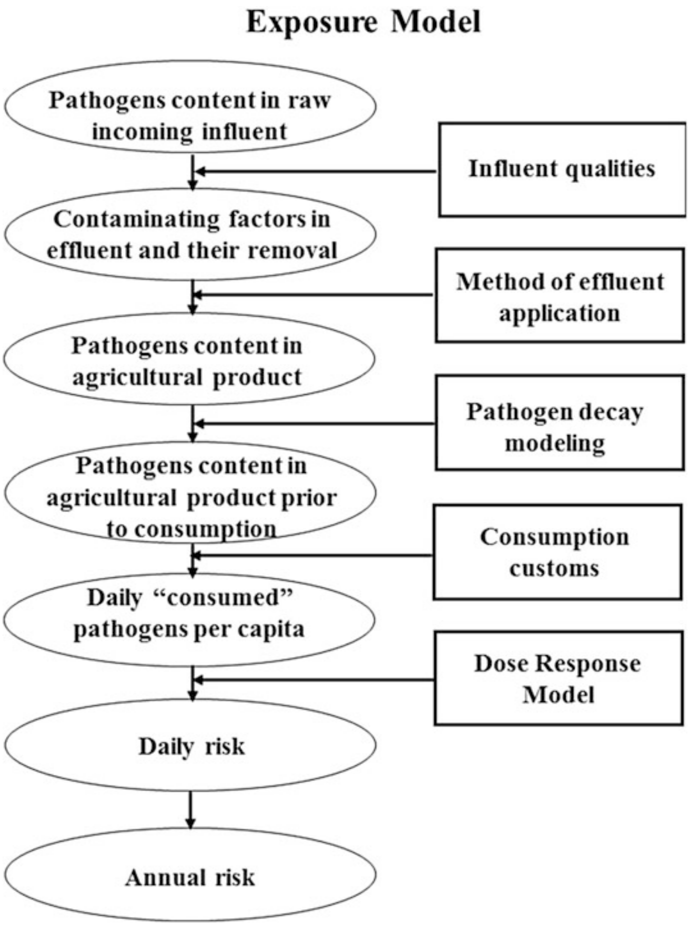

Fig. 39.4 The procedure for assessing annual infection risk by consuming fruits and vegetables irrigated with effluent

Other sources estimate an accidental ingestion of 100 mL of irrigation water per year, without specifying whether this concerns consumers or workers (Rose et al. 1996).

39.4.1 *Subsurface Drip Irrigation Characteristics*

Effluent reuse through SDI systems is a unique concept that refers to the issues of acceptable wastewater dispersal, water low quality reuse, and water conservation. The basic concept is to prevent any contact between the applied effluent and all elements and activities above the soil surface that include the workers and

Table 39.2 The decay coefficient (1/day) for the Waste Stabilization Pond temperature system (C°) in the City of Arad, Israel

Fecal coliform			F^+ phages			Somatic coliphaes		
Lower temper.	Upper temper.	Correlati. coefficient	Lower temper.	Upper temper.	Correlati. coefficient	Lower temper.	Upper temper.	Correlati. coefficient
0.100 at 11 °C	1.303 at 27 °C	$R^2 = 0.87$	0.199 at 10 °C	1.584 at 27 °C	$R^2 = 0.77$	0.112 at 10 °C	0.790 at 27 °C	$R^2 = 0.68$

agronomical operations, and between the applied effluent and the agricultural crops. SDI has a series of advantages that include minimal water losses through the soil surface due to reduced evaporation, no runoff, minimal weed germination, no rotting of spread-out fruits (e.g., melons), reduced need for herbicides application, elevated yields, and the option to cultivate the field even during irrigation. The primary limitations refer to the relatively high initial capital investment, the risk of the emergence of bores in the drip laterals due to rodent presence in the soil, and, in arid zones, the accumulation of the dissolved solids contained in the effluent in the upper soil layers (Palacios et al. 2007). Frequently, a special mobile spray or sprinkler irrigation system is required for germination of the seasonal crops.

39.5 The Risk Assessment Approach for Safe Effluent Reuse

39.5.1 The Exposure Model Characteristics

Exposure consists of a series of events in which a person (or a community) is in a close contact with biological, chemical, or physical agents. The prevailing route of exposure to reclaimed wastewater for human consumers is primarily through ingestion of food irrigated with reclaimed effluent and/or contaminated water. When modeling exposure of a community to a unique phenomenon regarding wastewater, the following are considered: (i) wastewater treatment characteristics and related effluent quality; (ii) the route of virus migration from the irrigation wastewater into and within the food plant; (iii) virus die-off during the period between last irrigation and agricultural raw product harvesting and consumption, and; (iv) the consumption pattern of the population.

The exposure route is based in this model on a human adult whose dietary intake of fruits and vegetables is based entirely on crops irrigated with effluent. The corresponding assumptions for the dose-response models are: (a) exposure only through ingestion is considered; (b) the virus concentration in raw sewage is log normally distributed, where the arithmetic mean is 1,000 Plaque Forming Units per liter (PFU/L), and the standard deviation is 300 PFU/L (Rose and Gerba 1991); (c) the decay of pathogens during storage of effluent before irrigation is part of the treatment system; (d) the total period between final irrigation and human consumption includes also the storage immediately after harvesting; (e) no cross-contamination of fruits and vegetables after harvesting is considered; and (f) commonly, consumers eat 50 % of their diet uncooked, unpeeled, and unwashed.

The dose response model explains the linkage between the rate of pathogens exposure to humans (e.g., virus dose) and the rate (actually exposure) of consuming products irrigated with effluent. It is based on the ß Poisson Distribution Model (ß-PDM), assuming rotaviruses are the dominant pathogen. Rotaviruses are the type of enteric viruses with the lowest infectious dose. The hypothesis is that an independent action of single organisms forms the base for the ß-PDM. The ß-PDM is considered the appropriate model for virus ingestion and infection probability assessment (Haas et al. 1999). The daily probability of infection by ingesting pathogens P_y is given by

$$P_y = 1 - (1 - Y_i/ß)^{-\eta} \tag{39.3}$$

where

Y_i – daily consumed dose of risk-carrying contaminant, PFU/d.
ß – the ß Poisson distribution coefficient. Poisson expresses discrete probability distribution of rare events with a known mean.
η – a model parameter for assessing the infection rate (η is in the range of 0.232–0.247 [Haas et al. 1999]).

Consequently, the annual probability R_s of infection by ingesting pathogens is given by

$$R_s = 1 - \left(1 - P_y\right)^{365} \tag{39.4}$$

39.5.2 Polluted Agriculture Product Consumption

Contaminated Fruit and Vegetable Consumption In order to be able to compare the two drip irrigation methods (ODI and SDI), the Effluent Equivalent Volume (EEV) concept was adopted. The EEV approach is implemented for ODI, with a triangular distribution, expressing variability and uncertainty. The triangular distribution is a conservative characterization of a normal distribution and takes into account a high level of uncertainty. Accordingly, the EEV has an average pathogen content of 0.16 mL in the applied effluent penetrating into 100 g of plant matter (the minimum is 0.016 mL/100 g and the maximum is 1.6 mL/100 g).

Fruits and vegetables are the major component of the human diet affected by irrigation with reclaimed wastewater. The US-EPA (1997) investigated the daily intake of fruits and vegetables per body weight in the United States. The US-EPA analysis is based on a mean common body weight of approximately 71 kg. The fraction of fruits and vegetables that is consumed uncooked, unpeeled, and unwashed can be described by a triangular distribution pattern (average 50 %; minimum 25 %; maximum 75 %). The combination of the data leads to a daily per capita consumption of raw fruits and vegetables that is affected by effluent application.

The Risks Associated with the Application Method Under SDI, the risk of crop contamination is reduced by minimizing direct contact between the upper parts of the plant and/or the soil surface and the contaminated applied effluent. The two possible mechanisms of contamination under SDI are either by over-head irrigation (probably adjacent fields), causing the effluent to reach the soil surface, or through penetration via the root system and internal migration to the upper parts of plants. The limited data regarding SDI revealed that very small amounts or no viruses at all can penetrate into the plants (Haas et al. 1999; Weber et al. 2006). In spite of this, the EEV concept was also applied for SDI and a triangular distribution. Under SDI and for a triangular distribution, the average EEV was 0.016 mL/100 mL, the minimum was 0.0016 mL/100 g, and the maximum was 0.16 mL/100 g. Comparisons with on-surface conventional ODI irrigation demonstrate that at least a 2 orders of magnitude reduction in pathogen levels in soil and crops can be attained under SDI.

39.5.3 Pathogens Die-Off After Last Effluent Application

Under adequate environmental conditions, pathogens (mainly viruses) can survive for extended periods of several months (Feachem et al. 1983). The survival depends on a series of surrounding conditions, however, and their multiplication needs a suitable host. The natural decay processes of viruses depend on moisture, salinity, temperature, pH, and radiation intensity. The fate of pathogens in the environment is usually represented by first-order rate die-off kinetics [Eq. (39.5)]. A decay constant k (d^{-1}) in the range of 0.65–0.73 d^{-1} is often used for viruses (Haas et al. 1999):

$$C_t = C_d[\exp(-k * t_d)] \tag{39.5}$$

where C_t is the virus concentration at elapsed time t_d after irrigation or at consumption, PFU/L, C_d is the initial virus concentration in the applied effluent, PFU/L and t_d is the elapsed time between final irrigation and consumption, given in days.

The simulation procedure was defined and tested for comparing the risks under ODI and SDI. The developed dose response model is based on previous literature data and diverse field data.

39.5.4 The Linkage with the Application Method

The exposure was defined and tested for comparing the risks of the effluent application under ODI and SDI. The model is based on previous literature data and diverse field data. The EM quantifies the relationship between irrigation effluent quality, irrigation policy, and the daily virus dose that a consumer ingests. The expected annual risk of infection is estimated stochastically by using the Monte-Carlo Simulation Method (MCSM) and the developed model (Thompson et al. 1992). The outcomes of the numerical computations are compared, including the given and obtained risks. The numerical simulation combines treatment characteristics and effluent quality applied for irrigation. The irrigation effluent quality and the exposure model lead concurrently to the daily virus dose that consumers ingest. The daily risk of infection is then calculated using a dose response model implementing data from the literature. Finally, the daily risk of infection is converted into an annual risk of infection taking into account the exposure frequency. The general modeling layout and data-processing procedure are described in Fig. 39.4.

39.5.5 Results of the Monte-Carlo Simulation

The exposure model was examined for various situations and conditions. A sample result for representative scenarios for different effluent qualities (primary and secondary quality, and advanced treatment) applied through the two considered drip irrigation methods are presented (Figs. 39.5 and 39.6). The number of simulation runs using the RiskMaster software (1995) ranged from 2,500 to 50,000. The simulation runs provide clear evidence that SDI is associated with reduced risks as compared to any other application method. One of the immediate conclusions is that, even when the applied effluent is of poor quality, under SDI the risk to consumers is still low.

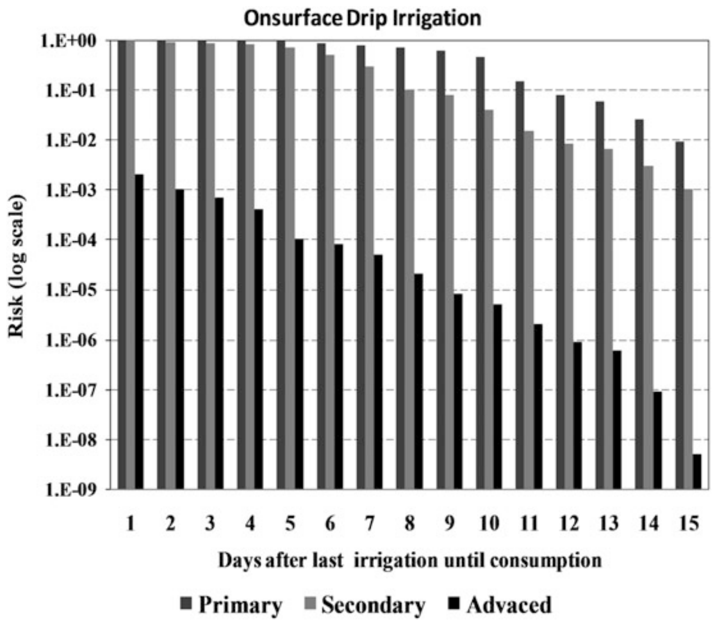

Fig. 39.5 Assessed risks based on simulation for applying different qualities via onsurface drip irrigation

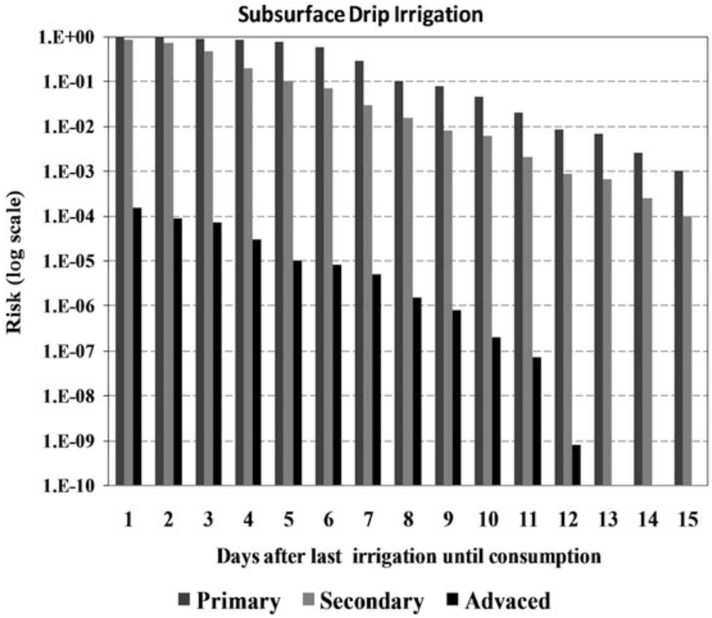

Fig. 39.6 Assessed risks based on simulation for applying different qualities via subsurface drip irrigation

Concluding Remarks

Numerical simulation of exposure scenarios of humans consuming agriculture products that were irrigated with various qualities of effluent under two drip irrigation methods provides the means to express the uncertainty and variability of the model input parameters by characterizing them with a distribution pattern. Variability is the impreciseness that occurs because of actual differences among segments of a population, which differs in resistance to diseases. Although the variability is not reduced, it provides extra information, thus increasing the accuracy of the analysis. Uncertainty stems from the limitation in the thoroughness of the measurement of the specific factor. The findings strengthen the main assumption that under SDI, even when low quality effluent is applied for irrigation of consumed agriculture products, the associated human risks are very low.

Acknowledgement The work was partially supported by The Integrated Water Resource Management (IWRM) – Sustainable Management of Available Water Resources with Innovative Technologies (SMART) project on development, modeling and providing tools for optimal water use in arid regions, which is supported by The Federal Ministry of Education and Research, Germany and The Ministry of Science and Technology (MOST) of the State of Israel.

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Chapter 40
Molecular Bioindicators of Pollution in Fish

Nancy D. Denslow and Tara Sabo-Attwood

Abstract The use of microarrays to assess pollutant responses in aquatic organisms has become widespread. In the field of ecotoxicology, the development of microarrays for fish models has served to advance our understanding of the mechanisms of action of numerous chemicals, including both those that are well studied and those that are emerging, singly in controlled laboratory settings, and in complex mixtures and field settings. This chapter chronicles the advent of using microarrays in the study of fish and provides notable examples of both laboratory and field studies where microarrays were instrumental in answering important contaminant-driven hypotheses. These examples will highlight how microarrays have been effective in defining unexpected actions and pathways of well-studied chemicals and in the toxicological assessment of emerging pollutants including nanomaterials, and whether this technology is useful for defining the response to complex mixtures in field settings. Global transcriptional data sets may help define key events for new state-of-the-art modeling of adverse outcome pathways (AOPs).

Keywords Microarrays • Fish • Endocrine disruptors • Adverse outcome pathways • Pollutants

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_40

40.1 Introduction

The advent of microarrays has expanded our ability to monitor global transcriptomic changes in organisms in response to environmental stressors. A microarray is a large collection of probes, segments of DNA sequences, each specific to a different gene (usually 15,000–60,000), which are fixed on a solid surface. To measure changes in the transcriptome as a consequence of contaminant exposure, total RNA is extracted from cells or tissues of control and exposed animals (usually the minimum number of individual animals required is four for each group). The total RNA is further processed to select mRNAs, which are then converted to copy RNAs (cRNAs) through a process of reverse transcription that enables the incorporation of fluorescently labeled nucleotides (or in olden times, radioactive nucleotides). The labeled cRNAs are then washed onto the solid surface where they can bind to the probes by complementation and in proportion to their concentration in the original tissue. Because exposure to contaminants alters transcriptional expression in aquatic organisms, it is possible to determine the specific genes that are altered and the biological processes and molecular pathways to which they belong. This is an extremely powerful method to identify biochemical pathways targeted by the contaminants. It is also possible to determine common regulators for the genes that are affected and to start to identify the molecular initiating and key events for toxicologic effects due to contaminants.

The first array showing the utility of this technology for fish was published by our group in 2002 and consisted of a 'macroarray' – a membrane-based solid support platform using radiolabeled cRNAs to detect expression level changes for 132 genes specific to largemouth bass (LMB, *Micropterus salmoides*) (Larkin et al. 2002). With technological advances, arrays have moved to glass slide fluorescent-based platforms, described above, containing thousands of genes for individual fish. Large scale sequencing efforts, including the availability of next-generation sequencing instruments, have led to the possibility of developing molecular tools, at affordable costs, for any fish species starting from total RNA isolated from tissues (Garcia-Reyero et al. 2008). These new sequencing methods have also been adapted to sequencing individual mRNAs directly on platforms that can analyze 500 million sequences in parallel, using a method called RNAseq. However, this method requires a relatively complete transcriptome for the organism of interest, which may be difficult to obtain for non-model species in ecotoxicology. Due to the limited use of RNAseq in environmental studies, as this technology is still in its infancy, we will focus in this chapter on the utility of microarray-based technology in pollutant responses specifically in fish.

In ecotoxicology, gene arrays have been widely utilized to assess the toxicologic impacts in fish that have been exposed to numerous pollutants, including single chemicals and complex mixtures. In fact, there are more than 30 species-specific fish arrays that have been constructed to date and used to monitor gene signatures of pollutant exposures (Table 40.1) with zebrafish, fathead minnow, rainbow trout, and Japanese medaka being the most widely employed species. Transcriptional

Table 40.1 Transcriptomics experiments performed with different fish species

Species	Pollutant	Reference
Atlantic cod, *Gadus morhua*	Chemically and mechanically dispersed oil and dispersants; by-product of offshore oil production (produced water), alkylphenols, 17β-estradiol; polluted waterways; weathered crude oil and/or a mixture of chlorinated PCBs/pesticides, polybrominated biphenyl ethers, fluorinated compounds	Bratberg et al. (2013), Olsvik et al. (2012), Lie et al. (2009)
Atlantic salmon, *Salmo salar*	Nonylphenol; brominated flame retardant congeners (BDE47, BDE153, BDE154); acetaminophen, carbamazepine, atenolol	Hampel et al. (2010, 2014), Søfteland et al. (2011), Robertson and McCormick (2012)
Atlantic tomcod, *Microgadus tomcod*	Mixture of coplanar polychlorinated biphenyls	Carlson et al. (2009)
Brown trout, *Salmo trutta m. lacustris*	Highway runoff; pulp and paper mill effluent; wood resin acids	Merilainen et al. (2007), Oikari et al. (2010), Meland et al. (2011)
Chinook salmon, *Oncorhynchus tshawytscha*	Sewage effluent	Osachoff et al. (2013)
Common carp, *Cyprinus carpio*	Perfluorooctane sulfonate; 17-β-estradiol, 4-nonylphenol, bisphenol A, ethinylestradiol; effluent; cadmium	Reynders et al. (2006), Moens et al. (2007), Hagenaars et al. (2008)
Delta smelt, *Hypomesus transpacificus*	Polluted water samples; ammonia; esfenvalerate	Connon et al. (2009, 2011), Hasenbein et al. (2014)
Eastern mosquitofish, *Gambusia holbrooki*	17β-trenbolone	Brockmeier et al. (2013)
Eelpout, *Zoarces viviparus*	Contaminated waters	Asker et al. (2013)
European eels, *Anguilla anguilla*	Polluted waterways	Pujolar et al. (2013)
European flounder, *Platichthys flesus*	Polluted estuarine sediment; polluted waters and estuaries; PDBEs, DE-71, Pentamix; cadmium chloride, methylcholanthrene, aroclor 1254, tert-butyl-hydroperoxide, lindane, perfluoro-octanoic acid	Williams et al. (2003, 2008), Falciani et al. (2008), Leaver et al. (2010), Williams et al. (2013)

(continued)

Table 40.1 (continued)

Species	Pollutant	Reference
Fathead minnow, *Pimephales promelas*	Pulp and paper mill effluent; diethylstilbestrol; Nebraska watersheds; 17β-trenbolone; lead; 17β-estradiol; urban waste water treated effluent; streams adjacent to sewage treatment plants; pulp and paper mill effluent; 17alpha-ethinylestradiol; flutamide and trenbolone; cyclotrimethylenetrinitramine; prochloraz; mixture of psychoactive pharmaceuticals (fluoxetine, venlafaxine & carbamazepine); propranolol; ketoconazole; methylmercury; 2,4-dinitrotoluene; Waters impacted by treated wastewater sprayfields	Klaper et al. (2006), Wintz et al. (2006), Larkin et al. (2007), Mager et al. (2008), Perkins et al. (2008), Dorts et al. (2009), Garcia-Reyero et al. (2009a, b, c, 2011), Popesku et al. (2010), Gust et al. (2011), Adedeji et al. (2012), Costigan et al. (2012), Lorenzi et al. (2012), Sellin Jeffries et al. (2012), Thomas and Klaper (2012), Weil et al. (2012)
Goldfish, *Carassius auratus auratus*	Lumiestrone; fadrozole; fluoxetene	Mennigen et al. (2008), Zhang et al. (2009), Trudeau et al. (2011)
Hornyhead turbot, *Pleuronichthys verticalis*	Wastewater treatment plant effluent; wastewater outfalls; 17β-estradiol, 4-nonylphenol	Baker et al. (2009, 2013), Vidal-Dorsch et al. (2013)
Japanese flounder, *Paralichthys olivaceus*	Heavy oil	Nakayama et al. (2008)
Japanese medaka, *Oryzias latipes*	Glyphosate agrochemical components (1,1,1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane (o,p′-DDT); 17α-ethinylestradiol, estradiol benzoate; silver nanocolloids; urban streams impacted by domestic sewage, n-propylparaben, n-butylparaben, methylparaben; PCB126, kanechlor-400; 17-β estradiol, 4-nonylphenol, 2-chlorophenol; 3,3′,4,4′,5-pentachlorobiphenyl (PCB126), PCB mixture (Kanechlor-400: KC-400); arochlor 1260; i-butylparaben, and benzylparaben	Kim et al. (2006), Yamamoto et al. (2007, 2011), Nakayama et al. (2008, 2011), Uchida et al. (2010, 2012), Yum et al. (2010), Pham et al. (2011), Hirakawa et al. (2012), Kashiwada et al. (2012), Miller et al. (2012)
Largemouth bass, *Micropterus salmoides*	Dieldrin; atrazine, cadmium chloride, PCB 126, phenanthrene, toxaphene; methoxychlor; progesterone; 17β-estradiol, 4-nonylphenol, 1,1-dichloro-2, 2-bis (p-chlorophenyl) ethylene	Larkin et al. (2002, 2003), Martyniuk et al. (2010, 2011, 2013), Sanchez et al. (2011)
Largescale suckers, *Catostomus macrocheilus*	Polluted waterways	Christiansen et al. (2014)

(continued)

Table 40.1 (continued)

Species	Pollutant	Reference
Mummichog, *Fundulus heteroclitus*	17-α-ethinylestradiol; arsenic; chromium-contaminated creek; highly polluted Superfund sites; trivalent chromium	Gonzalez et al. (2006), Roling and Baldwin (2006), Fisher and Oleksiak (2007), Roling et al. (2007), Gaworecki et al. (2012), Doyle et al. (2013)
Rainbow trout, *Oncorhynchus mykiss*	TCDD; Methylmercury; atrazine and nonylphenol; ketoprofen, diclofenac; sewage effluents; perfluoroalkyl acids; kerosene, gas oil, heavy fuel oil, crude oil; silver nanoparticles; pharmaceutical industry effluent; silver, copper, cadmium; cadmium tellurium quantum dots; diesel; 2,2,4,4-tetrabromodiphenyl ether, and chromium VI; perfluorooctanoic acid; 17 β-estradiol, diethylstilbestrol, dehydroepiandrosterone, dihydrotestosterone, cortisol; medetomidine; 17α-ethinylestradiol, 2,3,7,8-tetrachloro-di-benzodioxin, paraquat, 4-nitroquinoline-1-oxide; diquat, benzo[a]pyrene, trenbolone; polluted lakes; carbon tetrachloride and pyrene; beta-naphthoflavone; aflatoxin B(1)	Koskinen et al. (2004), Krasnov et al. (2005), Tilton et al. (2005, 2008a, b), Hook et al. (2006a, b, 2007, 2008, 2010a, b), Finne et al. (2007), Gunnarsson et al. (2007, 2009), Moran et al. (2007), Benninghoff and Williams (2008), Walker et al. (2008), Gagne et al. (2010, 2012), Cuklev et al. (2011, 2012), Ings et al. (2011), Lennquist et al. (2011), Benninghoff et al. (2012), Shelley et al. (2012), Liu et al. (2013a, b, c)
Rare minnows, *Gobiocypris rarus*	Perfluorooctanoic acid, perfluorononanoic acid, perfluorodecanoic acid, perfluorododecanoic acid, perfluorooctane sulfonate, 8:2 fluorotelomer alcohol and mixtures	Wei et al. (2008, 2009)
Sea bream, *Sparus aurata*	Contaminated field sediments; copper	Minghetti et al. (2011), Ribecco et al. (2011)
Small abalone, *Haliotis diversicolor*	Tributyltin	Jia et al. (2011)
Sheepshead minnows, *Cyprinodon variegatus*	17β-estradiol	Knoebl et al. (2006)
Sole, *Solea solea*	Contaminated sediments	Ribecco et al. (2012)
Striped seabream, *Lithognathus mormyrus*	Polluted waters; tert-butyl hydroperoxide; benzo[a]pyrene, pp-DDE, aroclor 1254, perfluorooctanoic acid, tributyl-tin chloride, lindane, 17β-estradiol, 4-nonylphenol, methyl mercury chloride, cadmium chloride	Auslander et al. (2010), Yudkovski et al. (2010)

(continued)

Table 40.1 (continued)

Species	Pollutant	Reference
Three-spined stickleback, *Gasterosteus aculeatus*	17α-Ethinyloestradiol, copper, di-benz(*a*,*h*)anthracene	Brown et al. (2008), Katsiadaki et al. (2010)
Turbot, *Scophthalmus maximus*	Fluorosurfactant mixtures	Hagenaars et al. (2011)
Yellow perch, *Perca flavescens*	Nickel and cadmium	Bougas et al. (2013)
Zebrafish, *Danio rerio*	Octocrylene; methylmercury; atrazine; 4-nonylphenol; 4-Nitrophenol; 11H-benzo(b) fluorene, 4-azapyrene; benz(a) anthracene, dibenzothiophene, pyrene; fluoxetine, sertraline; contaminated sediments; flusilazole, hexaconazole, cyproconazole, triadimefon, myclobutanil, triticonazole; bisphenol-A; PAH-rich soot generated from 1,3-butadiene; 1,2,4-triazoles; mercury; polybrominated diphenyl ethers, polychlorinated biphenyls, dichloro-diphenyltrichloroethane metabolites; titanium dioxide, hydroxylated fullerenes; aluminum nanoparticles; arsenic; fadrozole; flutamide, vinclozolin; 17β-estradiol; 2,2′,4,4′-tetrabromodiphenylether (BDE47), 6-hydroxy-BDE47, 6-MeO-BDE47; tetrabromobisphenol-A; copper; synthetic effluent from oil and gas production; sodium metam; chlorpyrifos, copper; genistein; fullerene C60; 17α-ethinylestradiol, fadrozole, 17β-trenbolone; aroclor 1254; mixture of pharmaceuticals; benzo[a]pyrene, 3-methylcholanthrene, 2,3,7,8-tetrachlorodibenzodioxin, diethylstilbestrol;,4-dichloroaniline, acrylamide, arsenic (III) oxide, tert-butylhydroquinone, cadmium chloride, 4-chloroaniline, 1,1-bis-(4-chlorphenyl)-2,2,2-trichlorethane, lead, 2,3,7,8-tetrachlorodibenzo-p-dioxin, valproic acid; 17-α-methyldihydrotestosterone; pentachlorophenol; mianserin; chlorpromazine	Hoyt et al. (2003), Andreasen et al. (2006), Lam et al. (2006), van der Ven et al. (2006), Kreiling et al. (2007), Martyniuk et al. (2007), Pomati et al. (2007), Santos et al. (2007), Voelker et al. (2007), Yang et al. (2007), De Wit et al. (2008), Hoffmann et al. (2008), Holth et al. (2008), Kausch et al. (2008), Ruggeri et al. (2008), Tilton et al. (2008a, b, 2011), Usenko et al. (2008), van Boxtel et al. (2008), Wahl et al. (2008), Wang et al. (2008a, b), Baker et al. (2009), Mattingly et al. (2009), Villeneuve et al. (2009), Duan et al. (2010), Leaver et al. (2010), Lyche et al. (2010), Ung et al. (2010), Hawliczek et al. (2011), Hermsen et al. (2011), Jovanovic et al. (2011), Lam et al. (2011), Martinovic-Weigelt et al. (2011), Richter et al. (2011), Bui et al. (2012), Hermsen et al. (2012), Kosmehl et al. (2012), Park et al. (2012), Christiansen et al. (2014), Goodale et al. (2013), Liu et al. (2013a, b, c), Bluthgen et al. (2014)

responses of numerous pollutants have been observed including metals, pesticides, pharmaceuticals, industrial products, and nanomaterials, among others. The earliest published studies focused on 4- nonylphenol (NP) and 1,1-dichloro-2, 2-bis (p-chlorophenyl) ethylene (p,p′-DDE), compounds that are considered 'endocrine disruptors' and are linked with estrogenic activity (xenoestrogens) (Larkin et al. 2002). It is this estrogenic activity that contributes to the commonly observed increase in hepatic expression of genes, primarily egg yolk proteins (vitellogenins, Vtgs), in male fish. In the case of p,p′-DDE and NP, it was not clear whether their potential toxic mechanisms of action were the same as those of the endogenous hormone, 17β-estradiol (E2), or whether they could also impact alternate signaling pathways. To answer this question, in part, we constructed, validated, and employed a 132-gene macroarrray specific to LMB to determine whether the hepatic expression profiles of these chemicals would be similar to that of E2. The novelty of this approach, at the time, allowed for confirmation of gene expression changes of well-studied E2-induced transcripts (i.e., vitellogenins) and minimally investigated several targets simultaneously, highlighting similarities and differences in their transcriptional profiles. What we learned from this study is that while E2 and NP shared similar expression patterns, transcripts such as signal peptidase were upregulated by NP but not E2. It was also discovered that while p, p′-DDE and E2 produced similar profiles in males, the signature generated in females exposed to p,p′-DDE was quite divergent. These data revealed the powerful nature of arrays and their utility as an important tool in fish toxicology. We now have knowledge to suggest that chemicals such as NP have alternate modes of action that seem independent of E2 signaling pathways (i.e., pregnane X receptor pathways) (Meucci and Arukwe 2006). Arrays have since been utilized in similar capacities to define mechanisms of action of single chemicals, mixtures and in response to multiple stressors (i.e., chemical and biological) (Burki et al. 2013).

Since then, microarrays have been applied to many different chemicals. For example, expression profiles have been created for synthetic hormones, such as ethinylestradiol (EE2), a major constituent of birth control pills (Finne et al. 2007; Moens et al. 2007; Garcia-Reyero et al. 2009b; Hirakawa et al. 2012; Miller et al. 2012; Doyle et al. 2013), androgens such as trenbolone (Dorts et al. 2009; Garcia-Reyero et al. 2009c), and progesterone (Garcia-Reyero et al. 2013). Other chemicals of interest have included metals, PCBs, industrial products such as surfactants (i.e., nonylphenol) and plasticizers (i.e., bisphenol-A), and a variety of pharmaceuticals, among others. In addition, specific patterns of gene expression have been identified for mixtures of chemicals found in surface waters and polluted sites, such as downstream from pulp and paper mill or sewage effluents. The patterns of gene expression vary considerably depending on the class of chemical, allowing for chemical class-specific profiles that may allow the identification of contaminants in complex mixtures.

40.2 Case Studies Using Microarrays in Laboratory Settings

Several convincing laboratory studies have examined global changes in gene expression in fish. They are excellent examples that showcase the utility of microarray data to decipher alternative pathways of toxicity in fish and to begin to define mechanisms of action for new emerging pollutants. Here, we will present three examples of laboratory-based studies and how microarrays have been effective in defining unexpected actions of known receptor agonists and antagonists, modulation of alternate physiological pathways (endocrine and immune), and toxicological assessment of emerging nanomaterials.

40.2.1 Laboratory Case Study 1: Exposure of Fathead Minnows to Ethinylestradiol

One of the initial experiments we performed with microarrays was to expose male fathead minnows to a relatively low (but within the environmental range) level of EE2 (5 ng/L) (Garcia-Reyero et al. 2009b). We also exposed fish to 100 ng ZM189, 154 (ZM)/L, a pure antiestrogen, and to a mixture of EE2 and ZM (5 ng/L and 100 ng/L). Both EE2 and ZM have similar affinities for the soluble fish estrogen receptors (ERs). We expected that the inclusion of ZM at 20 times the concentration of EE2 in the mixture would minimize the alterations of gene expression induced by EE2 alone. We found that this was the case and ZM did inhibit expression of EE2-induced genes, many of which are controlled in mammals by E2 through soluble ERs. The surprise was that a second group of genes was actually enhanced by EE2 and the co-exposure with ZM. These genes appeared to be regulated by membrane receptors and were highly enriched in non-genomic signaling pathways. Later, we discovered in the literature that ICI 182,780, another pure antiestrogen, similar in structure to ZM, actually acts as a ligand for E2-linked membrane receptors. This example and many others (Table 40.1) show convincingly that microarrays can be used to provide information about how chemicals might be causing toxicity within aquatic organisms at the mechanistic level.

40.2.2 Laboratory Case Study 2: Immune Effects of Atrazine and Nonylphenol on Rainbow Trout

In another study, microarrays were employed to answer questions about the immune effects of two well-known xenoestrogens, atrazine and nonylphenol (Shelley et al. 2012). While the impairment of sex steroid function by these chemicals has been well documented, including alterations in estrogen and testosterone levels and activation of estrogen receptors, few studies have probed alternate modes of action. Shelley et al. (2012), observed that exposing rainbow trout to atrazine and nonylphenol, followed by a pathogen challenge (*Listonella anguillarum*), resulted in higher mortality as compared to fish that were not chemically exposed. They then utilized a microarray approach to determine whether this mechanism of action could involve alterations in genes relevant to the immune system. This was indeed the case, as microarray analysis on liver tissues revealed genes with altered expression that are immune directed. Results of this study suggest that chemical exposure to these xenoestrogens, while impacting sex steroid pathways, could additionally play a role in disease susceptibility through modulation of the immune system at the gene level.

40.2.3 Laboratory Case Study 3: Assessment of Nanomaterial Toxicity in Medaka

Microarrays are also being employed to assess the toxicity of new emerging contaminants about which very little is known. Nanomaterials, defined as entities $\leq$100 nm in at least one dimension, have unique properties that may produce distinct toxicity as compared to classic chemicals. This raises questions, such as whether metal-based nanoparticles behave mechanistically like their metal counterparts. As an example, in one study we used the medaka model to determine the toxic effects and corresponding mechanisms of silver nanocolloids (SNC) (Kashiwada et al. 2012). Embryos were exposed through water to SNC, and transcriptional profiles were generated. Data from this study revealed that, while some genes, such as those involved in oxidative stress, were modulated similarly to what is known for silver (and other metals) exposures, a subset of novel gene targets were altered in terms of expression by the SNC that had not been previously documented. These included genes involved in embryonic cellular proliferation, and morphological development. This study is just one example of the utility of microarrays in understanding mechanisms of action of emerging or understudied pollutants.

40.3 Case Studies Using Microarrays in the Field

While microarrays have demonstrated their utility in controlled laboratory exposures, the extreme variability of biotic and abiotic stressors in the environment brings in to question whether this approach can say anything of value about pollution in the field. An important question is: How do fish sense the mix of stressors and can one identify a common set of biochemical pathways that are activated in a group of fish that are exposed to the same environmental conditions? Because fish are outbred, they are likely to have different genetic backgrounds and vary in their responses to chemicals, so some may be more sensitive than others. Does this variability in their sensitivities make this approach untenable? We have asked these questions and utilized microarray experiments in the field to help answer them with much trepidation. To our amazement, microarray approaches seem to work in the field and provide insight into molecular pathways that are activated by the stress. Three case studies will be summarized here, which vary in their sampling approaches, from bringing water from the site into the laboratory for experimentation, to using caged fish in the locations of interest, to catching feral fish in the polluted environments. In each of these case studies, the microarray analysis points to biochemical pathways that are consonant with the types of pollution that are known to be present at the various sites.

40.3.1 Field Case Study 1: Eglin Air Force Base and the Endangered Okaloosa Darter

The Okaloosa darter *(Etheostoma okaloosae)* is a small fresh water fish (<50 mm in length) that lives in only six streams, which are located in and around Eglin Air force Base, FL (Mettee and Crittenden 1979; Ogilvie 1980). The status of the fish was downgraded from endangered to threatened in 2011. Of concern was whether the darter populations were threatened by development and anthropogenic contaminants (Weil et al. 2012). Of particular interest was a spray field for wastewater from the City of Niceville that was located on one of the streams, Turkey Creek, just above the city. The goal of the study was to measure changes in gene expression in fish exposed to waters receiving input from the spray fields to determine whether there was exposure to anthropogenic contaminants. The ambient waters differed widely in pH and temperature, and therefore, rather than doing the exposures in the field, waters were trucked to the laboratory where pH, dissolved oxygen, and temperature could be controlled better. For this study, 20 Gal of water were collected at 4 different sites; above the spray field, within the spray field, below the spray field, and at another site on a parallel stream that did not appear to be impacted (Fig. 40.1).

One of the "control" sites selected was at the source waters for Long Creek. Only after we performed the experiment did we realize that Long Creek initiates in an area that is likely highly contaminated by unexploded ordnance due to use of the site for military testing and training. Fish exposed to these waters had the most divergent profiles of all. Because of the military use of this site and the aberrant gene expression profile, we excluded it from the analysis.

Analytical chemistry from SPMD and POCIS devices deployed directly at the other three sites showed low levels of anthropogenic contaminants at the spray field site (site 2) with the most elevated levels being those of Acenaphthene (28 pg/L) and Acenaphthylene (52 pg/L), and EE2 (51 pg/L) out of the 30 organochlorine pesticides (OCP), 16 polyaromatic hydrocarbons (PAH), and total polychlorinated biphenyls

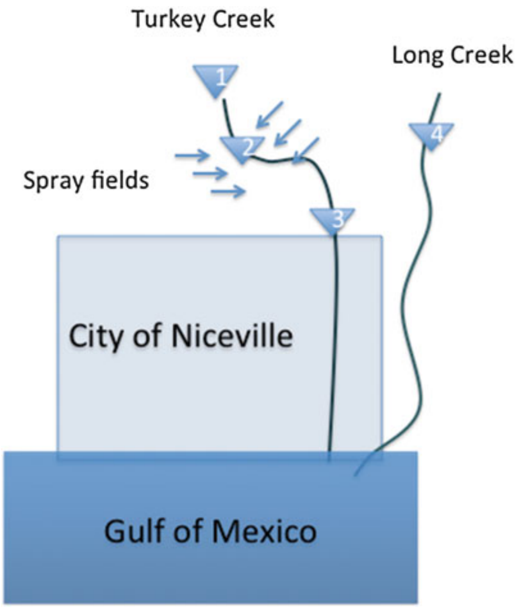

Fig. 40.1 Water collection sites on East Turkey Creek and Long Creek on the Eglin Air Force Base, FL. *Triangles* show approximate sites of water collection for exposures (Adapted from Weil et al. (2012))

(PCBs) measured by GC-MS (Weil et al. 2012). Metal analysis of tissues from sailfin shiners caught at the sites showed increases in Pb, Cd, and Zn at site 2, which is known to be influenced by wastewater.

Fathead minnows were used as a surrogate species and the exposures were performed for 48 h. Gene expression fingerprints produced from liver and gonadal tissues grouped by site, as determined by hierarchical clustering, indicating that there were differences in the water from each site (Fig. 40.2). Expression patterns for Sites 1 and 4 were closest to fish exposed to control conditions in the laboratory. Expression patterns at Sites 2 and 3 were different and suggested impacts of spray field runoff. The biochemical pathways affected included metabolism, cell cycle control, transcription, translation, remodeling of cellular structures, and cell signaling. These changes were consistent with a generalized stress response and point to survival of early life stages, as a likely higher order effect. Interestingly, Vtg was not elevated in male fish, probably because the levels of EE2 (and other xenoestrogens not measured) were below the threshold levels for induction of expression through the estrogen receptor. It is more likely that the changes in gene expression patterns were due to other chemical stressors and metals.

This study revealed that there was perturbation of gene expression patterns in fish exposed to the waters collected at the spray field sites and downstream from the spray fields. Clearly anthropogenic contaminants are present in streams and may be contributing to the decline of the sensitive Okaloosa darter. It is also clear that a limited set of additional studies should be performed to determine exactly how the

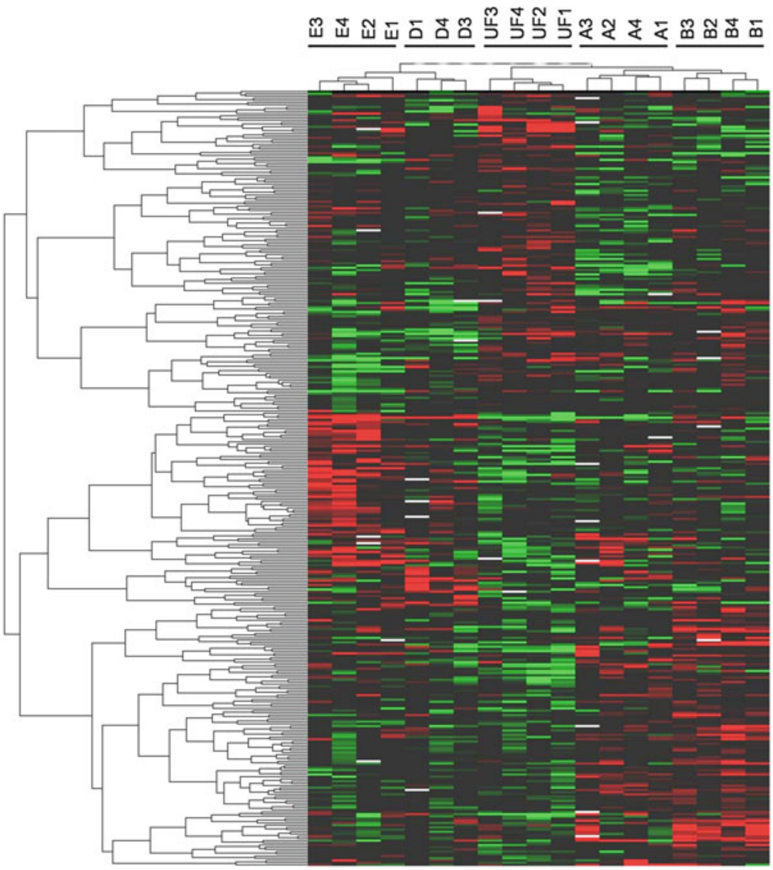

Fig. 40.2 Hierarchical clustering of sites at Eglin Air Force Base based on the gene expression data that are statistically significant as determined by ANOVA ($p < 0.05$; expression >1.5 or <1.5). Each *column* represents a different biological sample and each *row* is the expression of a single gene. *Red* is above average based on the median expression for the row. *Green* is below average based on the median expression for the row (Adapted from Weil et al. (2012))

darter is being affected, and whether it is at the early life stages (as suggested above) or at some other point in their life cycle. Studies such as this one help to create additional hypotheses for further testing.

40.3.2 Field Case Study 2: Behavior and Gene Expression Changes in Waters Influenced by Sewage Treatment in Minnesota

It is possible to test waters also by deploying a test fish species in cages at the sites of interest. In this study, fathead minnows (*Pimephales promelas*) were caged for

48 h in several rivers in Minnesota that had previously been studied by Kathy Lee and shown to have endocrine disruption effects in endogenous fish, mostly carp (Lee et al. 1999; Lee et al. 2004). In addition to domestic and industrial sewage, some of the locations tested received extensive agricultural runoff, particularly from pig, cow, and poultry farms, where anabolic androgens are used extensively. Alongside the gene expression analysis, male fathead minnows caged at these sites were also tested for their competitive behavior in protecting a nest. For fathead minnows, spawning is generally a competitive process, with the more aggressive males acquiring and protecting nest sites, and subordinate males being unable to reproduce. Previous studies have shown that environmental estrogens and androgens can influence these behavior patterns (Martinovic et al. 2007).

At one location that is primarily influenced by domestic and industrial waste, male fish appeared to be feminized, e.g., not able to compete with control males for protecting a nest (Garcia-Reyero et al. 2009a). This particular site has been shown in many studies to be influenced by estrogens (Folmar et al. 1996; Folmar et al. 2001). At other locations, fathead minnow males were more aggressive than control males (Garcia-Reyero et al. 2009a; Garcia-Reyero et al. 2011). These locations receive agricultural wastes. Vitellogenin induction was seen only in males that were feminized.

Hierarchical clustering of gene expression data from microarray analysis showed that fish clustered by site, suggesting that the waters at each site were sufficiently different from each other to change gene expression in the fish. Only one set of locations was on the same river, up-stream and down-stream from a sewage treatment facility, and they clustered together. Those where fish behavior was more aggressive clustered together and those with little effect on behavior clustered together, despite the sites being located on different rivers.

There was a clear pattern of gene expression changes that correlated with the behavior seen in fish. For example, fish that were more aggressive expressed a higher level of ornithine decarboxylase antizyme 2, which has been linked to the action of androgens and antiandrogens in the testis (Berger et al. 1984; de las Heras et al. 1998) and may be a good biomarker for contaminants with such activities. Other genes whose expression was elevated correlated with effects from exposures to complex mixtures of chemicals. For example, there was elevation of expression of the cytochrome P450s and of nuclear receptors such as RORa, known to be a ligand for cholesterol (Kallen et al. 2002), which is abundantly found at these locations (Kolpin et al. 2002; Lee et al. 2004).

In this study, the gene expression data helped to explain some of the behavior alterations in the fish and furthermore gave inferences and new hypotheses of how the exposures may be affecting higher biological levels in fish inhabiting these locations. This study also showed that molecular endpoints could add value to ecological assessments of rivers.

40.3.3 *Field Case Study 3: Determining the Effect of PCBs on Wild Largescale Suckers (***Catostomus macrocheilus***) on the Columbia River in the United States*

The objective of this study was to use wild largescale suckers collected at different locations in the Columbia River and analyze their gene expression changes as a function of contaminant load. In the case of the Columbia River, various regions are highly contaminated with organochlorine pesticides, polychlorinated biphenyls and the flame-retardants, polybrominated diphenyl ethers. Fish that inhabit the river are contaminated with these chemicals primarily through the food web, but also through direct interaction with the contaminants in the water column, and have been shown to suffer endocrine disruption from the exposures (Rayne et al. 2003; Feist et al. 2005; Hinck et al. 2006; Johnson et al. 2007). The goal of the study was to find gene expression changes that correlated with contaminant load in the tissues of the fish.

For this study, we first needed to develop a custom microarray for the largescale sucker, as no genomic sequences were generally available. We did this by constructing a normalized cDNA library (Garcia-Reyero et al. 2008) and sequencing the library on the Roche 454 GS-FLEX and the Illumina Genetic Analyzer IIX. Sequences were assembled and annotated by comparing them via BLAST to the nr and nt databases at NCBI. Out of the 54,386 sequences that had good matches, we picked 14,000 with the best annotation and representation for an oligonucleotide-based microarray (Christiansen et al. 2014).

In the case of this study, livers from the same fish were measured for contaminant burden, specifically for organochlorine pesticides, PCBs and PBDEs. Expression of 72 probes in the fish correlated with individual contaminants and 23 probes with multiple PCB and PBDE congeners (Christiansen et al. 2014). This suggested a general relationship with contaminant burden rather than a specific response to individual congeners. Among the key pathways that were altered in fish with high contaminant burdens were the usual suspects, CYP genes and others involved in drug metabolism and detoxification. Other genes associated with oxidative stress and cellular chaperones were also altered, again showing that the organisms are exposed to the contaminants and trying to re-establish homeostasis. More interesting was the increase in expression of Poly(rC)-binding protein 4 (PCBP4), a gene involved in apoptosis. The protein product of this gene binds to RNA sequences that are rich in C residues and is induced by P53 to induce apoptosis. This suggests that cellular responses to the contaminants had proceeded beyond the first level of response and that cellular damage was occurring. This progression is expected as the concentration and time of exposure cause damage beyond that from which the animal can recover.

40.4 Using Compiled Microarray Data Sets to Model AOPs

The new Adverse Outcome Pathway (AOP) paradigm proposed by EPA (Ankley et al. 2010) and adopted by the Organisation for Economic Co-operation and Development (OECD) proposes the use of many *in vitro* assays as surrogates for *in vivo* testing for xenobiotics as long as the molecular initiating event can be identified and linked through weight of evidence to key events on the path to adversity. Several pathways have now been developed in this context (Perkins et al. 2011; Williams et al. 2011; Yozzo et al. 2013; Villeneuve et al. 2014). A beautiful example for an AOP, is the one developed by Villeneuve et al. (2013) for aromatase inhibition by contaminants, such as fadrozole and prochloraz. Aromatase is the enzyme that aromatizes testosterone into E2. When this enzyme is inhibited, it leads to a general decrease in estradiol biosynthesis in the gonad, resulting in a reduction of this hormone in the blood. This then leads to reduction of Vtg synthesis in females, since this gene is under the control of estradiol in the liver. Decrease in Vtg in females has been directly linked to poor egg development and population level effects (Miller and Ankley 2004; Miller et al. 2007; Ankley et al. 2008; Ankley et al. 2009). This AOP was among the first developed to show how this paradigm could work.

Microarray information can lead to hypotheses for molecular initiators that can then be further tested by orthogonal experimental methods. In addition, as more microarray data have become available, investigators have begun to focus their efforts on developing analyses for compiled data sets in order to define AOPs across chemicals (Shoemaker et al. 2010; Ankley et al. 2012). For example, Villeneuve et al. (2012) used gene set enrichment analyses (GSEA), a computational method used to evaluate whether sets of genes have significant relationships between distinct biological states. In this case, gene sets from microarray data generated from fathead minnows and zebrafish exposed to chemical stressors were evaluated and compared. These gene sets were organized into tissue-specific lists and subdivided based on functional categories in order to compare transcriptional changes of brain–pituitary–gonadal-hepatic axis across separate experiments. In another study, Shoemaker et al. (2010) created a simulation model of ovarian steroidogenesis in the fathead minnow by mining existing microarray data to predict the effects of the aromatase inhibitor fadrozole (FAD) on steroidogenesis.

Conclusions

Microarray analyses of toxicant effects in laboratory and field settings have provided good insight into the mechanisms by which the health of aquatic organisms may be impacted. Confidence in using these methods is rising as studies report changes in gene expression of key genes already known to be altered in traditional toxicology studies (e.g., Vtg mRNA in response to estrogens). In addition, similar changes in gene expression patterns and

(continued)

pathways are found in multiple studies with the same toxicants indicating that the responses are fundamental to the mode of action of the chemicals in aquatic organisms and perhaps in vertebrates in general. It is important for this type of work to link changes in gene expression with phenotypic changes at higher orders of biological organization. Microarrays can also be used as semi-quantitative analyses, as the magnitude of response for some genes is in proportion to the dose. However, it is important to note that the number of genes that are altered also increase with dose, suggesting different thresholds of activation for different genes. In summary, this type of analysis can give rise to new hypotheses that can then be tested more thoroughly by mechanistic studies.

Acknowledgements This work was supported by the Superfund Research Project from the National Institute of Environmental Health Sciences, NIEHS (RO1 ES015449) and by the National Science Foundation (NSF CBET 1236029).

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Part XIII
Water Chemical Pollution

Chapter 41
Ocean Acidification and Related Indicators

Friedrich W. Meyer, Ulisse Cardini, and Christian Wild

Abstract Ocean acidification is one of the main consequences of global climate change. It is caused by the increasing input of atmospheric CO_2 in the world ocean, which in turn is affecting the marine carbonate system and resulting by now in a measurable decline in seawater pH. Thus, several key water quality parameters (alkalinity, partial pressure of CO_2, concentration of dissolved inorganic carbon – DIC, and the seawater pH) serve as environmental indicators for ocean acidification. In addition, many pelagic and benthic marine organisms, particularly those that are calcifying, negatively or positively respond to acidification so that their physiological parameters (calcification, photosynthesis, growth) may also act as indicators of this phenomenon. On the ecosystem level, potential environmental indicators for acidification can be found in the sedimentary record (mineralogy, crystallography), in the benthic community (relative abundance of calcifying versus non-calcifying organisms, rugosity), or in the overall production, cementation, and erosion of inorganic carbon.

Keywords Carbonate chemistry • Eutrophication • Photosynthesis • Calcification • Paleocene-Eocene thermal maximum • Saturation horizons • Cementation • Coral

41.1 Introduction

As fossil fuel emissions grow at an alarming rate, earth's climate is changing and temperatures are rising due to the increased concentration of greenhouse gasses. Carbon Dioxide (CO_2), one of the most significant greenhouse gases, also leads to

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_41

another problem: the so-called ocean acidification (OA). In this chapter, we refer to three sections where we select the main environmental parameters that serve as short and long term identifiers of ocean acidification from the early signs, and the organism level to the ecosystem level.

In the first section, we define the term OA and describe its causes and its detection in seawater. We also compare present and past acidification events in the Earth's history. We move along with a summary on the worldwide distribution of OA with an emphasis on most affected regions, while suggesting indicators that can be used to detect short- and long-term changes in seawater carbonate chemistry.

In the second section of this chapter, we outline the most important physiological processes affected by OA and identify which parameters can potentially serve as indicators. Coral reef ecosystems are found in areas of naturally lower intensity of ocean acidification (see Sect. 41.2.3). While providing ecosystem services for billions of people, at the same time they are being affected by the strongest human pressure through overpopulation, exploitation, and habitat destruction. Therefore, we decided to focus on the effects of OA in these systems, as their study and conservation should be of the highest priority for the above mentioned reasons (see also Sect. 41.4.3). In the description of physiological processes, we mainly focus on coral reef benthic communities and refer to related work in temperate and Polar Regions when knowledge on coral reef species is scarce. We distinguish between short- and long-term effects on organisms' physiology and identify the processes that lead to changes in community composition. By comparing present and predicted alterations in community composition with geological and sedimentary records, we identify indicators on the community composition level. Changes in productivity and shifts in carbon cycling are then discussed as potential indicators of acidification. Ultimately, the effects of OA on the ecosystem level and possible related indicators are discussed.

In the third section, we summarize the outcomes of previously employed OA indicators and provide an outlook on the future expected performance of organisms, communities and ecosystems. We finally conclude the chapter by suggesting priority fields for future research to elucidate management strategies for ocean acidification.

41.2 Definition, Causes and Distribution of Ocean Acidification

41.2.1 The 'Other CO_2 Problem' and Its Effects on the Ocean Carbonate System

Ocean acidification is a term commonly used to describe the changes in the seawater carbonate chemistry deriving from the ocean uptake of anthropogenic CO_2 from the atmosphere. Since global warming and ocean acidification are both caused by increasing atmospheric CO_2, acidification is commonly referred to as the 'other CO_2 problem' (Doney et al. 2009).

CO_2 in the atmosphere equilibrates with surface water through air-sea gas exchange within a timescale of approximately one year (Doney et al. 2009). Once dissolved, CO_2 gas reacts with water to form carbonic acid (H_2CO_3), which dissociates by losing hydrogen ions (H^+) to form bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions:

$$CO_{2(atm)} \leftrightarrow CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \quad (41.1)$$

These reactions are reversible and near equilibrium (Millero et al. 2002). Accumulating CO_2 in the oceans alters the seawater carbonate chemistry, increasing aqueous CO_2, bicarbonate, and hydrogen ion concentrations, with the latter lowering pH. On the other hand, carbonate ion concentration declines. This, in turn, cause a decrease in the saturation state (Ω) of calcium carbonate ($CaCO_3$), which is directly dependent on the concentration of dissolved carbonate ions:

$$\Omega = \left[Ca^{2+}\right]\left[CO_3^{2-}\right]/K'_{sp} \quad (41.2)$$

Calcium carbonate occurs in two common polymorphs, calcite and aragonite, the latter being approximately 50 % more soluble than calcite (Mucci 1983). In seawater, a natural horizontal boundary is formed as a result of temperature, pressure, and depth, known as the (aragonite or calcite, respectively) saturation horizon (Raven et al. 2005), which represents the transition depth between the supersaturated upper ocean ($\Omega > 1.0$) and the undersaturated deep ocean ($\Omega < 1.0$).

Increasing CO_2 levels (and the resulting lowering in pH and carbonate ion concentration) decreases the saturation state of $CaCO_3$ and raises the saturation horizons of both its mineral forms closer to the surface. This is an important threshold for marine calcifying organisms since $CaCO_3$ deposition generally occurs at $\Omega > 1.0$, while its dissolution occurs at $\Omega < 1.0$ (Fig. 41.1). However, reduced calcification rates following acidification occur for a variety of calcareous organisms even at $\Omega < 1.0$ (Ries et al. 2009). Aside from the slowing and/or reversing of calcification, organisms may suffer several other adverse effects, either indirectly through negative impacts on food resources or directly as reproductive or physiological effects (see Sect. 41.3).

Moreover, a decrease in seawater buffer capacity will arise as a result of the dissolution of anthropogenic CO_2 and the following increase in Dissolved Inorganic Carbon (sum of the dissolved carbonate species, denoted as DIC), causing much greater sensitivity to local variations in DIC and Total Alkalinity (TA) (Egleston et al. 2010). This is posing another threat to marine life, especially in shallow coastal environments in which high biological productivity drives the large natural variability in carbonate chemistry that will be amplified as the buffer capacity of the ocean will decrease (Shaw et al. 2013; see Sect. 41.3).

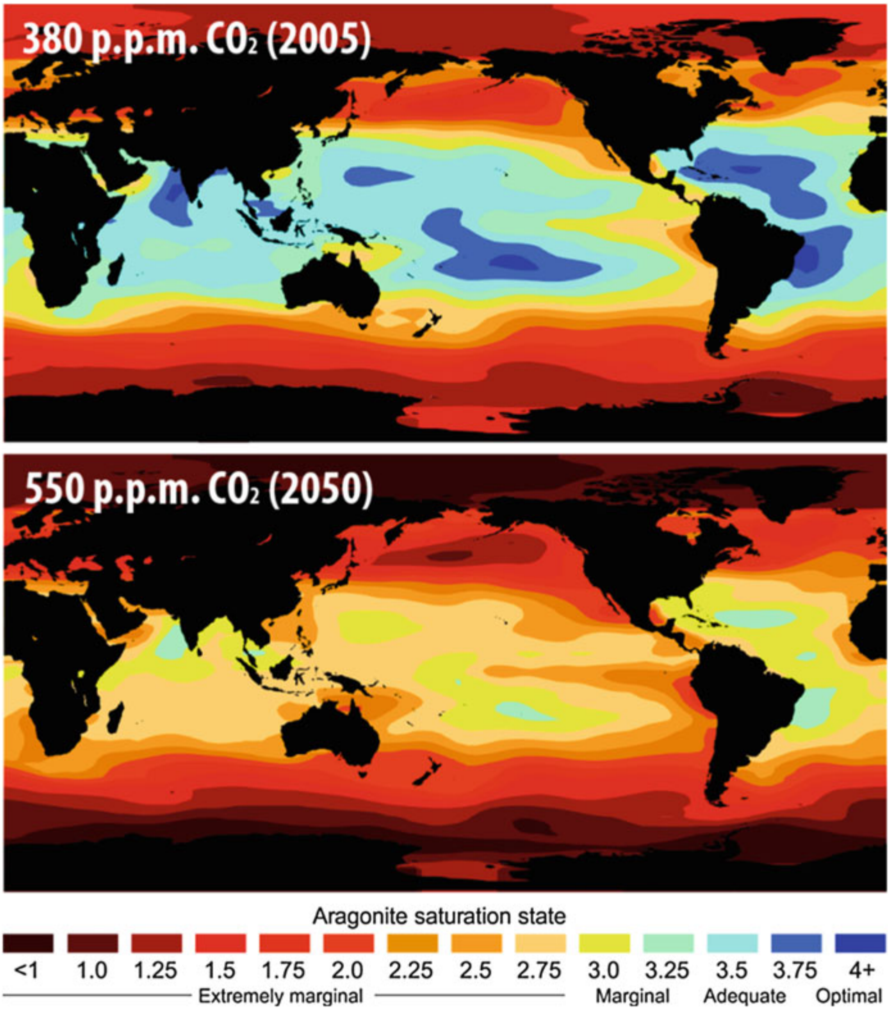

Fig. 41.1 Model showing expected changes in the surface oceans' aragonite saturation state by 2050 due to anthropogenic CO_2 emissions (Modified from Schiermeier (2011))

The solution chemistry of carbon dioxide in the seawater can be easily calculated and monitored by measuring any two of its four main parameters (TA, DIC, pH , and CO_2 partial pressure ($p\mathrm{CO_2}$)) for a given boron concentration, temperature, salinity, and pressure. This can therefore be used as an effective environmental indicator of ocean acidification, allowing to detect and investigate regional and local trends. Several Standard Operating Procedures regarding the measurement of each parameter are listed in Dickson et al. (2007), while Riebesell et al. (2010) provide a useful baseline for ocean acidification research and data reporting.

41.2.2 Past Acidification Events in Earth History Compared to Present Phenomenon

The earth already experienced episodes that involved geologically 'rapid' (<10,000 year) changes of ocean carbonate chemistry, such as the Paleocene-Eocene Thermal Maximum (PETM, ~55 Myr), during which global surface temperatures increased by 5–9 °C within a few thousand years (Zachos et al. 2003; Sluijs et al. 2006) and a substantial carbon release occurred, leading to ocean acidification and dissolution of deep-sea carbonates (Zachos et al. 2005; Zeebe et al. 2009; Ridgwell and Schmidt 2010). However, the present rate of carbon input is greater than during any of the geological ocean acidification events identified so far, including the PETM (Riebesell et al. 2010). A recent investigation provided further evidence that the current rate of ocean acidification is faster than at any time in the past 300 million years, and it is occurring at almost 10 times the rate of acidification experienced by the oceans during the PETM (Hönisch et al. 2012). Historically, sustained periods of acidification and CO_2 increase – which were similar, but not as extreme as in the last 1,000 years – have led to the collapse of coral reefs and, in one instance, to the extinction of 96 % of marine life (Hönisch et al. 2012).

There is little doubt concerning the link between anthropogenic emissions and ocean acidification, since the current anthropogenic trend already exceeds the level of natural variability by up to 30 times on regional scales (Friedrich et al. 2012). These results are further verified by hydrographical surveys and time series data (Feely et al. 2008; Wootton et al. 2008; Doney et al. 2009; Dore et al. 2009) that show a direct correlation between rates of increase in surface water pCO_2 and atmospheric CO_2 (Dore et al. 2009), thereby indicating uptake of anthropogenic CO_2 as the major cause for the observed long-term increase in Dissolved Inorganic Carbon (DIC) and decrease in $CaCO_3$ saturation state.

Over the past 250 years, atmospheric CO_2 levels increased by more than 40 % from pre-industrial levels of approximately 280 parts per million by volume (ppmv) to 393 ppmv in 2013 (Tans and Keeling 2014). The rate of increase, driven by human fossil fuel combustion and deforestation, was about 1.0 % year^{-1} in the 1990s and reached 3.4 % year^{-1} between 2000 and 2008 (Le Quéré et al. 2009). About one third of the carbon dioxide released by humans into the atmosphere dissolves into the oceans (Sabine et al. 2004).

Since the beginning of the industrial revolution, surface ocean waters have already experienced a 0.1 pH drop or more (representing an approximately 29 % increase in H^+), and a further 0.3–0.4 pH drop is projected for the end of the twenty-first century as the oceans absorb more anthropogenic CO_2 (equivalent to approximately a 150 % increase in H^+ and 50 % decrease in CO_3^{2-} concentrations) (Solomon et al. 2007).

Recently, several trace-element and isotopic tools have become available which have been applied as environmental indicators to study and compare past and present acidification events. It is possible to trace changes in seawater pH through the boron isotopic composition ($\delta^{11}B$) of marine carbonates, to estimate surface ocean aqueous [CO_2] using the stable carbon isotopic composition ($\delta^{13}C$) of organic molecules, and to reveal ambient [CO_3^{2-}] by means of the trace element (such as B, U, and Zn)–to-calcium ratio of benthic and planktonic foraminifer shells (Hönisch et al. 2012).

The assessment of past acidification events through geological records is essential to understand and predict the unknown territory of marine ecosystem change that we are facing. Hence, future studies will have to apply the available tools in order to expand geochemical estimates and reduce uncertainties of past ocean carbonate chemistry and ecological changes.

41.2.3 Regional Variability of Acidification in the World Ocean

Saturation states are highest in shallow, warm tropical waters and lowest in cold high-latitude regions and increasing water depths, reflecting the increase in $CaCO_3$ solubility with decreasing temperature and increasing pressure (Feely et al. 2004). Since high-latitude regions have naturally low carbonate ion concentrations and higher CO_2 solubility, these will be the first regions affected by ocean acidification and by undersaturated surface waters (Fig. 41.1) (Fabry 2009). Recent investigations showed that areas of aragonite undersaturation already exist in some Northern Polar Seas (Bates and Mathis 2009; Yamamoto-Kawai et al. 2009). Surface waters of the Southern Ocean, Arctic Ocean, and parts of the subarctic Pacific will become undersaturated with respect to aragonite by the end of this century if the current CO_2 emission rates are not mitigated (Orr et al. 2005; Steinacher et al. 2009).

Moreover, anthropogenic CO_2 penetration into the ocean has been concentrated in the upper thermocline (Sabine et al. 2004), which determined the shoaling of saturation horizons by 30–200 m from the pre-industrial period to the present. As a consequence, deep-sea regions will also be soon affected by ocean acidification and undersaturated waters, as the saturation horizons become shallower.

Although major changes are expected to occur only in the future, a recent report already found large quantities of upwelling water undersaturated in aragonite close to the Pacific continental shelf area of North America, a condition that was not predicted to occur in open ocean surface waters until 2050 (Feely et al. 2008). Much of the corrosive character of these waters is due to respiration processes occurring below the euphotic zone. However, in the absence of the anthropogenic signal, the aragonite saturation horizon would have been deeper, and no undersaturated waters would have reached the surface (Feely et al. 2008). Thus, these events are likely to occur more frequently and in the near future, because of the additional inputs of anthropogenic CO_2, exposing continental shelves and their benthic communities to acidified conditions.

Other peculiar point-source environments of low-pH waters are also used as natural laboratories to help unravel the ecosystem-level effects of ocean acidification. These are natural pH gradients, caused by the volcanic vents of CO_2-rich gases or by low-pH, low carbonate saturation groundwater springs, which have been exploited to investigate how species, communities, and ecosystems react to acidified conditions in a natural environment. Most studied are the ones in Italy (Hall-Spencer et al. 2008), Greece (Vizzini et al. 2010), Papua New Guinea (Fabricius et al. 2011; Uthicke et al. 2013), and Mexico (Crook et al. 2011, 2013).

Natural pH gradients, as well as high-latitudes or deep and upwelling areas of the oceans, are presently undergoing large and rapid changes in seawater carbonate chemistry. Therefore, their investigation may help in understanding ocean acidification effects on physiological processes, potential acclimation and adaptation strategies and future impacts at the population, community, and regional scales. This in turn may provide essential environmental indicators in the form of biological processes, species, or communities that, because of their moderate tolerance to pH and pCO_2 variability, can be effectively used to assess the quality of the environment and how ocean acidification changes over space and time (see Sect. 41.3).

41.3 Impact on the Physiological Parameters of Organisms and Ecosystems

The impacts of OA on the organisms' level have been studied intensively and a vast amount of literature is available for polar, temperate (see reviews by Riebesell et al. 2010; Gattuso and Hansson 2011), and tropical regions. In this section, we concentrate on the effects of OA in tropical regions and in particular on coral reefs and their related benthos, as these represent some of the most productive areas of the world's oceans, which provide a multifarious range of ecosystem services. As coral reefs are located in areas of naturally low acidification (please refer to Sect. 41.2.3), they should be the focus of management and conservation strategies. Furthermore, these areas are amongst the most populated worldwide, and the immense population pressure brings with it a potential cumulative effect of OA with other stressors such as eutrophication (please refer to Sect. 41.4.1). Therefore, the identification of indicators for expected acidification in coral reefs is especially needed.

41.3.1 Calcification

Due to the shift in the carbonate system and the lowering of the carbonate saturation state, one of the most apparent indicators of OA on the organism level is the change in calcification. As the forms of carbonate, as well as the calcifying mechanisms, differ across taxa, the response toward OA can vary. However, the most dominant observation is a loss in calcification rate or alteration of calcification structure with increasing OA conditions. This can be observed for temperate and polar species living in the areas most susceptible to OA (Feely et al. 2004; Fabry et al. 2008; Comeau et al. 2012; Hoppe et al. 2011; Cerrano et al. 2013). Many studies on tropical calcifiers, such as corals, calcifying algae, molluscs, echinoderms, and crustaceans, indicate similar effects of OA.

41.3.2 Corals

Corals form the basis and structure of coral reefs. They provide habitat and primary productivity for one of the world's most diverse ecosystems. Studies revealed that a reduced pH due to the increase of atmospheric pCO_2 impairs the ability of corals to calcify (Anthony et al. 2008; Krief et al. 2010). The overall trend of reduced calcification has also been identified in many other experiments (Marubini et al. 2003, 2008; Jokiel et al. 2008), which was also confirmed in field studies (Manzello and Kleypas 2008; Fabricius et al. 2011). Moreover, corals seem to be able to influence the carbonate chemistry on a small scale within their tissues and on a larger scale in the whole reef community. It has been shown that corals are able to elevate the pH of water close to and within their tissue by 0.2–0.5 (Venn et al. 2011), and due to calcification activity they modify seawater pCO_2 and alkalinity even downstream of their habitat (Kleypas et al. 2011). Asymbiotic cold water corals show more pronounced responses toward OA, and a decrease of calcification and reduced distribution can be found along natural pH gradients (Maier et al. 2012; Jantzen et al. 2013).

41.3.3 Algae

Calcifying algae, mainly crustose coralline algae (CCA), play an important role in a reef ecosystem as they strengthen the coral reef framework. Recent studies found that CCAs seem to be the most susceptible to dissolution and productivity loss under OA conditions (Kuffner et al. 2007; Anthony et al. 2008; Martin and Gattuso 2009). Similar results were observed in experiments with *Halimeda* (Robbins et al. 2009; Price et al. 2011), an algae providing important microhabitats and contributing to substrate/sediment production (Drew 1983; Muzuka et al. 2001; Jinendradasa and Ekaratne 2002). Specimens of Halimeda incubated for 3 weeks under pH of 7.5 showed reduced inorganic carbon contents and increased organic carbon contents, suggesting reduced calcification, while high productivity was maintained. The same holds true for other calcifying micro and macro algae (Langer et al. 2006; Martin and Gattuso 2009; Ries et al. 2009) and the results are also supported by recent field data from natural vent sites (Fabricius et al. 2011; Porzio et al. 2011; Johnson et al. 2012).

41.3.4 Other Benthic Invertebrates

Little is known about the impact of OA on gastropods in tropical reefs. Overall, calcification rates of adult *Littorina* and the whelk *Urosalpinx cinerea* decrease with increasing OA conditions (Ries et al. 2009). Crabs can play an important ecological role by reducing epiphyte growth on corals and calcifying algae (Coen 1988; Stachowicz and Hay 1996, 1999), as well as by influencing nutrient cycling and ecosystem health with their grazing, omnivorous, detritivorous or scavenging behaviour. Nevertheless, studies on brachyuran crabs and the impacts of OA are rare. A few studies on adult crabs suggest a lowered thermal tolerance of the spider crab *Hyas araneus* under OA conditions (Walther et al. 2009), while other species, such as the swimming crab *Necora puber*, showed a high compensation capability under strong (pH 6.74) OA conditions (Spicer et al. 2006). The high capacity to calcify under OA conditions and even the increased rate of calcification were unexpected results of studies on these organisms (Ries et al. 2009). Overall data on groups of benthic invertebrates from temperate regions show negative yet variable effects on the adults as well as on their reproduction and larval development.

41.3.5 Photosynthesis, Respiration and Other Metabolic Processes

With an increase in bicarbonate ions and a decreased pH, the substrate availability and the medium for many fundamental metabolic processes change under OA. Depending on the organism, different effects on these processes are observed.

41.3.5.1 Corals

The increase of CO_2 as a substrate for photosynthesis by coral symbiotic algae resulted in an increased productivity, although CO_2 concentrations above 1,000 ppmv resulted in productivity loss (Anthony et al. 2008). Isotopic and physiological measurements showed that, while calcification and zooxanthellae density decreased under OA conditions, coral tissue biomass and chlorophyll density increased (Krief et al. 2010), possibly compensating for the decreased photosynthetic capacity (Crawley et al. 2010). The impact of OA on the coral holobiont (i.e., the community of coral host and associated microorganisms) has just recently been addressed, and the first results suggest a drastic change in microbial composition on the coral mucus, tissue, and skeleton under OA conditions (Meron et al. 2011).

41.3.5.2 Algae

For CCAs, not only their calcification, but also the photosynthetic rate are negatively influenced under OA (Semesi et al. 2009). In contrast to calcifying algae, which are strongly affected, fleshy non calcifying algae and sea grasses flourish under OA conditions (Fabricius et al. 2011; Porzio et al. 2011) as the additional CO_2 acts as substrate for photosynthesis. Moreover, the decline in grazers and in calcifying epiphytes increases algae development (Hall-Spencer et al. 2008). Similar results can be observed for pelagic microalgae from tropical to polar regions, which show higher productivity under OA resulting from a higher uptake of CO_2 and consequently a higher build-up of organic material (Riebesell et al. 2007; Tortell et al. 2008). This leads to a higher organic material transfer to deeper waters, eventually leading to higher oxygen consumption rates and oxygen deficiencies (Riebesell et al. 2007; Hofmann and Schellnhuber 2009). This may in turn affect the biological pump in the open ocean (i.e., the fixation of inorganic carbon and its transport from the productive zone to the ocean interior), which eventually determine the fate of increased atmospheric CO_2 (Garrard et al. 2013).

41.3.5.3 Other Benthic Invertebrates

Many studies show that echinoderms are affected mainly by an altered acid base regulation. Adult sea urchins of the species *Strongylocentrotus dröebachiensis* and *Psammechinus miliaris* show poor ion regulation under OA conditions and uncompensated respiratory acidosis (Spicer et al. 2006; Miles et al. 2007). The species *Arbacia punctulata* and *Eucidaris tribuloides* showed a negative or no response in calcification to OA, respectively (Ries et al. 2009).

41.3.6 Reproduction and Recruitment

41.3.6.1 Corals

Studies on the embryology and juvenile development of corals showed that fertilization success, larval metabolic rates, and settlement rates are inhibited under OA conditions (Albright 2011). Both *Porites asteroides* and *Acropora palmata* suffered from reduced settlement rates and the number of corals settlers was estimated to be reduced to up to 73 % (Albright et al. 2010). As revealed by Fabricius et al. (2011), adults of the massive coral of the genus *Porites* are less susceptible to OA than others (such as tabulate corals), although the recruitment of juveniles was low. Another study found a growth rate reduced by up to 78 % in the early post settlement stage of *Porites asteroides* (Albright et al. 2008). A delay in the establishment of symbiosis, combined with a reduced growth of *Acroporid* corals, was also observed (Suwa et al. 2009). In addition, a suppressed metamorphosis rate for *Acropora digitifera* was described (Nakamura et al. 2011). These studies demonstrate that juveniles of corals seem to be even more directly affected by OA than their adult stage counterparts, as they suffer from mortality and decreased recruitment rates. Their recruitment success and early developmental stages can therefore act as an indicator of OA. However, adult corals seem to be also heavily affected. When other factors interacting with OA (such as increased nutrients or reduced grazing pressure) are present, this may lead to a transition from a coral- to an algae-dominated reef (Hoegh-Guldberg et al. 2007).

41.3.6.2 Algae

While the recruitment of CCAs was found to be reduced in a mesocosm study (Kuffner et al. 2007), little is known about the impact of OA on the reproduction of macroalgae. OA has not only direct effects on the coralline algae but also indirect negative effects on their interaction with coral larvae, for which they serve as a settlement substrate, eventually resulting in a reduced survival rate of the coral recruits (Doropoulos et al. 2012). On the other hand, in microalgae, higher productivity under OA leads to higher growth rates (Tortell et al. 2008; Hofmann and Schellnhuber 2009). Due to their short generation time, first evidence suggests that microalgae can adapt in a short period of time (Lohbeck et al. 2012).

41.3.6.3 Other Benthic Invertebrates

Larval development of sea urchins under OA conditions is more intensively investigated than the effects of OA on their adult stage, and shows mainly a reduced fertilisation rate (Havenhand et al. 2008; Havenhand and Schlegel 2009; Byrne et al. 2010). When exposed to OA, sea urchin larvae showed a reduced ability to react to thermal stress (O'Donnell et al. 2008), development delay (Catarino et al. 2011), reduced calcification and growth, and increased metabolic rate (Stumpp et al. 2012). In summary, sea urchins studied so far are negatively impacted by OA during their larval as well as during their adult stages. Impacts of OA include decreased somatic growth and development as well as decreased calcification. Research addressing the effects of OA on sea stars show a conflicting picture as both increased growth and larval survival has been observed under OA conditions (Gooding et al. 2009; Dupont et al. 2010; Schram et al. 2011). Studies focusing on gastropods investigated the effect of OA on the Abalone *Haliotis discus*, *Haliotis kamtschatkana* and the intertidal gastropod *Littorina littorea*. In the Abalone, fertilization, survival, and hatching rate were negatively affected, while the rate of malformation during larval development increased under OA conditions (Crim et al. 2011; Kimura et al. 2011). *Littorina littorea* produced thinner shells when exposed to OA conditions and at the same time showed an increase in predator avoidance behaviour (Bibby et al. 2007). Results comparable with those for *Haliotis sp.* were obtained for the larval development of other mollusk species reared under OA conditions. For example, blue mussels of the genus *Mytilus* showed a higher rate of abnormal development, smaller larval sizes, and a lower hatching rate (Kurihara et al. 2008; Gazeau et al. 2010). Seedlings of the clam *Ruditapes decussates* exhibited reduced feeding rates, clearance, and ingestion rates, as well as respiration rates, under OA conditions (Fernández-Reiriz et al. 2011). A recent study on the oyster *Crassostrea gigas* again revealed similar responses with regard to their larval development (Gazeau et al. 2011), although their sperm motility was not affected (Havenhand and Schlegel 2009). Interestingly, larvae of oysters pre-acclimatized to OA conditions reacted differently. Their size, development rate, and survival rate were similar to those of larvae from adults exposed to ambient pCO_2 (Parker et al. 2011).

Studies available on larvae and adults of crustaceans are also scarce. For the larvae of the lobster *Hommarus americanus*, no reduction in carapace mass, survival, or development rate was observed (Arnold et al. 2009). In contrast, larvae of the spider crab *Hyas araneus* reared under OA conditions and elevated temperatures showed delayed metamorphosis, lower survival rates, and a reduction in calcium incorporation as compared to larvae reared at ambient temperature and pH. This effect was more pronounced for larvae of adults living in cold habitats as compared to larvae of adults from warmer habitats (Walther et al. 2010, 2011). In summary, little is known about the effect of OA on crabs and their larvae. It seems that their calcification is little affected; however, comparative measurements of tropical reef species are still missing.

41.3.7 Effects of Ocean Acidification on the Ecosystem Level

If we are to understand the potential effects of OA in the global oceans, it is fundamental to scale up the scientific questions to the ecosystem level, therefore taking into consideration a complex array of both biotic and environmental interactions (Garrard et al. 2013).

Mesocosm experiments are used in order to study not only species-specific responses, but also the effects on the community. Data of calcification rates of entire communities reflect well the species-specific and show a decrease of community calcification with increasing OA (Leclercq et al. 2002; Langdon 2003; Kuffner et al. 2007). In contrast to calcification, the net production of the system did not change (Leclercq et al. 2002). Similar observations were made using a natural pH gradient at a field site in the Mediterranean (Hall-Spencer et al. 2008). These findings agree with field observations from another natural volcanic CO_2 vent site in which massive *Porites* colonies dominated the community, with a loss in the 3D structure of the system (Fabricius et al. 2011). At the same time, also bioeroder abundance was elevated, supporting other findings predicting higher bioeroding rates under future OA conditions (Wisshak et al. 2012; Reyes-Nivia et al. 2013). In accordance with the findings for the whole coral community (as named above), also the productivity on the microbial scale did not change under different OA conditions (Witt et al. 2011). In contrast, the bacterial community did react fast, and an increased abundance of several bacterial species, such as *Alphaproteobacteria* and *Flavobacteriales*, may serve as microbial indicators of OA-induced community changes (Witt et al. 2011).

In summary, the species-specific response in calcification rate and the high abiotic erosion rates observed under OA conditions (Manzello and Kleypas 2008) suggest that the net ecosystem calcification rate may serve as a good indicator for OA. This indicator, together with measures of $p\mathrm{CO_2}$ and alkalinity, could be used as a monitoring device for community and ecosystem change (Andersson and Gledhill 2013). As for benthic communities, measures of rugosity and cementation rates can be used as convenient indicators of OA impacts. In some cases, such measures already reflect the effects of OA in upwelling areas (Manzello and Kleypas 2008).

Good indicators of OA on the community level in coral reefs are a decreased carbonate accretion rate due to increased erosion, and a loss in biodiversity and structural complexity. In addition, a decrease in hard coral cover, CCAs, calcified invertebrates, and weak framework cementation, as well as an increase in sea grass and non-calcified algae abundance, may serve as biological indicators of increasing OA conditions.

41.4 Outlook

41.4.1 How Can Acidification Interact with Other Regional or Local Stressors?

In the future, the world's marine ecosystems will likely be simultaneously affected by a range of global stressors, such as acidification and warming, which will interact with a range of local factors, particularly eutrophication (e.g. Voss et al. 2013).

Literature is lacking with regard to the potential interaction of ocean acidification and eutrophication, but there is some indication that acidification may affect the bioavailability of essential nutrients in the marine realm (Shi et al. 2010). A potentially relevant surplus source of acidification comes from the anthropogenic inputs of nutrients in the coastal waters of the world oceans (Cai et al. 2011). Human activities, such as the use of chemical fertilizers, the discharge of human and animal wastes, and the inputs of oxides of nitrogen (NO_x) from fossil fuels burning, have increased the concentrations of inorganic nutrients and fuelled massive algal blooms in many coastal areas (Howarth et al. 2011). This pronounced marine eutrophication may stimulate ocean acidification via facilitation of CO_2

uptake by phytoplankton. In addition, microbial consumption of the organic matter produced by phytoplankton depletes bottom waters of oxygen (O_2) and releases CO_2, in turn increasing seawater acidity (Sunda and Cai 2012). Therefore, eutrophication and the related increase in bottom water CO_2 concentrations may exacerbate ocean acidification in coastal waters.

Knowledge about the interaction between such global and local factors and their consequences for the ecosystem functioning is scarce, but a few studies indicate cumulative aggravating effects (e.g. Lloret et al. 2008). Future research should, however, concentrate on these aspects.

41.4.2 Recommendation for a System of Indicators

A good system of indicators for OA should include a range of indicators of status and process that simultaneously characterize the water chemistry and effects on marine organisms and ecosystems. These indicators may benefit from a combination of measurements of seawater temperature, pH, and alkalinity (status parameters) on the one hand, and quantification of calcification rates and oxygen fluxes (process parameters) of key pelagic (e.g., coccolitophores) and benthic (e.g., corals, sea urchins, and calcifying algae) marine organisms on the other hand. As a supplementation, sedimentary carbonate contents and benthic rugosity (status parameters), along with benthic community changes (process parameter), may be used in order to contribute to the understanding of the consequences of OA on the ecosystem. Such a suggested system of indicators would have a good ratio between sampling effort and information outcome. It should be implemented best in a comparative way using identical methodology in an appropriate temporal and spatial resolution at several locations of particular interest.

41.4.3 How Can Management Target Ocean Acidification?

Science-based management of marine coastal ecosystems and their resources considers the interaction of global as well as local factors (refer to section above). This may be achieved through the use of appropriate systems of indicators, as suggested in the preceding section.

An urgent need is to assess the impacts of ocean acidification on the ecosystems. The understanding of the effects of ocean acidification on the interaction among different biotic components and on marine ecosystems is still limited (Fabry et al. 2008; Hall-Spencer et al. 2008). It is particularly important to evaluate possible negative socio-economic impacts that are reflected in decreases in ecosystem services, such as productivity, provisioning of associated biodiversity, and coastal protection (please refer to related publications on coral reefs: Moberg and Folke 1999; Wild et al. 2011).

As for ocean warming, there are no direct management measures for ocean acidification, because it is not feasible to isolate marine ecosystems against these global effects in their medium, the seawater.

However, as ocean acidification is predicted to increase in the mid-term under all IPCC scenarios, conservation priorities should include those areas that exhibit a naturally lower intensity of acidification, such as shallow tropical areas, which at the same time provide many ecosystem services and are among the densest populated areas in the world (for regional differences in ocean acidification please see Sect. 41.2.3). These areas could be protected at least against local stressors, such as overfishing and eutrophication, that act simultaneously with global factors, such as acidification.

Ocean acidification itself may be reduced by all general measures that limit CO_2 emissions. In addition, methods such as carbon capture or sequestration are discussed, but such elaborate and technically expensive measures, which require extensive development and trials, should rather be considered as symptomatic treatment and not as a sustainable management strategy against ocean acidification.

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Chapter 42
Mercury in Fish: History, Sources, Pathways, Effects, and Indicator Usage

Edward J. Zillioux

Abstract Methyl mercury is highly toxic to humans, particularly to the developing nervous system. Virtually all mercury in muscle tissue of naturally-occurring edible fish is in the form of methyl mercury, and fish consumption is the most common route of human exposure to methyl mercury. The monitoring of mercury in fish thus provides reliable indication of potential exposure of humans to mercury, and regulatory guidelines based on threshold levels of effects due to such exposure provides the best mechanism for effective avoidance of mercury toxicosis in populations throughout the world. This chapter traces the development of the use of mercury in fish as an indicator of potential harm to human health from early recognition of the dangers associated with methyl mercury, to the first records of major toxicity events attributable to fish consumption, through the sources of environmental contamination by mercury today, both natural and anthropogenic, and an overview of the mercury species, environmental conditions and pathways leading to uptake and bioconcentration of mercury in fish.

Keywords Mercury • Methyl mercury • Fish consumption • Bioconcentration • Indicator • Regulatory guidelines

42.1 Introduction

The concentration of mercury (Hg) in edible fish tissue is today perhaps the most broadly-applied indicator of potential harm to human health from any xenobiotic substance. Organic mercury, in particular monomethyl-Hg (CH_3Hg^+ or MeHg), is the most toxic form of mercury commonly found in the environment, and consumption of contaminated fish is the most common route of human exposure to MeHg. Virtually all Hg (>95 %) in muscle tissue of naturally-occurring (and commonly consumed by humans) fish is in the form of MeHg (Bloom 1992). Today, fish and products derived from fish and sea mammals are virtually the only sources of MeHg to humans (Clarkson 1997).

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_42

This chapter reviews the early history of organic-Hg toxicity events, the origin of our recognition of the value of fish as the primary indicator in determining potentially harmful human exposure to MeHg, the primary pathways of uptake by fish, bioaccumulation and bioconcentration of Hg in fish, factors that exacerbate or mitigate the uptake of Hg in fish, the toxic effects of Hg to the fish themselves, as well as to piscivorous species both wildlife and human, and how these translate into regulatory standards and action levels, or consumption advisories. This chapter is an overview of MeHg poisoning with a focus on the principal vector to humans and wildlife. It is not intended to be a comprehensive review of the literature relating to each subject, but it is my intent within each section to provide adequate references to assist students who wish to pursue more focused studies in greater detail.

42.2 Historical Background

42.2.1 Organic Mercury Poisoning

The earliest known deaths attributed to exposure to organic mercury, involving dimethyl mercury, occurred at St. Bartholomew's Hospital in Smithfield, London in the course of research on the valency of metals and metallic compounds. Details of the research that led to the lethal exposures were reported by Frankland and Duppa (1863); yet, inexplicably, their publication made no mention of the poisoning and deaths of two technicians involved in the research. The two technicians were apparently directly exposed to dimethyl Hg for periods of 3 months and 2 weeks, respectively. According to hospital reports, both men exhibited symptoms associated with ataxia and died 2 weeks and 12 months, respectively, after the onset of symptoms. Clinical details were reported in two internal hospital reports (Edwards 1865, 1866), which include the statement, "That the symptoms were due to the inhalation of [mercuric methide] is rendered almost certain." However, circulation of these reports was limited; Hunter et al. (1940) commented that "The story of these deaths has been handed down verbally from one generation of chemists to another."

Despite these early fatalities, a detailed clinical description of the toxicity of organic mercury to humans was not published in the scientific literature until shortly before a massive poisoning event, traced to the consumption of contaminated fish, occurred in Minamata, Japan. Hunter et al. (1940) reported four cases of human poisoning by inhalation of MeHg compounds that occurred in a factory where fungicidal dusts were manufactured. In all four subjects, only the nervous system was involved; symptoms included generalized ataxia, dysarthria (speech slurred, slow, and difficult to understand), astereognosis (unable to distinguish form of objects by touch), gross constriction of visual fields, inability to perform simple tasks, weakness of arms and legs, and unsteadiness in gait. Symptoms known to occur in cases of metallic Hg poisoning, salivation, stomatitis and erethism (abnormal physical sensitivity), were generally absent. All recovered with varying degrees of disability; the most severe, a 23-year-old man (Case 4), remained totally disabled 3 years after the onset of symptoms.

Hunter et al. (1940) also undertook four experiments with animals, which included a pathological study. The first three experiments exposed rats to methyl mercury nitrate through gavage feeding or vapor inhalation. The fourth experiment exposed a female monkey (*Macacus rhesus*) to MeHg vapor using the same box as previous inhalation experiments with rats, albeit at a much lower dose in proportion to body size. Symptoms in both exposed rats and monkey mimicked the general ataxia, involving severe neurological symptoms, as observed in human exposures. Neurological symptoms were far more severe in the monkey than in the rats, suggesting that primates may be more susceptible to organic mercury compounds than rats. Animals that survived through later stages of intoxication showed degeneration of the cells in the granular layer of the middle lobe of the cerebellum. This is of particular interest because similar cerebellar cortical atrophy was found when the first human exposure to MeHg (Case 4 above) came to necropsy, following the exposure that occurred 15 years before his death (Hunter and Russell 1954).

42.2.2 Minamata Disease

Minamata Disease (MD) was first described by McAlpine and Araki (1958) as "an unusual neurological disorder caused by contaminated fish," which attacked villagers living near Minamata Bay in Kyushu Island, Japan between 1953 and 1956. During this period, 40 families were affected, "causing death in more than a third of its victims and serious disability in most of those who survived." In addition, numerous animals in the immediate area died with similar neurological symptoms, including 24 cats, 5 pigs, 1 dog and many crows. The brains of 10 of the cats showed the granular layer of the cerebellum especially affected. Although the cause could not then be established, the authors noted that certain metals including MeHg had been shown to cause some of the neurological symptoms of the disease. In all cases, the disease was directly correlated with the consumption of fish caught in Minamata Bay. It was strongly suspected that the fish were contaminated by pollutants contained in the effluent from a chemical factory owned by Chisso & Company, which, in 1950, had diverted its former open sea discharge through a newly constructed channel discharging directly into Minamata Bay. The factory utilized a process discovered in 1881 in which mercuric sulfate was used as a catalyst in the conversion of acetylene to acetaldehyde (Clarkson 1997). MeHg compounds were produced as byproducts of the catalytic process, which were at first recycled but later discharged directly into Minamata Bay because of soaring recycling costs (Kondo 1999). The causative agent of MD was verified in 1959 as MeHg poisoning by a Kumamoto University team (Study Group of Minamata Disease 1968). During the life of the plant, an estimated 600 tons of Hg were discharged (Harada 1982). In 1965, a second outbreak of MD occurred far to the north of Minamata Bay in the Agano River area of the Niigata Prefecture. Again, the cause of the poisoning was the production of acetaldehyde and discharge of waste MeHg byproducts into the Agano River and the consumption of contaminated fish. In all, 2,920 cases of MD in the two areas were officially recognized before the acetaldehyde process was discontinued in Japan and elsewhere (Kondo 1999).

42.3 Sources, Speciation and Pathways of Hg in Fish

Hg in the global aquatic environment comes primarily from atmospheric deposition (Livett 1988; Fitzgerald et al. 1991; Iverfeldt 1991), either direct from wet and dry deposition or indirect through Hg deposition on watersheds or floodplains, which is subsequently transported to surface water bodies. The form in which it deposits is primarily as Hg^{++}, or HgII, which can be biotransformed to MeHg which, in turn, is efficiently taken up by organisms at the base of the food chain. Trophic transfer and resultant concentrations in higher trophic level organisms are influenced by food web dynamics, including length of the food chain. A portion of Hg entering the environment from both natural and anthropogenic sources is reemitted as gaseous elemental Hg, or Hg^0, which is eventually redeposited, reemitted, etc. This cyclical history must be considered when constructing source attribution budgets.

42.3.1 Natural Sources

The earth's crust naturally contains approximately 50 ppb Hg, varying from an average of 40 ppb in limestone to an average of about 160 ppb in the A soil horizon. Most natural waters contain <2 ppb Hg (Adriano 1986). Natural sources of Hg to the atmosphere include geological, vegetative and aquatic degassing, biomass burning, and volcanic (explosive, passive & calderas) and geothermal emissions. Oceanic and soil degassing are probably the most important contributions to the global atmospheric burden of Hg (Pirrone et al. 2010; Norton et al. 1990). Considerable uncertainty exists concerning the proportion of natural sources of Hg, as opposed to anthropogenic sources, contributing to the total atmospheric burden. Seigneur et al. (2003) reported the contributions of natural Hg emissions, direct anthropogenic emissions, and re-emitted anthropogenic emissions to be roughly equal. Thus, by these estimates, one-third of the total annual Hg emissions, estimated at 6,000–6,600 metric tons, would be attributed to natural sources. More recent models estimate the contribution from natural sources to be on the order of 10 % of an estimated annual total of 5,500–8,900 metric tons currently being emitted and re-emitted to the atmosphere from all sources (UNEP 2013).

42.3.2 Anthropogenic Sources

The earliest evidence of anthropogenic releases of Hg to the atmosphere is associated with mining. Cinnabar (HgS) has been used for the production of vermillion since about 1500 BCE, with early mining sites in China, Spain, Greece, Egypt, Peru, and Mexico (Rapp 2009). On the Iberian Peninsula, mat deposits built by the seagrass *Posidonia oceanica* provide a paleorecord of Hg fluxes to the marine environment going back 4,315 years (Serrano et al. 2013). The first European Hg increase attributable to an anthropogenic source was identified in the *P. oceanica* record at about 2500 BP, coinciding with the beginning of intense mining in Spain. Lake-sediment cores collected near Huancavelica, Peru demonstrate the existence of a major Hg mining industry at Huancavelica spanning the past 3,500 years (Cooke et al. 2009). Artisanal and small-scale gold mining (ASGM) is the largest source of global anthropogenic Hg emissions today (e.g., Cleary 1990) followed closely by coal combustion. Other large sources of emissions are non-ferrous metal production, cement production, disposal of waste from mercury-containing products, hazardous waste sites, and sewage treatment plants (UNEP 2013). The global distribution of estimated Hg emissions in 2010 from anthropogenic sources, ranked from highest to lowest regional emitters, is shown in Table 42.1.

Note that estimates of regional and total anthropogenic Hg emissions change with pollution control technologies, regulatory limits and enforcement, fuel choice, phase-out of Hg containing products, increased usage, etc. This is illustrated by comparing global inventories over different time periods. For example, in 1995, approximately 11 % of the total global anthropogenic emissions originated in North America (Pacyna et al. 2003). In the 2010 inventory given in Table 42.1, the estimated contribution from North America had decreased to 3 %, primarily due to advances in emission control technologies, particularly with respect to coal combustion. On the other hand, inventory data from South America show a clear increase from approximately 3 % of total global anthropogenic Hg emissions in 1995, to 4 % in 2000, 7 % in 2005, and 12.5 % in 2010 (Pacyna et al. 2003, 2006, 2010; UNEP 2013). This increasing trend, the largest global increase in Hg emissions over the 15-year period of record, is due almost entirely to ASGM (Cleary 1990). Indeed, as noted by Pacyna et al. (2010), "at least 100 million people in over 55 countries depend on ASGM – directly or indirectly – for their livelihood, mainly in Africa, Asia and South America."

42.3.3 Atmospheric Hg Speciation and Deposition

Mercury is emitted to the atmosphere in gaseous forms, as Hg^0 and HgII (also known as reactive gaseous Hg, or RGM) and as particulate Hg, or Hg_p. The majority of Hg emissions to the atmosphere is as Hg^0, including soil, vegetative, and oceanic degassing, volcanic and geothermal emissions, mining operations, biomass burning and approximately half of fossil fuel emissions (Pacyna et al. 2006). The atmospheric residence time for Hg^0 is approximately one year

Table 42.1 Mercury emissions from various regions, in tones per year, with the range of the estimate, the percentage of total global anthropogenic emissions, and the primary and secondary regional sources of emissions[a,b]

Region	Emissions (range), tones	%	Primary and secondary regional sources
East and Southeast Asia	777 (395–1,690)	39.7	1° Coal combustion; 2° ASGM
Sub-Saharan Africa	316 (168–514)	16.1	1° ASGM; 2° Coal combustion
South America	245 (128–465)	12.5	1° ASGM; 2° Non-ferrous metals
South Asia	154 (78.2–358)	7.9	1° Coal combustion; 2° Large-scale gold
CIS and other Eastern European countries	115 (42.6–289)	5.9	1° Coal combustion 2° Non-ferrous metals
European Union (EU27)	87.5 (44.5–226)	4.5	1° Coal combustion; 2° Cement production
Undefined	82.5 (70–95)	4.2	Global total from contaminated sites
North America	60.7 (34.3–139)	3.1	1° Coal combustion; 2° Product waste
Central America and Caribbean	47.2 (19.7–97.4)	2.4	1° ASGM; 2° Non-ferrous metals
Middle Eastern States	37.0 (16.1–106)	1.9	1° Coal combustion; 2° Cement production
Australia, NZ and Oceania	22.3 (5.4–52.7)	1.1	1° Large-scale gold; 2° Non-ferrous metals
North Africa	13.6 (4.8–41.2)	0.7	1° Non-ferrous metals; 2° Product waste
Grand Total	**1960 (1,010–4,070)**	**100**	

[a]UNEP (2013)
[b]Estimates based on 2010 inventory

enabling distribution on a global scale. The majority of Hg^0 is eventually oxidized to HgII, which is soluble and subject to washout. HgII is also emitted directly to the atmosphere from various industrial processes including fossil fuel combustion (primarily coal), municipal waste incineration, cement production, as well as crematoria. HgII and Hg_p, have much shorter atmospheric residence times, often depositing on a local or, at most, a regional scale from point sources. Other species of Hg are generally present at de minimis levels in the atmosphere and will not be considered further here.

42.3.4 Methylation and Uptake of Hg in Fish

Deposited HgII is the primary substrate for methylation by sulphate- and iron-reducing bacteria and/or methanogenic archaea under anoxic conditions found in sediments, as well as in periphyton and wetland catchment areas, and is highest in sediments moderately enriched by organics and sulfate (Poulain and Barkay 2013; Hamelin et al. 2011; Gilmour et al. 1992; Driscoll et al. 1994; Sunderland et al. 2006 [see also reviews by Zillioux et al. 1993; Porcella 1994 and references therein]). The efficiency of MeHg production varies greatly among species and between geobiological niches, however. Benoit et al. (2003), in an extensive review of MeHg production and degradation, made the case that sulfate-reducing bacteria (SRB) are the key Hg methylators in aquatic ecosystems. They cited studies using specific metabolic inhibitors where inhibition of methanogens increased Hg methylation, while inhibition of sulfate reduction dramatically decreased MeHg production in saltmarsh sediment (Compeau and Bartha 1985). In addition, Oremland et al. (1991), citing Mcbride and Edwards (1977), reported that "Hg methylation was not detected in whole cells of methanogens or in methanogenic sewage sludge suggesting that methanogens are not active in this reaction." However, Hamelin et al. (2011) presented findings that suggest "that methanogens rather than SRB were likely the primary methylators in the periphyton of a temperate fluvial lake." Parks et al. (2013), although acknowledging that SRB are the main producers of MeHg in nature, provided genetic evidence for "a common mercury methylation pathway in all methylating bacteria and archaea." Kerin et al. (2006), in a paper relating mercury methylation to dissimilatory iron-reducing bacteria (DIRB), implied that, since current models for methylation are based on relationships between methylation and sulfate reduction, the potential significance of methylation by iron reduction in certain environments may be undervalued or missed entirely. Kerin concluded that "the finding that DIRB can produce MeHg suggests that Hg methylation may be important in sediments and soils where these organisms are dominant, e.g., iron-rich sediments with low concentrations of sulfate." Regardless of the methanogenic species, MeHg produced in aquatic environments is taken up rapidly by the food web, with greater accumulation in higher trophic levels. Given that some methanogenic bacteria and archaea are among the oldest life forms on the planet, and that a shared evolutionary history for methanogenesis and sulfate reduction developing about 3.5 billion years ago has been postulated (Susanti and Mukhopadhyay 2012), and that inorganic Hg has always been present in Earth's biosphere, it seems that fish have accumulated MeHg throughout their evolutionary history (Clarkson 1997).

Calculations in dilute-water lakes from the ratio of total fish Hg to total Hg and aqueous MeHg measurements indicate accumulation of MeHg in fish by a factor of three million times, accounting for the observation that fish can contain more than one part per million Hg in water with less than one part per trillion of total Hg (Zillioux et al. 1993). Although accumulation of Hg in fish can occur through uptake across both the gills and the gut, dietary uptake seems to account for more than 90 % of total MeHg uptake with assimilation rates up to 80 % or higher. MeHg binds to red blood cells and distributes via the circulatory system to all organs and tissues, although much relocates to the skeletal muscle where it accumulates bound to sulfhydryl groups in protein (Wiener et al. 2003). This process is described by a bioaccumulation factor (BAF), i.e., the ratio of tissue chemical residue to chemical concentration in an external environmental phase (water, sediment, or food).

For equilibrium partitioning at steady state, the BAF may approximate the organism-water partition coefficient (K_b), although this varies with the degree of uptake through the dietary route (the bioconcentration factor [BCF] is equivalent to K_b since it describes the ratio of tissue chemical residue directly to chemical concentration in water with no food-web exposure). The bioaccumulation process results in a biomagnification of Hg, or increase in tissue chemical residues at higher trophic levels, primarily as a result of dietary accumulation (Spacie et al. 1995), although the degree of biomagnification in a given water body varies by species and with size and age. Figure 42.1 illustrates the range of fish species variations in average Hg tissue (primarily axial muscle) concentrations as reported by the U.S. Food and Drug Administration (USFDA) and the U.S. Environmental Protection Agency (USEPA).

42.3.4.1 Factors Affecting Methylation and Uptake of MeHg by Fish

Since methylation of HgII is a prerequisite for the efficient uptake of Hg in fish in most natural water bodies, an examination of the environmental factors that promote methylation, as well as demethylation, is important to understand the observed differences in Hg uptake between water bodies. Methylation and demethylation should be viewed within the context of the overall cycling of mercury species in the aquatic environment. The major compartments, fluxes, and reaction components of mercury in a lacustrine ecosystem are illustrated in Fig. 42.2.

Many authors have considered the influence of water chemistry on the uptake of Hg in fish. For example, Lange et al. (1993) reported that uptake of MeHg in largemouth bass in 53 Florida lakes was shown to be positively correlated with fish age (strongest correlation) and fish size (e.g., see Table 42.2), and negatively correlated with alkalinity, calcium, chlorophyll α, conductance, magnesium, pH, total hardness, total nitrogen, and total phosphorus. They found that pH accounted for 41 % of the variation in Hg concentration for standardized age three fish, while chlorophyll α and alkalinity accounted for 45 % of the variation. Fish Hg concentrations were significantly higher in lakes with either pH <7, alkalinity <20 mg/L as $CaCO_3$, or chlorophyll α <10 μg/L. Also, Hickey et al. (2005) studied the effects of water chemistry on Hg in 747 fish of mixed species from 31 Ontario lakes and 11 lakes in Nova Scotia, Canada. They found that pH alone explained 77.7 % of the variation in Hg concentration in fish, while MeHg in water and dissolved organic carbon (DOC) accounted for only 2.7 % of the variation. They concluded that “reducing acid rain and mitigation of pH levels will reduce Hg levels more than will reducing Hg deposition.” Although not directly addressing this relationship, it should be noted that, in a whole-ecosystem experiment where different isotopes of Hg were deposited directly to a Canadian lake surface and to upland and wetland components of its watershed and tracked over time, the Hg levels in fish responded rapidly and directly to the changes in atmospheric deposition (spike additions) when added directly to the lake surface (Harris et al. 2007; Engstrom 2007).

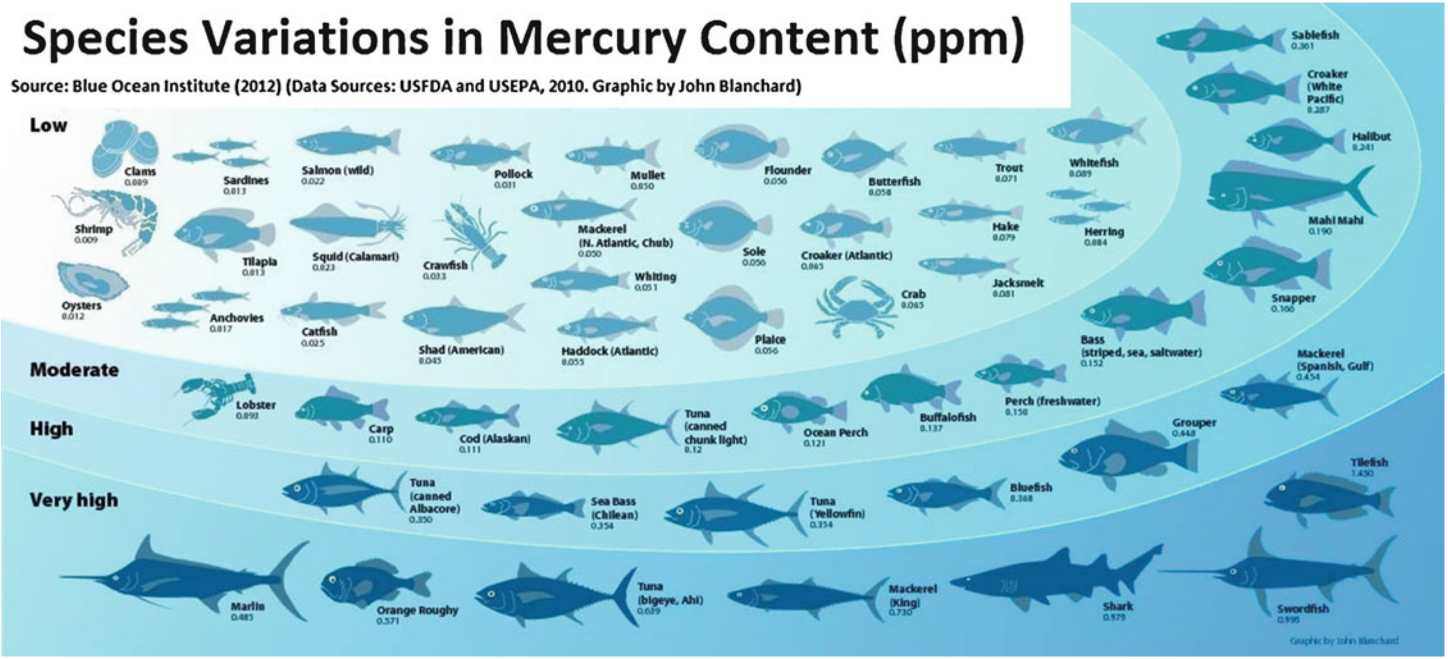

Fig. 42.1 Species variations in mercury content (ppm) (Source: John Blanchard (Sources: FDA and EPA), Sierra Magazine, Nov/Dec 2011)

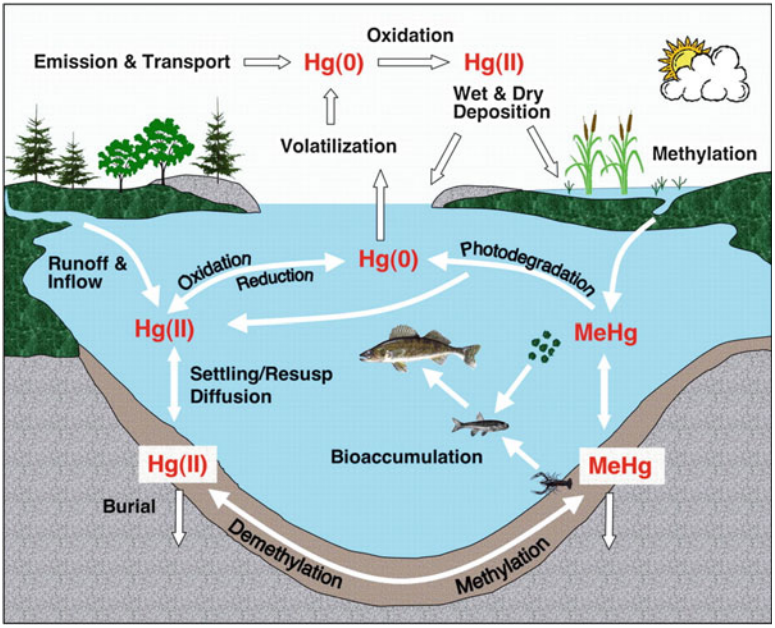

Fig. 42.2 Mercury cycling in a lake and its watershed (From: Engstrom (2007) (Reprinted with permission))

Table 42.2 The effect of size (age) on the mean Hg level in 181 king mackerel sampled in 1999 from North Carolina, South Carolina, Georgia, and Florida, USA

Size category (fork length) (in.)	Number of fish	Average (ppm)	Range (ppm)
<27	19	0.22	0.14–0.36
27–32	43	0.34	0.15–1.00
33–39	53	0.80	0.25–2.10
>39	66	1.54	0.40–3.50

Moore (2000)

A number of studies have developed statistical or inferential models in order to determine the biogeochemical factors that govern Hg bioaccumulation in aquatic food webs. For example, Pollman (2012) used a variety of multivariate modeling techniques to construct and validate empirical models relating the occurrence of Hg in fish to chemical and other potential determinants of the variability of fish tissue Hg concentrations. The modeling effort used data sets representative of over 7,700 lakes greater than 4 ha and 83,457 km of stream and riverine reaches in the State of Florida, and approaches including integrating principal components analysis with multiple linear regression and generalized linear modeling for the lake model, and classification and regression tree analysis for the streams and rivers model. The sequence of importance of independent variable contributions to the overall variability in Hg in largemouth bass was: for the study lakes, alkalinity > chlorophyll α > urban runoff disturbance > atmospheric deposition > sulfate; and, for the study streams and rivers, pH ≫ DO % saturation > conductivity > total Kjeldahl nitrogen > sulfate > total phosphorous. Considering uncertainties in model prediction and inferred distributions, the model results for the 90th percentile concentrations for largemouth bass Hg, in mg/kg, were: streams – 1.295; small lakes – 1.319; rivers – 1.136; the Everglades – 1.071; and large lakes – 0.694. The much lower predicted fish Hg concentration in large lakes reflects both higher alkalinities and higher productivity compared to small lakes.

Chemical and biological control of microbial methylation and demethylation of Hg is complex and not fully understood. The degree of complexity is perhaps best illustrated by the central role played in the biogeochemical cycling of Hg by interactions affecting Hg methylation/demethylation among dissolved organic matter (DOM), sulfate reduction, and sulfide inhibition (e.g., Benoit et al. 2003; Hickey et al. 2005; Miller et al. 2007; Graham et al. 2012, 2013). Sulfate and sulfide exert conflicting influences on the extent of Hg methylation such that the highest methylation rates are found at sites with intermediate sulfate-reduction rates and sulfide concentration, although the point at which the highest rates occur varies with other controlling factors. Sulfate additions increase Hg methylation rates until sulfate concentration reaches the point where sulfide buildup is sufficient to inhibit microbial methylation (Gilmour et al. 1998; Graham et al. 2013; Benoit et al. 2003). Correlations between DOM and MeHg production are positive in many aquatic sediments and wetland soils with low μM sulfide levels, and DOM concentrations below 8 mg C/L. DOM can strongly enhance the bioavailability of HgII to SRB under micromolar sulfide concentrations and anoxic conditions (Graham et al. 2012, 2013); however, the degree of enhancement is influenced by DOM size, hydrophobicity, and sulfur content. The interactions of Hg with DOM in the presence of sulfide complicate the Hg-sulfide complexation as predicted by thermodynamic models such that laboratory and field studies have not always been in agreement. DOM influences numerous processes in the biogeochemical cycling of Hg including HgII complexation and transport, MeHg complexation, transport, precipitation and dissolution of Hg-S minerals, and MeHg production by microorganisms (Graham et al. 2013 and references therein). In addition, Hg complexed with DOM dominates the speciation of Hg under oxygenated conditions and may influence the ultimate Hg substrate available to SRB at the primary site of methylation in aquatic sediments, just below the oxic/anoxic interface. Reported correlations between DOM and MeHg concentration also can be negative (e.g., Hickey et al. 2005; Driscoll et al. 1995), further reflecting the biogeochemical complexity controlling these interactions.

Other factors affecting MeHg formation and uptake of Hg in fish have been reported by many authors. Examples include: food-chain structure (Cabana et al. 1994, Greenfield et al. 2001); salinity (Compeau and Bartha 1987; Farmer et al. 2010); selenium (Southworth et al. 1999; Belzile et al. 2006; Peterson et al. 2009); acid rain (Richardson and Currie 1995; Richardson et al. 1995a, b; physical attributes of lakes (Richardson 1994); sulfate loading (Gilmour et al. 1998); algal blooms (Pickhardt et al. 2002); temperature and season (Benoit et al. 2003).

As mentioned above, demethylation occurs in natural aquatic systems in concert with methylation such that MeHg uptake by fish is a function of the *net* microbial production of MeHg. Bacterial demethylation through the *mer* operon pathway has been well characterized (e.g., Robinson and Tuovinen 1984; Liebert et al. 1999; Hobman et al. 2000; Barkay 2000). The *mer* operon contains the organomercurial lyase gene that cleaves the carbon-Hg bond of MeHg, producing methane and HgII; the HgII then is reduced to Hg^{o} through a second step involving the Hg-reductase enzyme (Benoit et al. 2003; Wiener et al. 2003). Oremland et al. (1991) described an oxidative demethylation process that derives energy from single carbon substrates in a wide range of environments including freshwater, estuarine, and alkaline-hypersaline sediments and in both aerobic and anaerobic conditions. Working in three environments that differ in the extent and type of Hg contamination and sediment biogeochemistry, Dipasquale et al. (2000) found that severely contaminated sediments tend to have microbial populations that actively degrade MeHg through *mer*-detoxification, whereas oxidative demethylation occurs in heavily contaminated sediments as well but appears to dominate in those less contaminated, under both aerobic and anaerobic conditions.

42.4 Effects

42.4.1 Effects of Hg on Fish

The effects of Hg in fish, as well as in other aquatic organisms, and piscivorous wildlife have been reviewed extensively (e.g., Eisler 1987). In two early reviews published in 1979 (Taylor 1979; Birge et al. 1979) a total of 50 discrete references that specifically addressed the issue of Hg in fish were cited. Since the completion of these two reviews, at least 447,000 publications have dealt with some aspect of Hg in fish (source: Google Scholar, extrapolated from a sample size of 1,000 citations).

Although diet is the primary route of Hg uptake in fish, most laboratory studies of Hg in fish have measured effects through gill uptake from concentrations in water much higher than typically observed in natural water bodies, where typical concentrations in lakes are measured in the low ng/L range (Watras et al. 1992). For example, Zillioux et al. (1993), in a review on the effects of Hg in wetland ecosystems, reported effects of organic Hg on fish derived from laboratory exposures at concentrations in water from 0.1 μg/L (zebrafish [*Brachydanio rerio*] – hatching success reduced) to 0.88 μg/L (brook trout [*Salvelinus fontinalis* embryo] – enzyme disruption). Sublethal exposures of fish to MeHg can result in impaired ability to locate, capture, and ingest prey, and to avoid predation (Kania and O'Hara 1974; Little and Finger 1990; Sandheinrich and Atchison 1990; Weis and Weis 1995; Fjeld et al. 1998; Samson et al. 2001, as cited in a comprehensive review by Wiener et al. 2003). However, Wiener and Spry (1996) in a review on Hg in freshwater fish concluded that reduced reproductive success was the most plausible toxicological endpoint in wild fish populations exposed to Hg-contaminated food webs. For example, Hammerschmidt et al. (2002) reported that exposure of fathead minnows (*Pimephales promelas*) to three concentrations of dietary MeHg of 0.88, 4.11, and 8.46 μg Hg g^{-1} dry weight prior to sexual maturity, resulted in reduced spawning success rates of 63 %, 40 %, and 14 %, respectively, down from success rates of 75 % for controls. Beckvar et al. (2005) linked fish tissue residues of Hg to biological effects thresholds, primarily of growth, reproduction, development, and behavior, using literature sources screened for data consistency. Based on an evaluation of several approaches, the threshold-effect level (t-TEL) best represented the underlying data. (The t-TEL is calculated as the geometric mean of the 15th percentile concentration in the effects data set and the 50th percentile concentration in the no-effects data set.) They concluded that a whole-body t-TEL of 0.2 mg Hg/kg wet weight of tissue would be protective of juvenile and adult fish, where the incidence of effects below the t-TEL is predicted to be rare.

42.4.2 Effects of Hg on Piscivorous Wildlife

Effects of Hg on piscivorous birds and mammals were reviewed by Wolfe et al. (1998), with emphasis on the mechanisms of Hg toxicity and interpretation of residue data. In both birds and mammals, MeHg readily penetrates the blood-brain barrier producing brain lesions, spinal cord degeneration, and central nervous system dysfunctions. A residue threshold for toxicity in mink is suggested at 5.0 ppm for brain and muscle tissue. From their review of the literature, Zillioux et al. (1993) concluded that residue thresholds for significant toxic effects in wading birds occur between 1 and 3.6 ppm wet weight (w/w) in eggs and 5 ppm w/w in liver. However, a study by Frederick and Jayasena (2011) suggested that dose-related increases in male-male bonding and altered sexual display behavior in the white ibis occur at mean residue levels as low as 4.3 ppm fresh weight in feathers (approx. equivalent to 0.37 ppm in wading bird eggs, from comparative feather/egg effects data in Zillioux et al. 1993) and 0.73 ppm in blood. Many investigations on ecosystem proliferation of Hg and the effects of Hg on piscivorous wildlife have been conducted in the Florida Everglades, the largest freshwater wetland in the continental United States. For example, Frederick et al. (1999) studied the diet of great egret (*Ardea albus*) nestlings exposed to dietary Hg during the breeding seasons of 1993–1996. By collecting and analyzing Hg in regurgitated food samples from large colonies throughout the central Everglades, where fish comprised >95 % of the nestlings' diet, Frederick et al. estimated that nestlings would ingest 4.32 mg total Hg (Hg_T) during an 80-day nesting period. In live tree islands, which are the primary habitat for wading bird colonies in the Everglades, the annual Hg deposition by bird guano was estimated at 148 μg m^{-2} $year^{-1}$, about eight times the atmospheric deposition of Hg in southern Florida (Zhu et al. 2014). Feather mercury concentrations in adults and nestlings of the great egret exceeded 30 ppm in environmental samples from the Florida Everglades in the early 1990s, when this area had the highest levels of Hg in fish in the entire USA (as high as 2.7 ppm in axial muscle tissue of largemouth bass, Wolfe et al. 2007).

During the same period, top predators of the fish-based food chain in the Florida Everglades also had high tissue Hg levels. Alligators (*Alligator mississippiensis*) collected on a transect through the Florida Everglades in 1999 were reported by Rumbold et al. (2002) with Hg_T mean concentrations (n = 28) in liver and tail muscle of 10.4 and 1.2 ppm w/w, respectively. A single Florida panther (*Puma concolor cori*), a critically endangered species in Florida, was found dead in the southern Everglades region with the highest Hg concentration ever reported of 110 ppm w/w in the liver; Hg toxicosis was strongly implicated in its death (Roelke et al. 1991). Other free-ranging panthers in the same region had mean hair, liver, and muscle concentrations of 56.4, 40.6 and 4.4 ppm Hg_T w/w, respectively. Roelke et al. concluded that Hg_T in panther hair greater than 57.3 ppm fresh weight would indicate toxicosis, and identified an "at risk" threshold value for Hg_T in panther hair as greater than 12.57 ppm. All of these panthers were known to be feeding on Hg-contaminated raccoons (*Procyon lotor*). Raccoons are opportunistic omnivores, but eat largely insects and crustaceans and some fish outside berry season, which peaks in January in the Everglades region. As is the case in fish, Hg in insects is essentially all MeHg (Mason et al. 2000). Roelke et al. (1991) reported a mean value of 1.8 ± 1.24 ppm Hg in raccoon muscle tissue in the central Everglades, while in a retrospective study across all of southern Florida, Porcella et al. (2004) found no statistical difference in raccoon Hg content over the past 50 years.

42.4.3 Effects of Hg in Humans

About 95 % of MeHg in fish ingested by humans is absorbed. In the blood, about 90 % is associated with red cells, probably bound to the sulfhydryl (SH) groups of hemoglobin. From the bloodstream, it is taken up by all tissues, and readily crosses the blood-brain and placental barriers. Early studies of the effects of MeHg on humans have been described above (Section 1.2.1). More recent studies have confirmed that the major human effects from exposure to MeHg are neurotoxicity in adults and toxicity in fetuses of mothers exposed during pregnancy. The cortex of the cerebrum and cerebellum are selectively involved in Hg toxicosis, with focal necrosis on neurons, lysis and phagocytosis and replacement by supporting glial cells. The over-all acute effect is cerebral edema, but with prolonged destruction of gray matter and subsequent gliosis, resulting in cerebral atrophy (see reviews by Clarkson 1997 and Goyer and Clarkson 2001, and references therein). However, the primary human health concern today is with more subtle effects arising from prenatal exposure, such as delayed development and cognitive changes in children. Myers et al. (2003) studied neurodevelopmental effects in a fish-consuming population in the Republic of Seychelles, investigating 779 mother-infant pairs. Mothers averaged 12 fish meals per week, with fish concentrations of MeHg similar to commercial ocean fish elsewhere. Children were followed from the prenatal period (mean prenatal MeHg exposure was 6.9 ppm, SD 4–5 ppm) to age 9 years. Neurocognitive, language, memory, motor, perceptual-motor, and behavioral functions were assessed at 9 years. Their data did not support the hypothesis that there is a neurodevelopmental risk from prenatal MeHg exposure resulting solely from ocean fish consumption. However, other studies of prenatal exposure related to fish consumption have shown effects in children, from an inverse correlation between maternal Hg hair levels and IQ in their children (Kjellström et al. 1989) to cognitive developmental delays at the age of 4 years (Freire et al. 2010). A WHO Expert Group concluded that there may be a low risk of prenatal poisoning at maternal hair levels between 10 and 20 ppm (corresponding to blood levels of 20–40 ppb). Two independent analyses of the same data base concluded that the lowest effect level may be anywhere from 7 to over 100 ppm in maternal hair. As a point of comparison, a study conducted in the Florida Everglades, during the period of highest reported concentrations of Hg in fish, measured Hg in the hair of sport fishermen, Everglades residents, and subsistence fishermen. Of 350 participants, 119 had levels above detection limits and, of these, the mean total Hg in hair was 3.62 (SD 3.0) ppm, with a range of 2.28–15.57 ppm (Fleming et al. 1995).

42.5 Use of Fish as Indicators of Human Hg Exposure

The practice of using fish as indicators of chemical exposure is relatively new. A permissible Hg content of 0.5 ppm in fish established in 1970 by the U.S. Food and Drug Administration (USFDA) was the first regulatory action level for any element in the USA (Hall et al. 1978). This temporary action level was later revised upward to 1 ppm MeHg in fish, which "was established to limit consumers' MeHg exposure to levels 10 times lower than the lowest levels associated with adverse effects (paresthesia)" (USFDA 1995). This new action level was based on the occurrence of adverse effects in adults "because the level of exposure was actually lower than the lowest level found to affect fetuses, affording them greater protection." Nevertheless, in January 2001 the U.S. Environmental Protection Agency (USEPA) in apparent contradiction to the USFDA action, established a water quality criterion of 0.3 mg MeHg/kg fish tissue screening value for fish consumption (USEPA 2010). This was the USEPA's first issuance of a water quality criterion expressed as a fish tissue value rather than as an ambient water column value. The more restrictive USEPA criterion is intended to be protective of recreational, tribal, ethnic, and subsistence fishers who typically consume fish and shellfish from the same local water bodies repeatedly over many years. Today, action levels for fish consumption advisories are common throughout the world. Table 42.3 provides the most complete compendium of these action levels available for 53 nation states, including the 27 member states of the European Union and 12 member states of the Commonwealth of Independent States as well as general guidelines issued by the World Health Organization/Food and Agriculture Organization of the United Nations.

Table 42.3 Examples of maximum allowed or recommended levels of Hg in fish in various countries and by WHO/FAO (based on submissions to UNEP, unless otherwise noted)

Country/ organization	Fish type	Maximum allowed/ recommend levels in fish[a]	Type of measure	Tolerable intake levels[a]
Australia	Fish known to contain high levels of mercury, such as swordfish, southern bluefin tuna, barramundi, ling, orange roughy, rays, shark	1.0 mg Hg/kg	The Australian Food Standards Code	Tolerable Weekly Intake: 2.8 μg Hg/kg body weight per week for pregnant women.
	All other species of fish and crustaceans and molluscs	0.5 mg Hg/kg		
Canada	All fish except shark, swordfish or fresh or frozen tuna (expressed as total mercury in the edible portion of fish)	0.5 ppm total Hg	Guidelines/ Tolerances of Various Chemical Contaminants in Canada	Provisional Tolerable Daily Intake: 0.47 μg Hg/kg body weight per day for most of the population and 0.2 μg Hg/kg body weight per day for women of child-bearing age and young children
	Maximum allowable limit for those who consume large amounts of fish, such as Aboriginal people	0.2 ppm total Hg		
China	Freshwater fish	0.30 mg/kg	Sanitation standards for food	
Croatia	*Fresh fish* Predatory fish (tuna, sword-fish, molluscs, crustaceans)	1.0 mg Hg/kg 0.8 mg methyl Hg/kg	Rules on quantities of pesticides, toxins, mycotoxins, metals and histamines and similar substances that can be found in the food.	
	All other species of fish	0.5 mg Hg/kg 0.4 mg methyl Hg/kg		
	Canned fish (tin package) Predatory fish (tuna, sword-fish, molluscs, crustaceans)	1.5 mg Hg/kg 1.0 mg methyl Hg/kg		
	All other species of fish	0.8 mg Hg/kg 0.5 mg methyl Hg/kg		

(continued)

Table 42.3 (continued)

Country/ organization	Fish type	Maximum allowed/ recommend levels in fish[a]	Type of measure	Tolerable intake levels[a]
European Community	Fishery products, with the exception of those listed below.	0.5 mg Hg/kg wet weight	Various Commission regulations	European Commission, Official Journal of the European Communities 7 February 2002
	Anglerfish, Atlantic catfish, bass, blue ling, bonito, eel, emperor or orange roughy, grenadier, halibut, marlin, pike, plain bonito, Portuguese dogfish, rays, redfish, sail fish, scabbard fish, shark (all species), snake mackerel or butterfish, sturgeon, swordfish and tuna.	1 mg Hg/kg wet weight	Commission regulation (EC) No. 221/2002	
Georgia	Fish (freshwater) and fishery products	0.3 mg Hg/kg	Georgian Food Quality Standards 2001	
	Fish (Black Sea)	0.5 mg Hg/kg		
	Caviar	0.2 mg Hg/kg		
India	Fish	0.5 ppm total Hg	Tolerance Guidelines	
Japan	Fish	0.4 ppm total Hg/kg	Food Sanitation Law – Provisional regulatory standard for fish and shellfish	Provisional Tolerable Weekly Intake: 0.17 mg methyl Hg (0.4 μg/kg body weight per day) (Nakagawa et al. 1997).
		0.3 ppm methyl Hg (as a reference)		
Korea, Republic of	Fish	0.5 mg Hg/kg	Food Act 2000	
Mauritius	Fish	1 ppm Hg	Food Act 2000	
New Zealand	Fish	1.6 μg MeHg/kg body weight per week	Food Standards Australian New Zealand (FSANZ)	Adopted 2003 JECFA PTWI (Karatela et al. 2011)
Philippines	Fish (except for predatory)	0.5 mg methyl Hg / kg	Codex Alimentarius	
	Predatory fish (shark, tuna, swordfish)	1 mg methyl Hg/kg		

(continued)

Table 42.3 (continued)

Country/ organization	Fish type	Maximum allowed/ recommend levels in fish[a]	Type of measure	Tolerable intake levels[a]
Slovak Republic	Freshwater non-predatory fish and products thereof	0.1 mg total Hg/kg	Slovak Food Code	
	Freshwater predatory fish	0.5 mg total Hg/kg		
	Marine non-predatory fish and products thereof	0.5 mg total Hg/kg		
	Marine predatory fish	1.0 mg total Hg/kg		
Thailand	Seafood	0.5 μg Hg/g	Food Containing Contaminant Standard	
	Other food	0.02 μg Hg/g		
United Kingdom	Fish	0.3 mg Hg/kg (wet flesh)	European Statutory Standard	
United States	Fish, shellfish and other aquatic animals (FDA)	1 ppm methyl Hg	FDA action level	US EPA reference dose: 0.1 μg methyl Hg/kg body weight per day
	States, tribes and territories are responsible for issuing fish consumption advise for locally-caught fish; Trigger level for many state health departments:	0.5 ppm methyl Hg	Local trigger level	
WHO/FAO	All fish except predatory fish	0.5 mg methyl Hg/kg	FAO/WHO Codex Alimentarius guideline level	2003 JECFA provisional tolerable weekly intake 1.6 μg MeHg/kg body weight per week
	Predatory fish (such as shark, swordfish, tuna, pike and others)	1 mg methyl Hg/kg		

From: Global Mercury Assessment, Chapter 4 (UNEP Chemicals 2002) unless otherwise noted. Revised

[a]Units as used in references. "mg/kg" equals "μg/g" and ppm (parts per million). It is assumed here that fish limit values not mentioned as "wet weight" or "wet flesh" are most likely also based on wet weight, as this is normally the case for analysis of fish for consumers

Compliance with regulatory guidelines, however, is often lacking. For example, in the study of Hg in hair of exposed populations in the Florida Everglades mentioned earlier, Fleming et al. (1995) found that, although 71 % of the 350 participants knew of the State Health Advisories concerning ingestion of Hg-contaminated fish from the Everglades, this did not change their consumption habits.

Conclusions

It would be difficult to find an indicator of potential harm more well-researched than Hg in edible fish within the HgII → methanogen → MeHg → fish → human pathway. For human consumption, the challenge is to balance regulatory guidance for protection against exposure to MeHg at potentially harmful levels with the well-known health benefits of fish consumption. Since this review has not focused on the latter, a brief summation of beneficial effects is warranted.

Clinical effects that support human health benefits of fish or fish oil intake have been shown for anti-arrhythmia, anti-thrombosis and the lowering of triglyceride, heart rate, and blood pressure. At moderate intake levels of <750 mg per day EPA/DHA (eicosapentaenoic acid and docosahexaenoic acid), the physiologic effects most likely to account for clinical cardiovascular benefits include modulation of myocardial sodium and calcium ion channels, and reduced left ventricular workload and improved myocardial efficiency as a result of reduced heart rate, lower systemic vascular resistance, and improved diastolic filling. The dose response for anti-arrhythmic effects is initially steep, reaching a plateau at intake levels of around 750 mg/day EPA/DHA. At increasing levels of intake up to at least 2,500 mg/day, beneficial effects continue to accrue with respect to triglycerides, heart rate, and blood pressure over a time course of months to years. In addition, fish or fish oil intake may provide important beneficial effects with respect to endothelial, autonomic, and inflammatory responses (Mozaffarian and Rimm 2008, and references therein).

Among piscivorous wildlife, the population and ecosystem-level risks from high environmental Hg concentrations in natural systems have proved to be demonstrably greater than the current risk to human consumers. For major health outcomes among adult humans, the benefits of fish consumption generally outweigh risks; this is true even for sensitive populations of women of child-bearing age and young children if health advisories and consumption limits are followed. Further development of the application of Hg levels in fish for the indication of potential threats to non-human species and to ecological health in general is needed.

Acknowledgement Thanks are due to Dr. Curtis D. Pollman, of Aqua Lux Lucis, Inc., for his review and helpful comments.

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Chapter 43
The Chronic POEDCs Ecotoxicological Impact: An Aquatic Environmental Indicator of Surface and Groundwater

Uri Zoller

Abstract The occurrence and persistence of anthropogenic pollutants in the environment showing estrogenic-endocrine modulating effects in aquatic organisms is a "hot" issue of major health- and environment-related concern worldwide. The population growth and the increasing scarcity of water in many regions of the world have led to a comprehensive reuse of treated wastewater that, ultimately, may cause a long-term concentration buildup of many toxic persistent organic pollutants (POPs) in the closed cycle of water supply and wastewater treatment and reuse. The endocrinic/mutagenic potencies of the EDCs-branched chain alkylphenol ethoxylates (APEOs), polycyclic aromatic hydrocarbons (PAHs) and their metabolites are well-documented. From ~5.5×10^8 m^3/year of sewage produced in Israel, ~70 % are reused, following a conventional, or advanced, activated sludge or sand aquifer treatment (SAT). A major related question is: Does this practice conform to sustainability? Our studies reveal that (a) the concentrations of APEOs and PAHs in Israel rivers and sediments do pose a potential health risk problem; and (b) the *synergistic* ecotoxicological impact of environmentally relevant mixtures of these POPs, in WWTP effluents, constitutes an inconsistency, health-wise, with sustainability practice.

Keywords Anthropogenic pollutants • Polycyclic aromatic hydrocarbons (PAHs) • Persistent Organic Endocrine Disrupting Compounds (POEDCs) • Persistent organic pollutants (POPs) • Toxicity • Water • Health

43.1 Introduction and Background

The occurrence and persistence of anthropogenic pollutants in the environment showing estrogenic-endocrine modulating effects in aquatic organisms is a "hot" issue of major health and environment-related concern worldwide (Sumpter and

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POEDCs: Persistent Organic Endocrine Disrupting Compounds

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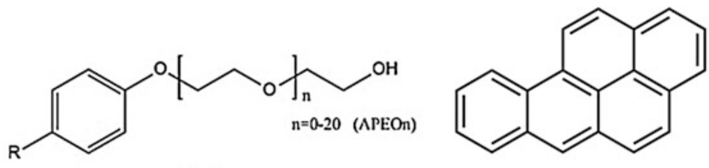
R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_43

Johnson 2005). The population growth and the increasing scarcity of water in many regions of the world have led to a comprehensive reuse of treated wastewater that ultimately may cause a long-term concentration buildup of many toxic chemicals in ecosystems and closed cycles of water supply and wastewater treatment and reuse (Caldas et al. 2013). Endocrine disrupting chemicals (EDCs) refer to chemicals affecting the endocrine system. Such an effect may be at the level of receptor-mediated hormone action, binding and activating, or not activating the estrogen receptor (estrogenic or antiestrogenic, respectively), hormone synthesis, or clearance. In the aquatic environment there are many well documented examples of EDC-s/persistent organic endocrine disrupting chemicals (POEDC-s) impact on wild life. As such, the EDCs-ecosystems-environmental condition-environmental indicators-sustainability connection is apparent.

Sustainability is a key demand in our world of finite resources and endangered ecosystems. Given the environmental imperatives, the potential ecotoxicological risk of anthropogenic chemicals, and the limited economic feasibility of large scale treatment and remediation technologies, the currently emerging corrective-to-preventive paradigms shift in production, development, consumption, and disposal is unavoidable. Following their use and disposal – into either sewage systems or natural receiving aquatic sinks – and/or the large scale reuse of wastewater for agricultural irrigation, persistent (nonbiodegradable) EDCs/POEDCs ultimately enter aquatic and terrestrial compartments of the environment and persist there as such, or as their (bio-) degradation/metabolites.

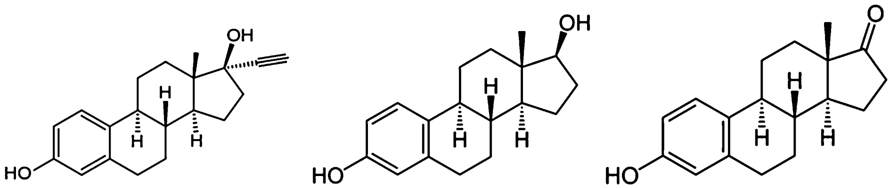
43.2 Potential Hazard and Fate of Endocrine Disrupting Chemicals in Wastewater

The occurrence and persistence of anthropogenic POEDCs in the aquatic environment that were found to affect aquatic organisms initiated both health and environment concerns worldwide (Pickering and Sumpter 2003; Sumpter 2008; Ternes et al. 1999; Lee et al. 2013). EDCs refer to those chemicals with a primary effect on the endocrine system. Such an effect may be at the level of receptor-mediated hormone action, binding and activating, or not activating the estrogen receptor (estrogenic or antiestrogenic, respectively), hormone synthesis or clearance. In the aquatic environment there are several well documented examples of EDCs that have been demonstrated to have an impact, such as male feminization and reduced productivity in fish and other wild life (Pickering and Sumpter 2003). The three classes of anthropogenic POEDCs that, ultimately, reach surface and ground water resources, largely via the reuse or disposal of municipal wastewater, are the nonionic alkylphenol ethoxylates (APEOs) (Naylor et al. 1992; Sarmah et al. 2006), polycyclic aromatic hydrocarbons (PAHs) (Mahler et al. 2005), pharmaceuticals (Ternes et al. 1999, 2004) personal care products (PPCPs), and hormones (Esperanza et al. 2004; Huang and Sedlak 2001; Kolpin et al. 2002a, b)



Alkylphenol polyethoxylate Benzo[α]pyrene

Fig. 43.1 APEOs and PAH representatives



Ethinyl estradiol 17β-Estradiol Estrone

Fig. 43.2 Anthropogenic and natural hormones in Israel's WWTP influents and effluents

(Figs. 43.1 and 43.2). Although the extent of the threat of human exposure to these EDCs still remains to be elucidated, they are naturally biodegradation-resistant and, therefore, environmentally persistent organic pollutants (POPs), creating a major ecotoxicological issue of concern. Since (a) these EDCs and other structurally-related compounds as well as/or their metabolites and/or degradation products do reach surface- and groundwater (Ashton et al. 2004; Bergman et al. 2013; Ying et al. 2002), and (b) they were found to affect the endocrine system of the susceptible animals, triggering a rather wide range of biological effects even at extremely low concentrations (ng-μg/L level), their persistent/survival in the aquatic environment, particularly in public water supply and treatment [activated sludge (AS), river bank (RB), wetland (WL) and soil aquifer treatment (SAT)] systems, constitutes an issue of importance with respect to public health (Heberer and Adam 2004; Zoller et al. 2004; Kidd et al. 2007). Indeed, there is a POEDCs-related environmental health risk problem (McCann 2004; Zoller 2004; Sumpter 2008).

Two major anthropogenic EDCs that, ultimately, reach surface and ground water resources via runoff and reuse or disposal of municipal wastewater (Berryman et al. 2004; Ying et al. 2002) are the persistent organic pollutants (POPs) PAHs and APEOs. The extent of the threat to humans being exposed to these mutagenic/carcinogenic (and also teratogenic) still remains to be elucidated. Thus, the fact that PAHs are structurally biodegradation-resistant and, therefore, environmentally persistent (Nagy et al. 2007) renders an environmental ecotoxicological issue of concern. These EDCs and their metabolites/degradation products, oxidatively or reductively, were found to affect the endocrine systems of the susceptible animals, hence triggering rather large biological effects even at low concentrations. APEO surfactants on their part, especially the branched congeners nonyl-and octylphenol ethoxylates and their metabolites, are known to elicit estrogenic response, i.e., they are capable of mimicking or antagonizing the action of steroid hormones, in both mammals and fish (Jobling et al. 1996). They were found in tissue of mature and juvenile fish (flounder), indicating an environmental /estrogenic exposure to wastewater discharges (Lye et al. 1999). Data on the chronic effects of actual environmental and/or sublethal concentrations of APEOs are available (Zoller 2008). The persistence of these POEDCs in the aquatic environment, particularly in public water supply systems and in reclaimed water where reuse for agricultural irrigation is extensively practiced, constitutes a major environmental health risk problem (Pickering and Sumpter 2003; Zoller 2006). Data concerning the synergistic effects of these two groups, *per se*, in the presence or absence of other EDCs, particularly as far as their synergistic ecotoxicological and health risk potential are concerned, are just starting to emerge (Zoller 2006; Zoller and Hushan 2010). Clearly, the increased solubility of the hydrophobic PAHs in the presence of the hydrophilic APEOs increases the bioavailability of the former, with all the ultimate chronic ecotoxicological impacts involved. The scope of the POEDCs problem is huge, since in addition to the APEOs and PAHs, PPCPs and natural steroidal estrogen hormones (Kolpin et al. 2002a, b; Ternes et al. 2002) are released to the environment after passing through conventional wastewater treatment plants (WWTPs), which, as such, are not designed to remove these compounds from the effluents (Kolpin et al. 2002a, b).

43.2.1 Wastewater Treatment

The continuing rise of the human population, accompanied by the increasing demand on the limited water reservoirs worldwide necessitates seeking alternative water resources. Domestic urban, industrial, and agricultural wastewater is considered to be one of the most important water resources and has gained much interest during the last years. Treated wastewater in WWTPs can be readily reused in agriculture or industry. Various conventional, e.g., active sludge-based, and advanced oxidation processes (AOPs) have been developed and are currently being used for wastewater treatment. However, the majority of conventional treatment processes have been designed, primarily, for reduction of organic and inorganic components in the WWTPs influents to a level permitting their safe discharge into the environment. However, the potential additive and/or synergistic chronic ecotoxicological impact (SCEI) of the POEDCs, such as pharmaceuticals, hormones, antibiotics, and personal care products (PCPs), persists in the effluents to be reused. Awareness of the environmental health hazard posed by such contaminants has resulted in increasing the related public concern and stimulated exploration of the EDCs' occurrence and fate in sewage influents and effluents of WWTPs. Conventional activated sludge (AS) and river bank (RB) systems are, at present, the most common for treatment of domestic wastewater in large cities. In rural areas, wetland systems are also used for wastewater treatment. Anaerobic lagoons are used to treat animal waste, such as that of swine. Since it is highly unrealistic to expect a reduction in the consumption of, e.g., pharmaceuticals (hormones and antibiotics), novel technologies for improving wastewater treatment are continuously being developed that significantly diminish the release of these endocrinic compounds into the environment.

The scope of the problem is huge (Khanal et al. 2006; Lohmann et al. 2007), since the anthropogenic POEDCs, APEOs, PAHs, PPCPs, natural steroidal estrogen hormones (Hanselman et al. 2003; Koplin et al. 2002a, b), and inorganic EDCs are released directly to the environment after passing through conventional WWTPs that are not designed to remove these compounds from the effluents (Halling-Sorensen et al. 1998; Kolpin et al. 2002a, b), and ultimately, reach surface- and groundwater. In fact, concentrations of (10–100 ng/L) of PPCPs and structurally related compounds were already found in wastewaters and surface water, e.g., propranolol and ibuprofen, more than a decade ago (Kolpin et al. 2002a, b; Hanselman et al. 2003; Ternes et al. 2004). Such concentrations of these EDCs, and >10 μg/L of APEOs have the potential to affect adversely the reproductive biology of aquatic wildlife (Tyler et al. 1998; Hanselman et al. 2003; Pikering and Sumpter 2003; Zoller et al. 2004). Thus, the importance of establishing these EDCs' environmental concentration profiles and their synergistic chronic ecotoxicological impact (SCEI) in soil and surface- and groundwater, is apparent.

43.2.2 Treatment Methods

43.2.2.1 Chemically Enhanced Primary Sedimentation (CEPS)

The removal rate of organic carbon load toward secondary treatment can be increased by chemically aided sedimentation, considering that a quite large amount of the organic load (up to 40–50 %) present in sewage is in the colloidal form. The expected increase in the removal efficiency of organic micro-pollutants can have a strong impact on further treatment stages and the ultimate effluent reuse. There have not been many data regarding the removal of POEDCs in CEPS. Some indication could be obtained based on the study of Sharp et al. (2005), who found that coagulation of natural organic matter (NOM) depends on the latter's polarity balance and the charge density. In accordance, a reduction in the CSEI of POEDs in WWTPs' effluents is to be expected.

43.2.2.2 Biological Treatment

It has been reported that various organic micro-pollutants have been removed in activated sludge (AS) systems by two main mechanisms: biodegradation and sorption to the biomass. Nevertheless, the data gathered are somehow controversial. Joss et al. (2006) reported, based on the degradation of a heterogeneous group of

35 compounds, that state-of-the-art biological treatment schemes for municipal wastewater are not efficient in terms of degrading pharmaceuticals. Several distinct categories of PPCs were surveyed along different units of a municipal WWTP, in Spain (Carballa et al. 2004). The overall removal efficiencies within the WWTP ranged between 70 and 90 % for the fragrances, 40–65 % for the anti-inflammatories, ~ 65 % for 17β-estradiol, and 60 % for sulfamethoxazole. However, the concentration of estrone increased along the treatment due to the partial oxidation of 17β-estradiol in the aeration tank. Conventional wastewater treatment has been found efficient in the removal of the potent 17α-estradiol (85–99 %), whereas estrone removal was relatively poor (25–80 %) (Khanal et al. 2006). A study in eight WWTPs in Germany found that the removal efficiency of the hormone ethnylestradiol (birth control pill) reached 90 % (Coors et al. 2004). Several reports depict hydrophobic interaction between aliphatic and aromatic EDCs and the lipophilic moieties of biomass-cell membranes (Thomas et al. 2006), indicating a significant hazard related to sludge application in agriculture.

43.2.2.3 Advanced Oxidation Processes (AOPs)

New emerging technologies utilizing combinations of UV, Ozone, and H_2O_2 are currently being applied for the removal of various contaminants in water and wastewater (Vieno et al. 2007). Ozone was reported to exhibit high removal efficiency of various pharmaceuticals and steroids (Ternes et al. 2004). The effectiveness of Ozone and UV/H_2O_2 for the removal of six medicines was found to be high for all six medicines tested, except clofibric acid. These processes, while being highly efficient, are relatively costly and may result in the formation of toxic intermediates (Thomas et al. 2006). Clearly, application of AOPs following the process in the biological treatment stage in AS-based WWTPs significantly reduces the "endocrinal potential" of the POEDCs SCEI in the discharged effluents.

43.2.2.4 Sorption

Activated carbon has been traditionally used for the removal of many toxic compounds in water works. In a related study, it was found that granular activated carbon could be used successfully for the removal of PPCPs and estrogenic flame retardants in surface waters and WWTPs effluents (Kim et al. 2007). The effect of the nature of the sorbents (i.e., surface charge), PPCPs (i.e., pKa, ionization, hydrophobicity) and aqueous solution (i.e., pH) impacted the sorption of pharmaceuticals (Lorphensri et al. 2006). A strong association was found between increased organic carbon content and increased sorption, or decreased mobility of, e.g., estradiol and testosterone, indicating that hydrophobic interactions are responsible for the sorption process (Casey et al. 2004; Das et al. 2004). As far as the pharmaceuticals are concerned, the more of them that are sorbed on the activated carbon, the less "endocrinic" the WWTPs effluents are expected to be.

43.2.2.5 Membrane Separation Processes

Pressure-driven membrane separation processes comprise microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). All these are considered to be emerging technologies for the potential removal of EDCs from WWTPs effluents. Membrane bioreactors (MBR) showed a limited removal of target compounds, but were shown to be effective for eliminating some PPCPs, e.g., acetaminophen, ibuprofen and caffeine; RO and NF showed a >95 % removal of all target substances studied (Kim et al. 2007). However, it was demonstrated that high molecular weight POEDCs, such as 17β-estradiol (MW: 279 g/mol), were still detected in the RO permeate, albeit at very low concentrations (Kimura et al. 2004). Negatively charged compounds are expected to be significantly rejected by NF/RO membranes due to electrostatic repulsion between the compounds and membranes. A high level of rejection (>90 %) associated with negative charge was observed even for low molecular weight compounds (e.g., 110) in NF. For neutral, uncharged compounds, rejection will depend on their physical/chemical properties. The relationship between the physical/chemical properties of compounds and the latter reactions of NF/RO membranes' systems affects the end results and, accordingly, the endocrinal impact of the effluents.

43.3 Synergistic Chronic Ecotoxicological Impact (SCEI) of Persistent Organic Endocrine Disrupting Chemicals (POEDCs)

Regardless of "climate change," the population growth, and the increasing scarcity of water in many regions of the world, arid and semi-arid, in particular, water reuse, mainly of municipal wastewater treatment plants effluents, has increased dramatically (Sumpter and Johnston 2005; Ternes et al. 2004). Consequently, the pollutants, mainly the POEDCs that survive the various treatments – physical, biological, chemical and/or natural environment systems-based (e.g., bank filtration, soil-aquifer treatment-SAT) – constitute an ever-increasing major environmental ecology- and health-related concern. This is due to the estrogenic-endocrine modulating effects of these POPs-EDCs, even in their surviving ng/L concentrations in the WWTPs' effluents, which, ultimately, reach surface- and groundwater resources. The main issue is not the LD_{50} of the separated EDCs in effluents mixtures, but rather the actual combined chronic ecotoxicological impact (SCEI) of this endocrinic mixture, which, in turn, also point at a potential toxic health risk (Fig. 43.3).

Although the extent of the threat to humans being exposed to POEDCs still remains to be elucidated (Zoller and Hushan 2010), their nature, namely their naturally biodegradation-resistance and environmental persistence, turn them into a major ecotoxicological environmental issue of health concern. These EDCs and their metabolites/degradation products were found to affect the endocrine system of exposed animals, triggering rather large biological effects even at extremely low

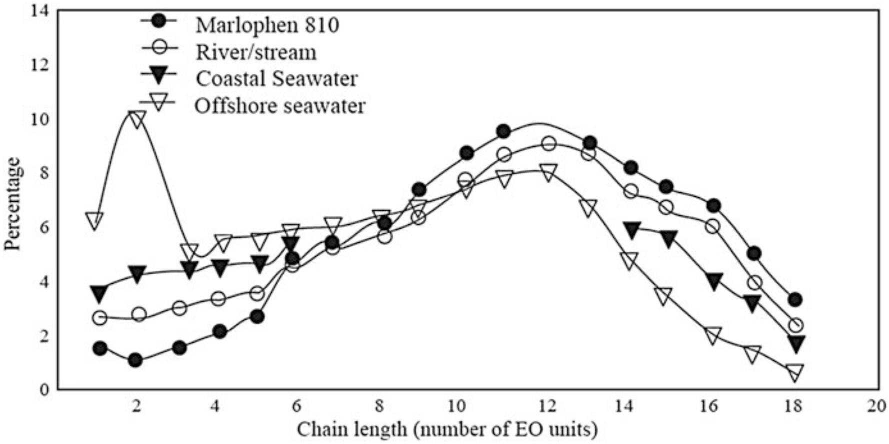


Fig. 43.3 The homologic distribution of APEOs (% of total distribution) in Israel's rivers, estuaries and Mediterranean seawater (Zoller et al. 2004)

concentrations (ng-μg level). The persistence of the POEDCs in aquatic environments, particularly WWTPs effluents reused for irrigation and public water supply systems in semi-arid regions (where reclaimed water reuse, mainly for agriculture irrigation is extensively practiced), constitutes an environmental health problem (Pickering and Sumpter 2003; Zoller 2004). Recently, the focus of the EDCs-related environmental research has been extended to PPCPs (Ternes et al. 2004; Zeng et al. 2005; Bayen et al. 2013; Lee et al. 2013) with respect to their and as well as their recalcitrant metabolites' persistence and estrogenic effects in aquatic environments, particularly whenever wastewater effluents are either being reused or discharged into surface waters (Huang and Sedlak 2001; Kolpin et al. 2002a, b; Yang et al. 2013; Esteban et al. 2004). Consequently, the health-related aspects, have become a major issue of concern, in particular the related SCEI-human health risk potential relationship (Zoller and Hushan 2010).

Many anthropogenic, e.g., APEO surfactants, especially the branched congeners nonyl- and octylphenol ethoxylates and their metabolites, are known to elicit estrogenic responses, i.e., they are capable of mimicking or antagonizing the action of steroid hormones in both mammals and fish (Gabriel et al. 2008; Lye et al. 1999). They were found in tissue of mature and juvenile fish (flounder), indicating environmental estrogenic exposure to wastewater discharges. Similarly, long term chronic exposure of Zebra fish to a mixture of PAHs resulted in substantial reduction in their fertility (eggs' production) (Zoller and Hushan 2010).

43.3.1 The Synergistic Chronic Ecotoxicological Impact (SCEI) of Selected POEDCs

Data on chronic effects of actual environmental and/or sublethal concentrations of POEDCs, the most relevant with respect to the potential public health risk, are

Table 43.1 AEPOs and PAHs concentrations in WWTP influents and effluents

STP	Influent (μg/L)		Effluents (μg/L)		Removal (%)	
	AEPOs	PAHs	AEPOs	PAHs	AEOPs	PAHs
Haifa	48.9	0.38	34.0	0.25	**30.5**	**34.2**
Netanya (Sharon)	49.9	0.38	35.0	0.24	**30.0**	**36.8**
Neve Shaanan Technion	42.1	0.36	27.4	0.23	**34.9**	**36.1**
Sakhnin	48.0	0.23	34.8	0.23	**27.5**	**30.4**

scarce. Clearly, more data concerning the quantitative chronic effects of each environmentally underestimated relevant POEDC and more so the synergistic chronic ecotoxicological impact (SCEI) of environmentally POEDCs' particularly are needed, targeted at the assessment of their ecotoxicological and health risk potential.

The SCEI of real POEDCs mixtures in WWTPs' effluents, surface- and groundwater via appropriate tests, e.g., the ZFEPT (Zoller et al. 2004), fill all the criteria of "environmental indicators" and can be used as "equivalents" to the latter. The related representative results of our research study recently conducted in Israel, based on our (experimentally) developed ZFEPT (Zebra fish Egg Production Test) and to be published shortly, are presented in the next Sect. 43.3.2 of this chapter (Table 43.1).

43.3.2 *The SCEI of POEDCs: The Israeli Research-Based Case Study*

Israel, a country in the eastern Mediterranean basin, is located in a semi-arid region. The country is experiencing an extreme shortage of water supplies. From the approximately 5×10^8 m^3 of annually produced sewage containing ca. 9–122 mg/L of anionic (mainly LABS) and 1–3 mg/L of nonionic (mainly APEO) surfactants, ~ 90 % is treated in (mainly) activated sludge (AS)-based WWTPs, and about 70 % is reused, mainly in agricultural irrigation. Given this, almost exclusively, secondary activated sludge treatment (AST) practice, the importance of establishing these EDCs' environmental profiles and synergistic ecotoxicological environmental impact in river sediments and water is apparent (Fig. 43.4).

43.3.3 *APEOs-PAHs in Israel (Representative) Rivers*

Given that about 70 % of Israel's ~550×10^6 m^3/Y of wastewater is being reused, following its treatment in AS-based WWTP or SAT, the remaining concentrations

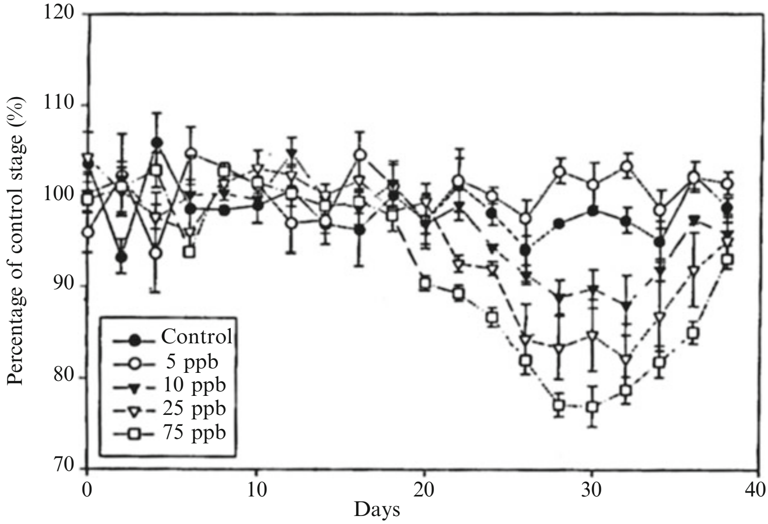


Fig. 43.4 Effect of APEOs mixtures (Marlophen 810) on zebrafish (*Danio rerio*) reproduction (Zoller 2004)

of the APEOS and PAHs in the effluents that ultimately reach surface and groundwaters, mainly via agricultural irrigation, are of particular relevance (Table 43.2).

It is worth noting that (1) the APEOs and PAHs loads in the two urbanic wastewater plants (Haifa and Netanya) were essentially the same, and (2) the percentage of removal of these two POEDCs in the activated sludge (AS)-based treatment was quite similar.

Based on our representative results presented here, the experimentally derived research does respond to the question concerning the potential synergistic ecotoxicological impact of APEO-PAH mixtures and their potential health risk. Similar conclusions have already been reached in many studies focusing on mixtures of hormones (natural and anthropogenic) and selected "representative" PPCPs in wastewater effluents that are actually being reused. Thus, the contemporary wastewater reuse practice constitutes a potential endocrine health risk. This, in turn, requires the application of advanced treatment technologies in WWTPs to ensure the sustainability of their effluents' reuse. In view of recent studies that demonstrated the potential deleterious effects of extreme abiotic factors on chemically-based toxicities/56/, toxicokinetics and toxicodynamics modeling studies may be needed in the future to understand the toxicologic-ecotoxicologic pathways that are involved in environmentally-relevant mixtures of POEDCs and relevant stressors. This would enable the usage of the related SCEI as a solid environmental indicator.

Table 43.2 The impact of APEOs + PAHs + hormones + Pharmaceuticals on zebra fish (*Danio rerio*) egg production

Chemical group	Average concentration in WWTP effluents	Average concentration in WWTP influents	Smaller concentrations which had impact
APEOs	32.6 μg/L	47.8 μg/L	10 μg/L
PAHs	0.23 μg/L	0.35 μg/L	50 μg/L
Hormones			
E1	28.8	73.4	75
E2	7.8	22.4	50
E3	5.8	11.0	1
Pharmaceuticals Sulfa	74.6	154.3	120
Carba	135.7	449.5	120
Diketo	93.6	1,143.6	150
Impact after Exposure (days)	4	4	8
Recovery after Cleaning (days)	Return to 25 % (of eggs) compared to start	Return to 22 %	Return to 40 %
Maximum reduction in egg production	12 %	8 %	16 %

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Chapter 44
Bioaccumulation and Long-Term Monitoring in Freshwater Ecosystems – Knowledge Gained from 20 Years of Zebra Mussel Analysis by the German Environmental Specimen Bank

Martin Paulus, Diana Teubner, Heinz Rüdel, and Roland Klein

Abstract With due regard to high standards, the zebra mussel (*Dreissena polymorpha*) has been utilized as an indicator of bioaccumulative substances in the German Environmental Specimen Bank for over 20 years. On an exemplary basis, the acquired time series of mercury and p,p′-DDE-concentrations underline their high value for freshwater ecosystem monitoring as well as their specific information content. The trends of mercury serve as a mirror of the industrial changes in Eastern Germany. A comparison with other sample specimens further emphasizes its usefulness in biomagnification studies. The p,p′-DDE concentrations demonstrate the diverse application history of the insecticide pp′-DDT, as well as the high persistency of this transformation product. Furthermore the mussel's biometric parameters highlight various water body specific developments, which in turn illustrate the different developments of its living conditions in the large German river systems. In the meantime, the severely lacking sample availability at many sampling sites partially underscores these changes. Reduced nutrient availability, predatory pressure, and competition by the invasive quagga mussel, *D. rostriformis,* are being discussed as possible causes. Overall, the sample availability is susceptible to considerable temporal discontinuities due to the complex dynamics of flowing water systems, which renders the latter crucial to the success of long-term monitoring studies.

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_44

Keywords Zebra mussel (*Dreissena polymorpha*) • Bioaccumulation • Monitoring • Mercury • pp′-DDT (p,p′-dichlorodiphenyltrichloroethane) • Freshwater • Biomagnification • Ecosystem

44.1 Introduction

The zebra mussel (*Dreissena polymorpha*) is native to the ponto-caspic region, from where it expanded north- and westwards in the late eighteenth century. Today, its invasive area stretches over large parts of Europe and North America, where it has successfully established large populations (Claudi and Mackie 1994; Herbert et al. 1991; Lowe and Day 2003; Mackie et al. 1989; Morton 1993; Ram and McMahon 1996). This alien species provided a great opportunity for environmental monitoring to study an effective plankton filter feeder as an indicator organism for bioavailable and bioaccumulative anthropogenic pollutants on a large geographical scale.

The successful invasion by the zebra mussel can be described as the initial spark for a great number of "Mussel Watch"-programs in the limnic waters of Eurasia and North America. Recent examples of these programs outside the native areas can be found in Belgium (Bervoets et al. 2004, 2005; Covaci et al. 2005; Voets et al. 2006), France (Bourgeault et al. 2010; Guerlet et al. 2010; Minier et al. 2006), Italy (Binelli et al. 2001, 2004; Camusso et al. 2001; Riva et al. 2008, 2010), Spain (Alcaraz et al. 2011), Canada (Renaud et al. 2004) and the United States (Kwan et al. 2003; Kwon et al. 2006; Richman and Somers 2005; Rutzke et al. 2000).

In the German Environmental Specimen Bank (ESB) (Federal Environment Agency 2008), the zebra mussel has been applied as an indicator organism for bioaccumulative substances for approx. 20 years. Therefore, routine operation profits from a multitude of experiences and a great amount of data from sampling and sample characterization. We here present the knowledge gained from this 20 years of zebra mussel analysis as an important tool for long-term monitoring in freshwater ecosystems.

44.2 The Zebra Mussel in the Frame of German ESB

44.2.1 Function of the Specimen Type

The ESB constitutes a system for surveying retrospectively chemical changes in marine, freshwater and terrestrial ecosystems in the long-term. Within the scope of the ESB, the zebra mussel represents the level of the first order freshwater consumers in running and stagnant waters. The following reasons substantiate the suitability of the zebra mussel as an indicator organism (Wagner et al. 2003):

– *D. polymorpha* has a wide distribution within Europe and North America and it has a continuous tendency to extend its spread.
– The adult mussels are sedentary.

– It is characterized by a great ecological valence, colonizes oligotrophic to mesotrophic waters, sustains in brackish water, occurs in stagnant and running waters, and survives short-term drying-up of the water body.
– The zebra mussel generally occurs in large population densities.
– It feeds mainly on vegetable and animal plankton-organisms, as well as on detritus particles in the size range 1–40 μm, which it filters from the circumfluent water. Thus, it is in close contact with all substances dissolved or suspended in the water.
– Due to its feeding habits, the zebra mussel is closely related to its environment. The continuous passing of water through its coat cavern and the large contact zone of the opercula and the coat, favor the direct uptake of pollutants from the water.
– It is easily to manipulate, which means that it is suitable for both active monitoring (exposure of substrata colonized with juvenile mussels) and toxicity and impact tests.
– It serves as nourishment for a number of fish species, part of which are used commercially, such as the bream, which itself serves as specimen for the ESB.

44.2.2 Sampling and Sample Treatment

Zebra mussels were sampled annually at 14 sites including the Rivers Elbe (E1–E5), Rhine (R1–R4), Danube (D1–D3) and Saar (S1–S2); one sample from Lake Belau (LB) was taken biannually (Federal Environment Agency 2008, Fig. 44.1).

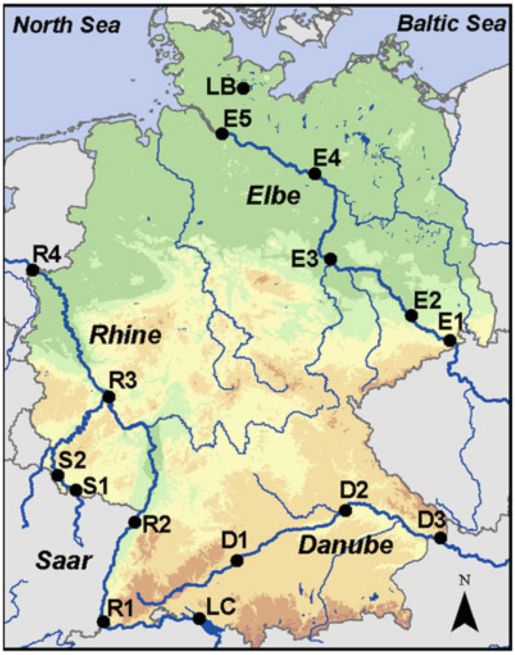

Fig. 44.1 Zebra mussel sampling sites of the German ESB. *E* Elbe, *R* Rhine, *S* Saar, *D* Danube, *LB* Lake Belau, *LC* Lake Constance (used for colonization of plate stacks)

Fig. 44.2 Zebra mussel plate stack with protective netting against predators after successful exposure

Zebra mussel sampling was conducted by means of stacks of polyethylene plates, which were exposed in Lake Constance (Fig. 44.1) at the beginning of the respective spawning season (Wagner et al. 2003). In autumn, when they were densely populated with young mussels, the plate stacks were removed and transported to the sampling sites, where they were exposed for 1 year (Fig. 44.2). In order to protect the plate stacks from predators they were covered with nets of approximately 10 mm mesh size.

A single plate stack remained in Lake Constance as control. If stack exposure was unsuccessful, effort was invested in gathering naturally occurring zebra mussels from substrate beneath the low water line. In order to achieve the required 2,000 g soft tissue of zebra mussel, 5,000–7,000 fresh mussels with a shell-length range of approx. 15–25 mm had to be collected at each sampling site.

For biometric characterization, 50 mussels are randomly selected from the sample in the laboratory. The soft-tissue of the remaining mussels is pooled and homogenized for each sampling site and subsequently divided into approx. 200 aliquots for long-term cryogenic storage. Chemical analyses are performed on the homogenates.

Further descriptions of the ESB, including standard operating procedures (SOPs), are provided at www.umweltprobenbank.de.

44.3 Long-Term Developments of Environmental Indicators

44.3.1 Chemical Indicators

The potential of zebra mussels as an indicator organism for long-term monitoring will be illustrated by two examples from the German ESB, mercury / methyl mercury and p,p′-DDE (p,p′-dichlorodiphenyldichloroethene), a transformation product of the insecticide p,p′-DDT (p,p′-dichlorodiphenyltrichloroethane).

Mercury (Hg) is a ubiquitous environmental pollutant, which enters aquatic ecosystems either directly via, e.g., industrial waste water and mining wastes, or through deposition of atmospheric emissions, for instance, from power plants or waste incineration. However, also natural sources contribute to the atmospheric burdens of mercury. Abiotic or biological methylations can eventually lead to the formation of monomethyl mercury (MeHg), which is more toxic and bioaccumulative than inorganic Hg species.

Figure 44.3 shows the concentrations of total Hg and MeHg in zebra mussels from the Elbe sampling site E3 between 1998 and 2011. E3 is located directly downstream of the Saale confluence and is influenced by metal burdens originating, e.g., from the industrial area around Leuna in Eastern Germany, but also by former mining activities in the Fichtel Mountains where the Saale has its source. The time series covers the period of changes in industrial structure in East Germany, which were induced after the German re-unification in 1990. Hg and MeHg both increased until 2003 and 2002, respectively, and decreased thereafter. For the entire study period, a significant decrease ($p < 0.05$, Mann-Kendall-Test) was detected for both parameters.

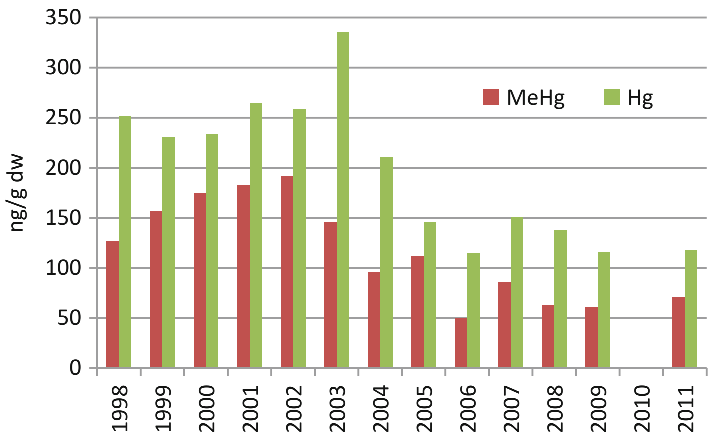

Fig. 44.3 Methyl mercury (MeHg) and total mercury (Hg) in zebra mussels sampled at the Elbe site E3. Concentrations refer to dry weight (dw). No data available for 2010

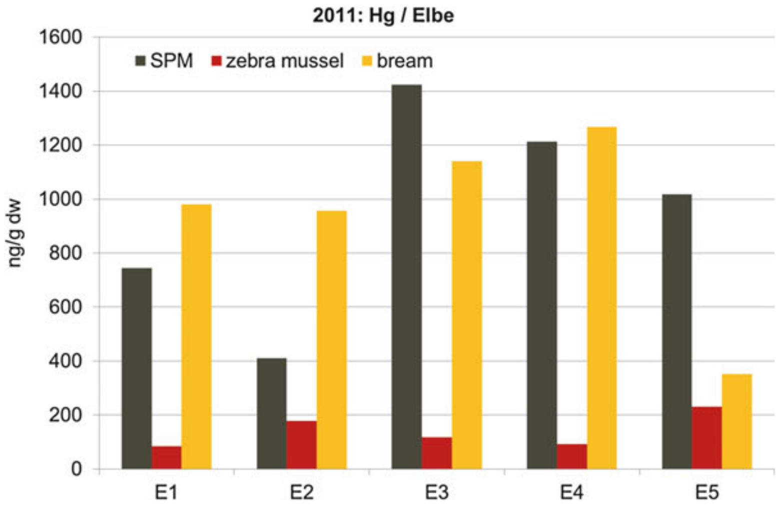

Fig. 44.4 Total mercury (Hg) concentrations (ng/g dry weight) in suspended particulate matter (SPM), zebra mussels and bream muscle sampled at the Elbe sites of the German ESB

The zebra mussel results are supported by ESB data for suspended particulate matter (SPM) and fish, for which decreasing trends were also observed at E3. Hg levels in bream were on average 8–9 times higher than in zebra mussels, thus highlighting the biomagnifying potential of Hg (e.g., Suedel et al. 1994, US EPA 1997).

An additional value of zebra mussels is their application as an indicator for biomagnifying compounds in food webs. This approach uses representatives of different levels of the aquatic food web. An example is shown in Fig. 44.4, which summarizes the total Hg levels in SPM, mussels, and bream at all the Elbe sites in 2011. The mercury contents of zebra mussel and bream reflect the bioavailable fraction of Hg, and the comparatively higher levels in bream indicate that Hg is biomagnified in the food web (zebra mussels are considered here as representative of the trophic level of primary consumers; however, due to their low abundance at most Elbe sites, zebra mussels probably do not contribute significantly to the diet of bream). In contrast, Hg levels in SPM are governed by different processes (SPM is assumed to contain mainly non-bioavailable Hg of geogenic origin bound in mineral particles) and are obviously not directly related to the bioavailable fraction.

The potential of zebra mussels as an indicator organism also for organic pollutants is exemplarily demonstrated for p,p′-DDE. p,p′-DDE is a very persistent metabolite of the pesticide p,p′-DDT, which was widely used globally until its environmental impacts became evident in the 1960s. Since 2004 the agricultural use of p,p′-DDT has been banned worldwide under the Stockholm Convention (Stockholm Convention 2001). In the Federal Republic of Germany, it was already banned in 1972, whereas it was still used in the former German Democratic Republic (GDR) in forestry and wood preservation until the late 1980s. These differences in use patterns are still reflected in environmental concentrations.

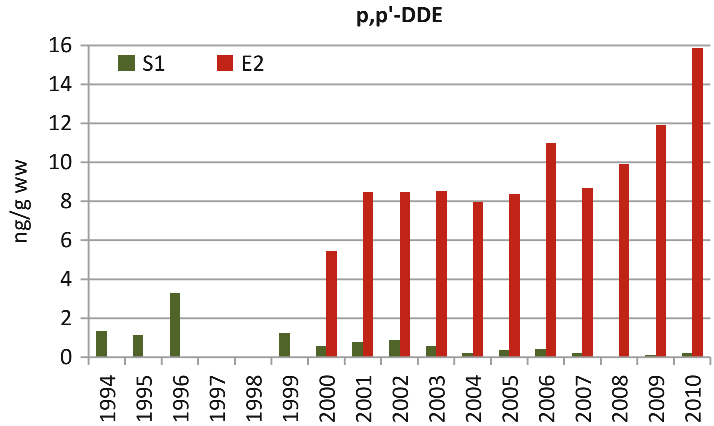

Fig. 44.5 p,p′-DDE in zebra mussels (ng/g wet weight) sampled at S1 and E2. No data available for S1 for 1997, 1998 and 2008; the routine sampling at E2 started only in 2000

Figure 44.5 shows the p,p′-DDE concentrations in zebra mussels from the Saar site S1 (Western part of Germany) and the Elbe site E2 (Eastern part).

The data refer to wet weight, even though p,p′-DDE is lipophilic and normalization to lipid weight would be a usual approach for biota residues. However, the lipid content of zebra mussels is relatively low (0.1–3 %) and highly variable depending on sampling time and location. This implies that wet weight is the better choice when reporting concentrations of organic compounds in zebra mussels (Metcalfe-Smith et al. 2002).

p,p′-DDE levels at E2 were 10–90 times higher than at S1. The p,p′-DDE loads at E2 probably stem from former intensive p,p′-DDT uses in agriculture and forestry and from its wide use as a wood preservative in the former GDR. During the monitoring period, levels in annually sampled zebra mussels at S1 decreased significantly to concentrations in the range of the limit of quantification ($p < 0.001$, Mann-Kendall-Test). However, levels still increased in mussels from the site E2 ($p < 0.01$, Mann-Kendall-Test). It is not clear whether the increase of p,p′-DDE levels at this site results from continuing emissions (e.g., from contaminated sites in the Elbe upstream area) or from a remobilization from the sediment. At site E1, the p,p′-DDE concentrations in zebra mussels increased to about 50 % of the level of an assessment criterion derived for the protection of predators from secondary poisoning by p,p′-DDT (30 ng/g prey tissue; Bursch 2003), under the assumption that both compounds exhibit similar (eco)toxicity.

In bream, much higher p,p′-DDE levels were detected at both sites (factor 4–100), which confirms the biomagnification potential of p,p′-DDE (Borgå et al. 2012; Metcalf et al. 1971). p,p′-DDE concentrations in bream from S1 also decrease over time ($p < 0.001$, Mann-Kendall-Test), while in contrast to the mussel data no trend is observed at E2. The different time patterns observed in bream and mussel at site E2 again seem to reflect different bioavailable fractions of p,p′-DDE and uptake pathways of the organisms.

Table 44.1 Time trends (Mann-Kendall-Test) of elements and organic compounds in zebra mussels (*D. polymorpha*) at ESB sampling sites; empty field: no trend; +: increasing trend; −: decreasing trend; levels of significance: +++/−−−: p = 0.001; ++/−−: p = 0.01; +/−: p = 0.05; gray shaded fields: insufficient data, no trend analysis possible

Water body	**Lake Belau**	**Saar**		**Rhine**				**Elbe**					**Danube**		
Sampling Site / parameter	LB	S1	S2	R1	R2	R3	R4	E1	E2	E3	E4	E5	D1	D2	D3
Co [dw]		+								+				+	
Ni [dw]	−					−						++			
Cu [dw]	−−	+										++		++	+
Cd [dw]		+		−		−				+					
Hg[dw]			−							−					
Pb [dw]	−								+						
As [dw]															
Se [dw]							+		−						
MeHg [dw]				+						−			+		+
HCB [ww]	−	−−							−	−−	−	−−			
OCS [ww]	−														
DDE[ww]		−−−	−−−						++						
DDD [ww]		−−	−−						++					−	
ß-HCH[ww]			−−			−			−						
Sum PCB [ww]		−													

Trends refer to the following sampling periods: LB: 1997–2011 (every second year); S1, S2: 1994–2011; R1–R4: 1995–2011; E1: 1999–2011; E2: 2000–2011; E3: 1998–2011; E4: 1998–2011; E5: 1995–2011; D1–D3: 2004–2011. Data from single years are partly missing in the time series due to sample losses or insufficient analytical data

The examples demonstrate that zebra mussels are well suited as indicator organism for bioaccumulative and biomagnifying substances and supplement monitoring data of fish and SPM.

Table 44.1 gives an overview of all elements and substances regularly analyzed in zebra mussels during real-time monitoring under the German ESB program and summarizes the results of time trend analyses using the Mann-Kendall-Test. These data underline the suitability of zebra mussels as an indicator organism for the detection of time trends and spatial differences.

44.3.2 *Biometric Indicators and Indices*

In the German ESB, selected biological characteristic values of the sampled indicator organisms are evaluated through biometric sample characterization.

These biometrical data are utilized for standard verification purposes, facilitate the comparison of samples of different spatial and temporal origin, and allow for normalization of analytic results. Bignert et al. (1993) elaborately demonstrated the importance of the biological variability of age, length, and weight for an accurate interpretation of chemical residue in biological samples, especially concerning the analysis of homogenates. Furthermore, biometric data can be used as endpoints for the monitoring of environmental effects. They thereby function as non-specific biometric indicators or indices that allow for the integrated assessment of the overall ecosystem condition (Paulus et al. 1996, 2005). This concept has been applied by Teubner et al. (2013) who demonstrated that biometric parameters and indices of bream (*Abramis brama*) are reliable indicators for long-term changes of fish health, which in turn, can also point to long-term changes in environmental quality. In zebra mussel monitoring, the biometric indicators shell length and width, shell weight, and soft tissue weight constitute the established measuring norms. The condition index can be calculated on the basis of the relationship between soft tissue- and shell weight (e.g., Bourgeault et al. 2010; Lowe and Day 2003; Minier et al. 2006; Nalepa et al. 2010; Richman and Somers 2005; Singer et al. 2005; Voets et al. 2006).

We tested these indicators and the condition index for time trends at the ESB sampling sites (Table 44.2). The shell parameters length, width, height and weight of shell, as well as the weight of soft tissue showed negative trends at the ESB sampling sites at the River Saar (S1, S2), at the River Rhine at R1, and at Lake

Table 44.2 Time trends (linear regression) of parameters and indices of zebra mussels (*D. polymorpha*) at ESB sampling sites; empty field: no trend; value: r^2 ($r^2 \geq 0.1$ and $p \leq 0{,}001$); red shaded field: negative trend, green shaded field: positive trend, gray shaded fields: insufficient data, no trend analysis possible

Water body	**Lake Belau**	**Saar**		**Rhine**				**Elbe**					**Danube**		
Sampling Site / parameter	**LB**	**S1**	**S2**	**R1**	**R2**	**R3**	**R4**	**E1**	**E2**	**E3**	**E4**	**E5**	**D1**	**D2**	**D3**
Length	0.51	0.40	0.51	0.55			0.15							0.39	0.19
Width	0.46	0.38	0.46	0.52										0.43	0.24
Height	0.44	0.38	0.44	0.58										0.43	0.25
Shell weight	0.57	0.44	0.57	0.52		0.15	0.10							0.42	0.20
Soft tissue weight	0.45	0.49	0.49	0.27			0.10		0.10					0.29	0.15
Condition index		0.18				0.16		0.37	0.20		0.14				

Belau (LB). Additionally, there was a negative trend of the condition index at S1. Furthermore, there were negative trends of the length, weight of shell and soft tissue at R4 and of weight of shell at R3. These negative trends imply a decline in the growth condition, which may be caused by different stressors. Potential stressors are pollutants, insufficient nutrition, competitive pressure, and predation (see Chap. 4). However, current findings suggest the decline of the contaminant burden of the Rivers Rhine and Saar (ICPMS 2001; ICPR 2002, 2007a, 2011; Rüdel et al. 2007; Wenzel et al. 2004). The temporal trends shown in Table 44.1 were also predominantly negative. There were only a few slightly positive trends at S1, R1, R3, and R4, which most likely did not cause the negative trends of the biometric parameters and condition index.

There was a positive trend of the condition index at R3. This was accompanied by a negative trend of shell weight, which in addition to the soft tissue weight was included in the calculation of the condition index. At this point, it is important to stress that a decrease in the shell weight and not an increase of the soft tissue weight contributes to a positive development of the condition index. Therefore an increase in the condition index due to the thinning of the shell has to be interpreted as a worsening of living conditions rather than a positive development of mussel fitness. This demonstrates that time series of the condition index alone, without consideration of the development of shell and soft tissue weight, do not provide comprehensive results.

The most powerful stressor for the River Rhine probably is the nutritional status, as discussed in Sect. 44.4.1. At R1, which is located at the Upper Rhine, the collection of sufficient amounts of sample material has always been difficult since the start of routine ESB sampling. Here, the food supply might have been poor at the initial sampling in 1995 and may have further deteriorated in the meantime. All parameters, except the condition index, declined until 2006. Since 2007, no mussels have survived on the exposed plate stacks. The negative trends at R3 and R4 may have been caused by the competitive pressure with the quagga mussel (*Dreissena rostriformis*) – formerly known as either *D. bugensis* or as *D. rostriformis bugensis* (name has been changed per Stepien et al. 2013) – which first occurred in 2004 at R3 and in 2005 at R4. In 2011 *D. rostriformis* reached abundances of 95 % and 80 %, respectively (Paulus et al. 2014). The quagga mussels compete for nutrition against *D. polymorpha*, which is in an inferior position to its opponent (see Sect. 44.4.3).

It remains uncertain why the growth of mussels in Lake Belau has declined.

An increase of zebra mussel fitness could also be established for the River Elbe close to Czech border at E1 and E2 and downstream of the estuary of the River Havel at E4. Concerning these sites, neither competitive pressure with other Bivalvia nor a lack of nutrition is a likely suspect. However, Teubner et al. (2013) indicated an improvement in the fitness of bream at the Elbe sampling sites E1 and E2. The water quality of the Elbe River is ameliorating due to a decline in the contaminant burden and increase in oxygen levels (Heininger et al. 2003; ICPER 2010). Thus, the increased fitness may indicate the improved water quality at these sampling sites.

There are positive trends of all shell parameters at D2 and to a lesser extent at D3. The reasons for this have yet to be elucidated. In contrast to the Elbe, where the improved mussel fitness was displayed by the increasing condition index, the Danube mussels increased in size without an improvement in their fitness. This suggests that other factors may play a role, as in the Elbe.

44.4 Long-Term Sample Availability

The preceding chapters have demonstrated the zebra mussels' ability to provide extensive information on bioaccumulation and biological effects in freshwater ecosystems. Together with the actual information content of an indicator organism, the continuous availability of the selected species is a vital key to the success of a long-term monitoring program. Against this background, the zebra mussel poses an ideal indicator organism as it rapidly reaches high and stable population densities within a short time following its arrival. However, as experience has shown, even under these conditions long-term sample availability can be precarious when large sample amounts are required (5,000–7,000 mussels per sample location, see Sect. 44.2.2). Oftentimes, only smaller sampling amounts were achieved at many sites, and in some cases even a complete loss of sampling material could not be averted.

These incidents might be explained by low growth rate, death, or migration, or direct influence of predators. The following factors might in turn be responsible for this development: (a) poor nutrition, (b) competitive pressure, (c) poor physicochemical water parameters and (d) high predatory pressure, all of which will be explained in detail subsequently. Thereby, we will focus on the Rhine River as most difficulties attaining the required sampling amount occurred there. As of now, neither the influence of pathogens nor the toxic effects of pollutants can be identified.

44.4.1 Nutritional Status

Bergfeld et al. (2009) were able to show that the biomass of plankton in river systems is the result of an interaction of benthic filter feeders and anthropogenically altered factors, such as river morphology, water retention time, and nutrient load. In comparison to other European rivers, such as the Meuse, Loire, and Elbe, the river systems of the Rhine, Moselle, and Saar feature a very low average biomass of all examined plankton groups. According to the results of Friedrich and Pohlmann (2009), who studied the changes in the Rhine since the 1970s, the Chlorophyll concentration dropped from 59 μg/l in 1979 to 31 μg/l in 1986 and further to 21 μg/l in 2004. The reduction of waste water influx containing high organic content has led to a clear decrease in coccoid green algae within phytoplankton. During the phase of high eutrophication, the Rhine River displayed two phytoplankton peaks per year; nowadays, this has decreased to a single peak a year. Scherwas et al. (2010) emphasize that in earlier years an increase in bacterial plankton could be observed along the Rhine, which is now at a relatively low and constant level throughout the course of the river. Likewise, the increase in phytoplankton along the length of the river is also reduced in comparison to earlier years. In addition to the decrease in eutrophication, the authors mention the impact of plankton filter feeders, in particular, during the main growth phases. The species composition of filter feeders is notably affected by invasive species. It is well known that, particularly in the main growth phases of the macrofauna during summer, the algae concentration tends to drop significantly (Scherwass et al. 2010). This might also relate to the zebra mussel, which according to current results is facing decreased nutrition availability, markedly in the Rhine and mildly in the Saar River. During the last years, the lower and middle parts of the Rhine are most evidently affected by this development. This matches the observations of the exposed plate stacks at sites R3 and R4, where predominantly during the main growth phases in August and September mass extinctions occurred in multiple years. Similar results were also obtained for R3 on natural substrate.

Based on these findings, it can be assumed that there is a clear connection between the altered nutrition situation and the reduced availability of the zebra mussel in the Rhine River. This demonstrates that the declining degree of eutrophication, which has been ongoing for the past years to decades in many freshwater ecosystems, can significantly affect the sample availability of the zebra mussel.

44.4.2 Physicochemical Water Parameters

In order to verify whether altered physicochemical water parameters have caused the reduced sample amounts, data from water monitoring stations of the federal states were analyzed. Data for ESB sampling sites were available for the years 2003–2009.

Oxygen concentration is considered the limiting factor for the presence of *D. polymorpha* (Naddafi et al. 2010). The occurrence of low oxygen concentrations, which are mainly induced by high water temperatures during the summer months, could therefore be linked to the death or migration of the zebra mussel. An analysis of the time series of water temperatures and oxygen concentrations at ESB sampling sites for the months June, July and August from 2003 to 2009 did not suggest any relationship between these parameters and the die-off of the mussels.

Calcium plays a vital role among the limiting factors for the presence of dreissinid species. It is required for metabolism and shell growth (Whittier et al. 2008). The authors base the risk for an invasion of dreissenids on calcium concentration. Concentrations below 12 mg/l are classified as very low risk areas, 12–20 mg/l low, 20–28 mg/l moderate, and above 28 mg/l as prone to high risk. The optimum concentration for *D. polymorpha* lies at 70 mg/l. A level in excess

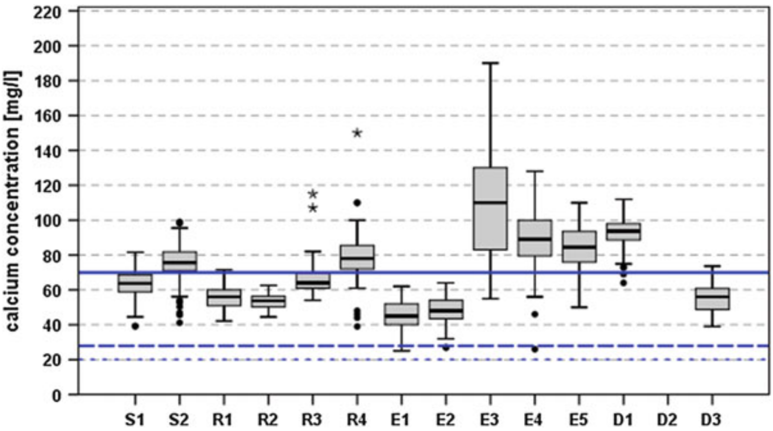

Fig. 44.6 Ca-concentrations at ESB sampling sites from 2003 to 2009 (Source: federal water monitoring stations). *Continuous line* Optimum for *D. polymorpha* (Zhulikov et al. 2010). *Dash dotted line* high invasion risk and *dashed line* moderate invasion risk by dreissenid species (Whittier et al. 2008)

of this value could mean an advantage for competing species particularly *D. rostriformis* (Zhulidov et al. 2010).

However, for the years from 2003 to 2009 calcium cannot be considered a limiting factor as the concentrations indicate a moderate to high risk of invasion (Fig. 44.6). This applies in particular to the sampling sites R1 and R2, which showed the lowest quantities and most intense loss of sampling material.

44.4.3 Competitive Pressure

In addition to the zebra mussel, the likewise invasive species *Corbicula spp*. and *Corophium curvispinum* have in recent years been described as important plankton-reducing organisms (Scherwass et al. 2010). Since the beginning of the twenty-first century, European *D. polymorpha* populations have also been increasingly displaced by the quagga mussel (D*reissena rostriformis)*. Studies in North America, where both species have coexisted for a long time, indicate a successive displacement of *D. polymorpha* by *D. rostriformis* (Baldwin et al. 2002; Diggins 2001; Peyer et al. 2009; Ricciardy and Whoriskey 2004). Zhulidov et al. (2010) describe a similar development in Eastern Europe.

The competitive advantage of *D. rostriformis* may arise from its superior ability to deal with low nourishment, higher water temperatures, and connected low oxygen levels. Compared to *D. polymorpha*, the quagga mussel has a lower respiration rate in varying seasonal temperature conditions. This allows it a stronger growth, as well as a larger allocation of energy toward the soft tissue under equal conditions of food supply (Zhulidov et al. 2010). Simultaneously, the quagga mussel also features a remarkably greater filtration rate than its dreissenid counterpart (Baldwin et al. 2002; Diggins 2001). These interspecific differences play an important role at common summer temperatures (Zhulidov et al. 2010). Peyer et al. (2010, 2011) were able to provide evidence that the quagga mussel can produce a shallow and deep-water shell type. Both morphotypes present an adaptation to hard or soft substrates, allowing it an improved locomotion, and thereby creating a competitive advantage.

The discovery of *D. rostriformis* in 2004 in the Rhine River near Koblenz (R3) presents the first record of this species not only in Germany, but also in Western Europe (Paulus et al. 2014). Today, there are numerous records from several German river and canal systems, indicating the high dynamics of its current expansion (bij de Vaate 2010; Haybach and Christmann 2009; Heiler et al. 2012, 2013; Imo et al. 2010; Martens et al. 2007; Paulus et al. 2014; Schöll et al. 2012; van der Velde and Platvoet 2007). The known invaded area includes the total navigable river Rhine, sections of the rivers Elbe, Main, and Danube, with single records from the river Neckar, the Rhine-Main-Danube-Canal, as well as canals connecting the rivers Rhine and Elbe.

Meanwhile, the quagga mussel has arrived at multiple ESB sampling sites and in some cases has reached high population densities. Recently, the abundance of the quagga mussel has exceeded that of the zebra mussel at some ESB sampling sites (Fig. 44.7) and is now the highest in the Rhine River. In the Danube and Elbe, *D. polymorpha* is still more abundant than quagga mussels. However, it is to be expected that within a few years all ESB sampling sites will be populated by *D. rostriformis*, further displacing the zebra mussel populations.

44.4.4 Impact of Predation

Naddafi et al. (2010) emphasize that for a long period the discussion on the limiting factors of population density, size, and success of invasion focused on

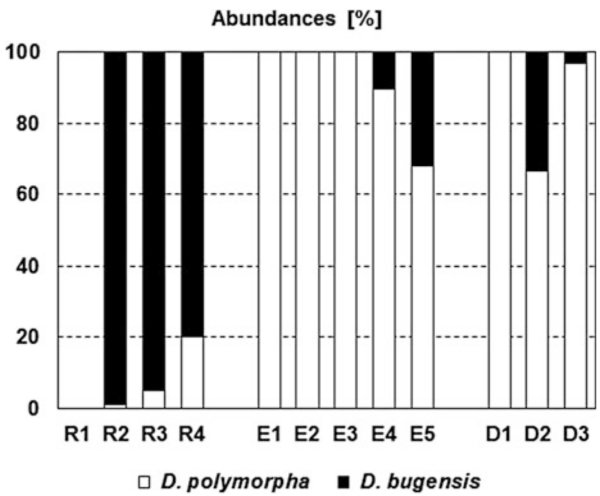

Fig. 44.7 Relative abundances [%] of *D. polymorpha* and *D. rostriformis* at Rhine (R; 2011), Elbe (E; 2012), and Danube (D; 2012) river banks (cf. Paulus et al. 2014)

physicochemical aspects. On the other hand, biotic factors were attributed merely a secondary role. Interestingly, although currently only a few studies have examined fish predation as a limiting factor, the authors consider it an underestimated component regulating *D. polymorpha*. According to their results, fish predation seems to be the controlling factor of zebra mussel development in Lake Erie. They identified roach (*Rutilus rutilus*) as the most important species, also one of the most common fish in German inland waters. Among the 67 fish species inhabiting the Rhine River, roach maintains the dominant position followed by bream (*Abramis brama*), chub (*Leucisus cephalus*), and perch (*Perca fluviatis*) (ICPR 2007b).

Zhulidov et al. (2010) regard both *D. polymorpha* and *D. rostriformis* to be a valuable food source for many Eurasian fish species. This includes the cyprinid species roach (*Rutilus rutilus*), bream (*Abramis brama*), orfe (*Leucisus idus*), and carp (Cyprinus carpio), all of which belong to the local German fish fauna. As the most important non-cyprinid species, they mention the round goby (*Neogobius melanstomus*). Zhulidov et al. (2010) assume that after both dreissinid species have expanded to a new area in considerably high population densities, the local fish fauna adapts to them as a new food source, thereby accounting for population crashes.

Within this process, the round goby seems to be of particular importance. Lederer et al. (2006) investigated the influence of *N. melanostomus* on invertebrates in the Green Bay area, Lake Michigan. They established a significantly negative relationship between the abundance of round goby and most invertebrates, including *D. polymorpha* and *D. rostriformis*. Therefore, the authors assume that the round goby is able to affect benthic macroinvertebrates substantially. Barton et al. (2005) studied the stomach content of the round goby at the northern shores of Lake Erie, revealing quagga mussels as their main food source. Meanwhile, zebra mussels are no longer found in that part of the lake. The allochthonous *N. melanostomus* has long been the most common fish species in the vicinity.

This species was first recorded in 2005 in the Rhine River (ICPR 2007b). Based on our own observations, the round goby has now also populated the Danube and Saar and reached considerable abundance. Due to its slim build, it can easily enter the plate stacks through the protective mesh, especially during its juvenile stage. Therefore, we suggest direct predation by the round goby to be an important factor in the loss of zebra mussels on the exposed plate stacks. Furthermore, the autochthonous perch is also regularly encountered on the plate stacks (Fig. 44.8).

Besides direct predation, an indirect influence induced by the presence of predatory fish might also cause the mussels to migrate. The zebra mussel can easily withdraw its byssus threads and crawl to new locations (Eckroat et al. 1992). Kobak et al. (2009) concluded that this spontaneous behavior of sessile mussel species displays a reaction to degrading environmental conditions, such as oxygen deficiency, siltation, poor water quality, strong light, or the decay of the underlying substrate (see Bodamer and Ostrofsky 2010). Furthermore, a stimulus caused by predator kairomones or alarming substances emitted by injured mussels may also trigger relocation mechanisms. Experiments revealed such a behavior in the

Fig. 44.8 Round goby (*N. melanostomus*, *left*) and perch (*P. fluviatilis*, *right*) as suspected predators of zebra mussels on ESB plate stacks

presence of roach and perch. Small mussels shifted considerably more often than large ones that cannot be cracked by predators (Kobak and Kakarenko 2009; Kobak et al. 2009). Apparently, mussels are also able to judge the size of the predator and evaluate their own vulnerability in connection with their individual size (Kobak et al. 2010). Consequently, the loss of young mussels on plate stacks may also be caused by migration to a safer location.

When we contemplating current information, fish are of primary importance among the potential predators for zebra mussels on plate stacks. A direct impact of mammals or aquatic birds (cf. Mörtl et al. 2010) is at most restricted to the margins of the stacks due to the mesh size of the netting. The Chinese mitten crab (*Eriocheir sinensis*) may also have to be considered an additional predator, especially in the Elbe River. Native to Eastern China, the crab was introduced to Europe by ballast water from merchant vessels. Its introduction history in Germany has been summarized by Domisch et al. (2010), Fladung (2000), Herborg et al. (2003), and Ojaveer et al. (2007). Accordingly, the crab was first recorded in 1912 in the river Aller. Shortly thereafter, in 1915 it was sighted in the tidal Elbe. In the meantime, it has rapidly expanded, in particular, in the rivers flowing into the North Sea: Elbe, Weser, Ems, and Rhine, as well as their tributaries. Riedel-Lorjé and Gaumert (1982) state that the Elbe presents an optimal habitat for the crab, resulting in high population densities. Its food spectrum includes aquatic plants, insect larvae, mussels, snails, small fish, and carrion. Oftentimes, fairly large crab carcasses are found inside the netting of ESB plate stacks, in particular, in the area of Hamburg Blankenese and Cumlosen. Most likely, the crab enters the plate stacks in a juvenile stage, residing and feeding on the mussels until it has reached a size too large to exit.

Conclusions

The examples of the German ESB show that zebra mussels are suitable for and can be used well as indicator organisms in environmental specimen banking and long-term monitoring studies. Since the exposure and physiology of zebra mussels is quite different from that of fish, they yield additional information on environmental contamination. For some elements, zebra mussels are even more suitable as indicators of environmental concentration levels than fish because they accumulate the respective element, whereas fish do not (e.g., lead). Furthermore, the assessment and detection of biomagnification requires more than one trophic level, and zebra mussels are valuable also in that respect. Finally, if, as in the case of ESBs, the main goal is to collect and store specimens for retrospective studies on yet unknown compounds, greater significance can be expected if more than one specimen is considered.

However, the results of the ESB also show that even with species such as the zebra mussel, which displays a large ecological valence, strong expansion tendency, high reproduction rate, and high population density, sample availability can be limited. This especially applies to long-term studies, which require large sample amounts. Concerning the zebra mussel, along with the reduced nutrient availability and predatory pressure by the round goby, the competitive stress caused by the quagga mussel seemingly stands out as a crucial factor.

Based on current findings from other colonized areas, it is not expected that *D. polymorpha* will be completely displaced by *D. rostriformis*. There are a number of arguments underlining this hypothesis. In comparison to the quagga mussel, *D. polymorpha* has a thicker shell and is able to withstand higher water velocities due to its stronger adhesion to substrate (Peyer et al. 2009). These features clearly provide a superior protection against predators. Zhulidov et al. (2010) concluded varying quagga mussel expansion scenarios for Eastern European river systems. According to their findings, *D. rostriformis* initially displaces *D. polymorpha* almost completely, thereby rapidly attaining a dominant position. This near-complete displacement is then conversely followed by a population crash of *D. rostriformis*. In that respect, the authors discuss predation by fish communities for which the width of the shell may be a decisive factor. It is assumed that, following the expansion of the quagga mussel, fish quickly adapt to this new food source and are then substantially responsible for the subsequent population crashes. Currently, the most urgent task for the biomonitoring of *D. polymorpha* is to elucidate the different accumulation behavior of both *Dreissenid* species. The studies dealing with this issue (e.g., Mills et al. 1993; Richman and Somers 2005; Rutzke et al. 2000; Schaefer et al. 2012) brought

(continued)

forth varying or partially contrary results, and hence no clear findings could be deduced.

According to Zhulidov et al. (2010), reasons for the competitive advantage of *D. rostriformis* might be found in specific differences in physiological characteristics between the two species (cf. Sect. 44.4.3). *D. rostriformis* has higher assimilation efficiency than *D. polymorpha*, which enables it to maintain higher growth and fecundity rates at low food levels. Additionally, *D. rostriformis* has a lower respiration rate under different seasonal temperature regimes. Lower respiration rates decrease metabolic costs, allowing *D. rostriformis* to have greater growth and greater allocations of energy to soft body mass than *D. polymorpha* at similar food conditions (Zhulidow et al. 2010). Due to their different physiology, it has to be expected that the mussels also show a dissimilar accumulation behavior.

If this was not the case, there would be nothing opposing an integration of both species in a *Dreissenid* monitoring of pollutants.

Acknowledgements The authors acknowledge the contributions of all past and present partners to the routine operations of the German Environmental Specimen Bank. The continuous funding by the German Federal Ministry of the Environment, Nature Conservation, Building and Nuclear Safety and the organization and permission to use the data of the ESB and the federal monitoring stations by the Federal Environmental Agency is gratefully acknowledged.

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Chapter 45
Viability and Reliability of Dense Membranes in Removing Trace Organic Contaminants for Wastewater Reclamation and Purification: Pros and Cons, Mechanisms, and Trends

Shirra Gur-Reznik and Carlos G. Dosoretz

Abstract Detection of synthetic organic contaminants in the water cycle worldwide, though at trace levels, has led to a growing concern regarding their environmental fate and the ability of current water and wastewater infrastructures to treat them. Combining simplicity, versatility and continuous process of aqueous streams, pressure driven-membrane separation systems, applying nonporous membranes such as reverse osmosis or nanofiltration, are a promising treatment generic technology for municipal wastewater reclamation, in general and specifically for treating trace organic levels. This chapter aims to review the application of pressure-driven membranes for removing trace organics indicators present in water and wastewater and specifically the role of nonporous membranes. The tradeoffs in choosing less dense nonporous membranes (i.e., nanofiltration) over denser nonporous membranes (i.e., reverse osmosis) were examined, and especially whether or not lowering operating pressures/increasing permeability would result in decrease of selectivity and therefore diminished permeate quality.

Keywords Pharmaceutical and personal care products (PPCP) • Micropollutants • Trace organics indicators • Synthetic organic carbon • Membrane filtration • Effluents desalination • Reverse osmosis • Nanofiltration

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_45

45.1 Background

For over more than two decades now a plethora of researchers have been continuously adducing unequivocal evidence as to the occurrence and persistence of anthropogenic trace pollutants, known as synthetic organic contaminants (SOCs), in surface water, groundwater, and in some cases even drinking water (Heberer et al. 1997; Halling-Sorensen et al. 1998; Daughton and Ternes 1999; Snyder et al. 1999; Kolpin et al. 2002; Carballa et al. 2004; Jones et al. 2001, 2005; Putschew et al. 2001; Westerhoff et al. 2005; Ternes et al. 2001; Ternes and Joss 2006; Joss et al. 2006; Pérez and Barceló 2007; Reif et al. 2008). In some sporadic cases they have even been reported in seawater (Miao and Metcalfe 2003). This group of compounds comprises, among others, products used in our everyday lives, such as human and veterinary pharmaceutically active compounds, personal care and household products, plasticizers, stabilizers, detergents, hormones, and industrial additives. This list includes also traditional organic micropollutants, such as pesticides, disinfection by-products (trihalomethanes and N-nitrosodimethylamine for example), and chlorinated flame retardants (Drewes et al. 2005). Some of these SOCs display endocrine disrupting activity characteristics.

SOCs enter the environment in several ways but the dominant route for their entry is primarily through discharges of wastewater-treatment plants (WWTPs) effluents, as presented in Fig. 45.1. Improved analytical methodologies have enabled researchers to lower the detection limits of these SOCs to a stringent reporting limit, ranging from µg/L (parts per billion or ppb) to ng/L (parts per trillion or ppt) levels, and for some individual compounds to pg/L (parts per quadrillion or ppq),

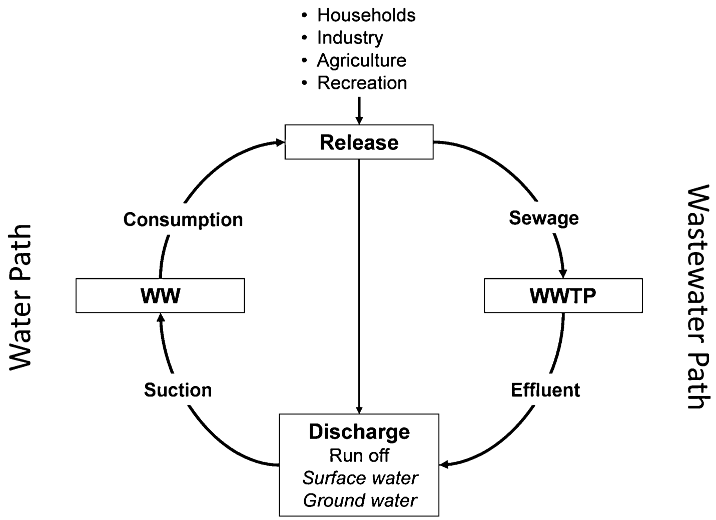

Fig. 45.1 Schematic diagram of synthetic organic compounds in the water cycle. *WW* water works, *WWTP* wastewater treatment plant

even in the most complex environmental matrixes. SOCs are referred to in the literature also as micropollutants, but due to their very low concentrations found in the environment they will be referred to as trace pollutants in this chapter. The establishment of SOCs' omnipresence in the water cycle around the globe led to a growing concern regarding the environmental fate of these compounds, in particular, with relation to the ability of current water and wastewater infrastructures to treat them, as well as to the ecotoxicological and human health risks associated with their occurrence. These questions arise particularly in the face of increasing demands for freshwater, which will probably lead to only greater incidences of indirect and direct water-reuse situations. As the required quality of the recycled water rises, pollution of drinking water sources with SOCs will be of great concern in such situations (Oliver et al. 2005).

The earliest reports on the presence of steroids and pharmaceuticals in United States wastewater effluents and even surface waters were published in the 1960s and 1970s, showing for the first time that steroids and human hormones were not completely eliminated via conventional WWTPs (Stumm-Zollinger and Fair 1965; Tabak and Bunch 1970; Garrison et al. 1976; Hignite and Azarnoff 1977; Aherne and Briggs 1989). Actually, at the beginning of 1990s researchers already showed that synthetic chemicals can interfere with the natural hormone system in the body (Walker and Janney 1930; Sluczewski and Roth 1948). However, until their occurrence in WWTPs effluents, especially that of a synthetic hormone, ethynylestradiol, used as a birth-control pharmaceutical, became linked to toxicological impact on fish found below wastewater outfalls, little attention was focused on these trace pollutants (Purdom et al. 1994; Gimeno et al. 1997; Arcand-Hoy et al. 1998; Kramer et al. 1998; Routledge et al. 1998; Snyder and Villeneuve 2001).

This chapter aims to review the application of pressure-driven membranes for removing trace organics present in water and wastewater and specifically the role of nonporous membranes, nanofiltration (NF), and reverse osmosis (RO). The tradeoffs in choosing less dense nonporous membranes (i.e., NF) over denser nonporous membranes (i.e., RO) were examined, and especially whether or not lowering operating pressures/increasing permeability would result in diminished permeate quality.

45.2 Advanced Wastewater Treatment Processes

Although it is infeasible to remove all trace pollutants to levels below the detection limit, especially of the modern analytical instrumentation, some treatment processes have been shown to be more effective than others. Secondary treatment, i.e., biological processes, such as conventional activated sludge (CAS), or even tertiary treatments, such as membrane bioreactors (MBR), sand filtration, biofiltration, or soil aquifer recharge, can only reduce the concentration of some of these compounds to a very partial extent, especially of those which are easily biodegradable and/or tend to sorb to sludge particles (Ternes et al. 1999a, b;

Table 45.1 SOCs transformation efficiencies for different wastewater treatments

Treatment technology	Removal range (%)
Primary settling	3–45
Coagulation, filtration, settling	5–36
CAS	0–99
MBR	0–100
Sand filtration	0–100
Extensive treatment (e.g., wetland, lagoon)	43–100
Activated carbon adsorption	25–99
Ozonation	54–100
UV irradiation	29
Photolysis (UV/H_2O_2)	52–100
Dark and light Fenton	80–100
UV/TiO_2	>95
Non thermal plasma (NTP)	70–100
Reverse Osmosis	85–100

Modified from Westerhoff et al. (2005), Oulton et al. (2010), Magureanu et al. (2010), WHO (2012), Gerrity et al. (2010), Gur-Reznik et al. (2011b)

Ternes and Hirsch 2000; Drewes et al. 2002; Petrović et al. 2003; Ashton et al. 2004; Snyder et al. 2004; Clara et al. 2005; Joss et al. 2005; Oulton et al. 2010; Kim et al. 2007; Kimura et al. 2007; Carballa et al. 2008; Stevens-Garmon et al. 2011). Primary treatments, such as coagulation, flocculation, and precipitation, are mostly ineffective in removing these trace contaminants (Ternes et al. 2002; Carballa et al. 2004, 2008; Westerhoff et al. 2005; Stevens-Garmon et al. 2011).

In Table 45.1, the ability of different wastewater purifying technologies to treat SOCs is compared. It should be taken under consideration that treatment conditions, SOCs type, or water matrixes were not always similar across the different treatments. The broad range of efficiencies, reported for CAS, MBR, and sand filtration in Table 45.1, highlights the inability of conventional wastewater treatment processes to remove trace pollutants. Indeed, WWTPs are not designed to treat SOCs, either by the conventional secondary treatment (CAS), or, with a slightly higher extent of treatment, by MBR or sand filtration. A somewhat narrower range found in wetlands may reflect some physical or physicochemical interactions with the solid matrix. Although many of the SOCs found in stream waters have chemical structures and physicochemical properties appropriate for microbial degradation, their negligible concentration (ng-μg/L) as compared to sewage organic matter (mg-g/L) makes them irrelevant for growth linked-microbial degradation.

Thus, in order to enable and ensure a safe wastewater recycle and a sustainable water cycle, advanced wastewater treatments, such as adsorption (i.e., activated carbon, organo-modified clays, chitosan composites), oxidation processes (i.e., wet and thermal oxidation, ozonation, advanced oxidation processes-AOP: UV/ TiO_2, H_2O_2/ozone, UV/H_2O_2, NTP), or tight membrane separation, have been studied in the literature. Trace organic contaminants present a particular challenge, since the treatment needs to combine high rate, efficient removal, and low cost. For most SOCs, the removal efficiencies are almost not known for post-treatment processes, such as membrane filtration, activated carbon adsorption/filtration, or advanced oxidation processes. Both adsorption and oxidation strongly depend on contact time, feed characteristics (chemical structure, initial concentration), background materials, and concentration (too low target-to-background material ratio makes treatment cost per unit mass excessive), and they leave behind inorganic contaminants. These characteristics explain the broad range of results reported (see Table 45.1), especially for AOPs in which some of the results refer only to initial oxidation whereas others refer to complete mineralization in pure water. Furthermore, in oxidation techniques partial oxidation may lead to toxic end products and, when applied directly to treat trace levels of pollutants in wastewater effluents, they often suffer from increased cost due to slow kinetics and high energy demand. Activated carbon is an expensive alternative because of the constant need for regeneration and the consequent loss of material. In addition, the removal capacity is limited by contact time, competition with organic matter, contaminant solubility, and carbon type (Westerhoff et al. 2005; Snyder et al. 2007; Gur-Reznik et al. 2008). Dense membranes, such as RO membranes, are a promising treatment configuration for the reclamation of municipal wastewater effluents with a median value of 98 % (Oulton et al. 2010) and with an important advantage, expressed in the range of the reported data, showing high and stringent removal efficiencies of 90–100 % (see Table 45.1).

Pressure driven-membrane separation systems using membranes such as RO or NF are being increasingly emphasized as a powerful tool for water and wastewater purification (Madwar and Tarazi 2003; Katz and Dosoretz 2008). They represent an important generic technology to deal with organic and inorganic effluent-derived contaminants, combining simplicity, versatility, and continuous processing of aqueous streams (Reith and Birkenhead 1998; Drewes et al. 2005; Watkinson et al. 2007). Furthermore, dense membrane separation does not require extensive use of chemicals and has small plant footprints (Schäfer 2001; Kunst and Kosuti 2008). Using dense membrane filtration, purified water can be obtained in a fast and continuous way, while trace pollutants and other organic contaminants are concentrated in a relatively small volume in the brines (concentrate). The actual costs of disposal or treatment of the resulting brine, which contains high concentrations of salts, organics, and biological components, constitute a limitation of this technique (van der Bruggen et al. 2003). The concentrations of SOCs might especially present a hazard with regard to potential (eco)-toxicological effects, if the brine is discharged directly into the aquatic environment. This makes it necessary to reduce brines' volumes and apply advanced low-cost-treatment technologies in order to reduce the concentrations of these trace pollutants in the concentrate, creating a full cycle of treatment and releasing innocuous brines to the aquatic environment. In addition, membrane fouling alters membrane surface characteristics, in addition to the permeate flux decline (Ivnitsky et al. 2005; Bishop 2007), and consequently impacts to some extent SOCs' removal (Xu et al. 2006; Agenson and Urase 2007; Nghiem and Coleman 2008; Verliefde et al. 2009). Likewise, changes in membrane characteristics due to chlorine (typically in the form of hypochlorite solution) or monochloramine residues, used for biofouling cleaning, have been shown to alter the separation process of trace organics by NF and RO membranes (Simon et al. 2009).

Over recent decades, the cost of membranes has decreased and fluxes have dramatically increased, making membranes an attractive technological solution for water and wastewater effluent treatment. Undoubtedly, effluents effective treatment is being increasingly emphasized as a strategy for conservation of limited resources of freshwater and as a means of safeguarding the aquatic environment. Indeed, the recycling of considerable amounts of wastewater from large cities can provide a reliable alternative supply to resolve the severe water shortages instead of other artificial water resources. Consequently, indirect potable reuse, through groundwater recharge and surface water augmentation, is expected to be the main focus of water reuse in the near future (Tchobanoglous 2009). Although dense membranes are the core technology for safe and sustainable water reuse and recycling, integrated processes are required to ensure maximal removal of all trace contaminants.

45.3 Membrane Separation Processes

A membrane process can be defined as the separation of a feed stream (containing pollutants that have to be removed) into a clean water stream (permeate) and a concentrated stream (concentrate or brine). Four membrane processes can be distinguished that apply hydraulic pressure as the driving force for the separation: microfiltration (MF) and ultrafiltration (UF), and nanofiltration and reverse osmosis. Two models are usually used to describe the dominant permeation mechanism through pressure-driven membranes (Fig. 45.2): the pore-flow model for microporous membranes (UF and MF) and the solution-diffusion model for separation in nonporous membranes (NF and RO). Electrical repulsion is also present to some extent, especially in nonporous membranes.

Pressure-driven separation membranes are often defined by the pressure applied across the membrane surface area and the molecular weight cut-off (MWCO) (or porosity) of the membrane, having a characteristic permeability (Table 45.2). While microfiltration (MF) and ultrafiltration (UF) are relatively capable of retaining particles colloids and macromolecules, NF and RO can also remove dissolved organic contaminants and single ions. Removal of solutes is usually referred to as rejection. Rejection of a given solute is defined as

$$\mathrm{R} = \frac{C_F - C_P}{C_F} \tag{45.1}$$

where, R is the rejection of the solute [%], and C_F and C_p are the mass concentration of the solute in the feed and permeate, respectively.

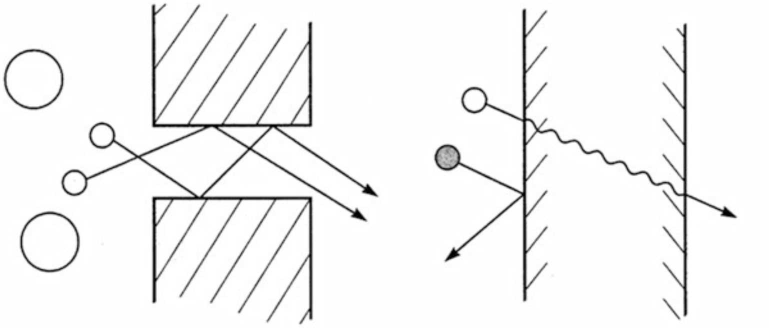

Fig. 45.2 Molecular transport through membranes (Reproduced from Baker 2004 with permission of John Wiley and Sons, 2014)

Table 45.2 Classification of pressure-driven membrane processes

Membrane	Applied pressure range (bar)	Permeability range ($L/m^2 \cdot h \cdot bar$)	MWCO		Application
			(nm)	Approximate Mw (kDa)	
Microfiltration (MF)	0.5–5	> 50	>100	>150	Removal of suspended particles
Ultrafiltration (UF)	1–10	10–50	10–100	10–150	Removal of suspended particles, viruses, and macromolecules
Nanofiltration (NF)	5–15	1.5–12	1–10	>0.2	Removal of multivalent salts, dissociated acids, and small organic molecules
Reverse osmosis (RO)	10–100	0.05–5	<1	≤ 0.2	Removal of all salts, undissociated acids and small organic molecules

Modified from Osmonics (1991), Baker (2004), Drewes et al. (2005), Verliefde (2008)

Most commercially available nonporous membranes for water and wastewater treatment are made of polyamide thin film composite (TFC) membranes, composed of three separate thin film layers: (i) a microporous polysulfone support layer, usually cast onto (ii) a nonwoven polyester inner web to contribute to the membrane overall mechanical strength, and (iii) an ultrathin polyamide active layer that is then applied by interfacial polymerization. The thickness and chemical structure of this polyamide skin layer range from 50 to 200 nm for a typical membrane, determining solute separation and permeate flux mainly by its morphology and chemical nature (Cadotte et al. 1980; Petersen 1993; Freger et al. 2002; Simon et al. 2009).

Cross-flow filtration is the most popular separation configuration in water and wastewater membrane-based purification processes. In cross-flow filtration, the feed stream flows parallel to the membrane walls, while the permeate stream flows perpendicularly toward the membrane walls, and the concentrate stream continues to flow to the exit of the membrane, parallel to the membrane walls. The permeate flux of an RO and ultra-low pressure RO system is generally limited to 13–20 Lm^{-2} h^{-1} in wastewater applications with operating pressures of 10–20 bar and a system recovery of 75–85 % due to fouling limitations. NF is still an evolving technology for wastewater reuse, and pilot-scale studies has reported a permeate flux of 20 Lm^{-2} h^{-1} with operating pressures of 4–5 bar and a system recovery of up to 82 % (Ivnitsky et al. 2005; Bellona and Drewes 2007).

45.4 SOCs Rejection Mechanisms and Trends

Knowledge of RO and NF's performance in rejecting trace organics has been acquired mainly through experimental work of bench- and pilot- to full-scale treatments, leading to a partial understanding of how trace organics are rejected by high-pressure membranes, and only a limited ability to predict rejections (Bellona et al. 2004). For example, bench-scale (Comerton et al. 2008; Kimura et al. 2009; Gur-Reznik et al. 2011a) as well as pilot- and full-scale studies (Snyder et al. 2007; Drewes et al. 2005) showed that in most cases dense membranes can provide an effective barrier for rejection of trace pollutants. However, several studies illustrated that some hydrophobic compounds, such as natural hormones and other neutrals and acid SOCs, can adsorb to the membrane and thus decrease to some extent the rejection, since upon saturation the compounds diffuse through the membrane (Salveson et al. 2000; Drewes et al. 2002; Kimura et al. 2004; Nghiem et al. 2004; Comerton et al. 2007). Thus, membrane preconditioning is essential to ensure that compound adsorption into and onto the membrane has reached equilibrium for a reasonable evaluation of the rejection. Nonetheless, Bellona and Drewes (2007) found during a pilot-scale study a high and constant rejection of approximately 95 % for nonionic hydrophobic solutes, such as steroid hormones, due to adsorption and partitioning. It was hypothesized that the organic fouling layer that was established over time served as an impermeable barrier for these compounds.

Removal of SOCs by membranes is a complex mechanism that can vary significantly. In general, there are three major interactions primarily affecting solute-membrane rejection, as summarized by Bellona et al. (2004) in a comprehensive literature review: *steric hindrance* (sieving effect), *electrostatic repulsion* (charge effect), and *hydrophobic-hydrophobic/adsorptive interactions* (Van der Waals) (Fig. 45.3). These solute-membrane interactions are determined by solute

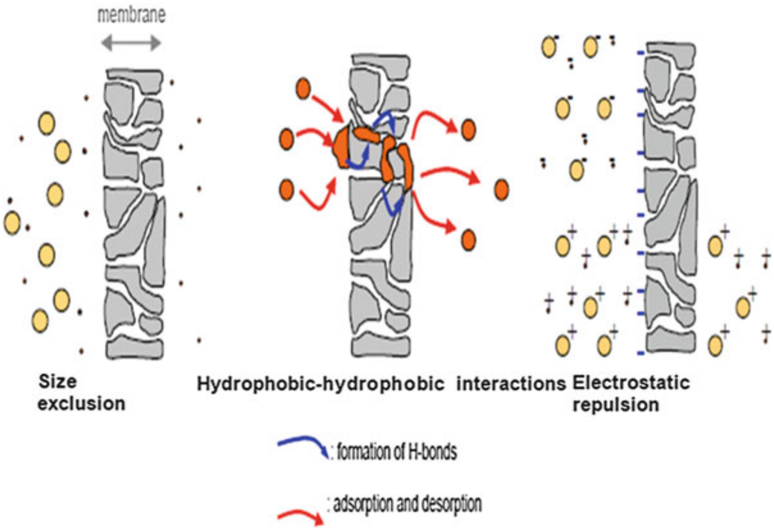

Fig. 45.3 Three major interactions primarily affecting solute-membrane rejection (Reproduced from Verliefde 2008 with permission of the authors, 2014)

properties (e.g., molecular weight, molecular size (length and width), charge (determined accordingly to the acid disassociation constant (pK_a) and the pH of the solution), diffusion coefficient and hydrophobicity (expressed by the octanol: water partitioning coefficient K_{OW}), membrane properties (such as MWCO/pore size, surface charge measured as zeta-potential, wettability measured as contact angle), surface morphology (measured as roughness) and operating conditions (e.g., pressure, flux, and permeate recovery), and solution chemistry (e.g. pH, temperature, DOC, inorganic matrix, and membrane fouling).

The rejection of SOCs by RO and NF membranes were reported in the literature on the background of different water matrixes; ultra-pure water (UPW), drinking water, wastewater influent and effluent, as well as synthetic and real matrixes. In general, organic matter has been observed both to increase and decrease compound rejection from these water matrixes (Kimura et al. 2004; Košutić et al. 2007; Nghiem et al. 2005; Park et al. 2004; Verliefde et al. 2009; Yoon et al. 2006; Yangali-Quintanilla et al. 2009). NF and RO rejections for different SOCs from either ultra-pure water or WWTP effluents gathered from different literature sources are summarized in Table 45.3. The comparison enables a true sense of the differences and tradeoffs when less dense (i.e., NF) and denser (i.e., RO) nonporous membranes are applied to remove trace pollutants.

Comerton et al. (2008) reported the rejection of 22 EDCs and PhACs as a function of water matrix properties (UPW, raw and filtered lake water, and MBR effluents) by two loose (NF270, Dow/Filmtec) and tight (TS80, TriSep/Goleta) NF membranes as compared to an RO (X20, TriSep/Goleta) membrane. They observed low and variable (1–70 %) rejections for the loose NF270 membranes (400 Da

Table 45.3 Comparative RO and NF reported rejections from UPW and WWTP effluents

	Membrane			
	UPW		Effluent	
Compound	Tight NF	RO	Tight NF	RO
Acetaminophen[a,b,c,d,e]	0	92 ± 1	0–95	50–100
Alachlor (Lasso)[a]	42 ± 3	97 ± 2	95 ± 1	97 ± 1
Atraton[a]	22 ± 9	97 ± 3	94 ± 2	97 ± 1
Bisphenol A[a]	26 ± 9	96 ± 2	87 ± 1	97 ± 1
Caffeine[a,b,c,d]	5 ± 4	95 ± 1	85–90	90–100
Carbadox[a]	2 ± 2	95 ± 1	91 ± 1	96 ± 2
Carbamazepine[a,f,g,b,c,d]	9–55	92–100	89–98	94–100
Clofibric acid[f,b]	73	100	93–100	79 ± 11
Diatrizoate[g]	97 ± 2	98 ± 1	98 ± 1	99 ± 1
DEET[a,b,c,d]	18 ± 6	96 ± 1	92–95	97–100
Diclofenac[f,b,c,d]	60	99 ± 0	98–100	95–100
Diethylstilbesterol[a]	75 ± 14	98 ± 1	90 ± 1	98 ± 1
Equilin[a]	42 ± 14	97 ± 1	91 ± 1	98 ± 1
Estriol[a,e]	24 ± 9	95 ± 2	50–94	50–96
Estrone[a,d]	39 ± 10	97 ± 1	93 ± 1	90–98
Gemfibrozil[a,b,d]	27 ± 14	97 ± 2	97–100	98–100
Ibuprofen[b,c,d,e]	–	93–100	98–99	95–100
Iopromide[g,d,e]	–	95–100	–	98–100
Ketoprofen[f,b,e]	55–85	100	78–100	93–100
Metolachlor[a]	51 ± 8	97 ± 1	95 ± 1	97 ± 1
Mefenamic acid[f]	70	98	94 ± 6	85 ± 10
Naproxen[b,c,d]	–	–	88–100	94–100
Oxybenzone[a,d]	95 ± 7	100 ± 0	94–100	94–100
Primidone[f,b]	60	100	85–100	100 ± 1
Sulfamethoxazole[a,b,c,d]	22 ± 4	96 ± 2	95–98	98–100

[a]Comerton et al. (2008). Tested membranes (TriSep/Goleta): NF (TS80); RO (X20). MBR effluent
[b]Bellona and Drewes (2007). Tested membrane: NF (NF4040, Dow/Filmtec). Tertiary effluent
[c]Kim et al. (2007). Tested membranes (Saehan): NF (NE4040-90-RF); RO (RE4040-FL). Tertiary effluent
[d]Snyder et al. (2007). Tested membranes: RO (Saehan, Hydranautics, Dow/Filmtec). MBR effluent
[e]Gur-Reznik and Dosoretz, unpublished results. Tested membranes (Dow/Filmtec): NF90; RO (XLE, BW, SW). Tertiary effluent
[f]Kimura et al. (2009). Tested membranes: NF (UTC60, Toray); RO (LF10, Nitto Denko). MBR effluent
[g]Gur-Reznik et al. (2011a). Tested membranes (Dow/Filmtec): NF90; RO (XLE, BW, SW). MBR effluent

MWCO), with higher rejections (0–93 %) when organic matter was present, whereas the RO membrane (MWCO <200 Da) provided an efficient (>90 %) and more steady removal. Kimura et al. (2009) also studied the influence of MBR and micro-filtered tertiary effluents (media filtration) on NF (UTC60, Toray) and RO (LF10, Nitto Denko) retentions of six pharmaceuticals. The membranes

(Dow/Filmtec) in this study were relatively dense, of 150 and 100 MWCO for NF and RO, respectively. They also observed an increase in the rejections when wastewater effluents were desalinated with an NF membrane as compared to UPW spiked with the pharmaceuticals. For the RO membrane, removal of the pharmaceuticals was high regardless of the pharmaceutical type or tested matrix. Complementary work by Gur-Reznik et al. (2011a) comparatively studied the rejection of carbamazepine and diatrizoate with three RO (BW, SW, and XLE) and two NF (NF90 and NF270) membranes. The findings showed that tight nonporous membranes (i.e., RO) exhibited high rejections of the compounds (>98 %), regardless of membrane resolution or conditions tested. In contrast, in loose nonporous membranes (i.e., NF), season and water matrix were both found to influence markedly the dissolved organic matter composition and consequently the rejection of low molecular weight compounds with medium hydrophobicity. These season-dependent interactions strengthened during the summer, increasing the removal of loose nonporous membranes, but weakened during the winter, reducing the rejection as a result.

The effect of membrane fouling on the rejection of trace organic contaminants has been addressed by several researchers and the conclusions drawn from these studies have been somewhat contradictory. Xu et al. (2006) determined that organic fouling resulted in an increased membrane surface charge as well as increased adsorption capacity, which resulted in an increased rejection of negatively charged organic solutes and hydrophobic organic solutes. They observed during bench-scale experiments a decrease in the rejection of hydrophilic nonionic organic solutes as membrane fouling increased, but found that the rejection of the majority of solutes investigated was enhanced by effluent organic matter fouling. Ng and Elimelech (2004), however, found during bench-scale experiments that colloidal silica fouling reduced the back-diffusion of organics present in feed water from the membrane surface to the bulk solution. Consequently, the buildup of solutes at the membrane surface resulted in a significant decreased rejection of hydrophilic and hydrophobic organic solutes, due to a higher solute concentration gradient across the membrane and a greater solute transport through the membrane as a result. The decline in hydrophobic steroid hormone rejection with time was more severe among the tested compounds when colloidal fouling took place.

Plakas et al. (2006) reported in the case of herbicides that calcium in the feed water lowered the removal in NF/RO membranes. Verliefde et al. (2008) showed that the addition of Ca^{2+} leads to a shielding of the NF membrane surface charge, which resulted in increased rejection values for positively charged SOCs and decreased rejection values for negatively charged compounds. For the neutral pharmaceuticals, neither Ca^{2+} addition nor the presence of natural organic matter influenced the rejection. Kimura et al. (2009) tested micro-filtered tertiary effluent (media filtration) versus MBR effluent and found that modification of the membrane surface due to fouling and association between the macromolecules and the pharmaceuticals contributed, in general, to the increase in removal of SOCs by the NF/RO membranes. They found that the more significant increase in NF retention as compared to the already high retention of RO following effluent filtration was mostly higher in the case of filtration of MBR effluent than in that of tertiary effluent and could be correlated to the zeta potential. The membrane surface became more negatively charged after fouling in the case of filtration of the tertiary effluent, whereas no detectable change in the zeta potential was seen after filtration of the MBR effluent. The membrane degradation affect due to chlorine attack on the rejection of three pharmaceuticals by NF and RO membranes was investigated by Simon et al. (2009). The RO (BW30, Dow/Filmtec) and the tight NF (NF90, Dow/Filmtec) membranes were much more resilient to chlorine exposure than the looser NF (TFC-SR2, Koch and NF270, Dow/Filmtec) membranes. Rejection of all three pharmaceuticals tested by the RO membrane remained largely unchanged after hypochlorite exposure, and further characterization did not reveal any evidence of compromised separation capability. In contrast, profound effects of chlorine degradation were observed for the two loose NF membranes, resulting mostly in reduced rejection, though a small increase in rejection was observed when exposed to a comparatively dilute hypochlorite solution.

Bellona and Drewes (2007) conducted a pilot-scale study employing NF (NF4040, Dow/Filmtec) membranes for treating 24 SOCs present in tertiary effluents at a water reuse facility prior to aquifer recharge. The NF membranes were compared to conventional full-scale RO (TFC-HR, Koch) membranes operating at the same water reuse facility. These researchers found a minimal amount of flux decline as a result of organic fouling during the total 1,200 h of NF operation. While the NF operating pressures were lower by a factor of 2–3 than the conventional RO membranes, rejection of SOCs varied between 80 and 100 % after 24 h of start-up, while the RO membrane had no detectable concentrations of any trace organic contaminants. Based on the MW of the nonionic compounds tested, they interpolated that the MWCO of the NF membrane was 200 Da. Interestingly, the NF rejections were observed to increase as operation continued and SOCs were rejected at a rate greater than 95 % after 800 h of operation. They hypothesized that organic fouling and to a lesser extent membrane compaction after a period of operation could lead to a higher degree of rejection for certain constituents by NF membranes. In an earlier work, Drewes et al. (2005) studied the rejection of 21 SOCs under conditions simulating full-scale ultra-low pressure RO installations. They compared a two-stage laboratory-scale membrane unit using single-elements vessels (TMG10, Toray versus ESNA1-LF, Hydranautics) with two full-scale facilities (both employing TFC-HR, Koch). They found rejections below the detection limit (ranging from 0.4 to 560 ng/L) with the exception of bisphenol-A (30 ng/L detection limit) in the laboratory experiments and caffeine (40 ng/L detection limit) in the full-scale studies. Snyder et al. (2007) extensively evaluated the rejection of 36 trace organic compounds present in wastewater effluents by RO at pilot- and full-scale. They tested the membranes of a variety of manufacturers (Saehan, Hydranautics, Dow, and Koch) and operation configurations. This group of researchers observed that RO was capable of removing nearly all target compounds to levels below method reporting limits (1–10 ng/L compound dependent), even though trace levels of some contaminants were still detected in RO permeates. The compounds that breached the RO membranes were not consistent, and no clear relationship between molecular structure and membrane breaching was established. The full-scale double-pass RO system showed that the second pass was able to remove compounds not entirely rejected during the first pass, demonstrating that a multi-barrier approach can be successful in the removal of SOCs.

Concluding Remarks

The findings presented here stress that dense nonporous membranes (i.e., RO) are required for a reliable and constant high quality of the effluents, whereas the rejection of less dense nonporous membranes (i.e., NF) is influenced by a variety of parameters, such as the SOC type, water matrix, and other operating conditions. Molecular sieving appears to be the main mechanism for the high rejection rate of most SOCs by RO membranes, regardless of the operating conditions and water matrix. This makes RO membranes the most generic core technology available for effluent purification, removing both organic and inorganic contaminants. A rejection diagram summarizing the key parameters affecting the rejection of SOCs by nonporous membranes is consequently presented in Fig. 45.4. This diagram intends to evaluate the true separation potential of nonporous membranes and therefore is based on a system following equilibration, thus neglecting adsorption phenomena on the membrane polymer. Some inconsistency may occur for very hydrophobic molecules with pKow > 4, which in any case have low to negligible water solubility. It should be noted that despite the numerous publications on SOC separation by nonporous membranes, there is still a lack of a systematic and comprehensive understanding regarding the factors affecting rejection in full-scale installations.

In conclusion, integrated advanced processes comprising dense nonporous membranes (i.e., RO) as a central stage are technologically feasible and environmentally compatible to ensure maximal removal of all trace contaminants from water and treatment process streams. Membranes are easily scalable as well as applicable to all kind of waters. While purified water is obtained in a fast and continuous way with membrane filtration, SOCs as well as other organic and inorganic contaminants are concentrated in a relatively small volume in the brine stream. Yet, treatment of RO brines is required for achieving a sustainable wastewater reuse, creating a full-cycle of treatment and releasing innocuous brines to the aquatic environment. Finally, we should bear in mind that advanced technologies will not be able to remove all trace pollutants completely to concentrations below the detection limits of the most sensitive analytical procedures at all times. Thus, advanced effluents treatment should be envisioned, with a reduction at source of synthetic chemicals and drugs, and treatment at source of concentrated streams.

(continued)

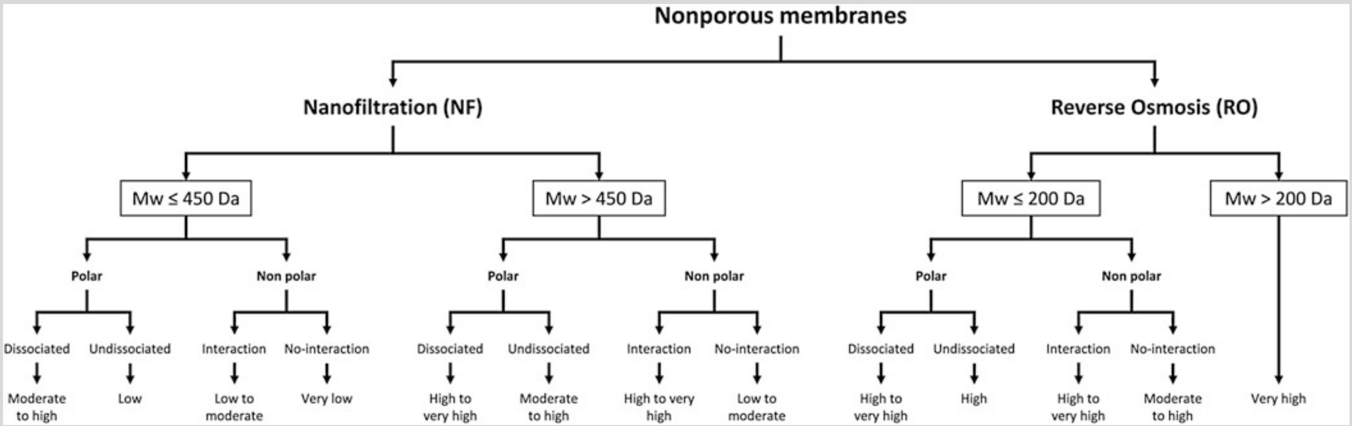

Fig. 45.4 Rejection diagram of SOCs by nonporous membranes following equilibration conditions (Modified from Bellona et al. 2004) *Mw* molecular weight

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Part XIV
Air Pollution

Chapter 46
Indoor Air Quality Indicators

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Abstract We spend almost 80–90 % of our time indoors and almost 2/3 of this time is spent at home. The built environment has been recognised as a key factor determining the overall exposure to airborne pollutants affecting human health and well-being. In this work the main indoor air pollution sources are outlined and the indoor air pollutants that require priority action in terms of management measures are described. These are the most prominent indicators of indoor air pollution to be used for comprehensive environmental management. Data requirements in terms of indoor air pollution indicators that may be used to understand better the source-to-exposure continuum and the interactions among the different components of indoor air are given in order to support the development of comprehensive approaches to indoor air health risks. Finally, recommendations on how to best fill the data gap with harmonized sampling and assessment methods at different spatial scales are given.

Keywords Indoor air pollution • Sources • Combined exposure • Harmonization • Data requirements • Sampling • Risk assessment • Spatial scales

46.1 Introduction

Millions of Europeans in modern society spend approximately 90 % of their time indoors, in their homes, workplaces, schools, and public spaces and it is estimated that approximately 2/3 of this time is spent at home. For many years, the housing environment has been acknowledged as one of the main settings that affect human health. Indoor air quality, home safety, noise, humidity, and mould growth, indoor temperature, volatile organic compounds (VOCs), lack of hygiene and sanitation equipment, and crowding are some of the most relevant health threats that can be found in dwellings (Saijo et al. 2004; Takigawa et al. 2004; Sarigiannis 2013). Many health problems are either directly or indirectly related to the quality of housing itself, because of the construction materials that were used and the

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_46

equipment installed, or the size or design of the individual dwellings, which affects disproportionally more vulnerable population groups in terms of socioeconomic status or class age (WHO 2007).

The most frequent exposure to health risks in the indoor environment pertain to chemical mixtures of pollutants that are almost ubiquitous in the indoor environment, such as carbonyls (e.g., formaldehyde and to a lesser extent acetaldehyde), volatile organic compounds such as phenolic compounds (e.g., benzene, toluene, ethylbenzene and xylenes, the so-called BTEX mixture,), and terpenes, particulate matter, and polyaromatic hydrocarbons; the latter are known carcinogens. Over the last decade a number of studies revealed the existence of a significant number of phthalates and brominated flame retardants in the indoor air. These substances, characterized as endocrine disruptors, have been associated with emissions from building materials, such as carpet lining and vinyl flooring, as well as emissions from consumer products that are now found at almost all residences, schools/kindergartens, and day care facilities, such as electronic goods and other inflammation-prone electric equipment. For the chemical mixtures identified as most frequent in the indoor space, additivity of effects was observed at the concentrations usually encountered in non-occupational settings.

The second most frequent combination of stressors includes the simultaneous and multiple exposure to air pollutant mixtures and biological stressors, such as mould/dampness and mite allergens. One can identify significant physicochemical and mechanical interactions mutually reinforcing the presence of these health stressors in the indoor environment. For example, the presence of dampness and mould in the walls of a residence tends to enhance wall brittleness and thus contribute to the indoor levels of ultrafine and fine particulate matter. Older, more brittle walls would be expected to release volatile and semi-volatile organic compounds at a higher rate than those in a younger house; at the same time adsorption of such compounds onto the walls increases due to the higher porosity and active surface of the wall material. More porous wall material, in turn, provides a very good substrate for mould growth when indoor humidity and dampness prevail. The epidemiological studies that have looked at the health effects of combined exposure to indoor chemicals (e.g., formaldehyde) and mould or mite allergens have shown that the actual effect on adverse health outcomes is more pronounced when compared to the effect observed after exposure to single pollutants.

In this chapter, the main indoor air pollution sources are outlined and the indoor air pollutants that require priority action in terms of management measures are described. These are the most prominent indicators of indoor air pollution to be used for comprehensive environmental management. Finally, the data requirements in terms of indoor air pollution indicators that may be used to understand better the source-to-exposure continuum and the interactions among the different components of indoor air are given as a contribution to the development of comprehensive approaches to indoor air health risks. In the closing section recommendations on how to best fill the data gap with harmonized sampling and assessment methods at different spatial scales are given (Cimino et al. 2008).

46.2 Indoor Air Pollutants and Their Sources

The causes of poor indoor air quality are many and diversified; they are of chemical and biological nature. Main chemical sources are combustion products of solid fuels, such as CO, CO_2, SO_2, NO_2, particulate matter ($PM_{1,}$ PM2.5, PM10), and volatile (benzene, toluene, carbonyls) or semi-volatile (phthalates, flame retardants, plasticizers) organic compounds and pesticides. Environmental tobacco smoke (ETS) represents another relevant source of indoor chemical pollutants. Finally, the so-called bio-pollutants, such as, animal dander, mites, and mould can be found in the indoor environment (Maroni et al. 1995).

There are, however, some differences between developing and developed countries, mainly related to energy consumption: the former still use crude biomass fuels (animal dung, wood, etc.) and coal, whilst the latter use mainly fossil fuels (natural gas, petroleum gas, petroleum products) (WHO 2005). However, both types of fuels produce toxic substances and dust, adversely affecting human health.

In developing countries, fuels represent the main cause of indoor pollution whilst in developed ones a major role is played by other sources, such as construction materials (e.g., asbestos), furniture (formaldehyde (HCHO) and acetaldehyde (CH_3CHO)), carpets, consumer products (e.g., varnishes, insecticides, detergents), moth clothes conservation and biocidal purposes (naphthalene), in-house insecticides and biocides, paper dust, and carbonless copy paper (Jaakkola and Jaakkola 2007).

Ventilation is one of the most important determinants of indoor air quality. Improper ventilation and presence of air-tight devices, installed for reducing energy consumption, prevent the indoor/outdoor air exchange and thus contribute to worsening indoor air quality. Low ventilation rates, as well as the carbon dioxide (CO_2) concentrations in indoor air, have been associated with health and perceived air quality outcomes (Seppänen et al. 1999). Ventilation rate has been associated also with work performance in office work and academic performance of school children (Seppänen et al. 2005; Schaughnessy et al. 2006; Wargocki and Wyon 2007). High temperature and humidity may also increase the indoor air levels of some pollutants and in particular of bio-pollutants.

There are three main domestic sources of indoor air pollution: loaded particle filters, computers and other electronic apparatus used indoors, and building materials (Fanger 2006). The former are very important because of their capacity to store chemical and biological pollutants. Ventilation, especially if mechanically forced, increases the emission of pollutants caught onto the filter, causing the paradoxical effect of not improving, but rather worsening, the air quality. Thus, it is recommended to frequently change or substitute them with other purifying air systems. Sources of poor indoor air quality may also be personal computers with CRT screens and building materials. Personal computers and other electronic apparatus can be strong emitters of brominated flame retardants. As regards building materials, concern is mainly raised by asbestos, a carcinogenic substance widely utilized in the past (IARC 1988, 2002); and phthalates, especially DEHP, emitted from materials such as linoleum (widely used in flooring).

Exposure to indoor air pollutants may occur directly by inhalation, or indirectly by ingestion of, e.g., dust, while volatile compounds such as formaldehyde and benzene are mainly present in the gas phase. Less volatile substances are also to some extent bound to particles and dust, and exposure via these carriers may contribute to the total exposure. Many semivolatiles, such as phthalates, flame retardants, PAHs, chlorophenols, pesticides, organotins, and metals, may be adsorbed to house dust (Butte and Heinzow 2002; Bornehag et al. 2004). Particles may abrade from materials containing the chemicals of interest, e.g., PVC particles containing phthalates. House dust forms a long-term sink, may be regularly resuspended, and represents a secondary source for pollutants. The particle size of house dust is, however, typically large and only a fraction of it is respirable (Butte and Heinzow 2002; Maertens et al. 2004). Ingestion is likely the main exposure route for house dust (Butte and Heinzow 2002) in small children due to licking and biting on articles and "hand-to-mouth" behaviour. Small children spend a considerable part of their time on the floor and may thus be more exposed to re-suspended dust than adults. The particle/dust pathway has been shown to be an important exposure route, e.g., for polybrominated diphenyl ethers (PBDEs). Exposure to dust may account for about 14 % of the external exposure of those substances for adults, but over 90 % for children in the age range of 1–4 years (Shoeib et al. 2004; Stapleton et al. 2005; Wilford et al. 2005). However, there is insufficient information in general as to the extent to which the exposure to dust actually leads to uptake of pollutants in children.

The following table summarises major indoor air pollutants and their sources (Table 46.1):

Table 46.1 Major indoor air pollutants and their sources

Pollutant	Emission source
Asbestos, MMMF (man-made mineral fibers)	Remodelling/demolition/deterioration of construction materials
PM10, PM2.5, other fine particles	Fuel combustion, cleaning, cooking, ETS, inkjet and laser printers
CO	Fuel combustion, ETS
NO_2	Fuel combustion
Ozone	Photo copiers, laser printers, air purifiers, from outside
PAHs	Fuel combustion, cooking, ETS
VOC/SVOC	Fuel combustion, consumer products, cooking, ETS, furnishings, construction materials
Formaldehyde	Building materials, cooking, furnishings, consumer products
Lead	Remodelling/demolition of painted surfaces
Pesticides	Consumer products, carpets, textiles, dust
Biological pollutants	Moist areas, ventilation systems, furnishings
EMF-ELF	Household appliances, electric cables
Radon	Soil under building, construction materials

46.3 Priority Indoor Pollutants in Terms of Level and Severity of Exposure

More than 900 organic compounds have been detected in indoor air in the EU, in addition to fine and ultrafine particles and biological material (microbes, allergens). Availability of data on exposures to specific chemicals, and their toxicity and associated health risks are highly variable. Therefore, a priority ranking of chemicals and exposures that cause concern is difficult and uncertain. However, the European Commission's Scientific Committee on Health and Emerging Risks (SCHER) considers that **formaldehyde, carbon monoxide, nitrogen dioxide, benzene, naphthalene, environmental tobacco smoke (ETS), radon, lead, and organophosphate pesticides** are compounds of concern in indoor environments.

According to the INDEX project (Kotzias et al. 2005), co-ordinated by the European Commission's Joint Research Centre, the highest priority chemicals were **formaldehyde, carbon monoxide, nitrogen dioxide, benzene, and naphthalene**. These may occur indoors in high concentrations due to indoor sources; they have uncontested individual and public health impacts, and effective risk management options are known. A second priority list includes **acetaldehyde, o-, m- and p-xylene, toluene, and styrene**. These chemicals are commonly found in indoor air and they do exhibit toxic characteristics. Their indoor air concentrations, however, are usually orders of magnitude below their lowest observed adverse effect levels (LOAEL). They do, nonetheless, contribute to annoyance, irritation, and ammonia, and also to the perception of poor indoor air quality, and they may contribute to the so-called "cocktail effects" (observable adverse effect of a complex chemical mixture in which each individual component exists clearly below its LOAEL concentration). A third list of chemicals, including **ammonia, d-limonene and α-pinene,** was identified, for which further research on exposure and dose-response relationships is required (Cimino et al. 2008).

Several studies have reported associations between VOCs and asthma symptoms. However, a recent comprehensive review found no consistent association between the commonly measured indoor VOC exposures and onset of new asthma cases (Nielsen et al. 2007). Altogether, the available evidence on VOCs as causing health effects in indoor environment is not conclusive; VOCs may, nonetheless, be indicators for the presence of other stressors contributing to health effects. More recently, reaction products formed in indoor air have been investigated. Terpenes may react with ozone to produce secondary reaction products (Wolkoff et al. 2006). Limonene reacts with ozone and has been reported to produce both gaseous reaction products and fine and ultrafine particles. The highest terpene concentrations also produced high particle levels (Sarwar et al. 2004).

Several other pollutants react in indoor air and on surfaces producing known and as yet unknown reaction products (Weschler 2006). In some studies, the reaction products have shown irritating properties (Clausen et al. 2001; Nøjgaard et al. 2005) and poor perceived air quality (Tamás et al. 2006) at terpene and ozone concentrations that can be present in indoor air. Adverse health effects have not been observed in all studies (Laumbach et al. 2005; Fiedler et al. 2005). Altogether, the concentrations of VOCs and ozone causing mixture effects are as yet poorly known (Weschler 2000). In addition to the compounds emitted from the intact materials in the indoor environment, there may also be new compounds formed due to decomposition of the materials. The glue used to fasten PVC flooring can be hydrolysed by water (dampness) from the underlying material, especially if it is concrete with a high pH. The compounds released from material decomposition should be identified and their potential health effects evaluated.

Typical micro-environmental and personal exposure concentrations as summarized from several population studies are given in the table below. These data cover priority organic compounds such as aromatics, aldehydes, and terpenes, as well as classical pollutants such as **CO** and $\mathbf{NO_2}$. A comparative view of the summary results indicates that indoor concentrations are significantly higher than outdoor values, while personal exposure concentrations are much higher than both. Work environments are generally characterized by slightly higher pollution levels than residential spaces, most likely due to the existence of strongly emitting sources in occupational settings (Table 46.2).

These compounds are of concern because they have caused adverse health effects as indoor pollutants or have a high potential to cause health effects. However, the concern is not similar all over in Europe due to different exposure levels (see Figs. 46.1 and 46.2). For example, limited data on air fresheners indicate that burning of incense may produce abnormally high benzene and formaldehyde emissions in indoor air (SCHER 2006).

Table 46.2 Typical European microenvironmental and exposure concentrations ($\mu g/m^3$, except CO, which is given in mg/m^3)

	In[a]	W[a]	Out[a]	P[a]
Aromatics				
Benzene	2–13	4–14	1–21	3–23
Naphthalene	1–90	2–8	1–4	2–46
Styrene	1–6	3–7	1–2	1–5
Toluene	15–74	25–69	3–43	25–130
m&p-Xylenes	4–37	25–121	2–23	25–55
o-Xylene	2–12	7–29	1–8	8–15
Aldehydes				
Acetaldehyde	10–18	3	1–2	8
Formaldehyde	7–79	12	2–4	21–31
Terpenes				
a- Pinene	11–23	1–17	1–7	7–18
Limonene	6–83	11–23	5–9	19–56
Classical pollutants				
CO	0.5–1	1	2	0.8–1.7
NO_2	13–62	27–36	24–61	25–43

[a]In, W, Out, P = Indoor, workplace, outdoor and personal exposure concentrations

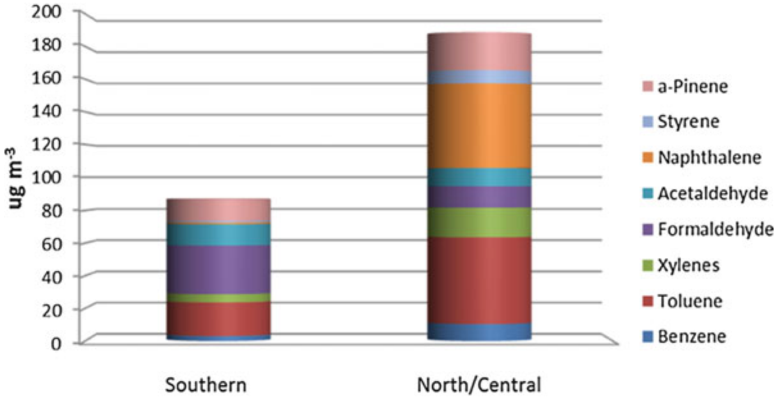

Fig. 46.1 Multiple exposures to major organic compounds in residential settings in Europe (Data from Sarigiannis et al. 2011)

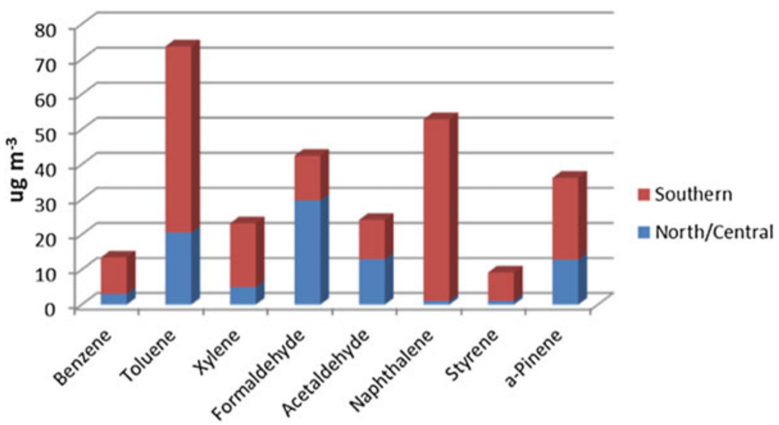

Fig. 46.2 Concentration of major organic compounds in residential settings in Europe (Data from Sarigiannis et al. 2011, 2012a, b)

Tobacco smoking is the primary source of several emissions (benzene, fine and ultrafine particles) indoors and associated health effects. Environmental tobacco smoke (ETS) is the mixture of smoke that comes from the burning end of a cigarette, pipe, or cigar, and smoke exhaled by the smoker. It is a complex mixture of over 4,000 compounds, more than 40 of which are known to cause cancer in humans or animals and many of which are strong irritants. In adults, ETS has been associated, e.g., with coronary heart disease, sensory irritation, and exacerbation of respiratory symptoms, including asthma (IARC 2004). In children, the association between infant sudden death syndrome and middle ear infections and ETS has been observed (Tamburlini et al. 2002; DiFranza et al. 2004). The evidence clearly indicates that **ETS** requires risk management and, as such, it should be used as a key indoor air pollution indicator.

Radon in indoor air has been associated with lung cancer (WHO 2009). According to a recent analysis of European epidemiological studies (Darby et al. 2005), radon may be a common problem in Europe. Radon gas diffuses through soil into residences in areas where bedrock contains an excess of uranium. Indoor radon concentrations can be decreased by technical means, even in existing buildings. Data on residential radon concentrations should be obtained by measurements in countries where such data do not yet exist in order to permit the comprehensive assessment of the associated health risk.

Paint-related **lead** still exists in indoor environment in old houses in some EU countries, although its use has been restricted or banned in indoor paints. Children are especially exposed through non-dietary ingestion of dust. Exposure from other sources may be significant (TNO 2005) and the evidence is increasing that low-level exposure of children to lead is already harmful (e.g., Lanphear et al. 2005). Therefore, it is essential to evaluate whether the lead level in indoor environments is still a problem in EU countries. The existing data on lead should be compiled, and thereafter, the need for further research considered.

The indoor use of **organophosphate pesticides** for treatment of cracks and crevices (Byrne et al. 1998) or the use of insect strips (Weis et al. 1998) may lead to high exposures to these compounds by inhalation or ingestion due to accumulation on surfaces, including children's toys (Hore et al. 2005) and house dust (Butte and Heinzow 2002). This uptake may contribute considerably to the overall uptake of organophosphates by children (Gurunathan et al. 1998). The acute toxicity of organophosphate pesticides is well known (WHO 2004); however, it is very unlikely that indoor levels can result in acute effects. Recently, neurodevelopmental effects have been reported both in experimental animals (Aldridge et al. 2005) and humans (Berkowitz et al. 2004), raising concern about possible effects in children from the use of organophosphates in the indoor environment.

Phthalates are common contaminants in the indoor environment, occurring both in house dust and indoor air, and di(2-ethylhexyl) phthalate (DEHP) is the dominant component (Øie et al. 1997; Rudel et al. 2003; Fromme et al. 2004). The PVC flooring material is an important source of phthalates, but several other sources contribute in indoor environments (Bornehag et al. 2005). PVC products indoors (different surface materials) have been associated with airway effects in epidemiological studies (Jaakkola et al. 2006).

Polybrominated diphenyl ethers (PBDEs) are classes of brominated hydrocarbons, also referred to as **brominated flame retardant** (BFR) chemicals. They are structurally similar, containing a central biphenyl structure surrounded by up to 10 bromine atoms, and they are used in a wide variety of products, including furniture, upholstery, electrical equipment, electronic devices, textiles, and others. Due to their physicochemical properties, when released into the air they tend to adsorb onto particulates and dust (Huber et al. 2011). Thus, many studies (Frederiksen et al. 2009) have shown that the indoor environment, mainly indoor dust, is a significant source of exposure to PBDEs, especially for younger children because of their behavioral patterns, e.g., putting fingers, toys, and other items in their mouth (Góralczyk et al. 2012).

Biological contaminants comprise bacteria, mould, mildew, viruses, animal dander and cat saliva, house dust mites, cockroaches, and pollen. There are many sources of these pollutants. Pollen originates from plants; viruses are transmitted by people and animals; bacteria are carried by people, animals, and soil and plant debris; and household pets are sources of saliva and animal dander. The protein in urine from rats and mice is a potent allergen. When it dries, it can become airborne. Contaminated central air handling systems can become breeding grounds for mould, mildew, and other sources of biological contaminants, and can then distribute these contaminants through the home.

46.4 Indicator Data Needed to Support Indoor Air Quality Management

Emissions of chemicals may occur from building materials, cooking activities, cleaning activities, heating, and combustion of biomass fuels in general, but the exposure patterns are not sufficiently known. Models have been developed to predict the emissions and distribution patterns of pollutants. Such models are essential for the development of indoor exposure and risk assessment (ECA 2006; Kephalopoulos et al. 2007). The INTERA project, supported by the European Federation of Chemical Industries long-range research initiative, offers a comprehensive validated general model for indoor air pollution risks (Sarigiannis et al. 2012b). Modelling of chemicals is the most advanced to date. At present, however, no reliable model for exposure to indoor air microbial pollution exists.

The frequent focus on VOCs and other selected compounds in measurement campaigns may neglect a possible impact of compounds with high toxicity present in low concentrations or of compounds that are difficult to detect by the procedures applied. The whole exposure range, not only average or median exposures, should be considered for risk characterisation and, if needed, risk management. Variations in exposure may expand over several orders of magnitude. Analysis of EXPOLIS study data on VOCs has shown that the group at the upper 95 % end of the distribution may get exposed significantly more than the median group (Edwards et al. 2005). This finding has been corroborated by later studies of the JRC and the Aristotle University of Thessaloniki (AUTh) on the basis of exposure data from the AIRMEX measurement campaigns (Kotzias et al. 2009; Sarigiannis et al. 2011). On the other hand, the most sensitive subgroups may react at notably lower exposures. Accordingly, the whole range of exposure concentration estimates (not only the central estimate) is useful. Considering the variability and complexity encountered in the indoor environment (which is compounded by differences in consumer behaviour and national/regional habits), the data for risk assessment (and therefore, science-based risk management) are scarce and to a large extent insufficient.

The main current gaps and data requirements for a science-based management of indoor air pollution are summarised here below.

Data requirements and gaps in knowledge related primarily to identification and exposure to pollutants:

- Comprehensive review of the existing data on the indoor air pollutants; definition of the major indicator pollutants and their concentrations range in each Member State of EU; and the setting up of a pan European database. The database could be a part of a relevant existing information source. The process would compile the existing information on indoor pollutants, including allergens, as background for future work, and would facilitate the use of the data at the EU and global levels, to identify differences among member states and data gaps. This information could drive both possible regular monitoring programs and future research.
- Source apportionment of the pollutants in indoor environments, including ambient air, preferably in quantitative terms. Identification of the main sources would help their mitigation.
- Research on emissions of chemicals from consumer products. More data on the levels of the emissions in realistic use situations are needed in view of the large part of population handling such products.
- Information on harmful emissions in water damaged buildings, including compounds from decomposing building material, contributing to toxicity.
- Evaluation of potentially harmful emissions from indoor combustion processes (e.g., halogenated dioxins). Low burning temperature may favour production of halogenated dioxins.

Conclusions

Currently, there is no Community or national legislation in Europe that prescribes explicitly a monitoring and control program for indoor air quality in non-occupational settings. Consequently, no EU-wide systematic indoor air monitoring data exist. Harmonized criteria on monitoring requirements and the development of harmonized protocols will improve exposure assessment of indoor air pollutants. The harmonized protocols must include pollutants to be measured, standardized analytical techniques to be employed, survey designs (including standardized questionnaires), target locations for measuring exposure (e.g., kindergartens, schools, offices, private dwellings, day care centres, hospitals, and transportation vehicles), periods and frequencies of measurements, range and distributions of concentrations, target population groups (general public, susceptible groups, etc.) and statistical tools for data evaluation. In view of optimizing the exposure assessment procedure, while containing the sampling/measurements cost, the following criteria are

(continued)

suggested for a sampling protocol framework towards harmonization in indoor air measurements (Sarigiannis et al. 2011):

- The number of samples should be representative of the population.
- The distribution of samplers within the city. This is very important since within the limits of a large urban agglomeration, the intra-urban variability of indoor air concentrations is in general seen to be higher than inter-urban or, even, inter-country variability for the same climatic zone.
- Sampling in residential and non-residential locations. Indoor air concentration data are needed from the majority of the locations encountered by the population; thus, besides dwellings, a significant number of samplers (about one third) should be placed in nonresidential locations. Special attention should be paid to children, considering that they constitute the most vulnerable group among the members of a population from the point of view of public health. At least half the sample taking efforts in non-residential locations should be devoted to assessing indoor air quality in schools and kindergartens. The following locations are characteristic for designing a representative indoor air survey:
  - City centre
  - Suburban/residential
  - Urban background
  - Rural background
  - Sites in proximity to major roads/streets
  - Sites in proximity to specific industrial site(s)
  - Specific source/target-oriented (e.g., garages, car parks, tunnels, schools, hospitals, kindergartens, public buildings, etc.).
- Sampling distribution within the country. Target cities should be clustered by relevance criteria; one city from each cluster should be the field of a measurement campaign as described above. The criteria for clustering the cities refer to either a) strong outdoor sources/high concentrations, which affect the indoor concentrations by penetration of ambient air indoors; or b) purely indoor emission processes and sources. Possible clustering criteria should comprise:
  - degree of urbanization and population density, which affects traffic volumes and ambient air pollution
  - meteorological conditions and local topography, which affect indoor-to-outdoor air interactions, as well as the use of ventilation, heating or cooling devices etc.
  - existence of industrial sites or power generation plants near the urban location

(continued)

  - socioeconomic status of the urban population, a parameter which affects consumer products choice, use pattern and consequently indoor air emissions
  - information on the specific building materials and consumer products/apparatus used in the indoor environment sampled.

- Duration and type of sampling. A combination of active and passive samplings as proposed by Karakitsios et al. (2010) is the method of choice. Passive sampling is adequate for giving an overview at low temporal resolution and wide areas can be included with relatively low cost. However, for optimizing the assessment procedure, active sampling should be applied in addition, in order to capture the indoor air quality dynamics under specific activities accompanied by strong emissions. In the frame of indoor air exposure assessment, active sampling measurements can target specific activities and microenvironments, elucidating thus their respective role in the definition of the overall exposure profile. On the contrary, passive sampling measurements demand a sufficiently high number of volunteers, making it difficult to represent homogeneously the exposure pattern of the population.
- Repetition of the sampling. Seasonal variation might significantly alter indoor concentrations due to differences in ventilation, indoor/outdoor interaction, use of space heating, etc. At least a two-season campaign (winter and summer) is necessary in each sampling location.

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Part XV
Environmental Health

Chapter 47
Environmental Burden of Diseases

Otto Hänninen

Abstract Environmental exposures are associated with a large variety of human diseases ranging from headaches and annoyance to cancer and premature death. Comparison of such risks and prioritization of preventive measures therefore cannot be based on incidence or prevalence rates. Environmental burden of disease methodology, developed by World Health Organization, accounts for both years of life lost due to mortality as well as years lived with various disabilities. The latter are quantified using, besides the duration of the condition, a severity weight. Such weights are inherently value-loaded, but in practice the resulting environmental burden of disease estimates have been found very useful.

Improved population health registries and harmonization of disease codes together with statistical methods such as population attributable fraction that can be estimated from epidemiological data, allow for rapid and comparable international assessments as demonstrated e.g. by the Institute of Health Metrics and Evaluation.

Recent estimates suggest that fine particles (PM2.5) are the leading environmental health risk in European countries by causing up to 10,000 non-discounted lost years of health per million people annually in the EU.

Keywords Burden of disease • Health risk characterization • Population attributable fraction • Disability adjusted life year • DALY

47.1 Introduction

Environmental indicators are designed to describe the state of the environment and its impact on human beings, ecosystems and materials, the pressures on the environment, and the driving forces and the responses steering the system. Indicators have gone through a selection and often an aggregation process to enable them to steer action (EEA 2012). First order environmental indicators focus on the state of the environment. However, comparison of the importance of the state descriptors across a wide range of indicators is not directly supported. Therefore, a second order of indicators is needed to translate the state into the magnitude of impacts.

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_47

This section of the book covers indicators that focus on impacts on human beings and especially on population health. This is achieved by combining information on the state of the environment, determining the population exposures to risk factors, with population characteristics, including age and gender distributions and health status, to generate a ranking of environmental stressors based on their population health importance. One of these approaches is called environmental burden of disease (EBD) and is the topic of this chapter.

47.2 Background

Prevention and control of disease and injury require information about the leading medical causes of illness and the associated exposures and risk factors (Murray and Lopez 1997). Assessment of the public-health importance of various risk factors involves comparisons of highly variable health conditions ranging from relatively mild diseases, such as the common cold or sleep disturbance, to serious life threatening and fatal conditions. Up to the 1990s, mortality statistics were used as a crude metric for serious health hazards and they have served quite well over the decades for tackling the most important causes of death. However, mortality counts can hardly be compared with less severe outcomes when investigating the overall burden over a wide range of diseases and risk factors.

The World Bank sponsored the first global burden of disease study in collaboration with the World Health Organization (WHO) in 1993. As well as generating a comprehensive and consistent set of estimates of mortality and morbidity by age, sex and region for the world, the study also introduced a new metric to measure the loss of health to quantify the burden of disease: disability adjusted life year (DALY) (Mathers et al. 2004). Burden of disease (BoD), measured in DALYs, combines health losses from premature mortality and from morbidity into a metric that allows comparisons of the health losses due to a wide range of different causes, accounting for morbidity as well as mortality. Moreover, also the quantification of deaths is enhanced from body counts to quantify the years of life lost due to mortality. Figure 47.1 depicts some examples of disability weighted health conditions.

47.3 Methods

Burden of disease is a measure of sickness and death in a population. The burden of disease methodology is based on making years lived with a disability (YLD) comparable with years of life lost (YLL) due to premature mortality. Summing

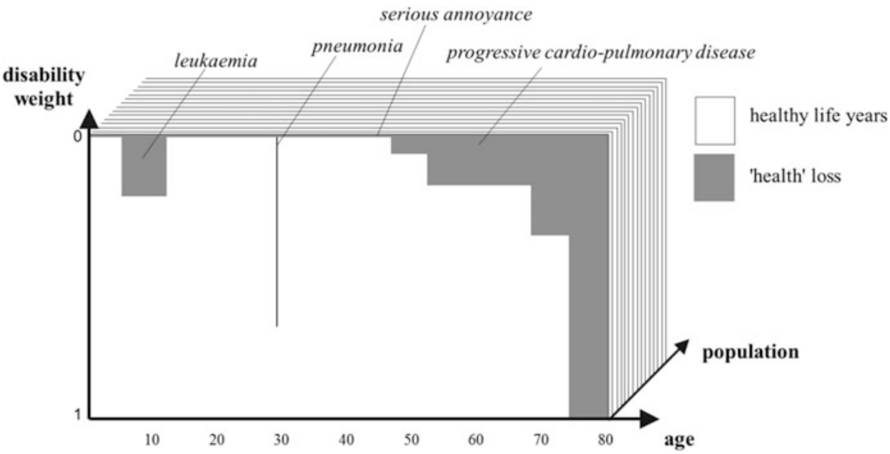

Fig. 47.1 Examples of disability adjusted life-year losses due to various diseases (*grey* areas) (Modified from de Hollander et al. 1999)

these two components produces disability adjusted life years (DALY) (Murray and Lopez 1997):

$$BoD = YLL + YLD \tag{47.1}$$

Years of life lost (YLL) in a case of premature mortality are calculated as the age-specific remaining life expectancy at the age of death. Mortality numbers, ages of death by causes, incidences of acute and chronic diseases and corresponding mean durations available in health registries are supplemented with disability weights.

Disabilities caused by various types of diseases are calculated by accounting for both the duration of the disease (L) and the disease severity expressed as a disease specific disability weight (DW):

$$YLD = DW \times L \tag{47.2}$$

The value of the time lived in non-fatal health states, in comparison with life lost due to premature mortality, is estimated using health state weights reflecting social preferences for different states of health.

Although the disability weights used in DALY calculations quantify societal preferences for different health states, the weights do not represent the lived experience of any disability or health state, or imply any societal value for the person in a disability or health state. Rather, they quantify societal preferences for health states in relation to the societal ideal of good health. The term “disability” is used broadly to refer to departures from good or ideal health in any of the important domains of health. These include mobility, self-care, participation in usual activities, pain and discomfort, anxiety and depression, and cognitive impairment (Prüss-Üstün et al. 2003). Examples of disability weight values, collected from dedicated

Table 47.1 Examples of disability weights (Adopted from Murray and Lopez 1996)

Disease	Disability weight	
	Untreated disease	Treated disease
AIDS	0.50	0.50
Infertility	0.18	0.18
Diarrhoea disease, episodes	0.11	0.11
Measles episode	0.15	0.15
Tuberculosis	0.27	0.27
Malaria, episodes	0.20	0.20
Trachoma, blindness	0.60	0.49
Trachoma, low vision	0.24	0.24
Lower respiratory tract infection, episodes	0.28	0.28
Lower respiratory tract infection, chronic	0.01	0.01
Cancers, terminal stage	0.81	0.81
Diabetes mellitus cases (uncomplicated)	0.01	0.03
Unipolar major depression, episodes	0.60	0.30
Alcohol dependence syndrome	0.18	0.18
Parkinson disease cases	0.39	0.32
Alzheimer disease cases	0.64	0.64
Post-traumatic stress disorder	0.11	0.11
Angina pectoris	0.23	0.10
Congestive heart failure	0.32	0.17
Chronic obstructive lung disease, symptoma	0.43	0.39
Asthma, cases	0.10	0.06
Deafness	0.22	0.17
Benign prostatic hypertrophy	0.04	0.04
Osteoarthritis, symptomatic hip or knee	0.16	0.11
Brain injury, long-term sequelae	0.41	0.35
Spinal cord injury	0.73	0.73
Sprains	0.06	0.06
Burns (>60 %) – long term	0.25	0.25

questionnaire panels, are shown in Table 47.1. Treatment of diseases further modifies the diseases and the disabilities. In many cases a treated disease is substantially less disabling than a non-treated disease. These differences are highlighted in the table, too. More data on disability weights can be found in Opasnet 2014.

47.4 Population Attributable Fractions

In practice, burden of disease estimates describe the overall burden in a population and generally only a small fraction of this is attributable to given environmental and other risk factors.

Burden of disease can be estimated using a bottom-up approach described in Eqs. 47.1 and 47.2. However, the mathematical properties of relative risks offer a lucratively easy way to estimate the fraction of disease burden associated with a given risk factor when epidemiological data are available. In 1953, Levin first proposed the concept of the population attributable fraction. Since then, the phrases "population attributable risk," "population attributable risk proportion," "excess fraction," and "etiologic fraction" have been used interchangeably to refer to the proportion of disease risk in a population that can be attributed to the causal effects of a risk factor or set of factors (Rockhill et al. 1998).

In this context, the environmental burden of disease associated with a given risk factor can be calculated simply from the overall population burden of a given disease by multiplying it by the epidemiological estimate of the population attributable fraction. National background burden of disease data are directly available from the World Health Organization (2013).

$$EBD = PAF \times BoD \tag{47.3}$$

As described in more detail in Hänninen and Knol (2011), the population attributable fraction (*PAF*) can be derived from relative risk (RR) as

$$PAF = \frac{f \times (RR - 1)}{f \times (RR - 1) + 1} \tag{47.4}$$

where f is the fraction of population exposed to a given factor and RR is the relative risk of the exposed population.

In the case of environmental exposures, the relative risk is commonly expressed per a standard increment of exposures, e.g., 10 μg m^{-3} as in the case of fine particles (in this case, exposure to e.g., 15 μg m^{-3} would be expressed as E = 1.5). The needed relative risk at the current exposure level can be directly calculated as

$$RR = e^{(E \ln RR^{\circ})} = RR^{\circ E} \tag{47.5}$$

47.5 Assessments

Murray and Lopez (1997) developed the first global burden of disease study. At that time, they considered two environmental risk factors: (i) poor water, sanitation, and hygiene, and (ii) air pollution. In the updates of the global burden of disease project for 2002 (World Health Report 2002) and 2004 (World Health Organization 2009), additional environmental risk factors included: (iii) lead, (iv) indoor air pollution from solid fuels, and (v) climate change.

One of the first more comprehensive analyses of environmental burden of diseases from a number of risk factors was conducted by de Hollander et al. (1999) in the Netherlands. The 19 environmental risk factors covered are

Table 47.2 Estimated health impacts of selected environmental risk factors in the Netherlands (Hollander et al. 1999), demonstrating that the population level health risks are dominated by a few risk factors (particulate matter and accidents in this case)

	Environmental factor	Included health end-points	Total health impact	Relative contribution (%)
			DALY/a/M	
1	Particulate air pollution (long-term exposures)	Total and cardiopulmonary mortality, lung cancer, chronic respiratory symptoms in children, chronic bronchitis	15,482	52
2	Domestic accidents	Hospital admissions, disability, mortality	6,390	21
3	Traffic accidents	Hospital admissions, disability, mortality	4,640	16
4	Noise	Severe annoyance, sleep disturbance	1,774	5.9
5	Lead (drinking-water pipes)		469	1.6
6	Foodborne	Acute gastroenteritis, symptoms and mortality	266	0.89
7	ETS	Lung cancer and ischemic heart disease mortality and morbidity, asthma aggravation, lower respiratory tract symptoms, otitis media, sudden infant death	262	0.88
8	Particulate air pollution (short-term exposures)	Respiratory, coronary heart disease, pneumonia, and other mortality, respiratory and cardiovascular hospital admissions, respiratory emergency room visits, asthmatic attacks, use of bronchodilators, upper and lower respiratory tract symptoms	172	0.58
9	Radon (indoor)	Lung cancer mortality and morbidity	114	0.38
10	Damp houses	Lower respiratory disease, asthma	109	0.37
11	Ozone air pollution	Respiratory, cardiovascular, pneumonia, and other mortality	87	0.29
12	UV-A/UV-B exposure	Melanoma mortality and morbidity	30	0.10
13	B(a)P	Respiratory disease hospital admissions and emergency room visits	16	0.053
14	Benzene	Leukemia mortality and morbidity	7.9	0.026
15	Large industrial accidents	Mortality	1.3	0.0044
16	Vinyl chloride	Hepatoangiosarcoma mortality and morbidity	0.79	0.0027
17	Ethylene oxide	Leukemia mortality and morbidity	0.11	0.0004
18	1,2-Dichloroethane	Cancer mortality and morbidity	0.10	0.0003
19	Acrylonitrile	Lung cancer mortality and morbidity	0.09	0.0003
	Total		**29,821**	**100**

listed in Table 47.2, with a leading contribution from long-term exposures to ambient particulate matter and domestic and traffic accidents. These results demonstrated that, while environmental concerns are presented regarding a large number of pollutants, the public health impacts are driven by a relatively small number of factors and that these factors may not receive as much attention as the disease burden associated with them would justify.

47.6 WHO Environmental Burden of Disease Programme

World Health Organization Headquarters in Geneva has continued to promote the environmental burden of disease methodologies actively for more than a decade. As part of their activities, they continue pushing the methodologies forward in the Environmental Burden of Disease series, with the latest contributions for inadequate housing (WHO 2011a) and environmental noise (WHO 2011b). These and other related WHO reports are available at http://www.who.int/quantifying_ehimpacts/publications/en/.

47.7 European EBoDE -Study

A more recent approach compared the environmental burden of disease over six European countries. The EBoDE-study (Hänninen and Knol 2011; Hänninen et al. 2014) covered nine environmental risk factors based on their presumed public health impact (e.g., particulate matter, second hand smoke, radon, traffic noise), individual high risk (several carcinogens), public concern (e.g., benzene, dioxins), and economic values (e.g., formaldehyde).

The overall annual environmental burden of disease was estimated to be 11,324 DALY/million, or 2.6 million DALY in total in the participating six countries. Fine particles were by far the dominating source of burden (Fig. 47.2), followed by second hand smoke, traffic noise, and radon. Fine particles were the leading cause in all countries, but the order of the following factors varied between countries due to the national conditions. E.g., in Finland, radon was the second most important factor due to the relatively high occurrence of uranium in the soil, producing radon in the radiological decay chain. In contrast, Finland had clearly the lowest impacts from second hand smoke due to proactive tobacco legislation already developed in the 1970s (Hänninen and Knol 2011; Hänninen et al. 2014).

Finland also had the highest formaldehyde exposures, but the associated health impacts were estimated to be almost negligible. However, formaldehyde very well demonstrates the various magnitudes of uncertainties in the estimates. Formaldehyde has been shown to be carcinogenic in occupational settings, where exposure levels range from 2 to 5 mg m^{-3}. However, later systematic reviews by WHO and others on studies in general populations rarely exposed to over 100 μg m^{-3} have

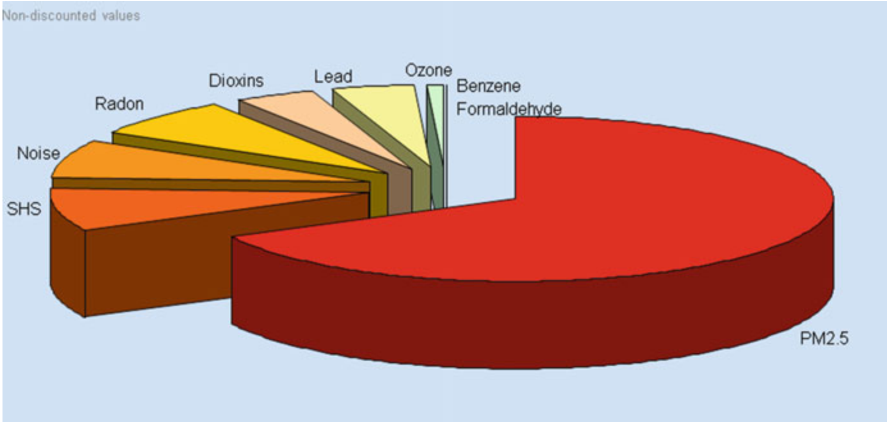

Fig. 47.2 Relative contributions of selected environmental factors on the environmental burden of disease in six European countries (Hänninen and Knol 2011; Hänninen et al. 2014)

concluded that nasal carcinogenic risk occurs only at substantially higher exposures, such as in occupational settings. Thus, the formaldehyde estimate did not include cancer as an outcome.

Uncertainties of the various environmental burden of disease estimates were evaluated in an expert panel, supported by a number of quantitative simulations of model and parameter uncertainties. Uncertainties for stressors like fine particles, for which the estimates were based on epidemiological data from large real populations at existing range of exposures were considered the smallest (Table 47.3). Pollutants for which even the selection of health end points contained substantial uncertainties, such as dioxins and formaldehyde, were classified as having the lowest certainty of the overall assessment.

More recently, environmental burden of disease methodology has been applied specifically to exposures in indoor spaces. Logue et al. (2012) combined the methodology with toxicological estimation of the dose-response coefficients. While the uncertainties of such estimates are much wider than when using epidemiological data, their results provided fresh insights into significant pollutants potentially missing from previous estimates, including acrolein, ozone, and acetaldehyde. Hänninen and Asikainen (2013) refined a similar assessment toward evaluating the effectiveness of ventilation and other risk management actions. They found that ventilation alone is not capable of reducing the burden much. However, combining ventilation with filtration of intake air and indoor source controls, over two million DALY could be saved annually in the European Union.

One of the advantages of environmental burden of disease methodology is that it can be readily used to compare also various endpoints against each other. Hänninen and Asikainen (2013) estimated the burden of disease of indoor exposures by endpoints in 26 European countries (EU27 excluding Malta), showing that cardiovascular diseases dominate the total impacts (Fig. 47.3).

Table 47.3 Relative uncertainties in the EBoDE estimates (Hänninen and Knol 2011; Hänninen et al. 2014)

Uncertainty level	Stressor	Sources of uncertainties
High	Dioxins	Endpoint uncertainty (total cancer)
	Formaldehyde	Endpoint uncertainty (limited evidence on asthma)
Medium	Traffic noise	Exposure data from early phase of European Noise Directive data collection
	Lead	Limited exposure data since abandoning tetraethyl lead additive
	Ozone	Loss of life uncertain (1 year assumed per death)
Low	$PM_{2.5}$	Strong evidence from large number of epidemiological studies in real human populations
	Second hand smoke	
	Radon	
	Benzene	

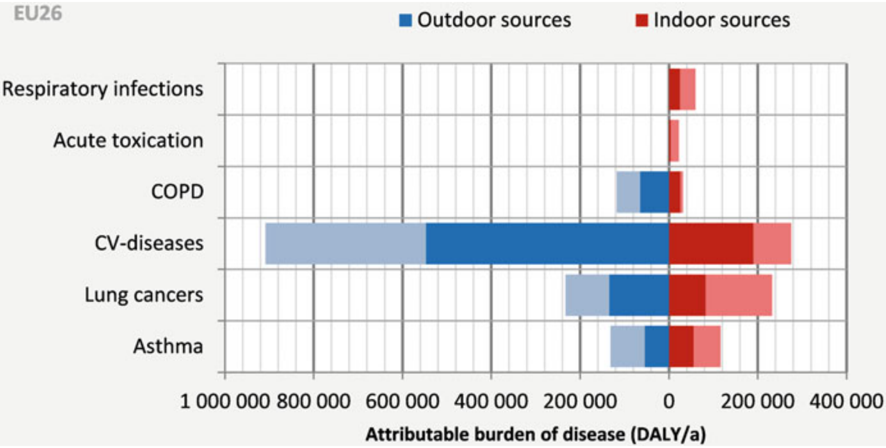

Fig. 47.3 Contribution of main disease categories to the burden of disease in EU26 caused by indoor exposures to pollutants originating from outdoor (*blue*) and indoor (*red*) air (Hänninen and Asikainen 2013). The estimated maximum reduction is shown in the *lighter shade* by disease category. *COPD* chronic obstructive pulmonary disease, *CV* cardiovascular diseases

47.8 Global Burden of Disease 2010 -Study

A recent major update of the global burden of disease study was coordinated by the Seattle-based Institute of Health Metrics, funded by the Bill Gates Foundation and published in a special issue of Lancet in December 2012. Lim et al. (2012) investigated the national and continental risks of 67 risk factors, now adding ambient ozone, residential radon, and a number of occupational risks to the palette of previous GBD assessments. Important methodological updates included dropping discounting and age weighting earlier used as a standard approach, and switching from incidence-based assessment to prevalence, i.e., focusing on current symptoms and not on the onset in the case of chronic diseases. The Institute for Health Metrics also developed impressive web-based tools to browse the results available at http://www.healthmetricsandevaluation.org/ numerically and graphically.

47.9 Discounting and Age-Weighting

Interesting methodological details debated actively in the past include discounting and age weighting. Originally Murray and Lopez (1996) used discounting to estimate the economic present values of future assets, such as lost life years. In the case of premature mortality, a substantial loss of life years may take place. According to economic models, the present value of lost life years needs to be adjusted by appropriate discounting. The World Health Organization adopted the approach and used a 3 % annual discounting rate. The present value (*pv*) of a future asset (*fv*) obtained after *n* years, using a given discount rate, is calculated as

$$pv = fv \times (1 + rate)^{-n} \tag{47.6}$$

In the case of multiple years of life lost, the cumulative sum of the present value of lost future years (the future value of each being 1) can be calculated, marking $q = 1 + rate$ as the geometric sum:

$$cpv(n) = \frac{1 - q^n}{1 - q} \tag{47.7}$$

As an example, using a 3 % discount rate ($rate = 0.03$), a year of healthy life gained 10 years from now is worth 24 % less than a year gained immediately.

Further, also an age weighing approach was developed by Murray (1996). BoD calculations involve judgments about standard life expectancy, severity (disability) weights, age weighting, and discounting over time. Murray (1996) also found originally that a year of healthy life lived at younger and older ages was weighted lower than that at middle age. In other words, Murray et al. chose to value a year of life in young adulthood more than a year in old age or infancy. This choice was based on a number of studies that have indicated there is a broad social preference to value a year lived by a young adult more highly than a year lived by a young child or at older ages (Fig. 47.4).

Both discounting and age weighting were heavily debated. For example, children's health has been given high priority in various international policies (e.g., WHO 2010), contrasting the age weights applied. In addition, discounting

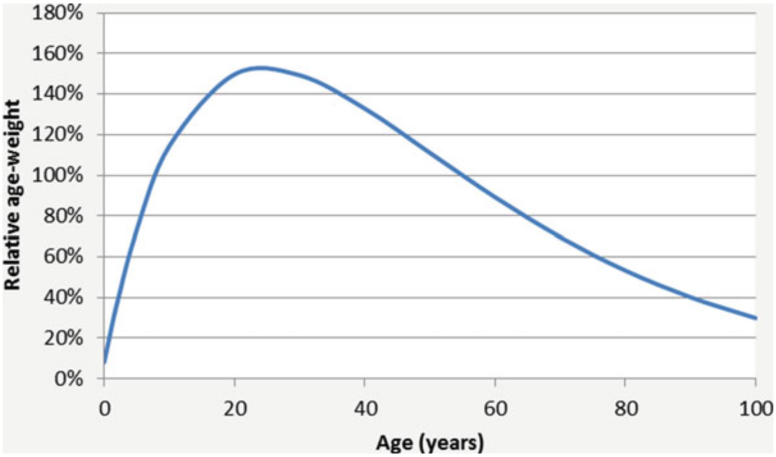

Fig. 47.4 Weights shown for 1 DALY as function of loss age

leads to the fact that childhood mortality, leading to up to 70–80 life years lost, is accounted for less than a similar amount of life years lost during a shorter period. As a reaction to the criticism, the Global Burden 2010 study (Lim et al. 2012) decided to drop both discounting and age weighting, giving equal values to the health of old and young and life saved now or later.

Conclusions

Environmental burden of disease is a useful indicator to quantify the population level health impacts of environmental factors, including chemical pollutants and noise. It allows quantitative comparisons of public health impacts associated with a wide range of environmental risk factors and targeting research and especially risk management to the major issues. However, the environmental burden of disease cannot directly be interpreted as a reducible burden. In many cases, exposures to natural sources of pollution or the existence of overlapping risk factors lead to the fact that exposures cannot be completely eliminated.

Further analysis may also be applicable for the cost effectiveness of various risk management actions. In some cases, reduction in exposures may require complex legislative changes as demonstrated, e.g., by removing lead from fuels, water pipes, canned foods, paints, and so on, over the past decades. Currently, similar challenges are being experienced, e.g., in controlling exposure to fine particles, which also have widely spread and have very heterogeneous sources. However, combining environmental burden of disease estimates with cost-effectiveness methodologies allows societies to target their environmental control efforts as efficiently as possible.

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Chapter 48
Textile Toxicants in Environmental and Human Health

Kaisa Klemola

Abstract The textile industry is a global activity. The production of fibres and manufacture of products takes place mainly in eastern countries, and the consumption of the products in western countries. A significant number of chemicals are needed in the production of fibres, to refine the materials in the processing stages, and to produce better quality products. In addition, different chemicals are used during their supply and transportation, and finally the consumers need chemicals to clean their textiles. A wide range of all textile chemicals is harmful to the environment, to the people working in the textile industry, and potentially to consumers. There is information about the toxicity of individual reagents, but limited information about the toxicity of textile materials and their adverse effects on textile workers. However, there are many studies on the environmental problems related to wastewater due to the presence of textile chemicals, and the removal of these chemicals is of importance. However, some chemicals from processing may remain on consumer products. Allergic reactions and irritation of the skin and respiratory tract are the most common harmful effects in workers in the textile industry. There is limited information about the toxic effects of different chemical combinations in textile materials. Different cell tests may be useful to indicate toxicity and to obtain information.

Keywords Textiles • Chemicals • Toxicity • Cell test

48.1 Health Risks by the Chemicals in the Production of Textile Fibres

The volume of the textile fibres produced during every year amounts to about 96.7 million tonnes (The Fibre Year 2009/10, A World Survey on Textile and Nonwovens Industry, www.oerlikontectile.com). Polyester is the most produced man-made fibre, while cotton represents the most produced natural fibre. Polyester is a plastic, and there is now a lot of information about the adverse effect of plastics

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_48

on humans. Monomers of polyester may cause severe health problems related to hormonal systems. These effects have resulted even in cancers (Sax 2010). In some cases, it has been claimed that polyester has caused miscarriages (Shafik 2007). The synthetic fibres, such as polyamide, polyester, and other synthetic fibres, are made using non regenerated natural resources. These fibres have many effects on the environment and humans that are similar to those of plastics.

For the most-produced natural fibre of cotton, a large scale of different chemicals is needed from the cultivation to the finishing stage of the products. For instance, zinc and copper salts and chlorinated phenols are used during cultivation. Residues of these compounds may still be present in cotton textiles (Suojanen 1995; Öko-Tex Standard 100 1977). Many fertilizers contain high concentrations of cadmium, a carcinogenic heavy metal (IARC 1993). Commonly, some fertilizers contain compounds resulting in allergic effects, poisoning, cancer, and hormonal changes. Synthetic pyrethroids clearly cause allergic reactions (Priha et al. 1988). Organophosphates have resulted in serious diseases of the central nervous system (Minton and Murray 1988; Marrs 1993; Lopez-Carillo and Lopez Cervantes 1993; Stevens et al. 1995). Women working with organophosphates are at risk of developing non-Hodgkin's lymphoma (Zahm et al. 1993). It has been found that exposure to organophosphates has caused low levels of cholinesterase activity in blood (De Peyester et al. 1993). In India, where many cotton farmers have committed suicide, organophosphates have been discussed (Sudeep Kumar 2006).

Many textile chemicals have been banned and lot of work toward safe products has been done. The Öko-Tex Standard 100, which has set limiting values on the amounts of many harmful chemicals whose presence is allowed, is used for labeling, (Öko-Tex Standard 100, 1997). However, it has been possible to find 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane, DDT in raw fabrics and also in clothes (Ahonen 1994; Suojanen 1995). During industrial processing, different chemicals used in cultivation are washed away, but some resins of chemicals may still remain in products.

During the cultivation of cotton, a farmer may become exposed to cotton dust. Prolonged exposure may result in the disease byssinose. This disease is a chronic pulmonary inflammation and it has been known over 200 years (Duffel 1985; Sigsgaard et al. 1992; Beckett et al. 1994; Hayes et al. 1994; Christiani and Wang 2003). Cotton dust may also produce a risk of nose and skin cancer developing (Lund 1991; Luce et al 1992).

In addition to chemical risks to human health, the cultivation of cotton causes large scale problems in the environment. The cultivation of cotton needs a lot of water; e.g., in EU-25 countries, we buy cotton from India. Every year about 7,000 million cubic meters of water are needed for our Indian cotton (Hoekstra and Chapagain 2008). Water foot prints are causing changes in the environment, as known in the case of the Aral lake, where the lake has dried and become saline and toxic because of irrigation and fertilizers. People have relocated because of health problems. However, water is not needed only for cultivation. In the textile process, hundreds of liters of clean water are needed for every kilogram of cotton. This water is necessary for washing the raw material, and for bleaching, dyeing, and finishing it

Table 48.1 Water footprints. Footprints of EU-countries, imported cotton between years 1997–2001, million m^3/year. Water was needed for cultivation and manufacturing of cotton products (Hoestra and Chapagain 2008)

India	6,623 million m^3/year
Uzbekistan	3,649 million m^3/year
Pakistan	1,423 million m^3/year
Turkey	1,277 million m^3/year
China	1,216 million m^3/year

(Table 48.1). These textile processes often cause difficult problems in water ways, if the wastewater is not purified. These textile wet processes should be conducted with care. The factories should have a good wastewater treatment system. The problems of wastewater emitted by the textile industry often include high pH, and many compounds are water-soluble and difficult to eliminate. Wastewater may include large scale different compounds, such as acids, alkalies, salts, detergents, and dyestuffs. The manufacturing of textiles that used to be located in the west has largely moved to developing countries. The textile processes may employ people, but on the other hand, these processes may cause difficult environmental problems.

In addition, a lot of energy is needed for the cultivation of cotton and for manufacturing textiles. The building of energy power plants causes changes in rivers and in the whole environment, including changes in nature and cultural changes in everyday life.

Viscose is a regenerated cellulosic fibre, and its consumption has become more and more popular. The process of producing viscose needs harmful chemicals, such as strong alkalies and sulphur compounds. Problems affecting the eyes and respiration have been found in persons who have been exposed to carbon disulfide. This compound is a known neurotoxic compound (Aaserud et al. 1990; Vanhoorne et al. 1991).

New innovations to avoid environmental problems are constantly being studied. In Finland, a new cellulose fibre, ioncell has been developed using an ionization method. This fibre should not cause as many environmental problems as viscose does. In the future, we will see whether it is possible to use this fibre instead of cotton and viscose.

48.2 Health Risks by Finishing Chemicals of Cellulosic Textile Materials

Finishing chemicals are used because cellulosic materials tend to shrink and wrinkle easily. Pure cellulose is flammable and burns with large flames. Many finishing chemicals are also used to avoid dirt and to make fabrics water repellent. In addition, the dyeing and printing of fabrics is included in the finishing processes. These processes include a wide range of different dyestuffs and auxiliaries for processing. In the finishing of fabrics, the main goal has been to achieve better quality, but it seems that in this development all the harmful effects have not been taken care of.

It is widely known that many fabrics may release formaldehyde, which is known to be harmful, and at high concentrations belongs to cancer causing chemicals Group 1 (James 1985; Priha et al. 1986, 1988, Priha 1992, 1995; Jahkola et al. 1987; Garcia et al. 1995; IARC 2004; Carlson et al. 2004). The known reactions caused by formaldehyde are mainly irritation of the skin, eyes, and respiratory tract. Asthma often follows exposure to formaldehyde (Piipari and Keskinen 2003). For instance, in the case of flame retardant cellulose, it may be a better choice to use fabrics that have material consisting of nonflammable manmade fibres. Thus, it is possible to avoid formaldehyde.

Bromide compounds used as flame retardants have now been found to be harmful and they are now largely avoided. It has been claimed that polybromide diphenylethers (PBDE) and polychlorinated PCBs cause neurobehavioral effects when exposure occurs in a critical stage of neuronatal development (Eriksson et al. 2006). Bromide compounds have been found to have effects in the cholinergic neurotransmitter system in adult mouse (Viberg et al. 2002). PBDE has been found in the environment and is even present in mother's milk. However, there is no information about the effects on the health of children (Hays and Pyatt 2006).

Studies have been conducted on the widespread use of phosphonium salts as flame retardants, but there is no exact information as to whether these chemicals are harmful. In dermal studies with rabbits, THP salts were proven to be promoters but not initiators of skin cancer (WHO 2000).

Textile fabrics are often finished by using antimicrobial treatments, if the material will be used outdoors. Many of these chemicals are relatively toxic and sensitize humans (Kanerva 1998; Kalimo and Lahti 1999; Yazdankhah et al. 2006).

Water repellents, stain repellents, dirt repellents and antistatic agents are available in aerosol form. These chemicals are combined with carbohydrates and fluorochemicals, and these have caused pulmonary inflammation (Wright and Lee 1986; von Essen 1996; Vernez et al. 2006). Consumers use these chemicals at home and these aerosols may be used inside rooms and without good protection.

During textile processes, in many cases a large scale of different tensides, dyes, and finishing chemicals are needed. Many of these chemicals are strongly corrosive and toxic to humans and the aqueous environment. Nonylphenol and nonylphenolethoxylates have been claimed to cause hormonal changes and their use should be limited (2001/838/EY, VNa 596/2004).

All pure textile dyestuffs are harmful chemicals in themselves and labeled by official labels indicating this. However, while the chemical itself is harmful, the same chemical in a fabric is not usually harmful. There is not much information available about fabric toxicity and textile dyes.

There is a large number of different textile dyes available. There are over 13,000 different compounds classified as dyes in the Colour Index (CI)2001. About 8,000 of these are used as textile dyes. Because cellulosic fibres are widely produced, there are also many dyes for cellulosic fibres, whose use is widespread. Reactive dyes react with cellulosic fibres and produce very constant bonds between the dye molecule and the fibre. This is the reason why these reactive dyes are now very popular in the manufacture of so-called high quality products. However, symptoms of asthma, rhinitis, and dermatitis have been detected in workers exposed to reactive dyes (Hatch 1984; Thoren et al. 1986; Nilsson et al. 1993; Manzini et al. 1996; Park et al. 2006). Reactive dyes themselves, before the reaction between the fibre and the dye molecule, are very active and toxic. The dermal problem is often difficult to trace because the dye usually acts as a delayed sensitizer and does not cause an immediate response.

The tests of mutagenicity, genotoxicity (Przybojewska et al. 1989; Schneider et al. 2004; Mathur et al. 2005a, b; Dogan et al. 2005), carcinogenicity (De Roos et al. 2005) and teratogenicity (Birhanli and Ozmen 2005) have proved toxicity for many textile dyes. In European countries, textile dyes releasing certain aromatic amines at concentrations of 30 ppm are forbidden (VNa 694/2003, 2002/61/EY and 2003/3/3EY). All these dyes are used not only for cellulosic textiles.

When the textile fabrics are printed, binders to bind the pigments on the fabric surface are needed. Both the pigments and the binders may cause health problems. Now and then, too high concentrations of phthalates have been found in the textile products. When the products have been tested, these harmful products have been removed from the market. Phthalates make plastics soft and these chemicals are needed for certain printing methods. For some time it has been known that these chemicals may be very toxic. It is clearly shown that phthalates cause hormonal changes. Allergic reactions and bladder diseases resulting from exposure to phthalates have been detected (IARC 2000). In European countries, phthalates are forbidden in baby toys and in materials for babies (European Commission IP/99/829 10/11/1999).

48.3 Consumer Products and Waste

Outside textile processes, we may become exposed to chemicals used for logistics. For supply and transportation, chemicals against microbes are typically in use. In some cases, these chemicals have caused difficult allergic reactions (Fig. 48.1).

We need to wash our clothes and other textiles. There are different washing chemicals on the market and these detergents contain different compounds of which some are sensitizers for human beings. Optic brighteners cause more brightness, but do not clean anything. These chemicals are not present in washing powders for baby clothes. In addition, perfumes clearly cause contact allergy, and baby washing powders do not contain them. Washing detergents contain a list of chemicals and not all the toxic effects have been studied. However, it is known that all these chemicals are not easily cleaned from wastewater and may enter our environment.

In Finland, the consumption of textiles is over 70,000 t for every year. In Sweden, consumption of textiles grew by over 40 % during the years 2000–2009. This causes large amounts of textile waste. These kinds of big molecules are not

Fig. 48.1 Reactions caused by dimethylene fumarate, a chemical against microbes. The product was a chair. Contact with the chair caused painful dermatitis. This irritation developed during 2 weeks and the skin healed during next 2 weeks. Some patients suffered for several months. During 2007, tens of cases were reported in Finland, and later, similar cases in UK (Rantanen 2008; the photo by Tapio Rantanen 2008)

easily broken down and it is not allowed to compost them. It is now important to plan the reuse and recycling of materials (Naoko et al. 2012).

In Finland, we have a new law. From the beginning of the year 2016, it will not be allowed to dispose of textiles together with other community waste. All textile waste shall be gathered separately. Later, this waste shall be burned, mainly at high temperatures, and used to generate energy. The aim of the new law is to avoid climatic changes, enthrophication, and toxication (331/2013).

48.4 Testing Toxicity of Textile Materials by Cell Tests

In vitro cell tests have been useful in the study of the overall toxicity of materials. Textile processes are complicated, consisting of a large scale of different process stages that use chemicals. The manufacture of the products, from fibre production to the consumer's use, is a long chain (Fig. 48.2). Typically it is often very difficult to obtain information about all the chemicals used during the textile process.

Analysing the possible toxicity of every single chemical may be impossible, because information about all the chemicals used is often limited. In addition, it may be useful to have information about which kind of effects the chemicals on the fabric cause all together. Cell tests are good indicators to show the toxicity, if some material of unknown chemical content is being studied. Thus, these tests are suitable for studying textile materials.

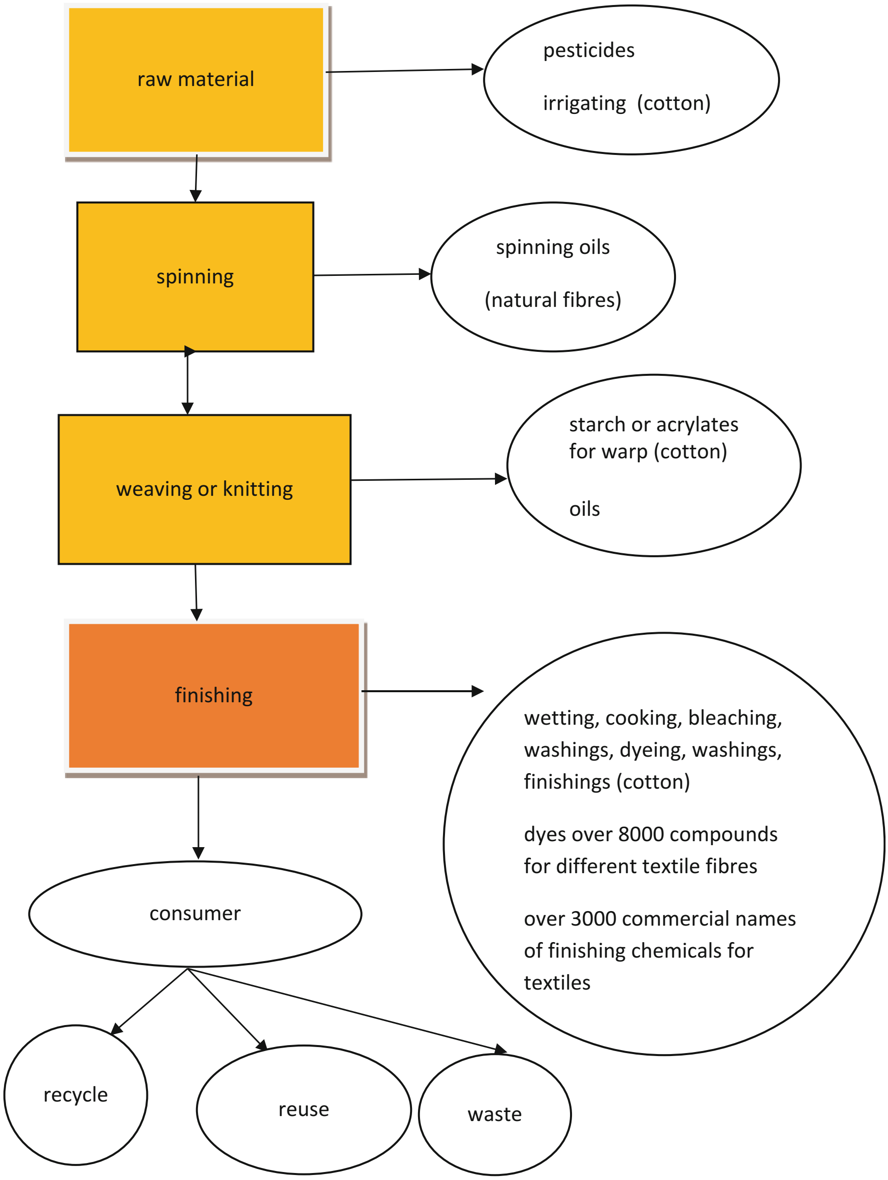

Fig. 48.2 Textile chain

The Öko-Tex Standard 100 shows whether some material does not contain too high concentrations of certain chemicals. However, the studied material may contain some harmful chemicals that are not included in the "test battery." In addition, the effect of the overall toxicity is not studied. The development of cell test use for textile material studies may provide useful information about the possible toxicity of textiles.

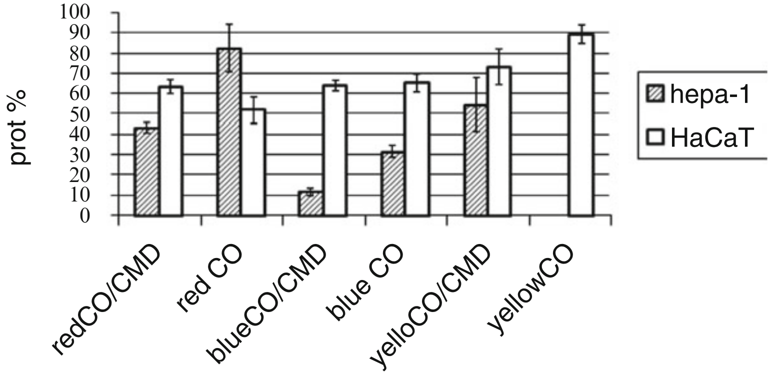

Fig. 48.3 The knitted fabrics studied by cell tests (Klemola 2008). The studied fabrics contained fibres of cotton and mixtures of cotton and modal (*CO* cotton, *CMD* modal). Textile dyes yellow, red, and blue belonged to the reactive dyes, which form a chemical bond between the fibre and the dye molecule

In order to assess the toxicity of fabric extracts, the hepa-1 cell cytotoxicity test was used (modified from INVITTOX protocol number 112). The same method was used for human ceratinocyte HaCat cells. These tests showed that some textile materials dyed by toxic reactive dyes were not toxic. If the protein contents in the results were higher than 80 %, the studied material was not toxic. These studies showed that where the protein content was high, the dyed material was not toxic. However, some knitted industrial materials dyed by reactive dyes were very toxic (Fig. 48.3). The chemical that caused the toxic effect was not known. These industrial materials were even Öko-Tex-Standard 100 labelled.

Conclusions

Thousands of chemicals are used in textile processes. In different stages, these have effects on the environment and on the people working in textile manufacturing. The textile industry consists of activities from agriculture and from the synthesis of plastics until to the washing of consumer products with chemicals. In addition, people may become exposed to chemicals that are needed for washing their own clothes and other textile materials. More studies and indicators to show possible toxicity or safety are needed. The textiles' toxic effects on nature, the living environment, and the consumers need to be investigated more thoroughly.

Because it is difficult to trace every compound used during processes and logistics, tests such as cell tests may be useful for finding toxic materials. These tests also show the toxic effects of chemical combinations. They reveal acute toxicity and are common indicators. However, it is difficult to show chronic and subchronic toxicity. The resulting health problems develop over a long time period, and patients find it difficult to detect the reasons for their diseases.

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Chapter 49
Biological Indicators of Ionizing Radiation in Nature

Anders Pape Møller and Timothy Alexander Mousseau

Abstract Ionizing radiation that consists of α, β and γ rays can directly damage DNA and other molecules and as such result in somatic or germline mutations. The consequences of ionizing radiation for living beings cannot be measured with a Geiger counter because it will depend on external dose, internal dose, and the extent of DNA repair. In addition it will depend on the environmental conditions under which living organisms exist. We list environmental indicators of ionizing condition that reveal immediate and long-term consequences ranging from changes in DNA, over damaged cells and organs to altered gene function and development, reduced fecundity and survival, and hence to negative population trends, and altered communities and ecosystems and perturbed ecosystem functioning. We test for consistency in biological indicator ability across spatial and temporal scales relying on long-term field data collected at Chernobyl and Fukushima, and we test for consistency in indicator ability among indicators. Finally, we address the direct and indirect effects of ionizing radiation and we discuss the species or taxa most susceptible to the effects of radiation.

Keywords Biological level of organization • Consistency across indicators • Direct vs. indirect effects of radiation • Environmental indicators • Spatial consistency • Temporal consistency

49.1 Introduction

Radiation is either non-ionizing (radio waves, visible light and heat) or ionizing with sufficient energy to ionize an atom. Ionizing radiation consists of α particles that cannot penetrate paper, β particles that can penetrate paper, but not an aluminium sheet, and γ rays that can penetrate paper, aluminium, and even layers of lead.

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_49

Both ionizing and non-ionizing radiation can damage organisms, although only ions produced by ionizing radiation can directly damage DNA and other molecules. Background radiation dose rates on Earth typically vary from 0.01 to 0.10 μSv/h, with the natural level in Chernobyl before the nuclear accident being only 0.01–0.02 μSv/h. However, some radiation hot spots have levels that exceed global mean levels by three orders of magnitude. The negative effects of radiation have been documented since the first studies of radioactivity by Becquerel and Curie, and the mutation effects of radiation were detected almost 90 years ago (Nadson and Philippov 1925). Thus, the negative consequences of ionizing radiation for living beings are a well-established fact. Still, very little is known about the biological effects of radiation on free-living organisms.

Why not just measure radioactivity with a Geiger counter and use these measures for predicting the consequences of radioactivity rather than investigate how living beings respond to radiation? The main reason is that the consequences of ionizing radiation for living beings will depend on a number of factors, including external dose, internal dose (the amount of radiation due to radionuclides that have been ingested or inhaled), and the extent of DNA repair. There are a large number of radiation hotspots around the world where natural levels of radiation have been shown to have negative effects on mutations, immunology, and disease, despite the opportunity for local adaptation to these conditions (Møller 2012).

A second major reason why the consequences of ionizing radiation cannot just be measured with a Geiger counter is that animals and other organisms that live under normal conditions commonly experience less benign environmental conditions than in the lab. They usually do not have ad libitum access to food and essential nutrients, making them experience trade-offs that are rare or non-existent in the lab. Likewise, field populations commonly suffer from predation, parasitism, or other interspecific interactions, while such effects are effectively controlled or eliminated in lab studies. In fact, most humans also live under such constrained conditions, making it unlikely that lab studies of the effects of ionizing radiation under benign environmental conditions will apply to humans. Indeed, lab studies generally indicate benign effects of low dose radiation, whereas field studies often show considerably increased negative effects (Garnier-Laplace et al. 2012).

Radiation accidents are common, making it of significant importance to document their effects on living beings. The number of radiation accidents runs into the hundreds, with 20 belonging to the grave categories on the International Nuclear Event Scale (INES) 4–7 (Lelieveld et al. 2012). Only Chernobyl and Fukushima have so far been designated as INES 7, which represents major accidents, with four Category 7 events, because of the meltdown of three reactors at Fukushima. Despite these events, there is only limited information available on the biological and health consequences of low dose radiation (reviews in Zakharov and Krysanov 1996; Møller and Mousseau 2006; Yablokov et al. 2009).

The objective of this chapter is to assess biological indicators of ionizing radiation under field conditions as a means of determining the extent to which radiation accidents have immediate and long-term consequences for living beings.

49.2 Environmental Indicators of Ionizing Radiation

49.2.1 Identification of Environmental Indicators of Ionizing Radiation

Mutations are changes in the sequence of DNA caused by single or double strand breakage of DNA. DNA repair can restore the original sequences of DNA, most readily single-strand, but even double-strand breakage of DNA can be repaired efficiently (Lehman 2006; von Sonntag 2010). Mutations are either somatic (i.e., occurring in ordinary body cells) or germ-line (i.e., occurring in gametes). Somatic mutations are sometimes the source of genetic diseases including different types of cancer, while germ-line mutations can be transferred to offspring and hence accumulate across generations. Radiation is a powerful mutagen as shown by classical laboratory experiments (Nadson and Philippov 1925; Muller 1954). Even a natural variation in levels of background radiation is a significant cause of mutation (e.g., Forster et al. 2002) and cancer mortality (e.g., Lubin and Boice 1997; Zhang et al. 2012).

Ionizing radiation can damage DNA either directly by causing single or double strand breakage, or indirectly by the production of free radicals that damage DNA, other molecules, and membranes. Indeed, barn swallows *Hirundo rustica* have germ-line mutation rates for neutral microsatellite markers increased by a factor 2–10 (Ellegren et al. 1997). Numerous other studies have shown increases in mutation rates from bacteria (Ragon et al. 2011) to humans (Dubrova et al. 1996), with contaminated areas around Chernobyl having mutation rates that are increased 2–20-fold relative to controls (Møller and Mousseau 2006). The effects of exposure to ionizing radiation may be long lasting due to genomic instability, causing DNA to be particularly susceptible to future environmental perturbations even after one or more generations (Morgan et al. 1996). Germ-line mutations are not readily quantified under field conditions, mainly because it is difficult to sample DNA from both parents and offspring. In addition, mutations may not have fitness consequences if DNA is repaired, or if offspring carrying mutations are spontaneously aborted, thereby preventing transmission to the next generation.

Mutations may result in the production of non-functional or damaged cells, as in sperm, pollen, red blood cells, and leukocytes. A large fraction of sperm cells has abnormal morphology and behavior, preventing them from fertilization. The frequency of such abnormal sperm is known to increase with the level of background radiation (Møller et al. 2005b), and such sperm cells have inferior swimming behavior, which may prevent fertilization (Møller et al. 2008; Bonisoli-Alquati et al. 2011). A similar production of abnormal germ cells occurs in pollen, which likewise have high frequencies of abnormalities that prevent fertilization. Indeed, the frequency of pollen abnormalities increases strongly with background radiation level in many plant species (Kordium and Sidorenko 1997). Somatic cells might likewise be affected by mutations, as shown for DNA damage to red blood cells in birds (Bonisoli-Alquati et al. 2010).

Ionizing radiation has significant negative effects on the normal development of organs, such as the brain and the lens of the eye. Birds at Chernobyl have brains that are on average 5 % smaller than birds in control areas, and there is strong selection against small brains (Møller et al. 2011). Likewise, the frequency of cataracts due to opacities of the lens is common in free-living birds in contaminated areas, but not in control populations (Mousseau and Møller 2013).

Mutations are a cause of altered DNA sequences that may have negative effects on gene function and hence development of normal morphology. Indeed, the frequency and the extent of abnormalities in plants and animals are elevated in Chernobyl as compared to control areas (Møller 1993, 1998; Zakharov and Krysanov 1996; Møller and Mousseau 2001, 2003). Detailed studies of barn swallows have shown high frequencies of abnormalities in populations in contaminated areas as compared to control populations (Møller et al. 2007). Abnormalities are rare under natural conditions because predators differentially eliminate individuals with aberrant phenotypes. Frequencies of aberrations and hard tumors in a diverse array of bird species reached levels that were many times higher than in control areas (Møller et al. 2013a). Similarly high frequencies of abnormalities have recently been reported for butterflies from Fukushima (Hiyama et al. 2012).

If ionizing radiation affects fertility, this may have negative effects on fecundity. Møller et al. (2005a, 2008) reported significantly elevated hatching failure in birds near Chernobyl compared to control populations, possibly due to embryo mortality caused by either damaged sperm and/or eggs, and hatching failure was also reported for butterflies at Fukushima (Hiyama et al. 2012). The main factors determining fecundity is whether an individual survives to the age of first reproduction and the number of subsequent years of reproduction. Detailed lifetime studies of barn swallows revealed annual adult survival rates reduced to 28 % in contaminated areas compared to 40 % in control populations (Møller et al. 2005a). Across 16 species of birds, adult survival rate was reduced by 21 % in contaminated as compared to control areas (Møller et al. 2012), and it was reduced in butterflies in Fukushima (Hiyama et al. 2012).

If fecundity and survival are reduced in contaminated areas, this translates into reduced abundance and species richness because uncommon species disappear due to random elimination of a few individuals. The underlying mechanisms are poorly understood, although individual birds are know to avoid nesting in the most contaminated areas (Møller and Mousseau 2007b), although contaminated areas that are partly empty due to the negative effects of radiation may be replenished through differential immigration (Møller et al. 2006). Surprisingly, the first standardized counts assessing the relationship between abundance and radiation were not conducted until 2007, more than 20 years after the Chernobyl accident. This is all the more surprising given that such research is inexpensive and does not require special equipment or training. We have made censuses of birds and other organisms (i.e., biotic inventories) at more than 1,000 census points in contaminated areas in Ukraine, Belarus, and Japan using standard procedures (Bibby et al. 2005). Indeed, species richness and abundance of birds (Møller and Mousseau 2007a, b, 2009), but also spiders, dragonflies, grasshoppers, bumblebees, butterflies, amphibians, reptiles, birds, and mammals, are reduced in more contaminated areas in Chernobyl (Møller and Mousseau 2007a, b, 2009, 2011b, 2013) and Fukushima (Hiyama et al. 2012; Møller et al. 2012, 2013b). We have controlled for the potentially confounding effects of habitat, soil, weather, and time of day, but still found highly consistent results (Møller and Mousseau 2011b).

Species and higher taxa differ in their susceptibility to radiation (Møller and Mousseau 2011; Galván et al. 2011). Bird species that have long dispersal and migration distances, pheo-melanin and carotenoid-based plumage, and high fecundity are the most strongly negatively affected by radiation, apparently due to the effects of radiation on the production of free radicals and hence on depletion of antioxidants. Interspecific interactions between species may be affected by radiation if one of the interacting parties is particularly susceptible to radiation. For example, plant-pollinator and prey–predator interactions are affected by radiation if the abundance of pollinators or predators changes. Indeed, mammalian prey were strongly aggregated in the least contaminated sites around Chernobyl, and predators were disproportionately common in those sites, presumably resulting in over-exploitation of prey (Møller and Mousseau 2013).

The effects of ionizing radiation on the abundance and diversity of species may affect interspecific interactions that constitute an integral part of ecosystem functioning. Chernobyl and other areas affected by radiation have perturbed ecosystems (Møller et al. 2012). Radiation reduces the abundance of pollinating insects, such as bumblebees and butterflies, with subsequent negative effects on fruit set of apples, pears, and other fruit bearing plants. In turn, frugivorous birds are less abundant in such areas with few fruit, which negatively affects seed dispersal and hence recruitment. Indeed, the recruitment rate of apples and pears was severely reduced in study plots with elevated background radiation.

49.2.2 Testing for Consistency of Indicator Ability Across Spatial Scales

Large-scale radiation accidents affect hundreds if not thousands of square-kilometers. Still, there have been few attempts to test whether there is consistency in responses to radiation across spatial scales. Møller and Mousseau (2011b) compared breeding bird census data obtained from the same years in Ukraine and Belarus and found highly consistent effects of radiation on the abundance of birds.

We have taken this analysis one step further by analyzing the slope of abundance of different taxa of animals in relation to radiation at Chernobyl and Fukushima (Møller and Mousseau 2013; Fig. 49.1). There was no significant interaction between radiation and area for species richness of birds, number of birds, and number of bumblebees, implying that the effect of radiation was similar in the two areas. In contrast, there were significant interactions for butterflies, dragonflies,

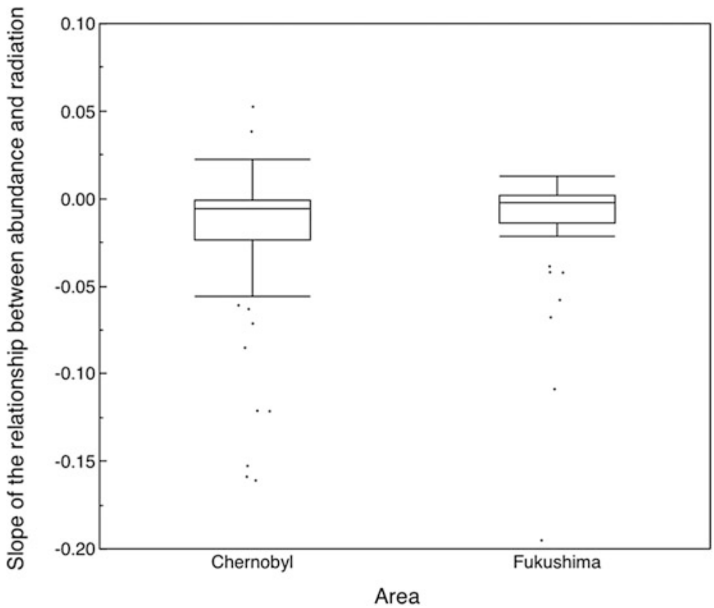

Fig. 49.1 *Box plots* of the slope of the relationship between abundance and level of background radiation for 80 species of birds at Chernobyl and 56 species of birds at Fukushima. The *box plots* show the median, quartiles, 5- and 95-percentiles, and extreme values. Note that slopes were generally negative, implying reduced population sizes at higher radiation levels, and slopes at Chernobyl were more negative than at Fukushima

grasshoppers, and spider webs, implying different effects in the two areas. We should not necessarily expect similarity because Chernobyl has been subject to chronic radiation for 27 years, whereas Fukushima has been exposed only for 2 years, and thus the composition of radionuclides differs.

Interestingly, many species occur both at Chernobyl and Fukushima, allowing a test of similarity in the effect of radiation on abundance at the two sites (Møller et al. 2012). The relationship between abundance and radiation in birds was on average −0.063 (SE = 0.007), N = 80 species in Chernobyl and −0.040 (0.008), N = 45 species in Fukushima. However, among the 14 species occurring at both sites there was a significant interaction between radiation, area, and species, implying that the abundance varied among areas and species, with radiation having different effects. The slope of the relationship between abundance and radiation for the 14 common species was −0.008 (0.001) at Chernobyl, but at −0.067 (0.011) much stronger at Fukushima (Møller et al. 2012).

49.2.3 Testing for Consistency of Indicator Ability over Time

We have conducted censuses of animals at both Chernobyl and Fukushima for more than 1 year, allowing for tests of relationships between abundance and radiation

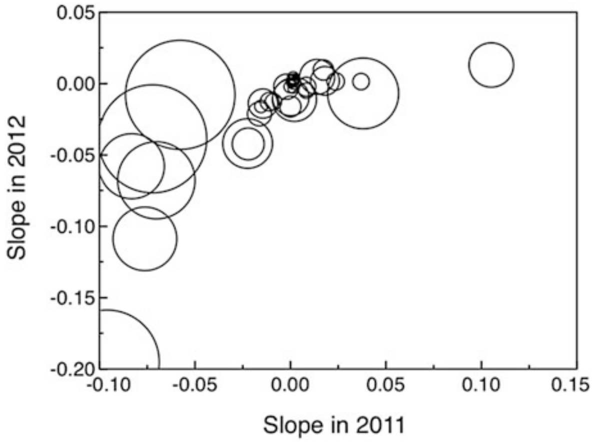

Fig. 49.2 Slope of the relationship between abundance and level of background radiation in 2012 in relation to 2011 for 35 species of breeding birds near Fukushima. The size of the *circles* reflects sample size. The slopes were generally more negative in 2012 than in 2011

among years. Indeed, we have documented temporal consistency for different taxa at Chernobyl and Fukushima (Møller and Mousseau 2011b; Fig. 49.2).

Laboratory experiments on the effects of radiation on living beings are usually based on acute radiation treatment, while the situation in the wild consists of chronic exposure with an accumulation of mutational effects over time. While such accumulation effects have not been demonstrated in Chernobyl because no or few studies were conducted immediately after the accident, Fukushima allows tests of whether there are increasingly detrimental effects over time. While the slope of the relationship between abundance of birds and radiation was −0.006 (SE = 0.005) for 45 species in 2011, it was −0.015 (SE = 0.005) in 2012 for the same species. Thus, the effects of radiation on abundance became much more severe 1 year later as compared to immediately after the accident. If many individuals with abnormalities die, as suggested by studies at Chernobyl (Ellegren et al. 1997; Møller et al. 2013a), we might expect a slight temporal trend toward fewer abnormalities over time due to radioactive decay. Indeed, Møller et al. (2007) showed that there was a trend toward reduced frequency of abnormalities over time in barn swallows, although this reduction could also be due in part to lower radiation doses in some areas following two decades of radioactive decay.

Exposure to radiation may result in adaptive responses to ionizing radiation if there is genetic variation in the underlying mechanisms (i.e., the mechanism(s) of adaptation are heritable), if there is selection against inefficient mechanisms, and if selection occurs for a sufficient number of generations. Recent studies of plants have suggested that DNA repair and specific proteomic patterns provide evidence of such adaptation (Boubriak et al. 2008; Danchenko et al. 2009; Klubicová et al. 2010). However, these experiments are based only on a single sample from a contaminated area and a second from a control area, providing no proper replication, thereby preventing firm conclusions about the underlying cause.

Table 49.1 Environmental indicators of ionizing radiation and their properties in terms of ease of use, consistency in response over space and time, reliability, and information content

Biological level of organization	Feasibility	Cost effectiveness	Consistency over space and time	Reliability	Informative
Mutations, DNA and other molecules	Relatively easy	High	?	?	Weakly
Germ cells	Easy	High	Yes	Yes	Yes
Organs	Easy	High	Yes	Yes	Yes
Populations	Time consuming	High	Yes	Yes	Yes
Species	Time consuming	High	Yes	Yes	Yes
Interactions among species	Time consuming	Medium	Yes	Yes	Yes
Ecosystems	Time consuming	Low	Yes	Yes	Yes

49.2.4 Testing for Consistency of Indicator Ability Among Indicators

Environmental indicators of the effects of radiation on different levels of biological organization have shown strong effects of chronic exposure at Chernobyl more than 27 years after the accident, and on-going studies at Fukushima show increasingly negative effects of radiation with time. Studies of the effects of ionizing radiation at different organizational levels differ in feasibility, cost effectiveness, consistency over space and time, reliability, and information content (Table 49.1). Thus, studies of mutations are relatively easy to conduct, although there are no studies showing consistency in response over space and time. More ecologically oriented studies focusing on populations, species, interactions among species, and ecosystems are time consuming with low cost effectiveness. However, if we require knowledge concerning the effects of radiation at different organizational levels for the characterization of direct and indirect effects and estimation of risks and injuries to individuals, populations, and ecosystems, we must conduct studies at these different levels.

49.3 General Discussion

We have briefly reviewed the literature on indicators of ionizing radiation at different levels of biological organization from molecules and cells, to individuals, populations, species, multi-species interactions, and ecosystems. There are many parallels between the effects observed in natural animal and plant systems and those documented for humans (review in Serdiuk et al. 2011). We have documented consistency in response to radiation over time and space, implying that our findings are not chance relationships, but rather consistent patterns of a pervasive impact of radiation on living systems. This raises two questions: First, what are the direct versus the indirect effects of radiation? Second, at which organizational level is the impact of radiation most efficiently and readily measured? Concerning the first question, there are so far no assessments of the relative direct effects of radiation and the indirect effects of radiation through food availability and interactions with conspecifics, predators, parasites, or pollinators. Clearly, such an assessment is urgently needed.

The second question concerns which species or taxa are most susceptible to radiation and hence most reliable as biological indicators of the effects of radiation (i.e., the canary in the coal-mine analogy). We have previously demonstrated that animal taxa with large mean population density and long natal dispersal distance are most strongly negatively affected by radiation (Møller and Mousseau 2011a). Rare bird species are more strongly negatively affected by radiation, and rare species are disproportionally found in the least contaminated sites around Chernobyl (Møller and Mousseau 2011b). Common species generally have long dispersal distances and occur at high average background radiation levels (Møller and Mousseau 2011b). This effect of dispersal may interact with mutation rate because species that disperse the farthest have the lowest frequency of mutations making it unlikely that mutations spread to uncontaminated areas through dispersal.

49.4 Future Prospects

It has been predicted that another nuclear accident at the INES 7 scale is likely to occur during the next 50 years in a heavily populated area affecting c. 30 million people (Lelieveld et al. 2012). Hence, there is great urgency to learn from past accidents to mitigate future effects. We consider this chapter to constitute a first necessary step toward the production of a tool kit for the assessment of the consequences of future nuclear accidents. Given the poor level of knowledge of the effects of radiation accidents on wild organisms, it is essential to retrieve information at a number of different scales. It is also essential to involve many different people, including citizen scientists, because knowledgeable citizens are numerous and dedicated.

We would like to emphasize the general lack of replication of most studies of low dose radiation. A second major problem is the general lack of proper experimentation with appropriate levels of replication, thus preventing inferences about causation. This precarious situation is mainly due to poor scientific methodology and a chronic lack of funding for research on the effects of low dose radiation. Construction and maintenance of nuclear power plants is hugely expensive, and allocation of even 0.1 per mille would represent a huge boost to research concerning the consequences of radiation accidents.

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Chapter 50
Health-Related Indicators of Outdoor Air Quality

Paul T.J. Scheepers

Abstract Episodes of air pollution such as in London in 1952 have killed thousands of inhabitants of urban or industrialized regions in a matter of days. Epidemiologists demonstrate that current much lower levels of air pollution also increase hospital admissions and daily mortality in individuals with pre-existent cardiopulmonary disease. For some gas phase components, such as carbon monoxide, ozone, nitrogen oxides, and sulfur dioxide, the etiology is well understood. For particles it is still unclear which size fractions and which components explain the observed health effects. There are some indications that traffic-related ultrafine particles are both linked to acute effects (cardiac dysrhythmias, respiratory complaints) and also increase the risk of chronic disease (lung cancer). Some specific gas phase compounds and indicators of particulate air pollution are useful environmental health indicators that could be used to reduce the impact of air pollution on short-term and long-term health effects.

Keywords Black smoke • Carbon monoxide • Diesel exhaust • Nitrogen oxides • Ozone • Particulate matter • Sulfur dioxide

50.1 Introduction

In London in 1952, a smog episode caused the death of approximately 3,700 inhabitants and possibly 25,000–100,000 individuals suffered from respiratory disease caused by the high concentrations of sulfur dioxide and smoke particles estimated as high as several thousands of μg/m^3 (Brunekreef and Holgate 2002, Fig. 50.1). Important contributors in this public health disaster were the stagnant weather conditions, combined with high emissions from the use of high-sulfur coal in domestic heating and power stations. Ironically, London had had a public transport system that relied on electric trams, which had recently been abandoned and replaced by the 'modern technology' of diesel-powered buses. From the time of this and similar reports of mortality attributed to air pollution (Meuse Valley 1930,

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_50

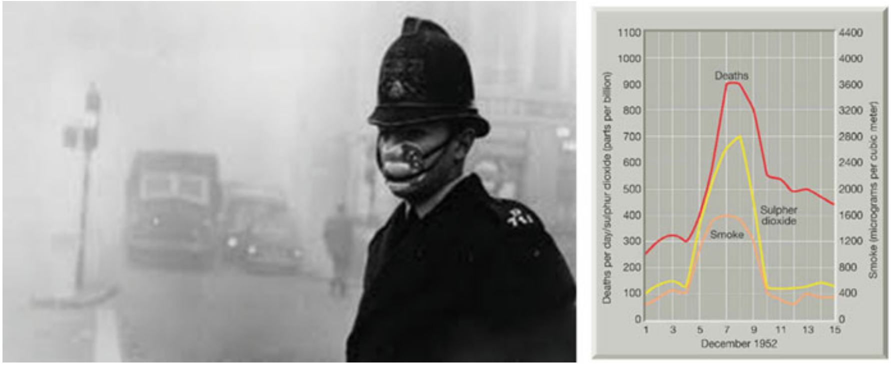


Fig. 50.1 A picture to the Great Smog which presented itself as a visible fog (*left*) and killed over 3,700 inhabitants of London in the winter of 1952 (*right*)

St Louis, Missouri, 1939 and Donora, Pennsylvania, 1948), not much attention was given to the impact of air quality on public health until epidemiology studies in the US made the scientific community aware that much lower levels of air pollution were also associated with health effects. In the early 1990s, two prospective cohort studies in the US suggested that outdoor air pollution is associated with increased all-cause mortality (Dockerey et al. 1993; Pope et al. 1995). Using time-series analysis, these studies showed that outdoor concentrations of fine, so-called PM-2.5 particles, sulfate, and sulfur dioxide could explain day-to-day variations in mortality and hospital admissions. In 1999, a third cohort study among non-smoking Seventh-Day Adventists suggested an effect of the thoracic dust fraction (PM-10) on non-malignant mortality and lung cancer mortality in non-smoking men (Abbey et al. 1999).

50.2 Gas Phase Pollutants

In addition to particulate matter, a number of gas phase air pollutants contribute to cardiopulmonary health effects.

50.2.1 Sulfur Dioxide

An important gas phase emission that causes upper airway complaints is sulfur dioxide and its atmospheric secondary reaction product sulfate, an ultrafine nucleation mode particle. Both are strong upper airway irritants, and asthma patients in particular will respond to it, even at levels as low as 0.1 ppm, during 10-min exposures (Goldstein and Weinstein 1986). The primary source of this pollutant is the combustion of fossil fuels. Emissions of sulfur dioxide from coal-fired power plants were reduced by the introduction of effective stack filters. Emissions can also be expected from road traffic, and the introduction of low-sulfur diesel further reduced the air levels of sulfur dioxide, which is no longer a problem in most modern cities. This pollutant may still be a problem related to natural sources such as volcanos (Ishigami et al. 2008) and forest fires (Wiwatanadate and Liwsrisakun 2011). Anthropogenic sources related to the respiratory health effects of sulfur dioxide may be related to the coal or high-sulfur oil still used, e.g., in ships (Winebrake et al. 2009), or to the local use of low-quality fossil fuels, such as brown coal, for house heating (Tayanç 2000).

50.2.2 Nitrogen Dioxide

Nitrogen dioxide (NO_2) is another gas phase pollutant that is elevated in urban areas because it originates from combustion sources, primarily road vehicles. This substance is formed from ambient air (i.e., nitrogen and oxygen) that is taken in by diesel engines for cooling and for the lean burn type of combustion commonly found in diesel engine technology (see Chap. 51). High exposures to NO_2 in indoor environments can cause serious lung trauma if this gas reaches the alveoli. This may happen in persons who inhale high concentrations of diesel exhaust in indoor settings (Ainslie 1993) or fire smoke derived from the combustion of materials rich in organic or synthetic nitrogen (see Chap. 54). For this gas in outdoor ambient air, the levels are so low that the effects on the respiratory system are mostly reversible and it is difficult to attribute such effects to NO_2 alone (Hesterberg et al. 2009), but ambient or personal monitoring of NO_2 can be useful as an approximation (a 'proxy') to characterize exposures of the general population to its emission from traffic. If ambient air sampling is combined with pollution dispersion modeling and geographical information systems, a direct link between emissions of this gas compound and traffic can be clearly demonstrated (see Fig. 50.2).

50.2.3 Ozone

For atmospheric ozone, it is important to make the distinction between the ozone formed in the outer part of the troposphere and stratosphere and the ozone at sea level. At an altitude of 10–90 km approximately, ozone is produced from the ionization of oxygen by the UV influx from sunlight and protects the earth crust from too high an intensity of UV irradiation at sea level, and reduces health effects from UV irradiation, such as melanoma skin cancer. At sea level, ozone formation is triggered by volatile organic compounds (VOC) having anthropogenic sources, which act as catalysts in a chain reaction leading to the formation of a range of secondary organic pollutants, including organic peroxides, aldehydes, and ozone. This atmospheric mixture of pollutants is commonly referred to as photochemical

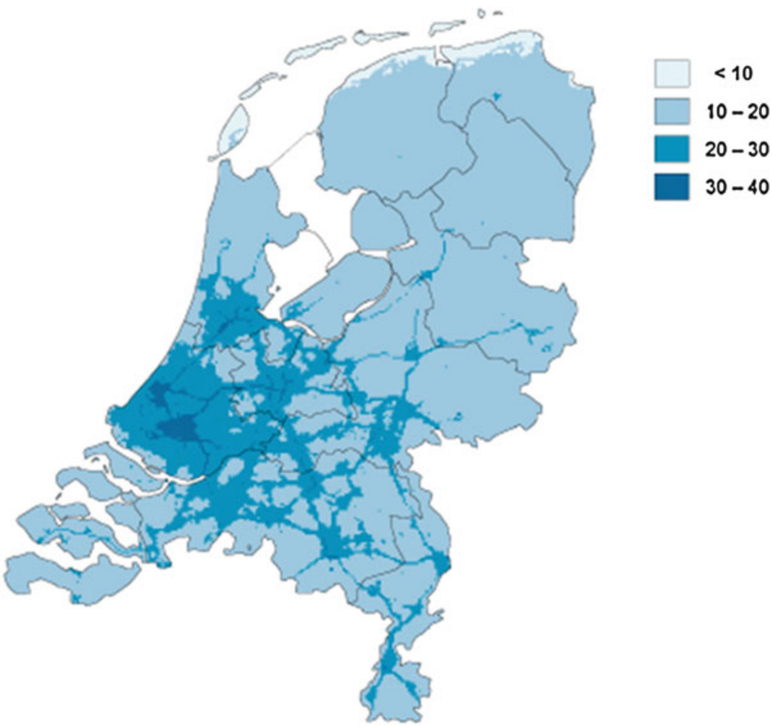


Fig. 50.2 Annual average level of NO_2 in The Netherlands in 2012 associated with urban areas (densely populated western part of the country). NO_2 is also elevated along major highways that run through less densely populated regions (eastern and southern parts of The Netherlands) (Source: RIVM, National Institute for Public Health and the Environment 2013)

smog. High levels of ozone can be expected when some meteorological and geographical conditions prevail. Meteorological conditions potentially leading to high ozone levels are a high intensity of sunlight, stable (non-turbulent) atmosphere, and an inversion layer in the lower part of the atmosphere, which reduces vertical dispersion. Because of the change in the sunlight's intensity, the occurrence of inversion, and the availability of VOC, ozone usually builds up during the day and tends to reach maximum levels during the afternoon and toward the evening, dropping quickly when the sunlight's intensity declines (Fig. 50.3).

With the change in gas phase pollutants over time (Fig. 50.3), an interaction between vehicle emissions and ozone concentrations was observed that has been attributed to scavenging of ozone by NO (see Eq. 50.1). A similar effect was observed when comparing weekdays with weekend days. Emissions from road traffic are on average 30 % lower on weekend days, resulting in a 10 % increase in ozone levels (Borrell 2013).

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{50.1}$$

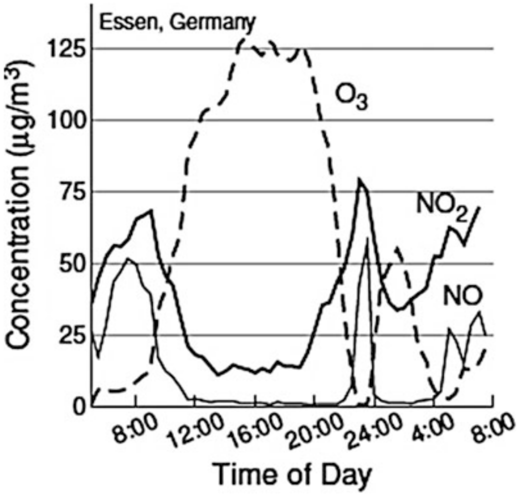


Fig. 50.3 The change in NO and NO_2 during the day indicates the high density of commuter traffic in the morning. Ozone increases with the intensity of sunlight during the afternoon and rapidly drops as the sun sets. In urban areas, the ozone levels may be attenuated as long as traffic emission as NO emissions are high and may cause a latency in buildup of ozone in the morning (Kuttler and Strassburger 1999)

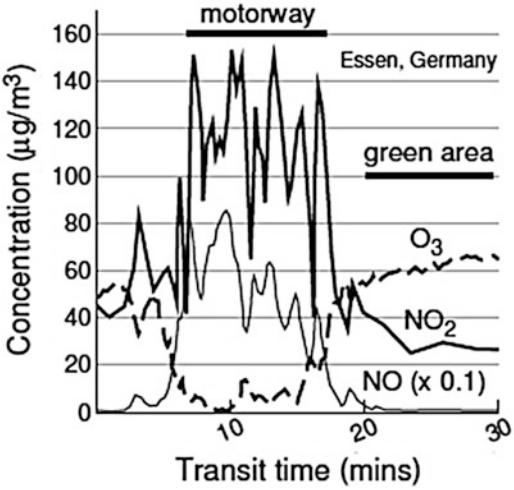
A second contributing factor is the consumption of hydroxyl radicals (that would normally contribute to formation ozone) reacting with NO_2 to form HNO_3 (see Eq. 50.2).

$$NO_2 + {}^{\bullet}OH \rightarrow HNO_3 \tag{50.2}$$

In space, Kuttler and Strassburger (1999) showed a remarkable difference in ambient air quality between driving on a highway compared to driving in less dense traffic in a green suburb (Fig. 50.4). They also indicate that vegetation has an effect on air pollutants (Liu et al. 2013; Brantley et al. 2014).

The geographical condition that tends to increase the formation of ozone is the enclosure of an area by a mountain range or river valley, as in Southern California, Mexico City, and Beijing. In these cities, it is likely that under the aforementioned meteorological conditions inhabitants of those cities will suffer from health consequences, such as respiratory irritation, in particular, if they have a susceptibility, such as asthma or COPD, and/or they engage in physical activity in the hours when ozone concentrations are high (afternoon and early evening). The effects of ozone on upper airway reactivity were confirmed in many studies and show a coherent exposure-response relationship in humans (Fig. 50.5).

Fig. 50.4 Driven transect through the city of Essen, Germany shows that the concentration of ozone on a motorway is attenuated by vehicle emissions, whereas the level tends to go up in a suburban area with decreasing levels of NO and NO_2 (Kuttler and Strassburger 1999)



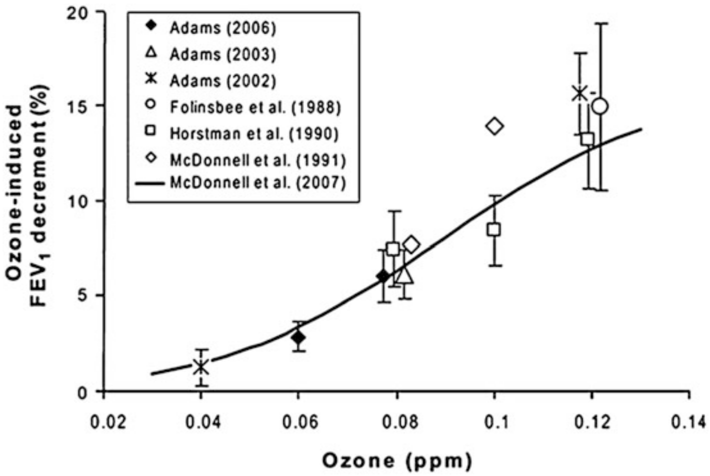


Fig. 50.5 Dose response curve for upper airway reactivity measured by the % of forced-expiratory flow reduction in 1 s (FEV-1) (Source: Brown et al. 2008)

50.2.4 Carbon Monoxide

Carbon monoxide (CO) is an incomplete combustion product emitted when coal, oil, gas, and other fossil fuels are burned. In outdoor urban air, such emissions are mostly traffic-related. It should be noted that for indoor exposures, this compound is related not so much to traffic as to poor combustion in domestic heating appliances (see Chaps. 53 and 54). Road vehicles that emit CO are primarily gasoline-powered engines, but also engines powered with liquefied petroleum gas or natural gas (see Chap. 51). They are primarily four-stroke engines used to power vans and passenger cars, but include also two-stroke engines in motorcycles. Hot spots of CO are roadsides and street canyons, in particular at traffic lights where engines are running in idle mode or are restarted. Other possible high-exposure locations are parking facilities, such as partially enclosed surface parking facilities in buildings and, in particular, completely enclosed underground parking garages that need an effective forced ventilation system to remove toxic fumes and provide fresh air. Flaws and technical problems with such ventilation systems can rapidly lead to life threatening situations (see Chap. 54). The general population is not commonly exposed to high CO exposures; workers in traffic-related occupations, such as traffic policemen, parking attendants, and tunnel booth officers, are. Persons working in the streets, such as street sweepers, street vendors, and persons in the informal sector, are also expected to be exposed at elevated levels (see recent review in IARC 2012). The health consequences are limited, as in healthy subjects the physiology can compensate for the hypoxic effects of CO exposure up to carboxyhemoglobin levels of 6 %, mainly by increasing the blood supply to tissues by coronary output, i.e., heart frequency. Individuals with a history of cardiovascular disease may suffer from acute symptoms, such as a tight chest or angina. In the case of long-term exposures, there are indications that much lower exposure levels are harmful and in part relate to direct interactions of CO with receptors. Some epidemiological studies have suggested health effects, such as increased hospital admissions and mortality from cardiopulmonary disease (Shah et al. 2013).

50.3 Particulate Air Pollutants

50.3.1 Definition of Particle Size Fractions

As shown in Fig. 50.6, the size fractions of ambient particulate matter are technical fractions. They do not correspond to the fractions that describe the penetration in a designated part of the airways, such as the inhalable fraction (particles that can pass through the nose and mouth), thoracic fraction (particles that can penetrate beyond the thorax), and respirable fraction (particles that can reach the alveoli). The latter conventions are often used to protect workers from the health effects of particle exposures and are laid down in European standard EN481. PM-10 is very similar to the thoracic fraction and PM-2.5 represents a particle size fraction with a high probability of reaching the part of the airways where – if deposited – they will not be removed by mucociliary transport, which means that their residence times will be more likely to be months than days.

It is also useful to know that the frequently used descriptors of PM-10 and PM-2.5 as particles smaller than 10 or 2.5 μm are not accurate. In the definition, 10 and 2.5 μm refer to the diameter that corresponds to a penetration probability of 50 % by

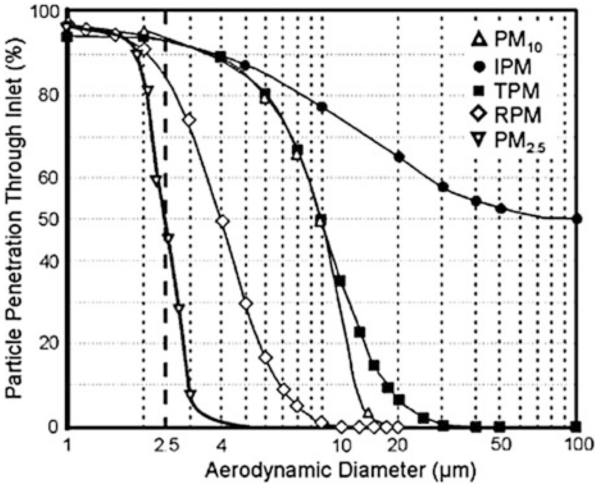


Fig. 50.6 Definitions for particle size fractions based on probability (expressed as % of mass) of penetration of particles through the inlet of an air sampling probe. PM-10 and PM-2.5 are technical fractions frequently used as standards for ambient air quality. The other fractions relate to the penetration of particles in the airways and are used to protect worker's health: inhalable particulate matter (IPM), thoracic particulate matter (TPM), and respirable particulate matter (RPM) (Wilson et al. 2002)

mass (below this diameter, this probability exceeds 50 %). Both definitions are mass-based. Reflecting recent knowledge that ultrafine particles (UFP) in particular have a high toxicity, some researchers suggest using particle numbers or particle surface area as an expression of dose. Because of the relationship between mass and volume and particle numbers by radius to the power 3 (R^3), it is clear that the relative contribution of ultrafine particles would become much greater if particle numbers or particle surface area were used instead of mass units in calculations.

50.3.2 Impact of Particle Emissions on Public Health

The closing and reopening of a steel mill in Utah Valley resulted in substantial changes in the air quality in a residential area close to this industry (Pope 1989). The industrial plant was shut down on August 1st, 1986 due to a labor dispute and reopened on September 1st, 1987 (Fig. 50.7). The average PM-10 was reduced by 50 % during the winter months. After reopening of the steel mill, hospital admission rates increased two- to threefold for children and by 44 % for adults. In months with PM-10 > 50 μg/m^3, admission rates went up by 89 % for children and by 47 % for adults. Regression analysis showed a stronger relationship with bronchitis and asthma than with pneumonia and pleurisy. Although Pope did not report on the composition of the ambient particles, it is suggested that particulate emissions from the steel mill contain PAH and oxides of metals (primarily ferrous), which are both likely contributors to the formation of reactive oxygen species (see section below).

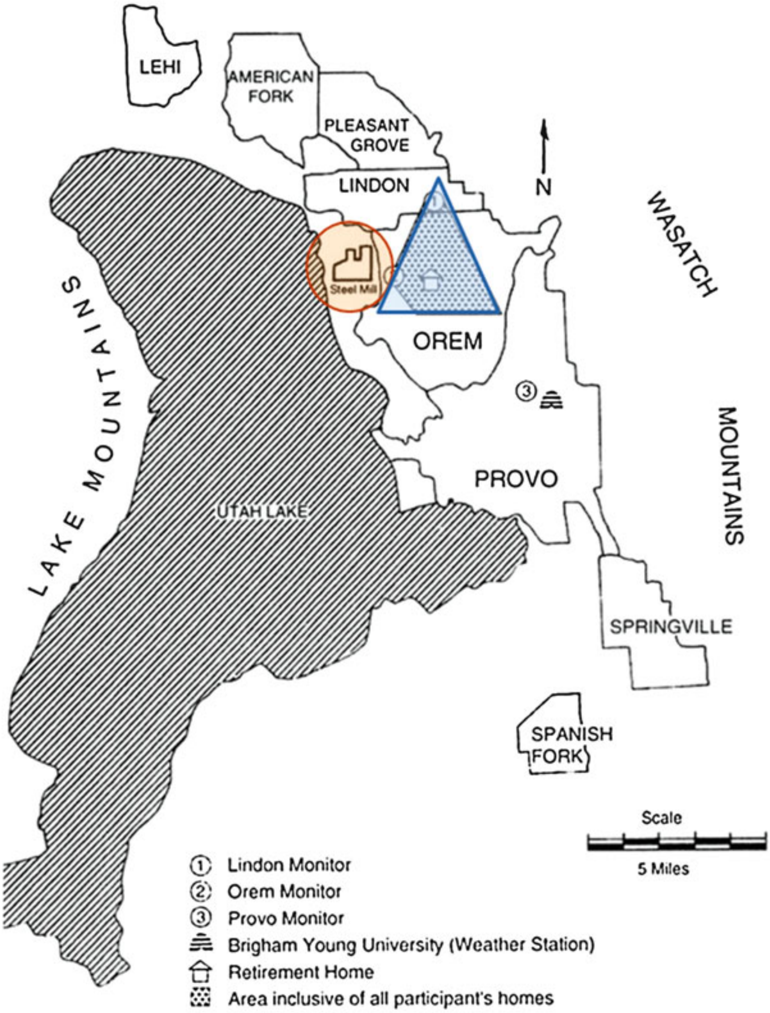


Fig. 50.7 Utah Lake valley with the location of a steel mill (*red shaded circle*) that changed the pattern of air pollution in a residential area (*blue shaded triangle*) when it was shut down for more than a year in 1986/1987 (Pope 1989)

50.3.3 Particle Composition and Source Apportionment

As discussed above, PM-10 and PM-2.5 are useful definitions of PM-fractions in terms of access to different parts of the airways. At the same time, it is difficult to assess the relevance of these air quality parameters in terms of source apportionment. Absorption of light of filter-loaded particles was introduced as a secondary

Table 50.1 Relative change (%) in cardiovascular and respiratory mortality and hospital admissions calculated from pooled epidemiology time series studies

Endpoint		Age group	No.	Percent change per 10 μg/m^3 increase (95 % CI)	
				PM-10	Black smoke
Mortality	All causes[a]	All ages	7	0.48 (0.18–0.79)*	0.68 (0.31–1.06)*
	Cardiovascular	All ages	7	0.60 (0.23–0.97)*	0.90 (0.40–1.41)*
	Respiratory	All ages	7	0.31 (−0.31–0.86)	0.95 (−0.31–2.22)
Hospital admission	All respiratory	> = 65	6	0.70 (0.00–1.40)*	−0.06 (−0.53– 0.41)
	Asthma + COPD	> = 65	5	0.86 (0.03–1.70)*	0.22 (−0.73–1.18)
	Asthma	0–14	5	0.69 (−0.74–2.14)	1.64 (0.28–3.02)*
	Asthma	15–64	5	0.77 (−0.05–1.61)	0.52 (−0.50–1.55)
	Cardiac	All ages	4	0.51 (0.04–0.98)*	1.07 (0.27–1.89)*
	Cardiac	> = 65	4	0.67 (0.28–1.06)*	1.32 (0.28–2.38)*
	Ischemic heart disease	> = 65	5	0.68 (0.01–1.36)*	1.13 (0.72–1.54)*

Modified from Janssen et al. (2010)
[a]Including cardiovascular and respiratory mortality
No. number of estimates
*$p < 0.05$

outcome in addition to gravimetric determinations of filter loads. This so-called black smoke is a proxy for the finer combustion-derived particulate matter. It is not surprising that black smoke is very different from PM-10, not only in terms of source apportionment but also in its use to relate air pollution constituents to health endpoints. An overview of the impact of PM-10 and black smoke on total mortality, and cardiovascular and respiratory endpoints is presented in Table 50.1 (Janssen et al. 2010). Air pollution parameters have also been linked to the risk of long-term effects, such as cancer, in particular, adenocarcinoma lung cancer in a meta-analysis of 17 European prospective cohort studies in the ESCAPE project (Raaschou-Nielsen et al. 2013). This study confirmed the findings of earlier studies and eliminated many of the methodological limitations of these earlier studies. The researchers were not able to pinpoint a threshold in the lung cancer risk and suggest that there might be an increased cancer risk even below current air quality guidelines in Europe (year average of 40 μg/m^3 for PM-10 and 25 μg/m^3 for PM-2.5). Although the hazard ratio of 1.22 (95 % confidence interval of 1.03–1.45 for an increase of 10 μg/m^3 of PM-10) is small as compared to the risk for current active smoking, the health impact is quite substantial due to the simple fact that the entire population is exposed. The shift of the tumor histology from squamous to a stronger association with adenocarcinoma could be indicative of the role of polycyclic aromatic hydrocarbons and their nitro-derivates (see Chap. 51, Raaschou-Nielsen et al. 2013).

Table 50.2 Life expectancy gain when shifting from car to bicycle

Factor	Relative risk	Gain in life (days/person)	95 % confidence interval (days/person)
Air pollution	1.001–1.053	−21	−0.8 to −40
Traffic accidents*	0.996–1.010	−7	−5 to −9
Physical activity	0.500–0.900	+240	90–420

Based on Hartog et al. (2010); * Related to a covered distance of 7.5 km

50.3.4 Contribution of Road Traffic

Exposure to particles near busy roads showed associations with respiratory health (Brunekreef et al. 2009). Separate traffic counts for automobiles and trucks revealed associations of lung function changes in children living less than 300 m from motorways with a high intensity of diesel-powered vehicles, such as trucks, suggesting that diesel exhaust particles have a contribution. Alternative expressions of particle-associated air pollution, such as 'black smoke' values in filters, are good indicators for traffic-related ultrafine particles (Janssen et al. 2010). A black smoke value can be determined by the reflection of light from particle-fractions loaded on filters during air sampling campaigns.

50.3.5 Particle Air Pollution and Life Expectancy

The cohort studies conducted in the US have suggested that the overall impact of particulate air pollution can be expressed in terms of a life-shortening estimated to be 1–2 years. Such calculations in European studies have resulted in similar effects, but not in Scandinavia (Boldo et al. 2006). Hartog and co-workers (2010) calculated the gain in life expectancy of using different vehicles when commuting (Table 50.2). The transition from using a car to travelling by bike over a distance of 7.5 km resulted in a somewhat higher risk (average loss of 21 days in life expectancy) due to exposure to traffic fumes and the risk of involvement in traffic accidents (average loss of 7 days). This relative loss of 1 month is compensated with a gain of 8 months due to the 10–50 % lower risk due to the increased physical activity that goes with riding a bike. The net life gain is estimated to be 7 months.

50.4 Discussion

Because of the large population at risk, there are substantial public health benefits to be gained by a reduction in air pollutants. These benefits should be traded off against the high cost in air pollution abatement. These high stakes have generated discussions about the scientific quality of the epidemiological studies presented earlier in this chapter. The earliest studies using time series analysis were criticized because of insufficient standardization for confounding factors, such as co-exposures to other components in the cocktail of air pollutants, and other factors, such as high air temperatures during episodes of poor air quality, for endpoints such as cardiovascular mortality (Ren et al. 2006). Following the introduction of standards for fine dust by US-EPA in 1997, a reanalysis of the data from the Six Cities study by Dockerey et al. in 1993 and the ACS study reported by Pope and co-workers in 1995 was performed, which showed that the results could be reproduced and that the results could be replicated using alternative models (HEI 2000). Similar findings from other studies in Europe were also reported (Hoek et al. 2009), which made it clear that the observed mortality involved mainly individuals with pre-existing cardiopulmonary disease. It was suggested that air pollution contributed to a shortening of life expectancy of those individuals who would have died of other causes. Over the past 20 years, observations from studies performed in the US have been replicated in Europe (Brunekreef and Holgate 2002; Raaschou-Nielsen et al. 2013).

Some indicators for exposure to air pollutants such as ozone are useful, because they represent hazardous constituents of air pollution and can be used to estimate the risk of respiratory health effects (Brunekreef and Holgate 2002) but not cardiovascular effects (Shah et al. 2013). Other indicators such as CO, NO, NOx, PM-10, and PM-2.5 are more controversial. CO may be useful as a chemical marker of the reductive type of emissions from combustion sources, such as exhaust from spark ignition combustion, but is not very useful for assessing health effects caused by this air pollutant. In outdoor air, CO is associated with particle emissions from road traffic (Shah et al. 2013). High exposure settings are most relevant to persons who spend much time near road traffic, such as in some occupational exposures (traffic policemen, street vendors, toll boot officers, et cetera). These workers may suffer from chronic effects of low exposure rather than hypoxic effects. For the general public, usually outdoor exposure levels are low relative to indoor exposures related to indoor use of open fire (see Chaps. 51 and 52).

There is not much evidence to suggest that there is a strong basis for proposing the use of NO_2 as an indicator for respiratory health effects (Hesterberg et al. 2009). Suggestions to use NO_2 as a proxy for traffic-related air pollution are also disputed, since abatement strategies such as particle filters may lead to an increase in emissions of NO_2 (Millstein and Harley 2013; see Chap. 51).

A recent meta-analysis indicated that particle fractions such as PM-10 and PM-2.5 are useful definitions because these particulate fractions relate to penetration in airways. They have been linked to cardiovascular effects (Shah et al. 2013) and lung cancer (Raaschou-Nielsen et al. 2013). With respect to source apportionment, these PM-fractions are less useful. For health impact evaluation of (traffic-related) abatement strategies, other indicators, such as black smoke, black carbon, and elemental carbon, may be more useful (Janssen et al. 2010). Increased chronic respiratory symptoms and lung function (measured by FEV-1) in children was associated with black smoke levels inside schools (Brunekreef et al. 2009; van Vliet et al. 1997). In addition, chemical markers for the organic mixture from combustions sources can be used for source apportionment or to study specific mechanisms, e.g., the use of hopanes from lubricating oils (Kleeman et al. 2006) or 1-nitropyrene to reflect genotoxic substances (Scheepers et al. 1995; Chap. 51).

Fig. 50.8 Equipment for measurement of ambient particulate matter for estimation of the exposure of commuters to traffic fumes in The Netherlands (Photo: Bas de Meijer)

Fig. 50.9 Example of using crowd sourcing to collect data on atmospheric particle concentrations. The technology was developed as the Spectropolarimeter for Planetary EXploration (SPEX) and designed to measure aerosol and cloud particles in the atmospheres of planets within the solar system. This technology was simplified and miniaturized to a setup-module for a smartphone supported by an app (www.ispex.nl). The goal is to involve 10,000 users in this citizens' science network in The Netherlands

In the near future, an improvement in exposure assessment strategies is expected. In the recent ESCAPE study, land-use regression models were developed for different pollutants, which used within-area contrasts in individual exposure estimates and were based on actual measurements (Raaschou-Nielsen et al. 2013). Such models may be further improved by including data on activity patterns. Recent studies of commuter behavior have shown differences in health risks, according to the use of different types of transportation (Fig. 50.8; Zuurbier et al. 2010). There are also some interesting initiatives based on crowd sourcing to acquire data that may be used in future studies of the health implications of air quality (see Fig. 50.9).

Conclusions
Outdoor air is a complex mixture derived from the interactions of anthropogenic emissions and atmospheric chemistry. Using the variability of exposure in space and time showed that air quality has a significant impact on the burden of disease and mortality in most parts of the world. The toxicity of individual gas phase components is generally well understood, but in the complex mixture of outdoor air linking toxic potency to health effects remains a challenge. The toxicity of particulate matter is less well understood and only recently studies have indicated that ultrafine particles have significant local and systemic health effects, even in a very low dose range (see Chap. 51). It is to be expected that different expressions of exposure and dose will further improve the use of indicators for air quality to predict early health effects and these markers will support abatement strategies to reduce the adverse health effects of air pollution.

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Chapter 51
Health Implications of Combustion Engine Exhaust

Paul T.J. Scheepers

Abstract The internal combustion engine is the primary power source in road traffic. Particulate matter, nitrogen oxides, hydrocarbons, and carbon monoxide engine emissions are regulated. New technology engines have much lower emissions of these exhaust components, but most vehicles currently on the road still rely on conventional engine technology. New biomass-based and non-petroleum synthetic components blended with conventional fuels may contribute to a reduction in exhaust emissions. Further reduction of regulated emissions is accomplished by exhaust after-treatment. However, even with these adaptations conventional engines produce exhaust fumes that have many toxic properties, and population-based studies show that exposure to emissions from road vehicles is associated with an increased burden of cardiovascular and respiratory disease and mortality, including lung cancer. Regarding the growing knowledge of toxicity mechanisms, additional markers and toxicity testing will be needed to evaluate the health impact of exhaust not only of improved and new engines concepts but also of retrofitted exhaust after-treatment and alternative fuels systems.

Keywords Combustion engine • Exhaust • Health effects • Emission • Respiratory diseases • Cancer • Alternative fuels

51.1 Introduction

The propulsion of road vehicles is currently dominated by combustion engines. These engines rely primarily on non-renewable petroleum-based fossil fuels as their energy source, but there is a trend toward reducing the use of conventional gasoline and diesel fuels and increasing that of biofuels and synthetic non-petroleum fuels, with gas fuels also playing a minor role (Fig. 51.1). There are some changes in the direction of reducing the share of fossil fuels, such as the use of biomass-based fuels as feedstock for gasoline (e.g., admixing of ethanol) or diesel (e.g., admixing of biofuels). They require the substitution of a conventional combustion engine by

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_51

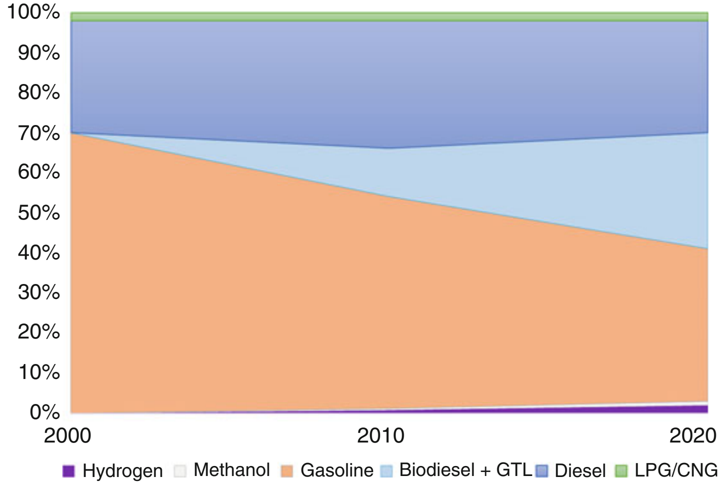

Fig. 51.1 Possible scenario in use of fossil fuels, biofuels and synthetic non-petroleum fuels in road vehicles. *LPG* liquefied petroleum gas, *CNG* condensed natural gas, *GTL* gas-to-liquid (see text for more details) (Modified from R. Clark et al. 2006)

alternative technology and fuel-supply technology, which will take a considerable time to realize.

For air quality, the development of zero emission solutions is promising, but it will take a considerable time for electricity and fuel cell-powered traction to penetrate the market of road vehicles. Biofuels and some synthetic fuels provide alternatives, because these new products can be blended with conventional fuels. This chapter will review the health implications of exhaust from the gasoline engine (Otto engine or spark ignition engine) and the engine concept developed by Rudolf Diesel. In this chapter the engine types will be named according to their conventional fossil fuel, i.e., gasoline engine and diesel engine. Other combustion engines, such as those used for the propulsion of airplanes, trains, and ships, will not be discussed, although such sources will also contribute to air quality and have implications for health in some particular settings.

51.2 Conventional Technology Engines

Before discussing the health effects of exposure to exhaust from combustion engines, some characteristics of engine technology will be briefly introduced. The difference in the composition of exhaust from gasoline and diesel engines is shown in Fig. 51.2. Figure 51.3 shows that the emissions from in-use conventional technology road vehicles in California, the rate of emissions of polycyclic aromatic hydrocarbons (PAH) from gasoline and diesel exhaust is similar. However, due to the fuel and engine characteristics, diesel-powered engines emit nitrated polycyclic

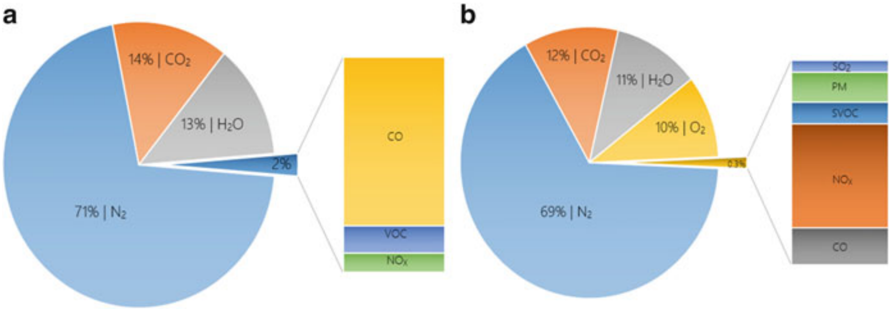

Fig. 51.2 Composition of exhaust from a gasoline-powered (**a**) and diesel-powered (**b**) road vehicle (Source: http://autoeco.info/)

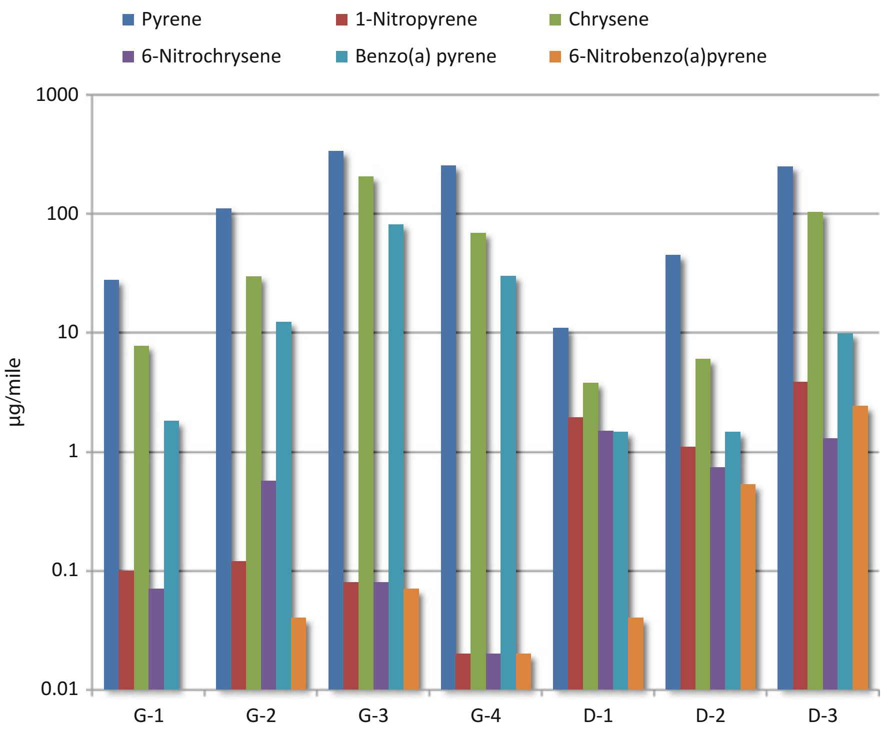

Fig. 51.3 Formation of a section of nitroarenes with their chemical precursors by multiple in-use gasoline-powered vehicles (G) and diesel-powered vehicles (D) in California, tested on chassis dynamometer in an Urban Driving Cycle (UDC). G-1: Mazda Millen, Ford Explorer, Nissan Maxima, GMC 1500 Pickup, Mercury Sable; G-2: Ford F-150 pick-up; G-3: Mitsubishi Montero; G4: Mazda Millenia, Ford Explorer, Nissna Maxima, GMC 1500 Pickup, Mercury Sable; D-1: Dodge Ram 2500 Pickup, Mercedes Benz E300, Volkswagen Beetle TDI; D-2: Dodge Ram 2500 Pickup; D-3: Dodge Ram 2500 Pickup, Mercedes Benz E300, Volkswagen Beetle TD (Data from Zielinksa et al. 2004)

aromatic hydrocarbons (nitro-arenes) at concentrations one to two orders of magnitude higher than gasoline-powered engines.

51.2.1 Gasoline Engine Exhaust

The engine most commonly used in road vehicles is a gasoline-powered four-stroke engine. A spark is used to ignite the fuel-air mixture leading to compression, which results in locomotion. Fuel injection is electronically regulated and improves the efficiency of the combustion, also leading to a more complete combustion. These engines require a fuel that contains low-boiling aliphatic and aromatic hydrocarbons, and the exhaust contains volatile organic compounds (VOC), carbon monoxide (CO), and nitrogen monoxide and nitrogen dioxide (NO and NO_2), together indicated as NO_X (see Fig. 51.2 and Chap. 50). The total mass emissions of gasoline engines are more sensitive to low temperatures than are mass emissions from diesel engines (Zielinska et al. 2004). In small road vehicles (usually with two or three wheels), such as motor cycles and scooters, two-stroke engines are used. The lack of a well-controlled fuel injection system contributes to the situation that many of these engines are not well-tuned and may produce high emissions of PM, VOC, and CO.

51.2.1.1 Tetraethyl Lead

To improve the performance of the fuel, tetraethyl lead is used as a fuel additive to prevent engine knocking. In most parts of the world, lead has been phased out due to health and environmental policies (see Fig. 51.4), and other organic compounds, such as Methyl-tertiary-butylether (MtBE), are now used to improve the fuel octane number. The combustion in gasoline engines is typically a ‘rich’ mixture, meaning that it uses a high fuel to air ratio. This leads to a type of combustion that tends to produce incomplete combustion products lower in oxygen as compared with the combustion in a diesel engine (see Sect. 51.2.1.3).

51.2.1.2 Volatile Organic Compounds (VOC)

Exhaust fumes typically contain incompletely combusted fuel components. The gasoline engine may produce gas phase as well as a condensate of liquid phase hydrocarbons (HC). In this and also other chapters (Chaps. 50 and 52), these exhaust components will be referred to as volatile organic compounds (VOC). These emissions were in part responsible for the formation of photochemical smog in large urban agglomerations (see Chap. 50). As the emissions from passenger cars and small vans were reduced, the attention shifted to the emissions from two-stroke engines in small road vehicles, which are much used in congested cities.

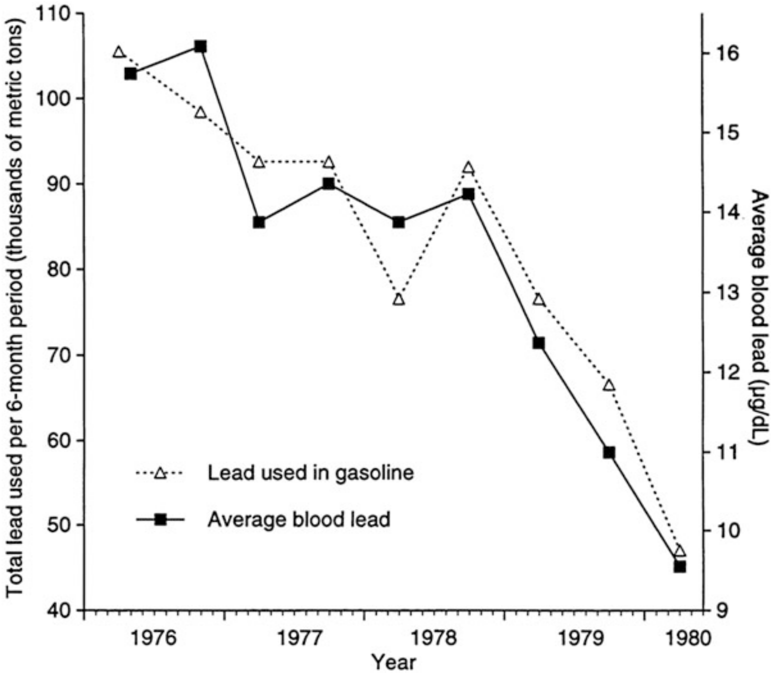

Fig. 51.4 Decreasing blood lead values in the US population attributed to phasing out of lead (Source: Reprinted, with permission, from J.L Annest, "Trends in the blood lead levels of the U.S. population: The Second National Health and Nutrition Examination Survey (NHANES II) 1976–1980," in Lead Versus Health, M. Rutter and R.R. Jones, eds., New York: John Wiley & Sons. ©1983, John Wiley & Sons, Ltd. NHANES)

These engines are not very efficient as compared to the car engine and may emit a considerable part of their fumes as non- or incompletely combusted fuel. Systems available for after-treatment did not improve this situation (Clairotte et al. 2012). As shown in studies of exhaust in two-stroke engines in chain saws, the emissions are dependent on how the fuel/air ratio is tuned (Nilsson et al. 1987). The relative contribution of these vehicles to the overall emissions from road traffic can be considerable. This situation, combined with the contribution of these vehicles to traffic accidents, resulted in restrictions on the use of motorcycles in some African and Asian countries.

51.2.1.3 Carbon Monoxide (CO)

Due to the limited supply of intake air, the combustion in a gasoline engine is characterized as a rich mixture (high fuel to air ratio). In terms of chemistry, the mixture is reductive and contains carbon monoxide as one of its incomplete combustion products. This toxic gas is emitted when gasoline is used but also when the engine is powered by other fuels, such as liquefied petroleum gas.

51.2.1.4 Lubricating Oil

Not many studies addressed the contribution of lubricating oil as a source of exhaust emissions. The pattern of PAH determined in a vehicle emitting visible black smoke corresponded to the profile of the PAH of the lubricating oil rather than that of the fuel (Zielinska et al. 2004). This suggests that the lubricating oil is a sink for PAH formed during combustion. These PAHs, which may contain some of the heavy > =6-ring PAHs, will be emitted as unburned lubricating oil. Hopanes and steranes can be used as chemical markers of environmental pollution caused by emissions of lubricating oils (Riddle et al. 2008).

51.2.2 Diesel Engine Exhaust

The concept of the diesel engine is much different from that of the gasoline engine. The fuel for a diesel engine is less volatile and after mixing with combustion air is ignited by high pressure and temperature built up in the cylinder. Unlike the gasoline engine, a diesel engine is cooled by intake air and runs at a much higher temperature. The fuel-air mixture is not as rich as in the gasoline-powered engine, as the term 'lean burn' is often used in the case of diesel combustion, and results in the emission of surplus oxygen in the exhaust (Fig. 51.2). The diesel engine also emits particulate matter (PM), nitrogen oxides (NO_X), semi volatile organic compounds (SVOC), and sulfur dioxide (SO_2). Each of these emission components will be discussed in greater detail below.

51.2.2.1 Nitrogen Oxides (NO_X)

Because of the high temperatures and large intake of ambient air for combustion, the engine produces high emissions of nitrogen monoxide and nitrogen dioxide (commonly jointly referred to as NO_X). In the combustion chamber, this high output of NO_x can be reduced by decreasing the temperature of the combustion, e.g., by admixing water to the diesel fuel (http://www.dieselnet.com/tech/engine_water.php). This results in these engines having a lower power-output. Moreover, in general, reduction in the emission of NO_X also leads to less effective combustion of PM (soot), which illustrates an important dilemma in diesel technology commonly known as the 'NO_X – soot trade-off' (see Fig. 51.5).

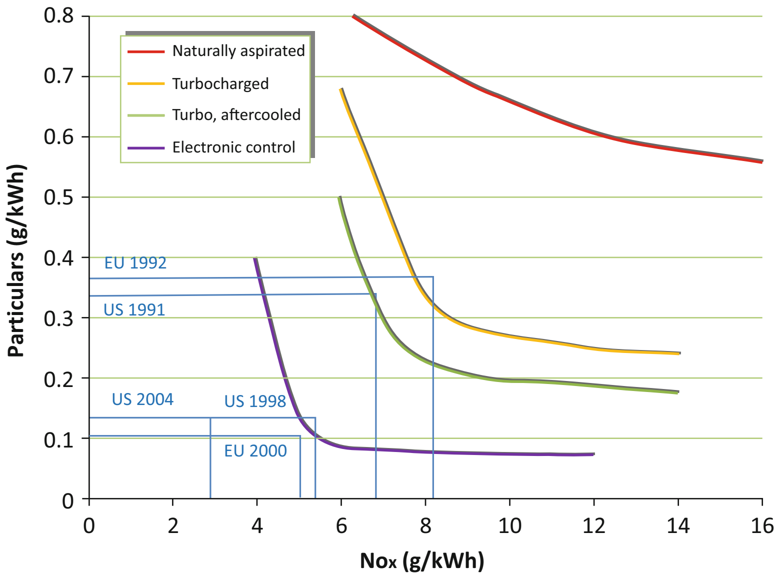

Fig. 51.5 Trade-off between NO_X and PM emissions for different generations of diesel engines. The *red lines* indicate the levels of new engine emission standards in Europe and the US (Source: http://www.dieselnet.com/tech/engine_design.php)

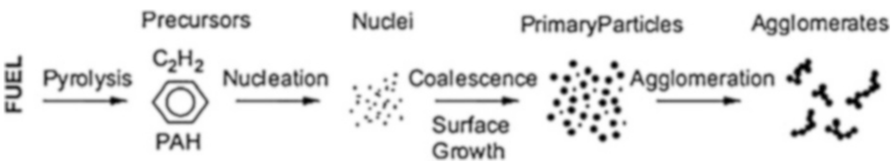

Fig. 51.6 Sequence of events leading to the formation of diesel exhaust particles (DEP) (Source: http://dc616.4shared.com/doc/aUPl6g-l/preview.html)

51.2.2.2 Particulate Matter (PM)

The particle phase is often referred to as particulate matter (PM) or diesel exhaust particles (DEP) and consists of solid particles with a mass median aerodynamic diameter of 0.124 ± 0.025 μm. These particles are formed by aggregation and agglomeration from unstable nanometer primary nuclei and ultrafine primary particles in a process referred to as aging. Their final morphology resembles grapes (Figs. 51.6 and 51.7) with a high specific surface (30–50 m^2/g) very similar to activated carbon used as an adsorbent in air sampling.

The core of the particles consists of elemental carbon (soot) and may carry a high load of adsorbed hydrocarbons, condensed SVOC, metals, and metal oxides and

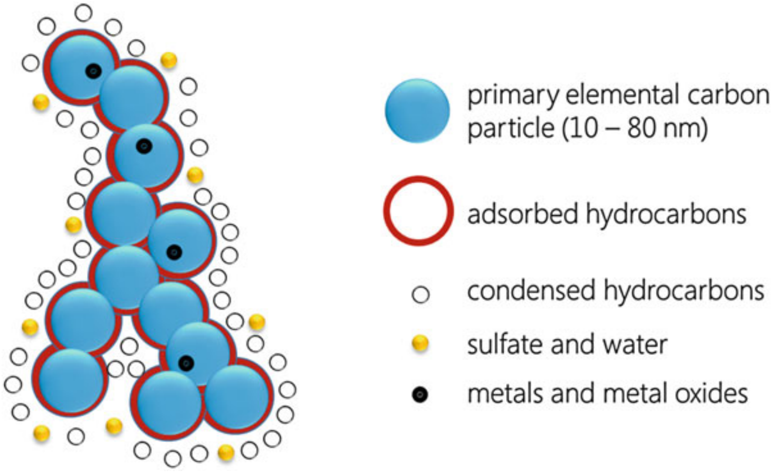

Fig. 51.7 Composition of a diesel engine particle (DEP) agglomerated by aging (Modified from: Avinash Kumar Agarwal et al. 2011)

sulfate with associated water (Fig. 51.7). These particles have the ability to remain airborne for a long time and the carbon surface tends to stabilize the adsorbed chemicals relative to other materials.

51.2.2.3 Semi Volatile Organic Compounds (SVOC)

The VOC produced by a diesel engine are likely to be much less volatile. This is due to the lack of low boiling-point hydrocarbons in the fuel, but also, because of the higher temperature of 500–600 °C reached in the combustion chamber, the engine will tend to produce primarily semi volatile organic compounds (SVOC) that are to some extent oxidized by a surplus of combustion air. In the gas phase, aldehydes are more abundant than in the exhaust from a gasoline engine. Like the gasoline engine, the diesel engine also produces incomplete compounds such as polycyclic aromatic hydrocarbons (PAH). The presence of small PAHs such as fluorene in diesel fuel increases the emissions of PAH dramatically whereas monoaromatic hydrocarbons such toluene have no influence on these emissions (Mi et al. 2000). It is suggested that the PAH content of the lubricating oil has less influence on the emission composition than in a gasoline engine (Zielinska et al. 2004). PAH are likely to be oxidized, leading to the formation of oxygenated species (oxy-PAH). In airborne PM, 9-fluorenone and 9,10 anthraquinone are the most abundant oxy-PAH derived from diesel exhaust (Albinet et al. 2006). Because of the high levels of NO_2 and HNO_3 in the exhaust manifold, some of the PAH are nitrated. These so-called nitroarenes are much more abundant in diesel than in gasoline engine exhaust (see Fig. 51.3). Because of their lower vapor pressure, these SVOC adsorb to PM. A diesel engine fueled with pure hexadecane produces

PAH (Abbass et al. 1988). This does not mean that the PAH content of fuel has no influence on incomplete combustion products. On the contrary, because PAH are very resistant to high temperatures, it is likely that PAH will survive the high-temperature conditions in the combustion chamber.

51.2.2.4 Sulfur Dioxide

As diesel fuel contains organic sources of sulfur, combustion leads to the formation of SO_2, which reacts with water vapor to sulfate and will absorb on the PM surface (Fig. 51.7). As the sulfur content is reduced to below 0.2 % in most diesel fuels, the particle sulfate content has reduced a lot over the past decades.

51.3 After-Treatment

In addition to changes in fuel and engine technology, systems were developed to change the emissions from the engine at the tailpipe using so-called after-treatment technology. These systems include oxidation catalysts and particle filters, and will be further discussed below.

51.3.1 Three-Way Catalyst

The contribution to exhaust of fuel components and incompletely combusted VOC was significantly reduced by the introduction of the three-way-catalyst. This catalyst also required the use of unleaded fuel, because the platinum catalyst surface is not compatible with lead. Platinum is a ubiquitous trace element because there is a natural background of this metal. The reduction in exhaust emissions has contributed to much lower VOC levels, and as a result, also to much lower ozone levels in densely populated urban areas (see Chap. 50).

51.3.2 Oxidation Catalyst

To remove PM from the engine exhaust, an oxidation catalyst can be effective because soot can be removed effectively by combustion. Sharp and co-workers (2000) studied the effect of a catalyst in the emissions of two different conventional technology engines tested on a chassis dynamometer in the US EPA heavy duty transient Federal Test Procedure (FTP) (for more details see http://www.dieselnet.com/standards/cycles/ftp_trans.php). As shown in Figs. 51.8 and 51.9, the emission of 1-nitropyrene goes up 10-fold when an oxidation catalyst is fitted to the engine. This is irrespective of the type of fuel (either diesel fuel, biofuel, or an 80:20 % blend). Both test engines were normally employed with this catalytic converter. These results suggest that the effect

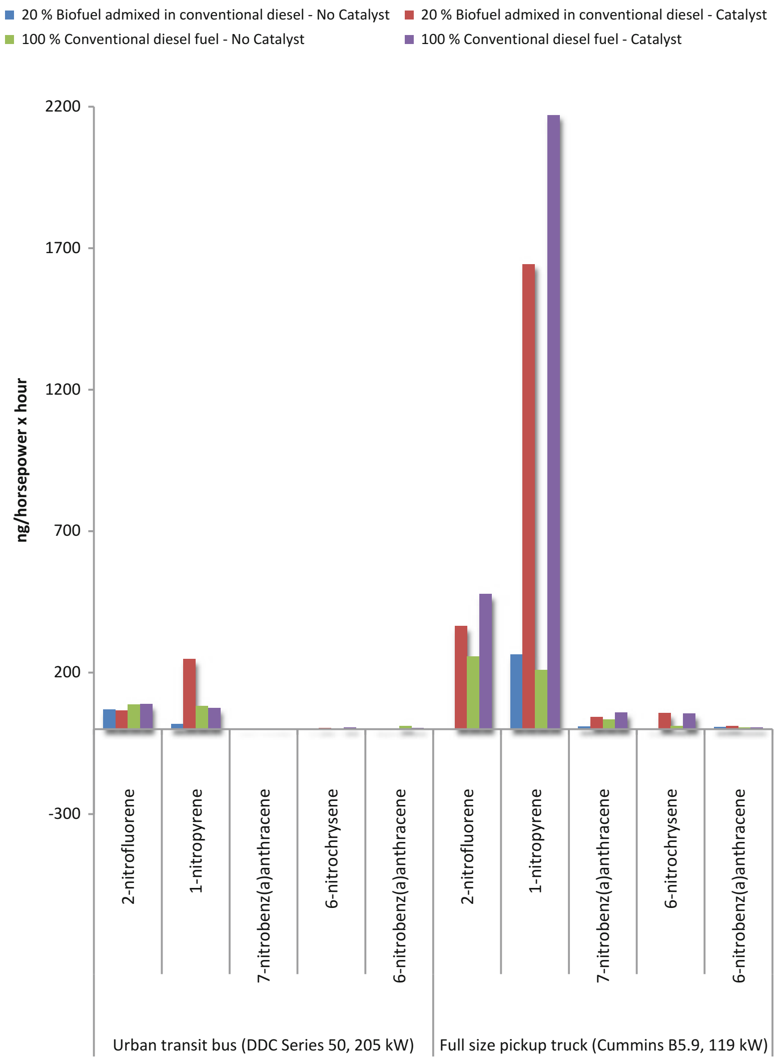

Fig. 51.8 Influence of removing an oxidation catalytic converter on two engines that are normally equipped with such a converter. For test conditions and discussion see text (Data from Sharp et al. 2000)

can be dependent on the type of engine and may not be the same for every specific nitroarene. It is also possible that the result is dependent on the type of driving cycle used in the test. In that respect, the increase of 1-nitropyrene may still be underestimated as compared to real-life use, since the used test cycle simulates a city traffic pattern with many stops, a low average speed of 30 km/h and an engine temperature not higher than 250–350 °C (with peaks of 450 °C during the hot sections in the cycle (www.dieselnet.com). Testing of in-use vehicles on a chassis dynamometer

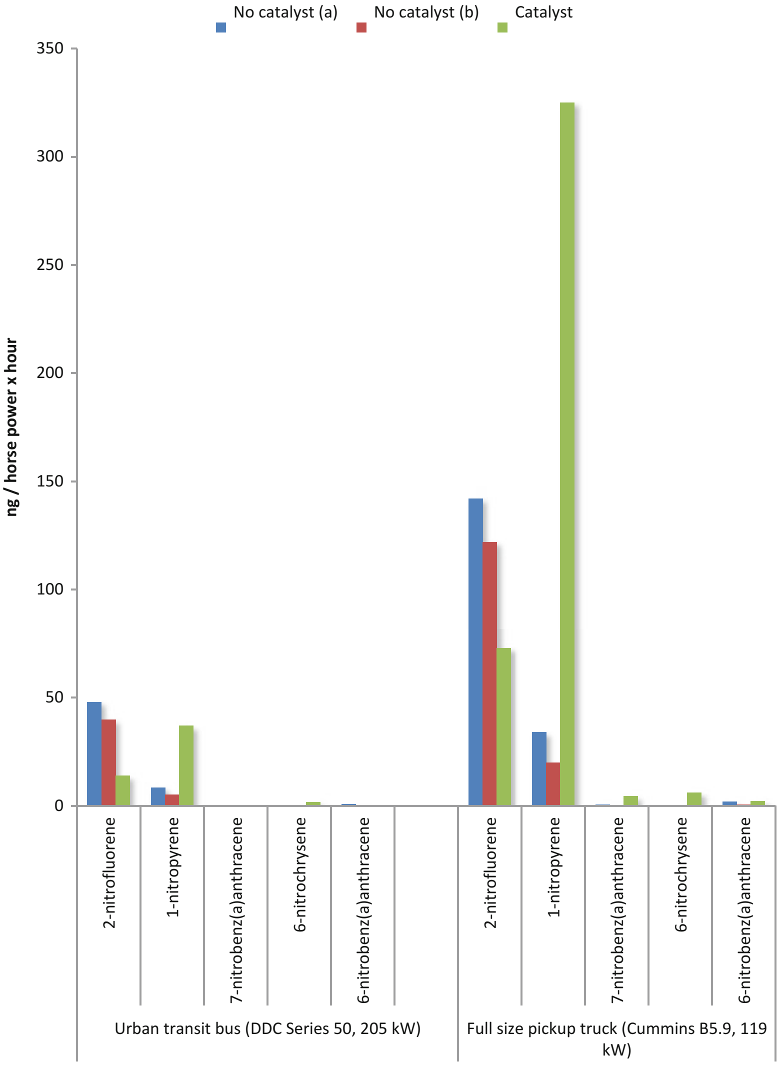

Fig. 51.9 Influence of removing an oxidation catalyst in two engines that are normally equipped with such a converter. For this test 100 % biofuel (methyl ester produced from virgin soybean oil) was used, which produced lower amounts of PAH and nitro-PAH as compared to conventional fuel. The engine was tested two times without the catalyst (**a** and **b**). For test conditions and discussion see text (Data from Sharp et al. 2000)

in a highway cycle suggested that emissions of nitro-PAH increase at higher speed, presumably due to higher levels of oxides of nitrogen produced in much hotter combustion and exhaust conditions (Scheepers et al. 2001).

51.3.3 Particle Filter

Particle filters using the wall flow filter principle are effective in reducing the emissions of soot and also of SVOC associated with PM up to efficiencies well above 99 %. Some particle filters may require a fuel-borne catalyst, such as iron, cerium, or copper. Traps may be placed on new engines but may also be retrofitted to conventional technology vehicles. In addition to removing PM from the exhaust emissions, particle filters may also function as chemical reactors (Mayer et al. 2003). Similar to oxidation catalysts, particle traps may increase the formation of nitroarenes. However, most of these substances are not present in the gas phase and will be captured in the filter with the particle. Only 2-ring gas-phase nitroarenes, such as nitronaphthalenes and nitrophenanthrenes, increase downstream of the trap up to tenfold compared with non-filtered exhaust (Mayer et al. 2003). When doping the fuel with chlorine, a particle trap can generate substantial amounts of polychlorinated dioxins and furans (Laroo et al. 2012). Mayer and co-workers showed that the addition of copper as a fuel borne catalyst gave rise to an increase in poly-chlorinated dioxins and furans by three orders of magnitude. Chlorine is not normally added to fuels, but may be aspired as airborne sodium chloride with the combustion air in an engine operated on a marine ship or in a car driving close to the coast. The continuous regenerating trap (CRT) is a special type of particle filter that uses a catalytic converter to convert NO to NO_2. The principle is based on unstable NO_2 that produces oxygen radicals and allows the regeneration of the trap at a relative low temperature. The surplus of NO_2 in the emissions from the CRT system leads to emissions of up to 500 ppm from the tailpipe (Mayer et al. 2003). A particle filter integrated into an exhaust gas recirculation loop resulted in a 50 % reduction of soot emissions (Gill et al. 2012).

51.4 Developments in Fuel and Engine Systems

51.4.1 Liquefied Petroleum and Natural Gas

Liquefied petroleum gas (LPG) and compressed natural gas (CNG) are attractive alternatives to gasoline in gasoline engines because of their high octane numbers (Delpech et al. 2010). However, the production capacity is limited (see Fig. 51.1). An ongoing development is the availability of non-petroleum fossil fuels, such as the biofuels ethanol (from grains or sugarcane) and butanol (from sugar beets) that are admixed to gasoline.

51.4.2 Liquid Fuels

Over the past decades, the production of synthetic liquid fuels, such as coal-to-liquid (CTL), gas-to-liquid (GTL) and biomass to liquid (BTL), has increased. For

GTL, oil companies are generating an enormous production capacity, suggesting that it will become possible to blend this product with conventional diesel fuel and also provide pure GTL for closed fleets, e.g., public transportation buses in cities where higher air quality standards are required. So far, laboratory-based tests have shown that admixing of 15 and 30 % to conventional fuel can have a beneficial effect on all of the regulated emission parameters, PM, SVOC, NO_X and CO, in current technology 1996–1999 engines compliant with Euro 2/3 emission standards (Clark et al. 2006). For new technology 2003 vehicles compliant with Euro 3/4 running on pure GTL diesel, the reductions were favorable for VOC and CO but ambiguous for PM and NO_X (Xinling and Zhen 2009). Optimization of new technology engines and engines dedicated to GTL are expected to achieve Euro 5 emission standards in vehicles registered for Euro 4 (Kind et al. 2010). It has been shown that GTL fuel extends the time to regeneration of the CRT type of particle filter that is fitted on new vehicles compliant with Euro 4 emission standards (Liebig et al. 2009).

The BTL solution for diesel engines is called biodiesel, which is often produced from a rapeseed oil or soybean oil feedstock. The fatty acids are usually entirely converted by transesterification by alcohol and catalysts into mono alkyl esters in the range from C_{14} to C_{20}, depending on the feedstock materials used. Biofuels contain oxygenated hydrocarbons and have the potential to reduce PM emission (Gill et al. 2012). Rapeseed methyl ester (RME) produced lower soot emissions than conventional diesel and GTL diesel but the concentration and diameter of nonvolatile nucleation mode cores was substantially greater (Heikkilä et al. 2009). Soybean- and animal-based biodiesel blended with a standard diesel fuel showed consistently increased NO_X with increasing biodiesel blend level (Hajbabaei et al. 2012). Since biofuels and synthetic fuels such as GTL contain no PAH, a reduction of such compounds in the emissions is to be expected. PAH can be generated de novo during combustion (see Sect. 51.2.2). A limitation of many studies of biofuels is that, when testing a biofuel, the oil compartment may still contain PAH derived in part from the previous use of conventional diesel. Nevertheless, a reduction of PAH ranging from 50 to 95 % and for the nitro-PAH from 50 to 90 % was observed only by changing from conventional diesel to soybean-based biodiesel in the engine of a highway truck (a 1997 Cummins N14) equipped with an oxidation catalyst (Sharp et al. 2000). Although it was suggested that the introduction of biofuels would increase emissions of formaldehyde (Salthammer 2013), tests performed so far showed that emissions of aldehydes (formaldehyde, acetaldehyde, and acrolein, accounting for 75 % of the aldehyde emissions) were generally lower, but no difference in exhaust emissions was observed when the relative contribution of small aldehydes was compared to that of conventional diesel fuels (Fig. 51.10).

51.4.3 New Engines Concepts

A new diesel engine technology introduced after 2007 showed much lower emissions of particles and incompletely combusted hydrocarbons compared to the

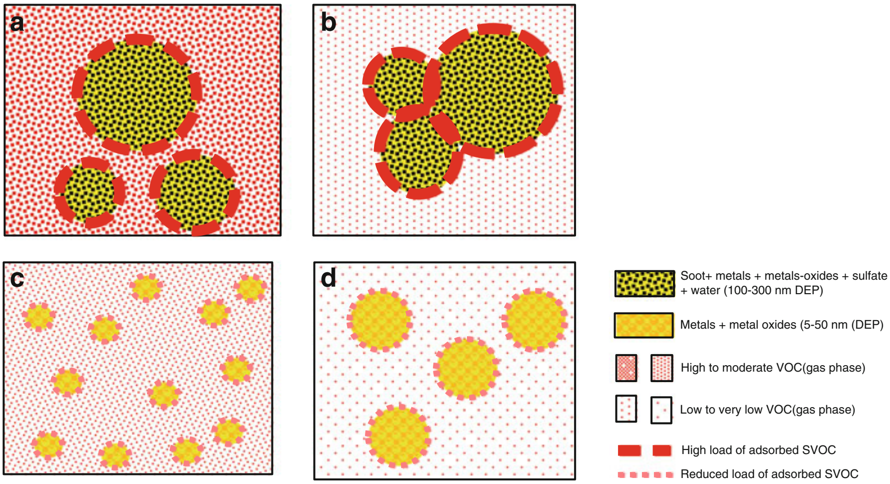

Fig. 51.10 Schematic representation of diesel engine exhaust emissions. Fresh emissions from conventional technology engines (**a**); aged emissions from conventional technology engines (**b**); fresh emissions from new technology engines (**c**); aged emissions from new technology engines (**d**)

conventional engine technology (Mc Clellan et al. 2012; Hesterberg et al. 2012). In addition to the two engine types discussed in this chapter, a possible third type of engine is the homogeneous charge compression ignition (HCCI) engine. It is a hybrid of the (basic) principles of the diesel- and gasoline-powered engines. The HCCI engine design is based on the principle of the Otto engine, but without the spark-ignition technology. The lean mixture of fuel and air is compressed to auto-ignition, which is typical for a diesel engine design. It is expected that this engine will be running on both conventional fuels, such as gasoline or diesel, and most alternative fuel systems discussed in Sec. 51.4.2. Fuel cells are introduced on a small scale and will allow the use of hydrogen as a fuel in road vehicles.

51.5 Toxicity Mechanisms

51.5.1 Local Effects

The effects of the outdoor air pollution mixture in the local upper airway are well described, but the attribution of these effects to specific components may not be feasible. For ozone, a dose-response relationship for a concentration range relevant to outdoor exposure is well established (see Chap. 50); however, ozone is not an exhaust component. Its formation is catalyzed by hydrocarbon emissions that may in part be vehicle-generated, and the levels are attenuated by emissions of NO_2 (see Chap. 50). Also, for sulfur dioxide, the local effects on airways are well understood, but current exposure levels are not expected to have a great impact. This is not the case for NO_2, and it is not known to what extent exposure will contribute to possible airway function. For other components, such as VOC, a direct contribution to respiratory complaints is uncertain. Perhaps if aldehydes increase, they may give local sensory irritation on mucous membranes of the upper airways and eyes (see Chap. 52).

51.5.2 Pulmonary Inflammation

The oxidant properties of air pollutants, such as ozone and reactive oxygen species (ROS) formed by quinones associated with particles, can have a direct local adverse effect on the lung epithelium, such as oxidation of membrane lipids (lipid peroxidation) and oxidation of proteins in the lung lining fluids and proteins embedded in cell membranes. A second source of oxidative stress is the alveolar macrophage that produces hydrogen peroxide upon phagocytosis of particles. The first line of defense against oxidative stress is the availability of antioxidants in the lung lining fluids (e.g., vitamin C and E and glutathione). In addition, high and/or repeated exposure to oxidant species may trigger oxidative stress signaling pathways in epithelial cells and resident cells in the lung lining fluid. This pathway involves the transcription factors NFκB and AP-1, which translocate to the nucleus, where they attenuate the expression of proinflammatory genes, resulting in the formation of cytokines (IL4, IL6, IL8 and TNFα). These cytokines initiate recruitment and activation of neutrophils and T-lymphocytes in the airways and the alveoli. Tissue damage activates cell proliferating activity mediated by growth factors such as EGFR and COX-2, which induce prostaglandin formation (Fig. 51.11).

51.5.3 Systemic Inflammation

The concept of systemic inflammation is supported by the use of numerous biomarkers in epidemiology studies. Increased levels of biomarkers, such as C-reactive protein (CRP), a plasma fibrinogen, and increased plasma viscosity and coagulation factor VII in panel studies suggested a contribution of a systemic effect in addition to local pulmonary responses. In the circulation, there are three targets (Mills et al. 2005): endothelium, atheroma, and platelets.

Mills and co-workers (2005) exposed human volunteers to diluted DEP in a double-blind, randomized cross-over design (Fig. 51.12). At 2 and 6 h following this exposure, the endothelial function was assessed by measurement of the forearm blood flow in response to different vasodilator drugs, such as bradykinin (BK), acetylcholine (ACh), sodium nitroprusside (SNP), and verapamil (VP). As anticipated, each of these vasodilators showed a dose-dependent increase in blood flow, but the exposure to DEP caused a decrease in blood flow, which persisted at 6 h following exposure for all drugs except VP. This experimental set-up supports the

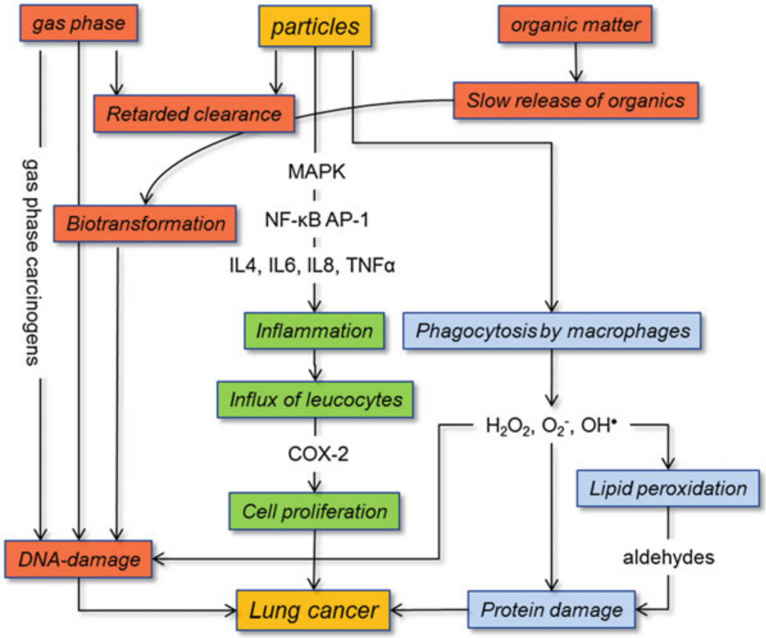

Fig. 51.11 Schematic representation of toxicity mechanisms of diesel exhaust particles in the lung (Source: Scheepers and Bos 1992)

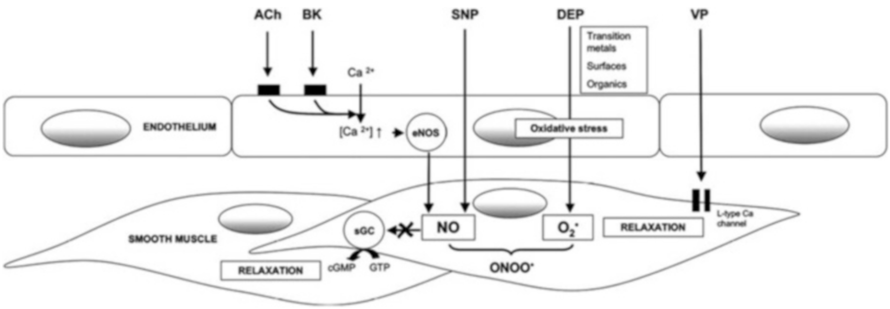

Fig. 51.12 Hypothetical mechanism of the influence of exposure to DEP on vasomotor function (see text for explanation) (Source: Mills et al. 2007)

theory that DEP-induced oxidative stress induces intracellular formation of superoxide. Superoxide reduces the availability of nitric oxide (NO) from peroxynitrite. NO is an important signaling molecule that prevents smooth muscle from relaxing. The effect of ACh, BK, and SNP drug therapy and not finding a difference in the VP-treated individuals supports the disruption of NO-mediated vasomotion as the mechanism to explain the reduced blood flow observed in the DEP-exposed volunteers. Mills and co-workers also observed a suppression of the fibrinolytic factors tissue plasminogen activator (t-PA), which normally degrades intravascular fibrin. The imbalance in the fibrinolytic system caused by DEP exposure may propagate microthombi, increasing the risk of arterial occlusion and tissue infarction. Mills and co-workers demonstrated that a reduction in the t-PA level in the DEP-exposed volunteers could be restored by BK.

An atheroma is an artery thickening and swelling consisting of lipids and macrophage, also indicated as an atheromatous plaque. Plaque expansion and disruption causes acute coronary symptoms such as angina and myocardial infarction. Only recently it was suggested that it is caused by endothelial dysfunction followed by an inflammatory process as indicated by an increase in CRP as an independent predictor of acute myocardial or cerebral infarction (Mills et al. 2007).

51.5.4 Genotoxicity

The genotoxicity of engines emissions is primarily associated with extracts from the particles phase. In SVOC mixture, nitroarenes and oxygenated nitrated PAH are the most potent direct bacterial mutagens (Scheepers and Bos 1992). That they are called ‘direct’ mutagens means that no enzyme activity is required for bioactivation. The other group of mutagens in the particle-phase of engine exhaust has ‘indirect’ mutagenic activity, depending on enzymatic activation. These are the non-conjugated or parent PAH (see Sects. 51.2.2.3 and 51.6.1). Both types of mutagenicity are found in both gasoline and diesel engine exhaust. The content in PAH and nitroarenes is not sufficient to explain the potency to induce tumors in animals (Grimmer et al. 1987). It is suggested that for the genotoxic damage to be expressed other factors are required. The most obvious mechanisms have been described previously in this paragraph (Sects. 51.5.1, 51.5.2 and 51.5.3) and involve inflammation and oxidative damage induced by reactive oxygen species (Fig. 51.11). The contribution of ultrafine particles and the higher content of strong direct mutagens may explain why diesel and not gasoline engine exhaust was classified as a human carcinogen (Benbrahim-Tallaa et al. 2012; IARC 2012).

51.6 Discussion

Engine exhausts have toxic properties that are well established, and with the population-based studies that associate exposure to vehicle-generated air pollutants to health effects the concern about health implications of road traffic emissions is justified. Improvement in engines technology resulted in a considerable reduction of regulated exhaust components, but road vehicles will be dominated by conventional technology for many years to come. There is some concern that solutions such as particle filters, oxidation catalysts, and alternative fuels will reduce one or more regulated exhaust components, but that other non-regulated exhaust components will not be reduced or in some cases even increase. Below, some possible environmental indicators for diesel and gasoline engine exhaust will be discussed that may help to evaluate the engine and fuel changes and addition to end-of-tailpipe solutions that will rule the air quality on the roads on short term.

51.6.1 Polycyclic Aromatic Hydrocarbons (PAH)

PAH represents a group of several hundred congeners that include genotoxic substances and some compounds that were classified as human carcinogens such as benzo(a)pyrene, which is representative of the heavier PAH with 5 to 6 aromatic rings, associated with PM in gasoline and diesel engine exhaust. Parent PAH needs bio-activation by liver enzymes (Fig. 51.12). In the case of benzo(a)pyrene, the ultimate carcinogenic intermediate binds to nucleophilic groups in the DNA to form addition products (adducts) which persist for several days to weeks before they are removed by DNA repair enzymes. If not removed, they may increase the risk of tumor formation. Benzo(a)pyrene and other PAH congeners are already much used in environmental health studies as chemical markers for the whole group of (parent) PAH.

51.6.2 Nitroarenes

Due to the formation of NO_2 and HNO_3, pyrene is converted to 1-nitropyrene, which is the most abundant nitroarene in diesel exhaust. At ambient temperature, pyrene is distributed over the vapor phase and particle phase. Nitration causes the nitrated daughters to remain entirely in the solid phase. Only a few percent of 1-nitropyrene is further nitrated to 1,3 – 1,6- and 1,8-dinitropyrene. 1-Nitropyrene was classified as a probable human carcinogen (Benbrahim-Tallaa et al. 2012; IARC 2012). Its content in diesel exhaust particle extracts was shown to correlate with the total extract mutagenicity of these extracts for a great variety of different types of in-use diesel engines (Scheepers et al. 1995). 1-Nitropyrene is a chemical precursor of dinitropyerenes, which are potent mutagens observed in diesel exhaust particle extracts (Ohgaki et al. 1985). It is not found in tobacco smoke and only in very low levels in gasoline engine exhaust (see Fig. 51.1). This substance is the most abundant nitroarene in diesel exhaust and one of the most abundant nitroarenes in primary combustion emissions. 1-Nitropyrene is exclusively combustion-generated as opposed to some other nitroarenes that are also produced by atmospheric reactions (e.g., nitrofluoranthenes). This compound may therefore serve as a chemical marker of combustion-generated nitroarenes and for source apportionment of diesel-generated genotoxic compounds (see Table 51.1).

Table 51.1 Source apportionment of diesel exhaust particles (DEP) in a busy and quiet street in city centre of Nijmegen, The Netherlands by use of 1-nitropyrene content. Data were collected on three weekdays in May (PM-10 and 1-nitropyrene are expressed as geometric mean ± geometric standard deviation of observations in triplicate)

Street	Vehicles[a]	Outdoor PM-10 (μg/m³)	Outdoor 1-Nitropyrene (pg/m³)	Outdoor DEP (μg/m³)[b]	Outdoor w %[c]	Indoor PM-10 (μg/m³)	Indoor 1-Nitropyrene (pg/m³)	Indoor DEP (μg/m³)[b]	Indoor w%[c]
Busy	4,556 ± 168[d]	58.0 ± 1.7	22.7 ± 1.3	22.1 ± 1.3	38[d]	36.1 ± 1.2	5.0 ± 1.5	4.5 ± 1.5	12.1[d]
Quiet	69 ± 9	36.8 ± 1.1	3.5 ± 1.1	3.9 ± 1.1	11	21.4[e]	1.8[e]	2[e]	9.3[e]

Source: Kimmel et al. 1996

[a]Arithmetic mean ± sd of total number of passing vehicles between 7:00 and 20:00

[b]Calculated DEP based on the following emission factors for PM: passenger cars 0.24 g/km, vans 0.3 g/km, buses 1.5 g/km and trucks 1.0 g/km (IARC 1989)

[c]Calculated of DEP to PM-10 based on the following emission factors for 1-nitropyrene: passenger cars and vans 2.5 μg/g, buses 1.13 μg/g and trucks 0.88 μg/g (IARC 1989)

[d]The sampling location was close to the bus station which explains the very high frequency of buses (25–30 % of all vehicle movements were city buses)

[e]Single measurement

In addition, this substance can be used to evaluate the possible side effects of the use of after-treatment, such as new fuels, oxidation catalysts, and particle filters, as 1-nitropyrene appears to be sensitive to chemical conversions caused by these after treatment technologies (Sharp et al. 2000).

51.6.3 Oxygenated Polycyclic Aromatic Hydrocarbons (oxy-PAH)

9-Fluorenone is an abundant oxygenated PAH that is also a precursor to mutagenic 2-Nitro-9-fluorenone (Bechtold et al. 1986) and di- and trinitro-9-fluorenones (Carré et al. 2004). With 9,10 anthraquinone, it was found as the most abundant oxygenated PAH in ambient air in Marseille, France (Albinet et al. 2006). Some oxy-PAH have a quinone structure and may generate reactive oxygen species (ROS) that may cause direct tissue damage, such as lipid peroxidation and oxidative DNA damage. ROS may also lead to proliferative growth, which increases the probability of expression of changes in the structure of DNA (Fig. 51.11).

51.6.4 Particulate Matter (PM)

The exposure to various fractions of PM near road traffic was associated with respiratory and cardiovascular health effects (see Chap. 50) and a risk factor in human cancer (Benbrahim-Tallaa et al. 2012). Although associations were found with many different expressions of PM, recent studies suggest that ultrafine particles (UFPs) are the most important determinants of acute and chronic health effects associated with exhaust emissions from road traffic. As alternatives to mass-based expressions of PM, the use of black carbon was suggested (Janssen et al. 2010) as a more specific and relevant approximation of combustion-generated particles. As the emission of soot is much reduced in new technology engines, the question is how long these soot-related parameters can be used. How conventional and new engine technologies compare with respect to fresh and aged particle emissions is postulated in Fig. 51.10. It is suggested that PM expressed in mass-based units will become less relevant as a regulated emission component, and also, for evaluation of environmental and health effects, alternative markers may have to be considered to evaluate the impact of particles in exhaust from new technology engines.

51.6.5 Carbon Monoxide

Carbon monoxide is a gas that is typically formed in emissions from gasoline engines powered with gasoline, natural gas, or liquefied petroleum gas. The emissions of this gas from diesel engines are much lower. Because this gas is odorless, an effective ventilation system needs to be in place in confined or enclosed facilities such as (underground) parking garages and in road traffic tunnels. In addition to sufficient air exchange, a reliable detection system for CO needs to be installed to monitor the air quality. In the case of failure of the ventilation system, immediate evacuation is required to prevent a risk of acute health effects such as hypoxia and possible secondary cardiovascular effects and central nervous system effects (see Chap. 54). CO was associated with hospital admissions and cardiovascular mortality in the general population (Shah et al. 2014). This effect may also be associated with other road traffic-related emissions such as PM. The main reason is that there are no other studies to support this type of health effect at the low concentrations of CO encountered in outdoor air.

51.6.6 Formaldehyde

Formaldehyde can be found in the gas phase of diesel engine exhaust. Because of its low threshold for sensory irritation (see also Chap. 52), it is related to the acute responses of humans to diesel engine exhaust. It could also represent the larger group of oxidation products that remain in the gas phase (many other oxidized products will become semivolatile and are associated with PM). This substance may be valuable for monitoring of possible increased emissions due to changes in fuel, or in engine after-treatment.

51.6.7 Bioassays

The combined PM and SVOC fractions of emissions from selected in-use gasoline and diesel-powered road vehicles (chemically characterized by Zielinska et al. 2004) were assayed in a battery of in vitro and in vivo toxicity assays, including in vitro bacterial mutagenicity testing and a battery of endpoints in bronchial alveolar lavage fluids (BALF) of rats that received an intratracheal instillation with the test material (Seagrave et al. 2002). These endpoints were related to inflammation, parenchymal changes, oxidative stress, macrophage function, lung weight, and histopathology tests. This comprehensive study showed that it is possible to use conventional toxicity assays to discriminate complex mixtures such as engine exhaust. In particular, the samples from so-called high emitters (‘white smoker’ or ‘black smoker’) could be discriminated from other emissions by one or more of these assays. This way of toxicity testing has been shown to be useful for studying the relationship between the physicochemical characteristics of complex mixtures and toxicity. For diesel exhaust emissions, the direct mutagenicity was attributed to nitroarenes, whereas indirect mutagenicity could be attributed to PAH (Kinouchi et al. 1988; Schuetzle et al. 1983). Bünger and co-workers (2007)

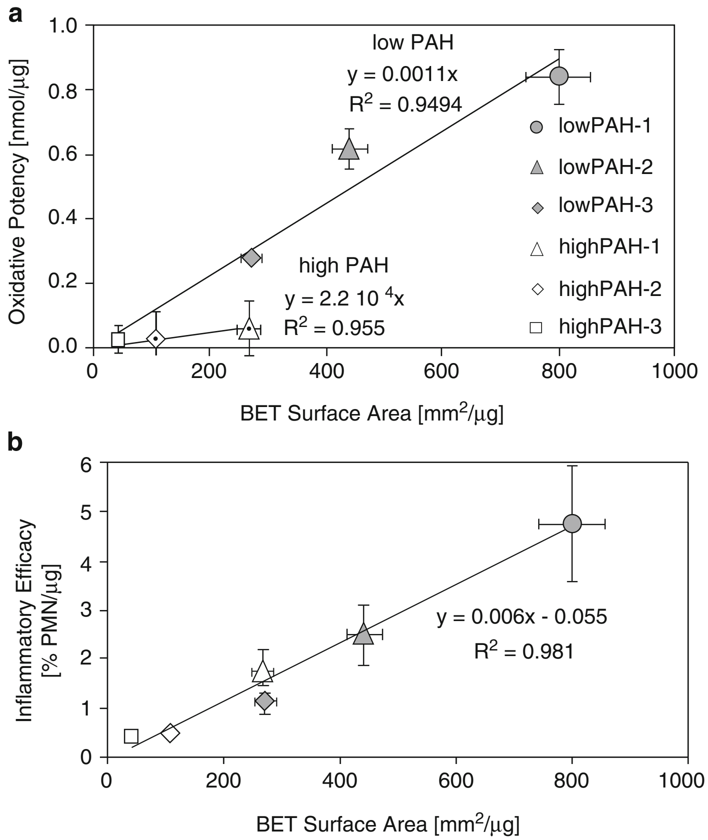

Fig. 51.13 Two particle toxicity parameters are shown in dependence of the surface area of the ultrafine particles (BET surface is an expression for the number of molecules absorbed on a surface). The oxidative potency (in vitro) is reduced by the PAH that cover the reactive carbon surface (**a**) and the inflammation efficacy in vivo in mice is compensated by metabolic activation of these PAH (**b**) (Source: Schmidt et al. 2009)

observed a sixty-fold higher mutagenicity of rape seed oil biofuel compared to conventional diesel fuel.

Seagrave and co-workers identified the emissions from G-3 (see Fig. 51.3) as the most toxic emission in most of the assays. A surprising finding was that the diesel and gasoline engine emissions at low temperature showed a much lower toxic potency than expected based on the high content of PAH and nitro-PAH. This is a similar finding to an earlier one of Schmidt and co-workers (2009) who suggested that surface-adsorbed SVOC like PAH may reduce the oxidative potency in vitro (see Fig. 51.13). From these attempts, it becomes clear that toxicology testing of complex mixtures is needed to complement our limited understanding of the molecular mechanisms involved in the toxicity of engine exhausts.

From the toxicity tests of high emitters, Seagrave and co-workers concluded that it may be possible that a limited number of vehicles produce abnormally high levels of emissions that may be responsible for a relatively large share of the emission-related health burden (Kurniawan and Schmidt-Ott 2006). A small percentage of vehicles (5 %) accounts for a high percentage (43 %) of pollution. Identifying these super polluters may have implications for the way the public health effects of air pollution can be mitigated.

Conclusions

Gasoline and diesel engine exhausts are associated with a wide range of health effects, such as lung function decrements, increased asthma complaints, increased vulnerability to respiratory infections, cardiovascular disease and mortality, and pulmonary disease and mortality. In addition, diesel exhaust was classified as a confirmed human carcinogen by the WHO (IARC 2012). New engine technology resulted in much lower emissions, but it will take decades before cleaner vehicles have influence on general air quality in the cities. In the meantime, a minority of the vehicles may be high-emitters and there are indications that the emissions of these super polluters have a much higher toxic potency.

Alternative fuels have the potential to reduce the health risk of engine exhaust. Oxygenated biofuels tend to reduced PM emissions, but some reports indicate an increase in emissions of NO_X. Within a few years, admixing of some new synthetic fuels with conventional fuels may result in lower emissions. Like natural gas pure synthetic fuels could be introduced sooner in closed fleets of public transportation systems. Dedicated vehicles are expected to use the full potential of emission reduction for these new fuel systems. Specifically the complete removal of aromatic hydrocarbons from fuel systems reduces PAH and nitro-PAH emissions.

New technology engines have much lower emissions and new engine designs may not need exhaust after-treatment. As new technology engines are penetrating the fleet at a slow pace, the current air quality is still determined by conventional technology engines with retrofitted oxidation catalysts and particle traps. These systems effectively remove particles, but some may also increase emissions, including NO_2 and nitroarenes. Particle filters may also generate hazardous chemicals. Emissions downstream of such retrofit systems should be scrutinized for potential health implications, before such after-treatment systems are introduced.

It is suggested that, in addition to particles and NO_X for diesel engine exhaust and CO for gasoline engine exhaust, some specific substances could be used as chemical markers to monitor specific toxicities. In the gas phase, formaldehyde is the most abundant aldehyde indicative of the sensory irritation of a large group of similar substances. In the particle phase, it is

(continued)

suggested that benzo(a)pyrene and 1-nitropyrene be used as chemical markers for PAH and nitroarenes, respectively. Because of its high specificity for diesel exhaust, 1-nitropyrene can also be used as a marker for source apportionment of diesel engine exhaust in environmental studies. It is suggested that the health-relevance of these and other markers could be validated by in vitro and in vivo toxicity testing of a representative sample of engine exhaust emissions.

Acknowledgements This chapter is dedicated to dr. Rob P. Bos. The author would also like to express his gratitude for fruitful discussions with working group members involved in preparation of IARC Monograph volume 105 on Diesel and Gasoline Engine Exhausts and Some Nitroarenes. The author would like to thank dr. Andreas Schmidt-Ott for his advice the preparation of Fig. 51.10. Jonathan M. Scheepers is kindly acknowledged for preparation of Figs. 51.1, 51.2 and 51.7.

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Chapter 52
Health-Related Indicators of Indoor Air Quality

Paul T.J. Scheepers and Stef van Hout

Abstract As buildings became more airtight in the 1970s, the health effects of the indoor air environment received more attention. Building materials and materials used in furnishing are potential determinants of air quality. Occupancy and activity patterns also have their impact on the quality of indoor air. This becomes apparent when occupancy rate is high relative to the intake of clean air, and even in a 'clean environment,' such as the home, school classroom, or office, users introduce many chemical substances, such as personal care products, air fresheners, and cleaning products. These chemicals are beneficial in most cases, but may be adverse in others depending also on the specific acquired susceptibility in a minority of the population. Other contemporary topics that will be addressed are the relative contribution of indoor and outdoor sources of air pollution, formation of pollutants by ozone-initiated chemistry, and the use of indicators to assess the health impact of indoor air quality.

Keywords Biological agents • Carbon dioxide • Carbon monoxide • Nitrogen dioxide • Formaldehyde • Ozonolysis • Particulate matter • Radioisotopes • Ventilation • Volatile organic compounds

52.1 Introduction

During the oil crisis in the 1970s, buildings were made more airtight and this aggravated problems of moisture and the accumulation of chemical and biological pollutants in homes. Health effects related to exposure to molds, endotoxins, irritant gases, and particles resulted in mostly non-specific health complaints. In offices, the most commonly reported health effects are tiredness, dry, irritated, or itchy eyes, and headache (Wolkoff 2013). Users may also find odors a nuisance or annoying. Since odor thresholds are several orders of magnitude below sensory irritation thresholds, such complaints are frequently reported. However, there is no evidence that unpleasant odors are associated with adverse health consequences (Rosenkranz and Cunnicham 2003).

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_52

At the same time, irritation can be confounded or masked by odor (Wolkoff 2013). Together with sometimes work-related mental stress, this resulted in an epidemic of sick building symptoms that received much attention (Apter et al. 1994). This drew attention to the use of low-emission building materials and introduction of decoration and furniture of homes with much lower emissions of radioisotopes, chemicals, and fibres (Jensen et al. 2001). Together with increased use of air treatment and forced ventilation, the indoor air quality (IAQ) has much improved over the past decades (WHO 2010). In the meantime, increased use of fragrance evaporators and changes in the composition of cleaning products and personal care products have resulted in changes in the composition of indoor air (Destaillats et al. 2006).

Outdoor pollutants, such as ozone, penetrating indoor environments may react with unsaturated organic compounds, leading to formation of products with low thresholds for sensory irritation. Because of the many hours spent indoors, the question is raised as to how known health implications for outdoor particulate air pollution influence the risk assessment of indoor exposure to particles. This discussion is not so much a discussion of dose, as more than 50 % of the outdoor pollutants penetrates the indoor space. The discussion is more about the evaluation of how the health hazards of indoor particles should be interpreted (Nazaroff 2010; Oeder et al. 2012).

52.2 Penetration of Outdoor Pollutants

52.2.1 Ozone

In outdoor air, ozone is continuously formed by atmospheric chemistry powered by sunlight and catalyzed by the presence of organic substances in the air (see Chap. 50 on outdoor air). Concentrations at ground level depend on the stability of the atmosphere which determines dilution by dispersion. In geographical enclosed areas, such as valleys and river beds, concentrations can reach values of several hundred μg/m^3. Other air pollutants, such as NO from motor vehicle exhaust, scavenge ozone (Lee et al. 2002). This causes the levels to be lower in high density traffic areas in city centres relative to lower-density traffic areas in the suburbs. If ozone penetrates buildings, it has only a limited lifespan with a half-life of 7–10 min (Weschler 2000). This rate of decay competes with that of air exchange and is caused by the reactivity of ozone with surfaces, particles, and hydrocarbons, primarily those with unsaturated carbon-carbon bonds in gas or condensed liquid phase (nanosized aerosols) (see Sect. 52.2.5).

52.2.2 Nitrogen Oxides

Oxides of nitrogen (NO and NO_2) are formed by natural or anthropogenic high temperature combustion sources. These substances originate primarily from the penetration of outdoor sources (see Chap. 50). This may occur if buildings are located in high density traffic zones. Indoor sources are relevant only if an exhaust extraction system for removal of gas stove emissions, cooking fumes, and emissions from unvented warm water appliances or heating systems is not present or is not effective (Dassen et al. 1987). In addition, other unvented blue-colored flames, such as those produced by kerosene heaters, tobacco smoking, and use of incense, can lead to increased indoor levels of NO and NO_2 (Gillespie-Bennett et al. 2008).

52.2.3 Volatile Organic Compounds (VOC)

VOC is an important group of chemicals contributing to indoor air odor. In the VOC mixture in indoor air, the most abundant species are usually ethanol and acetone, primarily derived from exhaled air (Kim et al. 2012). VOC are numerous and comprise saturated and unsaturated aliphatic and aromatic hydrocarbons. In the US, most VOC in indoor environments originate from air fresheners, general purpose cleaners, and floor care products (Nazaroff and Weschler 2004). Some aromatic VOC, such as benzene, toluene, xylene, and ethylbenzene (BTXE) can be related to fossil fuels and their derived products, such as cleaners, oils, and paints, and also incomplete combustion of, e.g., tobacco smoke and unvented indoor use of open fire (Kim et al. 2002; Pruneda-Álvarez et al. 2012). Phthalates may originate from flooring materials, specifically polyvinyl chloride floors (SCHER 2007). Personal exposure monitoring in children revealed that enhanced exposure to benzene, toluene and xylenes was associated with indoor smoking (specifically in cars), a home with a connected garage, and use of adhesives and paints (Thomas et al. 1993; Scheepers et al. 2010). Use of specific products may sometimes result in elevated levels of industrial chemicals, such as methanol and isopropylalcohol (cleaning products), musks (fragrances), acetates (food additives) toluene (some glues), acetone (nail polish remover), et cetera. VOC levels are highly variable and often related to the occupancy of indoor environments.

52.2.4 Aldehydes

Building materials, such as wood composite materials (e.g. plywood), are potential sources of formaldehyde (Hodgson et al. 2002). Precursors of formaldehyde are also added to consumer products for (antibacterial) preservation and can evaporate from surfaces and from the skin. In addition to primary sources, formaldehyde and other aldehydes may be formed from combustion and atmospheric ozone-initiated chemistry (see Sect. 52.4.2). Finally yet importantly, some small aldehydes such as formaldehyde and acetaldehyde are also products of endogenous metabolic processes and will be found in exhaled air (Kim et al. 2012).

52.2.5 Particles

The coarse particle fraction in indoor air may contain many different components. In homes, house dust is composed of crustal materials from street dust and also building materials, textile fibres from furniture, carpets, and clothes, and many other sources of mechanical wear (Butte and Heinzow 2002).

Depending on the season, some biological agents may also be found as particulate matter in indoor air. During the warm season, the contribution of pollen from trees, grass, and flowers may contribute significantly to mass concentrations of particulate matter. The course fraction may also contain biomaterials, such as dandruff, scabs, and hairs. Some agents may be derived from mites (excreta) or microorganisms, such as bacteria (endotoxins, spores, β 1 $\rightarrow$ 3 glucanes, lipopolysaccharide). In the cold or wet season, mold spores will increase (Douwes et al. 2003). Ambient particulate matter and its health implications are discussed Chap. 50. It is estimated that 30–60 % of outdoor particulate matter penetrates the indoor environment by natural ventilation. If an HVAC system is used, it is possible that particles may be captured in filters and that indoor fine particle concentrations are lower than outdoor levels. Ultrafine particles may penetrate much more efficiently than coarse particles, and for these particles the metaphor of the house as a cage is adequate. The indoor environment of buildings close to roads or parking lots may be influenced by outdoor particle emissions, depending on local weather conditions, such as wind direction and speed. Curtains hanging in the front of opened windows can often show dark traces of soot from traffic penetrating into buildings situated close to high-density traffic roads, as in street canyon settings.

As shown in Fig. 52.1, the pattern of indoor PM-10 and PM-2.5 tends to follow the changes in outdoor PM concentrations. Use of additional filtration may change this (Scheepers et al. 2012; Polidori et al. 2013). As concentrations reduce rapidly with the distance from a source, the direct influence of roads on IAQ cannot be determined at distances exceeding 200–300 m. However, the local concentrations of fine dust fractions may still be higher in urban areas as compared to suburban and rural areas. Particles may also be taken into a building by the users. Usually these are crustal and organic materials from street dust (Janssen et al. 1997). Other studies suggested that toxic materials, such as pesticides and asbestos, can also be carried into homes by residents as a result of surface contamination (Curwin et al. 2007; Driece et al. 2010). In the indoor environment, such materials can be dried, eroded, and be resuspended to become airborne and inhalable. That this may lead to extremely high particle concentrations was observed in classrooms of primary schools (Janssen et al. 1997; Blondeau et al. 2005; Scheepers et al. 2012; Madureira et al. 2012).

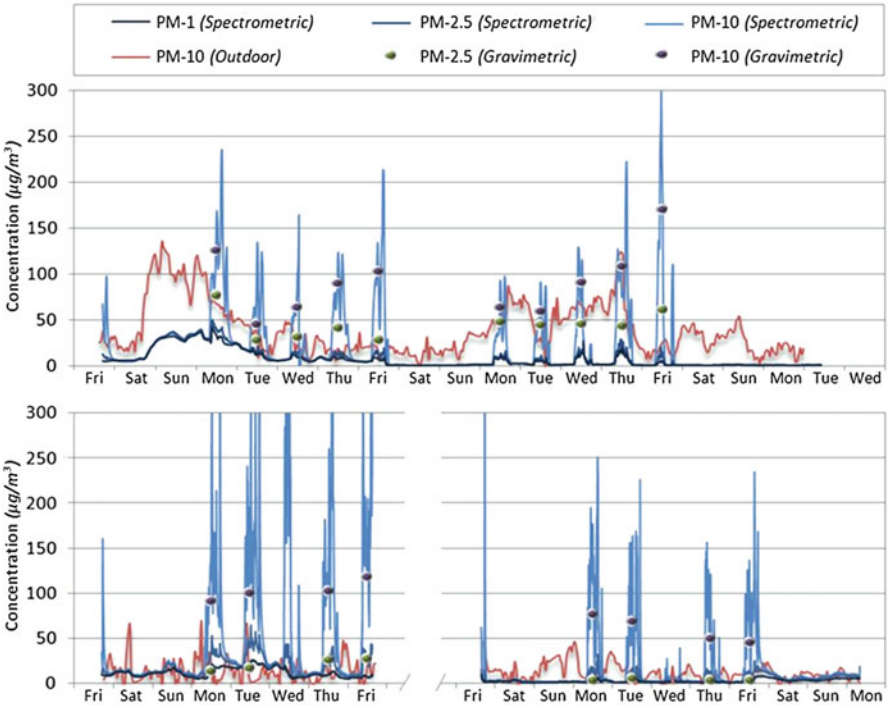

Fig. 52.1 Five minutes-time resolved registration of indoor aerosol spectrometric determinations of PM-10, PM-2.5 and PM-1 in a primary school classroom in The Netherlands. Average indoor concentrations of PM-10 and PM-2.5 during the lessons were based on filter measurements (gravimetrical). February (*upper panel*) and June (*lower panel*). In each of the panels in the second week an air filtration system was introduced to reduce indoor particle levels. The outdoor 1-h average concentrations of PM-10 (measured by beta attenuation monitoring) are presented as a reference for the general outdoor air quality. In February the influence of the general outdoor quality on indoor PM-levels is demonstrated. The high PM-10 levels on school days during the lessons are explained by particle resuspension due to the high occupancy and activity pattern of the children (Scheepers et al. 2012)

52.3 Indoor Sources of Air Pollution

52.3.1 Building Materials

Chemicals used in building materials can have a profound influence on IAQ. In old buildings, materials, such as PAH in parquet glue (Heudorf and Angerer 2001), PCBs in rubber sealants (Schettgen et al. 2011, 2012; Knobeloch et al. 2012) and lead in paint (Lucas et al. 2012), were introduced at times when the health consequences of such use were not known or were underestimated (see Table 52.1). The impact of fibres, radioisotopes, dust, and aldehydes will be discussed in more detail.

Table 52.1 Overview of health-relevant chemical and biological factors in indoor environments

Source	Factor	Substances	Suggested health implications	Risk management	Reference
Building location	Geological formations of granite rock downstream (river) clay formations	Radioisotopes (radon and thoron)	Cancer	Ventilation measures recommended	George (1996)
	Distance to high traffic locations	Particulate matter, NO_2, VOC, CO, aldehydes	Cardiovascular, respiratory, lung cancer	Air filtration treatment recommended	Brunekreef et al. (2009)
Building materials	Concrete	Radioisotopes (radon and thoron)	Cancer	Ventilation measures recommended	George (1996)
Maintenance	Oriented strand board	α-pinene, Δ(3)-carene and hexanal	Sensory irritation	Low emission materials preferred	Gminski et al. (2011)
Building materials	In situ isolation (spray foam applications)	Polyurethane and incompletely reacted products	Sensitization	Not recommended if not well controlled	Baur et al. (1994)
Interior	Asbestos	Asbestos	Cancer	Take precautions when damaged or removed	Driece et al. (2010)
	Moisture	Molds, endotoxins	Respiratory	Ventilation	Douwes et al. (2003)
	Synthetic materials (carpet, linoleum, paint, gypsum, ceiling, polyolefine, PVC)	Acetic acid, botanic acid, hexanal, nonanal, pentanal, propanal	Odor	Low emission materials preferred	Han et al. (2010)
	Plywood/wood composite in furniture	Formaldehyde	Irritant/cancer	Low emission materials preferred	Salthammer et al. (2010)
	Cleaning products	Terpenes, quaternary ammonium compounds	Irritant	Individuals with an allergy for terpenes	RIFM EXPERT Panel et al. (2008)
	Fragrances	Terpenes, musks and their oxidation products due to ozonolysis	Irritant	Individuals with allergy for terpenes	Destaillats et al. (2006)

	Microflora/intestinal flora	Alcohols, esters, ketones	Odor	Increase air exchange rate	Wanner (1993)
	Skin oils/lipids	Carbonyl-compounds including aldehydes	Odor/irritant (oxidation products[a])	Increase air exchange rate	Weisel et al. (2013)
	Exhaled air	Alcohols, carbonic acids, aldehydes	Odor	Increase air exchange rate	Wanner (1993)
		Carbon dioxide	Cognitive functions	Marker for air exchange rate in relation to occupancy	Bartlett et al. (2004)
	Air fresheners, cleaning products	Glycol ethers and terpenes and	Irritant and weak sensitizer to sensitive individuals	Not recommended to risk groups	Singer et al. (2006)
	Cosmetic products	Formaldehyde-precursors (dimethylol-dimethylhydantoin)	Irritant, cancer	Low emission materials preferred	Lefebvre et al. (2012)
Activities	Cooking	Cooking fumes, high temperature frying	Lung function, lung cancer	Fume hood recommended	Koo and Ho (1996); IARC (2006)
	Unvented heater	NO_2	Lung function	Fume hood recommended	Salome et al. (1996); Pilotto et al. (2004)
	Burning of incense	Volatile organic compounds, aromatic amines	Cancer	For indoor use	Manoukian et al. (2013)
	Use of essential oils	Terpenes	Airway irritant (oxidation products[a])	Individuals with allergy to terpenes	Umweltbundesamt (2010)
	Indoor storage of fossil fluids or indoor parking of vehicle(s)	Benzene	Cancer	No indoor storage of fuels	Thomas et al. (1993); Scheepers et al. (2010)
	Smoking	Cigarette smoke condensate, CO	Irritant/cardiovascular disease/cancer	No indoor smoking	Wanner (1993)

[a]Ozone-initiated chemistry (ozonolysis) giving rise to Criegee chemistry with resulting formation of irritant products such as carbonyls and aldehydes

The hazard of most particles, such as glass and stone wool, is low and health consequences are primarily reversible (Costa and Orriols 2012). However, there are also particles that are classified as human carcinogens: crystalline silica and asbestos. These particles should not be a problem in the normal use of a building, but during construction, reconstruction, and demolition these substances cause many problems to professional workers and also to the direct surrounding residential environment (Perkins et al. 2007). Workers are usually well-informed and likewise well protected as opposed to residents.

For radio isotopes such as radon and thoron there are two main sources: emission from soil and emission from concrete structures of buildings. Radioisotopes in the gas phase can penetrate into the indoor environment from the crawl space or basement (Nazaroff and Doyle 1985). Such problems arise in geographic areas with a natural background of radon and thoron, e.g., from granite rock (Scandinavia, Germany) or in houses built on river banks that contain clay sediments derived from similar geographic origin and taken downstream by rivers. Exposures were higher during the oil crisis in the 1970s, when energy was saved by increased insulation and reduced ventilation of homes. Nowadays, exposure of the residents is much reduced by an improvement in building requirements (Arvela et al. 2012).

Wood, floor coverings, urea-formaldehyde spray foam, and mineral wool insulation can all release formaldehyde (Hodgson et al. 2002; Salthammer 2013). Polymers such as polyvinyl chloride (PVC) floor materials are important sources of di(2-ethylhexyl)phthalate (DEHP) (Bornehag et al. 2005).

52.3.2 Occupancy as a Source of Air Pollution

Humans themselves are producing chemicals that they exhale, and their skin bacterial micro flora causes the formation of organic waste products (Nazaroff et al. 2012). In terms of particle emissions, the most important biological pollutants are dandruff and scabs. Persons are carriers of biological contaminants such as bacteria (Hospodsky et al. 2012) and allergens from cats and dogs (Instanes et al. 2005). Skin is also a source of squalene (2,6,10,15,19,23-hexamethyl-tetracosa-2,6,10,14,18,22-hexa-ene) from skin oil or sebum, a known precursor of oxidation products due to reactivity with ozone or hydroxyl (Wisthaler and Weschler 2010) (see Sect. 52.4.2). In addition to these endogenous waste products, the use of personal care products, as well as cleaning products, air fresheners, and adhesives, also causes elevated indoor concentrations of VOC and their oxidation products (Singer et al. 2006). Cosmetic products used by occupants contain dimethylol-dimethyl hydantoin (DMDMH), a precursor and secondary source of indoor formaldehyde (de Groot et al. 1988; Lefebvre et al. 2012). In addition, activities such as cooking may become a source of indoor air contaminants, such as particles, NO_2, and aldehydes, if not removed by ventilation (Evans et al. 2008; Salthammer et al. 2010).

52.4 Health-Related Indicators

52.4.1 Volatile Organic Compounds (VOC)

VOC represents a large group of volatile and semi volatile organic substances (VOC and SVOC). In addition to outdoor air as a source, building location, building materials, interior, maintenance, occupancy, and activity patterns all contribute to indoor VOC levels. VOC determines odor. Sometimes this is intended (fragrances in personal care or cleaning products), but in other cases, not (human excretion products and products from human microflora). The perception of odor can vary also depending on the context. Remarkably, occupants in a poorly ventilated room are often unaware of this whereas persons who enter a high occupancy room observe an unpleasant odor (Wargocki et al. 2004; Norbäck and Nordström 2008). Apart from odor, there is not much support for an influence of VOC on health effects (SCHER 2007). Observed effect levels for irritation were found to be higher than VOC concentrations normally observed in indoor environments (Andersson et al. 1997). Fiedler and co-workers (2005) simulated a workplace exposure to VOC and their ozone oxidation products, and found no significant effect on neurobehavioral performance, salivary cortisol, and lung function at relative high concentrations of VOC (26 mg/m^3) and ozone (40 ppb). As test subjects, they involved 130 healthy nonsmoking women recruited from the general population. For the aforementioned health endpoints, mental stress (a public speaking task) was observed to have a more significant impact than the chemical exposures. Other studies suggested an association between VOC concentrations in indoor environments and health effects (Hutter et al. 2006; Saijo et al. 2004; Takigawa et al. 2004; Delfino et al. 2003). In addition, for emissions from plastic polymers such as phthalates from PVC floors there are reports of associations with asthma and rhinitis in children (Bornehag et al. 2004), but exposures are low (Nielsen et al. 2007) and there were no indications of respiratory or skin sensitization (SCHER 2007).

52.4.2 Aldehydes and Other Oxidation Products

Unsaturated organic substances can be oxidized by ozone penetrating from outdoor air to form oxygenated species, such as aldehydes, ketones, carbonyls, dicarbonyls, carboxylic acids, and peroxides (Wells 2012). These reactions occur in the gas phase but also on surfaces (Wisthaler et al. 2005). A special case of the above described reactivity is the ozonolysis of terpenes, which has been studied extensively (see Wells 1012 for a review). In particular, carbon-carbon double bonds react fast in ozonolysis to form alcohols and aldehydes (Weschler 2000). Indoor use of air fresheners demonstrated the formation of secondary organic aerosols (Sarwar et al. 2004; Destailats et al. 2006). Ozonolysis of α- and β-pinene resulted in secondary aerosols containing numerous reaction products, most probably dimers of pinic acid and terpenylic acid (Gao et al. 2010; Claeys et al. 2009). Other studies also report oligomerization of intermediate or stable monomers, including Criegee intermediates, and H:C and O:C ratios also suggest polymerization of formaldehyde and acetaldehyde (Heaton et al. 2009). The acute effects in humans of these oxidation products are related to stimulation of the trigeminal nerve (5th cranial nerve) and lead to sensory responses in nose, eyes, and upper airways. So far, no indication was found that this response is indicative of a histological effect or tissue damage. The stimulation of the trigeminal nerve is often described as 'sensory irritation' or 'pulmonary irritation' but others dispute that this endpoint is predictive for irritation (Bos et al. 2002). Nevertheless, sensory irritation to the eyes is reported to be the most sensitive endpoint for terpene oxidation products, and this endpoint was studied in humans in well-controlled volunteer studies (Lang et al. 2008). In these studies, it was found that a mixture of limonene oxidation products and also five individual components of this complex mixture show a threshold for sensory and pulmonary irritation at concentrations tenfold lower than for formaldehyde (Klenø and Wolkoff 2004; Wolkoff 2013).

Formaldehyde may serve as a chemical marker for oxidant species that may be formed by ozone-initiated chemistry (Wolkoff 2013). A guidance value for formaldehyde based on chemosensory effects is much debated because most of the human data are based on subjective measures where there is a possible interaction with perception of odor intensity (Arts et al. 2006a, b, 2008; Appel et al. 2006; Kotzias et al. 2005). The evaluations of these tests yielded results different from those obtained using the Alarie assay. Long-term effects of formaldehyde exposure include nasopharyncheal and nasosinosal tumors (IARC 2006) and there is limited evidence of acute myeloid leukemia (IARC 2012), but epidemiological studies reported on increased cancer risks mostly involved occupational setting with high (peak) exposures of 5–10 mg/m^3 (Hauptmann et al. 2009).

52.4.3 Particles

In indoor air, the PM-10 and PM-2.5 conventions of particle fractions in the outdoor air are used. These definitions are explained in Chap. 50 and address particle size distribution and not the composition or toxicity of the particles. There is not much consensus on how to evaluate the health implications of indoor particle exposures. It seems obvious to follow the air quality standards of outdoor PM-2.5 to evaluate the health implications of the fine dust fraction and in particular the black carbon fraction (Janssen et al. 2010). Their penetration into indoor environments is high and their composition does not likely change. The composition and associated health hazard of coarser PM-10 may deviate from that of outdoor particles and represent a lower or higher hazard as compared to outdoor particles due to their chemical and biological composition (Oeder et al. 2012; Douwes et al. 2003). A systemic review and meta-analysis by MacDonalds and co-workers (2007) suggests that reductions in levels of house dust do not result in an overall decrease in the onset of upper airway complaints (wheeze) or severity of complaints. They noted that in some studies a reduction of physician-diagnosed asthma was recorded and a reduction in the number of symptom days. More studies should evaluate the health implications of indoor exposures to coarse particles, specifically in high occupancy settings involving young children, such as schools and daycare centres (Blondeau et al. 2005; Madureira et al. 2012; Scheepers et al. 2012).

The health implications of high concentrations of particulate matter such as observed in class rooms is difficult to estimate, but it is likely that bioallergens will contribute to upper airway symptoms in asthmatic children in those indoor environments (Douwes et al. 2003). Such indications were found in a study by Smedje and Norbäck (2001) who looked at the number of open book shelves and cleaning habits to study the association of allergen sedimentation in school classrooms in Sweden. Overall, it seems difficult to interpret indoor concentrations by using the framework of guidelines established for outdoor air quality (Nazaroff 2010). Because most of our time is spent indoors, it may be interesting to discuss a framework of IAQ guidelines for particulate matter.

There is discussion about the influence of carpets on the concentrations of airborne particles in homes. The common idea that hard floors are easily cleaned and therefore recommendable in homes of asthmatic patients is disputed (Morgan et al. 2004). It can be argued that once the floor is covered by soiling and sedimentation, such contamination may be resuspended more easily from a hard floor than from a carpet (Scheepers et al. 2014). On the other hand a carpet could act as a sink for particles (so-called deep dust) that may become airborne again due to activity on the carpet (Roberts et al. 2009). In addition to the properties of the used materials, it is likely that the maintenance and cleaning of such floor surfaces will have an influence on the particle concentrations. More research would be required to balance the merits and limitations of hard flooring and carpets.

52.5 Discussion

IAQ is only one out of many factors that can contribute to the wellness of users of an indoor environment.

Seasonal changes may have significant impact on IAQ and related health symptoms. Specifically relative humidity (RH) has its influence on perceived local symptoms, such as eye-irritation. Relative humidity of the air typically lower than 30 % may lead to perceived 'dry air' and sensory irritation of eyes and upper airways (Wolkoff 2013). These conditions are likely to occur at temperatures above 22 °C and during the heating season and are most likely related to water soluble air contaminants dissolving in a relative smaller volume of eye-lining fluid (desiccation and instability of the eye tear film) resulting in local higher surface doses (Wolkoff 2013).

Climate change may contribute to an increase of average hours of sun and subsequent higher average UV irradiation levels. This may lead to higher average outdoor ozone levels and result in ozone-initiated chemistry in the indoor environment. Since ozone-initiated chemistry is often skin, hair or skin-care products- or clothes-related, markers of ozonolysis are especially suited in high occupant density settings such as a school classroom interior or airplane cabin (Weschler et al. 2007). An increase in skin related allergies was reported in Germany and Austria from 0.5 to 3.1 % over a period of 5 years and attributed to the increased use of fragrances such as terpenes (Treudler et al. 2000). Sensitive individuals may respond to fragrances with skin symptoms at air levels well below the threshold for sensory irritation (Schnabel et al. 2010; Schnuch et al. 2010).

To control the levels of irritant ozonolysis products, systems may be equipped with catalyzers to reduce the ozone levels, especially in high-density occupancy indoor environments. It is not very practical to try to reduce substrates of ozonolysis, since most of these are used to increase the wellness of consumers or are naturally occurring skin oils/lipids (Wisthaler and Weschler 2010). In 2012, Wolkoff proposed markers with NOAELs below 1 mg/m^3 for sensory irritation (see Table 52.2). More research is needed to support the use of specific ozonolysis products as chemical markers for IAQ-related health complaints. Possible

Table 52.2 Environmental indicators for offices. Substances proposed as priority substances or recommended for measurement are labeled '+'

Indicator	Source	Health concern	Priority indicator[a]	Measurement[b]
Acetic acid	Wooden-based products	Comfort marker for perceived IAQ and sensory irritation	–	–
Acrolein	Combustion product, product of ozone-initiated chemistry and combustion	Sensory irritant	–	+
Ammonia	Common cleaning product and emitted from certain supporting flooring materials	Low odor threshold	–	–
Benzene	Reflects combustion and traffic	Human carcinogen	+	–
2-Butoxyethanol	Solvent used in many consumer products, reflects unsaturated fragrances	Respiratory irritant	–	+
Carbon dioxide	Reflects ventilation efficiency and odor dilution	No known concern	–	–
2-Ethylhexanol	Secondary VOC derived from hydrolysis of phthalate. Also product of microbial degradation	Sensory irritant	–	–

(continued)

Table 52.2 (continued)

Indicator	Source	Health concern	Priority indicator[a]	Measurement[b]
Formaldehyde	Wood-based products and product of ozone-imitated chemistry and combustion	Human carcinogen and strong sensory irritant	+	+
Glutaraldehyde	Disinfectant in cleaning products	Sensory irritant	–	+
Hexanal	Oxidation product of unsaturated fatty acids in building materials (linseed oils) an human debris (skin oil)	Comfort marker for perceived IAQ	–	
Hexanoic acid	Used for disinfection in cleaning products, and degeneration product from linseed oil and skin oil	Upper airway irritation	–	–
Hydrogen peroxide	Ozone-initiated terpene product and product of ozone-imitated chemistry and combustion	Oxidative damage	–	–
Isopropenyl-6-oxo-heptanal	product of ozone-imitated chemistry from limonene	Sensory irritant	–	+
Limonene	Common fragrance in consumer products and substrate for ozone-initiated chemistry	Sensitizer	–	–
Methacrolein	Combustion product from e.g. incense and product of ozone-imitated chemistry	Sensory irritant	–	+
Methylnaphthalenes	Combustion products and as co-solvents	Odor	–	–
Nitrogen dioxide	Reflects combustion and traffic	Respiratory irritant	+	–
Naphthalene	From heavy oil fraction (e.g. diesel and kerosene fuels and bitumen) also used in moth balls and other consumer products	Very low odor threshold	+	–
3-Octen-3-ol	Microbiological product	Concentration is probably too low to cause irritation	–	–
4-Oxo-pentanal	Product of ozone-imitated chemistry	Lower airway irritant	–	+
Ozone	Precursor for terpene oxidation products	Airway irritant	–	+

(continued)

Table 52.2 (continued)

Indicator	Source	Health concern	Priority indicator[a]	Measurement[b]
Peroxi-acetic acid	Photochemical product and also formed as product of ozone-imitated chemistry	Sensory irritant	–	+
Phenol	Common degradation product from flooring materials and phenol-formaldehyde resins	Sensory irritant	–	–

[a]WHO (2010) and SCHER (2007)
[b]Wolkoff (2013)

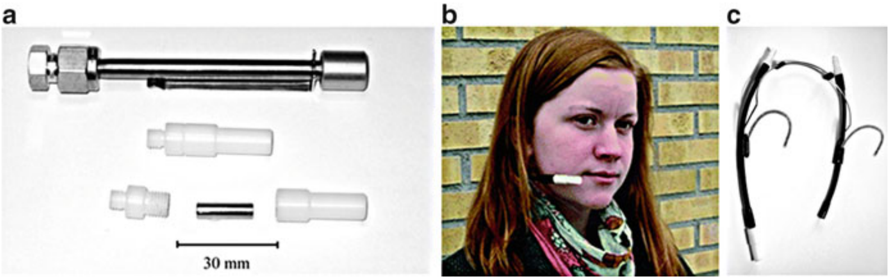

Fig. 52.2 Materials for personalized measurements of volatile organic compounds in the breathing zone (developed by Fenix Environmental, Sweden). Tube for sample storage small tube for sampling (**a**) headset for positioning of the sampling tube in the breathing zone (**b**) headset (**c**) (Photos by Roger Lindahl and Jan-Olof Levin)

additional indicators are labile species, such as secondary ozonides, reactive oxygen species, ultrafine particles, and black carbon particles (Wolkoff 2013).

Outdoor air quality is not a good indicator of personal exposure, because buildings are increasingly airtight and the vented air is more frequently treated in some way. At the same time, activity patterns indicate that most of a person's time is spent in buildings. For IAQ, this may lead to improved and miniaturized air sampling equipment. This will allow more personalized approaches to exposure assessment in homes (Fig. 52.2), such use of biomarkers of exhaled-air sampling to study exposures of residents (Fig. 52.3). New health indicators for indoor environments will probably be more likely to arise from self-assessment strategies and crowd sourcing using small electronic devices, such as smartphone-mediated sensors. In the coming decades this more compact equipment will become available to collect data on what is called exposome of residents (Ho et al. 2012).

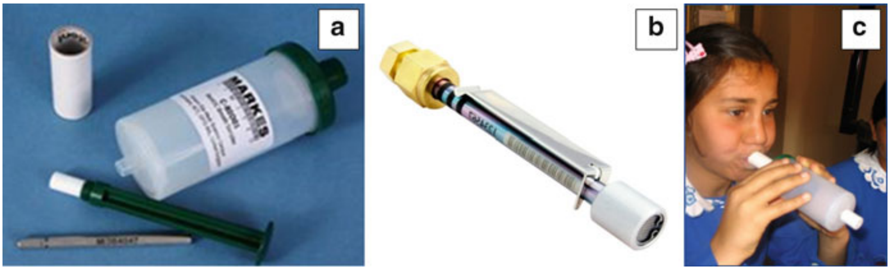

Fig. 52.3 Materials for self-assessment of exhaled air (**a**), adsorbent tube for transportation (**b**) and a child in primary school shows how an exhaled air sample is collected (**c**) (Photos by Markes (**a**), Camsco (**b**) and Joke de Koning (**c**))

Conclusions

On average, more than half of our lifetime we inhale indoor air. Over the past decades the composition of indoor air has become very different from the general outdoor quality. In part, this is the result of new building and (re) furnishing materials. Buildings have become more airtight, and, in part also because of changes in systems of climate control and air treatment, indoor air is much less related to outdoor general air quality. In part, this is also related to changes in activity patterns, including the use of consumer products such as air fresheners, surface cleaners, and personal care products. As fumes from open fires (smoking, room heating, and cooking) are reduced, the relative contribution of other chemicals increases. In the gas phase, carbon dioxide, ethanol, acetone and other odor-determining VOC will reflect endogenous products due to high occupancy, and their appearance may be used rather as a general indication of ventilation by number of air exchanges than as a health-related indicator of air quality. VOC represents a myriad of gas-phase components derived from building materials, occupancy, and activities. For VOC as a group, there is not much evidence to support an association with health effects. Some specific compounds may be of interest to specific health complaints. Formaldehyde may be a useful substance to monitor the formation of oxidation products that have a sensory response and can be used as indicator of perceived irritation. If high indoor ozone levels are expected, it is also useful to monitor the air concentration of reactive substrates in this process of atmospheric chemistry. One or more abundant terpenes present in cleaning and personal care products, such as limonene isomers, may be useful as chemical markers for substrates of ozonolysis. In the particle phase, coarse particles remain an important parameter as an indicator of biological agents and dust from mechanical wear that may also contain toxic ingredients, such as phthalates, polycyclic aromatic hydrocarbons, or polychlorbiphenyls, and flame retardants. The finer fraction may still be relevant as a marker of indoor process emissions, such as tobacco smoke and cooking fumes. If such sources are not contributing to indoor air levels, fine dust from outdoor sources is likely to reflect changes in general outdoor air quality.

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Chapter 53
Human Biological Monitoring and Public Health

Paul T.J. Scheepers

Abstract Environmental exposure to xenobiotic substances can be studied by analysis of biological media such as blood, urine, or exhaled air. Uptake from different sources and via different routes is integrated over time and can be reflected in concentrations of various types of biomarkers: the parent xenobiotic substance, a metabolite or the product of covalent binding to an endogenous macromolecule such as DNA or protein. The biological samples should be collected, pretreated, stored, and analyzed in a standardized manner. For interpretation of the biomarker levels, person characteristics, exposure patterns and the substance properties need to be taken into account. Such well-informed use of biomarkers is called human biological monitoring (HBM) and can be applied for different purposes: in occupational exposure surveys, exposure studies in the general population and unexpected exposures such as in chemical incidents. The aim of an HBM campaign should be introduced to the participants with care as some sample media require invasive collection methods. Less invasive methods such as urine and end-exhaled air should be considered if they produce equal results. For interpretation, models can be used to describe the kinetics of the biomarker of interest and estimate the target dose in one or more target tissues. For answering research questions, analysis on a group level is appropriate but the results should also be made available to individual study participants, upon request.

Keywords Bioactivation • Bioavailability • Biological tissues • Human biological monitoring • Toxicokinetics • Toxicodynamics

53.1 Introduction

This chapter describes the use of biomarkers in a public health context and also indicates that this wider scope of applications of biomarkers requires much more than just the analytical challenge of determining the concentration of the substance of interest in a body tissue.

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_53

In healthcare, biomarkers are often used for diagnostic and prognostic purposes in clinical practice. Outside the hospital biomarkers are often used to study interactions of xenobiotic factors from the environment with humans. The most important difference with clinical biomarkers is that for environmental exposure and public health purposes an association with the exterior risk factors should be verifiable. The most straightforward method to achieve this is the measurement of xenobiotic substances in human tissues. In 2009 in the Zamfara region in Nigeria, 460 children died of what was assumed to be an epidemic of malaria. Blood analysis confirmed that the neurological symptoms of surviving children could be attributed to lead intoxication from exposure to lead-containing dust released during gold mining (Bartrem et al. 2013). There are many more applications of the concept of biomarkers in the public health setting as will be discussed below.

In the context of public health applications, a single biomarker level is meaningless without additional data that can support interpretation of the biomarker level (Scheepers 2005). Each data point should be annotated with the proper contextual information that involves the person characteristics of the study subject and information on the exposure pattern. The determination of a biomarker level including this additional arrangement is described in the concept of human biological monitoring (HBM) or biomonitoring. A definition of this term was earlier postulated (Scheepers et al. 2011): The standardized and repeated systematic collection, pretreatment, storage, and analysis of body tissues in order to assess the internal dose of a xenobiotic substance by analysis of the parent substance and/or a product of biotransformation. In other words: biomonitoring is the application of biomarkers in a well-designed campaign or program aimed at answering a research question related to the impact of xenobiotic exposures on health in the general population or any specific sub population or individual.

53.2 Terminology and Classification of Biomarkers

Biomarkers can be classified in many ways. A classification earlier proposed by Zielhuis and Henderson uses three main categories: biomarkers of exposure, biomarkers of susceptibility and biomarkers of effect (Zielhuis and Henderson 1986). Examples of each of these types of biomarkers are presented in Table 53.1. Biomarkers of exposure are providing information on the uptake and systemic availability of a xenobiotic substance by representing the level of this xenobiotic substance or a product of biotransformation in the circulation (Manno et al. 2010).

Biomarkers of susceptibility represent parameters that reflect person characteristics that are inherited may also be acquired and modify the toxicokinetics and/or toxicodynamics of a xenobiotic (see Sect. 53.4 for more details). Such biomarkers usually reflect factors that modify toxicokinetics such as bioactivation or detoxification and that can explain why a susceptible person may respond to an exposure whereas other subjects (exposed to a similar dose) do not show a response at the

Table 53.1 Classification of biomarkers, which covers not all but most of its applications

Class	What it is	What it describes	Example	Reference
Biomarker of exposure	Parent substance or a product of (usually covalent chemical) interaction with an endogenous biomolecule	Related to a xenobiotic substance and reflecting a systemic internal dose in tissue relevant to the primary target organ or tissue	Blood lead	Skerfving et al. (1993)
Biomarker of susceptibility	An enzyme or enzyme activity or signal in the pathway between exposure and effect	Related to a constitutional property (genotype) attenuated by acquired characteristic (phenotype) that modifies the response of the physiology to a xenobiotic exposure	Activity of isoforms of enzyme systems, such as cytochrome P-450 isoenzymes (CYP), glutathione-S-transferase (GST), acetyltransferase, and UDP-glucuronosyl-transferases	Kadlubar et al. (1992), Autrup (2000)
Biomarker of effect	Any physiological change in structure or function of bodily constituents that can be interpreted as related to or leading to a potential or proven adverse event	Related to response of the body physiology that is not necessarily adverse but contains information on a biologically significant interaction of a xenobiotic factor with critical tissues or processes	Chromosome aberration	Hagmar et al. (1994), Norppa et al. (2006)

same exposure level. In this way, a high activity of a bioactivating system or a low activity of a detoxifying step in metabolism may result in a higher susceptibility of an individual within an exposed population.

Biomarkers of effect are a comprehensive group of markers of biochemical activity, physiological response, or effect. Most markers of effect reflect responses of a reversible nature that do not result in lesions that can be interpreted as 'adverse.' These biomarker are not necessarily good predictors of the probability of a disease to occur. There are also early indicators of a potential adverse effect that are considered biologically significant. On a population level, such effect biomarkers may explain a higher incidence or prevalence of a disease. For cancer, some biomarkers of cytogenetic damage such as chromosome aberrations have been demonstrated to be useful predictors of cancer in population-based studies (Hagmar et al. 1994; Norppa et al. 2006).

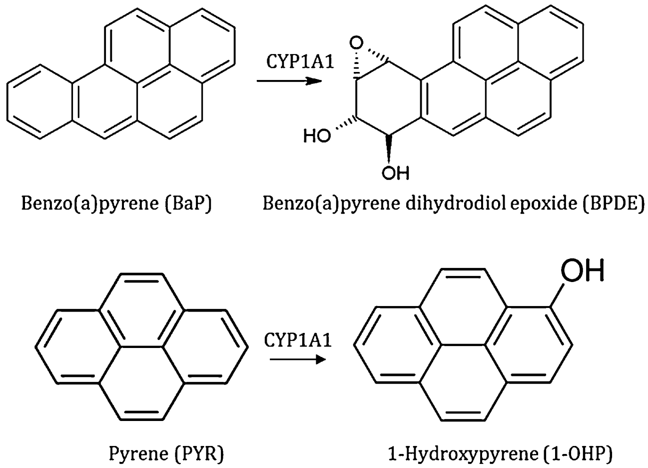

Fig. 53.1 Bioactivation of two congeners of polycyclic aromatic hydrocarbons (PAH) and their respective metabolites that are often used as biomarkers of exposure to PAH

Some biomarkers are not easily placed in one of the three aforementioned categories. An example is the addition product to DNA (DNA-adduct). Qualitatively, it supports a role of a particular substance in a target tissue. A good example is the DNA-adduct of benz[a]pyrene diolepoxide that supports a role of polycyclic aromatic hydrocarbons as a risk factor for lung cancer in active smoking (Garner et al. 1988; see Fig. 53.1). Finding this adduct in target tissue where a significant biological event is anticipated is a much stronger indication of a possible adverse outcome than just the presence of a parent xenobiotic substance in a target tissue. It demonstrates that the substance was taken up and distributed to that particular tissue. In addition, it demonstrates that the substance was bio-activated to produce a reactive intermediate capable of forming a covalent bond to a biomolecule with a critical role in human physiology. As DNA is a critical cell component, there are several biochemical mechanisms to prevent changes in the chemical structure of DNA, and (as relevant in this case) it also contains very effective systems to remove structure modifications. Most adducts will therefore disappear within days or weeks due to enzymatic DNA-repair. The adduct level may not be a good predictor of the health outcome (tumor induction): this may be much (more) dependent on how effectively the adduct can be removed by enzyme repair.

53.3 Body Tissues

In the field of HBM, the term body tissue as a medium of sample collection is widely interpreted to include organ tissue, blood, and urine but also exhaled air, saliva, buccal smears, hair, and nails.

53.3.1 Organ Tissue

There are limited possibilities for collecting samples from body tissues. Since skin, lung, and gastrointestinal tract represents a tissue that is in direct contact with the exterior and forms a first line of defense, these organs may be relevant for studying the local bioavailability and toxification or detoxicification in target tissues. Cells in direct contact with xenobiotics can be sampled by taking biopsies from skin (Roelofzen et al. 2012) or cells may be flushed, e.g., from the lung lumen, i.e., by a bronchial alveolar lavage or sputum (Talaska et al. 1996). Such procedures are invasive and must be performed with great care because of potential risk to the study subject. A less invasive method is the collection of epithelial cells from buccal smears or exfoliated cells from urine (Talaska et al. 1993). Both procedures are less invasive and also provide epithelial tissues, which may be targets for specific chemicals.

53.3.2 Blood

Collection of venous blood provides the possibility to study the systemic availability of a xenobiotic substance following absorption from different routes of uptake (inhalation, dermal absorption, and absorption via the gastrointestinal tract). Blood by itself represents a complex biological medium due to the presence of different cell populations that may contain target biomolecules such as DNA, RNA, and proteins, and also active metabolic pathways. Once a xenobiotic substance or its product of metabolism is taken up in a cell, the kinetics of elimination may be changed (see Sect. 53.4). Even without uptake in blood cells, the bioavailability of a xenobiotic substance may be influenced by protein binding in blood and organs and by partitioning between the blood circulation and perfused tissues. Because of the changes in bioavailability and metabolism over time, a plasma level can be an important source of information, especially if acute health effects are to be expected and treatment is considered (Chap. 54). Blood parameters reflect exposure but also bioavailability and, for xenobiotic species that require bioactivation, the cytochrome P-450 (CYP) enzyme system represents a comprehensive system of different iso-enzymes responsible for conversion of many substrates including xenobiotic substances. Many such conversions may lead to inactivation and rapid conjugation and elimination of toxic species but in some cases, such as polycyclic aromatic hydrocarbons (PAH), metabolites have a higher chemical reactivity and toxicity (Fig. 53.1).

For PAH reactive intermediates formed by CYP enzymes, adducts can be used as biomarkers of exposure. PAH epoxides represent the reactive intermediates responsible for covalent binding to nucleophilic groups in biomolecules such as DNA (Fig. 53.2). For those substances that form highly reactive intermediates, the most useful biomarkers may be DNA-adducts from peripheral blood lymphocytes, albumin adducts in plasma, or hemoglobin adducts in erythrocytes.

DNA-adducts have a limited half-life due to their repair, which normally takes a few days. For proteins, there is no known system of enzymatic repair and

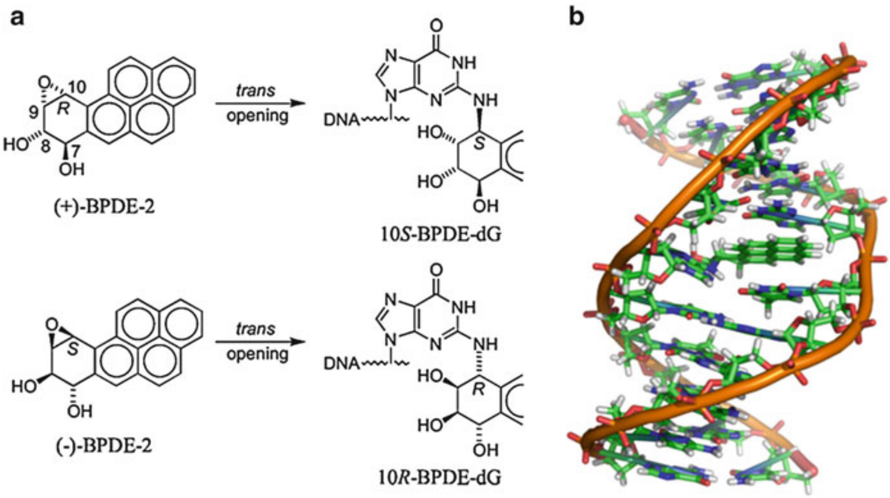

Fig. 53.2 (**a**) Structures of the trans-opened BPDE adducts at N^2 on the guanine base of DNA. A single site-specific trans-opened 7,8,9,10-tetrahydrobenzo[a]pyrene 7,8-diol 9,10-epoxide N^2-deoxyguanosine adduct (From Kramata et al. 2003). (**b**) Structure of an adduct of (+)-(7S,8R,9S,10R)-7,8-dihydroxy-9,10-epoxy-7,8,9,10-tetrahydrobenzo[a]pyrene in a DNA duplex (Wikimedia Commons, the free media repository)

these adducts are therefore more persistent and depend on the life span of the native protein. Chemically stable adducts of hemoglobin (Hb-adducts) have a persistence equal to the lifespan of the erythrocyte, which is 4 months in humans. Analytical methods have been developed for many different biomarkers based on Hb adducts (see Table 53.2). For specific xenobiotics, blood biomarkers may be used to assess exposure and potential health risk, e.g., formation of methemoglobin by amines and nitro-compounds, formation of carboxyhemoglobin by exposure to carbon monoxide or dichloromethane, and inhibition of acetyl cholinesterase from erythrocytes by organophosphor pesticides or carbamate pesticides and nerve agents. Porfyrine assays have been developed to assess the blood toxicity of different hazardous substances such as lead. Blood is also used to evaluate the toxicity of cytogenetic damage (Comets, micronuclei, sister chromatide exchanges, and chromosome aberrations). These cytogenetic markers demonstrate molecular lesions that reflect systemic bioavailability and bioactivation of xenobiotics. Some of these parameters reflect early biological responses that may be indicative of a potential risk if exposure extends over long periods (years) of time. For chromosomal aberrations, an association with cancer was suggested (Hagmar et al. 1994; Norppa et al. 2006).

53.3.3 Exhaled Air

The lungs effectively exchange gases providing bodily tissues with oxygen and removing excess carbon dioxide. In addition to oxygen, other substances can be

Table 53.2 New and improved biomarkers of exposure that were presented over the past 10 years (Scheepers and Heussen 2008; Scheepers 2011; Scheepers et al. 2013)

Chemical substance	Biomarker	Biological medium	Method[a]
Acrylonitrile	N-Acetyl-S-(2-cyanoethyl)cysteine (CEMA), N-acetyl-S-(1-cyano-2-hydroxyethyl)cysteine (CHEMA)	Urine	LC-MS/MS
Arsenic species	Arsenobetaine (AB), arsenite (As^{3+}), Arsenate (As^{5+}), dimethylarsinate (DMA), monomethylarsonate (MMA)	Urine	μLC-ICP-MS
Benzene and toluene	S-phenyl mercapturic acid (SPMA) S-butyl mercapturic acid (SBMA)	Urine	LC/LC-ESI-MS/MS
Benzene	S-phenylmercapturic acid (SPMA)	Urine	ELISA
	Benzene	Urine	SPME-GC-MS
Benzene, toluene and xylene-isomers	Benzene, toluene, ortho-xylene, para-xylene and meta-xylene	Exhaled air	GC-FID
Beryllium	Beryllium	Urine	Quadrupole ICP-MS
Bis(2-propylheptyl)phthalate (DPHP)	Mono-2-(propyl-6-hydroxyheptyl)phthalate (OH-MPHP), Mono-2-(propyl-6-oxoheptyl)phthalate (oxo-MPHP), mono-2-(propyl-6-carboxy-hexyl)phthalate (cx-MPHxP)	Urine	LC-MS/MS
Ethylene oxide	N-Acetyl-S-(2-hydroxyethyl) cysteine (HEMA)	Urine	LC-MS/MS
Nicotine	Cotinine (COT), trans-3′-hydroxycotinine (HCOT)	Urine	Online-SPE-UPLC-MS/MS
Decamethylcyclopenta-siloxane (D5)	Decamethylcyclopentasiloxane (D5)	Exhaled air	TD-GC-MS
1,1-difluoroethane, 1,1,1-trifluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,1,3,3-pentafluoropropane	1,1-Difluoroethane, 1,1,1-trifluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,1,3,3-Pentafluoropropane	Exhaled air, blood	GC-FID, ATD-GC-FID
N,N-dimethylacetamide and N, N-dimethylformamide	N-Methylacetamide and N-methylformamide	Urine	GC-MS

(continued)

Table 53.2 (continued)

Chemical substance	Biomarker	Biological medium	Method[a]
N,N-dimethylformamide (DMF)	3-Methyl-5-isoproylhydantoin (MIH, released from N-terminal Hb adduct), N-acetyl-S-(N-methylcarbamoyl) cysteine (AMCC)	Blood, urine	GC-MS (MIH), LC-MS/MS (AMCC)
Dithiocarbamates (DTC)	Ethylenethiourea (ETU), propylenethiourea (PTU)	Urine	UHPLC-ESI-MS/MS
2-ethoxyethanol	2-Ethoxyacetic acid (EEA)	Urine	GC-MS
N-ethyl-2-pyrrolidone (NEP)	5-Hydroxy-N-ethyl-2-pyrrolidone (5-HNEP); 2-hydroxy-N-ethylsuccinimide (2-HESI)	Urine	GC-MS
Ethylenethiourea	Ethylenethiourea	Urine	LC-ESI-MS/MS
n-Heptane	n-Heptane and its metabolites heptane-2-one, heptane-3-one, heptane-4-one, 1-heptanol, 2-heptanol, 3-heptanol and 4-heptanol	Urine	HS-SPDE and GC-MS
1,6-Hexamethylene diisocyanate	1,6-Hexamethyl diamine	Urine	GC-MS
Lead	Lead	Saliva	ICP-MS
Methamidophos	Methamidophos	Urine	LC-MS/MS
Naphthalene	Naphthyl-keratin adduct	Blood	ELISA
Octamethylcyclotetrasiloxane (D4)	Octamethylcyclotetrasiloxane (D4)	Exhaled air	TD-GC-MS
Polycyclic aromatic hydrocarbons (PAH)	1-Hydroxypyrene, 2-hydroxynaphthalene, 2-hydroxyfluorene, 2-hydroxyfluoranthene	Urine	HPLC-Flu
Polycyclic aromatic hydrocarbons (PAH)	1, 2-hydroxynaphthalene, 2-, 9-hydroxyfluorene, 1-, 2-, 3-, 4-, and 9-hydroxyphenanthrene, 1-hydroxypyrene, 6-hydroxychrysene and 3-hydroxybenzo[a]pyrene, naphthalene, acenaphtylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[a]pyrene	Urine	GC-MS
Pirimicarb	2-Methylamino-5,6-dimethyl-4-hydroxypyrimidine (MDHP)	Urine	LC-MS
(1S,6R)-(+)-3-carene	3-Caren-10-ol, 3-caren-10-carboxylic acid	Urine	GC-PCI-MS/MS

(1R,5S)-(+)-α-pinene, (1S, 5S)-(−)-α-pinene	(1R,2R,5R)-cis-verbenol, (1R,2S,5R)-trans-verbenol, (1S,5R)-(+)-myrtenol	Urine	GC-PCI-MS/MS
(R)-(+)-limonene	(1S, 5S)-trans-Carveol, (1R, 5S)-cis-carveol, (1S, 2S, 4R)-limonene-1,2-diol, perillyl alcohol, perillic acid, limonene-8,9-diol	Urine	GC-PCI-MS/MS
4,4′-methylenediphenyl diisocyanate (MDI)	5-isopropyl-3[4-(4-aminobenzyl)phenyl]hydantoin	Blood	GC-HRMS-NICI
Isocyanurate	Isotriamine	Urine	UPLC-MS/MS
Indium	Indium	Serum	ICP-MS
2- and 3-Nitrobenzanthrone	2-Aminobenzanthron-3-ylmercapturic acid (2-ABA-MA), 3-aminobenzanthron-3-ylmercapturic acid (3-ABA-MA)	Urine	LC-ESI-MS/MS
PAH	Parent polycyclic aromatic hydrocarbons	Urine	SPME-GC-MS
Phenyl urea herbicides	Parent phenyl urea herbicide, methyl urea, urea and aniline	Urine	LC-MS/MS
Styrene	S-(2-hydroxy-2-phenylethyl)cysteine adduct to globin	Blood	GC-EI-MS
Styrene	Styrene	Saliva	SHS-GC-MS
Tebuconazole	t-Butylhydroxy-tebuconazole (TEB-OH), t-butylcarboxy-tebuconazole (TEB-COOH)	Urine	LC-MS/MS
Terbuthylazine	Terbuthylazine (TBA), desethylterbutylazine (DET)	Urine, hair	LC-MS/MS
2,5-Toluylenediamine	2,5-Toluylenediamine	Urine	GC-MS
o-Tricresyl phosphate	o,o-Dicresylphosphate	Urine	GC-MS/MS
Bifenthrin/Cyhalothrin	3-(2-Chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclo-propanecarboxylic acid (TFP-acid); cis- and trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclo-propanecarboxylic acid (cis- and trans DCCA); cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylic acid (DBCA); 4-chloro-isopropyl benzeneacetic acid (CPBA); 3-phenoxybenzoic acid (3-PBA); 4-fluoro-3-phenoxybenzoic acid (F-PBA); 2-methyl-3-phenylbenzoic acid (2-MPA)	Urine	GC-MS/MS

[a] *ELISA* enzyme-linked immunosorbent assays, *GC-NCI-MS* gas chromatography negative chemical ionisation mass spectrometry, *GC-PCI-MS* gas chromatography positive chemical ionisation mass spectrometry, *GC-HRMS-NICI* gas chromatography high resolution mass spectrometry negative ion chemical ionisation, *ICP-MS* inductively coupled plasma mass spectrometry, *SHS-GC-MS* static head space gas chromatography mass spectrometry, *SPME* solid phase micro extraction, *μLC* micro liquid chromatography, *UPLC-MS/MS* ultra-performance liquid chromatography tandem mass spectrometry, *μLC-ICP-MS* micro liquid chromatography inductively coupled plasma mass spectrometry, *UHPLC-ESI-MS/MS* ultra high performance liquid chromatography electrospray ionisation tandem mass spectrometry

taken up by this route and in addition to carbon dioxide many other gases and vapors are excreted via the lungs. Due to the large surface and the short distance between the blood and air compartment in the alveoli, low-molecular substances in the gas phase equilibrate in a matter of milliseconds. The uptake and excretion are therefore ruled by the blood gas partition coefficient of any gas or liquid with a vapor pressure. The mixture of gases and vapors in the alveolar air volume will reflect the blood composition with respect to gases and volatile liquids. The relationship between alveolar air concentrations and arterial blood concentrations is known to be linear over a wide concentration range. This knowledge is used in the breath alcohol test to determine the blood percentage of drivers and can be applied to many other volatile organic compounds in industrial and consumer products. Substances that have low vapor pressure, such as most metal ions, can be captured from exhaled breath condensate and represent suitable noninvasive biomarkers of pulmonary exposure (Félix et al. 2013).

53.3.4 Urine

Most nonvolatile water soluble inorganic and organic xenobiotic substances are readily excreted in urine. In addition, traces of non-metabolized volatile organic compounds can be determined in exchange with the gas phase of urine (Fustinoni et al. 1999). Urine is continuously formed by the kidneys and collected in the bladder. If urine samples are required, it is useful to provide detailed instructions of how and when to collect the samples. Depending on the time and duration of exposure, it may be sufficient to collect only one urine sample (referred to as spot-sample) at a well-chosen time of the day (e.g. a first urine sample after awakening). If the exposure event cannot be pinpointed in time, it may be required to collect a number of urine samples over a defined period of time following an exposure event. Information on the time of the toilet visit (and the previous toilet visit) provides information on the period of time when the biomarker was excreted in the bladder. For standardization, it may be required to define the moment of sample collection, such as in workers (pre-shift and post-shift spot samples), or to collect urine of a defined period of time, i.e. a whole day and night (24 h sample). There is quite some variability in the density of urine samples due to the intake of beverages and loss of water vapor during exercise and/or in a warm climate. The creatinine adjustment is the most common approach to correcting for this variability (Garde et al. 2004). The half-life of urinary biomarkers is usually short but may be attenuated if there are sinks of poor water soluble depots, e.g., in the lungs (Scheepers et al. 2008) or due to binding to metallothioneins (metals).

53.3.5 Saliva, Hair, and Nails

Saliva is sometimes used as a biological medium for environmental exposure monitoring (Nigg and Wade 1992; Luconi et al. 2001). Hair and nails have been used to estimate exposure to metals (Kim and Kim 2011). The content of mercury in hair was used to reconstruct an intoxication in the general population in Iran (Crump et al. 1995). Recently, also organic substances have been determined from hair (Mercadante et al. 2013).

53.4 Toxicokinetics and Toxicodynamics

A popular expression to describe the contribution of toxicokinetics is: *what does the body do to the substance* as opposed to the contribution from toxicodynamics: *what does the substance do to the body*. Toxicokinetics describe the absorption, distribution, metabolism, and excretion of xenobiotics. These processes describe whether, when, and at what concentration a xenobiotic or one or more of its metabolites may reach a target tissue where it can do harm. For uptake, three routes have to be taken into account: inhalation, ingestion, and skin absorption. Substances can be taken up by only one of these routes, two of them, or all of them, depending on the substance properties and exposure situation. Inhalation is often fast, ingestion may be fast in most cases, and skin absorption is fast for only a few substances. For distribution, the partitioning between air and blood, between blood and organs, and between blood and adipose tissue is important. The lipophilicity expressed as the partitioning between octanol and water (Log $P_{o/w}$) is a useful parameter to predict the kinetics of uptake, distribution, and excretion. For some target tissues, such as the brain and the placenta, it is useful to know whether and to what extent a xenobiotic or its metabolite can pass the blood-brain or blood-placenta barrier, respectively. If a substance can be taken up efficiently, is taken up in the blood circulation, and can reach the target organ, it is said to have a high bioavailability.

Most organic substances are metabolized involving enzyme-systems that protect vital systems. Such enzyme systems can be found in all tissues but some organs such as the liver may be more important to overall metabolism because of higher concentrations and activity of enzymes or higher concentrations of substrates. For ingestion, the liver is the first organ to contribute to metabolism. If substances are taken up via inhalation or skin, the parent may reach other organs before passing through the liver or may be metabolized in lungs or dermis. There may be differences in iso-enzymes available in different organ systems and this may have consequences on the tissue dose of the parent and of one or more metabolites (Kadlubar et al. 1992).

53.4.1 Zero- and First Order Kinetics

For the study design of HBM campaigns, it is useful to know what kinetic pattern the biomarker of interest will follow. In this respect, the distinction between zero– and first order kinetics is the most relevant. First order kinetics applies to

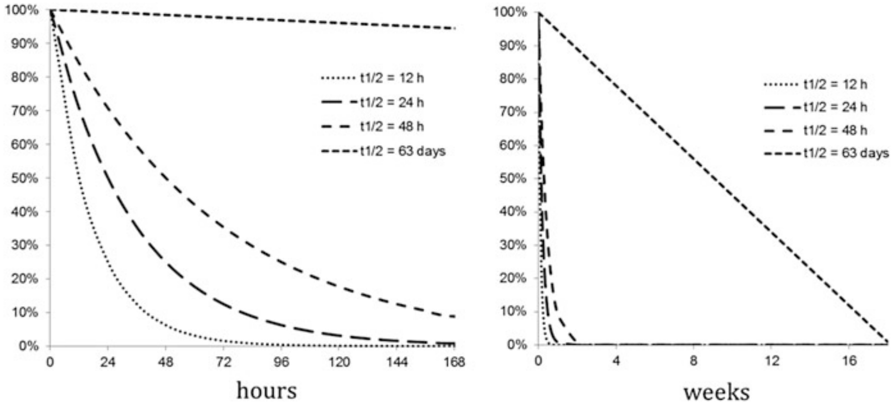

Fig. 53.3 Zero and first order elimination of biomarkers with different half-lives. The same data are shown over a time course of hours (*left panel*) and over the time course of weeks (*right panel*)

xenobiotics and their metabolites that are free in solution and dissolved in plasma and other body fluids. The half-life of excretion is determined by the overall effect of kinetic processes (see Fig. 53.3 for the influence of elimination half-life on the pattern of excretion of the biomarker). In contrast, zero-order kinetics applies to xenobiotics and their products of metabolism that are formed in the cell interior and that cannot leave the containment of the cell. This is the case for chemically stable addition products (adducts) of reactive intermediates with intracellular structures and biomolecules, such as DNA, RNA, and proteins. The half-life of these biomarkers is determined by the lifespan of the cell that contains the biomarker of interest. For white blood cells, this depends on the lifespan of the specific subpopulation of the cells. For red blood cells, this lifespan in humans is 126 days. The relative pattern of biomarker elimination over time is shown in Fig. 53.3. Such kinetic patterns can be measured and modelled. In practice, toxicokinetic models are often validated using data from analysis of body tissues and used for predictions of changes of concentrations in different body tissues over time. Kinetic information such as the pattern of elimination and the elimination half-life can already be used in the planning phase, e.g., to calculate the time available to collect a sample, regarding the anticipated type of elimination kinetics and the biological half-life $t_{½}$ of the specific biomarker. For biomarkers that follow zero kinetics (see Sect. 53.4.1), the time t_s available to collect a sample following an exposure event is equivalent to the estimated population-based life span of the cell that contains the biomarker. This life span is twofold the elimination half-life of the biomarker, only if the limit of quantification (*LOQ*) is much lower than the concentration of the biomarker in the available biological medium estimated at the time of exposure, C_e (Scheepers et al. 2011):

$$t_s \approx 2 \cdot t_{½} \text{ if } LOQ << C_e$$

For biomarkers that follow a first order pattern of elimination, the time t_s to collect an air sample is equivalent to (Scheepers et al. 2011):

$$t_s = t_{½}{}^2 \log\left(C_e/LOQ\right)$$

with $t_{½}$ as the elimination half-life of the biomarker of interest in a biological medium that is available for sample collection.

53.4.2 Modifying Factors

There are some person characteristics that should be considered when interpreting biomarker levels. In this section, the influence of gender and age, physical activity, and co-exposures will be discussed as some examples of factors that can modify biomarker levels quite substantially.

53.4.2.1 Gender and Age

Physiology in males and females is different. This relates to the distribution of adipose tissue and to differences in some hormone-directed processes. Young children are likely to have higher exposures than adults. In part, this is related to their body biometry and body physiology (body length and weight, high surface to volume ratio, somewhat higher lung ventilation frequency, etc.). Also, their behavior and activity patterns may attenuate internal exposures (e.g., personal hygiene, hand-mouth contact, sucking and licking of toys and other objects, etc.). It is obvious that it is relevant to register gender and age together with other useful person characteristics.

53.4.2.2 Physical Activity

Physical activity has a profound influence on the ventilation frequency and tidal volume. This may result in an increased uptake rate of xenobiotics from the gas phase. Post-exposure elimination of volatile xenobiotics or their metabolites by exhalation will also be much faster at an elevated level of physical activity due to a higher ventilation rate. A higher physical activity also results in an increased cardiac output that will enhance the distribution to and perfusion of organs. An increased liver perfusion will likely result in a much faster metabolism of xenobiotics (Jonsson et al. 2001). Obviously, when studying exposures of workers it is useful to determine and register their level of physical activity during different phases (pre-exposure, exposure, and post-exposure).

53.4.2.3 Co-exposure

Most exposures are not to single substances. In addition there may also be life style factors such as smoking of tobacco, drinking of alcoholic beverages, or other uses of stimulating or sedating substances. A particular interesting co-exposure is the use of prescribed or non-prescribed medical drugs. All of these exposures may interact with the toxicokinetics and the toxicodynamics of the substances of interest. Competitive inhibition of enzymatic conversions by medical drugs may alter metabolism (Campbell et al. 1988). Some other co-exposures provide substrates to an enzyme system, increasing the metabolic rate for the xenobiotic of interest. When applying biomonitoring, it is useful to keep track of these co-exposures by asking the study participants some specific questions related to their lifestyle and their use of medication.

53.4.3 Modelling

To some extent it is possible to simulate the toxicokinetics and toxicdynamic processes in a model. As long as exposures are low, most processes can be described in simple toxicokinetic models (TK-models) using linear differentiation equations. If exposures are higher, biotransformation pathways may become over-saturated resulting in more complex processes that require models based on more complex nonlinear differential equations. More accuracy is obtained using models that more precisely simulate human physiology in so-called physiology-based toxicokinetic (PBTK) models. Many substance and body-specific parameters have to be inserted before biomarker levels can be calculated. Once parameterized, the course of biomarker levels over time can be estimated for specific target organs by calculation. The recent introduction of generic PBTK models simplifies the use of these models in spread sheet-based software applications (Jongeneelen and ten Berge 2011a, b; LRI-CEFIC 2012). Such models could be used to derive biomarker levels to protect workers or the general public (Sect. 53.5.2). Another interesting application is the use of such models in reverse dosimetry related to chemical incidents. During follow-up to a high exposure, biological tissues are often available for analysis. Because biomarker levels change over time, it is useful to reconstruct the exposure level at the time of the incident. This information can be used in the medical support, for risk assessment, or for scientific research purposes (see Chap. 54).

53.5 Interpretation

The concentration of a parent, metabolite, or adduct provides information on the uptake of xenobiotics, taking into account the overall contribution from different routes of exposure and from different sources of the xenobiotic substance.

The level may vary over time and reflects the systemic uptake integrated over different toxicokinetic processes in time. Without additional contextual information on the study subject's person characteristics (gender, age, biometry, physical exercise, co-exposures, etc.), and about the exposure pattern, it is hardly possible to derive useful information from a biomarker concentration concerning the exposure or potential health effects (Edelman et al. 2003).

53.5.1 Individually and in Groups

Results of a biomonitoring campaign can be presented in descriptive statistics. If required, the results can be stratified according to gender, age, or anticipated exposure status. Stratification for life style factors such as smoking and drinking habits is recommended even if these co-exposures may not contain the xenobiotic of interest, as smoking and drinking of alcoholic beverages can attenuate the biomarker levels substantially by changing toxicokinetics such as enzyme activities (Sect. 53.4.2.1). Use of prescribed medical drugs may also interfere with toxicokinetics or toxicodynamics of the xenobiotic and such effects should also be treated in a separate analysis if possible.

53.5.2 Values for Reference

The most obvious reference level is a baseline level observed for the biomarker in individuals of the population of interest. A baseline is defined as the biomarker level observed when there is no known specific exposure other than background exposure. Such a baseline is determined by person characteristics and life style factors (VanRooij et al. 1994). Large population-based HBM programs were introduced in the US and Europe to describe the levels of biomarkers reflecting common and ubiquitous environmental contaminants (Kirman et al. 2012; Joas et al. 2012). If such values are not available for the population of interest, it is possible to determine the baseline by collection of samples before the start of a known exposure event. In populations of workers, a Monday morning sample, prior to the start of a work-shift, gives a suitable reflection of a baseline as long as the half live of elimination is sufficiently short and any traces from a previous workweek were eliminated. Biomarker levels in follow-up spot samples can be interpreted relative to this individually determined reference. For substances with fast toxicokinetics, the comparison of post-shift with pre-shift values is a suitable approach to identifying work-related factors as potential sources of uptake. For biomarkers with a much slower pattern of excretion, samples may have to be collected over several days up to a full workweek because of potential accumulation of the biomarker level over a workweek. The biomarker level in a post-shift sample on the last day of a workweek may provide a value that can be compared to a workplace standard, such as a biological guidance value (BGV), for workers. BGVs are specifically established for the desired type of biological sample, as well as the time of sample collection, relative to a period of exposure. BGVs have been published in the US, UK, Finland, and Germany (see for an overview Boogaard 2009). Most BGVs have been derived from maximum allowable air levels determined to protect worker's health (Bevan et al. 2012; Cocker 2014). Equations describing the numerical association between levels of inhalation exposure and biomarker levels have been published by the Deutsche Forschungsgemeinschaft (DFG 2012).

53.5.3 Pattern Over Time

Following the end of exposure, biomarker levels will normally gradually decrease towards background levels that are considered to be a background within a population (see Sect. 53.4.1). If the levels remain the same or go up in the post-exposure phase this may indicate a latency in uptake into the circulation from a depot in, e.g., skin, lungs, or intestine. Since skin absorption is a slow process compared to inhalation and gastrointestinal absorption, latency in skin absorption may cause the highest plasma concentration to be reached several hours following cessation of exposure. For substances with high acute toxicity, it is recommended that admission to a healthcare facility be considered because symptoms of intoxication may occur a considerable time after the exposure ended (see Chap. 52). If exposures do not decrease over a period of several days, there may still be an unknown or undetected source of exposure in the living or working environment. It is also possible that there a sink in the body from where a xenobiotic substance or a product of biotransformation is released into the circulation at a slow rate. This can be a depot of scarcely water-soluble material in the lung lumen, such as deposited ultrafine particles from e.g. welding fumes (Scheepers et al. 2008), a sink of a lipophilic substance in adipose tissue, such as in exposures to dioxin (Sorg et al. 2009), a substance that is protein-bound and slowly released due to the long life span of a cell in the case of hemoglobin adducts (Bader and Wrbitzky 2006), or a tissue depot of protein-bound xenobiotic substance in the kidneys, such as in the case of long-term exposure to cadmium (Sangster et al. 1984).

The use of HBM will be illustrated in a study of dermal absorption of PAH from coal tar. PAH represent a group of substances with a high molecular weight and high lipophilicity. Only judged by their substance properties, dermal absorption would be considered negligible. However, dermal administration of coal-tar in human volunteers demonstrated that benzo[a]pyrene (BaP) is effectively absorbed. As diffusion is the transport process in skin absorption, the concentration gradient over the stratum corneum is the driving force in skin permeation. Metabolism of BaP by CYP1A1 in the dermis increases the concentration gradient and explains the dermal uptake of BaP and other PAH (Fig. 53.4). The skin absorption of PAH in

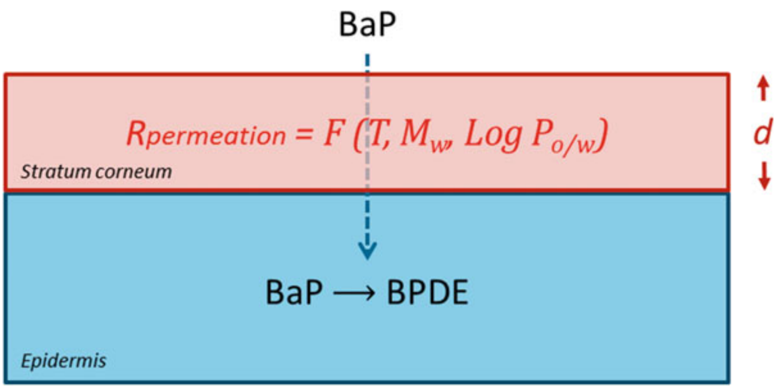

Fig. 53.4 Conceptual model for stratum corneum permeation of benzo[a]pyrene (BaP) that represents the most important rate-limiting step to skin absorption of BaP. The absorption is driven by a concentration gradient that is enhanced by biotransformation of BaP to BPDE by CYP 1A1 in the epidermis

Table 53.3 Median levels (range) of sum of PAH adducts and BPDE DNA adducts in volunteers and patients before and 96 h after the start of application of coal tar ointment (CTO). Adduct levels were measured by ^{32}P-postlabeling and expressed per 108 nucleotides

Study group	Before CTO administration ($t = 0$ h)		After CTO administration ($t = 96$ h)	
	Sum of PAH-DNA	BPDE-DNA	Sum of PAH-DNA	BPDE-DNA
Healthy subjects ($N = 10$)	3.5 (1.0–5.2)	< 0.1	21.1 (12.9–29.2)*	8.2 (3.9–13.3)*
Patients ($N = 10$)	1.0 (0.6–2.9)	< 0.1	3.6 (2.1–18.9)*	1.1 (0.5–6.7)*

*$p < 0.05$ compared to baseline (Roelofzen et al. 2012)

workers was demonstrated in road paving workers by using 1-hydroxypyrene as a biomarker of exposure and bioactivation (Fig. 53.1).

Urinary excretion increased from pre-shift to post-shift urine samples in workers exposed to coal tar-doped asphalt (Jongeneelen et al. 1988). That diffusion is the ruling physical process was also demonstrated in a well-controlled study by Roelofzen and co-workers (2012), comparing uptake of PAH in psoriasis patients who received coal tar therapy with the uptake following a similar treatment in healthy volunteers. The uptake in psoriasis patients was slowed down as reflected in a lower level of total PAH adducts, as well as specific BaP adducts (Table 53.3), and a lower urinary excretion of 1-hydroxypyrene over the entire period of the treatment compared to observed levels in healthy subjects (Fig. 53.5). The authors suggested that this was a direct result of a smaller distance to be covered in the stratum corneum of healthy subjects compared with patients who have a much thicker stratum corneum as a result of their disease.

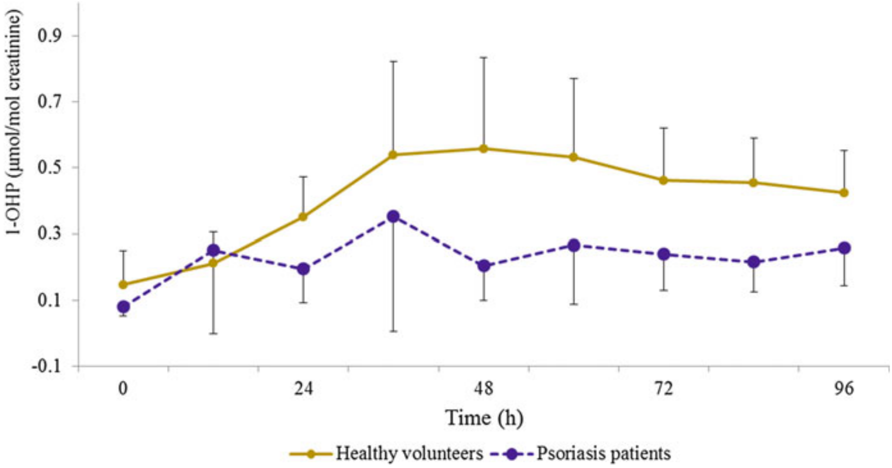

Fig. 53.5 Urinary excretion of 1-OHP (error bars indicate standard error of the mean). Time t = 0 h marks the time just before the start of topical application of coal tar ointment. Exposure continued over 96 h. The reduced uptake in psoriasis patients is explained by a disease-related increased thickness of the stratum corneum that contributes to a slower uptake of pyrene (Source: Roelofzen et al. 2012)

53.5.4 Communication Strategies

Despite a clear explanation prior to the start of an HBM campaign the meaning of the results of HBM may not be entirely clear. Following an analysis of body tissues, study participants often expect to receive information on their present or future health status. The researchers should explain that most biomarkers reflect uptake, bioavailability, and some also bioactivation. Only a few biomarkers reflect physiological responses that can be interpreted as a predictor of a health-related outcome. Also, these responses will likely disappear because the effects are most often reversible. Only those responses that can be interpreted as adverse in the short-term (e.g., elevated carboxyhemoglobin, inhibition of acetyl cholinesterase activity, elevated methaemoglobin level) may require therapy (see Chap. 54). A continued internal exposure over long to almost life-long exposure may be a risk factor for the occurrence of chronic disease and may also lead to different types of cancer or non-cancer related organ failure. For cancer, many of those exposures have been identified in populations of workers and are listed as human carcinogens by the WHO (see. http://monographs.iarc.fr/ENG/Classification/ClassificationsAlphaOrder.pdf). HBM may help to confirm a suspected exposure to a hazardous and potential reproduction toxic and/or carcinogenic risk factor and measures can and should be considered to take away or reduce the sources of such exposures to prevent the occurrence of disease. Only if exposures are extremely high, the elevated levels of biomarkers may explain the occurrence of clinical signs of intoxication that may earlier not have been attributed to a chemical exposure. Such results require immediate and appropriate treatment (see Chap. 54). In most cases, biomarker levels will be low and will not explain clinical symptoms. Often exposures are too short (accidents) or there was no direct contact, the direct contact did not lead to a significant uptake or the uptake did not result in a systemic exposure of any biological significance. Based on a well-informed interpretation, a physician can often reassure the study subject that health consequences are not likely in the short or long term (Scheepers et al. 2014). Physicians who are not familiar with the interpretation of laboratory results related to the biomarkers discussed in this section should consult a national or regional poison center for support in interpretation of lab results regarding how to communicate these results to the study subjects, including the consequences of engaging in some kind of treatment to reduce health implications and the potential side-effects of such medical interventions. In many cases, biomonitoring results will just confirm that supportive medical treatment is sufficient to prevent any adverse health effects resulting from toxic exposures (see Chap. 54). If requested, the results of HBM should be made available and explained to the individual study participant.

53.6 Discussion

Analytical capability, either sensitivity or specificity, augments the potential use of the analysis of body tissues in human health risk assessment. A positive finding of a xenobiotic substance in a body fluid does not represent a risk to health by itself. A positive biomarker finding should be put in perspective by use of contextual information, including both person characteristics and exposure information. This can be done by applying HBM in carefully designed population-based studies where data can become much more valuable if sample collection is repeated in time (Chadeau-Hyam et al. 2013). Temporal patterns of biomarkers can be studied and interpreted by use of mathematical models. In the near future, it is expected that bio-banks will provide valuable resources for the use of HBM approaches in population-based studies. HBM will contribute to studies aimed at describing the totality of environmental exposures from conception onward (Scheepers et al. 2013). These so-called exposome studies are trying to complement the interest in genome characterization by study of the individual's internal and external exposome in connection to temporal shifts in environmental exposures, so-called critical life stages, such as conception, adolescence, pregnancy, and major changes in working environment, such as a new job or in living environment such as migration (Vineis et al. 2013). Biomarkers will help us to understand the role of molecular mechanisms in associations between environmental factors and observed responses in human populations (Chadeau-Hyam et al. 2011). These changes result in physiological responses that lead to higher or lower risk in short- and long-term health effects that are of interest to public health policy.

Conclusions

The impact of environmental exposures is strongly dependent on the amount of a xenobiotic substance reaching a critical level in one or more internal organs. Analysis of biomarkers in body tissues demonstrates an internal exposure even in persons that do not have the clinical signs of intoxication. Such exposure may originate from different sources and reach the target tissue via different routes of uptake and biotransformation pathways. Biomarkers of susceptibility and effect can demonstrate an early response of human physiology to an exposure that may initially not be detected or evaluated as a health risk. Genes interact with the environment and explain differences in individual responses within a population, even if exposures across the population are quite similar. HBM deserves a prominent position within the field of contemporary public health research.

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Chapter 54
Chemicals Disaster Management and Public Health

Paul T.J. Scheepers

Abstract The release of chemicals may be the result of a natural or a man-made disaster. Hazardous materials involved in public health incidents most frequently contain irritants, and respiratory irritation is the most common health effect. Usually the release of hazardous materials is detected in an early stage and emergency response is organized around an incident location. In a silent release, victims may refer to healthcare facilities without an apparent event. The involvement and coordination of poison centers is often required to identify a common cause. To some extent all chemical disasters have a sociogenic component, which may in part be triggered by social media and require some specific communication strategies to mitigate the consequences. Available information from the event and from the involved victims determines an effective emergency response and the resulting impact. Fires and explosions cause most chemical intoxications. Support from environmental measurements and modeling can provide valuable information that can be used for interventions on the scene such as an evacuation. When health effects occur, this information can support on-site triage, support, and decontamination, followed by transportation of victims to a healthcare facility. Environmental monitoring and modeling can be complemented by results of analysis of body tissues and assessment of symptoms of intoxication made upon arrival in the hospital's emergency department. Information that the victim can provide or that is accompanying the victim can directly be used for medical care and treatment. If patients are presented without contextual information, treatment could be inappropriate or delayed. Often symptoms are difficult to interpret and only basic supportive care is provided. Analysis of biological tissues may support early decision making concerning targeted medical response in addition to supportive treatment. Exposure indicators from the incident scene should be combined with results of the physical exam, including biomarker levels that confirm the identity of the chemical hazard. All of these activities should be in the direct interest of a rapid assessment of the patient's situation, targeted treatment and risk communication.

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_54

Keywords Hazardous materials • Natural disasters • Technological disasters • Silent release • Risk communication • CBRN-incident • Decontamination • Emergency response

54.1 Introduction

The historical perspective of chemical disasters is strongly influenced by two chemical disasters: the release of dioxins and dibenzofurans in Seveso, Italy in 1976 and the toxic cloud of methylisocyanate from a pesticide plant in Bhopal, India in 1984, which have had a profound impact on the thinking about public health implications of technological disasters (Bader 1987; Baxter 1990). In Table 54.1, a profile description of these incidents is given. Both incidents generated much international attention for man-made chemical disasters with a public health impact.

This contribution will be limited to those disasters that involve chemicals. This field is often referred to as hazardous materials (hazmat) incidents as a subcategory within technological disasters. In addition, the possible consequences of the deliberate use of chemicals to inflict harm on the health of the public are receiving increased attention. This field is commonly referred to as chemical biological and radionuclear (CBRN) incidents. Such events can have many different consequences, but this chapter will be restricted to the public health implications of exposures resulting from accidental or intentional release of hazardous materials.

54.2 Classification of Incidents and Disasters

There are different parameters for classifying disasters, such as the geographical scale or the number of casualties (Baxter 1990). A useful system of classification is based on the type of response that is required to mitigate adverse consequences for human health and the environment. In this chapter, a simple classification will be used: natural disasters and technological disasters. These two main categories will be subdivided to include the most common disaster scenarios. An indication of the relative contribution of different types of events will be based on an analysis of 39,766 events registered in 1996–2001 in 13 states in the US as part of the Hazardous Substances Emergency Events Surveillance (HSEES) (Ruckart et al. 2004).

54.2.1 Natural Disasters

Natural disasters such as earthquakes, tsunamis, volcanic eruptions, hurricanes, tornados, and forest fires may cause breaches in industrial infrastructure, including transformers, vessels, pipelines, and storage tanks. The contribution of natural

Table 54.1 Characteristics of two prominent technological disasters

	Seveso	Bhopal
		
Date	July, 1976	December, 1984
Location	Seveso, Italy	Bhopal, India
Type of industry	Icmesa chemical company production plant of trichlorophenol (pesticide)	Union Carbid production plant of pesticides
Type of incident	Uncontrolled exothermic reaction in an overheated reactor resulting in emission of toxic cloud	Toxic cloud released following uncontrolled process emission
Emission	2,900 kg containing 2,3,7,8-tetrachlorodibenzo-para-dioxin (TCDD)	30 metric tons of methylisocyanate
Number killed in early phase	None	6,000–20,000
Type of injury in fatal cases	n/a	n/a Suffocation
Number injured	193 (acné) of which 88 % children	>15,000
Type of acute injuries	187 (acné)	Respiratory and eye irritation
Type of chronic injuries (f = female; m = male)	Lymphohematopoietic, rectum (m) biliary tract (f), lung cancer (m), shifted sex ratio, diabetes (f) and cardiovascular effects	558,125 injuries including 38,478 temporary partial injuries and 3,900 severely and permanently disabled, including blindness in many cases
Affected area (surface in ha and contamination in μg/m^2)	A-zone: 87 (15.5–580.4)	4,000
	B-zone: 270 (<50)	
	R-zone: 1,430 (<5)	
Number of inhabitants exposed	A-zone: 570	100,000–200,000
	B-zone: 5,000	
	R-zone: 30,000	
Effect zone (km)	6	8

Sources: Pesatori et al. (2003), Bader (1987)

causes to overall hazmat events may be small (estimated to be 3 % over a period of 1990–2008 in the US), but the large releases were most frequently caused by natural disasters. There are indications of an increase due to a recent rise in hurricane-related hazmat releases (Sengul et al. 2012). One of the largest natural disaster in terms of numbers of fatalities involved the killing of about 1,700 people in Cameroon in 1986 (Baxter et al. 1989; Wagner et al. 1988). This disaster involved the sudden and silent release of carbon dioxide from a volcanic source that was trapped in the water of the Nyos Lake. In vulnerable geographical areas, anticipated natural disasters are already included in the design of technical infrastructures, but, e.g., storage tanks are often not sufficiently resistant to hurricane damage (Sengul et al. 2012). Even if authorities are well prepared, natural disasters may still lead to releases causing a secondary chemical disaster such as fires secondary to an earthquake or environmental exposures secondary to a hurricane (Balluz et al. 2001). Even if such an event is predicted, the consequences of such incidents may not be mitigated by shutting down critical production facilities such as nuclear power plants. The recent Fukushima nuclear power plant disaster showed that such measures are not taken or may not be effective (Steinhauser et al. 2013).

54.2.2 Technological Disasters

54.2.2.1 Fixed Facility Event

Of all the events registered in HSEES, 76 % were classified as fixed-facility events (Ruchart et al. 2004). In 8 % of the reported events in the US, at least one victim was reported (mean of 4 with a range from 1 to 259 victims). Ammonia was involved in most events, but chlorine resulted most frequently in personal injury (12.6 and 28 %, respectively). Incidents involving acid were mostly of agricultural origin and involved victims in 14.8 % of the events. Pesticides were involved in only 2 % of the cases.

54.2.2.2 Transportation Event

Approximately 24 % of all HSEES events was related to transportation. For 8 % of the transportation events, at least one victim was reported, ranging up to a maximum of 65 victims per event (Ruckart et al. 2004). Transportation events mostly involved inorganic substances and often multiple substances. As in fixed-facility events, victims were most frequently involved in transportation incidents with release of ammonia (17.5 %) and chlorine (33.3 %). When hazardous materials are transported by rail, road, or waterway, a release may be triggered by a collision, which may rupture the containment such as a chemical tank, even if it is designed to resist heavy external strain. If a fire is involved, this may also cause the breach of the containment at a later moment in time if fire fighters are not capable of effective mitigation (see below). Such incidents may happen at a location that is not well prepared and may initially involve first responders who have received only basic training in responding to traffic accidents. Such an incident can have large secondary effects, in part determined by the type of interventions (see Box 54.1). Hsu and co-workers (2002) reported eight rail incidents requiring evacuation in 2000 and 2001 in the US, involving a wide range of hazardous chemicals, including acrylamide, ethylhexyl phthalate, glacial acetic acid, hydrochloric acid, hydrofluoric acid, propylene glycol, sodium hydroxide, tripropylene, and xylenes.

Box 54.1: Environmental: Release of Acrylonitrile from a Train in Wetteren, Belgium

On Saturday morning May 4th, 2013 at 2:00 GMT + a train derailed between Brussels and Gent near the town of Wetteren (24,000 inhabitants) and caused a chaotic scene. The train was driving at a speed of 87 km/h where 40 km/h was indicated as the maximum speed. The train was carrying chemical cargo from Barendrecht in The Netherlands to the seaport of Gent. The cargo load included 300 t of acrylonitrile. Six tanker wagons derailed. Three of them exploded and were set on fire. Two of the remaining tanks contained acrylonitrile and a third tank contained 1,3-butadiene but this tank remained intact. Known conversion products from fires involving acrylonitrile are oxides of nitrogen (NO_X), acetylene and hydrogen cyanide. Much water was used to put out the fire and also to scrub the toxic gases and vapors from the smoke (Fig. 54.1). Forty seven inhabitants living in 17 residences within a perimeter of 250 from the incident location were evacuated. The fire brigade used water to keep down the toxic smoke. A 64-year-old male living on the other side (North-West side) of the village died unexpectedly with no obvious cause. In his house which is situated on the bank of the river Schelde also his dog was found killed.

Fig. 54.1 The fire brigade attempted to keep down the toxic smoke (Photo: Gazette van Antwerpen)

(continued)

Box 54.1 (continued)

Fig. 54.2 Pattern of elevated CEV-Hb adducts levels measured in blood of inhabitants of Wetteren. The *blue line* indicates the main sewer system between the incident location and the river Schelde. Used cut-off values of 200 /g (smokers) and 10 pmol/g (non-smokers) (Source: WIV-ISP, Brussels)

From the inhabitants of Wetteren blood was collected for analysis of 2-cyano-ethylvaline (CEV) hemoglobin adducts (Fig. 54.2). These findings and the prevailing south-west wind suggest that the inhabitants were not exposed by inhalation from a toxic cloud. It is more likely that the inhalation exposure primarily occurred by emissions from the sewage system into the residences along the route of the main sewage from the incident location to the river Schelde. Acrylonitrile was presumably transported by the water that was used by the fire brigade to fight the fire rinsing off into the surface water and subsequently into the sewage.

54.2.2.3 Fires and Explosions

The heat of a fire and the force of an explosion can unexpectedly lead to exposures that by themselves can cause fatalities due, e.g., to heat or the force of a shock wave. With a frequency of 3 % of all events, a fire and/or explosions is not a very common event but it involves personal injury and fatality in approximately 40–60 % of cases (see Table 54.2). In addition to personal casualties, such force may also cause secondary damage to facilities in the vicinity. Fires and explosions change the chemistry of materials and may cause the formation a toxic cloud, such as in the

Table 54.2 Classification of chemical events according to type of release and substance (Ruckart et al. 2004)

Category	Type of incident	Fixed-facility		Transportation	
		Number	%[a]	Number	%[a]
Release type	Spill	11,165	6.2	8,020	6.5
	Emission into the air	17,280	7.1	945	18.3
	Fire	878	22.8	134	35.8
	Explosion	244	53.7	11	45.5
	Fire and explosion	98	57.1	5	40.0
Substance	Acid	1,832	14.8	–	
	Ammonia	2,150	12.6	280	17.5
	Chlorine	597	28.0	18	33.3
	Pesticide	810	14.8	–	–
	Other inorganic[b]	–	–	968	10.7
	Multiple substance	1,142	24.0	352	36.4
Factors	Beyond human control	1,076	2.2	–	–
	Equipment failure	15,193	4.5	–	–
	Human error	5,900	14.3	–	–
	Illegal dumping/deliberate damage	1,152	26.7	–	–
	Improper mixing or filling	771	22.6	–	–
	System problem	1,838	0.9	–	–
	Other	2,393	3.8	–	–

[a]Percentage of incidents involving one or more victims
[b]Paints, dyes, pesticides, polychlorinated biphenyls, volatile organic compounds and mixtures (excluding acid, base, ammonia, chlorine)

Bhopal disaster (see Table 54.1). Due to the increased use of synthetic materials in buildings, cars, and airplanes, emissions from explosions and fires may contain very toxic thermal decomposition products. Therefore, in addition to physical stressors, the toxicity of fire smoke contributes to explaining fatalities in fires, involving, e.g., carbon monoxide and cyanide as important toxicants (Alarie et al. 1983, 2002). Acute exposure to high levels of fire smoke has been implicated in the cause of chronic disease in residents and also first responders (Greven et al. 2009).

54.2.2.4 CBRN Incidents

A special type of incident is the deliberate silent or detected release of chemical, biological, and/or radionuclear agents in so-called CBRN incidents. In addition to assaults targeted at persons, such incidents may be targeted at crowded public places and thus will potentially have a large impact on public health. One of the best documented incidents is the sarin attacks in the metro of Tokyo, Japan (see Table 54.3). A CBRN incident may initially not be identified as a deliberate act. These assaults may be staged to look like a traffic incident or fire. Emergency responders may approach and encounter biological and chemical agents that were

Table 54.3 Deliberate use of hazardous materials in chemical incidents in Japan

Date	Location	Agent	Setting	Number killed	Number injured	Reference
27 June 1994	Matsumoto	Sarin	From truck in crowded residential area	7	586	Okudera (2002)
20 March 1995	Tokyo	Sarin	Five trains of subway system	12	>5,500	Okumura et al. (1998)
25 July 1998	Wakayama	Inorganic arsenic	Mixed in curry and rice meal served at summer festival	4	58	Kishi et al. (2001)
10 August 1998	Niitaga	Sodium azide	Added to contents of a teapot	9	–	Okumura et al. (2003)
31 August 1998	Nagano	Cyanide	Via pinhole in base of a teapot	1	–	Okumura et al. (2003)

designed and produced to disable persons (Box 54.2). It is much more likely that chemicals that are readily available for purchase on the market will be used. Most nations have persons especially trained to respond to these types of incidents in terms of mitigating the consequences for public health, both physically, mentally and in terms of communication (Okumura et al. 2003).

Box 54.2: CBRN-Incident: Moscow Theatre Hostage Crisis

On October 23rd, 2002 a performance of the Musical 'Nord-Ost' in the Melnivok Street Theatre in Moscow was brutally disturbed. Chechen terrorists took a group of 850 persons hostage. The terrorists demanded immediate and unconditional withdrawal of the Russian troops from Chechen territory. Early in the morning of October 26th the Russian Federal Security Service (FSB) dispersed a chemical substance into the building interior, followed by a storm of a special forces unit of the FSB. On November 12 and 13 two surviving English hostages were interviewed separately by the British police (Riches et al. 2012). They declared to have seen a white aerosol dispersed silently from a hole in the wall. Terrorists and many hostages were killed during and following the chemical release. Most terrorists were shot after falling unconscious due to the gas exposure. Members of the special forces unit rescued most unconscious hostages by taking them out of the theatre (Fig. 54.3).

Some of the hostages were killed by the terrorists but 125 were killed presumably involving the chemical exposure and due to delayed and inadequate medical response. It has been suggested that some of the hostages had

(continued)

Box 54.2 (continued)

Fig. 54.3 Members of the special forces unit carry casualties out of the theatre (Photo: EPA)

Fig. 54.4 Victim of the assault taken to hospital by public transportation (Photo: Justin Sutcliffe)

(continued)

Box 54.2 (continued)

airway obstruction aspirating vomit because of the way victims had been removed from the theatre lying on their back and later also transportation in buses normally used in public transportation (Fig. 54.4).

The care for the hostages was complicated by the position of the Russian authorities not to disclose the identity of the used chemical agent. Help from foreign embassies was offered to aid treatment of the hostages but there was no response to official requests on information on the used chemical agent. Three British hostages who survived have declared that the aerosol that was dispersed in the theatre was odorless (Riches et al. 2012). Another casualty reported the smell as 'indescribable' but people were not coughing or spluttering, even on the balcony from where the aerosol had been dispersed. From spotting the aerosol to being overcome by it took 10 to more than 30 s and none of the hostages had seen the assault team enter the theatre. Some of them regained consciousness in the hospital, were vomiting, had inhibited tendon, pinpoint pupils, bradycardia and hypotension, respiratory depression and cyanosis. Other victims regained consciousness during transportation from the theater to the hospital but dozed off. The British hostages declared that they were surprised to feel no pain when they regained consciousness. Sources in the hospitals have confirmed that hostages had been treated by oxygen administration, mechanical ventilation and injections of noxalone. Booij (2002) speculated that a fentanyl type of opioid anaesthetic had been used during the assault. It is 80–100 times more potent than morphine and these drugs are not approved for use in humans. Some fentanyl derivates are used to sedate animals such as in zoos. An important indication for involvement of a opioid is that naloxone was used in treatment and resulted in recovery of some of the hostages. Naloxone is a standard antidote in treatment of opioid overdose. Riches and co-workers (2012) reported on the analysis of clothing, blood and urine of the three British hostages. Those casualties were near an exit door which appears to have been a factor in their survival and they were among the first casualties evacuated from the theatre. From two casualties a leather jacket, jumper and shirt were available for analysis. Two blood samples were obtained from two of the casualties taken at 12 and 19 h after the chemical aerosol had been released into the theatre. No fentanyl was detected in the blood samples. From the leather jacket and jumper no chemical drugs were detected. However, extracts from the shirt were found positive for carfentanil and remifentanin in an LC-MS/MS analysis. The total amount of carfentanil and remifentanil recovered from clothing was estimated to be <5 ng with carfentanil being the primary drug. In urine norcarfentanil was detected, which is a metabolite of carfentanil. The identification of norcarfentanil is only tentative because only a single transition was monitored in mass spectrometry analysis. No traces of urinary remifentanil were recovered.

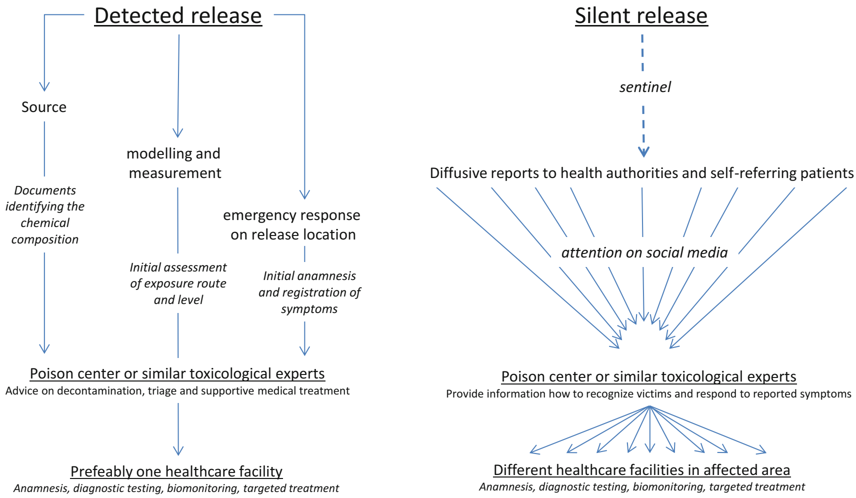

Fig. 54.5 Schematic of information flow in a detected and silent release involving hazardous materials. *Dashed lines* indicate no or limited availability of interpretable information

54.2.3 Silent Release

A silent release may present itself as a diffuse response to an earlier undetected event, e.g., an increase in patients reporting to emergency rooms of different hospitals with similar health complaints, or different reports of dead fish floating on the water surface. The problem is that individuals who pick up the early sign of the event may report such early signals to different healthcare centers/health authorities (Fig. 54.5). In a registration of 35 incidents of international importance, in 12 cases an illness of unknown origin was reported (Olowokure et al. 2005). Below, two common scenarios are described: a food-borne and an environment-borne silent release (see Table 54.4 for an overview).

54.2.3.1 Silent Release from Food and Other Consumer Products

In 9 out of 35 chemical incidents registered in international databases occurring between August 2002 and December 2003, food or other consumer products were suspected or known to be the source of an intoxication (Olowokure et al. 2005). A problem with the quality of a consumer product or medical drug may present itself over an extended period of time in a potentially large geographical area where the product is distributed via local retailers. Because of the wide distribution of consumer products, the number of victims can be very large (Macri and Mantovani 1987). As the cause often remains undetected, the number of cases with health consequences can grow rapidly. If the symptoms are not severe or nonspecific,

Table 54.4 Silent releases involving toxic substances

Cat.	Consumer product	Country	Year	Cause	Deaths	Numbers injured[a]	Type of injury	Reference
Food and consumer products	Ginger Jake (Jamaican ginger)	US	1920s and -1930s	Tri-ortho-cresyl phosphate added to cheap alcoholic beverage	Unknown	50,000	Axonal dying-back neuropathy affecting mainly large muscle groups causing impaired gate known as Jake Leg or Jake Walk	Woolf (1995), Morgan and Tulloss (1976)
	Rapeseed oil, Spain	Spain	1981	Traces of aniline, oleyanilide and other fatty acid anilides in limited no. of samples	>500	20,000	Admitted to hospital with fever, lung and skin complaints, later developing toxic pneumonia	Valenciano, et al. (1983), Altenkirch et al. (1988)
	Acetaminophen syrup	Haiti	1995–1996	Diethylene glycol-contaminated glycerol	85	86	acute anuric renal failure	CDC (1996)
	Contaminated wheat used for bread	Iraq	1971–1972	Alkyl mercury, fungicide	500	6,000	paresthesia, ataxia, dysarthria, diminution of vision and loss of hearing, coma, and death	Bakir et al. (1973)
	Milk powder	China	2008	Melamine	Unknown	51,900	Renal tube blockages and possible kidney stones	Qiu et al. (2010)
	Pesticide-contaminated cooking oil	India	2013	OP-Insecticide	22	Hundreds	Cholinergic symptoms	http://www.bbc.co.uk/news/world-asia-india-23342003
	Water proofing	Switzerland	2002–2003	Fine aerosol	Unknown	102	Chemical pneumonia	Vernez et al. (2006)

Environment	Fish contaminated by an industrial emission Minamata Bay	Japan	1956	Organic mercury	1,784[b]	2,265[b]	Neurotoxic syndrome known as 'Minamata disease'	Ekino et al. 2007
	Tunnel construction Hallandsås, Bjare	Sweden	1997	Acrylamide in grouting agent	Unknown	23	Cows and fish died and neurotoxic symptoms were found in workers	Kjuus et al. (2004), Hagmar et al. (2001)
	Transport	Spain	1985–1986	Soybean dust from unloading of ships in harbor	Unknown	Hundreds	Exacerbations of asthma on 10+ days over a period of several years	Antó et al. (1989), Pont et al. (1997)
	Small-scale gold mining	Nigeria	2010	Natural occurring lead (and other metals)	400	Hundreds	Neurotoxicity	Bartrem et al. (2013)

[a]Based on number of hospital admissions
[b]Source: http://www.env.go.jp/en/chemi/hs/minamata2002/ch2.html

it may take considerable time before a common cause is found and often the real cause remains unknown (Altenkirch et al. 1988; Vernez et al. 2006; Olowokure et al. 2005).

54.2.3.2 Environment-Born Silent Release

Minamata is probably one of the best known large-scale environmental incidents that occurred in the 1950s. Japanese authorities assume that 1,784 were killed and 2,265 suffered from a neurotoxic syndrome that was named the 'Minamata Disease' in 1956. The incident started with the release of elemental mercury from industrial activities in the Minamata Bay area. Elemental mercury was metabolized to organic mercury and bioaccumulated in fish that were also found floating in the bay. Many inhabitants in that region were exposed because fish is an important part of the diet of the local population. According to a recent study, a substantial number of inhabitants still suffers from the adverse health effects of this environmental disaster (Ekino et al. 2007). In Sweden, neurotoxic symptoms of an environmental acrylamide spill were first observed in cows in the Hallandås railway tunnel construction project. This was an early sentinel warning that health effects would later also appear in the tunnel construction workers (Hagmar et al. 2001; Kjuus et al. 2004).

54.3 Collection of Contextual Information

In contrast to the silent releases discussed above, most releases are detected at an early stage. Concerning the availability of interpretable information, a detected release follows a different pattern in terms of response as compared to a silent release. In such releases, the embedding and role of a centralized authority, such as a coordinating (poison) center, are different (Fig. 54.5).

54.3.1 Environmental Monitoring Networks

In locations where hazardous materials are stored, chemical sensors can be used to detect possible leakage of chemicals. Such networks of fixed air monitoring equipment lead to early detection and response to a problem, even before the hazardous materials cross the boundary of an industrial zone to a downwind residential area. In the case of a toxic cloud, immediate action is required since at a moderate wind speed a toxic cloud can cover a distance of 1 km to a residential area in a less than 5 min.

54.3.2 Ambulant Air Monitoring Systems

If air monitoring systems are not in place, such systems can be taken to the incident location, e.g., by fire fighters, to assess the potential risk to emergency responders at the incident location. Often such measurement systems do not provide useful data to assess the health risk for the general population in a much wider downwind area (Hsu et al. 2002). To assess the risk to the general population, hazmat teams need to collect data in the field using more sophisticated equipment for real-time and off-line analysis of the gas phase (gas chromatography mass spectrometry-based) or to detect hazardous materials on surfaces (XRF- and infrared-based instruments). These more sophisticated measurements can support an initial appraisal with confirmation of the type of chemicals involved but do not provide a very accurate quantification of air levels. Such measurements can be used to refine model predictions and support a targeted sampling strategy in a later phase during or after the incident. In the case of hazmat teams that carry more sophisticated instruments, it usually takes several hours before they arrive and another couple of hours before the first results can be reported and they may often arrive too late to be used in the acute phase of the incident (Baxter 1990). Therefore, some decisions have to be taken without proper confirmation, such as a first warning to the public, including pro-active interventions such as evacuation or shelter-in-place (Hsu et al. 2002). At a later stage, measurements are valuable to confirm the identity of hazardous materials with a high health risk profile. For some hazardous materials, such as asbestos or dioxin deposition, samples have to be collected for analysis in a specialized laboratory. This information can be used to inform the public, and in interventions involving agricultural activities. Previous disasters have indicated that unidentified chemical hazards reduce the prognosis of the victims of chemical intoxications (Riches et al. 2012; Okumura et al. 1998a, b). Confirmation of the identity of the specific chemical substances involved in an incident can support adequate decontamination, triage, treatment of victims on location, and safe transportation to a healthcare facility, and facilitates an adequate response upon arrival at the healthcare facility (see Sect. 54.4).

54.3.3 Modeling

Computer modeling of the dispersion of hazardous substances can complement measurements. The use of models is well-established for a toxic cloud release. During an incident, it can be used for initial appraisal of the geographical dispersion when the data of ambulant air monitoring teams are not yet available and decisions should be taken concerning evacuation or shelter-in-place (Scheepers et al. 2007). Modeling can support tactics as to when and where to perform ambient air monitoring. Modeling can also be useful to predict an alternative dispersion scenario if a change in weather conditions is anticipated. Models have been used to reconstruct the dispersion of chemical clouds to understand the health impact of incidents in retrospect, such as in the case of the Bhopal release of methyl isocyanate (Havens et al. 2012). Models do have some limitations in terms of predicting concentrations at street level in urban settings (Wang et al. 2013). This may in part be related to difficulties in predicting certain non-homogenous dispersions of high density vapors (Venetsanos et al. 2003).

54.3.4 Human Biological Monitoring

The analysis of body tissues for exogenous substances is widely used in the field of occupational and environmental health. The most common term for this is human biological monitoring (HBM) which is defined as is the standardized and repeated systematic collection, pretreatment, storage, and analysis of body tissues in order to assess the internal dose of a xenobiotic substance by analysis of the parent substance and/or a product of biotransformation (Scheepers et al. 2011). The determination of chemicals in body tissues may provide physical evidence of the exposure of an individual in a chemical incident or disaster. It provides information on the internal dose, that, if elevated, may be linked to a response to an earlier exposure. For some toxic substances, the clinical signs are difficult to interpret (carbon monoxide, cyanide and non-essential toxic metals) and analysis of biological materials is used to support a decision for medical intervention such as use of hyperbaric oxygen (carbon monoxide), specific antidote (cyanide), or chelation therapy (non-essential toxic metals).

Depending on the choice of the biomarker and body tissue, it is possible to evaluate the exposure status of an individual following the incident at a time point when concentrations in the environment at the incident location have fallen below levels that can be detected using environmental monitoring (Baxter 1990; Hsu et al. 2002).

One of the first attempts to apply HBM following a chemical incident was related to firefighters who responded to the WTC fire and collapse on 11 September 2001 (Edelman et al. 2003). In this incident, a shot gun strategy was used, involving the quantification of 110 chemicals in a cross sectional study among 321 exposed and 47 controls. As this study involved only one time point of sample collection for all biomarkers at 3 weeks following the disaster, the HBM results were difficult to interpret due to the different excretion half-lives of the selected biomarkers. It resulted in the possible contribution of previous exposures in biomarkers with a long half-life and the possible false negative results in biomarkers with a short half-life. In this study, the controls were selected from fire fighters assigned to office duties because of orthopedic injury and who did not have a recent history of firefighting-related exposures. The conclusion of this study was that the study did not provide any information concerning exposure or potential health effects (Edelman et al. 2003).

The time window between the onset of a chemical incident and the moment of sample collection may range from a few days to a period of several months, depending on the kinetic pattern of elimination and the sensitivity of the analysis. Simple algorithms can be used to calculate this time window, still resulting in a reliable outcome in terms of a biomarker level elevated above the limit of quantification and (if applicable) above the background level in a population (Scheepers et al. 2011). In addition, for each study participant the burden of sample collection should balance the benefit of the potential outcome of HBM and should be well motivated. An obvious motivation is the personal benefit to an individual if the HBM outcome has a role in the medical intervention leading to early recovery with reduced or no long-term health effects. A second motivation is the potential role of HBM in risk assessment and risk communication. Even if the individual does not have any clinical signs, there may be health consequences attributable to the incident. HBM may provide the supportive information to classify an individual or group as exposed or non-exposed. In addition, if followed up in time, a biomarker level will confirm the elimination of the noxious substances from the body, or perhaps show that there are still unexpected and or undetected (secondary) sources of exposure (Scheepers et al. 2014). HBM may involve individuals from the general public and also first responders. In the latter group, an additional purpose may be to verify the efficacy of personal protective equipment. In large-scale disasters, there may be questions about the feasibility and added value of HBM, and therefore, it would be useful to have a pre-developed matrix for decision-making on the use of HBM in a particular incident setting (Scheepers et al. 2011; Kitt et al. 2011).

54.4 Emergency Response

An analysis of 457 chemical incidents in 1993–1997 in the US revealed that 61 % of these events involved an evacuation (Burgess et al. 2001). In only 3 % of the incidents, the population at risk was advised to take shelter. Incidents involving three or more victims were much more likely to involve evacuation and shelter-in-place. Of the 2,654 victims, 70 % were transported but only 5 % were admitted to a healthcare facility for observation or treatment. Patient and event-related factors were involved in a decision to arrange the transportation of a victim. An appropriate triage and treatment at the incident location may save lives but requires adequate information about hazardous materials most likely involved (Okumura et al. 1998a; Hsu et al. 2002; Riches et al. 2012).

Respiratory symptoms are the most common effects due to the frequent release of irritants (see Fig. 54.6). Victims were less likely to be transported if triage could be established near to the incident location, such as in the case of inhalation exposure to irritants with a high water solubility (Burgess et al. 2001). Persons with trauma, gastrointestinal complaints, headache, dizziness, or other complaints of the central nervous system were more likely to be transported (than victims with local effects such as skin and eye injury), as well as victims presenting three or more health complaints simultaneously.

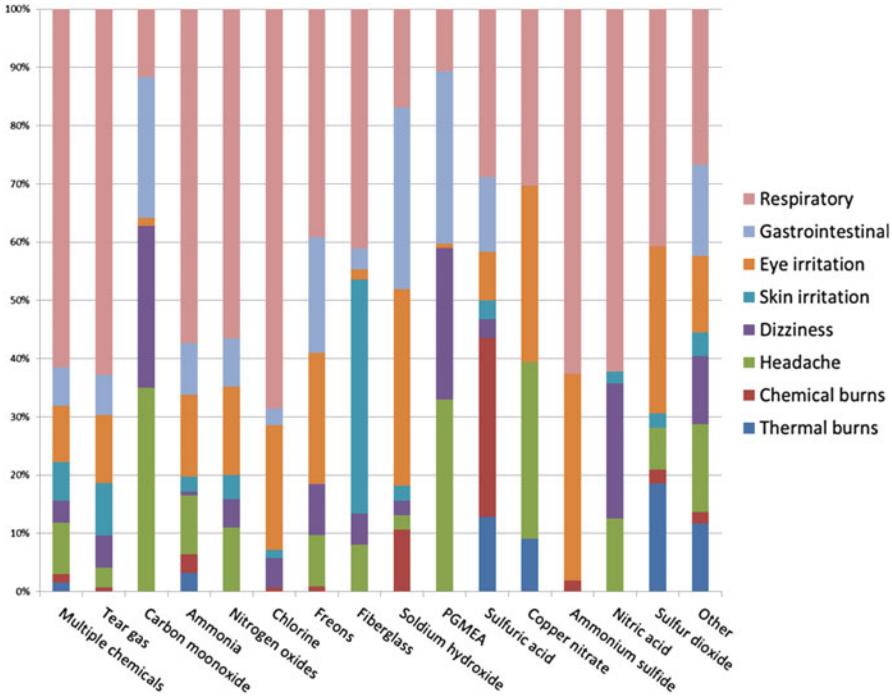

Fig. 54.6 Relative contribution of symptoms based on 2,617 chemical incidents with 25 or more victims (Burgess et al. 2001)

An incident has great impact on the available healthcare facilities (Runkle et al. 2012). The population is at risk for a variety of chemical substances. These incidents also include terrorism (Okumura et al. 2003). Technically, hazardous materials and chemicals used in deliberate acts, such as CBRN incidents, are one continuum (Okumura et al. 2003; Baker 2004) and the medical staff at emergency departments needs training to respond to all chemical exposure events (Baxter 1990; Okumura et al. 2003).

A specific problem is related to the need to decontaminate the victims who have been in direct contact with hazardous materials. Normally, the transmission of toxic substances from victim to medical personnel does not represent a health threat but even mild symptoms may lead to reduced functioning of medical staff (Burgess et al. 1999) and in some cases an emergency room had to be evacuated or medical personnel suffered severe symptoms (Thanabalasingham et al. 1991; Wing et al. 1991; Nozaki et al. 1995). This may be related to patients who transport themselves to the hospital, i.e., without pre-hospital decontamination (Freyberg et al. 2008). For those self-presenting or self-referring patients, it is important to make a sound judgment of the required decontamination as the patient may require stabilization without delay. This may include consultation with a toxicologist from a poison center (Baxter 1990). If possible, contaminated clothes can be removed. This will reduce the exposure of the medical staff substantially. Even if a very toxic industrial chemical is involved, removal of the clothes will already take away most of the risk of secondary exposure and the residual contamination on the skin of a victim will not likely present a risk to hospital personnel (Burgess et al. 1997). If pre-hospital or in-hospital decontamination is adequately organized, basic life support can be provided with minimum protection of medical staff.

Silent releases represent the most difficult scenarios related to diffuse cases of intoxication, e.g., those caused by use of contaminated consumer products or environmental exposures. Often, the early symptoms of chemical intoxication are misinterpreted as food poisoning or infection (Hartman 1998; Aniol 1992) and initial treatment is only supportive, potentially leading to complications and sometimes fatalities, such as described in cases of poisoning involving arsenic (Okumura et al. 2003), elemental mercury (Jung and Aaronson 1980; Moutinho et al. 1981), lead (Bartrem et al. 2013), and carbon monoxide (Raub et al. 2000). Victims may refer to different healthcare centers. It takes a while before signals are picked up that different cases of poisoning may be related to a common cause (Valenciano et al. 1983; Altenkirch et al. 1988). If information about the onset of an intoxication is shared among the healthcare facilities, this increases the probability of early identification of a common cause. The optimal situation is that labels of used products are provided to the medical staff and can be used in communications with a poison center. This center can manage the information and inform hospitals and general practitioners pro-actively to be alert for incoming patients with similar symptoms.

54.5 Risk Communication

Those persons close to the source of an unexpected chemical release, either an industrial emission or a fire, will be concerned about potential exposure to chemical components that might have health consequences, short-term or long-term. Whether an exposure is likely or not, the perception of being a victim warrants communication that does not withhold any information on the possible release of potentially hazardous substances. Usually, the classification of an individual or a group as exposed or non-exposed cannot be performed at an early stage. This means that communication will be to the general public, including those who (as may be shown later) have no reason to be worried.

All incidents will have some sort of social impact. In this text, these social factors are covered only to the extent that they may interfere with the response to a chemical incident or disaster. In some cases, they may even be the primary determinant of an incident or they may overwhelm other aspects of the incident and the response to it, also sometimes specifically in the aftermath. Silent releases may have a particular sociogenic component, which means that the response in the population may be (strongly) attenuated by social determinants such as gender, age and the social structure within groups. For emergency responders, sociogenic factors can complicate the interpretation of reported and observed symptoms. Individuals may report feeling 'unwell' and in a group an incoherent or diversity of different non-specific symptoms may be presented such as headache, light-headedness, nausea, and vomiting. On the other hand, victims may present very specific alarming symptoms, such as neurological symptoms, which should be followed up (Jones et al. 2000; Bartholomew and Wessely 2002). The first signals of a sociogenic component may be picked up in an early phase: symptoms may disappear quickly after the victims are removed from the incident location (e.g., by admittance to healthcare facilities). There are also factors that may cause the health complaints to persist or be aggravated such as (public) denial of a common cause (Jones 2000). These social elements may present themselves on a small scale, e.g., in a closed community, but there have been some recent examples of large-scale incidents that suggest that media attention may cause the number of involved individuals to rise rapidly and also the geographical area may grow (Nemery et al. 2002). This experience may have considerable implications for the type of response (see Table 54.5).

At the onset of this type of incident, there is usually a trigger that evokes some kind of response and sensitizes individuals, who may respond later (Boss 1997). As the trigger is usually a real and physical factor, even in the case that a sociogenic influence is suspected, the search for a possible cause should not be given up too easily.

Taking the health complaints seriously will help to identify a possible physical exposure that may have served as a trigger in a sociogenic event. Giving attention to victims of an incident with a sociogenic aspect will accelerate resolving the problems for the victims (see Table 54.5).

54.6 Discussion

Environmental indicators may have an important role in chemical disaster management. Their most useful role is related to supporting an assessment of the exposure of the public to potential hazardous materials (WHO 1997, 2009). The use of environmental indicators may be related to a diffuse exposure that presents itself as a silent release. In such a scenario, environmental indicators could provide the 'missing link' between an undetected event and the early signs of a public health problem. They may present themselves as sentinel environmental indicators (e.g., dead fish, cattle with symptoms) even before the occurrence of a response in the human population, e.g., health-complaints and/or clinical symptoms.

In other cases, the incident may start with a spill, toxic cloud release, fire, or explosion (or a combination of two or more). Information could be collected in the early phase of the event and be used to support the exposed population. This could and should start at the incident location by triage, decontamination, supportive treatment, and evacuation of the hot zone. There are two types of environmental indicators: the external indicator and the internal bio-indicator or biomarker. Table 54.6 provides an overview of examples for potential environmental indicators.

External indicators of chemicals are usually detected in air but may also be detected in water or soil. For public health-related disasters, it is very likely that

Table 54.5 Some factors that may improve or reduce effectiveness of emergency response to chemical incidents or disasters (Boss 1997; Jones 2000; Bartholomew and Wessely 2002)

Type	Type of available information	Effectiveness of emergency response	
		Improving factors – opportunities	Reducing factors – threats
Detected release[a]	Information on the origin of the hazardous material	Available product label or any other information about the identifying the substance, product or process emission and its composition	Contaminated victims that need admittance to a healthcare facility need appropriate decontaminated prior to transportation
	Information on the type of involved chemicals	Triage at the incident location may reduce demand for transport and emergency department capacity	Time delay caused by decontamination on incident location and/or healthcare facility may reduce survival
Silent release[b]	Scattered reports of individuals with health complaints in time and space	Media attention can help to identify characteristics that may lead to a common cause	Media attention may potentially cause the number of victims to increase due to sociogenic mechanisms (see below)
	Information on the geographical spread	Involvement of a centrally coordinated registry of health complaints (e.g. national poison center)	Lack of training of emergency department personnel to relate symptoms to a chemical hazard
	Development in time and dispersion in space	Central phone number and website to report new cases	Large number of self referring individuals potentially overwhelming response capacity
Sociogenic event[c]	Information on the social structure in a group of victims	Give attention to each of the victims individually but not at the (incident) location (see below)	Messages on social media may potentially increase the number of victims (see below)
	Hypothesis concerning a possible trigger or mechanism that could explain the development of the incident	Acknowledge that symptoms experienced by the victims are real and reassure each patient that recovery without any long-term health effects is to be expected.	Emergency response on the scene may potentially increase the number of victims
		Take victims away from the scene (take to different healthcare facilities or send home)	Sending victims home or to different healthcare facilities may prevent an a coordinated search of a common physical factor

[a]References: Burgess et al. (1999)
[b]References: Macri and Mantovani (1987)
[c]References: Nemery et al. (2002), Van Loock et al. (1999), Jones (2000)

Table 54.6 Examples of environmental indicators involved in chemical disaster management

Type	Indicators	Chemical	Type of event	Early detection
External indicators	Carbon monoxide	Incomplete combustion products	Malfunctioning heating system e.g. due to poor maintenance, malfunction of exhaust extraction system	Fire brigade and maintenance technician
	Formaldehyde, methyl bromide, et cetera	Fumigant	Transportation by sea containers	Customs at seaports
	Lead	Metals used in building materials such as paints	Neurotoxic symptoms in children	Environmental laboratory
	Volatile organic compounds	Industrial chemicals	Industrial emissions	Fire brigade, environmental or occupational hygiene service
	Asbestos	Mineral fibres	Demolishing, fire or reconstruction of buildings and industrial facilities and ships that contain asbestos	Fire brigade, environmental or occupational hygiene service
	TCDD	Dioxines and dibenzofuranes	Fire involving chlorinated plastics	Government laboratory
	PCB	Polychlorobiphenyl	Transformer fire or explosion	Government laboratory
Internal indicators	Blood mercury	Elemental mercury	Medicines, consumer products	Community healthcare centre and hospital
	Blood cholinesterase activity inhibition	OP- and carbamate pesticides, nerve agent	Agricultural, CBRN, residential	Community healthcare centre and hospital
	Blood CO-Hb	Carbon monoxide	Malfunctioning heating system e.g. due to poor maintenance, malfunction of exhaust extraction system	Community healthcare centre and hospital
	Blood Met-Hb	Nitrate, nitrite, organic nitro- or amines	Industrial, medicine	Community healthcare centre and hospital
	Urinary thiosulphate	Hydrogen sulfide	Work in confined space related to sewage, manure, water purification	Hospital

such indicators can be found in consumer products and food products. The occurrence of toxic substances can be related to an undetected technical problem in the chain of production, storage, and transportation of consumer products. Contaminations may also be the result of the intentional use of certain chemicals as medicine or for ritual purposes.

Internal indicators of chemicals can be detected using HBM. A decision to involve HBM should be well-informed, e.g., the identity of chemicals in environmental compartments or consumer products should be confirmed (Scheepers et al. 2011). Secondly, the type of toxic effect should be considered and also the toxicokinetic pattern of excretion in time, following the end of exposure. A biomarker should be available that can be detected and is sufficiently specific to the suspected exposure. In particular, when the parent chemical substance cannot be detected and a product of metabolism is considered as a biomarker, it is possible that the biomarker is not only a product of the substance of interest but may be produced from endogenous sources or may also be a metabolite of alternative chemical exposures that are common, e.g., as result of tobacco smoking or use of medical drugs.

Sensitivity is an important issue, especially if samples cannot be collected during the incident or at an early stage following the incident. Persistent biomarkers may still be collected weeks or months following the end of exposure but as their concentrations decrease over time it is possible that the levels detected will be in the same range as background noise of the population. Occupational exposures such as in firefighting and lifestyle factors such as smoking may mask a relationship with a specific incident.

Screening for a large number of parameters in a large scale incident may not turn out be very informative (Edelman et al. 2003). Instead, targeted approaches are much more likely to have added value for the medical treatment and also for risk communication (Scheepers et al. 2011). A good registration system for chemical disasters can provide the data to evaluate different strategies in follow-up health surveillance, including the use of environmental indicators (Olowokure et al. 2005).

Conclusions

There is no worldwide registration of chemical incidents and disasters with implications for public health. Attempts to collect data have shown that responding to such incidents requires information management. Environmental indicators are identified that could support an adequate response to mitigate health consequences for the general public and provide appropriate healthcare for those persons who suffer from direct contact with hazardous materials or may have other types of responses, e.g., related to the social impact of chemical incidents and disasters.

From the emergency response perspective, it is useful to make a distinction between a ‘detected release’ and a ‘silent release’ as these scenarios require a different type of information management (Fig. 54.5). A distinction between an accident and a deliberate event is less useful to guide initial emergency response from the healthcare perspective. Exposure assessment can be very useful for supporting well informed decision-making. Both environmental monitoring (directed at external indicators) and biological

(continued)

monitoring (directed at internal indicators) have a place in exposure characterization in support of determining optimal healthcare and risk communication. In both detected and silent release scenarios, it is useful to have well-trained duty officers to actively collect information from the field, guide modeling and measurement efforts, and interpret forthcoming data in the context of the rapidly changing incident and response scenario. Such use of information supports health authorities to take decisions for on-site response (e.g., shelter-in-place and evacuation and crisis management and communication) and decisions how to approach individual victims (triage, decontamination, anamnesis, transportation to healthcare centers, diagnostics, supported and targeted treatment of intoxications and risk communication).

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Chapter 55
On the Relationships Between Health Outcome and Urban Air Quality

David Broday

Abstract Environmental health indicators are used for assessing the impact on public health of exposure to environmental stressors. Air pollution is a complex phenomenon with considerable spatiotemporal and physicochemical variability and a high toll on the public health. In general, particulate ambient pollution is considered to be extremely hazardous, since different fractions (segments) of it were found to be associated with a variety of adverse health effects in humans. Specifically, numerous environmental epidemiology studies revealed associations between particulate pollutants and various cardiovascular disease (CVD) outcomes. Moreover, in the recent years some biological pathways that connect exposure to airborne pollutants and CVD outcomes were found, which provide the previously missing mechanistic link and specify toxicological routes that connect complex interactions among individual pollutants and attributed risk of CVD.

Keywords Air pollution • Particulate matter • Exposure • Cardiovascular outcomes

55.1 Introduction

Environmental health indicators (EHIs) are useful in a variety of research and decision-making settings to gauge the health consequences of exposure to ambient pollutants, summarize complex and interdisciplinary data that are characterized inherently by spatiotemporal and physicochemical variability, compare the impacts of policy across locations and times, and help convey reliable information to the public. In recent years, much effort has been made towards raising the public awareness to the deleterious effects of air pollutants across multiple scales (from local to global) and to encourage public participation in active data collection and interpretation (i.e., the citizen observatory concept). Moreover, today's social IT options provide an efficient and open platform for fast distribution of EHIs and

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_55

for effective empowerment of the general public and of community activists in demanding top-down abatement of air pollution (addressing regulators and administrators) as well as bottom-up behavioral changes to reduce exposure (addressing the people themselves).

In general, two types of EHIs are commonly used (Wills and Briggs 1995): health-related environmental indicators (i.e., exposure metrics) and environmental-related health indicators (i.e., outcome-based indicators). Environmental epidemiology focuses on exploring possible associations between these two types of metrics. For example, interest in the impact of air pollution on morbidity and mortality commenced in 1952 after the London fog incident, which showed a dramatic increase in all-cause mortality in parallel to a surge in air pollution. Since this event, a large number of studies revealed associations between different air pollutants and various health outcomes, from respiratory illnesses through cardiovascular diseases (CVD), metabolic syndrome, fetus and mother health, newborns and children growth and development, and up to different cancers. It should be appreciated that whereas the effect magnitude of ambient air pollutants on the individual's health is relatively small as compared to health effects of other stressors, such as smoking, malnutrition, infectious diseases, etc., for the whole population the attributable risk of air pollution is considerable and oftentimes much larger than that of, e.g., smoking and alcohol consumption (Martinelli et al. 2013; Bell et al. 2011).

Specifically, in its 2002 report the World Health Organization (WHO) estimated that about 800,000 premature deaths per year were caused by exposure to air pollution (WHO – World Health Organization 2002). The newer 2010 WHO Global Burden of Disease (GBD) report states that outdoor air pollution in the form of fine particles is a much more significant public health risk than previously thought, contributing annually to over 3.2 million premature deaths worldwide and to over 74 million years of healthy life lost (YLLs). Indeed, air pollution is now ranked among the top global health risk burdens as it has been linked to increased mortality and morbidity worldwide (Brunekreef and Holgate 2002; Pope and Dockery 2006). Whereas both gaseous and particulate matter (PM) air pollutants were found to be associated with adverse health effects in humans, PM appears as the more detrimental stressor and is therefore the most investigated airborne pollutant.

55.2 Air Pollution: Sources and Constituents

Air pollution consists of both gaseous and particulate pollutants, with many of them shown to have an effect on human health (either specific or non-specific). For example, cardiovascular morbidity was found to be associated with exposure to carbon monoxide (CO), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), ozone (O_3) and PM. Likewise, different adverse health effects have been associated with exposure to PM although the mechanisms by which particles influence human health are mostly still poorly understood and the question of causality is only seldom addressed.

55.3 Particulate Matter

Particulate matter (PM) is defined as material suspended in the air in the form of minute solid particles or liquid droplets. It is a mixture of many compounds that show both spatial and temporal variation, and is characterized by a myriad of thermophysical and biochemical attributes. Nonetheless, PM is classified primarily according to the size distribution of the particles that constitute it. Various PM fractions are commonly used as EHIs, since the toxic/pathogenic potential of PM was found to be critically related on its size. Total suspended particulate matter (TSP) refers to airborne particles smaller than ~30 μm, since larger particles remain airborne for only very short periods and are also mostly non-inhalable. Particles with diameter less than 10 μm are called PM_{10} and can easily penetrate the upper (thoracic) human airways, thus these particles are inhalable. This fraction is divided into three subgroups: the coarse fraction (PM with diameter between 2.5 and 10 μm, $PM_{2.5–10}$), the fine fraction (PM with diameter $\leq$2.5 μm, $PM_{2.5}$) and the ultrafine fraction (UFP, particles with diameter $\leq$0.1 μm). Specifically, the UFP fraction is a subgroup of $PM_{2.5}$ that accounts for most of the particles in terms of number concentration (rather than mass concentration). Fine particles ($PM_{2.5}$) are respirable, i.e., they can penetrate deep into the respiratory system. Generally, the different fractions have different sources and are therefore characterized by different composition and physicochemical properties. Apart from size, PM can also be classified in a few other ways, including PM of anthropogenic vs. biogenic origin, primary vs. secondary particles, products of combustion processes vs. those originated by mechanical wear, solid vs. liquid, soluble vs. insoluble, etc. The particle (size-specific) chemical constituents have been suggested as effective indicators of exposure and risk (Dominici et al. 2010; WHO 2003).

UFP result mainly from combustion of fossil fuels by traffic and industry. Due to fast atmospheric reactions in which they participate, their composition is often dominated by elemental and organic carbon and by oxides of metals. $PM_{2.5}$ result mostly from aging processes of the UFP fraction, in particular growth of nanoparticles formed by gas-to-particle conversion of primary gaseous emissions. Their composition is often dominated by sulfates and nitrates (Sarnat et al. 2006) and by the precursor UFP constituents. For instance, it has been proposed that industrial combustion processes are the main sources for $PM_{2.5}$ nickel, arsenic, chromium, sulfate, and vanadium; traffic is the main source for $PM_{2.5}$ bromine and organic and elemental carbon; soil and road dust are the main sources for $PM_{2.5}$ aluminum, silicon, and manganese; wood burning is the main source for $PM_{2.5}$ potassium; sea spray the main source for $PM_{2.5}$ sodium; and coal burning is the main sources for $PM_{2.5}$ selenium (Zanobetti et al. 2009; Laden et al. 2000). Moreover, due to condensation of semivolatile organic compounds (SVOCs), $PM_{2.5}$ tends to be also rich in polycyclic hydrocarbons (PAHs; PCBs, PCDDs, PBDEs, etc.)

The $PM_{2.5–10}$ fraction is generated primarily by mechanical shear and wear processes and is associated with resuspended surface/crustal matter and with fugitive releases by a variety of human (e.g., agriculture, construction, mining) and natural (e.g., erosion, forest fires, volcanism, sea spray) activities. Earth crust components, such as silicates, alumina, Ti, Fe, carbonates, chlorides, etc. represent a large fraction of these coarse particles (Brunekreef and Forsberg 2005), as well as bioaerosols such as pollen, mold spores, and plant and animal fragments. In terms of exposure, $PM_{2.5–10}$ deposits preferentially in the upper and larger airways whereas $PM_{2.5}$ can penetrate deep into the lungs and reach the smallest airways and alveoli. The UFP fraction tends to deposit efficiently along the airways and can cross the alveolar-capillary membrane relatively easily, spread through the systemic circulation and accumulate in various internal organs.

Studies that examined PM related health effects usually suggest that fine particles are the main culprit (Brook et al. 2010). This conclusion is supported by many epidemiological studies that suggested an association between exposure to $PM_{2.5}$ and various health outcomes, in particular cardiovascular mortality and morbidity. Recent studies suggested that $PM_{2.5}$ may also be related to an increased risk of cognitive impairment (Weuve et al. 2012). In contrast, the coarse fraction $PM_{2.5–10}$ received less attention. In most studies PM measurements of only one size fraction were available, with only a few studies reporting effect estimates for several PM size fractions (Pope and Dockery 2006). Normally for these studies, when the $PM_{2.5}/PM_{10}$ ratio was small cardiovascular mortality was associated with the coarse fraction (PM_{10}) whereas when the $PM_{2.5}/PM_{10}$ ratio was large it was associated with the fine fraction ($PM_{2.5}$). Clearly, with increasing contribution of fine particles to PM_{10} (as commonly found in north Europe and US) the probability to find significant relationships between health outcomes and coarse particles is small. Episodic high concentrations of coarse particles as a result of windblown dust were not linked to increased mortality (Schwartz et al. 1999). Yet, these findings may be specific to the outcome studied and their lag structure. Indeed, associations of health outcomes and mineral dust (coarse PM) are perplexing, with some studies showing clear evidence of adverse health effects (e.g., all-cause and cardiovascular admissions and hospitalization, Middleton et al. 2008; mortality, Jimenez et al. 2010; Castillejos et al. 2000; Villeneuve et al. 2003). In particular, $PM_{2.5–10}$ was also found to be associated with cardiorespiratory diseases (Burnett et al. 1997). Nonetheless, it is noteworthy that in both the Harvard Six Cities study (Dockery et al. 1993) and the American Cancer Society (ACS) study (Pope et al. 1995) the $PM_{2.5-10}$ fraction was not found to be related to mortality, unlike the $PM_{2.5}$ fraction (that was associated with mortality due to both cardiovascular and pulmonary causes).

To date, data about PM composition on a large scale are still generally sparse. Therefore, only a few investigations have examined the effects of different PM composition on human health, reporting that different PM species have different toxicity and bioavailability. For example, $PM_{2.5}$ from mobile combustion sources was found to account for a higher risk of daily mortality (3.4 % for a 10 μg/m^3 increase) than $PM_{2.5}$ from coal combustion sources (1.1 % for a 10 μg/m^3 increase) (Laden et al. 2000). Similarly, Ostro et al. (2007, 2010) and Ito et al. (2011) reported that $PM_{2.5}$, and in particular its organic and elemental carbonate constituents, were associated with cardiovascular hospitalization and mortality.

The risk of death has also been shown to increase with exposure to $PM_{2.5}$ aluminum, arsenic, sulfate, silicon, and nickel (Franklin et al. 2008). Hospital admissions for cardiovascular disease (CVD) were associated with bromine, chromium, nickel, and sodium, whereas high particulate concentrations of arsenic, chromium, manganese, organic carbon, nickel, and sodium modified the MI risk (Zanobetti et al. 2009a). These results support the notion that the chemical composition of particulate pollutants significantly affects the associations between respirable ambient PM and different health outcomes. In contrast, crustal $PM_{2.5}$ was not associated with mortality. Thus, fine PM can be regarded, in part, as a vehicle that transports toxic components into the lungs, where they can be activated and initiate molecular processes that lead to pathogenesis and cellular damage. Since size-specific PM composition is related to its toxicological potency (WHO 2003) and as both size and composition may have large geographical variation, PM-outcome associations found in one place may not necessarily be identical or consistent with results obtained in another place. This spatial PM-health effects variability is unlike the consistent associations found between exposure to gaseous pollutants and various health outcomes.

Deposition and uptake of particles in the respiratory tract are key mechanisms that lead to the toxicity observed in tissue target sites and organ systems (Donaldson et al. 2008; Wegesser et al. 2009). Apart from dissolution and activation of PM deposits, which lead to their penetration into the circulatory system, inhaled UFP can also translocate directly from their sites of deposition in the respiratory tract to secondary organs (Kreyling et al. 2009). Moreover, UFP deposited in the nose have been shown to traverse the olfactory nerve to the olfactory bulb. For example, ultrafine Mn oxide particles that translocate in this manner were found to induce inflammation and oxidative stress in specific regions of the brain (Elder et al. 2006; Ngo et al. 2010). Moreover, apart from PM many gaseous air pollutants, including carbon monoxide, nitrogen dioxide, sulfur dioxide, and ozone, were also associated with adverse health effects (Hoek et al. 2013; Sousa et al. 2013; Hesterberg et al. 2009; Chuang et al. 2009; Wang et al. 2011).

55.4 Particulate Carbonaceous Matter

Specific attention has been given in recent years to the PM carbonaceous content, which is normally divided into organic carbonaceous matter (OC) and its water soluble fraction (WSOC), and elemental carbonaceous matter (EC). Black carbon (BC), a global climate modifying parameter (Smith et al. 2009) and a hazardous agent (Janssen et al. 2011a), accounts for particulate products of incomplete combustion of biomass and fossil fuels. BC, black smoke (BS) and EC differ according to the analytical methods applied for their quantification. Since these fractions are highly correlated (Janssen et al. 2011b), they are oftentimes used interchangeably (Smith et al. 2009). Epidemiological evidence linking BC, EC, and BS to health outcomes is growing (Smith et al. 2009; Cao et al. 2012;

Lanki et al. 2006; Wang et al. 2013). For instance, significant positive associations were found between EC and ST-segment depression, daily hospital outpatient visits, emergency room admissions, and mortality (Lanki et al. 2006; Laden et al. 2006). Moreover, based on sufficient evidence that exposure to diesel exhaust particles (DEP) is associated with an increased risk of lung cancer, the International Agency for Research on Cancer (IARC), classified in 2012 diesel engine exhaust (which contains both EC and OC particulate fractions) as carcinogenic to humans (Group 1). Hence, BC/EC is a commonly accepted indicator when studying health risks from exposure to urban air pollution (Janssen et al. 2011a).

55.5 Exposure Considerations

The assessment of exposure to air pollutants suffers from several inherent limitations that bias derived risk estimates towards the null, including mostly unavailable direct measurements of exposure, unknown latency periods (the time lag between exposure and effect) for many outcomes, inseparable acute and chronic health outcomes as a result of an integrated body response to interacting pollutants, etc. (Künzli et al. 2001). In particular, the effect of short term exposure cannot be separated from people's past (lifelong) exposure (Englert 2004). Since time-series are often used to study acute effects but cannot account for long-term exposures, this has been suggested as an explanation for the normally lower relative risk estimates obtained in time-series studies as compared to cohort studies (WHO 2001). Specific to PM, open questions relevant to exposure estimation include: which fraction poses the highest risk for different health outcomes? What is the dose-response (concentration-response) relationship for various endpoints? Is PM the causal agent or is it just a pathway indicator (a carrier)? Is exposure to multiple PM species synergistic, antagonistic, or does it represent a complex mixture of effect modifiers? Etc. For example, the effect of $PM_{2.5}$ on lung cancer is known to be most distinct in people with low education, which is a proxy of their socioeconomic status, lifestyle, and accessibility to health care. Socioeconomic deprivation at the community level is a (non-chemical) stressor that plays an important role in shaping human health (Borrell et al. 2010; Factor et al. 2013; Robert 1999). Studies have shown that population health responds in a complex manner to socioeconomic factors, such that vulnerability in deprived populations expresses itself as variability in health outcomes (Karpati et al. 2002).

Whereas the relative risks associated with any single air pollutant are normally low, it should be appreciated that the population attributable risks are not negligible because of the wide exposure experienced by the general population (Mustafic et al. 2012). Nonetheless, it is equally important to acknowledge that, normally, exposure occurs to a mixture of airborne pollutants. Thus, the common single-pollutant approach for risk estimation may not necessarily suffice, and should be replaced by a multi-pollutant approach (Dominici et al. 2010). Integrated indicators (over time, space, or both) are commonly used when studying the effect of air pollution on human health. Unlike research that captures the independent impact of individual pollutants, composite indicators account for simultaneous exposure to multiple pollutants (Cairncross et al. 2007). The simplest indicators are obtained by a summation of the individual pollutant attributable risks, based on single-pollutant analysis, thus assuming biological uptake, activation, and toxicological pathways of non-interacting pollutants. Alternatively, aggregate exposure metrics account for multi-route exposure to mixtures of pollutants found in different environmental media (air, water, soil, food) (Fryer et al. 2006). It is noteworthy that the use of multi-pollutant exposure metrics is still limited, since most environmental epidemiology studies account for a single pollutant (with the other pollutants either omitted or incorporated as potential confounders) or for non-interacting pollutants (Mauderly and Samet 2009). Clearly, a true account for multi-pollutant exposure to potentially interacting pollutants requires an understanding of how the human body responds to simultaneous exposure and biological activation of a wide array of compounds. Currently, such approaches face numerous challenges, including inadequate exposure assessment methods and statistical modeling (Dominici et al. 2010).

PM has been shown to vary across geographical regions, and its effects were found to vary for people of distinct predisposition. Susceptibility refers to individual factors that increase the risk to obtain/develop adverse health effects at any given level of exposure. In contrast, vulnerability refers to factors that increase the potential to become exposed (Breysse et al. 2013). Both vulnerability and susceptibility are critical concepts for exposure assessment and environmental policy. Vulnerability is linked to the concept of environmental justice, since disadvantaged groups are more likely to have higher exposures. For example, vulnerable people at the lower socioeconomic status (SES) have been found to be at a particularly increased risk of cardiac outcomes (Brook et al. 2004; Lanki et al. 2006). In contrast, increased susceptibility implies a greater potential to develop a response at any given level of exposure. Many studies have suggested that certain groups of subjects are specifically susceptible to harmful effects triggered by exposure to PM, including the elderly, individuals with comorbidity (e.g., diabetics and/or obesity and coronary artery disease), and people with genetic predisposition. For example, it has been suggested that PM acts mainly as a trigger of acute events in individuals with underlying vulnerable vascular conditions (Pope et al. 2006), and that genetic host factors are plausible modifiers of the pathophysiological consequences of PM exposure. Many different polymorphisms in various candidate genes, particularly those involved in oxidative and inflammatory pathways, have been proposed as PM modulators (Zanobetti et al. 2011). For instance, variants on genes encoding for glutathione S-transferases (GSTM1, GSTP1, GSTT1), interleukin 6 (IL6), fibrinogen (FG-A/B/G), vascular endothelial growth factors (VEGF-A/B), apolipoprotein E (APOE) and the hemochromatosis protein (HFE) have all been found to show significant interactions with PM in determining heterogeneous cardiovascular phenotypes. Nonetheless, to date data on gene-environmental interactions is not yet conclusive because of low reputability of results across different studies.

As for vulnerability, the prenatal period and the first year of life are critical developmental periods when air pollution has been posited to influence fetal stress, fetal loss, fetal development, birth outcomes, and subsequent development of chronic cardiovascular, pulmonary, and cognitive dysfunction. Successive exposures to airborne pollutant during childhood may sustain or add to the adverse health effects accumulated during pregnancy and infancy, since children inhale greater volumes of air per body mass than adults and spend more time outdoors in intense activity, and since their lungs are still growing and developing. For example, preeclampsia (fetal stress), preterm delivery, low birth weight, and low weight for gestational age were all associated with pregnant women exposure to traffic-related air pollution after adjusting for community deprivation (Wu et al. 2009; Zeka et al. 2008). Likewise, Gryparis et al. (2009) and Bell et al. (2007) demonstrated trimester-specific associations of low birth weight with elevated traffic-related NO_2, CO, PM_{10}, and $PM_{2.5}$.

55.6 Air Pollution and Cardiac Outcomes

Epidemiological and toxicological evidence has demonstrated that air pollution, in particular PM, is associated with the occurrence of a multitude of terminal illnesses, including coronary heart disease, cerebrovascular disease, respiratory diseases, diabetes and cancer. Cardiovascular disease (CVD), and in particular ischemic heart disease, is the leading cause of morbidity and mortality in Western countries. Since 2004, the American Heart Association (AHA) recognized that exposure to high concentrations of PM is associated with an increased risk for cardiac outcomes such as cardiac arrhythmia, myocardial infarction (MI), stroke, heart failure and mortality due to heart failure, cardiac arrest and ischemic heart disease among both healthy and health-compromised individuals, hospital admissions and mortality due to CVD, electrocardiograph (ECG) features, etc. (Wellenius et al. 2006; Watkins et al. 2013; Hoek et al. 2013; Langrish et al. 2012; Martinelli et al. 2013). Consequently, in its recent scientific statement, the AHA defined exposure to $PM_{2.5}$ as “a modifiable factor that contributes to cardiovascular morbidity and mortality” (Brook et al. 2010).

PM effects on CVD vary between short- and long-term exposures, yet both show consistent associations with acute coronary syndrome, MI, and in particular with fatal events. Short-term exposure to $PM_{2.5}$ has been associated with increased risk of cardiac readmissions (Peters et al. 2004; Kloog et al. 2012), MI risk (Mustafic et al. 2012) and death. Positive associations were reported between autonomic dysregulation/arrhythmias and exposure to high levels of (mainly fine) PM among subjects with and without pre-existing cardiovascular disease (Watkins et al. 2013; Ebelt et al. 2005; Mann et al. 2012). Specifically, short-term exposure to increased PM concentrations has been associated with a higher cardiovascular mortality for both PM_{10} (0.3–0.9 % for an increase of 10 $\mu g/m^3$) and $PM_{2.5}$ (0.6–1.3 % for an increase of 10 $\mu g/m^3$) (Brook et al. 2010). Thus, $PM_{2.5}$ appears to have a higher impact on cardiovascular mortality than coarse PM ($PM_{2.5–10}$; Zanobetti and Schwartz 2009; Dominici et al. 2006). Similarly, long-term exposure to $PM_{2.5}$ has been associated with cardiovascular mortality and hospital admission for congestive heart failure (CHF), ischemic heart disease, acute coronary syndrome, peripheral arterial disease, heart failure, myocardial infarction (MI) and overall reduction in life expectancy (Zanobetti and Schwartz 2007; Brook et al. 2004; Laden et al. 2006), cerebrovascular disease, stroke, arrhythmias, and venous thromboembolism (Baccarelli et al. 2008; Martinelli et al. 2007, 2013; Dales et al. 2010; Mannucci 2010). These findings, in particular ischemic stroke (Brook et al. 2010; Miller et al. 2007) and recurrence of cardiovascular events in patients after a first MI (Koton et al. 2013), persist after adjustment for socio-demographic factors. Moreover, exposure to $PM_{2.5}$ was also found to be associated with frailty among CVD patients, providing a potential intermediary between air pollution and post-MI outcomes (Myers et al. 2013). The role of PM exposure in CVD becomes particularly evident when assessed as the population attributable fraction, which is a useful method to quantify the public health relevance of epidemiological findings, since it considers both the strength of the association between the risk factor and the outcome as well as the prevalence of the exposure within the population (Bruzzi et al. 1985).

Recent studies suggest that the PM-CVD relationship is likely more complex than a mere quantitative association between PM size-fraction concentrations and disease risk, and that the biological effects of PM vary according to its chemical composition as well as due to co-exposure to gaseous pollutants. For example, short-term exposure to dilute diesel-exhaust in men with coronary heart disease promoted myocardial ischemia fibrinolysis (Mills et al. 2007). To better understand the role of individual pollutants and of pollutant mixtures on arrhythmogenesis and to eliminate the lack of adequate controls on exposures in epidemiologic studies, controlled exposure studies on animal models have been conducted. In general, observable prevalence of arrhythmic events in toxicological studies was associated with exposures to diesel exhaust particles (DEPs) and to residual oil fly ash (ROFA).

55.7 Pathophysiological Mechanisms Linking PM and CVD

To date, the biological mechanistic processes that connect airborne pollutants to CVD outcomes remain mostly undetermined. Emerging evidence from controlled exposures generally does not support the concept of attributing health effects to any specific pollutant, mainly due to indeterminate toxicologic effects of individual pollutants and the complex interactions among pollutants in vivo. Yet, three PM-related mechanisms have been shown to play a role in pathways leading to CVD (Brook et al. 2010): pulmonary activation of pro-inflammatory and pro-oxidative arbiters that can mediate an indirect systemic response (e.g., release vasoactive mediators), direct transmural translocation of PM, in particular UFP, through the pulmonary epithelium directly into the circulation, and alterations of the autonomic nervous system (ANS) induced by PM interactions with lung receptors. Specifically, fine PM can trigger pulmonary oxidative stress and inflammation by means of heterogeneous and complex mechanisms with varying responses in relation to the distinct PM properties, leading to increased blood coagulability and the release of systemic mediators (Seaton et al. 1995). Inspired PM may cause a local inflammatory response in the lung within ~24 h, with blood markers of inflammation, coagulation, and oxidative stress increasing immediately after this pulmonary inflammatory response. In general, $PM_{2.5}$ and $PM_{2.5-10}$ can generate reactive oxygen species (ROS) and to activate ROS-generating pathways in both the pulmonary and vascular tissues (Martinelli et al. 2013; Weichenthal et al. 2013). Inflammatory cytokines, like IL-6, IL-1β, TNF-α, and interferon-γ, have been shown to be increased in bronchial fluid and in circulating blood after exposure to PM. The PM-induced vascular inflammation has a detrimental influence also on metabolic pathways, leading to insulin resistance and an increase in visceral adiposity (Sun et al. 2009).

Both particulate and gaseous pollutants can pass the alveolar-blood barrier and enter the systemic circulation. UFPs are more likely to penetrate the epithelium and infiltrate the bloodstream than larger particles, since they can translocate via non-phagocytic pathways. UFPs penetrating bloodstream can enhance platelet aggregation and endothelial cells activation, thus promoting atherothrombotic events independently of lung/systemic inflammation. For example, whereas exposure to traffic-related air pollution did not trigger inflammation, it lead to an elevation of plasma thrombogenicity by raising plasma microvesicles and their procoagulant properties (Emmerechts et al. 2012a, b). UFP has also been demonstrated to promote vascular calcification by activating NF-kB signaling (Li et al. 2013). Another potential mechanism is an abnormal alteration in the hemostatic balance and induction of prothrombotic diathesis. The biological plausibility of this association is supported by the well-recognized relationship between inflammation and hemostatic mechanisms (Bonzini et al. 2010).

PM can also stimulate the autonomic nervous system (ANS), impairing the autonomic balance and favoring sympathetic over parasympathetic tone (Pieters et al. 2012). Proxies of autonomic modulation include direct pulmonary neural reflex activation, autonomic stress as a result of circulation of pro-inflammatory cytokines, changes in the function of the cardiac ion channels, and hypertension. ANS modulation increases cardiovascular risk through the induction of pro-hypertensive vasoconstriction and the predisposition to arrhythmias. Tracking changes in heart rate variability (HRV) is the conventional approach for detection of impaired cardiac autonomic function. It is commonly accepted that markers of repolarization abnormality may indicate a propensity for arrhythmic events, and that alterations in the QT and T-wave segments of an ECG represent risk of arrhythmia. In particular, lengthening of corrected QT segment among unhealthy cohorts and significant modulation in the T-wave peak-to-end interval were identified in human with previous CVD after exposure to traffic-related air pollution and to BC (Watkins et al. 2013).

55.8 Reducing PM Exposure at Population Level: A Proof of CVD Causality

The crucial question arising from associations with risk factors found in epidemiological studies is whether there is proof of causality between the pollutant and the outcome. Despite biological plausibility of PM-induced adverse health effects, causality can be definitively established only through interventional studies that reveal a reduction of the burden of disease following a decrease in the environmental stressor that has been used as the risk factor (Martinelli et al. 2013). To this end, recent studies suggest that improvement in air quality has resulted in a decline in associated respiratory symptoms and in cardiorespiratory mortality (Hedley et al. 2002). A reduction in exposure to $PM_{2.5}$ contributed to a significant improvement in life expectancy (0.61 ± 0.20 years for a PM decrease of 10 μg/m^3; Pope et al. 2009). Coordinated interventions to reduce air pollution may include community education campaigns, law enforcement, and public participation in various ways (prioritization, design, and active/passive data collection and analysis). Indeed, emerging observations show reduced CVD mortality after coordinated community policies that result in lower PM exposure at population level (Pearson et al. 2001). In summary, air quality serves as a proxy for the good health-related environmental policy and in this sense it is an important health indicator.

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Chapter 56
Electromagnetic Radiation – Environmental Indicators in Our Surroundings

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Abstract All living tissues have magnetic properties that are affected to some extent by the existence of electromagnetic radiation in the environment. Therefore all living creatures including plants, microbes, animals and humans are environmental indicators of exposure to electromagnetic radiation. Radiation is the process through which energy travels in the form of waves or particles through space or some other medium. Electromagnetic radiation is the propagation of waves that have an electric (E) and a magnetic (H) field component. Biological cell proliferation and differentiation can be affected by both AC and DC magnetic fields.

Radiofrequency and microwave wavelengths can be made to carry information via amplitude, frequency, and phase modulation, such as data from television, mobile phones, wireless networking and amateur radio.

Chromosomal damage is a mechanism relevant to causation of birth defects and cancer. Long-term continuous or daily repeated EMF exposure has been found

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_56

to induce cellular stress responses at non-thermal power levels that lead to an accumulation of DNA errors.

Comparative studies in animals that rely on electromagnetic orientation provide valuable information. The effects of electromagnetic radiation on plants and animal life include the diminished radial growth of pine trees, lowered density of bird species and mammals, such as storks, sparrows and bats, effects on bees, effects on magnetic-based homing mechanisms of birds, and many other effects. Plants and animals can be monitored as environmental indicators to assess the effects of electromagnetic radiation.

Keywords Electromagnetic fields • Human antennas • Radiation • Sensing • Animals • Plants • Humans oxidative stress

56.1 Electromagnetic Fields and Electromagnetic Radiation – Background

Radiation is the process through which energy travels (or propagates) in the form of waves or particles through space or some other medium. Electromagnetic waves have an electric (E) and a magnetic (H) field component, that propagate in planes perpendicular to each other through space, at the velocity of light.

Waves propagate in a sinusoid shape. The number of times the electric or the magnetic field pulsates per second at a given point is called the *frequency* (f) of the wave. *Wavelength* (λ) describes the distance that the wave travels during the time corresponding to one period (1/f) of the wave, from peak to peak. Waves propagating to the *far field* become radiation. The wave is emitted from a transmitting source such as an *antenna*. The fields' intensities decay rapidly with distance away from an object, with an inverse square law.

There are electric and magnetic fields wherever there is electric power. These fields are created by the electric charges that are pumped into the power system by electric power generating stations. The electric power of 50–60 Hz frequencies that is used in our homes, offices and factories uses AC or alternating current. Biological cell proliferation and differentiation can be heavily affected by both AC and DC magnetic fields (Portelli et al. 2013). When inspecting health effects, both AC and DC fields need to be measured and understood.

Radiofrequency waves and Microwaves are in the range of 1,000 cycles per second (1,000 Hertz or Hz) to 1,000 Mega Hz (million cycles/ second). Radio wave wavelengths range from hundreds of meters to about one millimeter. Radio waves can be made to carry information via modulation, i.e. by varying a combination of the amplitude, frequency, and phase of the wave within a frequency band. Data from television, mobile phones, wireless networking and amateur radio are transmitted by radio and microwave frequencies.

56.2 Environmental Indicators of Electromagnetic Fields

Living organisms sense electromagnetic radiation. Eye receptors detect light in the visual frequencies, and the skin has heat receptors. These are examples of physiologic electromagnetic sensors. These are only a minor segment of the electromagnetic radiation we utilize.

The skin of humans and animals can carry electromagnetic fields. Electromagnetic radiation can couple to a conductor or a substance with dielectric properties such as the living tissues, and travel along it, inducing an electric current on its surface by exciting the electrons of the conducting material. The dielectric properties of a biological tissue result from the interaction of electromagnetic radiation with its constituents at the cellular and molecular level. *Permittivity* is the measure of the resistance that is encountered when forming an electric field in a medium. It is a measure of how much electric field (flux) is 'generated' per unit charge in that medium. Electric *conductivity* measures a material's ability to conduct an electric current.

Some wave frequencies can penetrate the skin and affect deeper tissues as well.

Microwaves and RF waves affect molecules that have a dipole moment. A dipole is established when two electrical charges in a molecule with opposite sign and equal magnitude are separated by a distance. The size of a dipole is measured by its dipole moment. In microwave heating, molecules and ions oscillate, aligning themselves to the applied alternating electric field. The resulting molecular friction generates heat. This process, called dipole rotation or dielectric heating is used to heat food in the microwave oven (Piyasena et al. 2003). Similarly, high power microwave devices can heat the water molecules in our body tissues. These are called Thermal effects, or heat effects, of microwaves.

Besides thermal effects, many researchers have demonstrated other, non-thermal effects of microwaves and RF waves. For example, Copty et al. (2006) demonstrated a specific microwave radiation effect on a molecule, the green fluorescent protein, that cannot be explained by heating alone. Pall (2013) has demonstrated in a review article that electromagnetic fields act via activation of voltage-gated calcium channels to produce beneficial or adverse effects, while no heating is needed for these effects.

Dielectric properties of biological tissues: The dielectric properties of biological tissues have been described (Gabriel et al. 1996; Peyman et al. 2001). Tissues with higher water-content exhibit higher permittivity and conductivity values (Schwan and Foster 1980), i.e. if there are more water molecules in the tissue then its response to passage of electromagnetic waves through it is greater.

Electromagnetic dosimetry is the simulation of electromagnetic exposure situations and the calculation of internal fields within the exposed structures. High-resolution, anatomically correct man and animal models derived from medical imaging data are available today for research (Dimbylow 1996). Over 30 tissue types can be uniquely identified.

SAR, or *Specific Absorption Rate*, is a measure of the amount of energy absorbed by our tissues, when exposed to RF/MW waves, although, it can also refer to absorption of other forms of energy by tissue. SAR is commonly used to measure power absorbed from mobile phones or during MRI scans. Different tissues absorb energy differently. One factor that influences SAR is the relative water content of the tissue, since water molecules are heated by microwaves. The SAR value depends on the geometry of the part of the body that is exposed and on the exact location and geometry of the power source.

Radio and television broadcasting use 100–200 megaHz frequencies. Mobile phone systems use 800 and onwards mega and Giga Hz frequencies. Micro-wave ovens use 2,4 GigaHz. Micro-ovens often leak; therefore it is not recommendable to allow children to be near when they are on. Radars used in naval and aviation applications cover a higher frequency range. Their actions are toxic to tissues as the water content of the tissues heat, causing damage to the tissue.

56.3 Electromagnetic Interference

When waves propagate through space and media, they undergo changes in polarization, reflection, refraction and diffraction. *Electromagnetic compatibility* is the ability of two or more devices to work together without interfering with each other. *Electromagnetic interference* is the production of unwanted RF energy, emitted intentionally or unintentionally from devices. For there to be electromagnetic interference, there must be a source of electromagnetic power, coupled by a transmission line to a radiating structure, or *antenna*.

Electromagnetic interference is regulated by governments, via regulatory agencies. This is important so that aircraft and military devices, for example, will not malfunction.

56.4 Electromagnetic Effects on Living Cells and DNA

The radiofrequency and microwaves from mobile telephony can cause genotoxic effects. Chromosomal damage is a mechanism relevant to causation of birth defects and cancer. Long-term continuous, or daily repeated EMF exposure has been found to induce cellular stress responses at non-thermal power levels that lead to an accumulation of DNA errors. It is possible that electromagnetic fields affect enzymatic reactions involved in the repair functions and as a result deformities are not corrected.

These findings have important implications with regards to potential dangers from prolonged and repeated exposure to non-ionizing electromagnetic radiation (Garaj-Vrhovac et al. 1991; Lai and Singh 1995; Balode 1996; Demsia et al. 2004; Diem et al. 2005; Gandhi and Singh 2005; Di Carlo et al. 2002; Leszczynski et al. 2002; Mirabolghasemi and Azarnia 2002; Friedman et al. 2007).

56.5 Plants as Environmental Indicators of Electromagnetic Radiation

Plants absorb electromagnetic radiation. Some plants can be used as indicators of its presence.

Davis et al. (1971), demonstrated the susceptibility of certain plants and weeks to ultrahigh-frequency electromagnetic field (2,450+/−20 MHz).

Balodis et al. (1996) used the Skrunda Radio Location Station, a site that had operated and emitted electromagnetic radiation continuously for more than 20 years, to study the effects of pulsed radio-frequency electromagnetic fields. Pine trees were the environmental indicator studied. The researchers demonstrated that the radial growth of pine trees had diminished in all plots that were exposed to electromagnetic radiation. This decrease in growth began after 1970, which coincided with the start of operation of the Skrunda RLS, and was subsequently observed throughout the period of study. The effects of many other environmental and anthropogenic factors were evaluated, but no other significant effects on tree growth were observed.

Ben-Izhak Monselise et al. (2011) and Parola et al. (2005) demonstrated a unique method for bio-monitoring of electromagnetic radiation exposure and cell stress, using plants. Water plants (Duckweed, *Landoltia punctata* also named *Spirodela oligorrhiza*) were exposed for 24 h to radiofrequency electromagnetic radiation between 7.8 V/m to 1.8 V/m, enerated by AM 1.287 MHz transmitting antennas. The researchers demonstrated accumulation of alanine in the plant cells, a phenomenon shown previously to be a universal stress signal. The magnitude of the effect corresponded qualitatively to the level of radiofrequency electromagnetic radiation exposure. In the presence of 10 mM vitamin C, alanine accumulation was completely suppressed, suggesting the involvement of free radicals in the process.

56.6 Animals – Electromagnetic Sensory Systems

Many animals, such as migrating butterflies, homing pigeons, honeybees, sea turtles and beluga whales have physiological magnetoreceptors of some kind. They use the natural magnetic fields to guide their travels over vast distances. Magnetite is found in the neural tissues, muscles, bones and teeth of humans, and also in insects – in the abdomen of honeybees and the heads and abdomens of some ants. Possibly other tissues have some concentration of magnetite crystals as well. At present, the mechanism by which these magnetite crystals transfer the electromagnetic signals they percept is not known (Kirschvink et al. 1992; Russel et al. 2008).

The orientation of honey bee dances is affected by the earth's magnetic field (Gould et al. 1980).

Exposure to cell phone radiations has been shown to produce biochemical changes in worker honey bees (Kumar et al. 2011) Reduced motor activity of the worker bees on the comb was initially demonstrated, followed by en masse migration and movement toward "talk mode" cell phone. The initial quiet period was characterized by rise in concentration of biomolecules including proteins, carbohydrates and lipids, possibly due to stimulation of body mechanism to fight the stressful condition caused by exposure to electromagnetic radiation.

Another study in India (Sainudeen Sahib 2011) exposed several bee colonies to mobile phones using a frequency of 900 MHz for 10 min for a short period of 10 days. After 10 days of exposure to electromagnetic fields the worker bees never returned to the hives in the test colonies. The researcher suggests that that navigational skills of the honey bees was harmed, preventing them from returning back to their hives. It was shown that the total bee strength was significantly higher in the control colonies being nine comb frames as compared to one in the test colony at the end of the experiment. The queens in the test colonies also produced fewer eggs/day (100) compared to the control hives (350).

56.7 Electrosensitivity in Animal Species

Practically all biological species are exposed to manmade irradiation. There have been studies on different species, insects and plants.

Balmori (2009) conducted a wide literature search presenting many studies that demonstrate animals as environmental indicators for electromagnetic fields. One example was an aversive behavioural response in bats exposed to electromagnetic radiation. Bat activity was shown to be significantly reduced in habitats exposed to electromagnetic field strength greater than 2 V/m (Nicholls and Racey 2007). During a study in a free-tailed bat colony (Tadarida teniotis) the number of bats decreased when several phone masts were placed 80 m from the colony.

Some birds are good indicators of biological and environmental effects, e.g. white storks. Their nests can easily be tracked and registered. Studies have shown that the population of white storks has been suffering lowered reproduction success (Balmori 2005). Another studied species is the sparrow, whose density has declined in areas with higher electrical field intensity (Balmori and Hallberg 2007; Everaert and Bauwens 2007). Reijt et al. (2007) found that electromagnetic fields may discourage some bird species from breeding in areas with higher RF EMF fields or might encourage other species to build their nests there. There is also some evidence that electromagnetic fields may modify the reproductive behaviour of insects that serve as food sources for various bird populations (Panagopoulos et al. 2007).

Birds like seagulls have been noted to leave their traditional resting sites when irradiation levels were increased by the introduction of a new phone base station(s) (Väkeväinen, personal communication).

56.8 Experimental Effects Recorded in Animals

Studies on animals may not be directly applicable to humans, but they rule out the psychosomatic effect that suggests that people develop symptoms only because they are worried by the antenna masts they can see.

Balmori reports Carpenter and Livstone's study, in which the researchers irradiated pupae of Tenebrio molitor with 10 GHz microwaves at 80 mW for 20–30 min and 20 mW for 120 min obtained a rise in the proportion of insects with abnormalities or dead (Carpenter and Livstone 1971).

Regoli et al. (2005) demonstrated the effect of low frequency 50 Hz electromagnetic fields on snails, both in the laboratory and under overhead power cables, employing a range of biological markers. The electromagnetic fields had particular dose dependant effects on markers of oxidative stress such as catalase and glutathione reductase both in the laboratory and in the field situations. A reduction in lysosomal stability and of DNA integrity was also demonstrated. The authors attributed the effects to the generation of free radicals.

Professor Andras Varga from the University of Heidelberg found that chicks exposed to microwaves in the egg died or hatched with deformities (Varga 1992). Youbicier-Simo et al. (1997) exposed chicken embryos to electromagnetic fields emitted by video display units and found that constant exposure was accompanied by significantly increased fetal loss (47–68 %) and markedly depressed levels of circulating anti-Tg IgG, plasma corticosterone, and plasma melatonin. Recently, Gabr from the Agricultural University of Athens demonstrated that exposure to 900 MHz electromagnetic radiation during the first 5 days of chick embryonic development resulted in increased morphological and anatomical abnormality rates as well as changes in embryo weight and impairment in behavioural pattern and long-term memory function (Gabr 2010). Cucurachi et al. (2013) have published a review of many papers demonstrating ecological effects of radiofrequency waves in birds and plants.

In the 1970s, behavioural studies were conducted on rats, to establish the existence of electromagnetic radiation induced effects (Korbel Eakin and Thompson 1965; Eakin 1970; Mitchell et al. 1977). Some of the abilities found to be affected in rodents were increased nocturnal activity, aggression, escape, avoidance, and sleep pattern (Smith and Justesen 1977; Frey and Feld 1975; Frey 1977; Monahan and Ho 1977; Monahan and Henton 1977; Ho et al. 1977; Laforge et al. 1978; Konig and Ankermuller 1970; Johnson et al. 1978).

Newer studies in rodents have examined spatial memory in mice (Fragopoulou et al. 2010; Narayanan et al. 2009), cognitive impairment (Li et al. 2008;

Nittby et al. 2008). Marino et al. (2003) have shown changes in EEG in rabbits, exposed to radiation from a 800MHz band cellphone. Blackman et al. (1979) demonstrated calcium-ion efflux from brain tissue by radio-frequency radiation.

Mobile phone exposure may have negative effects on sperm motility characteristics and both male and female fertility in rats and mice (Wdowiak et al. 2007; Ozguner et al. 2005; Forgacs et al. 2006; Gul et al. 2009). Oogesesis and spermatogenesis are very active and sensitive to external factors at different stages. Panagopoulos and Margaritis have shown alteration of cytoplasmic calcium concentration and an acceleration or retardation of cellular processes in insects. The observed effects could not be attributed to an increase in temperature (Panagopoulos and Margaritis 2002).

56.9 Deposition of Electromagnetic Energy in Tissues of Animals and Humans

Gandhi and others have raised concerns in multiple publications, that when electrical and dielectric properties are considered, different body parts of children and adults such as the brain, the testes and other sensitive organs, can actually absorb much greater levels of electromagnetic radiation than allowed by international regulations. For example, absorption of radiation from cellphone use in a child's skull bone marrow can be ten times greater than adults. Most contemporary cell phones do not comply with the existing certified SAR value when held directly at the head or kept in a pocket Gandhi et al. (1976, 1977, 1979), Gandhi and Riazi (1986), Gandhi (1989, 1990, 2002), Gandhi and Kang (2001), Dimbylow (1997), Beard and Kainz (2004).

Therefore, a new certification process for handheld devices that incorporates different modes of use, head sizes, and tissue properties is essential and urgent. Anatomically based models should be employed in revising safety standards and standards should be set by accountable, independent groups.

Table 56.1 presents the history of the regulation of human exposure to electromagnetic waves and radiation in various frequencies, by several organizations and regulation agencies. The data and the critical comments are adapted from Gandhi et al. (2011) review article and personal communication with OP Gandhi, and are based on the research and publications of: Gandhi (1974), D'Andrea et al. (1975), ANSI (1982), IEEE (1991), Cleveland et al. (1997), Chan et al. (1997), ICNRIP (1998), Means and Chan (2001) and Steneck et al. (1980).

Effects of human exposure to electromagnetic waves are described in detail in Chap. 57.

Table 56.1 Electromagnetic field effects – tissue environmental indicators – international regulation

Year	Data/regulation	Description	Comments	Source
1974	At certain frequencies resonance increases absorbed radiation up to nine times higher than previously assumed for humans			Gandhi (1974)
1975	Behavioral studies on rats determine hazardous levels of exposure to electromagnetic fields – impaired animal's ability to work for food reward	Exposure metric: Specific Absorption Rate (SAR), power absorbed per unit mass of tissue (Watts/kilogram)		D'Andrea et al. (1975)
	American National Standards Institute (ANSI) publishes first exposure NIR (non-ionizing radiation) exposure standard	Standard for whole body exposure of 0.4 W/kg averaged over 6 min, and a 20-fold greater spatial peak SAR exposure over any 1 g of tissue of 8 W/kg averaged over 6 min	Resonant frequency (70 MHz) "results in an approximate sevenfold increase of absorption relative to that in a 2,450 MHz field"	ANSI (1982, p. 11–14)
	Incorporates 10-fold safety factor for humans exposed to electromagnetic fields between 300 kHz and 100 GHz		Calls for a review of the standard every 5 years	
1987–1988	Setting of exposure limits handed to the Institute of Electrical and Electronic Engineers (IEEE), a professional society of electrical and electronics engineers from electronics industry and academia			
1991	IEEE first revised ANSI standard	Two-tier system:	Worker limit:	IEEE (1991)
	Comment: Specific Absorption (SA) is identical for the general population in an uncontrolled environment, as it is for workers in a controlled environment (0.08 W/kg*30 min = 0.4 W/kg*6 min)	General population within "uncontrolled environment"	Up to a whole body SAR of 0.4 W/kg for 1 g of tissue averaged over 6 min, Peak spatial SAR of 8 W/kg for 1 g tissue, averaged over 6 min	IEEE (1991, p. 17)
		Workers in "controlled environment"		
		For the general population, the IEEE revision of the ANSI standard reduced the average whole-body and spatial peak SAR by a factor of 5	General public:	
			0.08 W/kg averaged over 30 min	
		Concerns: wide range of ages, vulnerabilities and health status, potential of 24/7 exposures	Spatial peak SAR for 1 g tissue 1.6 W/kg averaged over 30 min	
1992	ANSI adopted the 1991 I.E. standard	Referred to as, ANSI/IEEE C95.1-1992		

(continued)

Table 56.1 (continued)

Year	Data/regulation	Description	Comments	Source
1997	FCC published the first U.S. regulations on maximum allowable cell phone radiation adopting the ANSI/IEEE C95.1-1992 standard	Became effective on October 15, 1997	Bulletin 65 described how to evaluate compliance to the FCC regulations	Cleveland et al. (1997)
1997	FCC Supplement C	Additional information for "portable devices" (cell phones) certification – no standardized process yet developed to evaluate RF exposure compliance with SAR limits	Lack of standardized test positions for evaluating handsets	Chan et al. (1997, p. 1)
			Liquid simulating the average electrical properties of an adult head not yet developed	
		Computer simulation: "Fnite-Difference Time-Domain" (FDTD) algorithm currently most widely accepted computation method for SAR modeling	Some models use "spacer" to represent the ear	
1998	International Commission on Non-Ionizing Radiation Protection (ICNIRP 1998), provided "guidelines"	Adopts the same two-tier system except that both the general public and occupational exposures are averaged over 6 min	Occupational exposure (far-field): "A whole-body average SAR of 0.4 Wkg^{-1}", SAR = 10 W/kg averaged over 10 g	ICNRIP (1998, p. 509)
	Comment: guidelines do not directly address product performance standards, which are intended to limit EMF emissions under specified test conditions, nor does the document deal with the techniques used to measure any of the physical quantities that characterize electric, magnetic, and electromagnetic fields	An additional safety factor of 5 is introduced for exposure of the public, giving an average whole-body SAR limit of 0.08 Wkg^{-1}	General public: (additional safety factor of 5) average whole-body SAR limit of 0.08 Wkg^{-1} maximum SAR = 2.0 W/kg averaged over 10 g	
		For general public exposures, the maximum spatial peak SAR = 2.0 W/kg averaged over 10 g, with occupational exposures, SAR = 10 W/kg		
2001	FCC's Supplement C revised	Standardized and repeatable, (although not necessarily accurate), industry designed cell phone SAR certification process	SAM [Specific Anthropomorphic Mannequin] cell phone certification process	Means and Chan (2001)

** Adapted from Gandhi et al. (2011), with permission

Acknowledgements This work was supported in part by the Environmental Health Trust, a non-profit and policy organization, and by the Yael Piton fund for support of research in Environmental Studies.

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Chapter 57
Electromagnetic Radiation and Health: Human Indicators

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Abstract Manmade electromagnetic radiation increases in the environment as new applications are frequently adopted. Humans serve as receiving antennas for electromagnetic waves. Thus various new responses can be expected. In addition to radio and television programs, mobile telephony, distant reading of electricity and water consumption and many other technologies load us electrically and magnetically both out- and indoors. Most exposures are active all the time, day and night, continuously or in regular pulses. Personal devices are also important sources, since they touch the skin and are held near the brain and heart. Humans are good bioindicators, as their physiological parameters, such as heart function and blood biochemistry, are frequently recorded. Data storage and analysis are getting better. Humans also report symptoms that cannot be directly measured, and carry valuable information on bioeffects. Studies from recent decades have shown that exposure to electromagnetic waves can break DNA chains, damage proteins,

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
DOI 10.1007/978-94-017-9499-2_57

even increase the blood brain barrier permeability, disturb sleep, and cause fatigue, memory and concentration problems. Neural, hormonal and psychosocial development is affected. An increase in human brain tumours has been described in correlation with mobile phone use on the exposed side of the head. The symptoms of electrohypersensitivity cause morbidity, but the interaction between multiple radiation frequencies and the mechanisms leading to frequency sensitivity are still poorly understood. Producers of mobile communication devices continuously warn users not to keep personal devices in skin contact. The Precautionary Principle that has been signed by many nations applies to all environmental risk factors, including exposure to electromagnetic waves.

Keywords City planning • Electromagnetic fields • Human antennas • Radiation • Sensing • Animals • Humans • Symptoms • Oxidative stress • Tumours

57.1 Introduction – Human Exposure to Electromagnetic Waves

Humans and all living organisms are *receiving antennas* for electromagnetic radiation (Adey 1981, 1986). Atoms, molecules and ions in human tissues interact with the electromagnetic waves, for example iron, present in many catalysts, haemoglobin and other carriers of oxygen, and magnetite crystals (Kirschvink et al. 1992; Russel et al. 2008). The antenna function of the human body can be directly registered in the same way data from physical antennas are recorded. Figure 57.1 presents radiation signals recorded with a spectrum analyzer from the skin of a sitting subject.

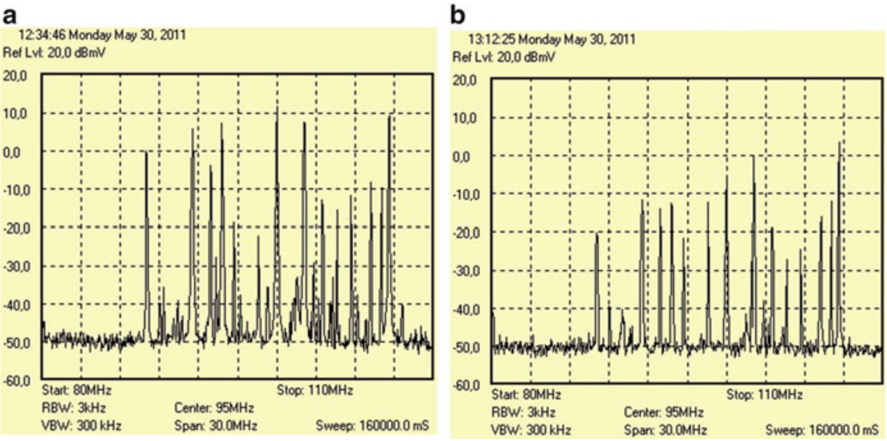

Fig. 57.1 Radiation spectra around the 100 MHz commonly used in frequency modulated (FM) radio transmissions, recorded with a spectrum analyzer (GW Instek GSP-827). (**a**) The horizontally polarized signals were captured with the aid of a 150 cm long dipole antenna. (**b**) Directly recorded from the same site level from the elbow skin of a sitting subject (one of the authors served as the receiving antenna). Without antenna, only minor noise was recorded (not shown) (Hänninen et al. 2013 reproduced with the permission of the J. African Association of Physiological Sciences)

Living organisms have been adapting to exposure to electromagnetic radiation from natural sources, and its effects, over millions of years. Outdoors, humans are exposed to the natural environment. We must start to consider that in the twenty-first century we have become too remote from the natural conditions to which humans and all other living organisms have adapted. The growing use of electromagnetic radiation by industry, the military, and the general public has raised the environmental baseline exposure to electromagnetic waves by several orders of magnitude. All species must now readapt to this new man-made artificial environment. Adaptation and evolution is not necessarily a fast process. Members of a species may show variation in their adaptation capacity. Therefore, precautionary measures must be taken rapidly to protect susceptible sub-populations in the general public.

Research results are still accumulating regarding the relatively new abundance of electromagnetic applications used by the general public since the last decades of the twentieth century. Synergistic or additive effects of interactions between different factors, and the long-term effects of low level exposure on humans, are even less known. Nevertheless new applications are adopted all the time, based on the assumption of safety. These are mostly controlled by regulations, but since much is still unknown, current exposure limits may not be protective. Indeed, there are many studies that show biological effects (bioeffects) at levels below current exposure limits. The planning of research is slow and the execution of studies is even slower than the rapidly advancing technology. Due to the scarcity of clear results and knowledge, lay findings and individual case reports are an additional important source of information, as they have always been, especially since modern information technology facilitates collection of these data.

A large part of our lives is spent indoors, protected from harsh climate conditions; but the indoor ambience exposes humans to multiple agents, such as cigarette smoke, chemicals and electromagnetic waves emitted from devices. It is notable that skin tumours are often seen in covered parts of the body and not only in the areas exposed to sunshine, as would intuitively be expected.

When people commute they are not in a natural environment either. Transportation vehicles like busses, trains, cars and ships have metal frames and their exterior is covered in metal. The lighting inside the vehicle is an artificial light. Many cars, trains, and busses operate wireless telecommunication or Internet connection inside the vehicle, e.g., cellphone antennas, Bluetooth or WiFi connections. Electromagnetic means are also used for tracking the transport of goods and of people, via satellites.

In many countries, regulations are not up to date with the most recent scientific knowledge on the possible human effects of electromagnetic radiation. Electromagnetic bioeffects were assumed in the past to be insignificant, and therefore regulations paid little attention to them. Recent studies and re-emerging data from the 1970–1980s from Eastern Europe and the United States indicate the significant existence of bioeffects of human exposure to electromagnetic radiation (see Bioinitiative Report 2012). Susceptible members of the general population, such as children, pregnant women, the sick and elderly, and those with a weaker immune system, are more at risk. The effect of long-term exposure, even at lower intensities, is not known.

57.2 City and House Planning

Increasingly more adults, children and teenagers spend their time indoors, at work and leisure. Populations live and act in buildings, in cities, and along their streets. The planning of areas is regulated.

Urban blocks of flats are usually made of steel-reinforced concrete. The roofs, and even the walls, are covered by materials that contain steel or other metals, which do not enable electromagnetic radiation to penetrate, but are reflective. Many small houses made of wood have roofs that contain iron or other metals.

Steel roofs of buildings help to protect the indoor inhabitants from exposure to an outdoor source of electromagnetic radiation. But electromagnetic waves can be reflected on the outer surface of the roof and redirected farther away, exposing others. Radiation from an external source can enter a building through the side walls. Radiation that enters a building is then reflected inside the building. Direct radiation and its reflections can interact, to form standing waves and hot spots. These can hamper the indoor electric processes. Figure 57.2 illustrates reflections of radiofrequency waves outside and inside a house.

Many common building materials enable electromagnetic radiation to penetrate the walls. There are, however, materials that can be used to damp the electromagnetic waves and their reflections. Insulation materials containing aluminium foil

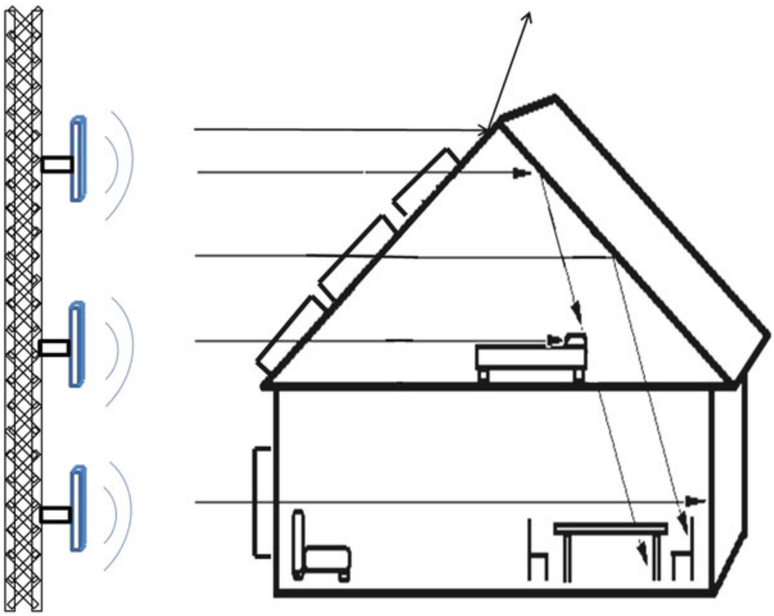

Fig. 57.2 Electromagnetic radiation and common house materials A European-type single family house with steel roof that prevents the penetration of radiation and reflects the radiofrequency radiation to air. However, when the steel structures create odd reflections *inside* the house, radiofrequency radiation gets in through windows (in high power densities)

are effective. If the building contains sensitive systems, it is possible to protect them by steel walls. Therefore, some factories install coverings made from metallic and other specialized materials to block the propagation of electromagnetic waves indoors. There are also metal-containing paints and curtains that limit radiation somewhat, but their efficacy is limited because the protective layer is very thin.

Electromagnetic radiation is emitted from radio and television systems, as well as, in higher frequencies, from radar transmission towers. In many urban as well as rural environments these and other sources, such as electric power lines, are activated all the time. Towers allow the radiation to reach a wide diameter. However, radiation beams are directional. If the beams are directed to the horizon, the immediate proximity of a tower may have lower exposure to the radiation. Negative health effects in the proximity of radiation emitting towers, if found, could be due to coexisting significant environmental exposures, e.g., chemical exposures (Atzmon et al. 2012).

Transmission towers and base stations are often located in densely populated areas. Small base stations, used for cellphone communication, can be found on roofs, on street poles, and inside shopping centers. In some countries, legislation still allows cellphone companies to rent space for use by base stations in vacant apartments or even on people's balconies, sometimes even without notifying the public about this exposure.

Recently, electric energy, water and gas companies have begun installing electronic wireless "Smart meters" instead of analog meters. Such wireless devices, installed on external or internal walls in people's houses, emit pulses of radio-frequency waves all day and all night, several seconds in every hour, or more. Chronic all-day every-day exposure is more likely than short and intermittent exposure, such as cell phone use, to produce harmful health effects. Although the exposure levels may be lower, the accumulated exposure over time has the potential to be greater, and to cause greater harm.

The discussion above has been about radiofrequency radiation and alternating current (AC) magnetic and electric fields. However, in many locations the static magnetic field can be generated or altered by ferrous structures and by direct current (DC) electrical currents. A typical example of this anomaly is a bed with metal springs occasionally causing a substantial DC magnetic anomaly. Man-made pollution created by extensive static magnetic field-generating structures has recently been reviewed and illustrated (Armadillo et al. 2012). Biological cell proliferation and differentiation can be heavily affected by both AC and DC magnetic fields (Portelli et al. 2013). When inspecting health effects, both AC and DC fields need to be measured and understood.

57.3 Testing for Short Term and Long Term Exposures

Exposure to electromagnetic radiation and fields continues, day and night, since radio and television broadcasts are continuous. Electric power lines and switch-boxes emit low frequency electromagnetic waves all the time. Surveillance of traffic, energy and water consumption is constantly transmitted from central locations or via remote “Smart” meters near every home. Electromagnetic waves from such devices, located on the external walls of homes, penetrate the normal building materials, exposing families and pets constantly. Cellphone towers, antennas and base stations emit electromagnetic waves all the time. Many people also expose themselves and their families voluntarily to WiFi wireless Internet network routers in their homes, or they may be exposed by their neighbours’ routers. Wireless technology is installed in coffee shops, at hospitals, in government buildings and large workplaces. In many large cities people are involuntarily exposed even in the streets.

We do not know the cumulative effects of these chronic, long term exposures. Commercial bodies continue to claim that there is no evidence of harm, but much evidence has accumulated, raising questions on the validity of current regulations that take only thermal effects into account and ignore all non-thermal reported health effects and bioeffects.

In required safety tests for cellphone communication, the electromagnetic waves emitted by cellular phones are tested only for short-term effects of heating. In 1975, research determined the heat levels caused by microwave heating that leads to damage to animals. The measurement currently performed is the specific absorption rate (SAR), i.e., the amount of power or heat energy absorbed per unit mass of tissue (Watt per kilogram). In the experiment, trained rats stopped working for food after their whole body exposure reached average SAR of 4 W/kg (D’Andrea et al. 1975).

Specific Anthropomorphic Mannequin (SAM) is the standard model used for radiation testing of mobile devices by their manufacturers. This is a large plastic head mannequin (Beard and Kainz 2004), with an opening at the top of its head, containing a liquid whose electrical permittivity and conductivity parameters are equivalent to the average electrical parameters of the 40 tissue types in the human head (Gandhi et al. 2011). The size of the model head was initially based on the 90th percentile of 1989 United States military recruits (Gordon et al. 1989). The model is exposed to electromagnetic waves in the radio frequency microwave range, from the device being tested, and the currents induced within the salt solution inside the plastic head are measured for 6 min. Then the values are averaged.

There are no official limit values for long term exposures, and therefore they are not measured.

One drawback of this system is that in reality, the human brain is a complicated network made of millions of neurons and other cells. No pathophysiological conclusion can be drawn by the Specific Absorption (SAR) tests recorded in this technique on long-term functions of neural networks. Another problem is that the test does not reflect the physiology of smaller individuals, including women and young children.

A different method for measuring and modelling tissue absorption using computational electrodynamics is the Finite-Difference Time-Domain (FDTD) method. According to several authors, the finite-difference time-domain (FDTD) algorithm is the most widely accepted computation method for SAR modelling, because this method simulates more anatomic tissue models derived from MRI or CT scans (Chan et al. 1997; Gandhi 2002; Gandhi et al. 2011). In the FDTD method, every cell is modelled according to specifically defined tissue characteristics. The area around the head is also modelled. This way, the interaction between different tissues and the emitting source are seen in the model, and we can identify "hot spots" in the tissues, which are areas that absorb more energy. The FDTD computer simulation cell phone certification process is immediately available and provides three orders of magnitude higher resolution than the SAM-based system for the head.

A serious health risk not taken into account by modern wireless technology is that functional neural networks take about two decades to develop in humans, beginning prenatally and continuing throughout childhood. In modern life, cell phones, radiation emitting tablet devices, computers, WiFi and other sources radiate all the time near the child's and teenager's constantly developing tissues. Brain neuronal networks must make an unnatural effort to meet the electric challenge in response to the abundant electrical signals of the environment, i.e., electromagnetic noise.

The best protection against exposure to radiation and electromagnetic noise is distance from the body. Radiation decreases in the distance squared. Terrain affects and especially rocks can provide measures of safety.

57.4 Mobile Technology

People use mobile technology to run their daily personal and business matters. Cellular phone and tablet devices are often kept in skin contact. Mobile computers, emitting electromagnetic waves, are held in people's laps, near their reproductive organs.

Wireless communication devices interact with transmission and receiver stations. Traditional high radiofrequency transmission towers are often complemented by smaller base stations. Both types are active day and night. Exposure from base stations depends on distance, direction, and use. If more personal mobile devices are sending and receiving data via the base station, it emits more radiation. The density of base stations is high in the cities, allowing the supply of fast mobile communication speed to more people. In rural areas the distance to the base station is greater. Therefore, the transmitted connecting signals from the personal devices must be stronger to reach the base stations and the receivers. The greater the distance, the more energy is needed in contacts.

As industry offers more and more services via wireless, people forsake the option of landline and wired communication and embrace the convenience of wireless technology, disregarding the warnings of potential hazards (Häninen et al. 2007). Medical associations have expressed concerns about the levels of electromagnetic load to which people are exposed. For instance, the Austrian Medical Association recommends that microwave radiation exposure levels should be less than 10 uW/m^2, one millionth of the limit value currently allowed in Finland (e.g. Johansson 2009).

Children are constantly exposed to electromagnetic radiation from cellphones carried by other children and by wireless Internet at school. Schools are areas where radiation limitations are important, as are homes, especially bedrooms. Constant exposure to electromagnetic fields from the proximity of mobile devices and their chargers, networks induced by routers, and exposure from Smart meters or external base stations can affect the learning process, disturb night sleep, and hamper the normal development of the brain.

57.5 Symptom Based Bioindication in Humans

Humans absorb electromagnetic signals and act as receiving antennas as shown in Fig. 57.1.

Humans are actually one of the most useful sensitive bioindicator species, as they are constantly exposed. In addition to measured reactions and health statistics, people can also express their sensations (Huttunen et al. 2009). Human data banks provide possibilities to follow health developments in different areas. In Sweden, it has been reported that the general public health markers have deteriorated with the increase in electromagnetic exposure (Hallberg and Johansson 2009).

Feldman et al. (2008, 2009) and Safrai et al. (2012) have suggested a unique environmental indicator for remote sensing of physiological effects in humans and primates. Eccrine sweat ducts in human skin are helically shaped tubes, filled with a conductive aqueous solution. The skin spectral response in the sub-Terahertz region is governed by the level of activity of the perspiration system and shows the minimum of reflectivity at some frequencies in the frequency band of 75–110 GHz. It is also correlated to physiological stress as manifested by the pulse rate and the systolic blood pressure. The technology for remote sensing of this physiological signal is under development.

It is important to note that human exposure to emissions in the sub-Terahertz frequency band may interact with this physiological mechanism, causing perception of pain or other yet unrecognized health-related or psychological consequence.

57.5.1 Oxidative Stress, Increased Brain Metabolism, and Cognitive Effects

Radiofrequency and microwave fields from mobile phones held close to the body have been shown to increase free radicals, especially in neural cells. These free radicals appear to enhance mainly lipid peroxidation, and change the antioxidase activities of human blood, thus leading to oxidative stress (Moustafa et al. 2001; Aitken et al. 2006; Friedman et al. 2007; Campisi et al. 2010.)

Volkow et al. (2011) demonstrated direct effects of RF radiation on the brain with cell phone use. In healthy participants, 50-min cell phone exposure was

Table 57.1 Reported main symptoms of electromagnetically hypersensitive persons during their acute phase (194 returned valid responses, 80.9 % women and 19.1 % men) (Hagström et al. 2013)

Symptom	%
Stress (nervous)	60.3
Sleeping disorders	59.3
Fatigue	57.2
Concentration problems	56.7
Memory problems	54.6
Anxiety	52.6

associated with increased brain glucose metabolism in the region closest to the antenna – as compared with no exposure.

Effects on sleep and cognitive performance in humans have been described by Regel et al. (2006–2007) and Hutter et al. (2006), as well as symptoms, such as Alzheimer's disease, migraine and vertigo (Huss et al. 2009 and others).

Highly electromagnetically exposed people complain of one or more of the symptoms described in Table 57.1, mostly due to neural-related problems. Many people connect their symptoms with their exposure to different sources, such as mobile phones, cordless phones, mobile phone stations, other electric appliances, television, computers, TV and radio broadcasting, and microwave ovens (Hagström et al. 2013). Cardiac arrhythmia has been reported by some to be increased when becoming sensitive, but this may also be due to increased age. The prevalence of implanted pacemakers increases steadily, e.g., in Finland, but again this may be due to population aging.

57.5.2 Cardiovascular System

Easiest to quantify are the cardiovascular and respiratory cycles. Cardiovascular responses are easy to register. Ancient Chinese traditional medicine has done so for 3,000 years or more Huang Ti Nei Ching Su Wen (1992). In ancient Chinese medicine the examiner compares the findings with his own pulse i.e. heart rate and arterial tonus, with respiratory cycles (Huang Ti Nei Ching Su Wen 1992, Veith 2002). Electrocardiograms are easily recorded by skin contact electrodes, or the signal can be recorded by mobile networks from a distance, even through a telephone connection. The blood pressure and respiratory cycles can be recorded remotely, although this is seldom done. With computer programs readily available, more data can be obtained and analysed. Figure 57.3 illustrates some cardiovascular responses to activation of a mobile phone in a person carrying a pacemaker.

57.5.3 Reproductive Effects

Animal studies indicate that electromagnetic radiation may have a wide range of damaging effects on the testicular function and male germ line (Dasdag et al. 1999; Davoudi et al. 2002; Mailankot et al. 2009). Men who used their cell phones the

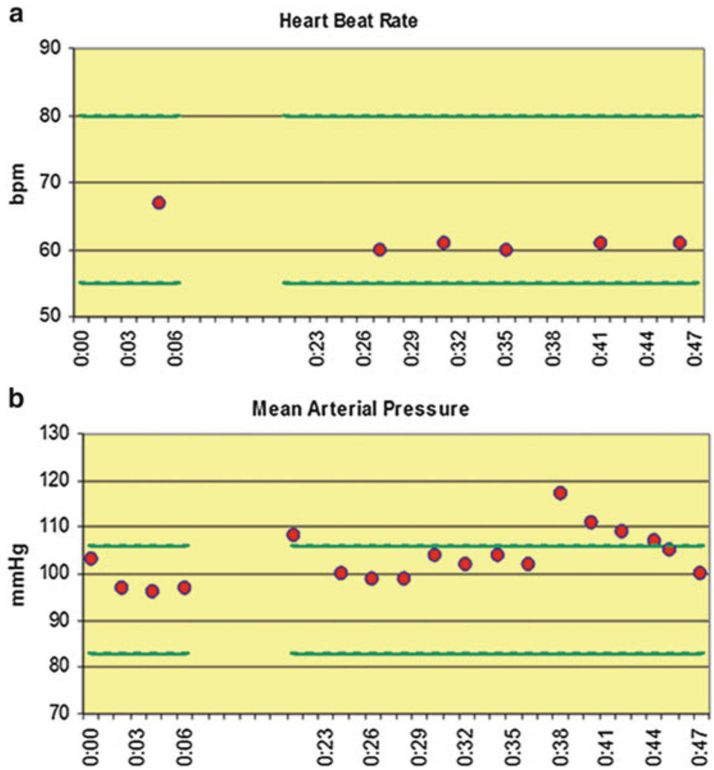

Fig. 57.3 The cardiovascular responses (heart rate (**a**) and mean arterial pressure (**b**)) in a person carrying a pacemaker, when a silent mobile phone was turned on and off to enable the phone to make contact with its base station. This experiment was performed in a laboratory Faraday cage. The phone was placed behind the occiput of the blinded person (Hänninen et al. 2013, reproduced with the permission of the Journal)

most had significant poorer sperm quality than those who used them the least. The lowest average sperm count was found in men who used their cell phone more than 4 h a day (Agarwal et al. 2009).

Purified human spermatozoa exposed to raised levels of RF/microwave radiation exhibited significantly reduced sperm motility and vitality (De Iuliis et al. 2009). Use of mobile phones may have a harmful effect on male and female fertility (Erogul et al. 2006; Wdowiak et al. 2007; Gul et al. 2009).

57.6 Electrohypersensitivity and Multiple Chemical Sensitivity

The interaction of electromagnetic fields with biological systems is known at different levels, but understanding and unravelling the cumulative effects are a big challenge (Blank 2009; Bioinitiative report 2012; Carstensen 1987).

Manmade radiation is constantly turned on, for example radio and TV transmissions, military, police and rescue personnel communication systems and naval systems. It has been shown that pulsed fields have an effect on the EEG and the central nervous system (Bawin et al. 1975; Rea et al. 1991; Marino et al. 2003).

One can expect to see responses in different species and in humans due to the electromagnetic changes in the environment that have taken place in recent decades. As we know, there is biological variation regarding human sensitivity and hypersensitivity to allergens. The brain has a central role in the allergy response. After hypersensitivity is initially triggered, the allergic or hypersensitive response to different allergens can broaden to include new agents, varying from chemical to physical agents and vice versa.

After a person has developed hypersensitivity to a chemical or to a certain frequency of electromagnetic waves, the patient's pattern of response stays the same whether the trigger is chemical, biological, particulate, nutritional, or electrical – it is characteristic of the patient. Typical subjective symptoms that have been described are drowsiness, malaise and headache, mood swings, tearfulness and eye pain, poor concentration, vertigo and tinnitus, numbness and tingling, nausea, convulsions, noise sensitivity, alteration in appetite, visual disturbances, restlessness, blushing, and muscle pain (Hagström et al. 2013; Bioinitiative report 2012).

Wireless networks, such as WLAN, Wi-Fi etc., in offices and in many homes, and wireless radiating Smart Meters, increase the environmental irradiation load. Indoor sources of radiofrequency waves, such as those emitted from portable computers connected to a network, or sources of electromagnetic waves in other frequencies, such as high frequency voltage transients from electricity lines, add to this load (Milham 2010).

A multitude of electronic devices is used every day in the homes for various tasks. Many of these devices also emit stray electromagnetic waves that have no useful function. The electric lines carry long distances transients, which are harmful. High frequency voltage transients affect individuals with Multiple Sclerosis, may elevate blood sugar levels among people with diabetes and prediabetes conditions, and contribute to triggering Electromagnetic hypersensitivity (Havas 2006).

Figure 57.2a gives the electromagnetic spectrum of a commonly used computer and Fig. 57.2b shows the huge increase in electromagnetic radiation of the attached WLAN in another computer (note the logarithmic scale).

57.7 Electrohypersensitivity – Recovery Is Possible

When a person has become sensitive, the first step towards recovery is to minimize the electromagnetic exposure. Many people who have become electromagnetically sensitive have previously suffered allergies to other agents, and know that they should avoid these exposures. Most important is to keep sources of electromagnetic waves such as mobile phones, TV sets, and computers turned off when not in use.

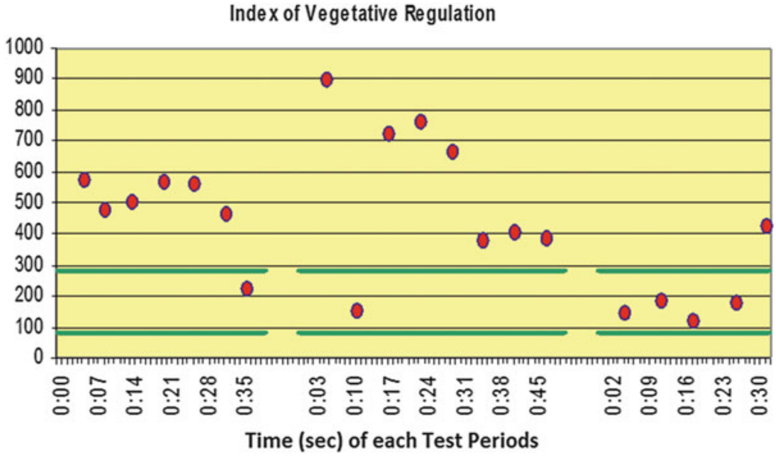

Fig. 57.4 Avoidance of electromagnetic exposure in a rural cottage outside a city. The cardiovascular abnormality of a sensitive person normalized in several weeks at least partially. The recordings of the heart rate and blood pressure were made in a Faraday cage, calculating the Index of Vegetative Regulation (Hänninen et al. 2013, reprinted with permission of the Journal)

Unfortunately, base stations and wireless networks cannot be turned off by individuals who wish to avoid this exposure, and therefore regulations must limit the installation of electromagnetic radiation emitting sources near people's homes, or near schools, where children, who are highly sensitive to all exposures, will be exposed. Figure 57.4 illustrates cardiovascular hyperactivity in an electrohypersensitive individual, and reduction of this response after avoidance of electromagnetic exposure for several weeks.

The major mobile phone producers have regularly issued warnings to their users, urging them not to keep their active mobile phones in skin contact. This may indicate a new turn in their attitude, possibly as an outcome of their failure to get health-related insurances for their products. However, these warnings are written in small font inside the device's user manual and therefore are not read by most users (Davis 2010).

Some devices emit more electromagnetic waves than others. Figure 57.5 compares the radiation spectra of two Hand Held Tablet Personal Computers. One device has extremely high emissions that cannot be tolerated by an electrohypersensitive person. The other device emits lower, more acceptable levels.

In the countryside one can find niches, e.g., rock surrounded valleys, where the electromagnetic load is weaker. The radiation "silence" can be recorded using the person her/himself as the antenna (see also Fig. 57.1). Food rich in essential components, such as amino acids, unsaturated fatty acids, vitamins and other elements, increases the endogenous defence against the attacks of oxygen free radicals.

One can also reduce the penetrating radiofrequency radiation by paint on walls and curtains with conducting threads in accordance with electric safety regulations in different countries. If the person avoids electromagnetic exposure

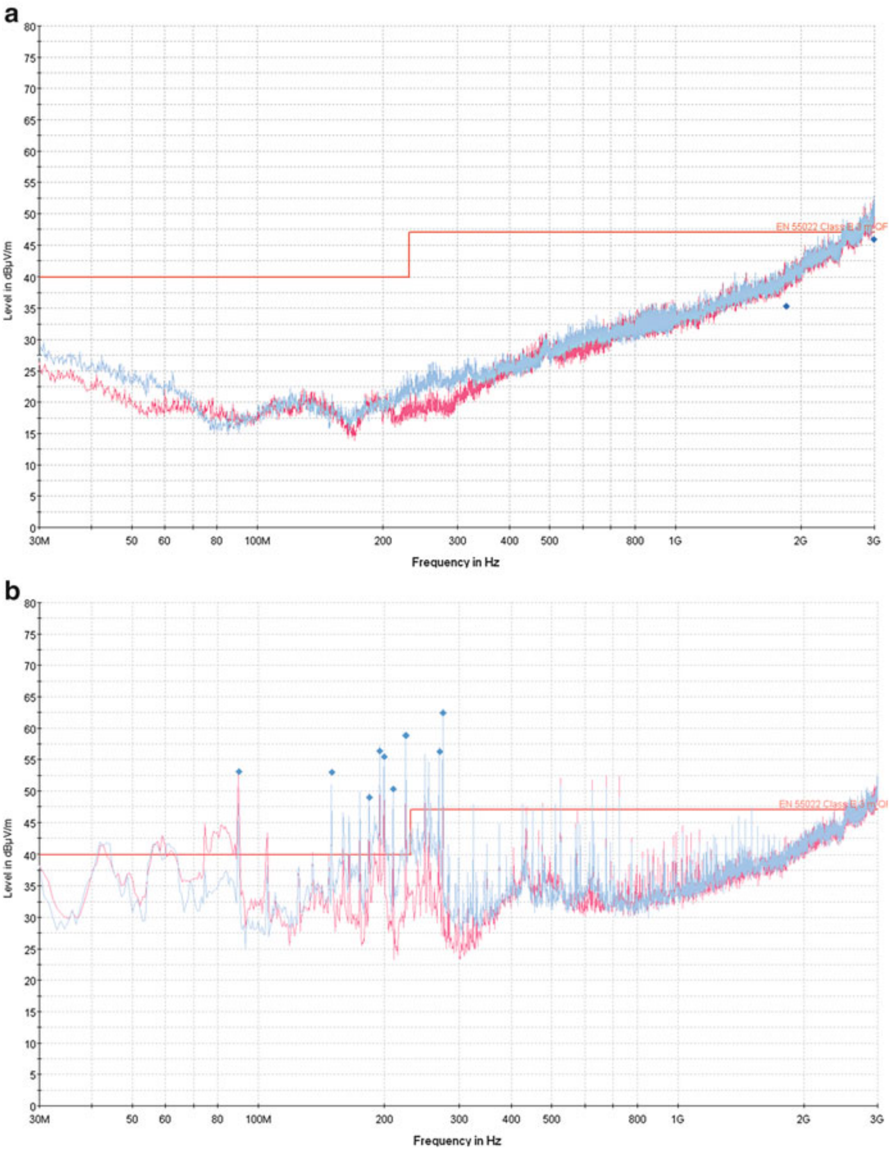

Fig. 57.5 Radiation spectra of two Hand Held Tablet Personal Computers measured in a Faraday room of a Radio laboratory. European Union EMC directive emission standard EN 55022 is indicated by the thin horizontal *red line*. According to the directive, one cannot sell dators exceeding this line, but these emissions were much exceeded in the lower tracing (**b**) of one tablet sold in Finland and sensitized persons cannot use it. The *upper curve* (**a**) shows that some devices emit more acceptable levels and can be used more safely

and uses nutritional supplements, positive results of reduction in hypersensitivity symptoms may be expected within about three months (Hagström et al. 2013, and Hagström, personal communication).

57.8 Discussion – Human Effects as Environmental Indicators

There are various ways to document the human abnormalities and effects caused by electromagnetic exposure. As the direct recording of the antenna function of the human body is possible, this would be recommendable, in order to demonstrate the exposure and to correlate body effects or responses with the absorbed radiation (Fig. 57.5).

As the skin is directly exposed to electromagnetic load, one can expect the greatest changes there, as one would expect skin cancers in skin exposed to the sun. Skin cancers are common, including melanoma, which has increased, possibly due to sunbathing. The electromagnetic exposure of a person can be detected by recording the signals directly, to identify the irradiation sources currently activated. For example, signals from the fingers during typing on a keyboard, as seen in Fig. 57.6.

In the skin or near it are various types of glands and glandular tissue. The breasts are a type of glandular tissue. The incidence of breast cancer has been rising and rising in the Western world. The causes of breast cancer are multifactorial. While the specific triggers for eruption of the disease in each person is difficult to specify, electromagnetic waves that have the ability to affect cells and chromosomes may act as an added factor or a catalyst in this morbidity.

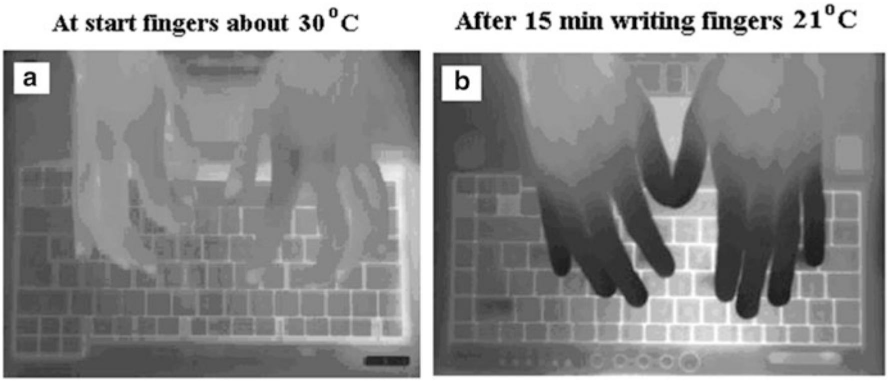

Fig. 57.6 The finger temperature of a sensitized person recorded by infrared camera during typing a heavily radiating laptop computer. While the increasing temperature can be seen from the keyboard the temperature of fingers was cooling. At the same time the person sensed pain and the hands got clumsy (Hänninen et al. 2011, J. Environmental Sciences, with permission of the journal)

The salivary glands are relatively superficial, near the skin. The parotid gland is particularly exposed to electromagnetic waves in the RF/MW range, due to the use of mobile phones near to, or in skin contact with, the ear and the head. A study from China has shown that parotid cancers have recently increased some 30-fold (Duan et al. 2011). A recent study from Israel (Czerninski et al. 2011) demonstrated that the total number of parotid gland cancers in Israel increased four-fold from 1970 to 2006 (from 16 to 64 cases per year), whereas other major salivary gland cancers remained stable.

Glandular cells are more exposed than cells of the central nervous system, i.e., the brain and the spinal cord. The brain is protected by the skull. Nevertheless, the incidence of brain tumours has doubled during the last decades, since the introduction of mobile telephony. A recent study demonstrated that use of a mobile phone for a total of 1,600 h seems to double the incidence of acoustic neuroma. Gliomas and astrocytomas are more common on the side of the head where the electromagnetic wave load has been greater than on the other side, i.e., the side that the person uses the phone (Hardell et al. 2010, 2013). A large epidemiological study found greater odds ratios for acoustic neuroma in those who used cellphones for 1640 and more cumulative hours. In some cases, use of over 5 h a day was reported (Interphone Study Group 2011). The tumour morbidity is expected to grow in the future, as young children actively use mobile phones extensively.

The permeability of the blood brain barrier against the entrance of harmful molecules has been shown to increase after mobile phone radiation exposure (Nittby et al. 2009). Children are especially susceptible to this effect, since the protective skull grows until the bone sutures have closed, and skull bone thickness continues to increase until adulthood (Gandhi and Kang 2001).

A unique mechanism in which electromagnetic waves of a specific frequency (Sub-terahertz) can enter the body through the skin is directly via the eccrine sweat glands that are found over most areas of the skin, in humans and primates (Feldman et al. 2009). The exact physiology and mechanism of function of this recently discovered frequency-specific biological sensor is currently being researched.

Biochemical responses in humans and other creatures can by analysed as indicators, e.g., hormones, such as cortisol, and melatonin (Burch et al. 1999). The release of iron has also been used as an indicator for effects and responses to exposure to both radio frequency and low frequency electromagnetic waves (Allen et al. 2000; Cespedes and Ueno 2009). The first step in this process is probably activation of plasma membrane NADH oxidase and generation of oxygen free radicals, followed by activation of protein kinases (Friedman et al. 2007). Fragmentation of DNA and other types of DNA damage have been shown to occur (Ahuja et al. 1999; Cohen et al. 1986; Phillips et al. 2009; Campisi et al. 2010) and genotoxic effects are expressed (Ruediger 2009). The exposure to electromagnetic waves also activates the synthesis of heat shock proteins which act as chaperons and transmute the three dimensional structures of proteins (Blank and Goodman 2009). These cause changes in cellular metabolism and can be seen also in the proteome findings. There may be differences between the responses to exposure to different wave lengths (Nylund et al. 2010).

Measurements help to quantify the sensations reported. For instance, a decrease in skin temperature is a sensation that a number of people have reported, and it can be followed with the aid of infrared thermography of the fingers. The person who is being monitored can report when feeling pain in the fingers and also the sensation that their hands are becoming clumsy, qualities that are more difficult to measure. Figure 57.4 a, b shows how exposure to electromagnetic waves constricts the circulation in the fingers and cools them within a few minutes to room temperature, although the computer induces heat that is expected to warm the fingers. Other people have reported a sudden feeling of heat in the head or neck or a sharp sensation of pain after exposure to electromagnetic waves. Huttunen et al. (2011) have reported Involuntary human hand movements due to FM radio waves. A testing mechanism should be developed to examine these phenomena.

Phone conversations while driving and especially text messaging distract the driver's attention. This affects the driver mentally and can cause car crashes (Drews and Stayer 2004; McEvoy et al. 2006).

Humans can sense the standing waves of some radio transmissions. People feel these waves in the form of a spontaneous muscle contraction. Some more sensitive individuals seem to be able to sense the differences of standing waves in different wavelengths, with a unique sensitivity, almost as most of us can differentiate between colours (Huttunen et al. 2009). Such people are specifically frequency sensitive.

57.8.1 Occupational Data on Human Exposure to Electromagnetic Fields (Mostly in Military Settings)

In 1972, Glaser published a 106 page report for the US Naval Medical Research Institute, reviewing over 2,300 articles (Glaser 1972) that assess biological responses and effects of non-ionizing radiation on humans. Many of these effects had been called microwave sickness. He classified the biological effects into 17 categories, listing both thermal and non-thermal effects. These include: changes in physiologic function such as blood and vascular disorders, biochemical changes (enzymes and others), metabolic, gastro-intestinal, and hormonal disorders, alterations in the nervous system, histological changes, genetic and chromosomal effects, psychological disorders, behavioural changes in animal studies, and others.

Cook et al. (1980) and Steneck et al. (1980) on research published during the years 1940–1960 in Russia and East Europe on the biological effects of microwave radiation. Justesen et al. (1978) presented research on health effects of nonionizing radiation to the United States House of Representatives.

In 1996 and 2001, Szmigielski published data on cancer morbidity of military personnel occupationally exposed to electromagnetic radiation from radar for a follow up period of 20 years (Szmigielski 1996; Szmigielski et al. 2001).

Grayson and Lyons (1996) found a slight excess risk for brain tumour after exposure to electromagnetic radiation (ELF and RF/MW) in the US air force. Robinette et al. (1980) looked at 20,000 US Korean War Naval Veterans 1954–1958 with occupational exposure to radar. The subgroup defined as the most intensely exposed, Aviation Technicians, had the highest level of crude death rates per 1,000. Groves et al. (2002), in a follow-up study of Robinette's cohort 40 years later, reported a difference in one high-exposure occupation group out of three, in which rates of non-lymphocytic leukemia were significantly elevated.

Degrave et al. (2005, 2009) found an excess incidence of hematolymphatic cancers in two retrospective cohort studies in Belgian male military personnel exposed to anti-aircraft radars in Western Europe between the 1960s and 1990s (Goldsmith 1995, 1997).

Occupational exposures to EMF have also been described by Goldsmith. In his report of 1997, Goldsmith presents evidence of chromosomal changes in lymphocytes cultured in vitro from employees who had worked in the U.S. embassy and had been unknowingly exposed to low levels of radiofrequency/microwave radiation.

Richter et al. reported exposures and cancers in several sentinel patients in a cluster of such workers and in patients. Some of the patients presented with brain cancer with short latent periods of less than 10 years (Richter et al. 2000, 2002).

Stein et al. (2011) reported a sentinel case series of 47 cancer patients, who had been occupationally exposed to RF/MW or ELF, in various mostly in military settings. Data analysis suggested a coherent and biologically plausible pattern of cancer latency in relation to the onset of exposure to EMF and accompanying agents, since latent periods for testicular tumours were very short, the latency was longer for Hemato-Lymphatic cancers and still longer in solid tumours.

57.9 The Precautionary Principle

The Precautionary Principle is a notion which supports taking protective action before there is complete scientific proof of a risk; that is, action should not be delayed simply because full scientific information is lacking. The precautionary principle or precautionary approach has been incorporated into several international environmental agreements, and some claim that it is now recognized as a general principle of international environmental law.

Currently, safety thresholds for electromagnetic exposure of the general public are being set mostly by engineers, not by public health experts, and are based on thermal effects only, totally ignoring reported bioeffects.

In view of the Precautionary Principle, the prudent conclusion is to reduce exposure of susceptible members of society, such as children, pregnant women, the sick and elderly and electrohypersensitive individuals, as a protective measure until the safety of the exposures is proven.

Conclusions

Ever-growing manmade electromagnetic radiation and fields cover the globe. This load has increased rapidly, by orders of magnitude, due to increasing mobile telephony, distant recording of services such as electricity and water services using wireless "Smart" meters, and Internet Wi-Fi networks applied in public spaces, including mandatory exposure of children in schools. All organisms are exposed to different degrees. Humans and other creatures serve as antennas. All people are passively exposed at least to some degree, but many are exposed much more, due to the active use of mobile telephones of other citizens including their neighbours at their homes.

Examples of animals, plants and humans indicate that they are harmfully affected. Human questionnaire surveys and epidemiological studies provide increasing evidence of risks of increased morbidity. Electrohypersensitivity is becoming more common. The worst signs are studies showing DNA damage and increased carcinomas.

Birds are able to leave high exposure areas. Humans seem to be able to recover, if they diminish use and avoid the presence of active radiating devices, or flee to radiation-free zones. Children need increased concern. The Precautionary Principle signed by many nations should be used and observed.

Acknowledgements This work was supported in part by the Environmental Health Trust, a non-profit and policy organization, and by the Yael Piton fund for support of research in Environmental Studies.

The occupational data was collected together with Prof. Richter from the Unit of Occupational and Environmental Medicine, Hebrew University – Hadassah School of Public Health.

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Chapter 58
Molds and Radon, Indoors Problems as Indicated by Diseases

Heikki Elonheimo, Osmo Hänninen, and Robert H. Armon

Abstract In old times people were aware of the health problems caused by visible mold marks on room walls. The prophet Moses instructed that such rooms must be emptied, cleaned, whitewashed and left empty for a while. If the mold marks still reappeared, the whole construction had to be demolished, and materials mold colored removed out of town. Such problems are still with us today. Many buildings are built in haste and not let dry well before use. Basement and floors interact with soil moisture and its microbes. Also roof and pipeline leaks can bring in biological harms as the mold growth is seen in few days in the worst scenario. Some people are sensitive to mold allergens and have serious health problems in such environments and have to seek new homes in healthier buildings. Radon that cannot be sensed promotes cancer development in inhabitants of buildings especially in smokers. Under very cold or hot weather conditions, homes need heating or cooling respectively both under close environment in order to preserve energy. For example in Finland, Finnish regulations require hypobaric condition to save energy. This pressure gradient sucks in radon, molds' spores, their toxins and allergens through leaks in the basements, floors, walls, windows and roofs' openings, waste pipes and electricity lines. Indoor hyperbaric pressure can prevent entrance of environmental allergens, dust, molds, and other toxicants and radon too and also helps drying the interiors. With present day sensors information can be collected from buildings, flats and even sole room to make safer indoor stay.

Keywords Indoor • Contamination • Mold • Radon • Allergens • Health problems

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DOI 10.1007/978-94-017-9499-2_58

58.1 Introduction

Traditional log buildings and their inhabitants were exposed to natural air streams. These houses were also above ground when standing on their basement stones to diminish exposure to natural radon or other radioactivity source. In this building type (not air tight), air flows could penetrate practically all indoor spaces. These log buildings are still popular, as logs balance the in and out air moisture transfer.

At present, the majority of buildings like brick as also wooden houses are built on concrete plates. They can also have extensive underground cellars (Ocon et al. 2011), parking lots etc. Soil moisture as rain water removal is recognized as an important condition for building health. Unfortunately these facts are often forgotten during short times of allotted tight buildings. Nowadays the buildings are also made physically air tight to save costly energy, which in turn may introduce harmful molds.

Presently there are simply usable sensors and computerized guidance to help control the ventilation, temperatures, humidity, spores, allergens and various toxicants and remove dust particles with proper filters and adjust the conditions optimal to meet the inhabitants' needs (even in each room and also to convey the basic levels of different parameters down when a room or the whole building is empty).

The expenses of buildings repairs are high. For example, in Finland the expenses are estimated to equal the national annual governmental budget (!) (indicating that repairs require years to happen with proper planning as necessary). The housing health should actually be a part of health education like immunization plan against common infectious diseases. Table 58.1 reveals that molds and their spores are among the key players in ruining peoples' health in many private houses including larger ones (multi-story ones).

Table 58.1 Hazardous sources biological, chemical, physical factors, dust and burning wood etc. used for heating and cooking and found in indoor air (Bernstein et al. 2008; Dales et al. 2008; Hulin et al. 2012). Let us remember that smoking is distributing carcinogens and should not be permitted indoors (Groves-Kirkby et al. 2011; Doll and Peto 1981; Scheepers 2015)

Source	Pollutant
Cooking and heating	CO, CO_2, NOx, PAH (polyaromatic hydrocarbons)
Dust (traffic and other harmful particles)	
Moisture and molds	Spores, toxins, aldehydes like compounds
Radioactive radon and uranium	Carcinogens in building materials and houses
Smoking	Carcinogenic materials and particles
Solvents and polymers	Carcinogenic volatiles

58.2 Impairments of Household Air

Around three billion people cook and heat their homes using open fires and simple stoves while burning wood, animal dung, crop waste as well as coal. In poorly ventilated dwellings, indoor smoke can have 100 times higher levels of harmful small particles than acceptable (Hulin et al. 2012). Women and youngsters are especially exposed at home. According to World Health Organization (WHO), 4.3 million people die yearly due illnesses attributable to household air pollution caused by inefficient use of solid fuels. Among these fatalities: 12 % are attributed to pneumonia, 34 % to stroke, 26 % to ischemic heart disease, 22 % to chronic obstructive pulmonary disease (COPD), and 6 % to lung cancer. Exposure to household air pollution almost doubles the risk for childhood pneumonia. Over half of deaths among children less than 5 years old from acute lower respiratory infections (ALRI) are due to particulate matter inhaled from indoor air pollution from household solid fuels. There is also evidence of links between household air pollution and low birth weight, tuberculosis, cataract, nasopharyngeal and laryngeal cancers. Approximately 17 % of annual premature lung cancer deaths in adults are attributable to exposure to carcinogens from household air pollution caused by cooking with solid fuels like wood, charcoal or coal. The risk for women is higher, due to their role in food preparation. However, active and passive smoking is, the main risk factor at homes, controllable by the people themselves (Hirayama 1981; WHO 2014a, b).

Too often and too commonly one can see rotten parts of houses in different corners of the world. Figure 58.1 (from Finland) illustrates an indoors source of molds and their spores, microbes and different toxins and allergens that use as seeds of diseases for humans and their pets.

WHO is leading efforts to evaluate which new household cooking technologies and fuels produce the least emissions, optimal for good health. WHO is also providing technical support to countries in their own evaluations and scale-up of health-promoting stove technologies.

The WHO Household Energy Database is used to monitor global progress in the transition to cleaner fuels and improved stoves as well as contribute to assessments of disease burden from household energy and energy access situation in developing countries.

WHO has recently reported on 4.3 million global deaths attributable to household air pollution (HAP). In 2004 an estimate ~2 million deaths took place from HAP (Fig. 58.2) (WHO 2014a). The large increase had been suggested to be related to several factors: (1) additional health outcomes were included in the new analysis such as: cerebrovascular diseases and ischemic heart disease (Smith et al. 2014) (Fig. 58.3); and (2) supplementary evidence on the relation between exposure and health outcomes and the application of integrated exposure-response functions (Burnett et al. 2014) and (3) estimated global increase in non- communicable diseases. An aerial mineral sensing has taken place due expectations of mining possibilities in many countries. There are publicly available maps on the rock beds

Fig. 58.1 Rotting corner of a wooden house due to frequent water leakage from roof

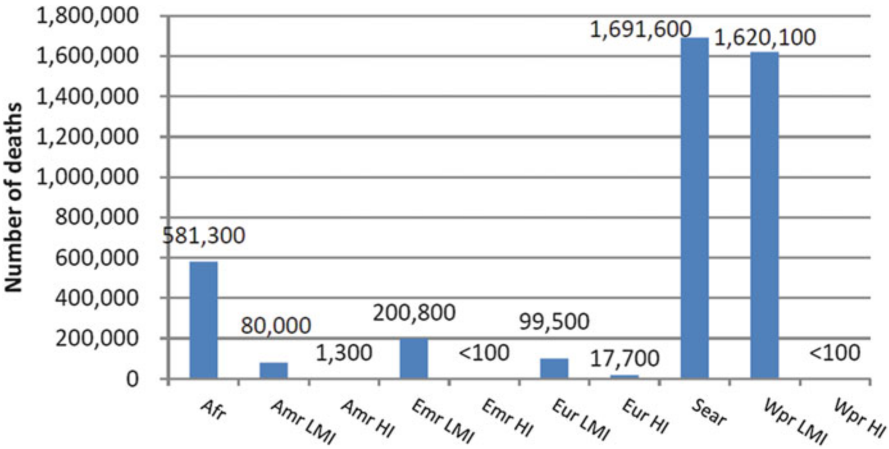

Fig. 58.2 Total deaths attributable to HAP in 2012, by region. *HAP* household air pollution, *Afr* Africa, *Amr* America, *Emr* Eastern Mediterranean, *Sear* South-East Asia, *Wpr* Western Pacific, *LMI* low- and middle-income, *HI* high-income (with permission from WHO 2014a)

and other soils which indicates a danger of radioactivity due to uranium and its physical decay products like radon. These health risks of miners are known (Möhner et al. 2010). The health of buildings has been mapped e.g. in Finland like in all Nordic countries nationwide.

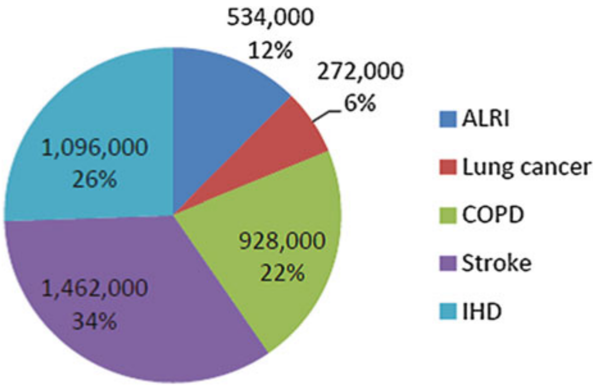

Fig. 58.3 Deaths attributable to HAP in 2012, by disease. Percentage represents percent of total HAP burden (add up to 100 %). *HAP* household air pollution, *ALRI* acute lower respiratory disease, *COPD* chronic obstructive pulmonary disease, *IHD* ischaemic heart disease (with permission from WHO 2014b)

58.3 Molds in Household and Diseases

There are several mold types that are commonly reported as a hazard in households: *Cladosporium* sp., *Penicillium* sp., *Alternaria* sp., *Aspergillus* sp. (Table 58.2). In a recent report by WHO presented as a review of epidemiological evidence, the authors based on a previous review by the Institute of Medicine and the quantitative meta-analysis of Fisk et al. (2007) concluded that "there is sufficient evidence of an association between indoor dampness-related factors and a wide range of respiratory health effects (Table 58.2), including asthma development, asthma exacerbation, current asthma, respiratory infections, upper respiratory tract symptoms, cough, wheeze and dyspnea". However, the authors emphasized that due to "limited data, broad lumping of diverse risk factors and multiple unverified assumptions", they should be interpreted cautiously; however, they do indicate that dampness-related risk factors may contribute substantially to the burden of respiratory disease (WHO 2009).

58.4 Biomarkers for HAP

Rylance et al. (2013) has summarized the potential promising biomarkers and their physiological relevance for the detection of household air pollution (HAP) (Table 58.3). Most of these biomarkers still have to be validated in large prospective studies as at the moment there are insufficient data.

It is estimated in Finland that molds form a problem in some 2.5–5 % of office space, in 7–10 % small living houses and in hospitals up to 20–26 %. These figures indicate that there are many problems already encountered and economic losses are significant as the repairs and the problem corrections are highly expensive and need much time to occur. For example, there is also need of space to keep functions running when repairs take place (e.g. offices building). It is also common that repairs are not always successful, and the advices already given by Moses in The Bible are to be implemented: final demolition (Moses, 2nd century BCE).

Table 58.2 Common household molds and their health effects

Mold type	Pathogenicity	Human health effects	Toxins	Other features
Cladosporium	Rarely	Skin and toenails infections, besides sinusitis and pulmonary infections	No major mycotoxins	Production of volatile organic compounds (VOCs) characterized by odors
Penicillium	Rarely. The thermally dimorphic *Penicillium marneffei*, from Southeast Asia	A threat of systemic infection into AIDS patients	Ochratoxin A by the species *Penicillium verrucosum*	
Alternaria	Rarely, mostly allergen	Common allergens in humans causing hay fever or hypersensitivity reactions that may lead to asthma Opportunistic infections in immunocompromised AIDS patients	A variety of toxic compounds (unknown for their action)	Normal agents of decay and decomposition. Ubiquitous spores are airborne and found in the soil and water, as well as indoors and on objects
Aspergillus	Aspergillosis caused by *Aspergillus*. *A. fumigatus* and *Aspergillus clavatus* subtypes associated with paranasal sinus infections as most common aspergillosis	Symptoms include fever, cough, chest pain, or breathlessness, (common in many other illnesses, therefore diagnosis maybe difficult). Susceptibility of weakened immune systems patients or with other lung conditions	*A. fumigatus* and *A. flavus*, produce aflatoxin (a toxin and a carcinogen), that contaminates foods such as nuts, peanuts, etc	More than 60 *Aspergillus* species are medically relevant pathogens For humans there is a range of diseases such as infection to the external ear, skin lesions, and ulcers classified as mycetomas

58.5 Roofs

All buildings need roofs as rain and sun protection. Old buildings had stone roofs. More common buildings have tiles either of burned clay or cement and also different tar impregnated materials has been historically made to enhance waterproofing as still used these days.

Presently steel is also a common roof material. It prevents effectively rains to enter the building, if uncorroded. Steel roofs block also the penetration of radiation used by the radio transmissions like mobile phones and their antennas. Unfortunately it works also in the opposite direction, i.e. steel roofs may also reflect

Table 58.3 A summary of promising biomarkers and their physiological relevance to detect HAP

Parameter	Biomarkers	Physiological relevance
CO-charcoal burning	Exhaled CO/transcutaneous COHb	Atherosclerosis and fetal effects may be explained due to High CO
Methoxyphenols-pyrolysis of lignins	Urinary syringyl methoxyphenols	Unmetabolized urinary product
Levoglucosan-burning of cellulose and starches		
1-Hydroxypyrene (1-OHP)- Incomplete combustion of biomass or fossil fuels	Urinary 1-OHP	Polyaromatic hydrocarbons acknowledged to be carcinogenic
DNA methylation-active tobacco smokers in pregnancy	DNA methylation in newborns	Long term epigenetic effects (e.g. ischaemic heart disease)
		Methylation effects on genes' promoters for inflammatory pathways (e.g. iNOS)
Malondialdehyde (MDA), 8-isoprostane- peroxidation of polyunsaturated lipid and interaction of arachidonic acid and free radicals, respectively	MDA and 8-isoprostane measured in urine, serum and exhaled breath condensate	HAP products are known to cause oxidative stress including lipid peroxidation and DNA strand breaks
Animal models- for chronic exposures	Different enzymes elevation	Pulmonary chronic exposure
Aldehyde-protein Compounds- Acrolein, an unsaturated aldehyde products of hydrocarbon burning	Specific metabolites (of lipid peroxidation such as Acrolein) affecting	Activation of pro-inflamma-tory signaling through NF-κ B and AP-1 transcription factors
	3-hydroxypropylmercapturic acid level, to be measured in urine	
PM2.5-Particulate matter measured as the concentration of particles less than 2.5 in diameter	Pulmonary macrophages isolation from spontaneously coughed or induced sputum, or directly by bronchoalveolar lavage	Low birth weight, myocar-dial infarction, cardiovascu-lar mortality, lung reduced function and cancer and total mortality
	Requires high technical skill and resources	

Adapted from Rylance et al. (2013)

back indoor generated radiation of such buildings triggering an indoors health risk. The outdoors reflected radiation is mostly harmless but harmful if reflected to neighboring buildings and their windows. Radiation penetrates into buildings through their roof windows. Therefore it is recommendable to clarify the location of base stations and other antennas (Stein et al. 2015, this volume Chap. 57). Whatever is the roof material made of all leaks are harmful as moisture may ruin the roof material with time, due to underneath rotting process, especially where wood consequently propagates the progress of mold growth (Fig. 58.1).

In the past, main building materials used to be wood, stone and bricks all of which are still in use. Wood products have usually been treated with chemicals to prevent microbial biodegradation, mostly with chlorophenols and polybrominated organics, the latter in order to prevent fire.

58.6 Radon

Every year, radon is estimated to cause about 21,000 lung cancer deaths in the United States. The U.S. Environmental Protection Agency (EPA) estimates that 1 of 15 homes in the United States (as many as 1 of 3 homes in some states) about seven million homes have high radon level (Krewski et al. 2006; Anonymous 2003; Mack et al. 2013). Particle size contributes also to danger of radon decay products (Ranamurthi 1989). Krewski et al. (2005) have conducted a systematic analysis of pooled data from 7 North American residential radon case-control studies (3,662 cases and 4,966 controls) to clarify the residential exposure to radon (at much lower levels compared to miners) and the risk of lung cancer. Using conditional likelihood regression to estimate the excess risk of lung cancer and based on the assumption that Odds Ratios (ORs) for lung cancer increases with residential radon concentration, the authors reported on an estimated OR following exposure to radon (100 Bq/m^3) in a exposure time window of 5–30 years, to be 1.11 (95 % confidence interval = 1.00–1.28) an OR compatible with the estimate of 1.12 (1.02–1.25) as predicted by downward extrapolation of the miner data (underground miners exposed to high levels of radon have an excess risk of lung cancer Möhner et al. 2010). These authors concluded that their results "provide direct evidence of an association between residential radon and lung cancer risk, a finding predicted using miner data and consistent with results from animal and in vitro studies".

Cement is made out of simple materials like chalk, quarts and clay. The main building material is crushed stone of different calibers and sand. Radioactive uranium as also its decay product common in nature, radon may be found, especially in granite rocks and also in cements. Furthermore drinking water originating from such rocks may contain radon. The radiation limit should be less than 100 Beckerels (Bq) per cubic meter and that can be directly measured.

In nature, molds are widely spread and due to their variability their identification are necessary only in special cases. Some of them are known to be toxic as such but many are powerful allergens. For example, the black mold (*Stachybotrys chartarum*) is directly toxic to both humans and animals (Pestka et al. 2008; Andersen et al. 2011).

Among the many construction materials, steel used to form and provide strength to cement constructions may contribute to magnetic properties of those buildings. In addition, there are also various chemicals used in cement and paints that may also release aldehydes (e.g. paints from surfaces and new furniture).

58.7 Heating and Areal Solutions

In most cold countries, especially in the Nordic ones but also in mountains inhabited areas, indoor heating is a necessity. Historically, it took place through fireplaces built from stones and/or bricks in one or more rooms. Wood was burned to warm the houses and also to allow food cooking. People were thus exposed to smoke and its particles PM_{10} or smaller being released both indoors and outdoors. When a fireplace generates warm air and the ventilation is closed the warm air may cause a mild over pressure indoors. The warm overpressure causes air to stream through the walls, ceiling as also floors. In warmer periods the air streamed through the rooms helps to ventilation.

Presently the buildings are made tight to save energy and keep the rooms proof from the increasing dust and pollutants carried indoors from outside traffic. Building needs many kinds of materials. Several such materials are practically sterile as being subjected to heat treatment as a common processes for preservation and are also often tightly plastic covered, a stage that lasts until the packages are opened. Unfortunately unfinished buildings with their materials are often soaked by rains and exposed to winds which carry many biological elements like molds and their spores from the surroundings.

In earlier times the buildings were naturally ventilated through doors, windows and chimneys by winds and gravitation. In modern buildings the incoming air is currently filtered to remove at least the main part of small particles. Different sensors are used to control ventilation and buildings' air travels in its own channels. The ventilation channels can, however, allow growth of organisms under warm and moist conditions. Therefore the ventilation channels are to be cleaned on a regular basis. Ventilation air also carries harmful components from environment, especially from outdoor traffic if not properly filtered. The particles around 10 μm in diameter can enter human lungs and particles smaller than 2.5 μm can enter as deep as the lung alveoli, while particles <0.1 μm can enter blood stream.

Earlier room air has been exchanged few times per hour at maximum. At the present one can calculate the air needed to meet the estimated or real room loads. In heavily loaded office and production rooms, several times these volumes are needed to be exchanged (e.g. when ozone is generated by different electric machines), hence the energy recovery is turning to be more important.

Traffic is one of the most common sources of pollutants as a result of gasoline burning and traffic dust released. This dust consists particles that carry a large variety of carcinogens, therefore filters are presently common in all ventilation systems. These filters need regular cleaning similar to old times' chimneys. Another source of dust and particles are streets and lawns commonly cleaned by air blowers that seriously redistribute the dust in air streams. Private houses had evolved similar to large flat-blocks. Besides to the traditional kitchen and bathrooms with its toilet, a flat can have other special spaces (e.g. sauna) In Finland, home saunas are highly popular. Such saunas with their humid and hot air can be a source of microorganisms that may affect elderly and immunocompromised persons, such in the case of *Legionella* contamination (Kura et al. 2006). In Finland, to save energy expenses several homes are centrally heated (in blocks of flats or in certain parts and even in the whole city). For this task, warm water travels through underground channels. As heating in cold climate is highly expensive also cooling is costly in hot environments. In future, temperature control will be highly requested for unexploited spaces in evenings when most humans are at home. Such a feature is possible in clever buildings which control through their sensors the human load and distribution per area. Obviously different rooms may have great differences in energy consumption that will require computerized adjustments. The regulation of room temperature is also possible by air pumping preheated air to individual rooms.

58.8 Ventilation and Room Pressures

Ventilation provides new air to buildings and individual rooms. Radioactive radon is one of significant environmental factor in sites where soil contains granite rocks and sands in ridges. Thus to prevent radon to enter the indoor air, the basements are constructed with air tight layers and specially organized outlets for basement air. It should be reminded that building materials like cement may be a source of radon. Although radon is an important factor in human neoplasm, it should be remembered that indoors smoking prevention is still much more important in every building, to prevent cancer. As already mentioned, in Finland the main parts buildings are requested to have a lower indoor pressure than outdoors to help the capturing the energy.

The entrance of moisture is blocked with the aid of plastic films. Due to wide variation in temperature indifferent seasons the plastic prevents the transfer of moisture and this may end up to condensation of water on the cold side. That may form a problem which promotes mold growth. On the other hand the higher indoor pressure would hinder the entrance of the harmful components in air in nature. Similar components can exist in the air released in basement, floors and walls and their materials. Keeping on ventilation is necessary to clean the air. This will also help in drying the unfinished structures. If the ventilation is cut off to save energy e.g. during nights and weekends, but the biological activity continues. The building mass maintains the warmth. The released heat of e.g. pipelines and home electronics may promote the biological activity. The warm and moist conditions promote the growth of microbes. There is biological activity in the air ventilation, and the generation of allergens and toxicants also continue.

58.9 Discussion

Majority of people spend some 90–95 % of their time in indoors, and every person consumes daily some 40 cubic meters of air. This means a need of some 15,000 l of indoor air per person and per day. The indoor air is a mixture of components available in the air near the house and its surroundings, if they get into the house through the filters and structural leaks. These mix with those generated in homes e.g. in kitchens and home office devices and other electronics, which generate radiation and ozone. This explains the deed of cleaning of filters of the building on regular basis. None of the electronic devices should be on if not used. Some people sense the impurities of the room air and are very sensitive to the components released by the molds and become so sensitive that they cannot work or live in those conditions. We know that dogs have much better ability that humans to sense the smells and they can be also further trained.

On the other hand radon and uranium cannot be sensed, but can be detected due to their radioactivity and are serious carcinogens released also in homes both from the building materials, but also from soil and rocks around homes (Möhner et al. 2010). Radon can enter homes also in drinking water, especially if there is a local well (Gray 2008). The showers are efficient in radioactivity distribution by means of water. As the radon is a common source or carcinogens in the indoor air, one should not have its concentration >400 Bq per cubic meter, and in new flats is should not exceed 200 Bq per cubic meter (Anonymous 2003; Bochicchio et al. 2014).

We need some 8–10 l of air per second per person at homes and some 10 l in office space. If there is unclean laundry at home, one should calculate one extra person than those who live in the flat. The same is true also to have untidy dish in kitchen. One must remember that the offices have several sources of electronics and thus sources of ozone. Of course office equipments are found also at homes. Of course the pets in hope need their respiration air. If you live alone, it is best to estimate that you need in you flat air for four persons. One should not have higher than 26 °C degrees, and 23–24 decrees in the room during the heating season. During building the protection against water and moisture of the building materials is essential for the future health of the construction as the drying on site is expensive and time consuming if they become wet.

Airborne exposure to different contaminants has been observed e.g. in flooded homes (Hoppe et al. 2014). High concentrations of endotoxin, glucan, spores, and culturable fungi have been detected in many of the homes which were affected by Hurricanes Katrina and Rita (Rao et al. 2007). The sampled microorganisms have been previously linked to human health effects especially in damped indoor environments where molds and bacterial growth is promoted (Institute of Medicine 2011). Exposure to molds, bacteria, fungal spores, allergens, endotoxin and fungal glucan through bioaerosols exposure have been linked to lung inflammation, organic dust toxic syndrome (that manifests as flu-like symptoms: malaise, cough, headache, nausea, etc.), allergic hypersensitivity, asthma (~20 % of US cases attributed to home dampness) etc. (Thorne and Duchaine 2007; Thorne et al. 2005; Institute of Medicine 2011). Inhabiting flood-damaged structures exposes individuals to high levels of bioaerosols with respiratory ailments such as persistent cough and sinus congestion (Tak et al. 2007).

Hoppe et al. (2014) carried an intensive study in the City of Cedar Rapids (Iowa, USA) where the river, that flows through, inundated the city after a snowy winter and prolonged rainfall, flooding 10 square miles of the city impacting 5,390 homes (Robinson 2010). These authors intended to address two aims: (a) to define the concentration of contaminants inside flood-damaged homes during and after remediation and (b) to determine whether the residents of these homes were experiencing higher rates of adverse health effects. Their results significantly emphasized the importance of "good remediation procedures"; two remediation levels have been tested: in-progress and completed. In progress level had significant higher airborne concentrations of molds, bacteria, iPM (inhalable particulate matter), endotoxin and glucan in comparison to the completed homes. Additionally, in-progress residents were found to have significantly higher prevalence of doctor-diagnosed allergies "(adjusted OR = 3.08; 95 % CI: 1.05, 9.02) and all residents had elevated prevalence of self-reported wheeze (adjusted OR = 3.77; 95 % CI: 2.06, 6.92) and prescription medication use for breathing problems (adjusted OR = 1.38; 95 % CI: 1.01, 1.88) after the flood as compared to before".

The thickness of insulation of the buildings is essential in cold climate. In the production the insulation materials are heated, and they are therefore practically sterile when coming out of from the factory process, but during the building process the rains can be common. It is strongly recommended that no wet insulation material is used when building. With water an unknown mixture of spores, germs and allergens will at the same time load the building and its air. It is easy to see that the improvement of housing is expensive and needs proper planning when such project must be carried out (Thomson et al. 2001).

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R.H. Armon, O. Hänninen (eds.), *Environmental Indicators*,
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