Eric Lichtfouse · Jan Schwarzbauer
Didier Robert *Editors*

Environmental Chemistry for a Sustainable World

Volume 1: Nanotechnology and Health Risk

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Preface

> *I was at a conference where someone said something about the Holocene. I suddenly thought this was wrong. The world has changed too much. So I said: 'No, we are in the Anthropocene.' I just made up the word on the spur of the moment. Everyone was shocked. But it seems to have stuck.*
>
> Nobel Prize-winner Paul Crutzen

To find rapidly chapters of interest in this book please see list of topics in Table 1 page ix.

Fukushima, Chernobyl and Climate Change

Nuclear Plants on Earthquake Zones

Everybody has been recently shocked by the major accident of the nuclear power plant on March 31, 2011 at Fukushima, Japan. Such a failure was both unexpected and expected. Unexpected because most thought that the 1986 nuclear disaster at the power plant of Chernobyl, Ukraine, could never happen again, especially in wealthy, high technology countries such as Japan. Expected because geology tells us that Japan lies on the cusp of the Pacific-Philippine-Eurasian triple plate junction, where the complex interactions of three tectonic plates is unpredictable and loaded with potential activity. As a consequence, Japan experiences regular, high intensity earthquakes, tsunamis and volcanoes since centuries. Similarly to the Chernobyl global 'event', the release of radioactive pollutants from Fukushima nuclear plant in water, air, and soil will most probably severely affect human health, food security and economy worldwide for decades. Therefore, one might just ask why nuclear plants are built on such high-risk areas.

Human Errors Are Repeatable

The global warming event has similar features – though less rapid and catastrophic – as the Chernobyl and Fukushima events on several rationales. First, the global warming is a worldwide event due notably to worldwide CO_2 emissions (Lichtfouse 2009a), a fact that is nicely coined by the popular saying "pollutants have no borders". Second, the effects of global warming are now clearly proven by many scientific trends (Feehan et al. 2009; Jones et al. 2009; Lavalle et al. 2009). Third, despite all such scientific evidence humans still use cars and planes that emit CO_2; they practice intensive, industrial agriculture that decrease soil carbon, and in turn emits CO_2; they cut forest, which in turn emits CO_2, and so on. Recent essays reports on global issues of and solution for society (Lichtfouse 2009a, b, 2010). From the scientist view, one might say ironically that "human errors are repeatable".

Social Chemistry

From those global issues several conclusions and advices can be drawn to improve society and the life of further generations. First, overwhelming scientific evidence is not sufficient to convince humans, notably decision-makers. Such a failure is due in particular to the lack of communication between science and society. In other words, scientists should not only publish in scholarly journals and attend high-level scientific meetings, but also communicate with the "real world". Here, a "social impact factor" to measure the impact of science on society – based for instance on web, facebook and blog usage data – would be very appreciated.

A second advice is that classical natural sciences such as chemistry, physics, biology, geology and medicine should integrate social, human and political sciences. In other words, the real world should be involved in the process of scientific discovery to bridge the gap between science and people. The integration of social disciplines is already occurring in agrosciences (Fleming and Vanclay 2010; Karami and Keshavarz 2010; Lichtfouse 2010; Lichtfouse et al, 2009, 2010). Indeed agriculture has always been historically closer to citizens, e.g. farmers, than chemistry and physics. The need for analysis of citizen discourses is nicely shown by the following survey answer: 'What's sustainable? You've got to look at our world as we know it. We're not in a sustainable position at the moment. That's why I say what is sustainable – I don't know' (Fleming and Vanclay 2010).

The concept of discourse was introduced in the 1960s by the French philosopher Michel Foucault. Foucault (1972) maintained that the way language is used has consequences for a whole range of things that go beyond the level of individuals or disciplines, to the very structures of society that shape and limit how people are able to speak, think, and act, and to the social structures that are developed accordingly. Now, environmental chemistry should use techniques of social sciences such as discourse analysis to discover novel findings that will be both innovative and accepted by citizens.

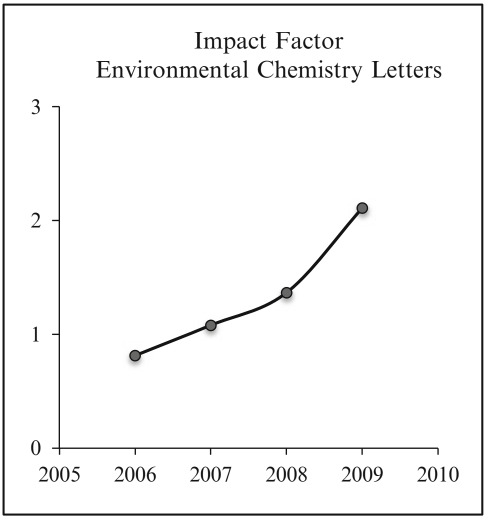
The Success of Environmental Chemistry

Association of Chemistry and the Environment

We founded the Association of Chemistry and the Environment in 2000 with a group of environmental scientists (www.europeanace.com). A "chemistry flower" logo was designed to symbolise positive benefits of chemistry for Nature (Fig. 1). The association was launched by the organisation of the two first European Meeting on Environmental Chemistry by Eric Lichtfouse, Brigitte Elbisser and co-workers in 2000 in Nancy, France, and in 2001 in Dijon, France. Meetings were immediately a success, with more than 300 attendants, due to several factors such as hard work from the organising team, willingness to create a new science community in a highly conservative science system, and gathering in a friendly location scientists from various isolated disciplines such as soil science, toxicology and chemistry. The first presidents of the association were Eric Lichtfouse (2000–2004) and Jan Schwarzbauer (2005–2009). Noteworthy, well established associations, in particular the Division of Environmental Chemistry and the Division of Geochemistry of the American Chemical Society (ACS), supported us, in particular by organising joint symposia sponsored by the petroleum research fund. We therefore thank very much the American Chemical Society.

Fig. 1 The "chemistry flower" was designed by Eric Lichtfouse and Guillaume Decaux to symbolise positive benefits of chemistry for Nature. Guillaume Decaux is a professional drawer living in Strasbourg, France (http://www.alcide.fr/)

Fig. 2 The impact factor of the journal Environmental Chemistry Letters (*ECL*) increased from 0.814 in 2006 to 2.109 in 2009. Article pdf downloads reached 36,549 in 2009 (100 per day)



Environmental Chemistry Letters

We founded the journal Environmental Chemistry Letters in 2003 to fill the science gap between chemistry and environment (www.springer.com/10311). Despite a tough selection by the Thomson Reuters agency to enter the Science Citation Index, we got our first impact factor of 0.814 for 2006, only 3 years later. The impact factor increased steadily to reach 2.109 in 2009 (Fig. 2) (www.thomsonreuters.com). The increase of the impact factor can be explained by a higher quality of articles, as a result of higher rejection that reached 73% in 2009. Given the rapid increase of submitted articles, more that 70% of articles are now declined at pre-screening stage. Journal articles are highly viewed as proven by the number of pdf downloads that reached 36,549 in 2009 (100 per day). This finding is both unexpected and expected. Unexpected because most articles are not in open access. Expected because Springer has about 30 millions scientists who access articles. Here, contrarily to the common thinking, articles published in restricted access by a major publisher are probably much more visible than open access articles published by a minor publisher.

Environmental Chemistry

We published the book Environmental Chemistry in 2005 (Lichtfouse et al. 2005b). The book includes 69 chapters sorted in seven sections: Analytical Chemistry, Toxic Metals, Organic Pollutants, Polycyclic Aromatic Hydrocarbons, Pesticides, Green Chemistry, and Ecotoxicology. The book is a success with over 35,000 chapter downloads from 2007 to 2010. Book chapters are still highly downloaded with 639

Table 1 Chapters of environmental chemistry for a sustainable world (Lichtfouse et al. 2012a, b)

1st author	Keywords			DOI
Tan	Nanotubes	Energy	Water	10.1007/978-94-007-2442-6_1
Landy	Cyclodextrin	Sequestration	Water	10.1007/978-94-007-2442-6_2
Chauhan	Nanotubes	Energy	Sensors	10.1007/978-94-007-2442-6_3
Liu	Photocatalysis	Remediation	Water	10.1007/978-94-007-2442-6_4
Visinescu	Polysaccharides	Metal oxides	Green chemistry	10.1007/978-94-007-2442-6_5
Ricking	DDT isomers	Remediation	Pesticides	10.1007/978-94-007-2442-6_6
Heim	Geochronolgy	Pollution history	Sediments	10.1007/978-94-007-2442-6_7
Anupama	Endocrine disruptors	Toxicity	Pesticides	10.1007/978-94-007-2442-6_8
Stankovic	Heavy metal	Toxicity	Seafood	10.1007/978-94-007-2442-6_9
Sarkar	DDT, PCBs	Toxicity	Seafood	10.1007/978-94-007-2442-6_10
Ribeiro	Pharmaceuticals	Remediation	Water	10.1007/978-94-007-2439-6_1
Sanjurjo	Buildings	CO_2, SO_2, NO_x	Air	10.1007/978-94-007-2439-6_2
Rene	Bioreactors	Remediation	VOCs	10.1007/978-94-007-2439-6_3
Etxebarria	Extraction	Pollutants	Water	10.1007/978-94-007-2439-6_4
Sharma	ClO_2, R-Cl	Oxidation	Water	10.1007/978-94-007-2439-6_5
Mondal	Dyes	Biodegradation	Water	10.1007/978-94-007-2439-6_6
Shukla	Heavy metals	Lichens	Air	10.1007/978-94-007-2439-6_7
Brillas	Pharmaceuticals	Remediation	Water	10.1007/978-94-007-2439-6_8
López	Biogas	Cleaning	CO_2, H_2S, R-Cl	10.1007/978-94-007-2439-6_9
Mudhoo	Heavy metals	Toxicity	Biosorption	10.1007/978-94-007-2439-6_10
Gasparatos	Heavy metals	Sequestration	Nodules, soil	10.1007/978-94-007-2439-6_11
Dabrowska	Arsenic	Remediation	Biosorption	10.1007/978-94-007-2439-6_12
Mahmood	Photocatalysis	Microbes	Disinfection	10.1007/978-94-007-2439-6_13

Keywords and DOI for fast access. *DDT* 2,2,-bis(4-chlorophenyl)-1,1,1-trichlorethane, *PCBs* polychorinated biphenyls, *VOCs* volatile organic compounds downloads in January 2011 (20 per day). The highest recent downloads can be freely viewed at Springer Realtime (www.realtime.springer.com). Here the most popular topics are heavy metals, bioremediation and green chemistry.

Environmental Chemistry for a Sustainable World

This new book series presents 23 chapters published into 2 volumes: Nanotechnology and Health Risk (Lichtfouse et al. 2012a), and Remediation of Air and Water Pollution (Lichtfouse et al. 2012b). Table 1 allows fast access to chapters by topics. All chapters have been reviewed and the rejection rate was 15%. The Nanotechnology section highlights carbon nanotubes for energy and detection; cyclodextrins for pollutant trapping; magnetic nanophotocatalysts for pollutant degradation; and polysaccharides for metal oxide green synthesis. The Health Risk section describes new findings on the old DDT pesticide; geochronology of river pollutants; toxic effects of endocrine disruptors; and heavy metals in seafood. The Air and Water Pollution section presents the selective degradation of chiral pharmaceuticals; the alteration of housing walls by CO_2, SO_2 and NOx; cleaning industrial waste gas and dyes wastewater; methods to extract and detect pollutants; and harmful chlorinated pollutants. The Remediation section highlights the electrochemical degradation of pharmaceuticals; methods to treat biogas CO_2, CH_4, H_2S and NH_4; heavy metal sequestration on biomass and soil nodules; As phytoremediation; and photocatalytic inactivation of water microbial pathogens.

Eric Lichtfouse,
Jan Schwarzbauer,
Didier Robert

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Part II Health Risk

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Part I
Nanotechnology

Chapter 1
Carbon Nanotubes Applications: Solar and Fuel Cells, Hydrogen Storage, Lithium Batteries, Supercapacitors, Nanocomposites, Gas, Pathogens, Dyes, Heavy Metals and Pesticides

Chin Wei Tan, Kok Hong Tan, Yit Thai Ong, Abdul Rahman Mohamed, Sharif Hussein Sharif Zein, and Soon Huat Tan

Contents

Abstract Energy and environment are major global issues inducing environmental pollution. Energy generation from conventional fossil fuels has been identified as the main culprit of environmental degradation from global warming effects, in addition to environmental pollution which arises from rapid industrialization and agricultural development. In order to address these issues, nanotechnology plays an essential role in revolutionizing the applications for energy conversion and storage, environmental monitoring, as well as green engineering of environmental friendly

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materials. Carbon nanotubes and their hybrid nanocomposites have received immense research attention for their potential applications in various fields due to their unique structural, electronic, and mechanical properties. Here, we review the applications of carbon nanotubes (i) in energy conversion and storage as in solar cells, fuel cells, hydrogen storage, lithium ion batteries, and electrochemical supercapacitors, (ii) in environmental monitoring and wastewater treatment as in the detection and removal of gas pollutants, pathogens, dyes, heavy metals, and pesticides, and (iii) in green nanocomposite design. Integration of carbon nanotubes in solar cells and fuel cells has increased the energy conversion efficiency of these energy conversion applications, which serve as the future sustainable energy sources. Carbon nanotubes doped with metal hydrides show high hydrogen storage capacity of around 6 wt% as a potential hydrogen storage medium. Carbon nanotubes nanocomposites have exhibited high energy capacity in lithium ion batteries and high specific capacitance in electrochemical supercapacitors, in addition to excellent cycle stability. High sensitivity and selectivity towards the detection of environmental pollutants is demonstrated by carbon nanotubes based sensors, as well as the anticipated potentials of carbon nanotubes as adsorbent to remove environmental pollutants, which show high adsorption capacity and good regeneration capability. Carbon nanotubes are employed as reinforcement material in green nanocomposites, which is advantageous in supplying the desired properties, in addition to the biodegradability. This paper presents an overview of the advantages imparted by carbon nanotubes in electrochemical devices of energy applications and green nanocomposites, as well as nanosensor and adsorbent for environmental protection.

Keywords Carbon nanotubes • Energy • Environmental monitoring • Wastewater • Biotechnology • Nanocomposites

List of Abbreviations

CNTs	Carbon Nanotubes
CV	Cyclic Voltammetry
DMFC	Direct Methanol Fuel Cell
DSSC	Dye-Sensitized Solar Cell
ITO	Indium-Tin Oxide
MEA	Membrane Electrode Assembly
MWCNTs	Multi-Walled Carbon Nanotubes
OTE	Optically Transparent Electrode
PEMFC	Polymer Electrolyte Membrane Fuel Cell
Pt	Platinum
QDSC	Quantum Dot-Sensitized Solar Cell
Ru(II)	Ruthenium Metalorganic Dye
SnO_2	Tin Oxide
SWCNTs	Single-Walled Carbon Nanotubes

TiO_2	Titanium Dioxide
VXC72R	Vulcan XC72R
WO_3	Tungsten Oxide

1.1 Introduction

Energy and environment issues have been the major global concerns in this twenty-first century, and they are both on the prioritized list of the top ten problems facing humanity (Smalley 2005). Undeniably, conventional fossil fuels, such as oil, gas, and coal have contributed to the energy prosperity in the past century till present days, but their overwhelming utilization has resulted in their depletion and exhaustion. Furthermore, the combustion of fossil fuels has been identified as the major cause of increasing atmospheric levels of greenhouse gases, which contribute to the global warming effects, such as abnormal climate change, increasing rate of natural disasters and ultimately, environmental degradation. Since the age of industrial revolution, environmental pollution issues have been greatly associated with the rapid growth in energy demand and production, industrialization and agricultural development. The main anthropogenic sources of pollutants are derived from industrial activities and agricultural activities, such as combustion of fossil fuels, metallurgical activities, transportation, livestock farming, application of pesticides and herbicides (Bashkin 2003). The environmental pollution of air, water, and soil has resulted in the degradation of our environmental quality and ecosystem health, giving rise to the human health concerns caused by pollutants toxicity. In order to enable future global energy prosperity and preservation of environmental quality, intensive efforts have been invested on the development of technology to solve the energy and environment problems. Recently, nanotechnology has been the field of interest, which promises in introducing scientific breakthroughs and revolutionary developments for addressing the energy and environment issues.

Nanotechnology involves the study, manipulation, creation and use of materials, devices and systems typically with dimensions smaller than 100 nm (Chen et al. 2004). It is based on the fact that some very small structures usually have new properties and behaviour that are not displayed by the bulk matter with the same composition. Carbon nanotubes (CNTs) were discovered in 1991 by the Japanese electron microscopist Sumio Iijima who was studying the material deposited on the cathode during the arc-evaporation synthesis of fullerenes (Iijima 1991). With the unique electronic, chemical, mechanical, and structural properties of CNTs, they are one of the most commonly used building blocks in nanotechnology and therefore, receiving intense investigation towards the development of their application. They represent one of the best examples of novel nanostructures derived by bottom-up chemical synthesis approaches. They are built from sp^2 carbon units in hexagonal networks or benzene-type hexagonal rings of carbon atoms, as in a graphene sheet (Merkoçi 2006). They can be essentially thought of as a rolled-up tubular shell of graphene sheet.

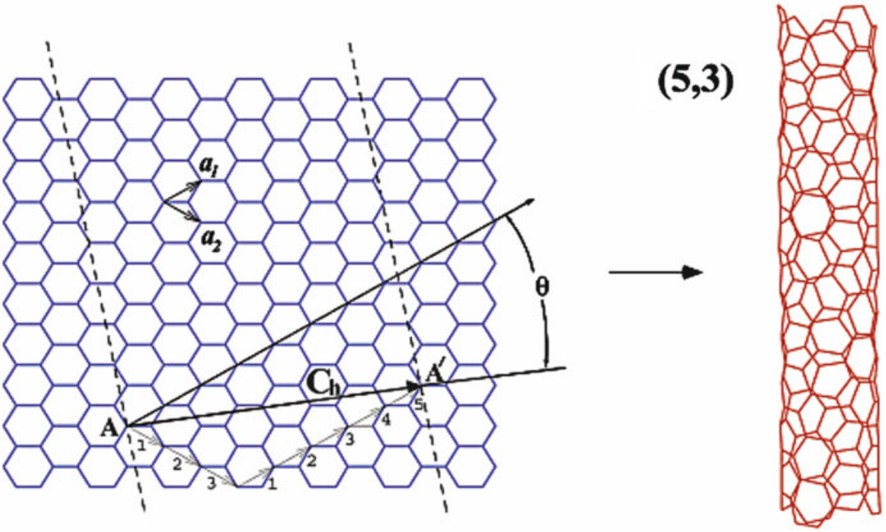

Fig. 1.1 Schematic diagram of the hexagonal honeycomb structure of a graphene sheet and formation of single-walled carbon nanotubes by rolling the graphene sheet along the lattice vector AA′. The chiral vector is defined as $C_h = na_1 + ma_2$ which connects two crystallographically equivalent sites, A and A′ on a graphene sheet, whereas the chiral angle is taken with respect to the zigzag axis (n,0). In the diagram: n = 5, m = 3, thus the chirality of the nanotube is (5,3) or $C_h = 5a_1 + 3a_2$ (Charlier 2002). Abbreviations: C_h chiral vector, θ chiral angle, A and A' crystallographic sites, a_1 and a_2 unit vectors of hexagonal honeycomb lattice

CNTs can be classified as either single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs). SWCNT is formed by rolling a sheet of graphene into a cylinder and capped by hemispherical ends, which is a result of pentagon inclusion in the hexagonal carbon network of the nanotube wall during the growth process. The diameter and chirality are the key parameters of CNTs, which are determined by the (n,m) indices in the graphene plane. The ways to roll graphene into tubes are mathematically defined by the chiral vector (C_h) and chiral angle (θ) as illustrated in Fig. 1.1. The chiral vector is defined as $C_h = na_1 + ma_2$ where *n* and *m* are the integers of the chiral vector considering the unit vectors a_1 and a_2, whereas the chiral angle is taken with respect to the zigzag axis (n,0). The relation between *n* and *m* defines three categories of CNTs, which are armchair, zigzag and chiral types of CNTs (Fig. 1.2a). The diameter of SWCNTs is around 0.4–3 nm and several μm in length (Balasubramanian and Burghard 2005).

MWCNT is a stack of graphene sheets rolled up in concentric cylinders (Fig. 1.2b). The diameters of MWCNTs are in between 2 and 25 nm, and the distance between sheets or inter layer spacing is about 0.34 nm (Ajayan 1999). The walls of each layer of MWCNTs are parallel to the central axis, and therefore it is called concentric MWCNTs. Some other inner textures may be found in MWCNTs,

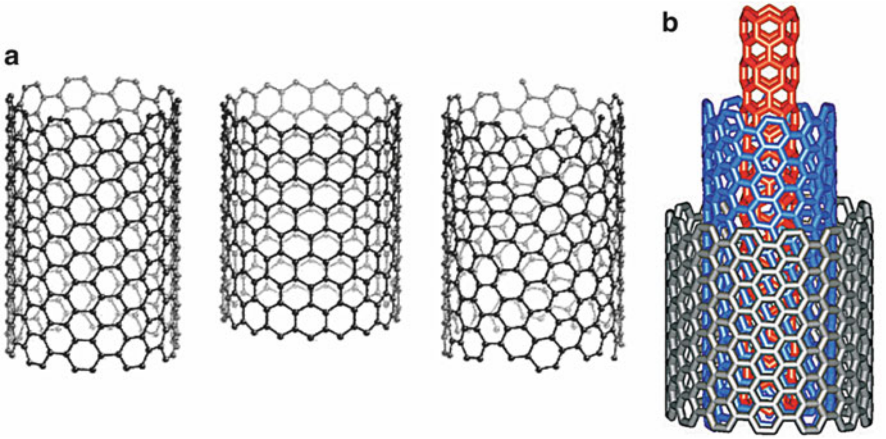

Fig. 1.2 Schematic illustration of (**a**) three categories of single-walled carbon nanotubes defined by its chirality, *from left to right*: armchair, zigzag, and chiral (Sloan et al. 2002) and (**b**) Multi-walled carbon nanotubes (Balasubramanian and Burghard 2005)

such as the herringbone texture and bamboo texture (Rodriguez et al. 1995). The herringbone texture, in which the graphene make an angle with respect to the nanotube axis and the angle varies upon the processing conditions, is obtained from process involving catalysts, generally catalyst-enhanced thermal cracking of hydrocarbons. The bamboo texture is described as the occurrence of limited amount of graphenes oriented perpendicular to the nanotube axis and it affects both concentric MWCNTs (Fig. 1.3a), and herringbone MWCNTs (Fig. 1.3b).

Arc-discharge, laser ablation and chemical vapour decomposition are the three main methods for the synthesis of CNTs (Ando and Iijima 1993; Guo et al. 1995; Che et al. 1998). In arc-discharge method, CNTs are synthesized through arc-vaporization of two graphite rod placed end to end, namely anode electrode and cathode electrode. Laser ablation method involves the sublimation of graphite target and condensation of laser-vaporized carbon/metal mixtures to form CNTs. As for chemical vapour decomposition, it involves the catalytic decomposition of a carbon containing gas and nanotube growth on metal catalyst particles impregnated on a substrate. Arc-discharge and laser ablation are widely employed for the synthesis of SWCNTs due to the high process temperature of around 1,200°C, which favours SWCNTs formation. Chemical vapour decomposition is suited for mass production of MWCNTs as it is a simple and economic technique at lower process temperature from 500 to 1,000°C.

Regardless of the synthesis method applied, as-prepared CNTs usually contain a significant amount of impurities, such as amorphous carbon, carbon nanoparticles, graphitic debris, catalyst particles and fullerenes (Baughman et al. 2002). These impurities often interfere with the desired properties of CNTs and impede CNTs for

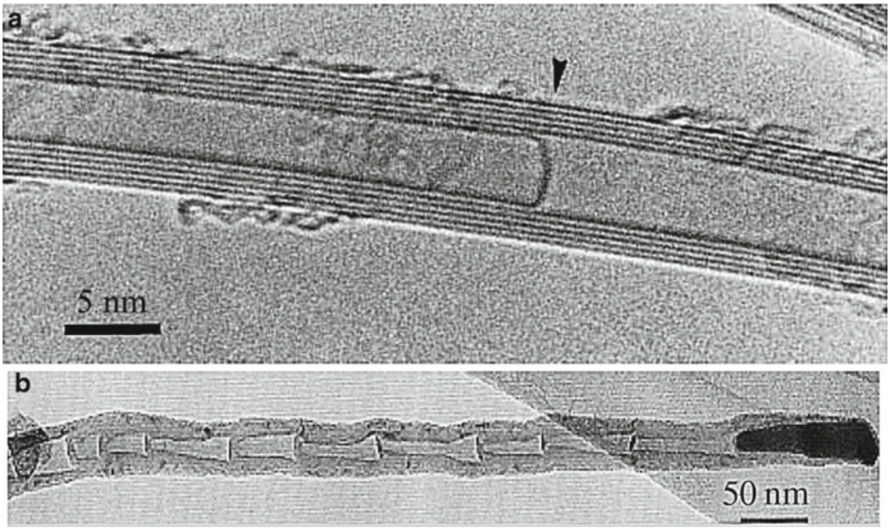

Fig. 1.3 High-resolution transmission electron microscopy images of (**a**) concentric multi-walled carbon nanotubes with bamboo texture, scale bar 5 nm (Harris 1999) and (**b**) herringbone multi-walled carbon nanotubes with bamboo texture, scale bar 50 nm (Saito 1995). The bamboo texture is described as the occurrence of limited amount of graphenes oriented perpendicular to the nanotube axis, which forms the internal cap across the central tube

detailed characterizations and advanced applications. Various purification techniques have been employed for the removal of impurities, which include flocculation, microfiltration, chromatographic, centrifugation, gas phase oxidation, liquid phase oxidation, and chemical functionalization (Vairavapandian et al. 2008). Typical purification process involves combinations of these protocols, in which first stage gas phase oxidation followed with second stage liquid phase oxidation are widely employed. Gas phase oxidation is an easy and fairly effective purification step to eliminate amorphous carbon and carbon nanoparticles (Shi et al. 1999). Subsequent liquid phase oxidation usually employs an acid treatment, which utilizes a strong oxidizing agent or acid solution, such as HCl, HNO_3, H_2SO_4 or a mixture of these acids. The liquid phase oxidation not only removes the catalytic metals together with some amorphous carbon, but it causes defects and/or shortening of CNTs (Vaccarini et al. 1999; Chen et al. 1998). The oxidation purification steps introduce carboxylic groups at defective sites of the open ends and the sidewall of CNTs, which are beneficial for further functionalization and increased solubility.

CNTs possess a framework structure of sp^2 hybridized carbon, therefore making its sidewall very hydrophobic and enriches π-stacking. These properties allow the functionalization of CNTs to prepare a wide range of nanotubes coupled with different types of materials, expanding their application range through novel nano-devices with new functions and applications. Functionalization of CNTs allows the unique properties of a nanotube to be coupled to those of other types of materials,

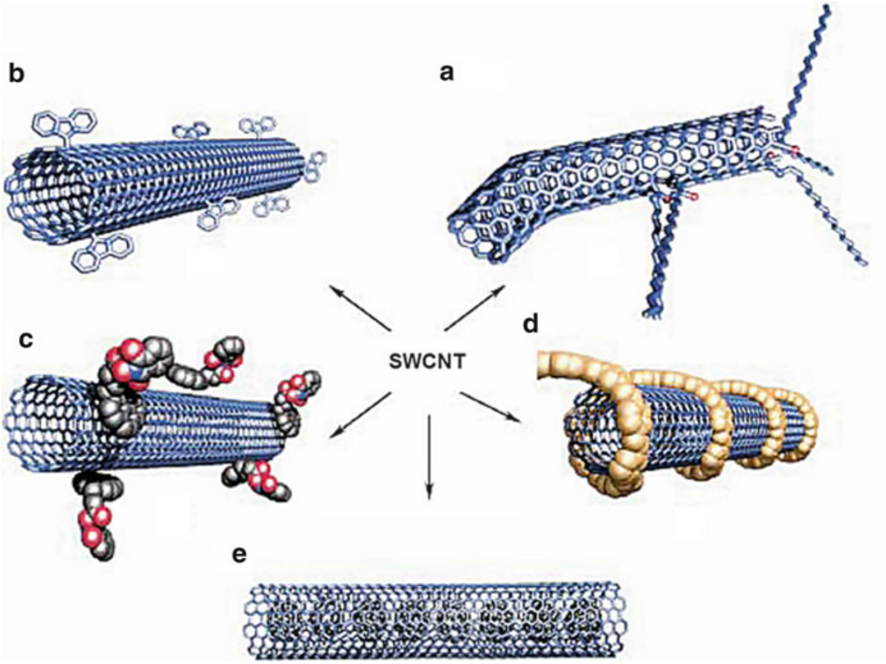

Fig. 1.4 Functionalization possibilities for single-walled carbon nanotubes: (**a**) defect-group functionalization, (**b**) covalent sidewall functionalization, (**c**) noncovalent exohedral functionalization with surfactants, (**d**) noncovalent exohedral functionalization with polymers and (**e**) endohedral functionalization. Defect-group functionalization involves the oxygenated functional groups at the defect sites along the sidewall or tube ends, whereas covalent sidewall functionalization involves the covalent bond formation between the materials and nanotube. Noncovalent exohedral functionalization involves either the aggregation of nanotube with surfactants or wrapping of nanotube with polymers, whereas endohedral functionalization involves incorporation of materials in the capillaries of nanotube (Hirsch 2002)

improves the solubility and processibility of CNTs. Several approaches have been developed to functionalize CNTs, which include defect-group functionalization, covalent sidewall functionalization, noncovalent exohedral functionalization with either surfactants or polymers, and endohedral functionalization as illustrated in Fig. 1.4. Defect-group functionalization involves the reactive groups which lie at the defect positions along the sidewall or tube ends of CNTs, such as vacancies, Stone-Wales defect, open ends of nanotubes closed by metal catalyst particles, etc. These reactive groups are oxygenated functional groups, such as carboxyl groups, which are produced during the purification of CNTs (Hamon et al. 1999). Covalent sidewall functionalization involves the covalent bond formation between the materials and nanotube with the presence of a highly reactive reagent. The direct sidewall functionalization of SWCNTs with organic groups is possible by reactive species such as nitrenes, carbenes, and radicals (Holzinger et al. 2001).

Noncovalent exohedral functionalization involves either the aggregation of CNTs with surfactants or wrapping of CNTs with polymers. With the presence of surface active molecules such as sodium dodecylsulfate or benzylkonium chloride, nanotubes can be dispersed in the aqueous phase without purification process (Krstic et al. 1998). Aggregation is due to the effective π-π stacking interactions between the aromatic groups of the surfactants and the graphitic sidewall of SWCNTs. The suspension of purified nanotubes in the presence of polymers in organic solvents will lead to the polymer wrapping around the nanotubes (Coleman et al. 2000). The properties of these polymer-functionalized nanotubes are markedly different from those of the individual components, such as higher conductivity. Endohedral functionalization involves incorporating or uptake of materials in the inner cavity or the capillaries of CNTs. One example is the incorporation of fullerenes in the sidewall of CNTs, in which the encapsulated fullerenes tend to form chains that are coupled by van der Waals forces and coalesce in the interior of SWCNTs upon annealing to produce new, concentric, endohedral nanotubes with diameter of 0.7 nm (Smith and Luzzi 2000).

CNTs possess some of the unique physical properties, such as one hundred times the tensile strength of steel, thermal conductivity better than other materials except the purest diamond and electrical conductivity similar to copper but carry much higher currents (Merkoçi 2006). SWCNTs can be either metallic or semiconducting (Louie 2001). All armchair SWCNTs are metallic, as well as those with $n-m=3$j and j being a nonzero integer. Metallic CNTs have relatively large band gaps, ~0.5 eV for typical diameter of 1.5 nm. All other zigzag and chiral SWCNTs are semiconducting, which have band gap inversely related to the diameters of nanotubes, ~10 meV. The conductivity of each layer of MWCNTs behaves like a SWCNT along the axial direction, but it is very poor between the layers. Nevertheless, CNTs have high electron transfer rate over the sidewall, which lead to the high electrical conductivity of CNTs.

Chemical reactivity of CNTs are derived mainly from the curvature of the sidewall and structural defects (Balasubramanian and Burghard 2008). The curvature of the nanotubes sidewall causes distortions to the normally planar C–C bonds of sp^2 hybridization, resulting in certain degree of sp^3 hybridization and the misalignment of π orbitals. The exohedral chemical reactivity at the convex surface of CNTs rises with increasing curvature of the wall or decreasing diameter. Defects on sidewall, such as vacancies and Stone-Wales defects profoundly alter the chemical reactivity of SWCNTs sidewall. Stone-Wales defect is formed from 4 adjacent heterocycles, which are 2 pentagons and 2 heptagons arranged in pairs opposite to each other. There is average one Stone-Wales defect every 5 nm along the nanotube length or approximately 2% of the carbons in a SWCNT involve in Stone-Wales defect (Monthioux 2002). The presence of defects at the sidewall allows localized double bonds to form between carbon atoms in the defect, which enhances the local chemical reactivity. Therefore, overall chemical reactivity of CNTs is strongly dependent on the synthesis methods, where the chemical reactivity is higher with more structural defects.

The adsorption properties of CNTs depend on the accessible surface area and the porous nature of nanotube. The surface area of a SWCNT is often larger than that of a MWCNT as proven experimentally, typically between 400 to 900 m^2/g for SWCNTs and 200 to 400 m^2/g for MWCNTs (Monthioux et al. 2007). Opening the nanotubes by removing the caps, as well as chemical treatment of CNTs can significantly influence the adsorption properties by altering the surface area and porous structure. For instance, chemical treatments of MWCNTs with KOH or NaOH activation are useful for promoting the microporosity and surface area to as high as 1,050 m^2/g (Raymundo-Piñero et al. 2005; Frackowiak et al. 2002). Modelling studies of SWCNTs have predicted that the adsorption properties are enhanced at the kink sites or nanotexture imperfections, such as vacancies and Stone-Wales defects (Lu et al. 2004; Park et al. 2003). Generally, CNTs were found to have higher condensation pressures and lower heats of adsorption than graphite (Masenelli-Varlot et al. 2002). This is due to the curvature of graphene sheets that leads to decreased lateral interactions between adsorbed molecules, therefore better adsorption properties.

The distinctive electrochemical properties of CNTs are due to their unique electronic structure. It is reported that the electroactive sites on CNTs are located at the tube ends with faster rate of electron transfer (Gooding et al. 2007; Liu et al. 2005). In addition, the alignment and the length of CNTs also have a significant effect on the electrochemical properties of CNTs, in which aligned CNTs and shorter length of nanotube show better electrochemical properties. Purification of CNTs, such as chemical oxidation or thermal treatment leads to the partial oxidation of CNTs to produce groups at the tube ends and defects along the sidewall (Gong et al. 2005). A pair of redox peaks is observed when the purified CNTs are subjected to cyclic voltammetry (CV) and the peaks are attributed to the redox process of oxygenated functional groups at the CNTs (Luo et al. 2001; Barisci et al. 2000). Therefore, the purified CNTs have two distinct regions that contribute to their electrochemical behaviour, which are the CNTs sidewall and the tube ends. The electrochemical behaviour of the CNTs sidewall is similar to the basal plane of highly oriented pyrolytic graphite and the electrochemical behaviour of the tube ends is similar to the edge plane of highly oriented pyrolytic graphite (Banks and Compton 2006).

Since the discovery of CNTs, they have been the subject of extensive research interest due to their outstanding structural, electronic, and mechanical properties such as unique tubular structure, high chemical and thermal stability, low weight, high electrical conductivity, good heat conductance, large surface area, and high mechanical strength. Several potential applications of CNTs have been explored in electrochemical devices, field emission devices, nanoscale sensors, and nanocomposite materials (Endo et al. 2008). In this paper, we review the recent advancements brought by CNTs in the field of energy conversion and storage, environmental monitoring and wastewater treatment, as well as green nanocomposite design. The advantages imparted by CNTs in enhancing the performances of solar cells, fuel cells, hydrogen storage, lithium ion batteries, and electrochemical supercapacitors, which serve as the future clean and sustainable energy source are discussed. We also discuss the potential applications of CNTs as sensors and adsorbents for environmental monitoring and the development of green nanocomposite based on CNTs for environmental protection.

1.2 Carbon Nanotubes in Energy Conversion and Storage

Global warming and depletion of natural energy resources are the current major concerns and are anticipated to become increasingly serious in near future (Smalley 2005). The abnormal climate shift and increasing rate of natural disasters occurring worldwide are clear signs of environmental degradation from global warming, in which the combustion of fossil fuels has been identified as the main culprit contributing to the global warming effects. In effort to limit the utilization of fossil fuels and to meet the ever-increasing energy demands of society, scientists are seeking for clean alternative renewable and sustainable energy sources. Potential candidates to substitute conventional fossil fuels include solar, wind, tidal, water, geothermal, and hydrogen energies, where extensive research has recently been carried out on these energy sources. In the past decade, nanotechnology with CNTs material has introduced revolutionary developments in several energy applications ranging from energy conversion such as solar cells and fuel cells, to energy storage such as hydrogen storage, lithium ion batteries, and electrochemical supercapacitors (Liu et al. 2008a). The advantages of CNTs and their hybrid nanocomposites in these energy applications are reviewed in this section.

1.2.1 Solar Cells

Solar energy has a great potential as a clean and sustainable energy source due to its abundance and more evenly distribution in nature than any other renewable energy sources (Wijewardane 2009). Photovoltaic is the technical term for a solar power technology that uses solar cells to convert energy from the sun into electricity. Conventional silicon solar cells can reach efficiencies as high as 24%, but high production costs limit their potential for economical applications (Green et al. 2008). New generation of solar cells based on thin films processing, include dye-sensitized solar cells, quantum dot-sensitized solar cells and polymer/organic solar cells, which are promising photovoltaic devices owing to their low fabrication cost and high energy conversion performance. Research and development in the past decade focus on the integration of CNTs, which possess the unique structural properties, excellent electronic properties, and fast electron transfer kinetics, to improve the photoconversion efficiency of these solar cells.

Generally, solar cell is made up of light-absorbing materials or sensitizer in mesoscopic semiconductor film on an optically transparent substrate as the working electrode, a conventional platinum (Pt) counter electrode, and an iodide based electrolyte (Green 2002). The operating principles of solar cells are charge injection, charge separation and reduction of electrolyte species as shown in the schematic presentation in Fig. 1.5. Upon illumination by sunlight, the sensitizer absorbs the photon and become photoexcited, subsequently injects the electrons into the conduction band of semiconductor. In the event of charge separation, the charge carriers

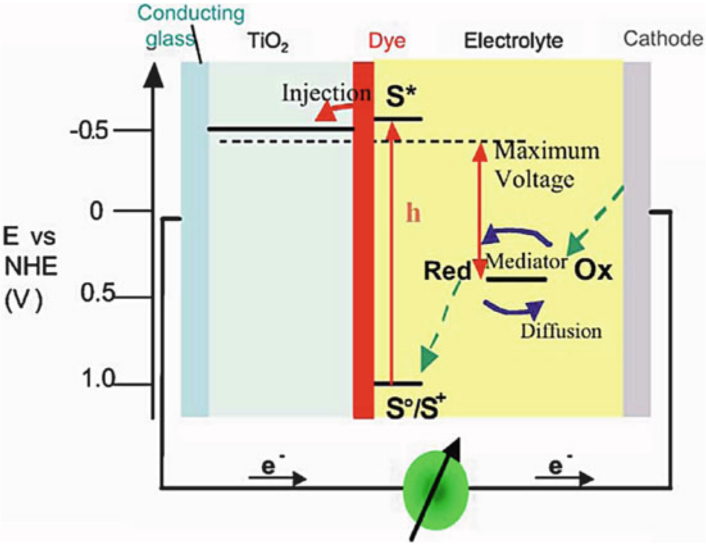

Fig. 1.5 Schematic presentation of operating principles of dye-sensitized solar cell. Photoexcitation of the dye molecule as sensitizer is followed by electron injection into the conduction band of an oxide semiconductor film, where the electrons diffuse across the semiconductor film and collected at the conducting glass electrode. The dye molecule is regenerated by the redox system, which itself is regenerated at the counter electrode by electrons passed through the load. Potentials are referred to the normal hydrogen electrode (Grätzel 2004). Abbreviations: *S* sensitizer, *TiO_2* titanium dioxide, *E* potentials, *NHE* normal hydrogen electrode, *Red* reduction, *Ox* oxidation, *e^-* electrons

diffuse via “mobile electron/hole pair” towards the transparent electrode surface. The oxidized sensitizer accept the electrons from iodide ions, I^- present in the redox electrolyte and resultant tri-iodide ions, I_3^- are reduced back to I^- at the counter electrode, thereby forming a closed electrical circuit.

Dye-sensitized solar cell (DSSC) is one of the most attractive solar cells due to the high photoconversion efficiency that can be achieved by simple and low cost fabrication methods (Umeyama and Imahori 2008). It uses typically, a ruthenium metalorganic dye, Ru(II) as sensitizer on a mesoscopic titanium dioxide (TiO_2) semiconducting film attached to the optically transparent electrode (OTE) to harness sunlight for conversion into electricity. The major hurdle in attaining high photoconversion efficiency is the photoinduced electron transport across the semiconductor network, as the grain boundaries encountered during the transit can result in charge recombination before they are efficiently collected at the electrode surface (Grätzel 2004; Kamat et al. 2004). This random transit path of electron enhances the probability of charge recombination with oxidizing species or photoexcited sensitizer and the tri-iodide ions in the electrolyte, thus inhibiting the photoconversion efficiency. Integration of CNTs into the electrode had been performed and the results showed that CNTs with one-dimensional nanostructural networks effectively direct the flow of photogenerated electron transport across the semiconductor network, and thus enhancing the electrical conductivity of the electrode and increasing the photoconversion efficiency (Kongkanand and Kamat 2007; Lee et al. 2007). Therefore, extensive research has been carried out to obtain high efficiency DSSC by introducing CNTs into the device, such as nanoarchitecture on electrode surface (Sawatsuk et al. 2009; Imahori and Umeyama 2009), CNTs composite as counter electrode (Mei et al. 2009; Ramasamy et al. 2008), and adding CNTs to the electrolyte (Lee et al. 2009a).

The employment of SWCNTs network on OTE as a one-dimensional nanoscaffold for dye-sensitized TiO_2 nanoparticles has been reported to improve the charge separation via promoting charge transport in mesoscopic TiO_2 films (Brown et al. 2008). Scanning electron micrographs of the OTE/SWCNT/TiO_2/Ru(II) electrode revealed that the TiO_2 nanoparticles attached to the SWCNTs network provide a complete coverage and retain its mesoscopic morphology. Both transient absorption spectra and emission lifetimes measurements of the OTE/SWCNT/TiO_2/Ru(II) and the reference OTE/TiO_2/Ru(II) electrodes indicated that the SWCNTs networks in the film have no significant influence on the charge injection process. Nanosecond laser flash photolysis results suggested that the photoinduced electrons in TiO_2 survive roughly 50% longer when embedded within the SWCNTs network, therefore reducing the rate of charge recombination. SWCNTs exhibited about 30% higher photocurrent in photoelectrochemical measurements and enhancement in the photoconversion efficiency, which suggest that the SWCNTs network improved the charge collection and transport, as well as the photocurrent generation.

Preparation of TiO_2-MWCNT composites on an indium-tin oxide (ITO) glass substrate for working electrode in DSSC by using simple direct mixing method has been reported, in which the authors claimed that the technique is suitable for large scale production (Sawatsuk et al. 2009). Photocurrent-voltage characteristics of electrode with different MWCNTs loading were studied, in which the photoconversion efficiency was increased by approximately 50% compared to the conventional DSSC at an optimal loading of MWCNTs at 0.025 wt%. The reproducibility of CV measurements up to 50 cycles showed that the direct mixing method is suitable for large scale production of electrodes with sufficient stability for DSSC. Recently, a novel solar cell was reported based on donor-acceptor nanoarchitecture on semiconducting electrodes, where CNTs were used as the electron acceptor material due to the unique one-dimensional nanostructure as the ideal charge transport pathway in the photoactive layer (Imahori and Umeyama 2009; Umeyama and Imahori 2008). The donor-acceptor multilayers were deposited electrophoretically or spin-coated onto nanostructured electrodes, therefore initial charge separation occurs at the blend interface of donor-acceptor molecules. The sequential electron transfer from the donor-excited state to the conduction band of semiconductor nanoparticles via CNTs as the electron acceptor minimizes the undesirable charge recombination and improves the cell performance.

The conventional Pt counter electrode has the advantage of high catalytic activity in reduction of the redox species, but it suffers from the high cost of noble Pt and the high temperature process to deposit on a flexible plastic substrate (Fan et al. 2008). CNTs show strong potential and simpler alternative counter electrode for its fast electron kinetics and large surface area. Preparation of a counter electrode with MWCNTs film sprayed coated on fluorine-tin oxide (FTO) glass substrate was reported, in which the film thickness was controlled by varying the spraying time (Ramasamy et al. 2008). In another report, conducting polymer/CNT composite was prepared as counter electrode by spin coating the composite on FTO glass substrate and the film thickness was controlled by adjusting the spin rate (Mei et al. 2009). Photoelectrochemical measurements of these CNTs modified counter electrodes exhibited high photovoltaic performance and the photoconversion efficiency is close to that of DSSC with conventional Pt counter electrode. The effect of film thickness on the photovoltaic performance of DSSC was studied with electrochemical impedance spectroscopy measurements. The results indicated that the charge transfer resistance reduced with increased film thickness of CNTs due to the medium catalytic function of the counter electrode, which resulted in increased photoconversion efficiency.

Quantum dot-sensitized solar cell (QDSC) is fundamentally similar to DSSC, except that it utilizes inorganic semiconductor quantum dots as sensitizer, instead of organic dyes (Kamat 2008). Quantum dots have the advantages of high extinction coefficient and quantum confinement effect, where the electronic and optical properties of quantum dots can be controlled by changing their size to improve the overall power conversion efficiency (Moreels et al. 2009, 2007). In addition, quantum dots possess high energy excitation, which can further boost the performance of QDSC through creation of hot electrons and/or multiple charge carrier generation (Nozik 2005) Despite the expected potential of quantum dots, the photoconversion efficiency of QDSC is still not satisfactory due to the rapid charge recombination that limits the charge collection at electrode surface (Lee et al. 2008). Therefore, integration of CNTs in QDSC plays the same role as in DSSC to facilitate the charge transport in the photoactive layer and to improve the photoconversion efficiency by reducing charge recombination.

The preparation of SWCNTs layer between ITO glass substrate electrode and lead (II) sulphide (PbS) quantum dots on porous TiO_2 films by successive ionic layer adsorption and reaction method has been reported to facilitate electron transport and reduce charge recombination in PbS/TiO_2 system (Lee et al. 2009b). Photocurrent-voltage characteristics of the solar cell were studied and the PbS/TiO_2/SWCNT/ITO electrode showed higher photoconversion efficiency as compared to the reference PbS/TiO_2/ITO electrode. Increment in the photoconversion efficiency was due to the suppression of charge recombination in the presence of SWCNTs in photoactive layer. The electron lifetime of PbS/TiO_2/SWCNT/ITO electrode was higher, which further verify the reduced charge recombination process, as more electrons survived from the charge recombination process. The increased photoconversion efficiency of the proposed QDSC was attributed to the reduced charge recombination and improved charge collection efficiency in the presence of SWCNTs.

Other recent advances in solar cell include research activities to fabricate CNTs thin films on various substrates (Kymakis 2006). The aim of the research to replace the commonly used ITO glass substrate with a promising alternative material, due to the high raw material cost of indium. This fabrication method involves the formation of very thin layers of highly-transparent conductive films based on CNTs dispersion on various substrates including polyethylene terephthalate, glass, poly(methyl methacrylate), and silicon (Zhou et al. 2006). Integration of CNTs into the electrode of solar cells had exhibited an increased photoconversion efficiency of 30–50%, which was attributed to the effective role of CNTs to facilitate the charge transport across the photoactive layer, to reduce the rate of charge recombination and therefore, to improve the photoconversion efficiency of solar cells. The current goal for the research community is to improve the lifetime and efficiency of solar cells, which will serve as the future clean and sustainable energy source.

1.2.2 Fuel Cells

The urgent needs for environmental friendly and sustainable energy has resulted in a tremendous increase of research effort on fuel cell technology, as fuel cells provide a clean alternative to other types of energy (Xu et al. 2008). Low temperature fuel cells, such as polymer electrolyte membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC) are promising alternative source of electrical power, owing to their high power density, low operating temperature and water as the only by-product. Pt and its alloys are used as anode and cathode catalysts in low temperature fuel cells (Antolini 2009). All fuel cells work on the similar basic principle except from the deviation of the fuel used (Fig. 1.6). Hydrogen molecules are provided at the anode side and then oxidized to protons and electrons as they passed through the Pt catalysts suspended on carbon-based support on the polymer electrolyte membrane. The electrons flow through the external circuit to produce electricity, whereas the protons permeate through the membrane and reduced with oxygen molecules at the cathode side to produce water.

There are several factors that greatly influence the reaction activities and kinetics of the carbon supported catalysts, such as the nature of the carbon support, catalytic particle size, and catalyst composition (Li et al. 2009). Recent studies have revealed that the physical properties of the carbon support can significantly affect the electrochemical activities of Pt catalyst and consequently, to improve the electrochemical efficiency of fuel cell (Wu et al. 2010; Antolini 2009). The key properties of carbon support to improve the catalyst activity include high surface area, high porosity, high electrical conductivity, and high stability in fuel cell environment. Despite the high surface area and low electrical resistance of the commonly used Vulcan XC72R (VXC72R) carbon black as carbon support, the Pt/VXC72R composite suffers from low Pt utilization and poor electrochemical stability (Tang et al. 2010a). Recently, CNTs have been exploited as an alternative catalyst support in fuel cell applications due to their unique properties. CNTs have the advantage of high surface area with high porosity, which enable the higher accessibility of catalyst particles deposited on CNTs to favour catalyst utilization (Jha et al. 2008). In addition, CNTs show higher electrical conductivity, better electrochemical durability and more resistant

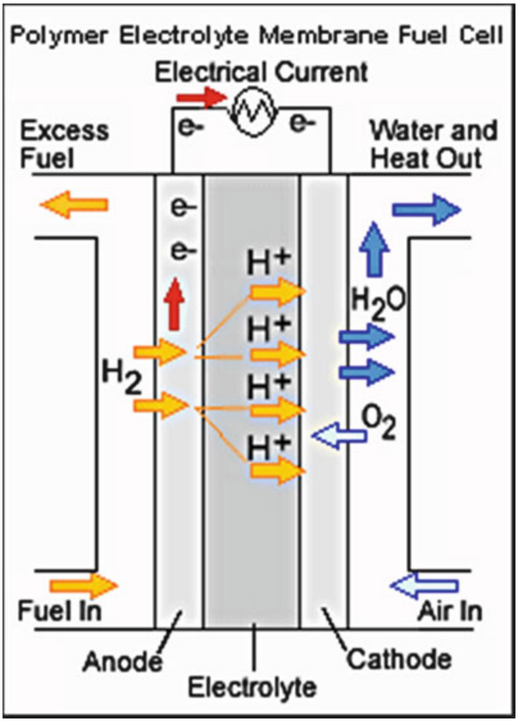

Fig. 1.6 Schematic presentation of operating principles of a polymer electrolyte membrane fuel cell. Oxidation of hydrogen molecules takes place at anode to produce protons and electrons, where protons flow through the electrolyte membrane and electrons through external circuit to cathode. Reduction of protons and oxygen molecules occurs at cathode to produce water and electricity (United States Department of Energy 2009). Abbreviations: H_2 hydrogen molecules, O_2 oxygen molecules, H_2O water, H^+ protons, e^- electrons

to electrochemical oxidation, as compared to carbon black materials (Li and Xing 2006; Li et al. 2003). As a result, fuel cells with CNTs as catalyst support material show higher performance in terms of fuel conversion efficiency, durability and stability (Mirabile Gattia et al. 2009).

The synthesis of Pt nanoparticles on MWCNTs as catalyst support was reported, in which a wet chemistry route, involving two-phase ion transfer followed by solution reduction approach to obtain the solid Pt/MWCNT nanocatalyst (Lin et al. 2010). The high-resolution transmission electron micrographs showed that the Pt nanoparticles are uniformly distributed on the surface of MWCNTs, which is essential for enhancing fuel cell performance and durability. The single cell testing of Pt/MWCNT based membrane electrode assembly (MEA) revealed that the Pt nanocatalyst based MEA performs better with higher current densities compared to that of the commercial catalyst with similar Pt loading, 0.2 mg/cm^2 at anode and 0.4 mg/cm^2 at cathode. In addition, the Pt nanocatalyst based MEA exhibited high durability by measuring the current density for a period of 100 h, as well as high stability by performing CV to measure the electrochemical active area before and after the 100 h durability test. The enhanced performance of the cell was attributed to the reduced catalyst particle size, improved chemical activity and stability of CNTs based catalyst support.

An efficient fabrication method of CNT-supported Pt catalyst for PEMFC has been reported, where the integrated Pt/CNT layer was prepared by in situ growth of CNTs layer on carbon paper using chemical vapour deposition followed by direct sputter-deposition of Pt nanodots onto the CNTs layer (Tang et al. 2010b). The transmission electron micrographs demonstrated that the Pt/CNT layer consist of a CNTs layer with high porosity and high surface area, covered by homogeneous distribution of Pt nanodots. Polarization curves measurement of MEA with Pt/CNT catalyst on cathode exhibited improved performance in power density, as compared to reference MEA with commercial Pt/VXC72R catalyst on cathode. Higher catalytic performance of Pt catalysts was attributed to the highly localized Pt distribution region at the membrane-electrode interface, which resulted in a higher Pt utilization for low Pt loadings.

Other than the development of carbon supports for catalyst, recent studies focus onto reducing the poisoning of Pt catalyst by carbon monoxide at anode and enhancing the electrocatalytic activity of Pt for oxygen reduction at cathode. Reports on utilizing co-catalyst with the transition metal oxides, such as ruthenium (IV) oxide (RuO_2), titanium dioxide (TiO_2), cerium (IV) oxide (CeO_2), tin oxide (SnO_2) and tungsten oxide (WO_3) have shown to increase the carbon monoxide tolerance of Pt particles and to assist the removal of the poisoning intermediate through carbon monoxide electro-oxidation (Zhou et al. 2010; Li et al. 2009). As for the application of CNTs in fuel cells technology, CNTs based catalyst supports had exhibited higher Pt catalyst utilization to increase the electrochemical efficiency of fuel cells, in addition to the higher durability and stability of catalyst supports in fuel cell environment. The current challenge is to develop CNTs based catalyst supports with high surface area, suitable porosity, and good electrical conductivity for enhanced performance of fuel conversion efficiency, durability, and stability in fuel cell environment.

1.2.3 Hydrogen Storage

Hydrogen is seen as an important new source of energy due to its inherent pollution free nature from clean combustion, resource availability and provision of the highest energy efficiency (Lim et al. 2010). However, hydrogen storage is a major barrier in the development towards feasible commercial use of hydrogen in fuel cells. Current strategies for hydrogen storage include compression and liquefaction, which have high storage volume efficiencies but fail to meet the criteria for on-board applications due to their individual drawbacks (Yürüm et al. 2009). The United States Department of Energy has revised the targets for on-board hydrogen storage medium in April 2009, where the medium should have a storage capacity of 4.50 wt% by 2010 and 5.50 wt% by 2015 (Miller et al. 2009). Nanostructured carbon materials especially CNTs have shown potential advantages to store hydrogen by physisorption and/or chemisorption mechanisms. Generally, physisorption has the advantages of higher energy efficiency and faster adsorption/desorption cycles but lower hydrogen storage capacity, whereas chemisorption results in higher hydrogen storage capacity but the process is not reversible in some cases or requires significant energy to release the adsorbed gas.

Hydrogen storage in CNTs via physisorption mechanism involves the weak van der Waals interactions between the hydrogen molecules as adsorbate and CNTs as adsorbent. The typical adsorption sites for hydrogen molecules are the interstitial sites between the tube arrays and the pores within the tube, in addition to the structural defect sites. Despite the reported high hydrogen storage capacity of CNTs from 4 to 10 wt%, the reproducibility of these high capacities of CNTs is poor and the actual mechanism of hydrogen storage in CNTs remains unclear (Liu et al. 1999; Ye et al. 1999; Dillon et al. 1997). In a recent work by Liu and co-workers, various CNTs samples, including SWCNTs and MWCNTs, with and without post-treatments, were employed for hydrogen storage measurements by a volumetric method with a specifically designed Sievelt apparatus (Liu et al. 2010) The results showed that CNTs had a hydrogen storage capacity of less than 1.7 wt% under the pressure of 12 MPa at room temperature. They claimed that investigation of hydrogen storage in pure CNTs for on-board applications should be discontinued, but instead, focusing on hybrid structures of CNTs and materials with potential high hydrogen storage capacity.

CNTs composite storage materials, such as SWCNTs doped with alkali or transition metals and SWCNTs coated with metal hydrides have shown better hydrogen storage capacities due to the chemisorption mechanism involved (Durgun et al. 2008; Dag et al. 2005; Yildirim and Ciraci 2005). These systems have the advantages of storing/releasing hydrogen at ambient conditions, as well as the ability of metal hydrides to adsorb certain amount of additional hydrogen molecules (Lochan and Head-Gordon 2006). Examples of metal hydrides that have been coated on SWCNTs to facilitate the adsorption of hydrogen molecules and to increase the hydrogen storage capacity are aluminium hydride, boron hydride, lithium hydride, and nickel hydride (Surya et al. 2010; Iyakutti et al. 2009; Surya et al. 2009). Iyakutti et al. (2009) reported a first principle study on the hydrogen storage in aluminium hydride (AlH_3) coated SWCNTs. First principles plane-wave calculations were carried out within density functional theory with the generalized gradient approximation to evaluate the hydrogen storage capacity of SWCNTs at half coverage and full coverage of AlH_3. There were 5 AlH_3 molecules attached around SWCNTs at half coverage and each AlH_3 molecule can adsorb up to 4 hydrogen molecules, denoted as $C5(AlH_3+4H_2)$, and the system qualified as a hydrogen storage medium with a hydrogen storage capacity of 8.3 wt%. The full coverage system denoted as $C10(AlH_3+xH_2)$ though exhibited higher storage capacity, it was not suitable for storing hydrogen due to the lower hydrogen binding energy and clustering of AlH_3.

Surya et al. (2010) reported the first principles study based on density functional theory of the hydrogen storage capacity of SWCNTs coated with lithium hydride (LiH) and nickel hydride (NiH_2) in their recent work. In half coverage system of

LiH, SWCNTs were coated with 5 LiH molecules with each capable of holding up to 5 hydrogen molecules, and the CNT-5(LiH + 5H_2) system showed an optimum hydrogen storage capacity and binding energy of 7.36 wt% and 0.14 eV, respectively. The CNT-10(LiH + 3H_2) system at full coverage of LiH exhibited high hydrogen storage capacity of around 7 wt% but with slightly lower binding energy. Both half and full coverage cases of CNT-NiH_2 system were not suitable for storing hydrogen due to the strong bond formation between CNT and NiH_2 molecules, which resulted in low hydrogen storage capacity and binding energy. These interactions reached a saturation level such that the CNT-NiH_2 system was not capable of adsorbing more hydrogen molecules and changes in clustering pattern upon adsorption of successive hydrogen molecules. The study highlighted the CNT-LiH system as a potential hydrogen storage medium with the advantages of high hydrogen storage capacity and storing/releasing hydrogen at ambient conditions.

Despite the expected potential advantages of CNTs to store hydrogen, the reproducibility of hydrogen storage capacity in pristine CNTs is poor. Nevertheless, CNTs composite storage materials, such as CNTs doped with metal hydrides had proven to be the potential hydrogen storage medium with higher hydrogen storage capacity, in addition to the advantage of sorption-desorption of hydrogen at ambient conditions. Intensive research studies are underway to optimize and to improve the performance of CNTs based hydrogen storage medium in terms of storage capacity and the sorption-desorption kinetics.

1.2.4 Lithium Ion Batteries

Lithium ion batteries are becoming the main power source in today’s portable electronic devices and hybrid electric vehicles, due to their high energy density, high operating voltage, and low self-discharge rate (Yang et al. 2009). The basic principle of rechargeable lithium ion batteries is the electrochemical intercalation and de-intercalation of lithium in both electrodes. During intercalation or discharging process, lithium ions from cathode are inserted or intercalated into the lithium insertion materials of anode, thus producing a current flow; whereas during de-intercalation or charging process, an external electrical power source forces the current flow in the reverse direction, lithium ions are extracted from anode back to cathode. The commercialized lithium ion batteries have graphite anode and a cathode of metal oxide, such as $LiCoO_2$ with high columbic efficiencies, but rather low discharge capacities of 372 and 145 $mAhg^{-1}$, respectively (He et al. 2010). Many efforts have been invested to develop new electrode materials or to design novel structures of electrode materials, so as to improve the performance of lithium ion batteries, such as high energy capacity, excellent cycling stability and rate capability (Zheng et al. 2008; Hu et al. 2006; Yang and Wu 2001; Gao et al. 2000).

CNTs have been employed as the alternative anode material in lithium ion batteries due to their unique structural properties, high electrical conductivity, mechanical strength, and chemical stability. It is expected that CNTs to exhibit high energy density as anode material if all or majority of the interstitial sites in CNTs are accessible for lithium intercalation. The electrochemical intercalation of SWCNTs with lithium was demonstrated and the effects of processing on the structure and morphology of SWCNTs on the performance of lithium intercalation were investigated (Gao et al. 2000, 1999). The purified SWCNTs showed a reversible capacity of 600 $mAhg^{-1}$, which was significantly higher than the capacity for graphite. The reversible capacity increased to 1,000 $mAhg^{-1}$ while the irreversible capacity reduced to 650 $mAhg^{-1}$ when SWCNTs bundles were fractured and cut into smaller segments by impact ball-milling. However, the large irreversible capacities and voltage hysteresis, as well as the absence of voltage plateau observed in all SWCNTs materials have limited the application of CNTs as the electrode material in lithium ion batteries.

Recently, intensive research efforts are focusing on developing CNTs nanocomposites with CNTs acting as an intercalation host or matrix for dispersion of lithium insertion materials (He et al. 2010; Xu et al. 2009). Several metals and metal oxides are investigated as lithium insertion materials in anode owing to their high theoretical capacities. However, large volume changes and agglomeration of these metals or metal oxides during charging and discharging process lead to the rapid pulverization of the electrode and the decrease of electrical conductivity, which in terms limit the cycling capability or cycle efficiency (Hu et al. 2008; Yang et al. 2007; Choi et al. 2004). CNTs appear to be one promising candidates for intercalation matrix to restrain the volume expansion or pulverization of electrode materials, while retaining their high capacities. This is because CNTs exhibit high electrical conductivity, high aspect ratio, remarkable thermal conductivity, and superior mechanical strength, which could improve the reversible capacity, cycling stability, and rate capability of the electrode (Landi et al. 2009).

The preparation of SnO_2/MWCNT composites by solvothermal method as anode materials in lithium ion batteries has been reported since SnO_2 shows a high theoretical capacity of 782 $mAhg^{-1}$ (Du et al. 2010). The SnO_2/MWCNT composites were prepared in two different SnO_2 content, low SnO_2 loading and high SnO_2 loading with molar ratios of Sn:MWCNT of 0.1:1 and 0.3:1, respectively. Characterization of the composites by scanning electron microscope, X-ray diffraction, and transmission electron microscopy revealed the deposition of very fine SnO_2 nanoparticles on the surface of CNTs and the nanoparticles formed a uniform layer on the surface of CNTs in the case of high SnO_2 loading. CV measurements were performed to investigate the cycling performances of the samples up to 100 cycles. Bare SnO_2 electrode showed the highest initial discharge capacity of 1,665 $mAhg^{-1}$ but poor cycling stability as the capacity gradually decreased until the 60th cycle due to the agglomeration of SnO_2 particles and the associated volume change of SnO_2 particles. Both SnO_2/MWCNT composites showed stable capacity retention, in which the composite with high SnO_2 loading demonstrated an initial reversible capacity of 709.9 $mAhg^{-1}$ and capacity retention of 402 $mAhg^{-1}$ up to the 100th cycle. The improved performances of SnO_2/MWCNT composite in terms of reversible capacity and cyclic capacity retention were attributed to CNTs as the intercalation host for SnO_2 nanoparticles that reduced the absolute volume change and prevented the agglomeration of SnO_2 nanoparticles.

Germanium (Ge) is one of the promising lithium insertion materials, owing to the high theoretical capacity of 1,600 mAhg^{-1} and high diffusivity of lithium (Graetz et al. 2004). The preparation of novel Ge/CNT nanocomposites by a facile precursor method through a pyrolysis technique was reported and applied as anode materials in lithium ion batteries (Cui et al. 2010). Characterization via X-ray diffraction and Raman spectroscopy verified the formation of crystalline Ge nanoparticles supported by CNTs, as well as transmission electron microscopy which revealed the carbon coatings around Ge nanoparticles inside CNTs. The electrochemical performance of Ge/CNT nanocomposites were evaluated in galvanostatic discharge-charge experiments, in which the nanocomposites showed high initial discharge and charge capacities of 1,740 and 696 mAhg^{-1}, respectively. The nanocomposites exhibited a highly stable and reversible capacity of 750 mAhg^{-1} and a columbic efficiency of 95% after a few cycles, which were attributed to the nanostructure of highly dispersed Ge nanoparticles in CNTs.

Despite the high theoretical capacities of lithium insertion materials, they suffer from rapid pulverization during charging and discharging process, leading to poor cycling stability. With CNTs acting as an intercalation host, high dispersion of lithium insertion materials can be achieved to increase the reversible energy capacity, in addition to restraining the pulverization of the electrode materials and therefore, to improve the cycling stability and rate capability of the electrode. Integration of CNTs had proven to improve the performance of lithium ion batteries in terms of energy capacity, cycling stability, and rate capability.

1.2.5 Electrochemical Supercapacitors

Electrochemical supercapacitors are considered as the ideal energy storage and power output technologies for portable electronic devices, digital communications, hybrid electric vehicles, and renewable energy systems, due to the advantages of high power and energy density characteristics, high cycle efficiency and long cycle life (Simon and Gogotsi 2008; Winter and Brodd 2004). Electrochemical supercapacitors based on carbon are of two different mechanisms of energy storage, namely the electrochemical double layer capacitor and pseudo-capacitor (Frackowiak and Béguin 2001). Electrical double layer capacitor involves solely a pure electrostatic attraction between ions and charged surface of the electrode, which is commonly obtained from activated carbons, carbon aerogels and CNTs. As for pseudo-capacitor, it involves faradaic redox reaction of electroactive materials at the electrode/electrolyte interface, which give rise to the pseudo-capacitance effects in addition to the electrostatic charge separation capacitance.

Recently, CNTs have been explored as electrode materials for hybrid supercapacitors, which combine the electrical double layer capacitive electrode and the pseudo-capacitive electrode, due to their high electrical conductivity, chemical stability, low mass density and large surface area (Du and Pan 2006; Pandolfo and Hollenkamp 2006). Chemical activation of CNTs by KOH has enhanced the capacitance, due to the increase of specific surface area and micropores volume for improving the electrical double layer charging (Frackowiak et al. 2002; Jiang et al. 2002). Electrochemical conducting polymers for instance, polyaniline, polypyrrole, and polythiophene derivatives, as well as the metallic nanoparticles or transition metal oxides, such as manganese dioxide (MnO_2) and zinc oxide (ZnO) are deposited onto CNTs to increase the total capacitance through faradaic pseudo-capacitance effects (Yan et al. 2010; Wang et al. 2009; Zhang et al. 2009).

Graphene nanosheet/carbon nanotube/polyaniline (GNS/CNT/PANI) composite was prepared via in situ polymerization and applied as electrode materials for electrochemical supercapacitors (Yan et al. 2010). Scanning electron micrographs and transmission electron micrographs revealed the growth of PANI particles on the surfaces of GNS as support material and CNT as conductive wires interconnected among GNS/PANI particles. Both CV and galvanostatic charge/discharge measurements indicated that the energy consumed by the internal resistance is reduced with good rate capability and improved effective energy storage in GNS/CNT/PANI composite electrode. The GNS/CNT/PANI composite exhibited a high specific capacitance of 1,035 Fg^{-1} but slightly lower than GNS/PANI composite, 1,046 Fg^{-1} as more PANI agglomerations were observed in GNS/CNT/PANI composite resulted in lower electrochemical utilization of PANI. However, the specific capacitance of GNS/CNT/PANI composite was larger than other porous carbon materials supported PANI composite and it exhibited excellent cycle stability with only 6% lost of initial capacitance up to 1,000 cycles. The high specific capacitance of GNS/CNT/PANI composite was attributed to the highly conductive GNS support for deposition of PANI particles and CNT as highly conductive path in the composite, whereas the excellent cycle stability was attributed to the CNT conductive network with improved mechanical strength during long term charge/discharge process.

Investigation of CNT-ZnO nanocomposite electrodes for electrochemical supercapacitors was reported (Zhang et al. 2009). ZnO nanodots were deposited onto the CNT films by ultrasonic spray pyrolysis and the deposition time was adjusted to obtain different amounts of ZnO nanodots in the nanocomposite. The surface morphologies of ZnO nanodots on CNT film were observed in scanning electron micrographs and transmission electron micrographs, where the increase in deposition time resulted in the densely packed ZnO grains on CNT film. The results from CV and galvanostatic charge/discharge measurements showed that the CNT-ZnO nanocomposite electrode exhibited higher specific capacitance compared to bare CNT electrode due to the presence of ZnO that contributed to the pseudo-capacitance. However, excess ZnO in nanocomposite showed deteriorating capacitive performance as the network structure of CNT matrix was destroyed and the electrode conductivity was lowered. The CNT-ZnO nanocomposite with optimum deposition time of 5 min achieved a specific capacitance of 323.9 Fg^{-1} and demonstrated good cycle stability.

Deposition of CNTs with conducting polymers and metal oxides as the electrode for electrochemical supercapacitors had exhibited an increased specific capacitance through faradaic pseudo-capacitance effects and due to the high electrical conductivity of CNTs. In addition, integration of CNTs had improved the mechanical strength of the electrode materials, which lead to the enhanced cycle stability of the electrode. With CNTs as the conductive filler in the electrode, higher energy capacity and cycle efficiency of electrochemical supercapacitors can be achieved.

1.3 Carbon Nanotubes in Environmental Monitoring and Wastewater Treatment

With the rapid development and economical growth in nations across the globe, the associated environmental pollution issues are becoming more serious and receiving much attention in seeking solutions to overcome the issues. Pollution by means of air, water, and soil has resulted in the environmental degradation of air quality, water quality, and soil composition, in addition to the adverse effects to the ecosystem. The effect of pollutants on the environment is very complex as undesirable transfers occur continually among different environmental sections. Pollutants that are released to the air may end up in soils or water, which may be washed off by rain into nearby natural water bodies and consequently, jeopardize our drinking water and food supply. Humans are often exposed to the myriad adverse health effects caused by pollutants toxicity, mainly through the ingestion of contaminated food and drinking water, as well as the inhalation of ambient air with high concentrations of pollutants. Obviously, there is an urge for the development of technology and techniques to detect the presence of these pollutants in any medium, as well as to remove them or to reduce their concentrations to safe and permitted levels.

CNTs with their unique properties, such as high electrical conductivity, good chemical stability, high mechanical strength, and high aspect ratio appear to be very attractive for electrochemical sensing to detect pollutants (Injang et al. 2010). Furthermore, CNTs with large surface area and easily modified surface have opened up exciting research opportunities for the development of CNTs based adsorbent to remove pollutants, especially in wastewater (Yao et al. 2010). The potential applications of CNTs as sensing material for the detection of pollutants and CNTs as adsorbent for the removal of pollutants are reviewed in the following section.

1.3.1 Gas Sensors

Air pollutants have been the major factor contributing to the degradation of air quality, leading to chronic effects on human health, such as chronic obstructive pulmonary diseases, cardiovascular diseases, asthma, and cancer (Yang and Omaye 2009; Kampa and Castanas 2008). Air pollutants, such as carbon monoxide (CO), carbon dioxide (CO_2), sulphur oxides (SO_x), nitrogen oxides (NO_x), ozone (O_3), volatile organic compounds (VOCs), heavy metals, and particulate matter (PM2.5 and PM10) are generated from human-derived anthropogenic activities, especially combustion of fossil fuels. Noteworthy that some of these hazardous air pollutants are greenhouse gases, such as CO_2, N_2O, and O_3 that contribute to the global climate change and global warming. Concerning the adverse effects of these air pollutants on environment and human health, the detection of these air pollutants by means of miniature and portable sensors with good sensing performance is of great importance for environmental pollution analysis, public security, industrial emission monitoring and control, medical diagnosis, and agriculture (Goldoni et al. 2010).

Conventional solid-state gas sensors based on semiconducting metal oxides and conducting polymers are highly sensitive and relatively selective, but they suffer from the disadvantages of elevated working temperatures and long-term stability problems (Bai and Shi 2007; Barsan et al. 2007). In efforts to develop a miniaturized sensor with high sensitivity and fast response time, CNTs show promising potential as gas sensing nanomaterials due to their gas adsorption capability and large active surface area (Wei et al. 2010; Penza et al. 2009). The basic principles of gas sensing by CNTs is to measure the changes in conductivity of CNTs when the adsorbed gas molecules participate in charge transfer with CNTs either as an electron donor or acceptor that would produce a change in electronic structure or conductivity properties of CNTs (Fam et al. 2009). In fact, CNTs based gas sensors have already demonstrated their advantages of high sensitivity, fast response, real-time analysis, good reversibility, low power consumption, small size, and low operating temperature (Penza et al. 2010; Zhang and Zhang 2009). These features of miniaturized CNTs based gas sensors are advantageous in hazardous gas detection and environmental pollution monitoring.

Basically, there are two sensor configurations commonly employed in CNTs based gas sensors, which are the field-effect transistor chemical sensor and chemiresistor (Zhang and Zhang 2009). The field-effect transistor chemical sensor utilizes a single semiconductive CNT, whereas the chemiresistor utilizes a thin film of CNTs networks as the active sensing element and the conductivity of CNTs are monitored when the sensors are exposed to chemical environment. Gas sensors based on pristine CNTs including SWCNTs, MWCNTs, and aligned CNTs are reported to show good responses to NO_2, NH_3, SO_2, and NO, despite their poor selectivity and slow recovery at ambient conditions (Moon et al. 2008; Goldoni et al. 2003, 2004; Valentini et al. 2004). The selectivity of CNTs based gas sensor can be enhanced by functionalization of CNTs with organic polymers, catalytic metals, and metal oxides that serve as sensing elements (He et al. 2009; Hoa et al. 2009; Penza et al. 2009). Furthermore, intensive investigations are carried out in developing sensors based on CNTs functionalized with metal oxides, such as SnO_2, WO_3, and TiO_2 due to the fact that these metallic clusters are mechanically and chemically robust and stable, which enable the sensors to operate at higher temperature and harsher environment.

Preparation of a MWCNT-doped SnO_2 thin film gas sensor by radio frequency reactive magnetron sputtering has been reported, in which the sensor showed a very good selectivity and a higher sensitivity than a pure SnO_2 thin film gas sensor to ultra-low concentrations of NO_2 in the ppb range, up to 100 ppb NO_2 (Wei et al. 2010). Gas sensing characterizations implied that the calcination temperature, film thickness and working temperature for MWCNT-doped SnO_2 composite thin film should be optimized for practical applications to obtain high sensitivity and faster response time. The improved performance of MWCNT-doped SnO_2 thin film gas sensor was attributed to the effects between p-type semiconductor of MWCNTs and n-type semiconductor of SnO_2 as the depletion layer at the p-n junction was modulated by the changes in barrier height and conductivity of the SnO_2/MWCNT sensitive layer by adsorbed NO_2. A gas sensor based on hybrid nanomaterials of oxygen plasma treated MWCNTs decorated with SnO_2 nanoclusters was reported to show superior performance in detecting NO_2 in the ppb range and CO in the low ppm range (Leghrib et al. 2010). It was derived from the gas sensing properties of hybrid nanomaterials that an optimal ratio between the amounts of MWCNTs and SnO_2 should be used during preparation to maximize the responsiveness towards NO_2 and CO. In addition, the optimal hybrid nanomaterials showed a significantly reduced moisture cross-sensitivity compared to pure SnO_2 or hybrid nanomaterials with high content of SnO_2. The detection mechanism of the optimal hybrid nanomaterials varied with activation at different working temperatures, as a p-type semiconductor at room temperature, whereas as an n-type semiconductor at 150°C.

The fabrication of a novel antimony-carbon nanotube-tin oxide (Sb-CNT-SnO_2) thin film by sol-gel method and ultrasonic dispersion technique has been reported, which could be potentially applied as gas sensor for detecting indoor air pollutants emitted from building and decoration materials (Liu et al. 2008b). The sensor was applied to the detection of formaldehyde, ammonia, benzene, and toluene, in which an improved gas sensing performance, such as higher sensitivity and shorter response time was observed compared to pure SnO_2 and Sb-SnO_2 thin film. The effect of CNTs as growth guider and energy buffer was proposed as the mechanism for the enhancement of gas sensing performance, where the crystal growth is oriented by CNTs and protrusions formed with crystallites growth along surface of CNTs. The existence of electric field on the thin film with array-like protrusions was proposed to accelerate the adsorption and transfer of polar gases, resulting in rapid response to formaldehyde, ammonia, benzene, and toluene. CNT-modified WO_3 gas sensor was demonstrated and it was capable of detecting 500 ppb NO_2 or 10 ppm CO under ambient conditions, and 10 ppm NH_3 at 150°C, far below the typical operating temperature of WO_3 sensor (Bittencourt et al. 2006). Oxygen plasma functionalized MWCNTs were added to WO_3 by drop-coating deposition method and the morphology characterizations revealed that MWCNTs were embedded in WO_3 matrix. It was derived that the adsorption at the surface of CNTs modifies the depletion layer at the n-WO_3/p-MWCNT heterojunctions and this results in the modulation of the depletion layer at the surface of WO_3 grains. This change in the depletion layer at the n/p junction that induces a change in the WO_3 matrix may explain the improvement in responsiveness shown by hybrid sensors.

The ultimate goal of gas sensor research is to create ‘electronic noses’ that can detect a wide range of gases at low concentration levels under ambient atmosphere with sufficient reproducibility, sensitivity and selectivity (Fam et al. 2009). Research studies have revealed that the functionalization of CNTs with metal oxides to serve as sensing elements had exhibited high sensitivity and selectivity towards many air pollutants, in addition to the advantages of fast response time and low operating temperature. CNTs based gas sensor have proved to meet all the criteria and are receiving much attention for development to exploit their application in various fields, such as environmental pollution monitoring, hazardous gas detection, food processing, agricultural and medical diagnostics.

1.3.2 Pathogens

Conventional water treatment methods, such as filtration and disinfection have become less effective especially for bacteria and virus removal due to the reasons that (i) most of the systems are equipped with insufficient technology for pathogens removal to provide adequate protection against these biological water contaminants, (ii) some pathogens are highly resistant to disinfection techniques, and (iii) some pathogens may contaminate the water distribution systems, downstream to the water treatment systems (Nuzzo 2006). Furthermore, most pathogens are colourless, tasteless, and odourless, which add up the difficulty and complexity in their detection and treatment to remove pathogens. In recent years, nanotechnology with CNTs has demonstrated potential applications in water treatment industry with promising outcomes. Several numbers of studies have explored the applications of CNTs for bacteria and virus removal. Generally, the affinity of CNTs to bacteria and virus has made them an efficient adsorbent and hence, creating potential applications for wastewater treatment.

Recent studies are focussing on the antimicrobial activity of CNTs towards *Escherichia coli (E.coli)* and *Staphylococcus aureus (S.aureus)*. Upadhyayula et al. (2008a, b) reported that SWCNTs had high adsorption affinity towards both *E.coli* and *S.aureus* bacterial cells. The high adsorption and selectivity of these bacteria might be due to the unique fibrous mesoporous structure of SWCNTs that provides higher accessible surface area. The results also showed that the adsorption capacity and diffusion kinetics of *S.aureus* were higher compared to *E.coli*, which was attributed to the smaller diameter size and cocci-shaped of *S.aureus*. Moreover, it was suggested that the diffusivity was dependent on the concentration and types of bacteria.

The adhesive activities of MWCNTs were also studied by using *Streptococcus mutans (S.mutans)* (Akasaka and Watari 2009). MWCNTs with diameter of 30 and 200 nm, denoted as 30-MWCNTs and 200-MWCNTs had been reported to present a high adhesive ability for bacteria. However, 30-MWCNTs were more suitable for applications in wastewater treatment as 200-MWCNTs showed poor precipitation. Clearly, the results showed that the adhesive activities of CNTs were diameter dependent. The high precipitation efficiency may be attributed to the differences in the flexibility of CNTs, which contributed to the pathogens capturing by winding CNTs to ensure stronger adhesion and to inhibit the release and budding of captured bacteria.

Both SWCNTs and MWCNTs have been used in filter fabrication. A filter using a poly(vinylidene fluoride)-based microporous membrane covered with SWCNTs has been reported to remove pathogens, such as *E.coli K12* and MS2 bacteriophage, which is a model virus particle (Brady-Estévez et al. 2008). The SWCNT-hybrid filter was not only very effective for pathogens removal but also allowed high water fluxes at low operating pressure. Besides that, development of a nanofilter based on MWCNTs by using spray pyrolysis method was reported (Mostafavi et al. 2009). The nanofilter was used for MS2 virus removal. Similar to SWCNTs-hybrid filter, it showed good performance in virus removal, water permeability, and filtrate flux.

Due to the high bacterial adsorption capacity possessed by CNTs, research studies have revealed their applications as an efficient adsorbent or nanofilter to remove pathogens. Furthermore, intensive research efforts are currently focusing on the functionalization of CNTs to develop a biosensor to detect pathogens. Since CNTs possess antimicrobial properties, the biosensor will have the ability to concentrate and detect pathogens, in addition to the selective differentiation of bacterial strains attributed to the recognition properties of biomaterials. Therefore, CNTs are gaining much research interest into developing treatment-based and sensor-based applications in water and wastewater treatment industry.

1.3.3 Dyes

Dyes are colour organic compounds that are used to colourize other substances, which have been used extensively in many industries. Effluents contaminated with dyes are associated with a number of industrial processes, such as paper, textile, cosmetics, and plastics. The existence of dyes in natural water bodies is extremely undesirable as some of which are mutagenic and carcinogenic to human beings, in addition to their environmental concern (Crini 2006). The conventional methods used for dyes removal in wastewater treatment are biological oxidation and chemical precipitation, but these processes are effective only in treating wastewater with high concentration of dyes. Obviously, there is a need for a highly efficient, low cost and simple process to remove dyes in waste effluents prior to discharge into natural water bodies (Wu 2007).

Adsorption techniques has proven to be an effective process for dyes removal, of which CNTs have been receiving much attention as the material of interest as adsorbent due to their large specific surface area and unique structural properties. The utilization of CNTs for Methylene Blue removal has been demonstrated and the results verified the potentials of CNTs as adsorbent for dyes removal (Yao et al. 2010). It was shown that the equilibrium adsorption of CNTs increased when both concentration of Methylene Blue and temperature increased. Increase in equilibrium adsorption with increasing temperature indicated that the adsorption process of dyes into CNTs was an endothermic process.

With the rapid development in both nanotechnology and biotechnology, it is now possible to combine these two exciting fields to modulate the physical properties of nanomaterials with the molecular recognition and catalytic functional properties of biomaterials. To date, CNTs have been impregnated with chitosan hydrogel beads for the removal of Congo Red (Chatterjee et al. 2010). The impregnation of CNTs with chitosan had proven to be an effective biosorbent material with enhanced adsorption capacity for Congo Red as the amino and hydroxyl functional groups of chitosan show high affinity towards many classes of dyes (Bhatnagar and Sillanpää 2009), in addition to the improved mechanical properties of chitosan by adding CNTs. Furthermore, large surface area, hollow, and layered nanosized structures of CNTs have also made them an excellent adsorbent. In the study, maximum adsorption of CNTs impregnated with chitosan hydrogel beads for Congo Red occurred at (i) 0.01% CNTs since at higher concentration, CNTs tend to aggregate and block the access of Congo Red to the adsorption sites, (ii) pH value of 4 for Congo Red solution. It was also shown that the equilibrium isotherm of CNTs impregnated with chitosan hydrogel beads best fit the Langmuir isotherm model. Similar observations were obtained by investigating the adsorption efficiency of CNTs towards Procion Red MX-5B, where the adsorption capacity decreased with increased CNTs dosage and pH (Wu 2007). However, the adsorption capacity of CNTs increased with temperature suggesting that the adsorption of dyes into CNTs was an endothermic process.

The potential of CNTs as adsorbent to remove dyes was verified with the ability of CNTs to adsorb dyes with good adsorption capacity. Moreover, the adsorption capacity of CNTs can be further enhanced by functionalization of CNTs with biomaterials, which show high affinity towards dyes. The current goal for the research community is to develop a CNTs based adsorbent for dyes removal with outstanding adsorption capacity and regeneration capability, in addition to low production cost, non-toxic characteristics and biocompatible.

1.3.4 Heavy Metals

Heavy metals can be defined as metals with a density above 5 g/cm^3, especially those that are poisonous such as lead (Pb), cadmium (Cd), mercury (Hg), copper (Cu), zinc (Zn), nickel (Ni), etc. (Nies 1999). Sources of wastewater containing heavy metals are mostly from metallurgical industries, such as mining, smelting, metal finishing, electroplating, automotive, battery and electric cable manufacturing (Yilmaz 2007). Heavy metals are considered as one of the major toxic pollutants due to its long persistency in the environment as they cannot be degraded. Moreover, ingestion of heavy metals-contaminated food and drinking water as well as the inhalation of ambient air with high concentrations of heavy metals will lead to myriad adverse health effects caused by heavy metals toxicity, including allergic reactions, neurotoxicity, nephrotoxicity, cancer, cardiovascular disease, and many others (Ismail et al. 2005; Nies 1999). Therefore, extensive research are carried out to develop techniques for the detection of heavy metals at trace amounts, as well as to remove heavy metals in the wastewater.

The unique structure and high surface area of CNTs have made them a good adsorbent for the removal of heavy metals. However, it was reported that pristine CNTs had low adsorption capacity of Pb^{2+} due to the absence of functional groups on the surface of CNTs (Li et al. 2002). The adsorption capacity of CNTs was improved by oxidation with oxidized acid to introduce functional groups on the surface of CNTs. In addition, the pH value of the solution significantly influenced the adsorption capacity of CNTs. It was reported that the adsorption capacity of CNTs was weak at pH below 3 and pH above 7. This was due to the reason that H^+ and Pb^{2+} tend to compete for the adsorption sites at pH below 3, whereas at pH above 7, precipitation tends to occur between Pb^{2+} and OH^-. Therefore, the best adsorption condition was reported to be at pH value of 5.

Study on the adsorption efficiency of CNTs towards divalent heavy metal ions, such as Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} has been performed (Rao et al. 2007). Adsorption of heavy metals by different CNTs roughly followed the sequence: $Pb^{2+} > Ni^{2+} > Zn^{2+} > Cu^{2+} > Cd^{2+}$. It was shown that oxidation of CNTs with acid solutions significantly improved the adsorption capacity of CNTs as the adsorption mechanism was mainly attributed to the chemical interaction between metal ions and surface functional groups. It was reported that heavy metals adsorption did not have a direct correlation with the specific surface area, mean pore diameter, and pore specific volume of CNTs. Instead, the surface total acidity of CNTs was a key parameter that influenced the adsorption capacity of CNTs, where an increase in surface total acidity will increase the heavy metals adsorption capacity of CNTs. Furthermore, comparison between SWCNTs and MWCNTs in Zn^{2+} removal also showed that SWCNTs required lower activation energy of adsorption (Lu et al. 2006). This may be due to the fact that SWCNTs consist of single atomic layer structure and hence, require less energy for diffusion of Zn^{2+} ions.

Due to the unique electronic structure of CNTs, many studies have been carried out to investigate their electrocatalytic behaviour towards many substances and to exploit their potentials as sensing material. Recently, modified carbon paste electrode based on MWCNTs and nanosilica was prepared for lead determination (Ganjali et al. 2010). MWCNTs in the carbon paste electrode not only improved the conductivity of the sensor, but also increased the transduction of the chemical signal to electrical signal. Results showed that the electrode had long term stability with more than 2 months, fast response time of 10 s, and performed satisfactorily in the pH range of 4–8.

Recent research activities focus on combining the specific recognition properties of biomolecules with the unique electronic properties of CNTs to produce hybrid sensing composite material with high sensitivity for the detection of trace levels of heavy metals (Janegitz et al. 2009; Morton et al. 2009). Morton et al. (2009) reported the functionalization of MWCNTs with $_L$-cysteine for Pb^{2+} and Cu^{2+} detection, since cysteine is an amino acid with high affinities towards some heavy metals. The principle of detection was explained, where the proposed mechanism of accumulation, reduction, and anodic stripping analysis is outlined in Fig. 1.7. Accumulation step involves complex formation between cysteine and heavy metal ion, M^{n+}, where cysteine acts as a chelator to complex heavy metal ions, prior to reduction and stripping analysis. Second step is the reduction of accumulated M^{n+} to elemental metal, M by application of negative potential. During stripping analysis, M is stripped back into the solution with an anodic potential scan, giving rise to a stripping current peak, which indicates the concentration of M^{n+} in the analyte solution. The high

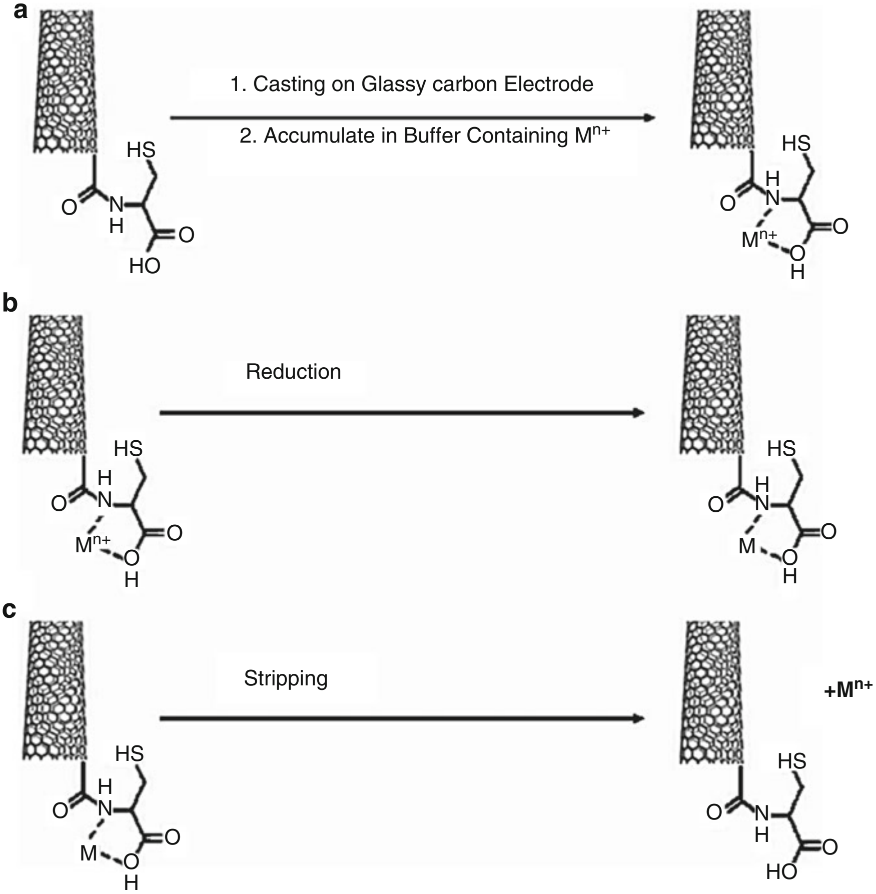

Fig. 1.7 Proposed accumulation and voltammetric mechanism of carbon nanotubes functionalized with $_{\mathrm{L}}$-cysteine for heavy metals detection, which involves three steps: (**a**) accumulation and complex formation between cysteine and heavy metal ion, M^{n+}. (**b**) Reduction of accumulated M^{n+} to elemental metal, M by application of negative potential. (**c**) Stripping of M from the complex back into the solution with an anodic potential scan. The stripping current peak provides the quantitative analysis of the concentration of heavy metals in the analyte solution (Morton et al. 2009)

sensitivity of CNTs modified electrode was attributed to cysteine as a chelator to accumulate the heavy metal ions and the detection limit were found to be 1 and 15 ppb for Pb^{2+} and Cu^{2+}, respectively. Therefore, the composite can be modified with appropriate chelates for simultaneous detection of other heavy metals with high sensitivity and selectivity.

CNTs upon oxidation had exhibited exceptional adsorption capacity and high adsorption efficiency, which suggest that CNTs are promising adsorbent material for the removal of heavy metals. Furthermore, recent research activities focus on exploring the functionalization of CNTs with different biomaterials to develop their applications in the detection of heavy metals. The CNTs based biosensor had shown high sensitivity and selectivity attributable to the high affinity of biomaterials towards heavy metals and excellent electronic properties of CNTs. Therefore, intensive research efforts are being invested to develop the potentials of CNTs as adsorbent and biosensor to remove and detect heavy metals in environmental protection applications.

1.3.5 Pesticides

Agriculture has played an important role in the development of human civilization. Pesticides are used in agricultural activities to increase the production yield and for the purpose of pest control. However, pesticides are well known as toxic pollutants, which are hazardous to human health. Current studies are concentrating on the detection of organophosphate pesticides. Many researchers have introduced CNTs into Acetylcholinesterase (AChE)-based electrochemical biosensor for pesticides detection (Gao et al. 2009; Chen et al. 2008; Du et al. 2007; Kandimalla and Ju 2006). The detection was based on the inhibition of AChE. Du et al. (2007) reported that AChE was covalently bound to a crosslinked chitosan-MWCNT composite. When AChE was immobilized on the electrode surface, it will interact with the substrate of acethylthiocholine, which will be further hydrolysed to obtain thiocholine. Oxidation of thiocholine will produce detectable signal which was catalyzed by MWCNTs and thus, increase the sensitivity of the sensor.

A biosensor was fabricated by covalent immobilization of organophosphorus hydrolase (OPH) enzyme on both SWCNTs and MWCNTs for organophosphate pesticides detection (Pedrosa et al. 2010). Two covalent immobilization approaches were applied, which are (i) direct coupling of ethylenediamene with the carboxyl groups on oxidized CNTs to introduce amino groups via amide formation (EDC-NHS), and (ii) direct coupling of the carboxyl groups to amine group modified with glutaraldehyde. SWCNT-OPH immobilized by EDC-NHS chemistry showed better activity and stability as the sensor retained 75% of the initial signal after 7 months of storage. The sensor exhibited high sensitivity, good reproducibility and was able to preserve the enzyme activity efficiently, which were attributed to the covalent functionalization of CNTs with OPH enzyme.

In addition, MWCNTs were used as solid phase extraction adsorbent to remove organophosphate pesticides by using methyl parathion as representative (Du et al. 2008). It was reported that MWCNTs allowed fast and simultaneous extraction and electrochemical detection of organophosphate pesticides, as well as the possibility to control adsorption and desorption by electrochemical methods. These properties suggested the potential of MWCNTs as an excellent adsorbent of organophosphate pesticides removal. Development of MWCNTs as solid phase extraction adsorbent was reported to evaluate its extraction efficiency towards chloroacetanilide herbicides, such as alachlor, acetochlor, metolachlor, and butachlor (Dong et al. 2009).

Results showed that both the amount of MWCNTs used and the pH of water samples had significant effect on the efficiency of MWCNTs to adsorb and elute chloroacetanilide herbicides. 100 mg of MWCNTs and a pH value of 7 for water samples were found to be the optimum condition for extraction of chloroacetanilide herbicides as good recoveries can be achieved. MWCNTs also showed a good adsorption capacity and recoveries without being affected by sample volume.

Functionalization of CNTs with biomaterials, especially enzyme had proven to be advantageous in the development of CNTs based biosensor to detect pesticides. The biosensor had exhibited high sensitivity and stability with good reproducibility, which was attributed to the function of CNTs as an effective scaffold for biomaterials, in addition to its remarkable structural, electronic, and mechanical properties. Moreover, CNTs had shown good adsorption capacity and regeneration capability as a solid phase extraction adsorbent to remove pesticides. Intensive research activities are underway to develop these applications in wastewater treatment industry.

1.4 Carbon Nanotubes in Green Nanocomposites Design

Advancements in nanotechnology and the widespread of environmental friendly products have found the potential application of CNTs as reinforcement material in green nanocomposites. Green nanocomposites mainly comprised of biodegradable polymer and CNTs, which is viewed as a wave of next generation materials. CNTs in green nanocomposites design have received a considerable interest from the researches worldwide since synthetic polymers create a lot of issues in waste management and if without proper disposal, will lead to the pollution and degradation of our environment.

CNTs play an essential role in supplying the desired properties of green nanocomposites due to their remarkable physical, mechanical and functional properties. Compared with traditional fibers, such as carbon or glass, CNTs manage to produce high strength green nanocomposites as their load bearing capability greatly exceeds those traditional fibers (Yeh et al. 2009). Moreover, their high aspect ratio and low mass density contribute to the extremely light weight of green nanocomposites. Nonetheless, CNTs possess high electrical and thermal conductivity, which improve the charge and heat transportation of green nanocomposites (Song and Qiu 2009; Misra et al. 2007).

The improved properties of green nanocomposites by CNTs can greatly increase the potential commercial value of green nanocomposites and expand their potential applications. For instance, the enhanced mechanical properties of poly(propylene fumarate) after reinforcing with ultra-short SWCNTs, had created potential application of SWCNTs/poly(propylene fumarate) nanocomposite to serve as a prototype bone tissue engineering scaffold (Sitharaman et al. 2008). Apart from that, CNTs reinforced poly($_L$-lactide-co-ε-caprolactone) can be used as a high load bearing application in medical field as the polymer alone may not possess sufficient strength to sustain high loading (Chakoli et al. 2009). In addition to the application of green

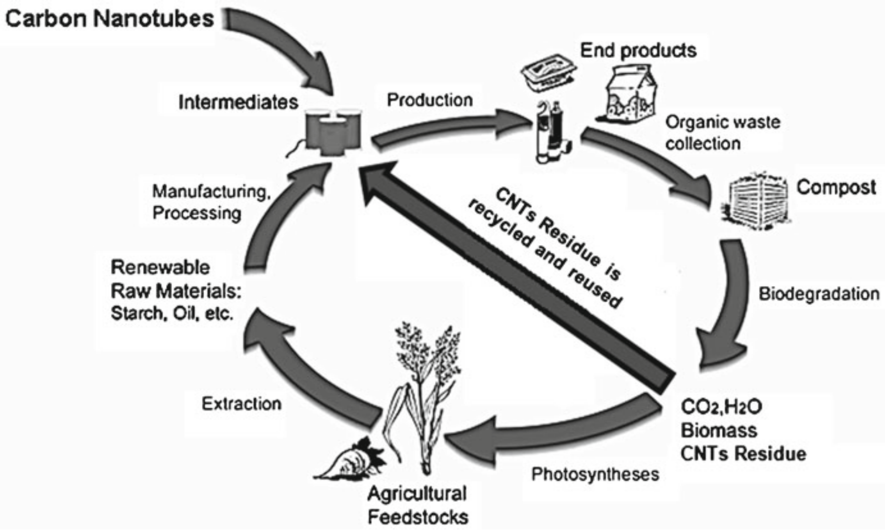

Fig. 1.8 Schematic illustration of life cycle of green nanocomposites. The source materials of green nanocomposites are from natural renewable resources, such as agriculture feedstocks. After extraction and processing with carbon nanotubes as reinforcement material, they are processed into end products. Upon disposal, they are biodegraded into biomass through enzymatic or microbial activities. The carbon nanotubes residue are recovered and reused for the production of new composites (Adapted and modified from Biokam Co. (2008))

nanocomposites in biomedical field, CNTs reinforced chitosan foreseen potential applications in catalysis and environmental protection (Ke et al. 2007). Poly(butylene succinate)/MWCNTs nanocomposite was found to show potential application as electronic packaging materials since the nanocomposite exhibited high antistatic efficiency (Shih et al. 2008).

In order to maximize the advantage imparted by CNTs, it is required to ensure the well dispersibility and alignment of CNTs in green nanocomposites (Camponeschi et al. 2007). Dispersion and alignment of CNTs prevent the formation of large CNTs aggregates and supplying large surface area to induce strong interaction between CNTs and biodegradable polymer matrix. However, CNTs are chemically inert and indispersible in almost all solvents due to their van der Waals interaction. Recent research activities have found functionalization of CNTs as an effective strategy to overcome this limitation (Lahiri et al. 2009; Sobkowicz et al. 2009). Owing to local strain that arises from pyramidalization and misalignment of π orbitals of the sp^2-hybridized carbon atoms, CNTs are more susceptible to be attached with other chemical species. The introduction of suitable functional moieties, such as carboxylic group enables the covalent coupling with biodegradable polymer through the ester bond, hence increase the solubility and compatibility of CNTs in biodegradable polymer matrix. As to unify the orientation of CNTs in green nanocomposites, there are several different methods available to align CNTs, including mechanical stretching

(Dai et al. 2007), nematic liquid crystal technique (van der Schoot et al. 2008), application of magnetic fields (Camponeschi et al. 2007; Garmestani et al. 2003; Kimura et al. 2002), and bubble blowing approach (Yu et al. 2008).

Unlike synthetic polymer nanocomposites, green nanocomposites are not resistant to degradation and are susceptible to significant change in chemical structure under specific environmental conditions (Kolybaba et al. 2003). From the aspect of life cycle assessment evaluation as shown in Fig. 1.8, the source material of green nanocomposites can be available from renewable resources, usually in the form of starch or cellulose. When come to disposal, they are capable to be degraded through the action of enzymes or chemical decomposition associated with microbial activities. The degradation temperature, which usually falls between 20°C and 60°C, depends on the type of active microorganisms, such as fungi, bacteria, actionmycetes, etc. with the presence of oxygen, moisture, and mineral nutrient as well as the neutral or slightly acidic pH conditions. The degradation process will ultimately leave behind carbon dioxide and water, which are environmentally friendly products, in addition to the CNTs residue. The recovered CNTs are still valuable to be reused for the production of new composites.

1.5 Conclusion

The applications of CNTs in the field of energy conversion and storage, environmental monitoring and wastewater treatment, as well as green nanocomposite design are research area of growing interest from their potential uses in future technologies point of view. This review examines the attributes of CNTs as the electrode material or conductive filler in the electrochemical devices of energy applications. The potential development of CNTs as sensing material in nanosensors for environmental monitoring, in addition to the development as adsorbents to remove pollutants in wastewater treatment are discussed. The advantages imparted by CNTs in green nanocomposite materials and their impacts on the environment are explained in the last section.

Integration of CNTs in the field of energy applications has brought revolutionary developments in the conventional electrochemical devices. In solar cell technology, CNTs are employed as the conductive filler for sensitizer with the advantages of lower fabrication cost but photoconversion efficiency comparable to or higher than the conventional silicon solar cells. The improved performance is attributed to the ability of CNTs to facilitate charge transport and reduce charge recombination in the photoactive layer, therefore increasing the photoconversion efficiency. CNTs are utilized as the alternative carbon support material for Pt catalyst in fuel cells, which show enhanced catalytic performance in fuel conversion efficiency and improved stability in fuel cell environment compared to the conventional carbon black. The improved conversion efficiency and stability are attributed to the high surface area of CNTs with high porosity which favours catalyst utilization, in addition to the better electrochemical durability of CNTs. CNTs doped with metal hydrides have been studied as hydrogen storage medium, which show better storage capacities due to the chemisorption mechanism involved and possess the advantages of storing/releasing hydrogen at ambient conditions. CNTs are employed as the host or matrix for the dispersion of lithium insertion materials in lithium ion batteries and for the deposition with metal oxides or conducting polymers in electrochemical supercapacitors, in which the hybrid nanocomposites have exhibited high energy capacity or specific capacitance and excellent cycle stability. The improved performance of these energy storage devices is attributed to the combined properties of high energy capacity or specific capacitance possessed by the metal oxides or conducting polymers with the high electrical conductivity and mechanical strength of CNTs.

CNTs have attracted extensive research interest for the development of sensors and adsorbents, due to their unique structural, electronic, and mechanical properties. In gas sensing applications, CNTs are selectively functionalized with metal oxides to act as the sensing elements, which have exhibited high sensitivity and selectivity towards many air pollutants. On the other hand, the development of CNTs based biosensor has been receiving immense research attention for their application in trace levels detection of pathogens, dyes, heavy metals, and pesticides. Functionalization of CNTs with biomaterials enables the modulation of the unique physical properties of CNTs with the molecular recognition properties of biomaterials, which in turn improve the sensing properties of the hybrid composite in terms of sensitivity, selectivity, and stability. Compared to the conventional sensors or detection methods, CNTs based sensors offer the advantages of portability, fast response and recovery time, good reversibility, long-term stability, low power consumption and analytical resources requirement, and the ability for real-time analysis, in addition to the high sensitivity and selectivity. CNTs have shown high adsorption capacity and good regeneration capability as an adsorbent to remove pollutants or contaminants in wastewater, such as pathogens, dyes, heavy metals, and pesticides. Furthermore, CNTs can be functionalized with materials that shows high affinity towards pollutants to enhance its adsorption capacity, which suggest that CNTs are promising adsorbent material for the removal of pollutants. Therefore, intensive research efforts are being invested into developing treatment-based and sensor-based applications of CNTs in environmental monitoring and wastewater treatment industry.

Green engineering is the process and design of products that conserve natural resources and impact the natural environment as little as possible. In efforts to replace the synthetic polymer which have caused issues in their waste management, the design of green nanocomposite is receiving much research attention. CNTs have been applied as reinforcement material in green nanocomposites to supply the desired properties, such as enhanced mechanical strength, light weight, improved electrical and heat conductivity. However, the well dispersion and oriented alignment of CNTs in biodegradable polymer matrix are pre-requisite for the desired properties of green nanocomposites imparted by CNTs. Green nanocomposite is degradable under specific environmental conditions, which is an advantageous tribute for environmental protection. Through life cycle assessment evaluation, the polymer matrix is degraded into environmental friendly products, whereas CNTs residue can be recovered for production of new composites.

As reviewed, CNTs have demonstrated advantageous potentials in energy and environmental applications with their outstanding structural, electronic, and mechanical properties. Development of CNTs integrated energy conversion technologies implement with efficient energy storage system have shown promising progress in efforts to address the energy challenge for future clean and sustainable energy source. In addition, CNTs represent a great alternative for the development of sensors and adsorbents with advantageous applications in environmental pollution analysis, industrial emission monitoring and control, as well as wastewater treatment. Moreover, the development of green nanocomposite will overcome the environmental issues posed by synthetic polymer and are finding exciting potential applications in various fields. In summary, CNTs offer exciting opportunities for development in energy and environmental applications with advantageous potentials. Intensive research efforts are required to further improve the performance of CNTs integrated device applications towards commercialization and practical applications for environmental protection and preservation.

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Chapter 2
Cyclodextrins for Remediation Technologies

David Landy, Isabelle Mallard, Anne Ponchel, Eric Monflier, and Sophie Fourmentin

Contents

Abstract Human activity and the modern way of life are responsible for the increase of environmental pollution. Industrial processes generate many substances that pollute air, water and soils with negative impacts for ecosystems and humans. The development of innovative remediation technologies has thus emerged as a significant environmental priority. Supramolecular chemistry can provide promising

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remediation methods to solve pollution issues. In particular, cyclodextrins (CDs) are a family of cyclic oligosaccharides that are composed of α-1,4-linked glucopyranose subunits. Cyclodextrins have thus a low-polarity cavity in which organic pollutants of appropriate shape and size can form inclusion complexes. This unique property makes cyclodextrins suitable for application in environmental protection by pollutant trapping. Accordingly, the present review lists the advantages of using cyclodextrins in soil, groundwater, wastewater and atmosphere remediation. The inclusion mechanism have been used in soil, water and air, either as solubilizing agent when the cyclodextrin is diluted in aqueous solution, or as trapping agent when cyclodextrin is immobilized on various supports. Resulting processes are highly versatile, since the complexing ability of cyclodextrins includes a wide range of pollutants. Remediation using cyclodextrins is a green processe due to cyclodextrins innocuity. Moreover, since inclusion involves reversible equilibriums, a major trend in the cyclodextrin environmental application field is to develop methods that combine both supramolecular chemistry and irreversible processes such as advanced oxidation or biodegradation. Such processes could lead to a complete remediation of pollutants and to cyclodextrin recycling.

Keywords Cyclodextrins • Remediation • Soil • Water • Atmosphere • Degradation • Pollutants

2.1 Introduction

Environmental pollution abatement is one of the most severe challenges worldwide. Indeed, industry has become an essential part of modern society, and waste production is an inevitable outcome of the developmental activities. The pollutants emitted from different sources contaminate air, water and soil environment with impact on both human health and ecological system. Maintaining and improving soil, water, and air quality represent some of the most formidable challenges facing society in the twenty-first century. Hence, the development of more efficient and less costly remediation technologies is required for the global environmental preservation.

Organic pollutants encountered in air, soil and water e.g. Polycyclic Aromatic Hydrocarbons (PAHs), Volatile Organic Compounds (VOCs), pesticides or dyes are mainly slightly soluble or insoluble in water. For that reason, it is necessary to use solubilizing agents that have affinity with these various pollutants and that are themselves non-toxic.

Cyclodextrins (CDs) are natural molecules derived from starch that have a remarkable capacity to form inclusion complexes (microencapsulation) in solution or in solid state with organic molecules, especially aromatics, through host/guest interaction. The increasing number of publications on complexation of pollutants and development or improvement of remediation technologies using CDs shows that there is a significant interest in the synthesis and applications of CDs and CD derivatives for environmental depollution. The main goal of this review is to provide a summary of the environmental uses of CDs in recovery based and catalytic remediation processes. Except in few studies concerning soil and groundwater remediation, for which large scale demonstrations have been realized, all the studies where demonstrated on a laboratory scale. A description of the structure and properties of CDs will be presented, as these data are important to understand the role of CDs in environmental applications.

2.2 Fundamentals of Cyclodextrin Chemistry

2.2.1 Structure and Properties

The enzymatic degradation of starch leads to the formation of cyclic oligosaccharides containing 6–8 glucopyranose units, called respectively α-, β- and γ-cyclodextrins (α-CD, β-CD and γ-CD) (French 1957; Szejtli 1982, 1996a, 1998). The molecular structures and characteristics of these three analogues are described in Fig. 2.1 and Table 2.1. Other CDs, with less than six and more than eight units, may also be isolated or synthesized at the laboratory scale (French et al. 1965; Nakagawa et al. 1994; Saenger et al. 1998).

On a three-dimensional point of view, CDs look like truncated cones, with an approximate C_n symmetry. This structure is characterized by a rather hydrophobic cavity and two hydrophilic peripheries, the narrower and wider side implying respectively the primary (6-OH) and secondary hydroxyls (2-OH and 3-OH). CDs are rather flexible macrocycles, even if the complete rotation of a glucosidic unit along the C_1-C_4 axis is not allowed for steric reasons (Saenger 1980), and if intramolecular hydrogen bonds may reduce the mobility of two consecutive glucoses. Such a combination of hydrophobic and hydrophilic area associated to a moderate flexibility confers to CDs their ability to include various organic guests in water.

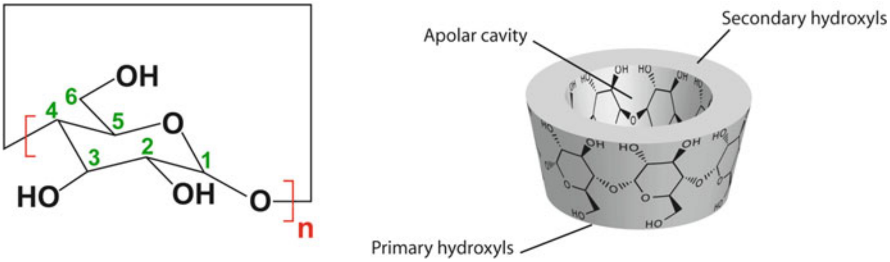


Fig. 2.1 Schematic drawing of α-CD (n = 6), β-CD (n = 7) and γ-CD (n = 8). CD: cyclodextrins

Table 2.1 Main features of α-CD, β-CD and γ-CD. CD: cyclodextrins

	α-CD	β-CD	γ-CD
Number of glucose units	6	7	8
Molecular weight (g/mol)	972.9	1135.0	1297.1
Aqueous solubility, 298.2 K (g/l)	145	18.5	232
Cavity volume ($Å^3$)	174	262	427
Peripheric diameter (Å)	14.6	15.4	17.5
Height (Å)	7.9	7.9	7.9
Number of water molecules within cavity	6–8	11–12	13–17
pKa, 298 K	12.3	12.2	12.1

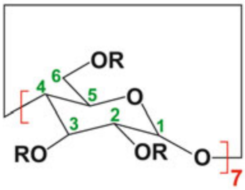
If the schematic drawings of α-, β- and γ-CD are analogous, their structural behavior are not strictly equal. Indeed, while a rather continuous crown of hydrogen bonds is observed for β-CD, even in DMSO-*d6* (Gillet et al. 1982), this is not the case for α-CD, which presents a distorted glucose in consequence of steric constraint, nor for γ-CD, for which the greater unit number allows a greater flexibility. As a consequence of these increased intramolecular interactions, β-CD experiences lower aqueous solvation and thus shows a lower solubility than the α- and γ-analogs (see Table 2.1). Aqueous cosolvent may increase CDs solubility, especially for alcohol or acetonitrile mixture (Szejtli 1996a). Besides, native CDs are generally insoluble in organic solvent, if we except DMSO, DMF and pyridine.

On the toxicological point of view, none of the α-, β- and γ-CD shows major harmful effects for human being (Szejtli 1982, 1996a). No mutagenic, teratogenic or carcinogenic effects have been observed. As a result, an increasing number of commercial products or processes involves native or modified CDs.

2.2.2 Cyclodextrin Derivatives

The presence of 3n reactive hydroxyl groups on CDs allows various modifications of such macrocycles (Khan et al. 1998; Jicsinszky et al. 1996; Easton and Lincoln 2000). It becomes thus possible to modify the CD features such as solubility, inclusion ability or to induce new properties e.g. chromophore introduction, immobilization on solid support.

Selective modifications might be realized, with the aim to control the number and position of introduced groups. It is indeed possible to activate preferentially primary or secondary alcohols, and to induce mono-functionalization or per-functionalization on a particular position (Takahashi et al. 1984; Brown et al. 1993; Defaye et al. 1998; Rong and D'Souza 1990; Gadelle and Defaye 1991; Gorin et al. 1996). Activation is generally realized by means of tosylation or halogenation, leading to versatile intermediates (Melton and Slessor 1971; Brown et al. 1993; Martin and Czarnik 1994), which allows a wide range of synthetic pathways. Protection/deprotection strategies are also envisaged (Takeo et al. 1989; Bansal et al. 1998).



R	Substitution Degree	Name
$-CH_3$	5	CRYSMEB
$-CH_3$	12-14	RAMEB
$-CH_2-CHOH-CH_3$	4-6	HPBCD
$-CH_2-COOH$	3-7	CMCD
$-(CH_2)_4-SO_3^-Na^+$	4-7	SBE

Fig. 2.2 Description of some modified β-CDs: methylated, hydroxypropylated, carboxymethylated and sulfobutylated. CD: cyclodextrins

Nevertheless, selectively modified CDs imply higher cost of production, and as a result most of environmental applications are based on native or randomly modified CDs, such derivatives being available on an industrial scale. Random modifications are realized by means of direct etherification. For instance, methylated (CRYSMEB or RAMEB), hydroxypropylated (HPBCD), carboxymethylated (CMCD) or sulfobutylated (SBE) β-CDs might be obtained with different degrees of substitution, in satisfactory yields (Fig. 2.2) (Pitha et al. 1987; Uekama et al. 1987; Stella and Rajewski 1991; Kenichi et al. 1996).

2.2.3 *Inclusion Phenomena*

Inclusion phenomena inside CDs might occur in solid, liquid or gaseous phase. Nevertheless, most studies are devoted to aqueous solutions, especially because of the central role that water plays in this complexation process. Indeed, the presence of water molecules inside the apolar cavity of CDs leads to a relative instability, which favors their displacement by less polar molecules. As a result, each compound, which presents a steric complementarity, even partial, with CD cavity, might be included. Complexation of molecules as diverse as aromatic compounds, ions, or polymers has been reported (Fenyvesi et al. 1996a; Landy et al. 2000).

The host/guest complex is stabilized by weak forces, in such a way that inclusion is a dynamic phenomenon which implies an equilibrium between free and complexed species (Connors 1997) (Fig. 2.3). Formation and dissociation are generally fast, on the micro- to millisecond scale (Bergeron 1977). Besides, the interactions that take place are diverse: if van der Waals forces are systematically present, since steric complementarity is required, electrostatic interactions often constitute additional stabilization sources (Liu and Guo 2002). Dipole-dipole interactions are often expected, as CD dipole is not negligible although highly depending on the macrocycle conformation. With adequate guests, hydrogen bonds might also occur, and charge transfers are more and more invoked.

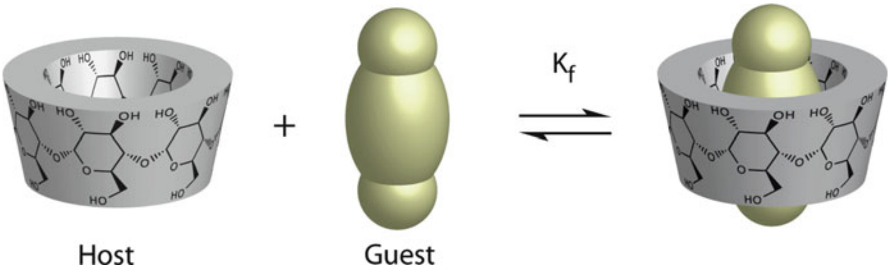


Fig. 2.3 Schematic drawing of aqueous equilibrium between free and complexed forms of a host/guest mixture

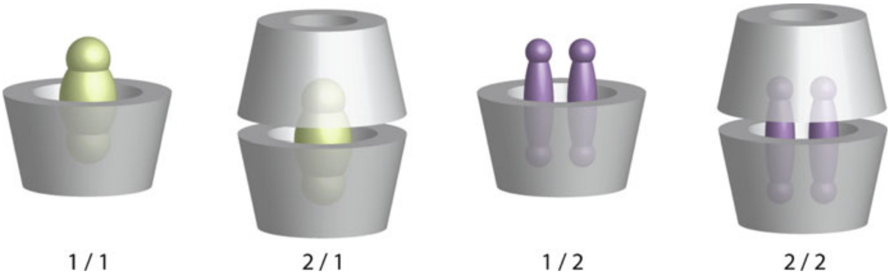


Fig. 2.4 Schematic drawing of main CD complexes stoichiometries. CD: cyclodextrins

The steric complementarity, which is a crucial parameter for host-guest affinity, also controls stoichiometry (Fig. 2.4) (Szente 1996; Szejtli 1996b). If 1/1 complexes represent the major class of inclusion compounds, it is also possible that one CD encapsulates two guest molecules or that one guest is included within two CDs (Fenyvesi et al. 1996a). It has to be mentioned that the formation of such 1/2 or 2/1 complexes generally takes place in presence of 1/1 complexes, in such a way that a mixture of complexes is observed. Higher stoichiometries might also occur.

The association and dissociation of the cyclodextrin/guest complex are governed by a thermodynamic equilibrium. In the case of a 1/1 inclusion complex, the formation constant is defined by the following equation (guest G):

$$K_f = \frac{[CD/G]}{[CD]*[G]} \tag{2.1}$$

While stoichiometries are often characterized by means of Job plots, affinities are generally determined by titration, competition or solubility procedures (Connors 1996). Many techniques have been used for the complexation study of organic compounds in general (Connors 1996), and also of organic pollutants: headspace gas chromatography (Baek et al. 2003; Saito et al. 2004; Lantz et al. 2005; Szaniszló et al. 2005; Fourmentin et al. 2007), isothermal titration calorimetry (Qiu et al. 2007), UV-visible (Sanemasa and Akamine 1987; Wang and Brusseau 1993; Hamai and

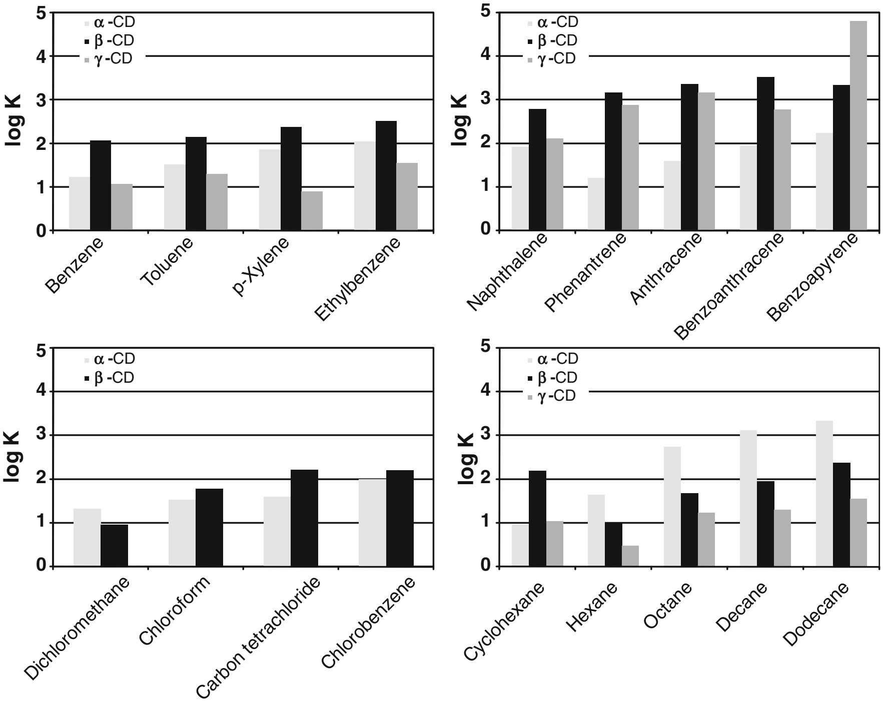


Fig. 2.5 Formation constants, in logarithmic form, of the complexes formed between α-CD, β-CD, γ-CD and some BTEX (*left upper part*), PAH (*right upper part*), chlorinated species (*left lower part*), alkanes (*right lower part*) (Sanemasa and Akamine 1987; Fujiki et al. 1988; Blyshak et al. 1989; Sanemasa et al. 1989, 1990; Takuma et al. 1990; Osajima et al. 1991; Szaniszlo et al. 2005; Fourmentin et al. 2007)

Satoh 1997; Hanna et al. 2003; Manolikar and Sawant 2003), fluorescence (Sanemasa et al. 1989; Murai et al. 1998; Veignie et al. 2009), circular dichroism (Ishiwata and Kamiya 1999) or NMR spectroscopies (Debouzy et al. 2000; Leyva et al. 2001).

If formation constants are due to be identical from one study to another, discrepancies are often observed. For instance, formation constants ranging from 8 to 910 M^{-1} have been reported for the β-CD/pyrene complex (Connors 1995). As a consequence, each published value should be taken into account with caution. Nevertheless, the knowledge of formation constants is of crucial importance, as it generally controls the efficiency of remediation process. For instance, the percentage of complexed pollutant, for a 0.001 M equimolar host-guest solution, approaches 90% for a formation constant equal to 10^5 M^{-1}, but it drops to 1% for a value of 10 M^{-1}. The lower the percentage of complex, the weaker the physico-chemical modification which could be observed.

As pollutants are characterized by an important diversity of their molecular shapes, measured affinities between CDs and pollutants cover a wide range. A sample of these stabilities is listed in Fig. 2.5, for BTEX (Sanemasa and Akamine 1987), PAHs (Fujiki et al. 1988; Blyshak et al. 1989; Sanemasa et al. 1989), chlorinated species (Takuma et al. 1990; Fourmentin et al. 2007) and alkanes (Sanemasa et al. 1990; Osajima et al. 1991; Szaniszlo et al. 2005). Values have also been reported for herbicides such as 2,4-dicholorophenoxyacetic acid (Ginés et al. 1996), pesticides such as parathion (Ishiwata and Kamiya 1999), polychlorinated biphenyls (Femia et al. 1985), surfactants (Qiu et al. 2007), phtalic acids (Murai et al. 1998), or chemical weapon like yperite (Debouzy et al. 2000), within the same range of stability (typically around 10^3 M^{-1}).

According to their cavity volume, CDs binding ability is generally increasing with the guest size, as can be seen in Fig. 2.5 from benzene to ethylbenzene, from naphthalene to benzo[a]pyrene, from dichloromethane to carbon tetrachloride or from hexane to dodecane. The greater the organic guest, the higher the van der Waals interactions between the complexation partners. However, such an increase in the stabilization of the inclusion complex is not only depending on the guest size but also on its molecular shape.

Data presented in Fig. 2.5 are also characterized by mean values of log K_f equal to 1.88, 2.32 and 1.87 for α-CD, β-CD and γ-CD, respectively. A similar tendency was previously evidenced for cohorts of data not restricted to pollutants (Connors 1995), with values respectively equal to 2.11, 2.69 and 2.55. If such mean values have no strict physical meaning, they underline the general trend of a slightly better efficiency of β-CD compared to smaller and wider analogs. This tendency is especially observed for both monoaromatic and polycyclic compounds, but also for chlorinated species. Only very large guest such as benzo[a]pyrene favors γ-CD, while α-CD shows greater binding properties for very small guests like dichloromethane, and for aliphatic species such as hexane. Moreover, β-CD constitutes a good compromise if a large range of pollutant is to be treated, as its cavity presents an intermediate size between α-CD and γ-CD. This greater complexation ability, associated to a lower cost (around 5US$ per kg), explains why β-CD is generally the CD of choice for environmental studies.

Nevertheless, the lower solubility of β-CD might limit its application to remediation. As a result, modified β-CDs appear to be promising hosts for environmental purposes. For instance, methylated or hydroxypropylated derivatives show binding ability analogous to native β-CD, but they are characterized by significantly higher aqueous solubility, up to 500 g/l against only 18 g/l for β-CD (Szaniszlo et al. 2005; Blach et al. 2008).

2.3 Cyclodextrins in Recovery Based Processes

Taking advantage of their inclusion capacity, CDs can play a major role in environmental science in terms of (i) solubilization of organic contaminants or (ii) enrichment and removal of organic pollutants and heavy metals from soil, water and atmosphere (Singh et al. 2002). This section will focus on environmental applications of CDs in recovery based processes for soil, groundwater, wastewater and atmosphere remediation.

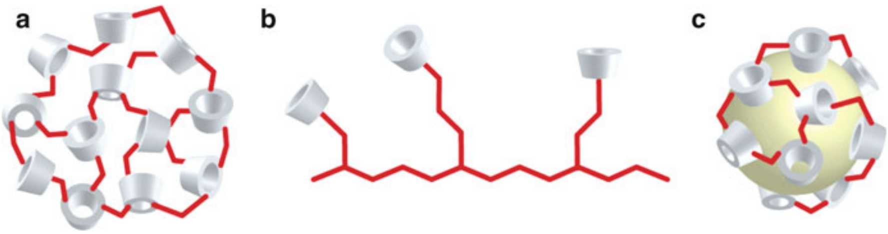


Fig. 2.6 Different approaches developed for the preparation of cyclodextrin (CD) functionalized materials: (**a**) CD polymers (**b**) grafting of CD onto insoluble matrix and (**c**) coating of CD onto insoluble matrix. CD: cyclodextrins

2.3.1 Removal of Water Contaminants

Removal of pollutants from water is a serious challenge for water supplying companies and municipalities. In fact, heavy metals, organic compounds like aromatic derivatives or synthetic dyes harmful to organisms are toxic and recalcitrant pollutants, that tend to accumulate in water. It is now well established that for the wastewater treatment, adsorption is a much better process than other physical techniques because of its efficiency and economy (Dabrowski 2001).

The parental CDs are soluble in water, therefore they cannot be used directly in the adsorption of pollutants from water. For these reasons, several workers have attempted to immobilize CDs on appropriate supports, including organic, polymeric and mineral materials. Different approaches have been developed for the preparation of CD functionalized materials, like the synthesis of CD polymers (Fig. 2.6a) and the grafting or coating of CD onto insoluble matrix (Fig. 2.6b, c) (Crini 2008).

These materials present several advantages in wastewater treatment like high stability, recoverability, reutilization, low cost, sorption capacity increase (Li et al. 2010).

2.3.1.1 Cyclodextrins Coupled with Insoluble Support

Several insoluble supports (organic or inorganic matrix) have been studied to produce materials containing CDs. All these studies were demonstrated on a laboratory scale, only a few of them reported the removal of pollutants from industrial wastewater (Chen et al. 2007; Fan et al. 2003a).

The coupling between CDs and natural materials has been extensively investigated for the removal of pollutants because they are abundant, renewable and biodegradable (Crini 2005, 2006). Chitosan bearing CDs are efficient sorbents for selective extraction of *p*-nonylphenol, bisphenol (Aoki et al. 2003), phenol (Li et al. 2009a) and *p*-nitrophenol (Tojima et al. 1999). They have also been tested for the decontamination of water containing textile dyes, with a rate of sorption and a global efficiency superior to that of the parent chitosan polymer and of the well-known CD-epichlorohydrin (CD-EP) gels (Martel et al. 2001). α-CD-linked chitosan beads were used to remove various phthalate esters from aqueous solution both in batch and continuous column tests (Chen et al. 2007). The α-CD-linked chitosan beads could be reused 15 times in the real wastewater at least.

Cellulose is also a natural carbohydrate polymer, insoluble in water. Crini and Peindy (2006) used β-CD-carboxymethylcellulose (CD-CMC) for the removal of C.I. Basic Blue 9 (BB 9) from aqueous solutions. Bonenfant et al. (2010) have shown that CD-CMC could constitute a good adsorbent for removing nonylphenol 9 mole ethoxylate (NP9EO) from wastewater with adsorption capacity of 83–92 wt% depending on the initial NP9EO concentration in liquid phase.

The efficiency of CD derivatives grafted or coated onto silica for aromatic pollutants has been compared (Phan et al. 1999, 2000, 2002). Sorption capacities were closed to each other independently of the synthesis procedure for a given pollutant. They were affected by the same parameters e.g. contact time, CD content, structure and concentration of pollutant. The mechanism of sorption is both physical adsorption in the polymer network (for supports obtained by coating) and/or the formation of an inclusion complex between CD and guest molecules. With respect to environmental (preparation in a water medium) and financial aspects (one-step reaction, fewer and inexpensive reagents), coating seems better. Unfortunately, the low CD loading of these CD-coated (178 μmol/g) or grafted materials (159 μmol/g) limit their absorption capacities.

Bibby and Mercier (2003) developed high CD loading materials by incorporating CD groups inside the pore channels of mesoporous silica with uniform channel structure (denoted CD-HMS). Adsorption studies on CD-HMS materials have shown that their open-framework structures promote unhindered interactions of organic guests with their CD binding sites because they easily permeate the material and reach the abundant CD groups inside the adsorbent.

Sawicki and Mercier (2006) have described the efficiency of CD-silica nanocomposites for the removal of pesticides like DDT (dichlorodiphenyltrichloroethane) which could be removed from water in low levels typically encountered in environment.

Other siliceous materials were synthesized between CDs, aminopropyltriethoxysilane (APTES) and tetraethoxysilane (TEOS) to remove remazol Red 3BS from aqueous solution (Asouhidou et al. 2009). Results showed a good adsorption of the dye and an efficient regeneration after repeated sorption-regeneration cycles. Aromatic compounds like phenolic derivatives were also removed from water by CD bonded silica under solid phase extraction (Fan et al. 2003a, b).

Adsorptive interaction of mercury ions with silica chemically modified by β-CD was demonstrated as well by Belyakova (Belyakova et al. 2008a, b). It has been established that isotherm of mercury(II) adsorption on the β-CD-containing silica is given by isotherm of Langmuir type.

More exotic supports were also synthesized. Salipira et al. (2007, 2008) have polymerized CDs and carbon nanotubes. Even if carbon nanotubes are expensive, the synthesis needs a small percentage of it. These supports were promising because they match the properties of CDs and carbon nanotubes for absorption. They absorb trichloroethylene (TCE) from water at concentration loads of part per million.

Shao et al. (2010) have followed the same idea but with a different procedure. They synthesized multiwalled carbon nanotubes grafted with β-CD by N_2 plasma induced grafting technique, an environmentally friendly technique, and applied the new material for the removal of polychlorinated biphenyls from aqueous solutions.

Cationic exchange textiles have been developed to remove heavy metal (Pb, Cd, Zn, Ni) from water (Ducoroy et al. 2008). Compared to other supports, they are less expensive and non-toxic.

Ceramic membranes impregnated with CDs polymers removed polycyclic aromatic hydrocarbons (up to 99%), monocyclic aromatic hydrocarbons (up to 93%), trihalogen methanes (up to 81%), pesticides (up to 43%) and methyl-tert-butyl ether (up to 46%) (Allabashi et al. 2007). Filters based on CDs were able to remove a wide range of pollutants. They have a lot of advantages like chemical inertia, long working life and thermal stability.

Table 2.2 summarizes some examples of the supports used to anchor CDs with the associated pollutants.

Table 2.2 Examples of supports used to anchor cyclodextrins and associated pollutants

Support	Pollutant	Reference
Organic compounds		
Chitosan	Phenol, phenolic derivatives	Tojima et al. (1999), Aoki et al. (2003), Li et al. (2009a)
	Textile dyes	Martel et al. (2001)
	Phtalate esters	Chen et al. (2007)
Cellulose	Textile dyes	Crini and Peindy (2006)
	Phenolic derivatives	Bonenfant et al. (2010)
Silica	Phenol, phenolic derivatives	Phan et al. (2000, 2002), Bibby and Mercier (2003), Fan et al. (2003a, b)
	Acetic acid	Phan et al. (2000, 2002)
	Textile dyes	Phan et al. (2000), Asouhidou et al. (2009)
	Chlorinated pesticides (DDT)	Sawicki and Mercier (2006)
Carbon nanotubes	*p*-nitrophenol, TCE	Salipira et al. (2007)
	Polychlorinated biphenyls	Shao et al. (2010)
Ceramic membranes	Aromatic hydrocarbons, trihalogen methanes, pesticides	Allabashi et al. (2007)
Heavy metals		
Silica	Hg^{2+}	Belyakova et al. (2008a, b)
Cationic exchange textiles	Pb^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+}	Ducoroy et al. (2008)

Generally, the sorption mechanism combines the inclusion complex formation resulting from the presence of CD but also from physico-chemical interactions. These interactions depend on the chemical structure of the pollutant, the type of sorbent and the contact time (static or dynamic). All these new adsorbents showed a good stability, satisfactory recoveries and low detection limits. They tended to be useful in the production of environmentally friendly materials.

2.3.1.2 Cyclodextrin Polymers

Numerous works involving the synthesis of insoluble CD polymers using bifunctional cross-linkers have been reported. Various linkers have been utilized such as epichlorohydrin (EP), toluene-2,4-diisocyanate (TDI) and hexamethylene diisocyanate (HMDI) in the formation of these nanoporous CD polymers (Li and Ma 1999; Crini and Morcellet 2002; Crini 2003; Mhlanga et al. 2007; Trotta and Cavalli 2009). The most thoroughly studied polymerization is the cross-linking reaction with epichlorohydrin (Murai et al. 1997; Crini 2003, 2008; Crini et al. 2007; Romo et al. 2008; Li et al. 2010). Many studies were completed on laboratory made hand water; only one of them was done with industrial water (Yamasaki et al. 2006).

Crini studied the kinetic and the equilibrium on the removal of dyes (Crini 2003, 2008; Crini et al. 2007). The mechanism of adsorption was demonstrated as both physical adsorption and hydrogen bonding. The adsorbent exhibited high sorption capacities between 30 and 54 mg of dye per gram of polymer.

Yilmaz et al. (2010) have also described the use of CD polymers for dye removal. In this case, 4,4′-methylene-bis-phenyldiisocyanate (MDI) and HMDI were preferred to EP. The polymers showed high affinity towards azo dyes (Evans Blue, Chicago Sky Blue, direct violent 51, methyl orange and Congo Red) and aromatic amines (Ozmen and Yilmaz 2007; Ozmen et al. 2008; Yilmaz et al. 2007, 2010).

Several studies have been published so far concerning the sorption of phenol or phenol derivatives (Mamba et al. 2007; Romo et al. 2008; Li et al. 2010). The efficiency of crosslinked CDs towards phenol as low as 0.8 ppm has been demonstrated (Yamasaki et al. 2006, 2008). Romo et al. (2008) have shown that the extraction efficiency of β-CD polymers is comparable to other conventional sorbents. Abay et al. (2005) described the suspension polymerization method to made microsphere of CDs. They could manage the diameter of their beads and trap phenolic compounds.

Nanospheres of CDs exhibit also a high ability to absorb aromatic organic molecules like phenol and toluene (Baruch-Teblum et al. 2010). Nanospheres were synthesized under miniemulsion polymerization. They can be used under various forms like granular solids, powders, and thin films. The same procedure was also employed for styrene and chlorinated volatile organic compounds (Kammona et al. 2008).

It has recently been reported that, by reacting CDs with suitable cross-linking agents, a novel nanostructured material consisting of hyper-cross-linked CDs can be obtained; these are known as nanosponges (Trotta and Tumiatti 2003). Polluting agents, like heavy metals and many organic substances can easily be removed from water with these nanosponges with performances many times superior to that of active carbon. Furthermore, the properties of the nanosponges can easily be restored

Table 2.3 Examples of pollutants trapped by cyclodextrin polymers

Pollutant	Cross-linking agent	Reference
Organic compounds		
Textile dyes	Epichlorohydrin	Crini (2003, 2008), Crini et al. (2007)
	Diisocyanate	Ozmen and Yilmaz (2007), Yilmaz et al. (2007, 2010); Ozmen et al. (2008)
Phenol and phenolic derivatives	Epichlorohydrin	Yu et al. (2003), Romo et al. (2008), Li et al. (2010)
	Diisocyanate	Mamba et al. (2007), Romo et al. (2008), Yamasaki et al. (2008), Mahlambi et al. (2009), Baruch-Teblum et al. (2010)
	Succinyl chloride	Romo et al. (2008)
Benzene derivatives	Epichlorohydrin	Yu et al. (2003)
	Diisocyanate	Baruch-Teblum et al. (2010)
Aromatic amines	Diisocyanate	Yilmaz et al. (2010)
Ionic surfactants	Epichlorohydrin	Murai et al. (1997)
Halogenated compounds	Meta-diisopropylbenzene	Kammona et al. (2008)
Naphthalene derivatives	Epichlorohydrin	Orprecio and Evans (2003)
Heavy metals		
Cr^{6+}	Diisocyanate	Mahlambi et al. (2009)

simply by washing them with ethanol, changing the pH, modifying the ionic strength or by mild warming (Trotta and Cavalli 2009).

Other typical aromatic compounds were also investigated like naphthalene (Orprecio and Evans 2003), benzene derivatives under solid phase extraction attempts (Yu et al. 2003) or ionic surfactants (Murai et al. 1997).

Another type of polymers based on β-CD-ionic liquid polyurethanes has shown good ability for heavy metal and phenol derivatives removal (Mahlambi et al. 2009). These polymers were insoluble in water and organic solvents and show a high percentage of removal (up to 80% for organic pollutant and up to 100% for Cr^{6+}). Table 2.3 summarizes the different family of studied pollutants associated with the cross-linking agent used in the studies.

The adsorption mechanism was not dependent on the nature of the linker. The proposed adsorption mechanism involved several kind of interactions: physical adsorption in the polymer network, hydrogen bonding and formation of an inclusion complex due to the CD molecules through host-guest interaction. The CD molecules played the most important role in the mechanism. The polymers could be used as beads or powders. In addition, the adsorbent can be easily regenerated by extraction with solvents. The complexing abilities remain unchanged after many regeneration cycles.

2.3.2 *Soil and Groundwater Clean Up*

Every year, millions of tonnes of hazardous waste are generated in the world. Due to inefficient waste handling techniques and hazardous waste leakage in the past, thousands of sites were contaminated by heavy metals, organic compounds and other hazardous materials, which made an enormous impact on the quality of groundwater, soil and associated ecosystems (Virkutyte et al. 2002).

Among existing methods, *in situ* technologies have become very attractive for treating contaminated soils and groundwater because of lower cost, less disruption to the environment, and reduced worker exposure to hazardous materials. However, organic pollutants are generally poorly soluble or insoluble in water. Addition of solubilizing agents such as cosolvents and surfactants is known to increase the transport of low-polarity organics from soils (Mulligan et al. 2001). The solubilization effect of cosolvents is usually not significant until their volume fraction concentrations are above 10%. Conversely, surfactants have a large solubilization power, but they may form high-viscosity emulsions that are difficult to remove (Wang and Brusseau 1993).

CDs have been proposed as an alternative agent to remove the organic pollutants from contaminated sites (Brusseau et al. 1994; Fenyvesi et al. 1996b; Shixiang et al. 1998; Tick et al. 2003). Numerous works showed that CDs enhanced the aqueous solubility of Hydrophobic Organic Compounds (HOCs) through the formation of water-soluble inclusion complexes. Consequently, HOCs complexes formation with CDs was proposed as a way of enhancing removal of these pollutants from soil and groundwater (Boving and Brusseau 2000).

The advantages of the use of CDs over organic solvents and non ionic surfactants for HOCs extraction are: (i) their much lower toxicity for soil microbial populations and their higher biodegradability and (ii) no critical micelle concentration and no formation of high viscosity emulsions, minimizing reagent residuals left in situ. Moreover, it appears that CDs are becoming comparable in cost with surfactants (Viglianti et al. 2006).

The most studied CD is the hydroxypropyl-β-CD. HPBCD has been used for the solubilization and desorption of PAHs and pesticides from contaminated soil in laboratory experiments (Fenyvesi et al. 1996b; Brusseau et al. 1994, 1997; Pérez-Martínez et al. 2000; Badr et al. 2004; Viglianti et al. 2006; Zeng et al. 2006) and for *in situ* flushing of HOCs (McCray and Brusseau 1998). The solubilization power of HPBCD as well as its removal capacity from soil are greater than those of β-CD.

The desorption rate of HOCs from soil depends on their hydrophobicity, CD type and soil organic matter content. Wang and Brusseau (1993) have reported that the solubilization power of HPBCD was parallel to their octanol-water partition coefficient.

The first pilot-scale field test using CD as a flushing agent was reported by McCray and Brusseau (1998) on a military site contaminated with petroleum hydrocarbons, chlorinated hydrocarbons and PAHs. The remediation technology tested in this study is termed a “complexing sugar flush” (CSF). A 10 wt% HPBCD solution was injected into the source zone and pumped out successfully with contaminants on the subsurface.

Blanford et al. (2001) reported the performance of a CD-enhanced vertical flushing for TCE contaminated aquifer. The results of this pilot test indicated that the CD solution increased the rate of TCE removal from the aquifer. The enhanced factor estimated from the field data can be compared to values determined from laboratory experiments.

Furthermore, Tick et al. (2003) demonstrated, on an another field site, that CD could be recycled using an in-line configuration, which will enhance the cost-effectiveness of the CSF technology.

In all these field experiments, the CD solution significantly increased not only the apparent solubility for the studied contaminants, but also the rate of dissolution. As a result of these effects, the CD-enhanced flushing technology reduced significantly the remediation time compared with the conventional pump and treat technology. An indirect benefit of CDs is that they have the potential to enhance *in situ* bioremediation (see Sect. 2.4.3). Thus it is possible that CDs may increase solubilization as well as *in situ* bioremediation.

CDs solutions have also been used for desorption and extraction of munition wastes and energetic compounds like RDX, 2,4-DNT and TNT (Hawari et al. 1996; Khodadoust et al. 2008).

A major factor complicating the cleanup of many sites is the co-occurrence of organic compounds and heavy metal, the so-called mixed wastes. Carboxymethyl-β-CD (CMCD) was used successfully for simultaneous solubilization of heavy metals and organic compounds from contaminated soil (Wang and Brusseau 1995; Brusseau et al. 1997; Skold et al. 2008, 2009). Examples of studied pollutants are given in Table 2.4.

Table 2.4 Examples of pollutants and associated cyclodextrins in soil and groundwater remediation

Pollutant	Cyclodextrin	Reference
Organic compounds		
TCE, chlorobenzene, naphthalene and DDT	HPBCD	Wang and Brusseau (1993)
TCE, naphthalene, biphenyl, anthracene, pyrene	HPBCD	Brusseau et al. (1994)
PAHs and pesticides	HPBCD and RAMEB	Fenyvesi et al. (1996b)
RDX	HPBCD	Hawari et al. (1996)
PAHs	β-CD and CMCD	Shixiang et al. (1998)
2,4-Diclorophenoxyacetic acid (2,4-D)	HPBCD	Pérez-Martínez et al. (2000)
Naphthalene and phenanthrene	β-CD and HPBCD	Badr et al. (2004)
Methyl-parathion	HPBCD	Zeng et al. (2006)
2,4-Dinitrotoluene (2,4-DNT)	HPBCD	Khodadoust et al. (2008)
Heavy metals		
Ba, Ca, Cd, Ni, Pb, Sr and Zn	CMCD	Skold et al. 2009
Mixed wastes		
Anthracene, trichlorobenzene, biphenyl, DDT and Cd	CMCD	Wang and Brusseau (1995)
Phenanthrene and Cd	CMCD	Brusseau et al. (1997)
Perchloroethylene and Pb, Sr, Zn	CMCD	Skold et al. (2008)

Fenyvesi et al. (2005) investigated the biodegradation of several CDs in soil. All the CDs were found to be more or less biodegradable. HPBCD was completely biodegraded after 280 days.

Electrokinetic (EK) remediation is an emerging technology that can remove heavy metals and organic compounds when they exist individually in low permeability soils (Maturi and Reddy 2006). Recently, the potential of HPBCD for the removal of coexisting heavy metals and HOCs by EK was evaluated. Pilot-scale EK test indicates that it is difficult to achieve great removal of HOCs or HOCs and heavy metal mixed contaminants with HPBCD (Li et al. 2009b).

2.3.3 Volatile Compounds Trapping

VOCs are widely used in industry as solvents, dry-cleaning agents, degreasers, and intermediates in the production of plastics, synthetic resins or pharmaceuticals. From an environmental point of view, it is necessary to limit and control their emissions because they affect the change of climate, the growth and decay of plants, and the health of human beings and all animals (Khan and Ghoshal 2000).

New regulations regarding volatile organic compounds emissions demand more efficient and less costly technologies (Liebscher 2000). There are many techniques available to control VOCs emission (destruction based and recovery based) with many advantages and limitations. Sorption is used to remove VOCs from gas streams by contacting the contaminated air with a solid (adsorption) or a liquid solvent (absorption) with high removal efficiency. CDs were used as solid support in order to enhance the adsorption capacity of sorbents or as aqueous solution to improve the transfer between gaseous and aqueous phase during the absorption process.

One of the first studies investigating the use of solid support modified by CDs in the sorption of organic contaminants in air showed that the trapping of low-molecular weight organic vapors by β-CD polyurethane resins were improved compared to polyurethane resins containing no CD units (Mizobuchi et al. 1981).

Butterfield et al. (1996) have shown that solid β-CD spread over a glass fiber filter could extract volatile PAHs from air by the formation of inclusion complexes. β-CD has been also immobilized on PEGylated Merrifield resins to study the trapping capacity of this new material for a mixture of VOCs (Siu et al. 2005). The resin modified by β-CD absorbs 60.1% of the VOCs against 29.3% for the unmodified. Considering relatively low % loading of CD, these values indicate a high efficiency of trapping.

Szejtli (1989) suggests the use of aqueous solutions of CD to scrub gaseous effluent, but very few studies were done on this subject (Uemasu et al. 1996; Blach et al. 2008). Uemasu et al. used aqueous solutions of branched β-CD to remove volatile chlorinated hydrocarbons. Blach et al. used α-CD, β-CD and β-CD derivatives e.g. RAMEB, CRYSMEB, HPBCD, SBE to trap toluene and showed that temperature, concentration of the waste gas and CD concentration have an influence

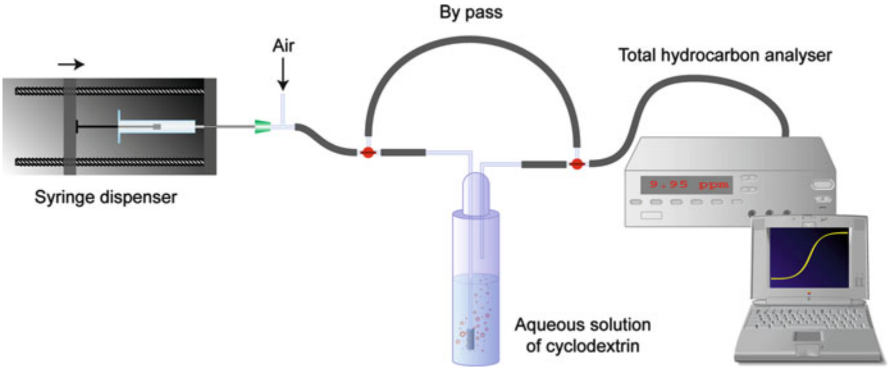


Fig. 2.7 Experimental setting for the study of dynamic absorption (Blach et al. 2008)

Table 2.5 Henry's law constants (H_c, dimensionless) and formation constants (K_f, M^{-1}) of toluene at 30°C determined by static headspace gas chromatography

	H_2O	[CD] M	α-CD	β-CD	HPBCD	CRYSMEB	RAMEB	4-SBE-β-CD
H_c	0.268	0.01	0.198	0.086	0.107	0.115	0.090	0.131
		0.05	–	–	0.031	0.035	0.025	0.048
K_f	–	–	38	142	163	165	171	155

Blach et al. (2008)

on the absorption capacities of the absorbent. In both studies, production of solid support was not observed and regeneration of used absorbent can be achieved by heating the solution. The experimental setting used by Blach et al. is presented in Fig. 2.7.

The trapping of gaseous radioactive iodine, from the fission of uranium 235 isotope, was investigated by using aqueous solution of α-, β- and γ-CD as well as their methylated analogs and insoluble crosslinked polymers (Szente et al. 1999). The methylated α-CD leads to a 200-fold increase in the aqueous solubility of iodine, the methylated β-CD to a 100-fold increase while the methylated γ-CD does not provide iodine binding.

The immobilization of VOCs in aqueous CDs solutions were also investigated by using static headspace gas chromatography analysis for single or multiple contaminants (Saito et al. 2003; Yang et al. 2006; Fourmentin et al. 2007; Blach et al. 2008; Gao et al. 2009). Henry's law constants (H_c) as well as stability constants were determined for different pollutants. In all cases, H_c decrease with increasing CD concentration (see Table 2.5). This behavior should be directly linked to the formation of an inclusion complex between the CDs and toluene, improving the apparent solubility of toluene. These data have demonstrated that the volatility of toluene could be greatly reduced in the presence of β-CDs, in comparison with α-CD. The use of RAMEB at a concentration of 0.05 M leads to a reduction of volatility up to 95%.

More recently, soluble and insoluble crosslinked CD polymers were synthesized by using a low methylated-β-CD (CRYSMEB) and epichlorohydrin with and without guest as template and were used to trap toluene in the gas phase (Mallard-Favier et al. 2011). Insoluble imprinted polymers trapped more efficiently toluene than insoluble polymers in gas phase and in water, showing that polymerization in the presence of toluene limits the blocking of CD cavities.

2.4 Catalytic Remediation Processes

The molecular encapsulation of a molecule in CD changes its physicochemical properties like volatility or solubility. Due to this feature, CDs are also associated with catalytic remediation processes. This section will focus on the applications of CDs in advanced oxidation processes, hydrodechlorination and biodegradation.

2.4.1 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) attract increasing interest as promising powerful methods to efficiently removing non bio-degradable pollutants from contaminated water or soils. Thus, AOPs are environmentally friendly methods, which are based on the *in-situ* production of hydroxyl radicals ($^{\bullet}OH$) as the main oxidizing agent. Among the different approaches to generate the active oxidizing radicals, much attention has been devoted to the environmental applications of CDs in Fenton-based processes and phototreatments.

The most popular chemical AOP is likely the Fenton method where a mixture of Fe^{2+} and H_2O_2 (Fenton's reagent) is used to degrade the pollutant into harmless products. The possibility of using CDs to promote the Fenton reactions was first reported by Lindsey et al. (2003). These authors studied the effect of native β-CD and CMCD on the effectiveness of the Fenton degradation of various HOCs (phenol, PAHs and polychlorinated biphenyls has been evaluated). The effectiveness of the process was found to be dependent both on the chemical nature of CD and pollutant. The best results were obtained for the degradation of PCB-80 (3,3′,5,5′-tetrachlorobiphenyl) in the presence of CMCD, showing a 13-fold increase in the decontamination rate over the control experiment. It was assumed that, the CMCD could form a ternary supramolecular complex (pollutant-cyclodextrin-iron) and that the degradation of the pollutant in the complex would be enhanced by the proximity of the pollutant to the hydroxyl radical formation site. These complexes have been identified by electrospray-MS and by absorbance spectra.

This pioneering work has led other researchers to investigate the destruction of toxic and refractory organic pollutants by means of Fenton-type processes assisted by CDs. Thus, an extension to this approach was recently reported by Matta et al. (2008) for the oxidation of 2,4,6-trinitrotoluene (TNT) by Fenton-like systems in the presence of naturally occurring iron-bearing minerals. In particular it was clearly shown that, at neutral pH, the combined used of magnetite-based systems (mixed Fe^{II}/Fe^{III} phase) and CMCD resulted in a threefold increase in the mineralization of TNT. Additional experiments have evidenced that CMCD increased the iron dissolution rates in aqueous phase by metal chelating and that this phenomenon was responsible for the enhancement of the degradation of TNT.

The ability of CDs towards degradation of TNT by Photo-Fenton has been also explored in contaminated soil extract solutions (Yardin and Chiron 2006). Photo-Fenton was carried out by applying UV light ($\lambda = 254$ nm, 150 W) to the Fenton process. The use of 5 mM methylated-β-CD flushing solution showed the highest potential since the removal of TNT from soils was significantly enhanced. However, the catalytic methodology led to a modest improvement of the degradation rate of TNT. Accumulation of short-chain carboxylic acids, such as formic and oxalic acids, was detected during the mineralization process.

Recently, Veignie et al. (2009) investigated the effect of native β-CD and its derivatives HPBCD and RAMEB on the solubilization of benzo[a]pyrene (BaP) and on its degradation by Fenton's reaction. Results showed that BaP apparent solubility and degradation was significantly increased in the presence of CD in the following order: β-CD < RAMEB < HPBCD.

The effect of CD was further investigated to promote indirect electrochemical methodologies for the elimination of pesticides in soil. Indeed, Hanna et al. (2005) showed that HPBCD was an efficient flushing agent for treating pentachlorophenol (PCP) contaminated soil extract solutions by using electrochemically generated hydroxyl radicals *via* the presence of Fe^{3+} in the O_2-saturated solution**.** A total disappearance of the pesticide and 90% abatement of the chemical oxygen demand were achieved after 11 h of electrolysis ($I = 200$ mA).

Gemeay et al. (2004) studied the oxidative degradation of thionine dye (3,7-diamino-phenothiazin-5-ylium acetate) in aqueous solutions, catalyzed by H_2O_2 and supported transition metal ion complexes for the treatment of industrial wastewater streams. A number of parameters were studied, showing that the degradation of the dye was strongly dependent on the nature of metal ion, ligand and support. The highest reaction rate was observed with the $Ni(NH_3)_6^{2+}$ complex supported on the Dowex-50 W cation-exchange resin with 8% divinylbenzene of cross-linkage degree. The effect of native β-CD on the oxidative degradation of thionine dye was also evaluated using $Cu(NH_3)_4^{2+}/SiO_2$ as catalyst. When the amount of β-CD was too low (<0.5 mM), a significant inhibition of the catalytic activity was observed and this phenomenon was ascribed to the inclusion of the thionine in CD cavity, which would lead to a shielding of the dye molecule from attack by the oxidant. This limitation was partly circumvented with further increasing the β-CD loading (>0.5 mM). This rate enhancement was attributed to the formation of a 2/1 inclusion complex (β-CD/dye) complex or stabilization of the catalytically active species formed from the reaction between H_2O_2 and the catalyst.

The utilization of more sophisticated transition metal ion complexes with CD has also been described in the literature. For instance, the behavior of HPBCD toward the catalytic oxidation of pentachlorophenol in soils suspensions has been recently explored by Fukushima and Tatsumi (2007) *via* the use of tetra(*p*-sulfophenyl) porphineiron(III) complex as the catalyst. The authors reported that, at $pH = 4$ or 6 in the presence of potassium monopersulfate as the single-oxygen donor, the addition of HPBCD in the reaction medium allowed not only to enhance the mineralization of the pollutant, but also to substantially slow down the rate of self-degradation of the Fe^{III}-porphyrin catalytic system thanks to the formation of a supramolecular complex with the oligosaccharide. Alternatively, Huang et al. (2003) developed the successful use of a β-CD covalently functionalized by an iron-porphyrin complex (hemin) for the degradation of toxic pollutants like Rhodamine B (RhB) and 2,4-dichlorophenol (DCP). This iron supramolecular complex was shown to be highly stable and active, with H_2O_2 and under visible irradiation, thus showing that RhB and DCP could be mineralized at 72% and 85% with low ratios of catalyst to substrate of 1:200 and 1:1,000, respectively.

CD-assisted photodegradation of pesticides and environmental contaminants has been currently used for the destruction of organic compounds, under homogeneous or heterogeneous conditions and without any additional oxidizing agent. Kamiya et al. (1994) investigated the inclusion effect of α-, β- and γ-CDs on the photodegradation rates of parathion and paraoxon and reported that the effectiveness of the process was strongly dependent on the nature of the CD. For instance, they found that γ-CD resulted in a considerable inhibition on the photodegradation rates of the both pollutants while α-CD exerted a small promotion effect.

Villaverde et al. (2007) studied the potential of native and functionalized CDs to act as photosensitizers for the degradation of the herbicide norflurazon (NFL) in soil colloidal suspensions and under irradiation. The irradiation was carried out with a Xenon lamp equipped with a permanent filter ($\lambda \geq 290$ nm, 500 W/m^2). In particular when methylated-, hydroxypropyl- and β-CD were added to the soil suspensions, the authors observed significant increases in the rate of NFL photodegradation, especially in the case of montmorillonite as shown by the measured $t_{1/2}$ values (6.4, 5.3 and 4.6 *vs* 16.5 h without CD). This photocatalytic effect was connected to the ability of these CDs to form inclusion complexes with NFL according to following order: methylated-β-CD > HPBCD > β-CD > α-CD > γ-CD.

In a similar context, Wang et al. (2007) reported that the formation of 1/1 inclusion complex of bisphenol Z with β-CD allowed the enhancement of its aqueous photodegradation in the presence of β-CD under UV irradiation ($\lambda = 254$ nm, 35 W). It was postulated that the enhancement effect by a factor 9 was connected to the moderate inclusion depth, facilitating the formation of $^{\bullet}OH$ radicals under irradiation thanks to the proximity of bisphenol with the secondary hydroxyl groups of the β-CD.

Over the last decade, the use of photo-irradiated semiconductors as photocatalysts, such as titanium dioxide in the anatase form, has also been examined for remediation processes. TiO_2 has been intensively studied in the field of photocatalysis owing to its non-toxicity, low cost, high chemical stability and superior photoelectronic properties (Linsebigler et al. 1995). Notably, the possibility of coupling CDs and TiO_2 in suspensions for enhancing environmental photocatalytic reactions was independently reported in 2004 by different authors (Anandan and Yoon 2004; Hanna et al. 2004; Lu et al. 2004).

Thus, Lu et al. (2004) showed the beneficial effect of native β-CD on TiO_2 photocatalytic decolorization of diazo dyes and photoreduction of Cr(VI) under

UV-light ($\lambda = 254$ nm, 30 W). The formation of surface complexes between the β-CD and the dyes or Cr(VI) anions onto the TiO_2 surface *via* hydrogen bonding and this hypothesis was supported by means of additional sorption and FTIR experiments. In these experiments, no degradation of β-CD was observed.

Hanna et al. (2004) evaluated the behavior of native β-CD and HPBCD in the degradation of pentachlorophenol in contaminated soil extract solutions irradiated by a mercury medium UV pressure lamp (125 W) using TiO_2 as a photocatalyst. However, the authors observed an inhibition of the photoactivity, which gradually increased with increasing amounts of CD. Nevertheless, by adjusting the experimental conditions, this method was considered as promising for the efficient PCP removal from contaminated soils, with preservation of the microbial activity.

In the same time, Anandan and Yoon (2004) reported that TiO_2-β-CD colloids prepared by hydrolysis of $TiCl_4$ in aqueous 1% β-CD solution could be successfully used in the photocatalytic degradation of the Nile red dye carried out in the visible region with a xenon lamp ($\lambda \geq 320$ nm). Near 70% Nile red conversion could be achieved after 1 h test in the presence of the TiO_2-β-CD system and this value was about two times higher than that obtained in the same conditions with colloidal TiO_2.

Interestingly, the photodegradation of bisphenol A and analogues was further investigated in aqueous suspensions containing β-CD and TiO_2 under irradiation in the visible region ($\lambda \geq 365$ nm, 250 W) (Wang et al. 2006a, b; Zhang et al. 2009). Apart from the possible promotion of degradation of organic pollutants in aqueous medium, β-CD could play a role of "nanochannel" or "bridge" to improve the kinetics of charge transfer from the photoexcited TiO_2 semiconductor to the electron acceptor groups of the organic guest retained in its cavity (Fig. 2.8).

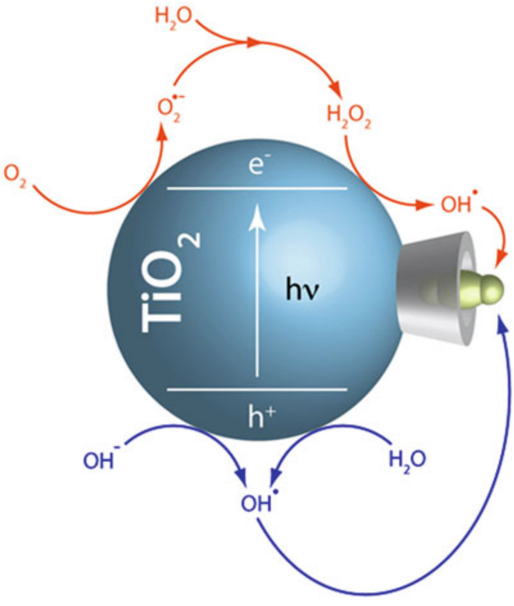


Fig. 2.8 Mechanism of the enhancement of pollutant degradation in presence of cyclodextrins

Interestingly, more sophisticated approaches involving the attachment of CDs to TiO_2 surfaces have been performed. For instance, the ability of CMCD to be chemically anchored onto titanium dioxide has already been demonstrated.

Thus, Tachikawa et al. (2006) reported that the amount of grafted CMCD onto the TiO_2 particles could be five times higher than the value obtained with native β-CD. However, it should be emphasized that these CMCD/TiO_2 particles facilitated the electron transfer in photocatalytic oxidation reactions of aromatic sulfides, studied by laser-flash photolysis. Toma et al. (2006) also showed that the surface modification of nanocrystalline TiO_2 films with CMCD could be successfully employed to improve selective photodegradation reactions. According to these authors, the chemical anchorage of CMCD on TiO_2 occurred through chelating of the carboxyl groups with the surface titanium ions. This new functionalized hybrid film has proven to be efficient in the UV-light photobleaching of a model guest organic species, i.e. $[Fe(Brphtpy)_2](PF_6)_2$.

It has also been reported that native CDs could be coated on the surface of anatase TiO_2 particles under UV irradiation. Thus, Feng et al. (2005) reported that UV-light illumination of an aqueous mixture of TiO_2 nanorods and native CD molecules (α-, β- or γ-CD) in a pH range of 5–7 could result in the formation of self-assembly of photoactive hybrid nanowires of TiO_2-CD, with lengths up to several millimeters. TEM data of the TiO_2-CD indicated that the thickness of the organic layer between the TiO_2 rods was about 1 nm. More recently, Zhang et al. (2010) have used a grafting procedure to anchor native β-CD on titanium dioxide through a photo-induced self assembly process. This method implied the UV-irradiation ($\lambda = 254$ nm, 15 W) of the TiO_2 suspension in the presence of β-CD under air bubbling. After 24 h under irradiation, the β-CD/TiO_2 material was recovered by centrifugation and the solid particles carefully washed with water to remove the excess of CD. Tested in the degradation of paracetamol under visible irradiation, this new β-CD/TiO_2 hybrid material led to a substantial increase of the photocatalytic activity compared to the control materials. The reusability was clearly demonstrated by three consecutive runs.

2.4.2 Hydrodechlorination

Cassez et al. (2006) have reported that catalytic hydrodechlorination of carbon tetrachloride into methane and chloride salts can be efficiently performed in the presence of chemically modified CDs in aqueous basic medium at room temperature. In this eco-efficient process, the organic pollutants are trapped in water by various chemically modified CDs via the formation of inclusion complexes and dechlorinated by a supported heterogeneous palladium catalyst (Fig. 2.9).

Catalytic investigations demonstrate that CDs act as efficient CCl_4 solubilizers and, much more interesting, as protective molecules against side reactions. The case of degradation of $CHCl_3$, which is the first reaction intermediate issued from the

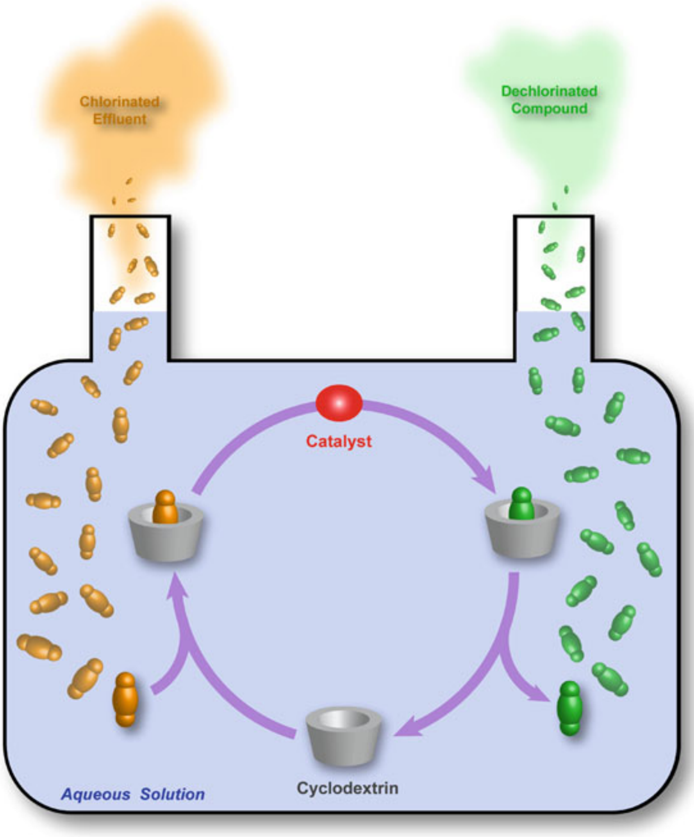


Fig. 2.9 Illustration of the dechlorination process of gaseous effluent through an aqueous solution containing cyclodextrin as a solubilizing agent and a catalyst

degradation of CCl_4 is particularly interesting. Actually it has been demonstrated that addition of chemically modified β-CDs such as the RAMEB in the reaction medium increases the stability of the chloroform in aqueous basic medium by impeding the basic attack of the hydroxide anions.

The dechlorination of trichloroethylene by iron powder in the presence of various substituted β-CDs has been investigated by Shirin et al. (2004). It was found that, in the presence of 100-mesh (0.145 mm particle size) zero-valent electrolytic iron powder, reaction rate decreased as the CD concentration increased. A satisfactory interpretation of the kinetic data could be given by the formation of an inclusion complex between β-CDs and trichloroethylene and also by a novel mechanism involving CD binding to the iron-surface. More precisely, the overall rate was governed by the extent of binding of CD with the iron surface (which depended on the

CD unsubstituted -OH groups), the binding constant between CD and the substrate, and the degradation of the CD-included trichloroethylene, the CD being associated with the ion surface. These observations were made both in batch (static) and column (dynamic) systems.

2.4.3 Biodegradation

Bioremediation is considered to be a cost-effective treatment option among the conventional treatment methods. The ability of CDs to interact with HOCs and form inclusion compounds was exploited in bioremediation processes to increase the bioavailability of pollutant and/or to decrease the toxicity of substrates towards cells.

Degradation of toluene and *p*-toluic acid by a *Pseudomonas putida* strain in the presence of β-CD was investigated by Schwartz and Bar (1995). The authors reported that the toluene toxicity towards *P. putida* was reduced when β-CD complexed toluene was provided as the substrate. The latter was fully degraded at a concentration of up to 10 g/l. Degradation of toluene vapors can also be enhanced in the presence of β-CD as a result of reduced molecular toxicity and facilitated absorption of the gaseous substrate. Similarly, β-CD alleviated the inhibitory effect of *p*-toluic acid on *P. putida*. This protective effect of CD was remarkably more prominent when the microbial culture was shock loaded with an otherwise toxic dose of *p*-toluic acid (1.8 g/l).

An enhanced effect of RAMEB for the biodegradation of toluene by activated sludge has been also observed by Furuta et al. (2007). The presence of RAMEB increased the activated sludge concentration and prevented toluene from evaporating during incubation.

Beneficial effect of CD on the bioremediation was also reported by Qiu et al. (2009). The biodegradation of *p*-nitrophenol by a soil bacterium strain (Arthrobacter) was greatly accelerated by addition of β-CD at a concentration of 0.5%. One explanation for the enhancement of biodegradation is that the soluble β-CD/*p*-nitrophenol complex reduces the effective concentration of *p*-nitrophenol, so that the bacterium is exposed to less toxic concentration of *p*-nitrophenol.

Interestingly, phenol derivatives can also be efficiently degraded by bacteria immobilized on supports containing CDs. Thus, Pluemsab et al. (2007) have reported that calginate beads covalently linked with α-CD can serve as a supporting matrix for bacterial degradation of nonylphenol. In fact, *Sphingomonas cloacae* immobilized on α-CD/alginate beads degraded nonylphenol more efficiently than that immobilized on alginate beads. In addition, the cell leakage from α-CD/alginate beads was not observed. Sevillano et al. (2008) used an insoluble CD polymer as a biomass carrier for the degradation of aqueous phenol in a fluidized bed biological reactor. The elimination capacity was about 1.0 kg-phenol/m^3 day.

Effects of β-CD, HPBCD and CMCD on the solubility and biodegradation of 2-nitrobiphenyl by an *Acinetbacter sp.* have been reported by Cai et al. (2006). Results showed that β-CD, HPCD and CMCD cannot be utilized by *Acinetbacter sp.*

as sole carbon source and none of the CDs had toxic effects on the growth of the bacteria in the experiments. Interestingly, all the CDs could enhance the apparent solubility and accelerate the biodegradation of 2-nitrobiphenyl. The biodegradation-accelerating effects of CDs on 2-nitrobiphenyl were correlated with their solubility-enhancing effects.

The biodegradation of decabromodiphenyl ether in liquid culture medium by white rot fungi in the presence of β-CD has also been evaluated by the same research group (Zhou et al. 2007). Their study indicates that β-CD had positive effects on the degradation rate of decabromodiphenyl ether but the effect was less than that of Tween 80 at the same concentration. It was also found that β-CD can also enhance the growth of white rot fungi, and the enhancement was directly correlated to β-CD concentration, suggesting that β-CD may be used as a carbon or energy source in these experiments.

The ability of CD to promote the biodegradation of aliphatic and polycyclic aromatic hydrocarbons was also observed by Bardi et al. (2000). Thus, the biodegradative activity of a microbial population isolated from a petroleum-polluted soil towards dodecane, tetracosane, anthracene and naphthalene was greatly enhanced in the presence of β-CD. It was also found that β-CD influenced the growth kinetics as shown by a higher biomass yield and better utilization of hydrocarbon as a carbon and energy source.

The use of CD for the intensification of bioremediation of contaminated soils has also been investigated by Fava et al. (2002). RAMEB appears as a promising bioavailability enhancing agent for the treatment of polychlorinated biphenyls contaminated soils, not only for its positive effects on the polychlorinated biphenyls biodegradation, but also for its biodegradability, non-toxicity and relatively low cost. RAMEB was also successfully applied as an additive in the bioremediation of different transformer oil-contaminated soils in laboratory and field experiments (Molnar et al. 2005). The environmental risk associated to the use of RAMEB appears much lower than the risk associated to the use of synthetic surfactants or solvents for mobilizing and improving the bioavailability of hydrophobic contaminants. The biodegradation of field-aged PAHs and phenolic compounds in municipal gas plant site soils can also be enhanced though HPBCD amendments (Allan et al. 2007). Experiments demonstrated that the biodegradation was not limited by the catabolic activity of the indigenous microorganisms but rather by processes resulting in limited availability of contaminants to degraders. Interestingly, β-CD enhanced bioremediation process can further be improved by phytoremediation. Indeed, Bardi et al. (2007) have reported that the content of PAHs in soybeans growing in contaminated soils was greatly increased in the presence of β-CD.

The degradation of hydrocarbons or mixture of hydrocarbons by *Pseudomonas* like species isolated from bilge oil contaminated waters has been investigated by Sivaraman et al. (2010) in the presence of native CDs. The percentage of residual hexadecane remaining in a 2.5 mM β-CD supplied medium at 120 h was found to be 15% in comparison with the biotic control which was 43%. Degradation of mixture of hydrocarbons (tetradecane, hexadecane and octadecane) by *Pseudomonas* like species was also found to be more efficient in the presence of β-CD. So, the residual percentage of tetradecane, hexadecane and octadecane remaining in a 2.5 mM β-CD supplied medium at 120 h was found to be 32%, 43% and 61% in comparison with the biotic control 50%, 58% and 67%, respectively.

Surprisingly, Stroud et al. (2009) have reported that the introduction of HPBCD into soils did not enhance the biodegradation of hexadecane or phenanthrene. In their study, soil was spiked with [9-^{14}C]phenanthrene and [1-^{14}C]hexadecane at 50 mg/kg and aged for 1, 25, 50, 100 and 250 days. At each time point, the microcosms were amended with aqueous solutions of HPBCD at a range of concentrations (0–40 mM). Mineralisation assays and aqueous HPBCD extractions were performed to assess the effect of the amendments on microbial degradation. The results showed that amendments had no significant impact on the microbial degradation of ^{14}C-contaminants. Inefficiency of CD to accelerate bioremediation has also been reported by Purwaningsiha et al. (2004). Indeed, although mass transfer was identified as the rate limiting step, the addition of HPBCD failed to improve the bioremediation of naphthalene particles by a pure strain of *Pseudomonas putida* in a water.

Finally, the interest of combining chemical and biological treatments to accelerate degradation of persistent pollutants has been recently demonstrated by Rafin et al. (2009). Indeed, BaP can be efficiently degraded in the presence of HPBCD by combining Fenton's oxidation and microbial degradation by *Fusarium solani*. Thus, when Fenton's treatment was combined with biodegradation, a beneficial effect on BaP degradation (25%) was obtained in comparison with biodegradation alone (8%) or with chemical oxidation alone (16%) in the presence of HPBCD for 12 days of incubation.

2.5 Conclusion

This review shows that CDs are a versatile tool for environmental remediation because CD chemistry offers various possibilities for preparing various CD derivatives (monomers and polymers) or materials (grafted or coated). CDs can be used in all areas of remediation technologies including soil, groundwater, wastewater and atmosphere. The number of papers that appears each year in the literature shows recent and continuing interest in applications of CDs in environmental protection. The large-scale commercialization of CDs and CD derivatives leads to a reduction of the cost, favorable to environmental applications. The future of CDs and CD derivatives in environmental remediation seems to be bright.

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Chapter 3
Carbon Nanotubes for Environmental Protection

Sippy K. Chauhan, Anuradha Shukla, Simpi Dutta, S. Gangopadhyay, and Lalit M. Bharadwaj

Contents

Abstract Nanotechnology is based on the fact that very small structures usually have new properties and behavior that are not observed in bulk matter of the same composition. Carbon nanotubes are one of the most striking nanometric structures. Their properties depend upon diameter and chirality. Carbon nanotubes have high length to radius ratio, high degree of mechanical strength and flexibility. Carbon nanotubes can behave like metallic, semi-conducting or insulating material. Carbon nanotubes have attracted major attention in latest applications such as nanodevices, field emission, gas adsorption, composite reinforcement, metal composites, and as a catalyst supports because they possess exceptional mechanical properties, unique electrical properties, high chemical and thermal stability and a large specific surface area.

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The properties of carbon nanotubes can be altered by encapsulating metals to make electrical or magnetic nanocables structures. Carbon nanotubes may therefore be suitable for sorbing hydrogen or separating gases and also can be used as energy storage, membranes for gaseous adsorption and sensors for environmental application. This review discusses the main concepts behind the role of carbon nanotubes for the special application in the field of environmental protection. The major points which are discussed in this review are:

- Introduction to carbon nanotubes: in this section we discuss the main synthesis routes of nanotubes and their properties
- Use of carbon nanotubes for energy storage: hydrogen storage is considered to be an ideal for its clean and abundantly reserved. Storage and transportation of hydrogen is an important challenge which has been focused on the use of carbon nanotubes.
- Use of carbon nanotubes as a sorbents: carbon nanotubes are thought to be very good sorbent for various toxic gases, dioxins, and volatile organic compounds.
- Use of carbon nanotubes as sensors: carbon nanotubes are thought to be promising candidate for nano scale sensing material for the detection of various pollutants in air like volatile organic compounds such as benzene and toluene.

Keywords Nanoscience • Carbon nanotubes • Nanosensors • Energy Storage • Membranes • Environmental protection

3.1 Introduction to Nanoscience and Nanotechnology

Nanoscience and nanotechnology study the structure of matter with at least one dimension of the order of less than 100 nm. This is the standard way of classifying what belongs to the nano world. However, properties related to low dimensions are more important than size. Nanotechnology is based on the fact that some structures usually smaller than 100 nm have new properties and behavior that are not exhibited by the bulk matter of the same composition.

This is because particles that are smaller than the characteristic lengths associated with the specific phenomena often display new chemistry and new physics that lead to new properties that depend on size. Perhaps one of the most intuitive effects is due to the change in the surface/volume ratio. When the size of the structure is decreased, this ratio increases considerable and structure phenomena predominate over the chemistry and physics in the bulk. Therefore, although the reduction in the size of the sensing part and/or the transducer in a sensor are important in order to better miniaturize the devices, nano science deals with new phenomena. New effects appear and play an important role that is often related to quantum mechanics and quantum mechanisms. Consequently, important characteristics and quality parameters of the nanosensors can be improved over the case of classically modeled systems merely reduced in the size. For example, sensitivity can increase due to better conduction properties, limits of detection can be lower, very small quantities of samples can be analyzed, direct detection is possible without using labels and some reagents can be eliminated. Sensors have been classified according to multiple criteria (Rodriguez-Mozaz et al. 2004). The most common way to group sensors considers either the transducing mechanism like electrical, optical, mass, thermal, piezoelectric etc., the recognition principle like enzymatic, DNA, molecular recognition etc. or applications like environmental, food, medical diagnosis etc.

3.2 Carbon Nanotubes for Environmental Protection

In 2004, US Environmental Protection Agency (EPA) announced that research was needed to identify opportunities and applications of nanoscale science and technology to address environmental problems (www.epa.gov). Three research topics were identified

- Environmental benign manufacturing and processing,
- Remediation/treatment,
- Sensors.

Nanotechnology refers to the use of materials and structures of nanoscale dimensions. Nanotubes are relatively new but broadly studied materials in the nanotechnology field. Due to their outstanding mechanical, electronic and chemical properties, carbon nanotubes offer great promise of delivering new and improved environmental technologies as sensors and sorbent materials to detect and treat existing contaminants and prevent new pollution which is significant challenges to environmental scientists and engineers. Nanotubes, present as small particulate material, may also present environmental hazards in their own right. Clearly nanotechnology brings many opportunities and challenges that scientists have only just begun to explore.

Environmental control agencies, researchers and the general public are concerned about the increasing mobilization and release of trace elements to the environment. Substances of significant concern in the remediation of soils, sediment and ground water include heavy metals (e.g. mercury, lead, cadmium) and organic compounds (e.g. benzene, chlorinated solvents, and toluene). Although nanotubes have been applied to adsorb several kinds of trace contaminants, (Li et al. 2002, 2003a, b) from water, there is a lack of fundamental understanding of the physics and chemistry of nanotubes surfaces related to sorbent capacity, and interference of other components in the gas mixture.

Nanotechnology could make many products lighter, stronger, cleaner, less expensive and more accurate. Nanotechnology has the potential to significantly improve environmental protection (http://es.epa.gov/ncer/nano/index.html). Specifically carbon based nanostructures exhibit unique properties and morphological flexibility, which renders them as inherently multifunctional and compatible with organic and inorganic systems. Carbon nanotubes have aspect ratio on the order of 1,000, which coupled with high conductivity, makes them ideal candidates for low voltage emitters.

Carbon nanotubes are the building blocks of Nanotechnology and are shinning everywhere like a diamond because of their special physicochemical properties. Therefore, this review article is an attempt to explain the status of carbon nanotubes for environmental protection.

3.3 Carbon Nanotubes: Synthesis and Properties

Carbon nanotubes have been the focus of much research since their discovery in the early 1990s' (Iijima 1991). Simply speaking, a carbon nanotube is analogous to a sheet of graphite rolled into a cylinder closed at either end with caps containing pentagonal rings. Depending on the twist direction of the graphite sheet, nanotubes can be metallic or semi conducting. Cartoons in Fig. 3.1 (Saito et al. 1998; Odom et al. 2000) illustrate the idea of rolling. Due to their special structure, perfect carbon nanotubes are light, flexible, thermally stable and chemically inert (www.pa.msu.edu/cmp/csc/ntproperties/equilibriumstructure.html, 2004). Several methods have been applied to produce nanotubes. Laser ablation and HiPco are two effective methods (Saito et al. 1998; Odom et al. 2000). A laser is used in laser ablation technique to vaporize a composite graphite/transition metal target inside a heated quartz flow tube. Nanotubes form in the condensing vapor. HiPco stands for catalytic decomposition of CO at high pressure and temperature.

Carbon nanotubes are self assembled nanoscale tubular structure of carbon atoms. There are two types of carbon nanotubes (a) Single Wall nanotubes (b) Multiwalled nanotubes. Single wall carbon nanotubes are the simplest of these nanostructures, being a single graphite plane rolled into a thin tube. The single wall carbon nanotubes are one dimensional wires consisting of only surface carbon atoms. The multiwalled carbon nanotubes are composed of concentric cylinders of various

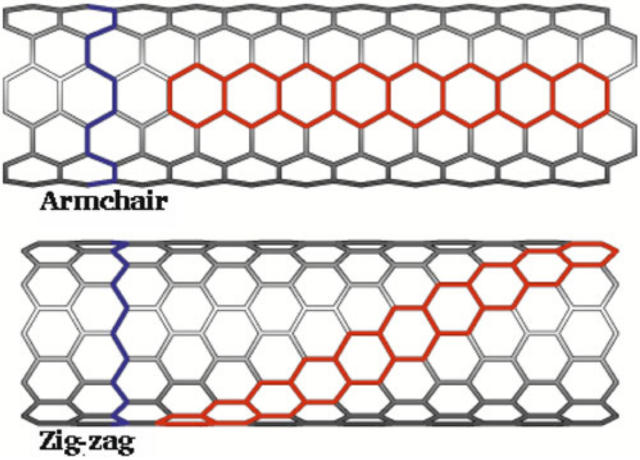

Fig. 3.1 Semi metallic/metallic structure of carbon nanotubes

single wall carbon nanotubes. The electronic structure of single walled nanotubes can be either metallic or semi conducting depending on the chiral vector (n, m) where n and m are integer (Thostenson et al. 2001; Dai 2002). The multiwalled carbon nanotubes could be formed by combining metallic and semi conducting nanotubes elements with different electronic properties (Varghese et al. 2001a, b).

The synthesis methods for single walled carbon nanotubes and multiwalled carbon nanotubes include arc discharge (Shi et al. 2000), laser ablation (Zhang and Iijima 1999), pyrolysis (Yang et al. 1999), chemical vapor deposition (Bower et al. 2000), gas phase catalytic growth (Nikolaev et al. 1999). These methods for the synthesis of carbon nanotubes do not produce a mono disperse product with physical and chemical properties controlled. During nanotubes synthesis, impurities in the form of metallic catalysts, amorphous carbon, fullerenes, graphitic carbon are also deposited. Hence subsequent steps of purification are required to separate the carbon nanotubes from non – tubular impurities by post treatments. Particular care must be applied to purification methods, which could give rise to structural changes in the carbon nanotubes by altering their chemical and physical properties mainly gas adsorption behavior and nano structural characteristics. Recently, the purification methods proposed for the carbon nanotubes are one step process with hydrochloric acid washing and two step processes with hydrochloric washing after air oxidation at temperature above 350°C (Yang et al. 2002a, b, c).

Carbon nanotubes are hundreds of times stronger than steel. This is partly due to their hexagonal geometry, which can distribute forces and stresses over a wide area and partly due to the strength of carbon – carbon links. They have unusual electronic properties derived from the free electrons left at the surface of the tubes after sp2 hybridization of the carbon orbital. Simple electronic devices including diodes, switches and transistors have recently been made using nanotubes. These devices are much smaller than their silicon equivalents that are currently used in computer chips. Several fields now take advantage of the exceptional properties of carbon nanotubes. The extraordinary properties of carbon nanotubes are as follows –

- Carbon nanotubes have high length to radius ratio, which allows for greater control over the unidirectional properties of the material produced
- Carbon nanotubes can behave as metallic, semi conducting or insulating material depending on their diameter, their chirality and any Functionalization or doping
- Carbon nanotubes have high degree of mechanical strength and flexibility
- The properties of carbon nanotubes can be altered by encapsulating metals inside them to make electrical or magnetic nanocables or even gases, thus making them suitable for sorbing hydrogen or separating gases.

Carbon nanotubes constitute a promising class of advanced nano materials with outstanding electronic, chemical, structural, optical, mechanical and thermal properties (Dresselhaus et al. 2001) for practical applications including nano devices (Collins et al. 1997; Avouris 2002), nano actuators (Baughman et al. 1999), nano sensors (Kong et al. 2000; Chopra et al. 2003a, b; Someya et al. 2003; Penza et al. 2004a, b, c, 2005a; Wong et al. 2003). Due to their peculiar hollow structure, nano sized morphology (diameter 1–10 nm), high surface area (100–2,000 m^2/g), high carrier mobility, high chemical reactivity at walls and mainly at caps, excellent stability, the carbon nanotubes are ideal candidates for highly sensitive gas adsorption, hence they are strongly attractive as gas sensors nano materials and used as advanced functional nano materials to fabricate high performance innovative gas and vapor phase chemical nano sensors (Cantalini et al. 2003; Qi et al. 2003; Penza et al. 2004a, b, c, 2005a, b; Li et al. 2003a, b; Bekyarova et al. 2004; Chen et al. 2005; Wei et al. 2003) in various configurations demonstrating that carbon nanotubes are appealing sensitive nano materials for molecular sensors. The single walled carbon nanotubes are building blocks aggregated in one dimensional tubular nano wire with only surface arranged carbon atoms. These are considered as the most promising nano materials for future miniaturized electronic nano devices. The single walled carbon nanotubes based sensors exhibit advantages over existing conventional sensor materials in performance terms of high sensitivity, very low sub ppm limit of detection, on – line and real time analyte detection, fast response, high resolution, specific chemical interactions between carbon atoms and targeted gas molecules at room temperature.

The excellent mechanical, electronic and chemical properties of carbon nanotubes have stimulated some work by environmental scientists and engineers (Masciangioli and Zhang 2003). Most work until now has been performed on the laboratory scale. So far, there are three main environmental applications of nanotubes, i.e. energy storage, sorbents and sensors. Nanotechnology has the potential to be used to develop new, “green” processing technologies that minimize or eliminate the use of toxic materials and the generation of undesirable byproducts and waste streams. However, the present cost of nanotubes, at hundreds of dollars per gram, limits large-scale applications of nanotubes in the near future. Novel production techniques may change this in the future.

3.4 Carbon Nanotubes for Energy Storage

Energy is the integral part of human life since ancient time. In recent years, the world energy consumption has been increasing at a much faster rate due to growing population, modern lifestyle and rapid industrialization. Fossil fuels, nuclear power, wind energy, solar energy is some of the primary sources of energy.

From the beginning of industrialization, humankind has been consuming natural resources without thinking about the environmental impact and possible consequences of their exhaustion. A major effect of using fossil fuels is global warming, which causes hundreds of deaths in warm climate countries, increasing levels of sea water worldwide which threatens seaside cities and numerous other natural disasters such as floods, hurricanes, forest fires and so on. At this point we have to think which way to choose: stop the exhaustion of resources, accelerate the transition to renewable energies or continue consuming fossil fuels and accelerate the world toward a disastrous end. We hope we choose the first option.

Clean technologies like solar energy, wind energy, hydro power, biomass energy, geothermal energy, tidal energy and wave power technologies are improving rapidly. The main problem of these technologies is that energy produced from these sources is difficult to store or transport. Significant amounts of electricity are lost while moving long distances on electric lines. It is obvious that an energy carrier is needed for all of these energy sources, which will be hydrogen. So, energy resources and environmental pollution are essential problems that are concerned with sustainable development and demand prompt solution. Hydrogen is considered to be an ideal energy source and carrier, since it is clean and abundantly reserved. To store and transport hydrogen safely and cheaply is a key step to the utilization of hydrogen energy thus effective means for hydrogen storage and transportation have been continuously investigated. The storage of hydrogen, particularly for the development of fuel cells, is an important challenge which has been recently focused on the use of carbon nanotubes. Carbon nanotubes which consist of 1 – D nano material/nano tunnel and unique intertube pore structures have attracted interest for their prospects as effective hydrogen storage materials (Chen et al. 1999).

Although currently expensive, carbon nanotubes are also considered promising materials for hydrogen storage, an application that will be crucial in the development of efficient hydrogen-based vehicles. (Dionysiou 2004) The reversible storage of hydrogen on nanotubes has attracted much attention from the energy and environmental protection field. Using hydrogen as an alternative energy carrier is rapidly developing due to an increasing demand for renewable and environmentally friendly energy sources (Forster et al. 2003; Gordillo and Marti 2001; Huang et al. 2002; Zhu et al. 2003; Jin et al. 2002). It is reported that crystalline SWNTs have a capacity for hydrogen sorption of 5–10 wt% at pressures less than 1 bar near room temperature (Dillion et al. 1997). Such a hydrogen storage capacity would be a significant advance for the use of hydrogen as a fuel as high gravimetric density of hydrogen is a figure of merit. The Department of Energy (DOE) target for vehicular fuel cells is 6 wt% for gravimetric and 60 kg/m^3 for volumetric densities (Hynek et al. 1997). Simonyon et.al has presented a review of experimental and theoretical work on hydrogen adsorption in graphite nano fibers and single walled carbon nanotubes (Simonyan and Johnson 2002). They found that adsorption of hydrogen onto alkali- metal doped nanotubes increased in comparison to the identical bundle without the metal and concomitant charge transfer. However, the total adsorption of hydrogen on metal-doped SWNT bundles is still a rather modest 2 wt% which is significantly smaller than the DOE target (Simonyan and Johnson 2002). Extensive exploration of hydrogen storage has been performed by several research groups. However, the claimed hydrogen uptake capacity varied from less than 0.5% up to 10% (Simonyan and Johnson 2002). Nanotubes are produced by different methods and under different conditions such as pressure and temperature make comparisons sometimes difficult. However, the uniform pore size distribution, high surface area and excellent electronic properties make nanotubes promising materials for hydrogen storage (Simonyan and Johnson 2002).

Storage of other fuels in nanotubes also has been studied. Natural gas (methane is the primary constituent) adsorbed on porous materials is a promising alternative to compressed natural gas as a clean vehicular fuel, and for bulk transportation. The adsorption of methane gas on isolated SWNTs and idealized carbon slit pores at 303 K was studied by non local density functional theory. (Valentini et al. 2004; Cao et al. 2003; Tanaka et al. 2002). Based on the research already done, (Valentini et al. 2004; Cao et al. 2003; Tanaka et al. 2002) nanotubes appear to be promising materials for energy storage.

The main flaw for the commercialization of carbon nanotubes based hydrogen storage technology is the high cost of carbon nanotubes which is ~50–600 Euro/g depending on the purity. Even they are good potential for storing hydrogen as compared to other technologies for hydrogen storage.

3.5 Carbon Nanotubes for Sorbents

Carbon is well known as one of the better adsorbents for gases. This property is due to (i) the ability of this material to exist in a very fine powdered form with highly porous structure and (ii) the existence of particular interactions between carbon atoms and gas molecules. During recent decades, many improvements have been accomplished to obtain micro porous and ultra micro porous carbonaceous materials having very high adsorbing properties for the most current gases

Graphite has a hexagonal structure with an in plane lattice parameter $a=0.24612$ and $c=0.6709$ nm and assuming that all the atoms are in one single plane the maximum specific surface area is $S1=1{,}315\ m^2\ g^{-1}$ or if both the sides of plane are considered $S2 = 2{,}630\ m^2\ g^{-1}$. For a nanotubes sample, the specific surface area exposed to the gas depends on the numbers of shells.

The adsorption of a gas on a surface is a consequence of the field force at the surface of the solid called the adsorbent, which attracts the molecules of the gas or vapor, called adsorbate. The forces of attraction emanating from a solid may be of two main kinds, physical or chemical and they give rise to physical i.e. vanderwaals or chemisorption respectively.

Carbon nanotubes have been proposed as superior sorbents for dioxin removal (Long and Yang 2001). Due to the extreme toxicity of dioxins, it is desirable to have a more efficient sorbent than activated carbon so that the dioxin emissions can be reduced to lower levels. Long et al. found the interactions of dioxins with carbon nanotubes are much stronger than that with activated carbon (Long and Yang 2001). The origin of these strong interactions is not clear but the authors suggest that it may be attributed to the unique structure and electronic properties of carbon nanotubes (Long and Yang 2001).

Because of the higher bond energy between dioxin and carbon nanotubes compared to other sorbents (315 kJ/mol for nanotubes vs. 119 kJ/mol for ZX-4 carbon), the removal efficiency for dioxin by carbon nanotubes is much higher than other sorbents. Nanotubes can also be used as aqueous phase adsorbents. Peng et al. used as-grown nanotubes and graphitized nanotubes as adsorbents to remove toxic 1, 2-dichlorobenzene (DCB) from water (Peng et al. 2003). Nanotubes can be used as adsorbents in a wide pH range (3–10) (Peng et al. 2003). The experiments demonstrated that it takes only 40 min for nanotubes to attain equilibrium and that the adsorption capacity is relatively high, thereby making carbon nanotubes good adsorbents for the removal of DCB from water. Nanotubes were also evaluated as adsorbents for trapping volatile organic compounds from environmental samples. For example, Li and co workers found that nanotubes have much higher breakthrough volumes for toluene, xylene, dichloromethane, 1, 2-dichloroethane and so on than graphitized carbon black with the same surface area (Li et al. 2004). This was ascribed to the more porous structure of SWNTs. The results indicate that nanotubes are potential useful adsorbents for direct trapping VOCs from air samples.

The adsorption of heavy metals by nanotubes has been studied by Li group (Li et al. 2002). They found that nanotubes show exceptional adsorption capability and high adsorption efficiency for lead removal from water. The adsorption is significantly influenced by the pH value of the solution and the nanotubes surface status. Their work also showed that the oxidation dramatically increase the cadmium adsorption capacity. The Cd(II) adsorption capacity of the as grown nanotubes is much smaller than H_2O_2, HNO_3 and $KMnO_4$ oxidized nanotubes

Using carbon nanotubes in computer displays may further diminish environmental impacts by eliminating toxic heavy metals and dramatically reducing material and energy use requirement. Moreover, multi-walled nanotubes demonstrated good properties as solid phase extraction adsorbents for the extraction and quantification of several chemicals in water including bis phenol A, 4-n-nonylphenol, 4- tert-octylphenol and phthalate esters (Cai et al. 2005).

It is realized that this is very good material for the sorption purposes but it is also found that the cost of carbon nanotubes is very high. It may be one of the main flaws for the commercialization of the technologies related to sorption.

3.6 Carbon Nanotubes for Nano Sensors

Carbon nanotubes have very peculiar properties, especially high surface area and atomic structure; make carbon nanotubes promising candidates for nanoscale sensing materials. Infact the electronic properties of nanotubes, especially semi conducting carbon nanotubes are very sensitive to chemical environment. The presence of electron donor or electron acceptor gas molecules in the ambient can either donate or remove electrons from carbon nanotubes by changing their overall electrical conductivity. Charge transfer between carbon nanotubes and adsorbed molecules produces a chemical gating effect that can be used for molecular sensing. Nanotubes sensors offer potential and significant advantages over traditional sensor materials like semi conducting metal oxides in terms of sensitivity, operation at room temperature, small sizes for device miniaturization massive sensor arrays.

Novel monitoring technologies and devices are needed for pollutants and microbial detection. Protection of human health and ecosystem requires rapid, precise sensors capable of detecting pollutants at the molecular level. Recently, several papers about nanotubes sensors have been published (Villalpando-Paez et al. 2004; Suehiro et al. 2003; Kong et al. 2000; Goldoni et al. 2003; Collins et al. 2000). The electrical resistance of semi-conducting SWNTs is dramatically changed upon exposure to ammonia and nitrogen dioxide molecules (Kong et al. 2000). This result provided the basis for research into the use of nanotubes as chemical sensors. Goldoni and coworkers showed that gas molecules could directly affect the nanotubes properties via physisorption or chemisorption, but they could also have an indirect effect by interacting with contaminants bonded to the nanotubes (Goldoni et al. 2003). Residual contaminants in purified single-walled carbon nanotubes bundles may be responsible for the reported sensitivity of the electronic and transport properties to oxygen (Goldoni et al. 2003). Strong sensitivity to NO_2, SO_2 and NH_3 was observed which confirmed the possible application of nanotubes as powerful sensors capable of measuring environmentally significant levels of toxic gases.

Recently, it has been experimentally demonstrated that the electrical conductance of carbon nanotubes can be modulated upon exposure of gaseous molecules of NO_2 and NH_3 (Kong et al. 2000) ; resistive gas sensors based on carbon nanotubes for sub – ppm NO_2 detection have been reported (Valentini et al. 2003) impedance spectroscopy was used to study the gas sensing properties of carbon nanotubes for NH_3, CO and CO_2 detection (Varghese et al. 2001a, b) a carbon nanotubes based gas sensor has been successfully proposed for wireless monitoring of CO_2, O_2 and NH_3 (Ong et al. 2002).

Most sensors based on carbon nanotubes are field effect transistors. Many studies have shown that although carbon nanotubes are robust and inert structures, their electrical properties are extremely sensitive to the effects of charge transfer and chemical doping by various molecules. The electronic structures of target molecules near the semi conducting nanotubes cause measurable changes to the nanotubes electrical conductivity. Nanosensors based on changes in electrical conductance are highly sensitive, but they are also limited by factors such as their inability to identify analytes with low adsorption energies, poor diffusion kinetics and poor charge transfer with carbon nanotubes. Greenhouse gases are especially important for monitoring the environment and are an important target for nanosensors made of carbon nanotubes. Other gases, such as contaminating gases like NO_2 or NH_3 or interesting analytes like aqueous vapour, have also been widely studied as potential target analytes for nanosensors. Several authors have used carbon nanotubes sensing devices to detect a wide range of gases without functionalizing carbon nanotubes which means that since carbon nanotubes are sensitive to many surrounding compounds, there must be no interference if the gas of interest is to be reliably detected.

Sumanasekera et al. (2002) created a thermoelectric chemical sensor to measure the easily detectable and reversible thermoelectric power changes of single walled nanotubes when they are in contact with Helium, Nitrogen and hydrogen. Chopra et al. (2003a, b) developed a circular disk resonator coated with single walled nanotubes using a conductive epoxy, which selectively detects the qualitative presence of several gases like ammonia, carbon mono oxide, argon, nitrogen, oxygen due to changes in the dielectric constant and shift in the resonant frequency. Penza et al. (2004a, b, c) developed a surface acoustic wave sensor coated with single walled carbon nanotubes and multiwalled carbon nanotubes and used it to detect volatile organic compounds such as ethanol, ethyl acetate and toluene by measuring the downshift in the resonance frequency of the surface acoustic wave.

Carbon nanotubes can be easily functionalized with molecules that interact specifically with target analytes. The procedure involves first adsorbing a polymer onto the surface of the nanotubes. The non covalent Functionalization of carbon nanotubes with polymer keeps the electronic structure of the carbon nanotubes intact. Also the nanotubes are protected against non specific interactions with unwanted analytes and specific molecules can be covalently attached to the polymer in order to interact specifically with the targeted analytes. In this way, different type of sensors can be developed based on molecular recognition interactions can be developed. These types of interactions allow for the development of nanosensors that are highly selective and sensitive. Moreover, the traditional problem of the lack of signal when the target analyte interacts with the recognition molecule is overcome. The presence of the analyte is enough to induce an input or withdrawal of electrical charges that produce changes in the conductivity in nanotubes. Directly, detecting the analytes i.e. without using reagents or markers is a significant advantage over other types of sensors. Finally, electrical detection allows for simple and inexpensive instrumentation, which improves the portability of these type of devices.

Therefore, the presence of functional groups or adsorbed oxygen species on single-walled carbon nanotubes (SWNTs) is known to affect properties of these materials (Kuzmany et al. 2004; Zhao et al. 2004). Functionalities influence the electronic properties of SWNTs by disrupting the graphitic-like sp^2 network of carbon in the SWNTs. This disruption produces local sp^3 defects which can introduce an impurity state near the Fermi level (Boul et al. 1999) and perturb the electronic spectra of these materials (Halicioglu and Jaffe 1999).

The conductivity (Boul et al. 1999) and solubility (Sun et al. 2001; Yang et al. 2002a, b, c) of SWNTs have also been shown to change as a result of functionalization. Ultimately, the performance of SWNTs as adsorbents, catalysts (Liu et al. 2002), capacitors (Hafner et al. 2001), microscopy tips (Wong et al. 1998; Yang et al. 2002a, b, c; Nguyen et al. 2002) and sensors (Kuznetsova et al. 2001) depends on understanding and controlling surface functionalities.

Normally, as-received nanotubes contain few heteroatom functional groups. However, during various purification steps, oxygen containing functional groups is introduced (Zhang et al. 2003; Bower et al. 1998). Some purification procedures use aggressive oxidizers like HNO_3, H_2SO_4, or H_2O_2 to crack the passivating carbon shells encapsulating residual catalyst particles and to remove unwanted carbons (Yang et al. 2002a, b, c; Hernadi et al. 2001; Chiang et al. 2001). Newer procedures use more gentle steps which expose the catalyst by heating in moist air followed by an acid removal (Novak et al. 2003). As one might expect, the amount and wash for catalyst type of functional groups introduced by these purification steps vary drastically with each different type of procedure employed. According to specific application one can modify carbon nanotubes. This is the biggest advantage of using nanotubes for environmental protection. Although, toxicological effects of carbon nanotubes yet have to be studied in more systematic way. Toxic effects of carbon nanotubes are reported but all available articles give very contradictor y results. Some authors suggest that functionalized nanotubes are toxic some says that nanotubes are not toxic in environment. Therefore there should some systematic studies for the toxicology of carbon nanotubes.

3.7 Future Direction

Among all the reviewed types of nanostructures, nano particles and carbon nanotubes probably stand out. Most of the reviewed nanostructures have successfully shown a great potential for being used in nanosensors, but the versatility and high applicability of nano particles and carbon nanotubes makes them clear candidates to be further used in nanosensors. But there are certain issues which must be considered for future work particularly for environmental application of nanotechnology. Some of those few are as follows:

- Nanotechnology may benefit the environment both indoor and outdoor is through detection devices that are more sensitive than existing devices. However more research for new material for such devices is the challenge.
- Nanotechnology has enormous potential for social, economic and environmental benefits from innovative medical technique to savings on materials and energy as well as advances in detection and remediation of pollution. However, with environmental impact as yet largely unknown and public controls largely absent, more systematic research and sector specific policies are necessary.
- As carbon nanotubes are the building blocks of nanotechnology further research should be concentrated on the cost effective synthesis route for carbon nanotubes and their purification. Above all, their functionalization route according to application in nanosensors, sorption membranes etc. should be improved.
- Human toxicology particularly for carbon nanotubes should be studied in depth. Because there are various reports or research papers are available with contradictory results. So there should be proper and systematic toxicological study for carbon nanotubes.
- The sorption properties of carbon nanotubes including the possibility of their chemical functionalization can be utilized in developing new micro separation methods and techniques. All these aspects of growing field of nanotechnology should in the near future lead to significant progress in instrumentation for chemical analysis.

3.8 Conclusion

One can find different environmental application of carbon nanotubes because of its unique properties, structure, surface area, high aspects ratio etc. We can also functionalize nanotubes according to our specific need. So we can change little properties and apply according to our requirement. Even one can synthesize nanotubes according to application vertically aligned, random etc.

A network of single walled nanotubes has been used to construct thin film transistors for detecting chemical nerve agents. These sensors obtained are reversible and capable of detecting at sub ppb concentration levels and they are intrinsically selective against interference signals from hydrocarbon vapors and humidity (Novak et al. 2003).

In this review we have discussed the use of carbon nanotubes for environmental protection. Carbon nanotubes based several types of nanosensors, sorbates membranes; hydrogen adsorption in nanotubes is discussed. Although fundamental developments in the Nanoscience field are still appearing, the well known effects arising only when the size of structures is reduced are being applied to develop new sensing devices. We can also conclude that the main problem associated with the development of the techniques for environmental protection using carbon nanotubes is the high cost of the material. So there is need to do research for the reduction of cost of carbon nanotubes as well as modification of tubes according to application.

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Chapter 4
Magnetic Nano-photocatalysts: Preparation, Structure, and Application

Shou-Qing Liu

Contents

Abstract Photocatalytic degradation of organic pollutants using suspended and dispersed nanosemiconductor photocatalysts in wastewater has unique advantages including high activity, low cost, solar utilization, and complete mineralization. However recovery and reuse of photocatalysts are difficult because fine particles are easily discharged in the waterflow. Immobilization of photocatalysts on supports such as glass and zeolite decreases activities due to the low specific area and slow mass transfer. Furthermore, a large amount of photocatalysts will lead to color contamination if they are released at industrial scale. Therefore, it is necessary to develop photocatalysts with separation function for reusable and cyclic application. The concept of magnetic photocatalysts with separation function was raised to benefit from high activity and enable nanosemiconductor photocatalysts to be reused.

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We review the photocatalytic principle of magnetic semiconductor catalysts, the classification of magnetic materials, the preparation, structure and application of magnetic semiconductor catalysts. The major points are: (1) suspended and dispersed composite nano-photocatalysts are a miniature of the photoelectrochemical cell. Semiconductor photocatalysts can nearly decompose all pollutants including refractory organic pollutants by hydroxyl radicals formed under light irradiation due to the high redox potential of the hydroxyl radicals with 2.8 V. (2) For the fabrication of magnetic photocatalysts the three most widely used magnetic materials are magnetite, maghemite, and MFe_2O_4, where M stands for Ba^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} divalent metallic cations. (3) The three-component photocatalysts are predominant because the structure maintains the high activities of the catalysts and endows the photocatalysts with the separation function. The core structure of the three-component photocatalysts comprises a magnetic core with the separation function, an interlayer (SiO_2) with the insulation function preventing the recombination of photogenerated electron-hole pairs, and a shell layer (TiO_2) with the photocatalytic function for the degradation of organic pollutants. The core magnetic photocatalysts possess great activities whereas the core magnetic photocatalysts have low activities. Compared with that of pure photocatalysts, the core magnetic photocatalysts may have an enhanced activity with magnetic separation function under optimal conditions. (4) In order to prepare the core photocatalysts with a magnetic separation function, one needs to synthesize the magnetic particle as a magnetic core first. Then a sol-gel method is often used to coat the silica insulator on the magnetic core. Finally, the semiconductor nanoparticles are bound to the interlayer insulator. Thus, a core photocatalyst with both magnetic separation function and photocatalytic function can be obtained. The prepared photocatalysts can be recovered using external magnetic force.

Keywords Photocatalysis • Magnetic photocatalyst • Magnetic separation • Cyclic utilization

4.1 Introduction

The photochemical utilization of solar energy includes three main processes: splitting water for hydrogen energy (Esswein and Nocera 2007; Youngblood et al. 2009), reducing carbon dioxygen to fuel molecules (Takeda and Ishitani 2010), and the photocatalytic removal of environmental pollutants (Akpan and Hameed 2009; Sakkas et al. 2010). The photocatalytic removal or degradation of environmental organic pollutants involves the photocatalytic oxidization process. This process, similar to ozonation and to electrochemical and Fenton oxidation, is one of the advanced oxidation processes that treats and degrades refractory organic pollutants. The major advantages of the photocatalytic oxidation process are as follows. First, it offers a good route for the use of broadly available renewable and pollution-free solar energy. Second, this process does not have waste disposal problems. Third, the photocatalytic process is a non-selective oxidation process for most organic pollutants;

therefore, it can destroy a variety of hazardous organic compounds in different influents. Fourth, it can transform organic pollutants into innocuous products by redox reactions and complete the mineralization of the organic pollutants. Fifth, it is inexpensive (Bhatkhande et al. 2001). Furthermore, photocatalysts can oxidize ammonia, another prevalent environmental problem in the wastewater, to nitrogen gas (Besten and Qasim 1964; Lee et al. 2002; Pretzer et al. 2008; Kolinko and Kozlov 2009), and destroy bacterial cells (Wakamura et al. 2003), viruses (Josset et al. 2010), cancer cells (Fujishima et al. 2000), and so on. Thus, the photocatalytic degradation of environmental pollutants is an interesting topic to study.

However, the application of photocatalysts for wastewater treatment still needs to tackle a variety of technical problems. For example, the recovery and cyclic utilization of the nano-semiconductor catalysts is still a major obstacle hindering practical application in industrial processes. Environmental scientists are working on the subject by integrating magnetic particles with photocatalysts to retain the high reactive performance of nano-photocatalysts from high specific areas, and to enable renewable utilization by magnetic force separation. The aim of this paper is to review the progress of the research on magnetic photocatalysts based on the photocatalytic principle.

4.2 Principle of Photocatalysis

Fujishima and Honda developed a photoelectrochemical cell (PEC) (Fujishima and Honda 1972) that can split water into hydrogen at an inert platinum electrode and oxygen gas at a titanium dioxide semiconductor electrode by a small given potential of 0.2 V under light irradiation. The photoelectrochemical cell is based on an electrochemical cell where at least one electrode is a semiconductor, generating electron-hole pairs when irradiated, which can be used to produce a current and drive redox reactions (Bard 1979, 2010) The device is shown in Fig. 4.1. Under irradiation, an oxidation reaction occurs at the n-type semiconductor, whereas a reduction reaction occurs at the counter electrode, because the photogenerated electrons flow to the counter electrode to reduce hydrogen ions into hydrogen gas through the external circuit. The photogenerated holes leave to oxidize the water molecules to release oxygen gas in the aqueous medium.

This device helps explain the photocatalytic redox reactions in cases where the semiconductor particles are suspended in an aqueous solution. If the external circuit is shortened sufficiently so that the platinum electrode comes in direct contact with the n-type semiconductor, and the inert platinum electrode becomes nanometer in size. The photoelectrochemical cell is shown in Fig. 4.2.

The photoelectrochemical cell becomes a micro-photoelectrochemical device. Actually, it becomes a semiconductor composite nanodevice. The oxidation reactions occur on the n-type semiconductor surface of the nanodevice, whereas the reduction reactions take place on the inert metal particle of the nanodevice, which functions as the counter electrode in the suspended photocatalytic system.

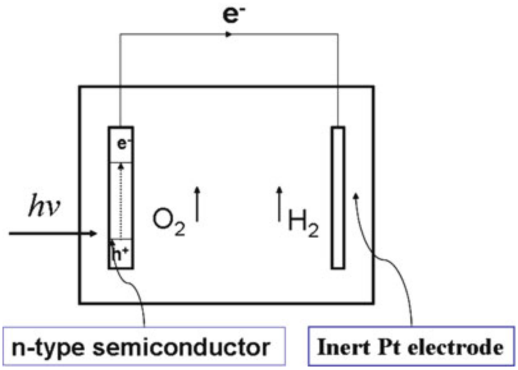

Fig. 4.1 A typical photoelectrochemical cell. The photo-generated electrons flow into the inert platinum electrode to reduce hydrogen ions into hydrogen gas and the photo-generated holes leave to oxidize the water to release oxygen gas upon irradiation

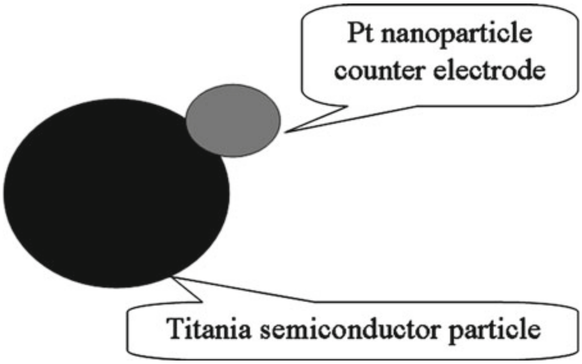

Fig. 4.2 Semiconductor photocatalyst suspended in aqueous solution. This composite nanodevice is similar to a small photoelectrochemical cell. The platinum particle serves as an inert cathodic electrode and the titania particle works as an anodic electrode

For example, when platinum particles were loaded onto the titanium dioxide particles, the acetic acid was not only oxidized to release carbon dioxygen, but was also reduced to form the products CH_3CH_3, CH_4, and H_2 (Kraeutler and Bard 1978). Another example is that sugar can be decomposed into carbon dioxide and hydrogen gas using titanium dioxide powders loaded with RuO_2 (wt10%) and Pt (wt5%) particles under irradiation (Kawai and Sakata 1980). Moreover, the photocatalysts loaded with noble metal particles in the suspension aqueous solution were broadly utilized to degrade the refractory organic pollutants (Serpone and Pelizzetti 1989; Kamat 1993; Pelizzetti et al. 1993; Rajeshwar 1995; Hoffmann et al. 1995; Halmann 1996; Fujishima et al. 1999; Kozlova and Vorontsov 2006; Ren et al. 2009; Iliev et al. 2010; Rupa et al. 2009) in the presence of oxygen, and the catalytic activities

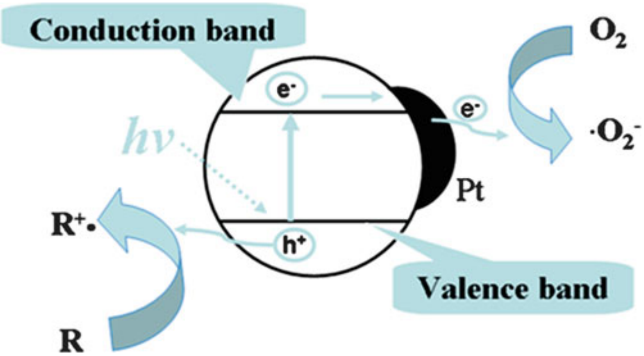

Fig. 4.3 Scheme of semiconductor photocatalytic principle. The electron at the VB is elevated to the conduction band upon irradiation. Then, the electron (which is called as the photogenerated electron) moves into the platinum particle to react with the O_2 molecule. The photogenerated hole leaves to oxidize the organic pollutants into intermediate

of the nanodevices loaded with noble metal particles are much greater than those of the corresponding pure semiconductor catalysts (Dawson and Kamat 2001; Li et al. 2008; Wang et al. 2008; Lin et al. 2009; Priya et al. 2009; Kozlova et al. 2010; Wodka et al. 2010). This is because the noble metal particles on the semiconductors facilitate the separation of the electron-hole pairs and block their recombination. This idea can be explained according to the band theory of the solid, as shown in Fig. 4.3. A filled valence band (VB), an empty conduction band (CB), and a bandgap between the VB and the CB exist in the electronic structure of the solid semiconductor. For titania, the filled VB is composed of O 2p orbitals, and the empty CB is composed of Ti 3d, 4s, and 4p orbitals. The Ti 3d orbitals dominate the lower portion of the CB (Linsebigler et al. 1995).

An electron is promoted from the VB into the CB when it is irradiated by a photon with *hv* energy greater than the energy of the bandgap. Thus, the semiconductor works as an electron pump. The electron promoted at the CB is referred to as the photogenerated electron, which can act as a reducing reagent. The positive charge being generated at the VB is known as a hole, which can work as an oxidizing reagent. For example, an oxygen molecule can accept one photogenerated electron from the platinum particle into reactive radical$\cdot O_2^-$, and an organic pollutant R can be oxidized by one photogenerated hole into reactive radical R·. Moreover, the photogenerated holes can oxidize water molecules adsorbed on the semiconductor surface to form the highly reactive hydroxyl radical ·OH. The hydroxyl radical decomposes nearly all the organic pollutants because the redox potential of the ·OH/H_2O is very high (2.8 V vs. NHE). The photo-physic process is shown as Eq. 4.1

$$TiO_2 \xrightarrow{hv} h^+ + e^- \tag{4.1}$$

The photogenerated electron attacks a molecular oxygen to form a superoxide radical O_2^-, which subsequently combines with a hydrogen ion to produce a hydrogen superoxide HO_2. The superoxide radical continues to undergo dismutation extremely rapidly. As a result, hydrogen peroxide is formed, as in Eq. 4.2:

$$O_2 + e^- \rightarrow \bullet O_2^- \xrightarrow{H^+} HO_2^\bullet \xrightarrow{H^+ + O_2^-} H_2O_2 + O_2 \tag{4.2}$$

Under irradiation, the hydrogen peroxide produces highly reactive hydroxyl radicals:

$$H_2O_2 \xrightarrow{hv} 2 \bullet OH \tag{4.3}$$

In contrast, the photogenerated hole from Eq. 4.1 can oxidize both the water adsorbed on the surface of the semiconductor to hydroxyl radical, as shown in Eq. 4.4, and the organic compounds to reactive intermediates. The highly reactive hydroxyl radicals are very strong oxidizing reagents that can nearly decompose the organic pollutants.

$$H_2O + h^+ \xrightarrow{hv} \bullet OH + H^+ \tag{4.4}$$

$$\text{Organic} + h^+ \longrightarrow \text{intermediates} \tag{4.5}$$

$$\text{Organic} + \bullet OH \longrightarrow \text{intermediates} \tag{4.6}$$

According to Eq. 4.1, the effective elevation of the electron from the VB to the conduction band and the isolation of the photogenerated electron-hole pairs initiate a series of subsequent reactions. Although the semiconductor nanoparticles have the advantage of high activity due to the specific area of fine particles, reuse remains a challenge.

Briefly, the semiconductor photocatalysts can decompose nearly all the pollutants, including the refractory organic pollutants, by the hydroxyl radicals formed under light irradiation due to the high redox potential of 2.8 V vs. NHE.

4.3 Background of Magnetic Nano-photocatalyst Appearance

The suspended and dispersed photocatalysts have some unique advantages: (1) great specific area for fast degradation rate of the pollutants; (2) effective absorbance of light irradiation for the efficient utilization of solar energy; and (3) facilitating fast transportation of pollutants between the powder surface and aqueous medium due to its small diameter. However, the recovery and cyclic utilization of photocatalysts are limited due to the difficult separation of the small particles from the medium. To overcome these drawbacks, the photocatalysts are immobilized on supports such as glass beads (Serpone et al. 1986; Al-Ekabi and Serpone 1988; Sakthivel et al. 2002), lamp walls (Sabate et al. 1991, 1992b), glass plates (Anderson et al. 1988), fiberglass mesh (Al-Ekabi et al. 1991; Horikoshi et al. 2002), porous films (Sabate et al. 1992a, b; Aguado et al. 1994), fiber optic cable reactor (Peill and Hoffmann 1996), cellulose matrix (Zeng et al. 2010), silica (Ilisz et al. 2004), alumina (Ding et al. 2001;

Torimoto et al. 1996), zeolite (Reddy et al. 2003; Anpo et al. 1997; Noorjahan et al. 2004). Although the immobilization can make them recoverable, the photocatalytic activities undergo a large decrease due to the low specific area caused by the supports and the limit of mass transfer. The photocatalysts are incorporated in the activated carbon, leading to an increase in catalytic efficiencies due to the synergistic effect; however, the composite materials are still difficult to recover (Matos et al. 2001; Ao and Lee 2004; Tsumura et al. 2002; Herrmann et al. 1999). In the background, the magnetic photocatalysts are desired because of their advantages of high catalytic activities from large specific areas and facile separation by the external magnetic force. The magnetic photocatalysts are defined as catalysts that possess both photocatalytic functions under light irradiation and magnetic separation functions by using an external magnetic force. The magnetic separation is referred to as the separation of fine particles dispersed in air, water, sea water, oil, organic solvents, etc., using a magnetic force.

In short, the suspended and dispersed fine photocatalysts have high activities due to their large specific areas; however, their recovery and reuse are difficult because fine particles are easily discharged with waterflow. The immobilization of photocatalysts on the supports results in decreased activities due to the low specific area and slow mass transfer. Therefore, photocatalysts with the function of magnetic separation are needed.

4.4 Structural Model of Magnetic Nano-photocatalysts

4.4.1 Features of Magnetic Particles

The first magnetic separation was described by William Fullarton, who used a magnet to separate iron minerals in 1792 (Yavuz et al. 2009). In 1873, Hay received the first US patent for a water treatment device that employed a magnetic field (Hay 1873). Currently, magnetic separation techniques are used in a variety of areas, ranging from steel production to biotechnology and environmental protection (Ambashta and Sillanpāā 2010). During the fabrication process of the magnetic photocatalysts, magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and MFe_2O_4 (where M stands for Ba^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} divalent metallic cations) are the three most widely used magnetic materials.

The bulk magnetic material consists of domains, each having its own magnetization vector, which arise from an alignment of atomic magnetic moments within the domain. The magnetization vectors of all the domains in the material may not be aligned, leading to a decrease in the overall magnetization (Teja and Koh 2009). Magnetite is a soft ferromagnetic material that can be oxidized to maghemite and has a Curie temperature of 850 K (Cornell and Schwertmann 2003). Its magnetic properties strongly depend on the methods used in its synthesis (Margulies et al. 1996; Voogt et al. 1998). Magnetite particles smaller than 6 nm are superparamagnetic, and have no hysteresis loop at room temperature.

Maghemite is ferromagnetic at room temperature, unstable at high temperatures, and loses its susceptibility with time. The Curie temperature of maghemite is believed to be between 820 and 986 K. However, its Curie temperature is difficult to determine experimentally because maghemite undergoes an irreversible crystallographic change to hematite at approximately 400°C, with a consequent dramatic loss of magnetization. Maghemite particles smaller than 10 nm are superparamagnetic at room temperature (Neuberger et al. 2005). The aggregation of ultrafine maghemite particles sometimes leads to the magnetic coupling between particles and the ordering of the magnetic moment, which is termed superferromagnetism (Cornell and Schwertmann 2003). Barium ferrite and zinc-nickel ferrite are two hard magnetic materials that are more difficult to magnetize. However, once magnetized, they can maintain their magnetic characteristics, as opposed to the spontaneously induced magnetic behavior of soft magnetic materials. Unfortunately, they may suffer from the same oxidation-related decrease in magnetic properties (Lee et al. 2006). Hard magnetic materials can be recovered using a magnet, similar to soft magnetic materials; however, they have the additional capability of being agitated using an oscillating magnetic field gradient.

In summary, the three most widely used magnetic materials are magnetite, maghemite, and MFe_2O_4 (where M stands for Ba^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} divalent metallic cations) for the fabrication of the magnetic photocatalysts.

4.4.2 *Structure of Magnetic Photocatalysts*

The first magnetic photocatalyst was designed by Hiroshi et al. and was prepared through the deposition of titanium dioxide onto a magnetite core in 1994 (Hiroshi et al. 1994). Atsuya and Mutsuo developed photocatalyst particles containing ferromagnetic metal particles in 1997 (Atsuya and Mutsuo 1997). In 1998, Beydoun synthesized titania-coated magnetic photocatalysts, in which titanium dioxide particles were directly coated with the Fe_3O_4 magnetic material (Beydoun et al. 1998, 2000) to form the core/shell structure. Other core/shell magnetic photocatalysts studied include $BaFe_2O_4/TiO_2$ (Lee et al. 2004), $NiFe_2O_4/TiO_2$ (Rana and Misra 2005; Xu et al. 2008b), $SrFe_{12}O_{19}/TiO_2$ (Fu et al. 2006a), $BaFe_{12}O_{19}/TiO_2$ (Fu et al. 2006a, b), $ZnFe_2O_4/TiO_2$ (Zhang et al. 2008), and Fe_3O_4/BiOCl (Zhang et al. 2009b).

At this initial stage, the as-synthesized magnetic photocatalysts were composed of two components: a magnetic core with the separation function by an external magnetic force, and a semiconductor shell with the photocatalytic function under irradiation. Although the two-component composite materials met the requirement of the separation of the photocatalysts from the suspended slurry system by the external magnetic force, the photocatalytic activities and stability were decreased because the direct contact between the magnetic particles and photocatalysts led to the photogenerated electron-hole recombination and the photodissolution of the Fe_3O_4 magnetic particles under the irradiation. The recombination process is shown in Fig. 4.4 (Beydoun et al. 2000).

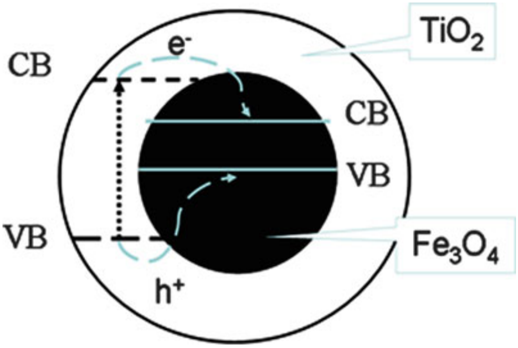

Fig. 4.4 Diagram of recombination of the photogenerated electron-hole pairs and photodissolution. The photogenerated electrons easily flow to the CB of magnetite and the photogenerated holes move to VB of magnetite because the energy level of the CB is lower, whereas that of the VB is higher, in magnetite than the corresponding energy levels in titania. CB: conduction band, VB: valence band

The photogenerated holes at the VB of the TiO_2 semiconductor are transferred to the VB of the Fe_3O_4, while the photogenerated electrons move to the CB of the magnetic core. The transfers in the direct contact prevent the photogenerated electrons from reaching the O_2 molecules. As a result, the radicals O_2^- cannot be formed. Similarly, the photogenerated holes can oxidize neither the organic molecules nor the water adsorbed to hydroxyl radicals. Therefore, the direct contact core/shell catalysts have low activities.

To overcome the drawbacks of the low activities and the photodissolution, Cao and Chen pioneered a three-component magnetic photocatalyst of γ-$Fe_2O_3/SiO_2/TiO_2$ in 1999, in which γ-Fe_2O_3 was used as the magnetic core, SiO_2 interlayer as insulator, and TiO_2 as photocatalytic shell (Chen and Zhao 1999). Beydoun also developed a relatively stable magnetic photocatalyst comprised of three components: a Fe_3O_4 magnetic core that functions as the separation after use, a silica insulator layer between the core and the shell which blocks direct electrical contact between the photocatalyst and the magnetite, and a titania photocatalytic shell (Beydoun et al. 2002; Rose et al. 2003) A three-component model of the magnetic photocatalyst, magnet-core/insulator-interlayer/catalyst-shell was designed and constructed. This three-component composite structure is shown in Fig. 4.5a, b.

According to the structural model, several three-component magnetic photocatalysts were synthesized, such as γ-$Fe_2O_3/SiO_2/TiO_2$ (Chen and Zhao 1999; Chen et al. 2001; Gao et al. 2003; Tawkaew and Supothina 2008; Abramson et al. 2009; Wang et al. 2010), $Fe_3O_4/SiO_2/TiO_2$ (Beydoun et al. 2002; Rose et al. 2003; Watson et al. 2005; Xu et al. 2005, 2008a; Song and Gao 2007; Kurinobu et al. 2007; Gad-Allah et al. 2009; Wang et al. 2009; Ye et al. 2010), $MFe_2O_4/SiO_2/TiO_2$ (Shchukin et al. 2004; Chung et al. 2004; Fu et al. 2005; Lee et al. 2006; Xu et al. 2007a, b; Zhang et al. 2009a; Kostedt et al. 2010), and others (Belessi et al. 2009; Li et al. 2009; Chen et al. 2009). Their components are listed in Table 4.1.

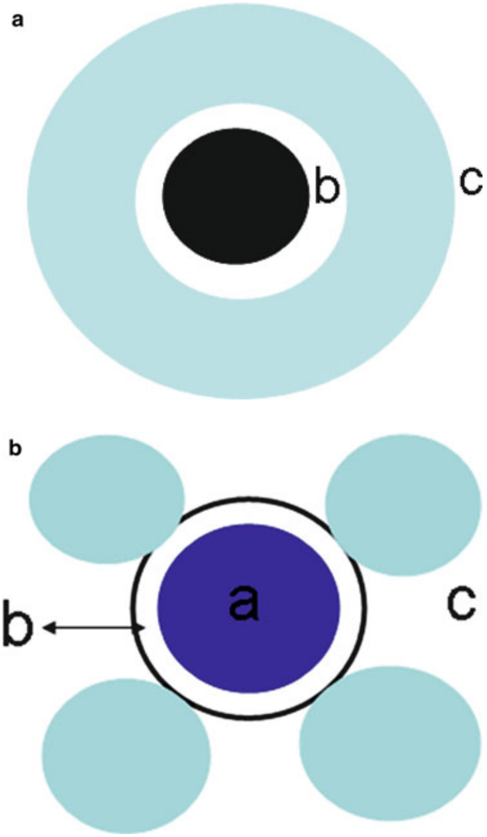

Fig. 4.5 Structural models of magnetic photocatalyst, (**a**) a magnetic core with the separation function; (**b**) an insulator interlayer to inhibit the recombination of the photogenerated electron-hole pairs for improving the catalytic activity; (**c**) a photocatalyst shell with the function of the degradation of pollutants

Silica is often used as an interlayer for insulation in the preparation of the magnetic photocatalysts. Other insulators, such as Poly(methyl methacrylate) and poly(sodium 4-styrene sulfonate) (PPS^-) polyanion coupled with poly (diallyldimethylammonium) (PDD^+) cation, were also investigated. The experimental findings indicate that the introduction of the interlayer can effectively inhibit the photodissolution of magnetic cores and greatly improve the photocatalytic activities and nanodevice stability. Thus, the insulators prevent the injection of charges from TiO_2 to the magnetic particles (Chen et al. 2001; Beydoun et al. 2002; Belessi et al. 2009). The interlayer materials are chemically inert and electronically passive toward photocatalysts.

Another three-component magnetic photocatalyst is the titania-coated magnetic activated carbon or titania-coated magnetic porous carbon (Huang et al. 2006; Hsu et al. 2010; Ao et al. 2008a, b, c, 2009). The photocatalytic efficiencies of these

Table 4.1 Components of core/insulator/shell magnetic photocatalysts

Magnet Core	Insulator	Photocatalyst shell	Reference
γ-Fe_2O_3	SiO_2	TiO_2	See the text
γ-Fe_2O_3	PPS^-/PDD^+	TiO_2	Belessi et al. (2009)
Fe_3O_4	SiO_2	TiO_2	See the text
Fe_3O_4	SiO_2	AgBr	Li et al. (2009)
Fe_3O_4	Poly(methyl methacrylate)	TiO_2	Chen et al. (2009)
$Zn_{0.35}Ni_{0.65}Fe_2O_4$	SiO_2	TiO_2	Shchukin et al. (2004)
$NiFe_2O_4$	SiO_2	TiO_2	Chung et al. (2004) Xu et al. (2007a, b) Xu et al. (2008a)
$CoFe_2O_4$	SiO_2	TiO_2	Fu et al. (2005) Zhang et al. (2009a)
$BaFe_2O_4$	SiO_2	TiO_2	Lee et al. (2006) Kostedt et al. (2010)
Black sand	SiO_2	TiO_2	Lou et al. (2009a, b)

PPS⁻ poly(sodium 4-styrene sulfonate) polyanion; *PDD*⁺ poly(diallyldimethylammonium) cation

materials are greater than those of the neat TiO_2 due to the synergistic effect between the carbon component and titania. The porous carbon component can take the preconcentration of organic pollutants and facilitate the separation of the photogenerated electron-hole pairs like the inert metals. The introduction of carbon component to the magnetic photocatalysts improves the degradation activities on organic contaminants.

In short, the three-component photocatalysts are predominant because the structure maintains the high activities of the catalysts and endows the photocatalysts with the separation function. The core/interlayer/shell structure of the three-component photocatalysts comprises a magnetic core with the separation function, an interlayer with the insulation function preventing the recombination of photogenerated electron-hole pairs, and a shell layer with the catalytic function of degradation of organic pollutants.

4.4.3 Comparison of Photocatalytic Activities

As mentioned above, in the case of Fe_3O_4, γ-Fe_2O_3, MFe_2O_4 as the magnetic core, the activity of the core/insulator/shell magnetic photocatalysts is greater than that of the corresponding core/shell magnetic photocatalysts because the insulator between the magnetic core and the photocatalyst shell can inhibit the recombination of the photogenerated electron-hole pairs. In the case of the direct contact core/shell structure, the heterojunction structure formed is shown in Fig. 4.4. The bandgaps of Fe_3O_4, γ-Fe_2O_3, and $NiFe_2O_4$ are 0.10, 2.30, and 2.19 eV, respectively, which are smaller than 3.20 eV for the TiO_2 bandgap. Therefore, the positions of the CBs for the narrow band-gap semiconductors are lower than that of TiO_2, and the position of the VBs

Table 4.2 Positions of CB and CV for Fe_3O_4, γ-Fe_2O_3, TiO_2 at pH 7.0 and their bandgaps

	E_{CB} (V vs. NHE)	E_{CV} (vs. NHE)	Bandgap (eV)
${}^{a}Fe_3O_4$	0.17	0.27	0.1
γ-Fe_2O_3	0.1	2.4	2.3
TiO_2	−0.5	2.7	3.2

[a] pH 3.5

are higher than that of TiO_2. The photogenerated electrons are transferred to the lower lying CBs of these magnetic materials from the CB of TiO_2, whereas the photogenerated holes are transferred to the upper VBs of these magnetic materials from the VB of TiO_2. The potentials of the CB and the VB for Fe_3O_4, γ-Fe_2O_3, and TiO_2 at pH 7.0, as well as the bandgaps, are shown in Table 4.2 (Gao et al. 2003; Beydoun et al. 2000).

For $Fe_3O_4/SiO_2/TiO_2$, Song and Gao reported the photocatalytic activity close to that of pure TiO_2 (Song and Gao 2007). In the γ-$Fe_2O_3/SiO_2/TiO_2$ system, the activities are comparable to those of pure TiO_2 or Degussa P25, although they are slightly lower (Tawkaew and Supothina 2008; Chen et al. 2001; Gao et al. 2003). The $NiFe_2O_4(CoFe_2O_4)/SiO_2/TiO_2$ system also displayed similar behaviors: the activity of pure TiO_2 or Degussa P25 is slightly greater than that of $NiFe_2O_4(CoFe_2O_4)/SiO_2/TiO_2$ system; however, their activities are comparable with each other (Xu et al. 2007a, b; Fu et al. 2005; Zhang et al. 2009a, b). Ye et al. prepared a $Fe_3O_4/SiO_2/TiO_2$ composite nanodevice with an activity equal to that of Degussa P25, and higher than that of the corresponding pure titania (Ye et al. 2010). The high activity could be ascribed to the small size of the anatase nanocrystals. The optimal size of an anatase particle is approximately 10 nm (Anpo et al. 1987; Chae et al. 2003). Chung et al. also reported that the titania-silica layer-coated composites had 3.5 times more enhanced photocatalytic activity compared with that of Degussa P25 (Chung et al. 2004), and attributed the enhanced activity to the dispersion of coated titania particles. Therefore, the carefully controlled conditions may improve the activity of magnetic photocatalysts.

The core/insulator/shell magnetic photocatalysts possess great activities, whereas the activities of the core/shell magnetic photocatalysts are low. Compared with that of pure photocatalysts, the core/insulator/shell magnetic photocatalysts may result in enhanced activity with magnetic separation function under optimal conditions.

4.5 Preparation and Cyclic Applications

Common procedures for preparing magnetic photocatalysts are as follows. First, magnetic particles are synthesized as the core of nanodevices being coated. Second, the interlayers are coated on the magnetic particles as insulators for improving the photocatalytic activity and stability. Third, the photocatalysts are bound onto the insulator layer. The method for synthesizing bare magnetic particles is common, and the sol-gel route is often used for coating the silica insulator on the magnetic cores. This route is also adopted for binding titania to the surface of the interlayers. In the desired case, the calcinations are carried out by crystallizing the amorphous titania layer into the anatase phase. The detailed procedures were shown in previous reports (Abramson et al. 2009; Chung et al. 2004; Lee et al. 2006; Kostedt et al. 2010; Song and Gao 2007; Fu et al. 2005; Lou et al. 2009a, b; Li et al. 2009; Ye et al. 2010; Zhang et al. 2009a, b). The resulting magnetic photocatalysts did not only gain the activity comparable to the pure titania, but could also be repeatedly reused using the external magnetic force for recovery.

In summary, to prepare the core/interlayer/shell photocatalyst with the magnetic separation function, one needs to synthesize the magnetic particle as a magnetic core. Then, a sol-gel method is often used to coat the silica insulator onto the magnetic core. Finally, the semiconductor nanoparticles are bound to the interlayer insulator. Thus, a core/interlayer/shell photocatalyst with both magnetic separation function and photocatalytic function can be obtained. The as-prepared photocatalysts can be recovered and reused by the external magnetic force.

4.6 Conclusion

In this article, the photocatalytic principle was discussed in detail. The magnetic particles were combined with photocatalysts to meet both the requirement of photocatalytic degradation and that of recovery for cyclic utilization. The insulator was introduced between the magnetic core and photocatalytic shell to greatly improve the photocatalytic activity. The introduction of porous carbon or activated carbon can also enhance the photocatalytic degradation efficiency due to the synergy. The size, as well as the dispersion of photocatalyst particles, is essential for the activity. The cautiously controlled conditions may be used to prepare highly active magnetic photocatalysts. As the next step, the improvements of stability for magnetic photocatalysts and developments of magnetic catalysts for visible light utilization may be interesting topics.

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Chapter 5
Polysaccharides Route: A New Green Strategy for Metal Oxides Synthesis

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Contents

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Abstract The present paper reviews some of the most important polysaccharide-based synthetic strategies of metal oxides, highlighting the polysaccharides multi-tasking abilities in the synthesis of nanosized oxide particles. The perspectives but also the unexplored areas of this new and promising green chemistry topic are also examined.

Keywords Polysaccharides • Starch • Cellulose • Dextran • Alginate • Carrageenan • Chitosan • Metal oxides synthesis

5.1 Introduction

Polysaccharides have found novel applications in green chemistry. Known also as glycans, polysaccharides are a large family of natural carbohydrates which includes both compounds glycosidically-linked sugar residues and polymeric saccharides structures bound to amino-acids, peptides, proteins or lipids. The most important quality is their eco-friendly character: non-toxic, renewable and widely available in great amounts. Several polysaccharides (bio)-chemical properties, such as biocompatibility, biodegradability, bioactivity, multiple functions, hydrophilicity, high chemical reactivity, chirality, chelation/coordination, assembling and adsorption abilities, have opened the gates of a new non-polluting and very promising chemistry of materials. An additional, but also a crucial feature, is the benign water-solubility of some of the polysaccharides, which transform them in suitable and active ingredients for green alternatives of the classical solution synthesis of materials [(co)-precipitation, sol-gel, hydrothermal, combustion methods].

The involvement of polysaccharides in metal oxides synthesis is a new, interesting and promising application in materials science. Fusing the above-mentioned polysaccharides topics with highly available *chimie douce* approaches (Schmid 2004; Ozin and Arsenault 2005; Sugimoto 2000), new advanced nanosized oxide-based materials with superior magnetic, opto-electronic and catalytic properties could be obtained. Polysaccharide-assisted oxides synthesis provides not only an eco-friendly reaction media, but also represents a straightforward route to control the nucleation and the crystal growth stages of the particles, a critical demand for specific (nano)sizes and structures of the oxides. Their "chameleonic" behaviour in the oxides nanoparticles wet procedures is illustrated by the single or combined polysaccharides actions: stabilizing, coating, template, functionalizing, chelating/

coordinating, assembling and/or fuel agent. The aim of this paper is to review and highlight some of the most successful polysaccharides-based strategies for the metal oxides synthesis developed in the last years. An inspection of the multiple roles played by polysaccharides in the oxides synthesis, the mutual influence of the intrinsic properties of reactants (metal salts, polysaccharides) and also the physico-chemical characteristics of the obtained oxides are also described in each section.

5.2 Polysaccharides in Our World

If the carbohydrates dominate our world, representing a three quarters from the biomass materials produced in nature (175 billion tons), we could say that the polysaccharides rule in the carbohydrates family (*ca.* 90% from the total amount of carbohydrates). The varied polysaccharides origin explains the richness of their structures and corresponding properties: from plants (*e.g.* starch, cellulose, pectin, guar gum), algal (*e.g.* alginate agar, carrageenans), microbial (*e.g.* dextran, xanthan gum), and animal (chitosan, chondroitin) (Sinha and Kumria 2001; Rinaudo et al. 2004; Geremia and Rinaudo 2005).

These carbohydrates are essentially natural macromolecules build up from monosaccharides units (from hundreds to thousands units) connected through glycosidic bonds. Each sugar residue carries multiple hydroxyl groups, able to act as acceptor of glycosyl substituents, leading to branched or mixed linear-branched polysaccharides structures. The most common constituent of polysaccharides is D-glucose, but D-fructose, D-galactose, L-galactose, D-mannose, L-arabinose, and D-xylose are also frequent monomeric units. Some monosaccharide derivatives found in polysaccharides include the amino sugars (D-glucosamine and D-galactosamine) as well as amino acids (*N*-acetylneuraminic acid and *N*-acetylmuramic acid), and simple sugar acids (glucuronic and iduronic acids).

Several features make the difference between the polysaccharides: the nature of the constituent monosaccharides building-blocks, the length of the polymeric chain and the degree of the chain branching. Their large variety makes very difficult a classification of these biopolymers. One criteria is their functionality in biological systems: storage polysaccharides, *e.g.* starch in plants, and structural polysaccharides, *e.g.* cellulose, which is the most abundant biopolymer in the world (Anglès and Dufresne 2001; Cima et al. 1996). The two polysaccharides have similar compositions, their properties are distinct and could be related to their structural differences, for example the mixed linear-branched and flexible structure of starch versus the linear and rigid skeleton of cellulose.

Polysaccharides are also divided into polyelectrolytes and nonpolyelectrolytes, the former class being further divided into positively (e.g. chitosan) and negatively charged polysaccharides: alginate, heparin, hyaluronic acid or pectin. From rheological standpoint, some of the polysaccharides form gels as the temperature is rising (*e.g.* starch), or under very mild conditions, upon contact with metal cations (alginate and carrageenan) or anions (chitosan).

5.3 The Role of the Polysaccharides in Metal Oxides Synthesis

Polysaccharides are used for a long time in the water-soluble polymers domain as thickening, gelling emulsifying, hydrating and suspending polymers. Polysaccharide-based oxides, with biocompatible and non-toxic features, represent a new class of hybrid materials with potential applications in medicine, pharmacy, biology, agriculture, on waste water and water treatment. Polysaccharides biomaterials were already used tissue engineering, drug vehicles, controlled release of drugs (Liu et al. 2008), cell culture, cancerous cell treatment, separation of biomolecules or immobilization of enzymes (Dumitriu 2002; Rinaudo et al. 2006; Gupta et al. 2009; Kato et al. 1997).

The metal oxides chemistry has encountered in polysaccharides the ideal non-polluting organic additives. Along with their already known biocompatibility, the polymeric structure of polysaccharides is suitable for solution-based chemical procedures (Rabelo et al. 2001; Qu et al. 1999; Si et al. 2004; Ditsch et al. 2005; Liu et al. 2006; Cocker et al. 1997; Lin et al. 2003a; Breulmann et al. 1998) to achieve and tune the size, morphology and structure of the oxides or oxides-composites nanoparticles. Polysaccharides could be used as: (i) stabilizer to control particle size preventing the spontaneous agglomeration of nanoparticles, (ii) templates to direct the structure of particles and (iii) metal oxides surface functionalizing agents to allow their covalent linking, a critical feature in order to load desired biomolecules.

The primary association between a polysaccharide and a metal ion affords usually an intermediate precursor which, depending on several factors (the chemical composition of the polysaccharides and structure, nature of the metal cation and experimental conditions namely pH value, raw materials concentration, and the presence of an auxiliary ligand) could be a colloid, a gel or a mixture of raw materials.

The polysaccharides interfere in various stages of the synthesis of metal oxides. The biopolymer, which is dispersed in the liquid media, behaves like an organic matrix, binding through their functional groups (for example hydroxylic, carboxylic, or amino groups) many metal cations. The initial association of the metal cations to polysaccharide determines a homogenous dispersion of the ion in well confined spaces. After the change of the initial reaction conditions, in the presence of a precipitation agent, these binding positions provide preferred nucleation and growth sites for the hydrolyzed M^{n+}-containing particles, due to the high local suprasaturation in M^{n+} cations. The conversion oxide precursor → oxide needs heating treatments. Since, some of the polysaccharides are decomposed at temperature lower than 300°C (Khairou 2002; Zohuriaan and Shokrolahi 2004), the combustion of their organic scaffolds can be expected to form dispersed oxides only when the sintering is not favored. The homogeneous dispersion of the cations within the polysaccharide matrix and the low temperature of its thermal degradation shifts the balance between nucleation-growth toward the formation of a larger number of smaller oxide crystals.

The initial metal cation linking to polysaccharides is a complicate process that involves different physico-chemical interactions which can act individually or simultaneously (at least some of them) (Ravi Kumar 2000; Lee et al. 2001) namely coordination/chelation, ion-exchange, electrostatic interactions, acid-base interactions, hydrogen bonds, hydrophobic interactions, physical adsorption. During the precipitation/maturation stages, the polysaccharides act also as "nanoreactor", as a template and stabilizing agent of the nanoparticles: the heterogeneous nucleation and subsequent controlled growth occuring in well-defined sites. An additional surface coating/functionalization is also obtained.

The polysaccharides may function either as hard or soft template to form 1D and/or hierarchical structures. It is known that, under certain kinetic conditions, the soft templates (for example long chain polymers, Fendler 1987) have self-assembled into well-defined aggregated entities which will restrict and direct the growth of the quest molecules. The growth of these molecules leads to 1D nanostructures, and if these are metastable, they can further organize themselves into hierarchical structures in liquid media (Wang et al. 2006; Dong et al. 2005; Seelig et al. 2003; Oliveira et al. 2003; Privman et al. 1999; Park et al. 2001). A beautiful example is the nanofabrication of functional ZnO architectures in the presence of sodium alginate (Gao et al. 2006).

A special role is played by polysaccharides when they act as hard templates in the synthesis of core/shell and hollow nanostructures (Caruso et al. 1998). The synthetic strategies are straightforwards and involve three main steps: (i) the preparation of the original template by dehydration/condensation of the polysaccharide molecules under hydrothermal conditions; (ii) the deposition of the target shell material onto the surface of the template with the formation of the core-shell composite either by direct surface reactions or by controlled precipitation (Wang and Zhang 2007), and (iii) the removal of the original template (after calcination treatments or selective etching) with the formation of the hollow structures.

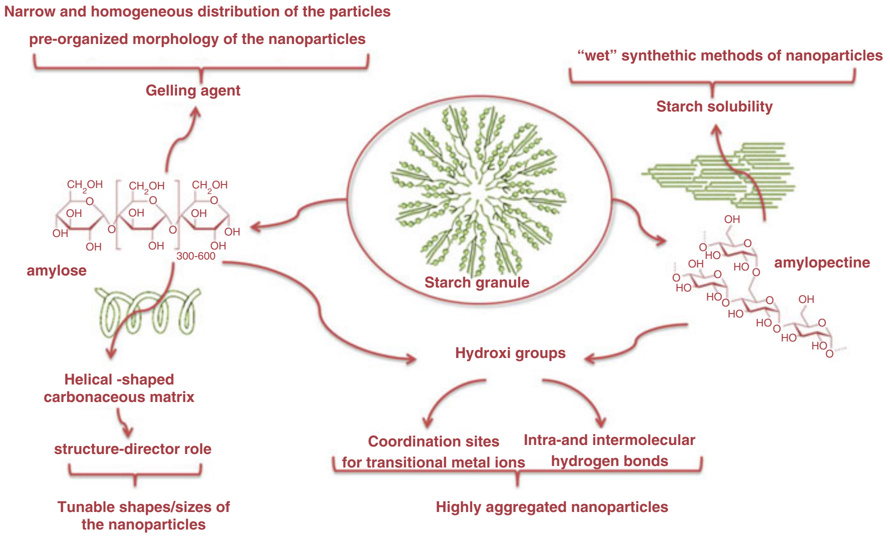
The success of the polysaccharide template routes is provided by the integrity and the uniformity of the outer functional layers of the carbonaceous templates which preserve the shell homogeneity without any surface modification. The template could be tuned controlling the experimental conditions (concentration of the starting material, reaction time and temperature), (Wang and Zhang 2007) and directs the shape and the size of the final product.

The polysaccharides-assisted strategies take also the advantage of the reducing abilities of some carbohydrates due to their high content in hydroxyl groups: the oxidation of polyol groups to the carboxylates may occur simultaneously with the reducing of M^{n+} cations to M^{m+}/M^{o} ($n>m$) (Gao et al. 2008a). This property was used in the synthesis of the magnetite, Fe_3O_4, (starting only from trivalent iron metal salts) and also for metal particles (Ellid et al. 2003; Raveendran et al. 2003).

It deserves to mention here the capacity of the polysaccharides to function as fuels in combustion synthesis of oxide materials. Polysaccharides belong to the low temperature flame fuels category, taking into account their large value of the heat of formation. Depending on the targeted oxide system, polysaccharides may be used either as single fuel (Li et al. 2003) or in a mixture with high temperature flame fuels (Tahmasebi and Paydar 2008) in solid state or solution combustion synthesis.

5.4 Starch

Starch is one of the most appealing bioresource for nanotechnology. The carbohydrate polymeric chains are build up from glucose units and parted in linear amylose (α-1,4 glycosidic bonds) and branched amylopectine (α-1,4 and α-1,6 glycosidic bonds), these peculiarities representing the key structural elements for the new alternative nanomaterials synthesis. Scheme 5.1 illustrates the specific roles played by the two starch fractions in nanosized oxides synthetic methods. On one hand, the linear and helical-shaped amylose could create a protective and functionalized surrounding shield for nanoparticles, being also responsible for gelling properties of starch, at temperatures ranging between 50°C and 90°C. The formed gel will be able to incorporate and disperse, in a uniform fashion, the incipient centers of nucleation of the nanoparticles. The branched amylopectine chains expose an important number of hydroxyl groups, giving a strong hydrophilic character to starch granules. It also assures the biopolymer solubility which makes it a suitable additive in solution synthesis of nanomaterials. The constituent hydroxyl groups of the carbohydrate could be involved both in intra- or intermolecular supramolecular associations, but are also able to coordinate transitional metal ions, maintaining the nanoparticles highly aggregated. Thus, their actions in materials synthesis are multiple: coating/capping, functionalizing, stabilizing, poring and/or coordinating agent. In fact, any starch-assisted synthetic route of materials gathers some of the above-mentioned carbohydrate actions, and essentially is directed by the combined and/or competing chemical/supramolecular interactions metal-polysaccharide. The starch is also a very interesting candidate as fuel for combustion methods due to its large heat of formation which significantly reduce the reaction exothermicity.



Scheme 5.1 The multiple roles of starch in the synthesis of nanomaterials

Several early attempts related with drug carrier systems, in which the coated and functionalized-starch particles has become biocompatible and able to react with various end standing functional groups for binding other molecules, have highlighted the great potential for the chemistry of nanomaterials of in this carbohydrate (Lübbe et al. 1996). Starch-protected homogeneous nanoparticles of noble (silver, gold and silver-gold) or nickel metals with large surface to volume ratio and nanosizes, features that are strongly required especially in some catalytic processes, have been obtained using the carbohydrate as reducing-modifier and/or protecting-dispersing agent (Raveendran et al. 2003; Raveendran et al. 2006; Vigneshwaran et al. 2006; White et al. 2009; Purcar et al. 2009; Yan et al. 2009).

The most wide used application of the starch in nanotechnology is by far related with the metal-oxides. Further we will review some of the remarkable starch effects in different *chimie douce* approaches of the nanosized metal oxides.

5.4.1 (Co)-Precipitation Synthesis

The starch-coated colloidal superparamagnetic magnetite, Fe_3O_4, nanoparticles (SPION), *via* a controlled co-precipitation of Fe^{2+}/Fe^{3+} hydroxides (Kim et al. 2003; Mikhaylova et al. 2004; Huong et al. 2009; Hai et al. 2008). These types of magnetite particles are mainly used in biomedical applications (magnetic resonance imagining, drug delivery, drug targeting and hyperthermia agent), thus they must fulfill several demands: they should have small and narrow sizes (<50 nm), with a uniform distribution of the particle sizes and they should be coated with nonimmunogenic, nonantigenic and protein-resistant materials, which facilitate their transport in biological membrane system. Starch provides these biocompatible surrounding layers which allow the particles transport in extracellular space. In addition, some of the outer-shell amylopectine layers from starch are swollen to a certain degree and interconnected through hydrogen-bonds with neighboring molecules. The carbohydrate granules build thus, in water, a three-dimensional glucose-based skeleton which could easily host and bind particles of metal oxides. Its hydrophilic polymeric matrix embeds the reactants and has multiple functions: prevents the agglomeration of particles and their further oxidation, assures their homogeneous distribution, hinders the cluster growth after nucleation and limits the size of the particles. The SPION nanoparticles are distributed in starch polymeric matrix in an uniform fashion, have cores diameters of 6 nm and clusters sizes of 42 nm and proved an extremely stable behaviour for 1 year (aqueous media room temperature deposition conditions).

Active functional groups could be inserted on the starch skeleton by oxidizing the carbohydrate with periodate, $NaIO_4$, which induce the cleavage of the glucose rings and the formation of polyaldehyde-starch coating layers (Jiang et al. 2009; Yang et al. 2009). The average diameters of magnetite particle cores, obtained through a co-precipitation route, is *ca.* 8 nm, the peroxidation treatment having no influence over their crystal structure. The change of the chemical environment of the surface atoms has effect on the relaxation behaviour of the iron oxides.

The type of iron salt used in synthesis has a significant influence over the final nanoparticles morphologies. The particular layered structure of iron(III) chloride has afforded, following a coprecipitation method in the presence of starch, highly crystallized hematite (α-Fe_2O_3) particles with spherical or tubular shapes, depending on the calcination temperatures and/or pH value of the solution (Chowdhury et al. 2008; Chowdhury et al. 2007). The hydroxi-functionalized layers of iron(III) chloride interact with polyol groups from starch, most likely by means of hydrogen-bonds, of which helical structure encapsulates the iron(III)-containing colloids in a cage-like structure. The combined structure-director roles both of the iron(III) salts and polysaccharide have led to highly regulated materials in which the particles are monodispersed, with controllable shapes and a well-defined morphology (spherical and tubular). The sizes of particles are *ca.* 30 nm with specific surface areas ranging from 24 to 126 $m^2\ g^{-1}$ and depending on the Fe^{3+}-precursor concentrations.

When iron(II) sulfate is involved in precipitation solution procedure, the Fe^{2+} cations are bound to the available hydroxy-coordination sites from the carbohydrate polymer, the centers of particles nucleation being well-separated one to each other. The multiple polyol groups of starch may also be involved in supramolecular hydrogen-bond contacts, these two coupled molecular-supramolecular effects giving rise to oxides-containing aggregates, in which the cores of nanoparticles and the carbohydrate-based coatings are strongly associated. The controlled starch removal, through heat treatment, converts the iron(II)-based complex precursors into non-agglomerated and highly crystalline nanoparticles of iron oxides with sizes around 64 nm and with a uniform distribution of their morphology (Janardhanan et al. 2008; Nidhin et al. 2008). Spherical nanoclusters of magnetite (200–300 nm in sizes) have been stabilized following a similar route and using transparent starch vermicelli as template. The thermal decomposition of the iron oxides nanoparticles has led to hybrid species iron oxide/composite with reduced magnetic properties, a useful effect for some biomedical applications (Chairam and Somsook 2008).

Spherical well-dispersed starch-capped Mn_3O_4 nanooxides, with 35 nm in sizes, are obtained through a solution method, by a low temperature controlled precipitation of $Mn(OH)_2$ in the presence of starch, in basic solution. The presence of an oxidant such as H_2O_2 is very important for the crystallinity and the purity of Mn_3O_4 phase (Mu et al. 2006).

Nickel(II) cations chemically interacts in solution with the hydroxy-functional groups of the starch and will be closely incorporated within the carbohydrate molecules. The NH_4OH titration causes the homogeneous nucleation of the $Ni(OH)_2$ particles localized on the coordination sites. A calcination treatment in air at 380°C, determines nickel(II) hydroxide decomposition into NiO oxide with H_2O evolving, while the starch ligand is converted into CO_2 and H_2O. The final NiO crystalline oxide presents a porous structure (the pore sizes are mainly in a range of 2–30 nm) and an average crystallites size of 11 nm. The specific surface areas and the pore volume of the sample are 76 m^2g^{-1} and 0.16 cm^3g^{-1}, respectively. The sample calcination at 550°C, in nitrogen, gives rise to a unique Ni/C composite material (Chen et al. 2006). Using a simple precipitation method, ZnO with spherical like shape and crystallite sizes of ~55 Å were relatively easy obtained (Fig. 5.1) (Tirsoaga Unpublished results). The purity of the ZnO phase, shape and crystallite size is strongly dependent on the precipitation pH value and starch concentration.

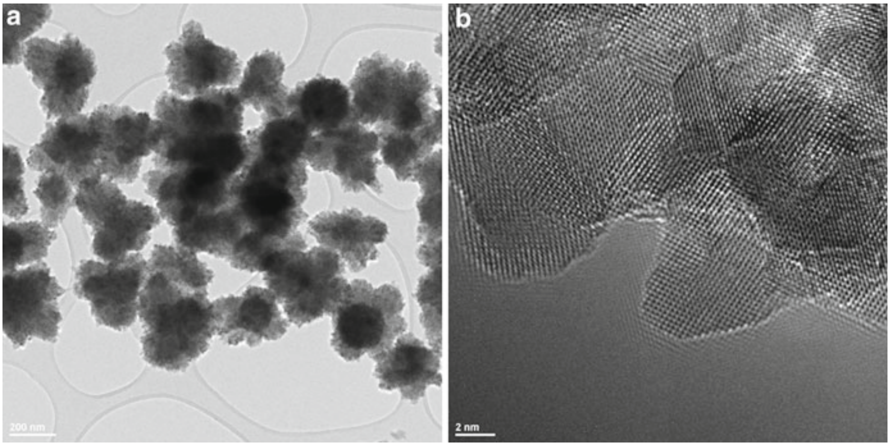


Fig. 5.1 (**a**) TEM and (**b**) HRTEM images of the powder of ZnO spheres obtained following a coprecipitation method in the starch presence. TEM: transmission electron microscopy, HR: high resolution

5.4.2 Sol-Gel Synthesis

One of the remarkable feature of the starch is its gelling abilities in aqueous solution in the temperature range of 50–80°C, due to its content of linear amylose component. The mechanism of starch gelatinization is still an issue question, but nowadays it is accepted that gelation causes starch anionic, either by producing fatty acids or causing –OH group to dissociate (Yamamoto et al. 2006; Whistler et al. 1984; Chen and Jane 1994; Bertuzzi et al. 2007). This special characteristic of starch could be efficiently exploited in the less-expensive and highly-available variant of a sol-gel synthesis, in which the starch-gel acts also as a template for nanoparticles aggregations. It has in fact multiple functions, such as hosting, protecting, separating, binding and tailoring agent for the precursors and their corresponding nanooxides. The chelating action of the carbohydrate is essential for the starch-based sol-gel synthesis. The resulted colloidal complex precursors are usually obtained from the reaction of the inorganic salts of divalent ions or metal-organic compounds and starch that pre-organizes the morphology of the nanoparticles. Starch is removed by decomposition at significantly lower temperatures than the classic sol-gel chelators (ethylenediaminetetraacetic acid-EDTA, citric acid). The thermal decomposition of starch generates sometimes pores, being a well-known consolidating agent for porous ceramics (Kim et al. 2002; Garridoa et al. 2009; Alves et al. 1998; Gregorová and Pabst 2007; Lyckfeldt and Ferreira 1998; Kim 2005).

A typical sol-gel synthesis uses the complexing abilities of the starch in order to produce non-spherical particles, the particle shape being suitable to preserve the magnetic phase. γ-Fe_2O_3 oxide (maghemite) crystallizes in the cubic inverse spinel structure, with vacancies distributed on the octahedral sites. For example, the ferrimagnetic behaviour of maghemite demands elongated ellipsoidal particles, for which nucleation could be controlled by complexing agents with a tailoring effect. A starch/ethyleneglycol mixture creates a suitable complexing medium to synthesize ellipsoidal mesoscopic γ-Fe_2O_3 particles with an average size of 19 nm, while 10 nm in diameter spherical-shaped particles are obtained in a water/starch solution. The size/shape have a decisive influence on the optic and magnetic properties of the oxides, a red shift of the band-gap and an enhanced coercivity, induced by anisotropy, being observed for the non-spherical nanoparticles (Narayanan et al. 2008).

The reactions of $KMnO_4$ and starch, with the formation of an intermediate gel, followed by a heating treatment at 400°C for 2 h, have afforded a layered-type structure of birnessite manganese oxide, MnO_6 (Ramalingam et al. 2006). The resulted oxide is made-up from sheets of edge-sharing MnO_6 octahedra, the interlayered distances, filled with water molecules and $MnO(OH)_2$ species (identified in thermal analysis by decomposition processes in the 172–396°C temperature range) being approximated at 6.5 Å.

An adapted sol-gel method, which consists in a reaction of titanium(IV) alkoxide with starch, under the mild conditions and non-polar cyclohexane, has led to mesoporous nanocrystalline TiO_2 materials (Kochkar et al. 2007). The starch that has only a stabilizing effect, was removed following two procedures: heat treatment and solvent extraction, the calcinated samples exhibiting superior textural properties. Nanosized TiO_2 particles of 23 nm mean crystallite sizes, with a specific surface area of 94 $m^2\ g^{-1}$ and pores dimensions varying between 9 and 15 nm, influenced by the Ti(IV)-alkoxide have been obtained.

One of the most interesting applications of starch-assisted gel template synthesis is the cobalt-containing blue inorganic pigments. Thus, the gradual controlled insertion of Co^{2+} cations, the source of blue color, within the inorganic gahnite (zinc aluminate, $ZnAl_2O_4$) host lattice, in the presence of starch, have afforded nanosized $Co_xZn_{1-x}Al_2O_4$ ($x=0$, 0.1, 0.2, 0.4, 0.6, 0.8 and 1) (Visinescu et al. 2010). The formation of the starch-gel is crucial for keeping a higher degree of homogeneity, purity and also a narrow distribution of the oxide nanoparticles, while the combined complexing, structure-director and gelation effects of the carbohydrate is a powerful tool for controlling the aluminates particle shapes and sizes. The formed (Zn, Al, Co)-starch complex, which initially was encapsulated within the helical polysaccharide (in excess) matrix were converted, after a heat treatment of 800°C for 1 h, into spinelic mixed cobalt aluminates. The mean crystallite sizes vary with the cobalt amount in oxides, the higher is the Co^{2+} cations content the lower is the particle dimension [from 250 Å for $ZnAl_2O_4$ ($x=0$) to 146 Å for $CoAl_2O_4$ ($x=1$)] (Fig. 5.2a). TEM investigations indicate the formation of small particles, homogeneous as shape and size and with a pronounced tendency to form agglomerates and even aggregates.

Several useful information have been extracted from the analysis of NIR-UV-Vis spectra, depicted in Fig. 5.2b: the tetrahedral sites are mainly occupied by the Co^{2+} cations and give the blue colored material (a three-structured band, with maxima centered at *ca.* 544, 595 and 622 nm in visible region assigned to the ${}^4A_2(F) \rightarrow {}^4T_1(P)$ spin allowed transition for the tetrahedral Co(II) chromophores), the purity of the

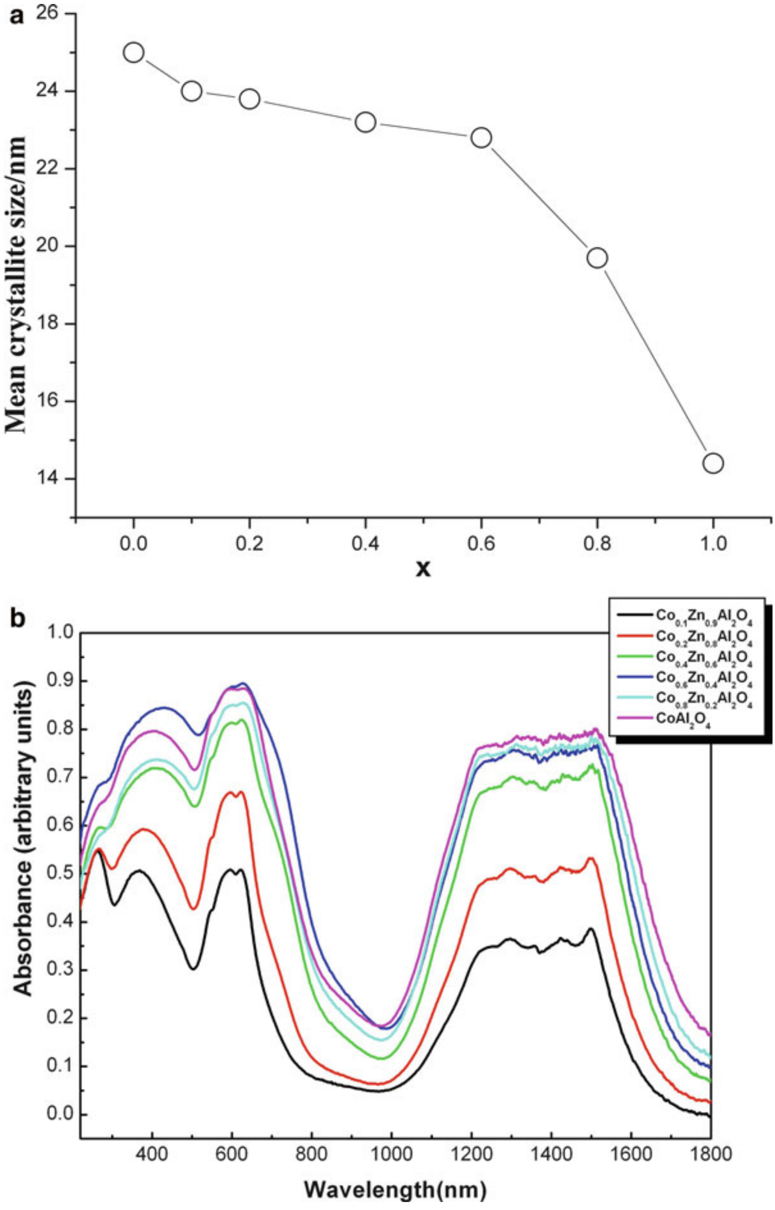


Fig. 5.2 (**a**) Diagram of the mean crystallites size of $Co_xZn_{1-x}Al_2O_4$ oxides (calcinated for 1 h at 800°C) vs. the cobalt (x) content; (**b**) Visible and near-infrared spectra for $Co_xZn_{1-x}Al_2O_4$ ($x=0.1$, 0.2, 0.4, 0.6, 0.8, 1) oxides calcinated for 1 h at 800°C (Reproduced by permission from Visinescu et al. © 2010 Elsevier)

spinelic phase (the absence of the Co_3O_4 is confirmed also by the XRD spectra) and the spinel-disorder dependence of the cobalt content. Thus, the rich-Co(II) oxide samples are characterized by the highest degree of spinel disorder, in which a percent of the Co(II) cations adopt an octahedral stereochemistry.

Doped nanocrystals of YVO_4:Ln (Ln = Sm, Dy, with a concentration of Dy^{3+} and Sm^{3+} ions kept constant at 1%) have been obtained using starch as suitable and, at the same time, labile chelator in an adapted sol-gel routine (Zhang et al. 2008). The oxidation of some polyol (–OH) groups of the carbohydrate to aldehyde (–CHO), with an excess of HNO_3, enhances the coordination abilities of the polysaccharide. The formation of a carbonylic gel-intermediate has been confirmed by the vibration spectra, in which the broad and strong band centered at 1630 cm^{-1} is attributed to the asymmetrical -COO^- stretching frequencies, while its complete thermal conversion into the oxide is proved by the strong absorbtion at *ca.* 844 cm^{-1} characteristic to the orthovanadate anion (VO_4^{3-}). The exothermic reaction between the NO_3^- anions (oxidant) and starch (reducing agent) at temperatures of 600–800°C, allow the rapid crystallization of the tetragonal pure phase of YVO_4, with crystallite sizes ranging from 50 to 100 nm and with a nearly cobblestone-like morphology, at temperatures lower than in the analogue solid-state reaction.

Starch gel templates coupled with colloidal nanoparticles titanium(IV) oxide have been used to prepare TiO_2 materials with a hierarchical meso/macropore organization (Iwasaki et al. 2004). The elasticity of starch, illustrated by its capacity to swell in water and to gradually shrunk by freezing without loosing its structural integrity, build a three-dimensional sponge-like structures with tunable pore sizes. The immersing of starch blocks into the TiO_2 colloidal dispersions has led to macroporous TiO_2-starch composites with extremely high photocatalytic activities for air purification.

5.4.3 Combustion Synthesis

The combustion method is a simple, fast and low-energy procedure which allows the control of the homogeneity and stoichiometry of the nanozised crystallite oxides. The starch, with its large heat of formation, is suitable for a two-fuel mixture combustion, which could properly adjust and control the flame temperature and, implicit the size, surface area and agglomeration of the particles of the final product.

A urea-starch mixture combustion experiment was used to produce Al_2O_3–ZrO_2 nanocomposite powder of small crystallite sizes (<20 nm) (Tahmasebi and Paydar 2008). A direct consequence of reaction exothermicity decrease is a diminished tendency of material agglomeration and thus an increase of the specific surface area (from 3.56 up to 13.16 $m^2\ g^{-1}$). These starch peculiarities will turn it into an alternative and non-toxic low-temperature flame fuel.

Pure spinelic phase of the oxide zinc aluminate, $ZnAl_2O_4$, has been obtained through the N-methylurea/starch two-fuels combustion method (Visinescu et al.

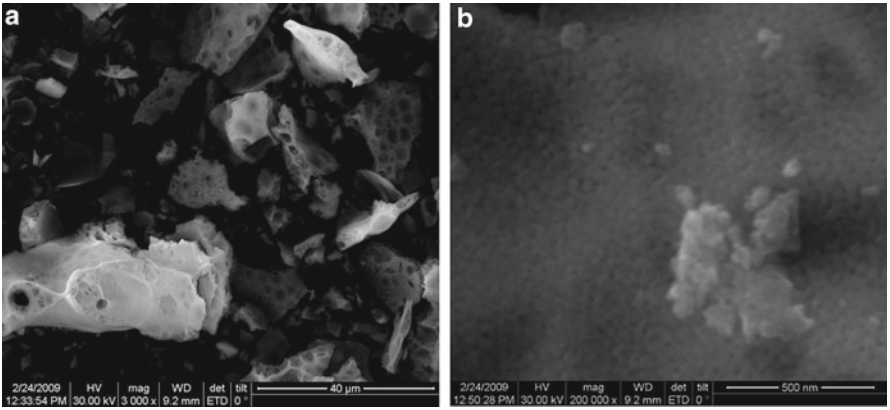


Fig. 5.3 Scanning electron microscopy (SEM) images of powder for zinc aluminate derived oxide obtained following a two-fuels mixture (25% starch and 75% N-methylurea) combustion procedure: (**a**) general view; (**b**) detail

2011) Assuming that combustion process is complete, the theoretical equations for the $ZnAl_2O_4$ formation is:

$$\begin{aligned}&2Al(NO_3)_3\cdot 9H_2O + Zn(NO_3)_2\cdot 6H_2O + 3.33C_2N_2H_6O_5 + 0.415C_6H_{10}O_5\\&\quad +2.47O_2 \longrightarrow ZnAl_2O_4 + 9.15\ CO_2 + 7.33N_2 + 36.06H_2O\end{aligned} \tag{5.1}$$

The phase crystallization temperature is strongly related with the starch amount from fuels mixture, lower values being recorded for the higher values of the starch/NMU ratio. The detailed SEM images show a fine-grained structure of small particles, with a particle average size of ~19 nm (Fig. 5.3). The use of a two-fuels mixture (25% starch and 75% NMU) and a stoichiometric fuel/oxidant ratio determines an extension of the surface area from 9.52 up to 20.69 $m^2\ g^{-1}$. This increase may be explained by a complete decomposition of the organic/carbonaceous residue.

The use of starch in a mixture urea/starch/ammonium acetate fuels have also significantly reduced the reaction exothermicity and the flame temperature comparing with urea single-fuel combustion, affording fine agglomerates of α-alumina-θ-ZrO_2 (ZTA) nanoceramic powders (Tahmasebi and Paydar 2008). The mean diameter of crystallites is lower than 20 nm and have an enhanced specific area of 13.16 $m^2\ g^{-1}$ than the urea as single fuel (3.56 $m^2\ g^{-1}$) or the urea/ammonium acetate two-fuels (7.3 $m^2\ g^{-1}$) cases (Aruna and Rajam 2004).

A 1:1 triethanolamine/starch mixture, have proved to be a suitable combination of fuels for the synthesis of spinelic $LiMn_2O_4$ (Fey et al. 2004). A further calcination for 10 h at 800°C is necessary to achieve a fine-structured product with the largest specific surface area (4.56 $m^2\ g^{-1}$) and with interesting electrochemical properties.

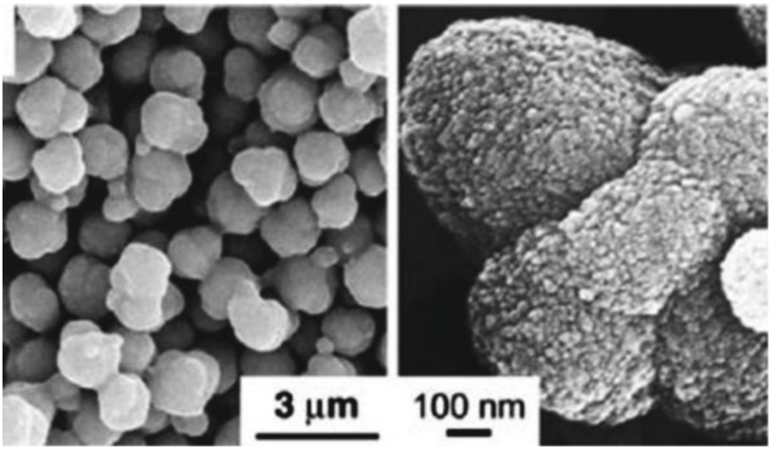


Fig. 5.4 Scanning electron microscopy (SEM) images of sample precipitated with starch, in the presence of hexamethylene tetramine (Reproduced by permission from Taubert and Wegner © 2002, Royal Society of Chemistry)

The natural polysaccharide could also act as single-fuel in a starch-assisted combustion of pure mono-dispersed $LiNiVO_4$ phase (Kalyani et al. 2002). The starch use as certains as any other common fuel decreases the calcinations temperature below 400°C and, supplementary, its presence prevents the agglomeration of the particles and hinders the grain growth. The carbohydrate amount used in reaction is crucial to assure the formation of crystalline spherical particles of single-phase $LiNiVO_4$, with a uniform distribution of the particle sizes (1.2–1.6 µm). The inverse spinel structure of $LiNiVO_4$ has been confirmed by the XRD data, while its remarkable electrochemical activity (acceptable capacity, good cyclability and improved reversibility) has a very useful application as cathode material in lithium batteries.

Macroporous foam oxides with tunable pore shapes/sizes have been prepared through combustion method in which the fuel used is urea, while the starch plays only a role of binder (Venugopal et al. 2009).

5.4.4 Alternative Solution-Based Synthesis

A relatively new and less-used method to obtain ZnO nanoparticles is the one-pot reaction between a zinc salt, starch and a base, refluxed at 100°C. Hexamethylene tetramine is decomposing slowly at 90°C and forms ammonium hydroxide, acting as a basic agent in reaction, while the majority of zinc cations are closely associated with the starch molecules (especially through coordinative bonds). The metal-occupied sites with a high concentration of starch become centers of nucleation and initial crystal growth which will aggregate and finally form spherical particles of ZnO with crystallite sizes of *ca.* 10 nm (Fig. 5.4). The presence of the carbohydrate in reaction enables the formation of a single-phase zinc oxide, with well-defined shapes and size distribution (Taubert and Wegner 2002).

The involvement of ionic liquids in the synthesis of the inorganic materials represents a new trend in green chemistry approaches. The non-polluting character together with the solvent-reactant-template triple function of the ionic liquid open non-conventional and eco-friendly routes to obtain metal oxides nanoparticles. In an one-pot reaction carried on at 80°C and 100°C, involving a mixture of zinc salt, ionic liquid and starch, the polysaccharide has a tailoring action and affords large ZnO/starch hybrid "sponges" with a broad size distribution ranging between 10 and 150 nm (Mumalo-Djokic et al. 2008).

A new class of hybrid composite materials, namely glycerol plasticized-pea starch (GPS)/ZnO (Ma et al. 2009), or starch-stabilized zinc oxide nanoparticles supported on polypropylene polymer (PP) (Chandramouleeswaran et al. 2007) with reinforced characteristics have been synthesized using the complexing/stabilizing conjugated effects of the carbohydrate on the metal oxides. Essentially, the polysaccharide-protected particles of oxides, called the "nano-fillers", are incorporated into a polymeric matrix (including modified starch) and impart their properties to the substrate, the resulted material exhibiting enhanced mechanical, optical or magnetical properties. The origin of these superior features of bionanocomposites lies on the strong molecular and supramolecular interactions oxide particles-starch which lead to a kind of cluster associations, which further interact one to each other.

5.5 Cellulose

Cellulose is the most abundant natural polymer in the world and is known to provide physical structure and strength to the cell walls of plants (Krishnan 1975; Belton et al. 1989; Anglès and Dufresne 2001; Cima et al. 1996). It has been found also in invertebrate sea animals (tunicin which contains highly crystalline cellulose) or in some bacteria secretion, in which the cellulose forms biofilms (Brown 2004). Cellulose, $(C_6H_{10}O_5)_n$, is a linear chain polymer, assembled from several hundred to over ten thousand D-glucose units, connected through β-(1–4) glicosidic linkages. The neighbouring glucose residues are rotated with −180° one to each other and preserve the linear configuration of the molecule.

Figure 5.5 depicts the cellulose fiber and its internal structure. The intra- and intermolecular hydrogen-bonds involving the constituent polyol groups of cellulose are the driving assembling force of the cellulose fibers. The polymer chains, associated by means of hydrogen-bonds are organized in highly-ordered structures (crystalline region), which together with the amorphous regions, assemble into a microfibril. The microfibrils build up a macrofibril and several microfibrils aggregate in a cellulose fiber. This hierarchical internal organization of cellulose provides its main physico-chemical properties: a decreased reactivity, good mechanical characteristics and insolubility in common solvents including water. Cellulose, unlike starch does not gelatinize in water, but undergoes at high temperature and pressure a crystalline-to-amorphous transformation (Deguchi et al. 2006).

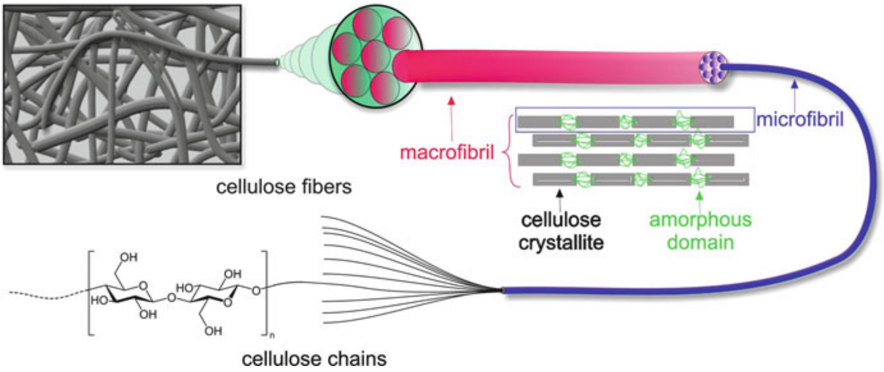


Fig. 5.5 Schematical representation of the hierarchical internal organization of cellulose fiber

The existence of microfibril disordered regions determines two important properties of cellulose. First, it is swelling in water, as a result of the new hydrogen bonds formed between its less ordered regions and water molecules. Secondly, it forms, by cleavage or partial acid treatment, rod-like nanocrystals – the so-called "cellulose whiskers" (de Souza Lima and Boursali 2004).

Another cellulose peculiarity is its rigid backbone and the asymmetric structure, the colloidal suspension of polysaccharide nanocrystals displaying isotropic transition to liquid crystals.

Learning from the bio-evolution processes, natural molecules could be combined with the synthetic procedures developed in materials science. The synthetic replication of some biological structures following biomimetic or bio-inspired approaches might introduce original properties of biologic structures to the artificial materials. In this context, the porous fibers of cellulose could act as suitable biotemplate for the synthesis of different materials.

The common idea was to incubate the material fibers with metal inorganic salt solutions (precipitation, sol-gel, hydrothermal methods) followed by a calcinations treatment, to remove the organic templates and to crystallize the oxides. The synthetic procedures closely replicate the morphological hierarchies of natural cellulosic substances from macroscopic to nanoscale levels. The strategies are based on the adsorption/coordination of metal-containing raw materials from solution onto/on cellulosic hydroxylated substrate surfaces, followed by subsequent heating treatments. The oxides are replicas (positive and negative) of natural cellulose fibers and are usually called "artificial fossil".

5.5.1 (Co)-Precipitation Synthesis

Disk-shaped maghemite nanoparticles, with a diameter around 24 nm and a thickness of 2.5–3.5 nm were obtained following an *in situ* coprecipitation procedure in the presence of cellulose film support (Liu et al. 2006a). The organic/inorganic nanocomposite films display anisotropic magnetic properties due to the ordered alignment of iron oxide nanodisks in the cellulose matrix (Okada et al. 1990). After the removal of the organic matrix, at 450°C, monodisperse maghemite nanoparticles with mean size of 28 nm have been obtained.

Cotton derived cellulose fibers, previously oxidized, were used as template in the synthesis of metallic iron, iron oxides and Fe/C composites, all materials reproducing the texture of the starting fabric (Bashmakov et al. 2008). Depending on the applied thermal treatment (temperature and pressure) and the magnetite contents different oxides and composites are obtained. The cellulose composites with various magnetite contents afforded, *via* a self-propagating combustion reaction, after a heating treatment in air at 520°C finely dispersed α-Fe_2O_3 particles with the average of crystallite sizes of *ca.* 30 nm. The iron oxide-containing cellulose/Fe_3O_4 with a magnetite mass fraction r of 0.54 have a mean crystallites size of 5 nm and a specific magnetization about 14.3 $Am^2\ kg^{-1}$. A vacuum annealing treatment at 800°C transforms the composite into a porous metallic fibrous structures. A similar thermal treatment of the hybrid materials with $r<0.54$ allow the formation of Fe/C composites with a mean crystallites size of 30 nm and an improved magnetization, equal with 160.3 $Am^2\ kg^{-1}$.

Cube-shaped and mesoporous TiO_2 nanoparticles were also prepared using colloidal suspensions of cellulose nanocrystals. Zhou et al. (2007) have involved cellulose rod-like nanocrystals as a morphology-tailoring and coordination agent. Regular TiO_2 nanocubes with 200 nm in particle diameter and a narrow sizes distribution have been obtained after a low-temperature precipitation (90°C). The thermal decomposition of titanium complexes containing rod-like cellulose nanocrystals generates mesoporous TiO_2 with interconnected irregular channels (Shin and Exarhos 2007). The mesoporous titania material consists in nanocrystalline clusters of 5–7 nm with specific surface area ranging between 170 and 200 $m^2\ g^{-1}$.

Wood cellulose fibers were also used as efficient hydrophilic substrates for the nucleation/growth of $BiVO_4$ microparticles in the presence of the cheating agent EDTA (Barata et al. 2005). Plate-like $BiVO_4$ particles of micronic sizes, attached both on external and internal cellulose surface, are obtained.

A carboxylate-functionalized cellulose, namely carboxymethyl cellulose (CMC) could direct the growth of molybdenum oxide nanoplates (Shao et al. 2008a, b) with large area surfaces and smaller sizes than those obtained through a similar procedure using aromatic amines (Mohammed et al. 2006; Shao et al. 2001). The precipitation of molybdenum oxide chains packed into thick layers occurs under acidic aqueous conditions. In the presence of CMC, regularly packed organic polymer/molybdenum oxide hybrids superstructures were obtained by an *in situ* self-assembly process. This organic/inorganic hybrid material was transformed at temperatures of 500°C into orthorhombic phase of MoO_3 nanoplates with 100 nm in thickness and 10–100 μm in length and width. These nanoplates are composed both from nanofibers of *ca.* 20 nm in diameter and 200 nm in length and nanoparticles ~50 nm in diameter.

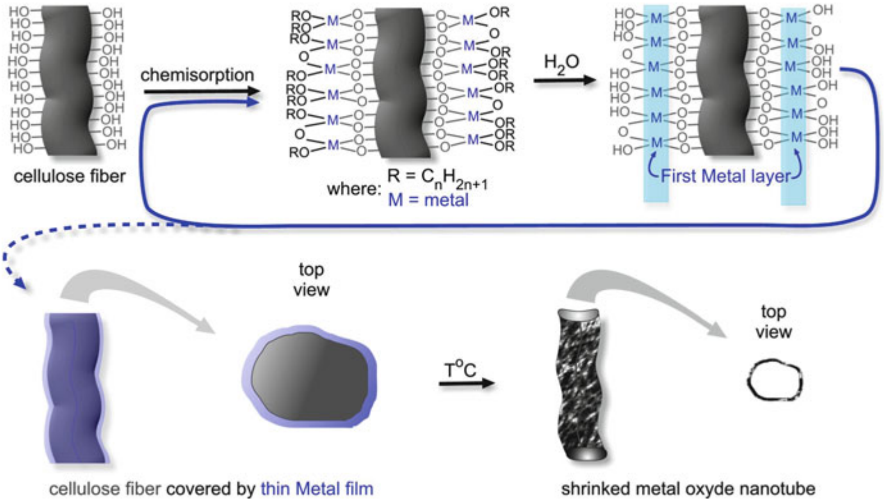


Fig. 5.6 Oxides replicas of natural cellulose fiber by surface sol-gel method

5.5.2 *Surface Sol-Gel Synthesis*

Nanosized particles of cellulose-based oxides with large surface areas, enhanced stability have been obtained following a surface sol-gel procedure (Caruso and Antonietti 2001): ZrO_2 (Huang and Kunitake 2003; Caruso and Schattka 2000), SnO_2 (Huang et al. 2005), $Sn_xIn_yO_z$ (Aoki et al. 2006), TiO_2 (Huang and Kunitake 2003; Caruso and Schattka 2000) and Au-TiO_2 (Huang et al. 2004). The oxide particles are hierarchically organized into nanostructures, the mechanism of the adapted surface sol-gel method being represented in Fig. 5.6.

A modified sol-gel method involving cellulose acetate membranes as template, was developed by Caruso and Schattka 2000. Two different strategies were employed: (i) the soaking method, in which homogenous TiO_2 and ZrO_2 films with small specific surface area (about 22 $m^2\ g^{-1}$), but with a substantial porosity have been obtained (ii) the filtering method (Holland et al. 1998) which is a quicker process than the first case, resulting materials with an increased surface area (about 74 $m^2\ g^{-1}$) but with smaller pores.

Rod-like cellulose nanocrystals, known as cellulose whiskers act as versatile templates in oxides synthesis (Revol et al. 1994). Depending on cellulose concentration the suspensions are highly, partially or randomly ordered. The type of suspensions used as templates in oxides synthesis tailors the morphology of the obtained oxide: mesoporous, nanotubes and nanowires, respectively. Silica oxides represent an illustrative example. Thus, using liquid crystalline cellulose nanorod gels, accurate silica replicas of the cellulose mesostructure template were obtained, the chiral mesoporous silica having co-aligned cylindrical pores of *ca.* 15 nm in diameter and wall thickness of 10 nm (Dujardin et al. 2003). On the other hand, randomly suspensions of cellulose whiskers have led, depending on the heating treatment, either to silica nanotubes (600°C) or nanowires (900°C) (Scheel et al. 2009).

The morphology of the oxides could be controlled also through the experimental conditions of the sol gel synthesis, mainly the pH value. This is the case of tungsten oxide ($Na_2W_2O_7$) (Chai et al. 2007) obtained in the presence of cellulose material which function as template in an one pot sol-gel method: nanotubes of 50 nm diameter and 400 nm length were produced at a $pH=6$, while at $pH=3$ oxide nanoparticles with sizes of 1–10 nm are assembled into a dendritic structure.

Hydroxypropyl cellulose (HPC) is a soluble cellulose derivative. This property together with its ability to convert itself into a liquid crystalline phase makes it a very useful organic additive in oxides synthesis. The data extracted from literature (Shimamura et al. 1981; Wojciechowski 2000) mentions that the HPC solutions are thermotropic (temperature dependent order, phase transition temperature 160–180°C) or lyotropic (concentration depended order) liquid crystalline mesophases. The anisotropic order of the HPC crystalline liquid could be exploited in template synthesis of the oxides, but some cautions should be taken into account (for example the control of the temperature and concentration) in order to avoid the crystalline liquid mesophase transformation.

Concentration restrictions of HPC template have been applied in the synthesis of mesoporous titania films (Zhao et al. 2005; Halamus and Wojciechowski 2007). Titania-HPC composite films containing oxide particles with low sizes, large specific surfaces enhanced photocatlytic activity and photo-induced hydrophlicity have been synthesized by keeping the concentration under a critical value (Zhao et al. 2005). Part of composite photocatalytic activity could be attributed to the hydroxypropyl cellulose, with an intrinsic photoactivity due to the presence the isopropanol groups. After the composite calcinations at 550°C, mesoporous nanocrystalline anastase TiO_2 particles with 30–40 nm in diameter were obtained. The temperature control in an adapted sol-gel method in a polysaccharide template synthesis of ZnO nanocrystalline films is useful to prevent the phase transformation of the HPC (Kamalasanan and Chandra 1996; Bobowska et al. 2008). The synthesis was performed at 160°C in order to accelerate the condesation process that grows the ZnO nanoparticles into the HPC matrix and also to disable the phase transformation. Dense and nanocrystaline ZnO films obtained after a calcination treatment at 500°C of the ZnO/HCP composites have shown a good transparency for the visible light and high absorbance for UV light.

Nano (<100 nm) and submicron (>100 nm) fibers of HPC, previously obtained by electrospinning approaches were used as template during an *in situ* or post synthesis sol gel procedures. ZnO nanorods were perpendicularly grown on a hybrid ultrafine fiber of polyethylene oxide/cellulose acetate following a direct *in situ* electrospinning method (Changangam et al. 2009). A post synthesis example is the preparation of nano and submicron SnO_2-HPC fibers composite with a reduced typical “bead-on-string” morphology of the HPC fibers (Shukla et al. 2005). Subsequent annealing treatment at 450°C has led to a porous network of nano and submicron fibers of SnO_2.

5.5.3 Hydrothermal Synthesis

The synthesis of carbonaceous microsphere starting from cellulose or methylcellulose, have received a special attention in the last decade. They could function as hard and/or sacrificial template for the obtaining of coated microspheres and hollow spheres materials (Bobleter et al. 1976; Huber et al. 2006; Sakaki et al. 1996; Bonn et al. 1983; Karagöz et al. 2005; Sevilla and Fuertes 2009; Wang et al. 2005). The carbohydrate microspheres are formed under hydrothermal conditions, at temperatures ranging between 150°C and 400°C. The chemical transformations involve several decarboxylation, hydrolysis and polycondensation reactions following the reaction model of noncatalytic decomposition, characteristic for carbohydrates (Sakaki et al. 1996). Most of the prepared microspheres have diameters ranging from 2 to 5 μm.

One-dimensional ZnO nanorods self-assembled into hierarchical cage-like structures have been obtained using water-soluble sodium carboxymethyl cellulose (CMC) as crystal growth modifier and assembling agent, under hydrothermal conditions (Yin et al. 2010). The number of the assembled hollow cages may vary from single-cage to multiconnected-cages, depending on the reaction conditions. Sodium carboxymethyl cellulose contains a large number of carboxymethyl groups, impeding thus the hydroxyl groups of polysaccharides to form hydrogen-bonds with water molecules. As a consequence, the "empty channels" described within the CMC structure will be available for oxide particles growing. Nanorods-type structures will develop on the top and bottom faces of previously formed hexagonal zinc oxide. In order to decrease the surface energy, these formed ZnO nanorods would organize themselves into broccoli-type structures (Fig. 5.7). The lengths of these nanorods vary in the range of 500–1000 nm while their diameters are between 50 and 100 nm. The obtained compounds present good catalytic abilities, decreasing the decomposition temperature of ammonium perchlorate. The increase of the cage number improved the photoluminiscence characteristics.

Spherical perovskite oxide powders ($PbTiO_3$, $BaTiO_3$, $SrTiO_3$, $PbZrO_3$, $Pb(Zr_{0.5}Ti_{0.5})O_3$ and $Ba(Zr_{0.5}Ti_{0.5})O_3$) were obtained from hydroxypropyl cellulose containing gel precursors (TiO_2, ZrO_2, and $ZrTiO_4$ respectively), under hydrothermal conditions (Choi et al. 1998).

Titania nanoparticles with a particle size of 10–20 nm are prepared using hydroxypropyl cellulose as pore agent (Beusen et al. 2007). The synthetic procedure implies two steps: the formation of TiO_2 by a low temperature (100°C) hydrothermal reaction and, a post synthesis by mixing the oxide with hydroxypropyl cellulose. Homogenously distributed pores are induced through burning out the cellulose derivative at 450°C.

5.5.4 Combustion Synthesis

The combustion synthesis using cellulose as fuel (single or in combination with other fuels) is based on the self propagated combustion of metal nitrates trapped in

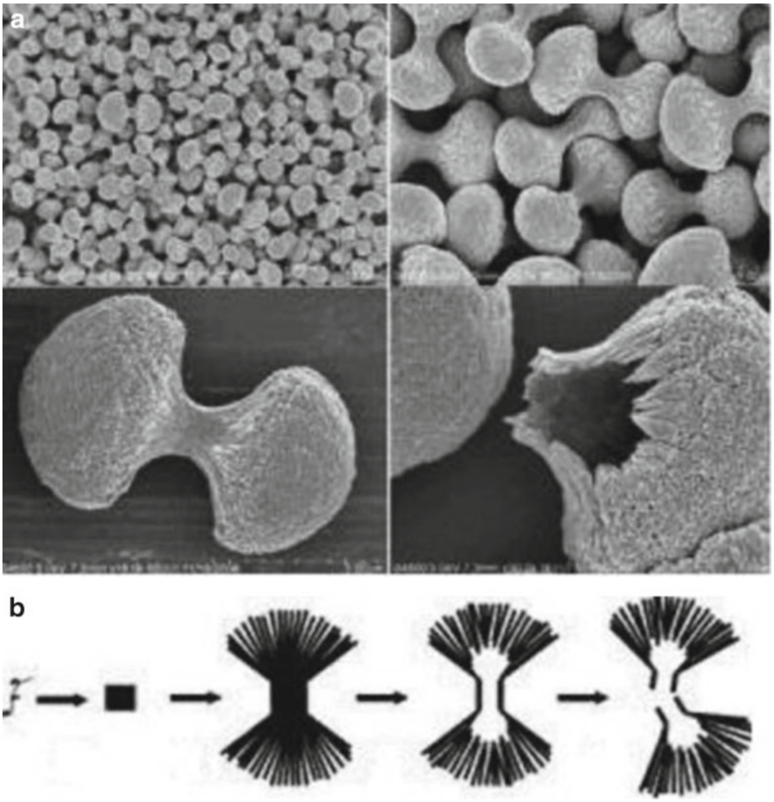


Fig. 5.7 (**a**) Scanning electron microscopy (SEM) images of double-cage ZnO nanorod self-assembled superstructures, obtained in the presence of sodium carboxymethyl cellulose under hydrothermal conditions; (**b**) Scheme of proposed growth mechanism of the double-cage superstructures (Reproduced by permission from Yin et al. © 2010, American Chemical Society)

various types of nanometer cellulose pores and capillaries (fibers). This particular combustion method is known as impregnated layer combustion synthesis (ILCS).

High phase purity MgO with particle size varying in the range of 3–7 nm were obtained by a high yield combustion synthesis, using magnesium nitrate and cellulose fibers (Maliyekkal et al. 2010). The nanosized MgO exhibits good adsorption capacity of groundwater fluoride.

The combustion of the impregnated cellulosic fibers with copper, zinc, zirconium, and palladium nitrates delimitates two reaction regions upon ignition: one for the amorphous metal oxide layer, a second for a crystalline one (Kumar et al. 2010). These oxides are active and selective catalysts for hydrogen production by the oxidative reforming of methanol.

Pure, well-crystallized $Li_4Ti_5O_{12}$ with quasi-spherical shaped crystallites were obtained through a cellulose- glycine-nitrate combustion process at 750°C, starting from anastase type TiO_2 (Yuan et al. 2009a, b). The sequence of impregnation has a strike effect on the phase formation and on the electrochemical performance of oxides. The optimal process succession involves first the cellulose impregnation with a mixed solution of $LiNO_3$ and glycine followed by the TiO_2 and HNO_3 impregnation. The newly synthesized oxides exhibit a better electrochemical behaviour at high charge/discharge rates than similar oxides obtained in solid state.

Synthesis of $La_{1-x}Sr_xCoO_3$ (x = 0.2) perovskite is carried on following a combustion method assisted by cellulose as single fuel (Shao et al. 2000). Both the purity of the perovskite and its mean crystallite sizes are influenced by the cellulose/nitrate ratio and calcination temperature. The perovskite starts to crystallize at 500°C, but a pure phase is obtained only at temperature higher than 800°C.

An interesting synthetic procedure was applied for the obtaining of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ perovskite powders, namely a combination of two methods: a freeze-drying one followed by the self-ignition of an aqueous solution of metal nitrates containing the soluble hydroxypropylmethyl cellulose (Traina et al. 2007). The precursor powder annealed at 1200°C exhibits a coral-like structure which collapses under low uniaxial pressure, resulting in a narrow grain size distribution suitable for sintering (98.8% relative density for a pellet sintered at 1400°C for 1 h). The fact that no milling step is necessary is a supplementary advantage of this method, which represents a promising opportunity for the synthesis of other multicationic oxides.

5.5.5 Alternative Synthesis

Oxides synthesis in ionic liquid media in the presence of cellulose have been also tested. Mesoporous TiO_2 films were prepared after the calcination of the ionic liquid solution namely 1-allyl-3-methylimidazolium chloride, that contain titanium tetrabutyloxide and cellulose (Miao et al. 2006). The surface area and pores size could be tuned by modifying the cellulose concentration.

Beaded chain ZnO nanostructures with superior photocatalytic activity and interesting photoluminescence properties were prepared by a complexation reaction between zinc acetate and hexamethylenetetramine in the presence of filter paper, followed by a calcination treatment at 700°C (Dutta and Basak 2009). The filter paper made up of fibrous cellulose material, acts as template: the nucleation of beaded ZnO is initiated along the fibers, the subsequent growth occurring into a highly organized fashion. ZnO nanostructures synthesized without the template are lumped together without any definite shape. The beaded nanochains obtained after an annealing treatment show superior photocatalytic activity than the template-free samples.

5.6 Dextran

Dextran is a branched polysaccharide composed from glucose units connected through α-1,6- glycosidic bonds, only a small percentage of monosaccharide being linked through α-1,3- or α-1,4- glycosidic bonds (Fig. 5.8).

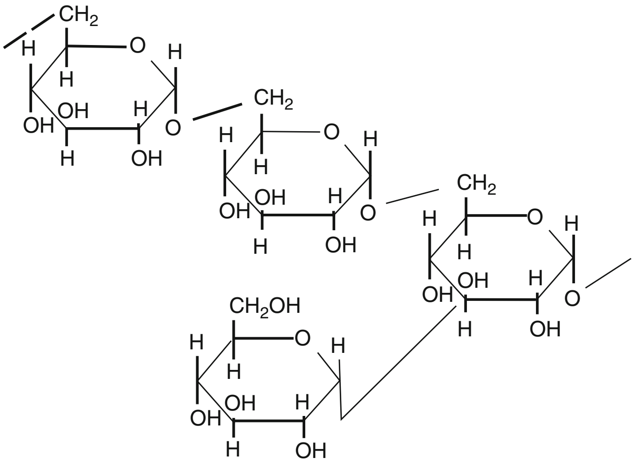


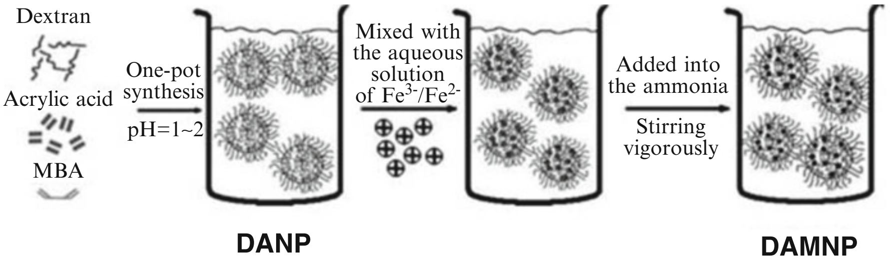
Fig. 5.8 Chemical structure of dextran with α -1,3 branching

Dextran has some unique properties useful in preparing nanoparticles through solution procedures: (i) a flexible structure; (ii) high solubility due to the high proportion of the D-glucose units linked by α-1,6 bonds; (iii) high stability; (iv) a reductive character of the constituting aldehyde groups that make possible an *in situ* reducing of the metallic cations (Shen et al. 1993; Laurent et al. 2008; Lin et al. 2003b) and (v) its controlled release using dextranase (Kim et al. 2009b).

The polysaccharide is considered an attractive biopolymer and is already used in medical fields, as drug delivery vehicle (Cristallini et al. 2001; Chauvierre et al. 2003), blood volume expander (Terg et al. 1996) or in gel permeation chromatography (Porsch and Sundelof 1994).

5.6.1 (Co)-Precipitation Synthesis

The stabilization/capping of iron oxides, magnetite, and maghemite has been the main application of dextran in chemistry of oxide materials (Laurent et al. 2008), dextran coatings being considered as an eco-alternative to the polyethylene glycol (Weissleder et al. 1989, 1990; Stark et al. 1988). Along with its biocompatibility (Berry et al. 2003; Laurent et al. 2004; Gamarra et al. 2005), the polysaccharide and its derivatives have a high affinity (polar interactions, complexation/chelation and hydrogen bonds) for iron oxide surfaces (Tartaj et al. 2006). Dextran-coated colloidal magnetic iron oxides are used in magnetic resonance imaging (Stark et al. 1988; Josephson et al. 1991) cell labeling and tracking (Arbab et al. 2004; Bulte 2006; Frank et al. 2003) and cell sorting (Radbruch et al. 1994; Ito et al. 2005). Most of the dextran coating procedures are performed *in situ* (Palmacci et al. 1995; Molday and MacKenzie 1982) but post-synthesis methods are also used, namely the grafting of the polymer on the magnetic particles (Hafeli et al. 1997; Okassa et al. 2005).



Scheme 5.2 The schematic representation of the synthesis of dextran-based nanoparticles containing carboxyl group (*DANP*) and dextran-Fe_3O_4 nanoparticles (*DAMNP*) (*MBA* N,N′-methylenebisacrylamide) (Reproduced by permission from Dou et al. © 2008, Springer)

The *in situ* dextran coating was first used by Molday and Mackenzie (1982), the procedure being applied also for various dextran derivatives, including carboxydextran and carboxymethyl dextran (Laurent et al. 2008).

Carp et al. (2010) have investigated the thermal behaviour of two types of dextran (with the molecular mass of 40.000 and 70.000)-coated magnetites obtained by a post synthesis procedure, the polysaccharide being connected to the iron oxide surface by means of hydrogen-bonds, with a lower thermal stability and through the coordination bonds with higher thermal stability.

Since, the most iron oxide-dextran interactions are of hydrogen-bonds types, the release of polymer may easily occur. In these conditions in order to improve the coatings stability, dextran crossslinking strategies, which involve for example epichlohydrin were elaborated (Josephson et al. 1999). The toxicity of epichlohydrin has led to the development of alternative cross-linking strategies. An interesting method to obtain ultrasmall superparamagentic iron oxide (VUSPIO) was developed by Mornet et al. (2004, 2005). It consists in a succession of oxidation/reduction reactions involving silane compounds and dextran. The maghemite surface is modified with aminopropylsilane (APS) groups that are subsequently coupled with partially oxidized dextran *via* condensation reaction and the formation of Schiff bases. The versatility of the iron oxide nanoparticles arises from the easiness of dextran derivatization, *e.g*. by polyethylene glycole.

Single domain magnetites with a homogeneous spatial distribution were formed through an *in situ* coprecipitation using carboxyl-functionalized dextran-based nanoparticles (DANP) as coating agent and template (Dou et al. 2008, see Scheme 5.2). The DANP hosts for the growing and organization of Fe_3O_4 nanoparticles (DAMNP), were previously synthesized by an one-pot approach, without using any organic solvent and surfactants (Tang et al. 2006). The magnetic nanocomposites exhibit saturation magnetizations similar with those of the magnetite and have a great potential in many biomedical fields.

A biocompatible ferrofluid containing dextran-modified Fe_3O_4 magnetic nanoparticles (MNPs) has been prepared following an one step method which involve hydrated hydrazine as reducing and precipitating agent (Hong et al. 2008). The dextran-coated MNPs molar ratio and the molecular weight of dextran strongly influence the coating efficiency, the size, dispersibility and magnetic properties of coated oxides.

Kim et al. (2009b) have recently reported a general and simple synthetic route of dextran stabilized oxides (Fe_3O_4, Co_3O_4 and Mn_3O_4), combining a coprecipitation and microwave heating procedures (Walsh et al. 2007a). The obtained stable suspensions of dextran – metal oxide particles (with average diameters of *ca.* 10 nm) could be cast as flexible transparent films. The enzymatic treatment of the coated metal oxides with dextranase provides an effective and simple method to remove the carbohydrate (Kim et al. 2009b). Monodispersed metal oxide cores, with diameters lower than 6 nm and stabilized by a low level of residual polysaccharide have been obtained. The amount of the remained dextran is still sufficient to inhibit the particles aggregation and growth, being also a basis for new nanoparticle assays.

Dextran assisted precipitation methods were used also to obtain iron oxide nanorods. Nath et al. (2009) have recently reported a simple, high-yield, room-temperature and water-based post synthesis method of dispersed dextran-coated iron oxide nanorods. This procedure differs from the above-mentioned methods by a quick addition of dextran, in the time range 1–60 s, after the nucleation process is complete. The geometry of the oxides is strongly influenced by the polymer purity, a high degree of purity affords a rod-shaped development (Manna et al. 2000).

The iron oxides properties, especially the magnetic properties, could be modified by various substitution of iron cations localized either on the octahedral or tetrahedral sites. Dextran-coated iron oxides doped with rare-earth cations can be prepared using methods that are very similar to those used to prepare analogues iron oxide colloids. Therefore, using an *in situ* synthesis, in which octahedral Fe^{3+} cations are substituted with lanthanide ions (Ln^{3+} = Er, Sm, Tb and Gd) in an amount ranging from 1 to 100 mol%, lanthanide-containing oxides have been obtained (Groman et al. 2007). The substitution of the iron cations with trivalent lanthanide ions had minimal effects on the colloid size. The effective diameters of most ultrasmall mixed iron oxides (USMIOs) colloids range between 20 and 40 nm. The presence of lanthanides ions (europium and terbium) in the iron oxide matrix induces interesting optical properties for the long-term multilabelings. These oxides have high photostability, a narrow emission band, and a broad absorption band combining the high sensitivity of time resolved fluorescence with the high spatial resolution of MRI (Matsumoto and Yuan 2003).

The substitution of the tetrahedral iron cations with manganese, gadolinium and zinc metal ions influences the superparamagnetic features of the iron oxide nanoparticles and provides control of properties important for biological applications (Groman et al. 2007; Lai et al. 2003; Drake et al. 2007; Latore-Estevez et al. 2009). In addition, the doping process could allow an additional control of the used material amount and implicit its toxicity in some therapeutic applications.

5.6.2 Gel Template Synthesis

Dextran is an interesting biotemplate molecule as a result of its complex and multi-branched structure.

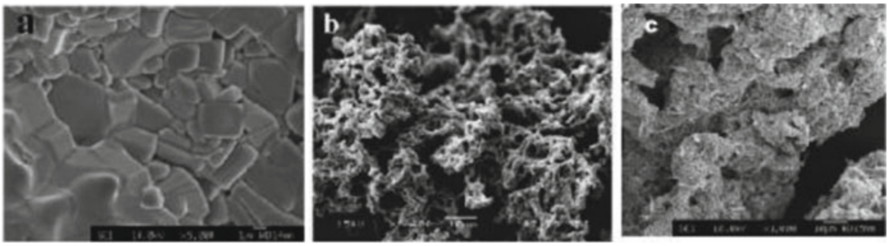


Fig. 5.9 Scanning electron microscopy (SEM) images of (**a**) $YBa_2Cu_3O_7$ sample; (**b**) a dextran template $YBa_2Cu_3O_7$ sponge and (**c**) a silver-doped dextran templated $YBa_2Cu_3O_7$ sponge. Scale bar in part a is 1 µm, in parts (**b**) and (**c**) is 10 µm (Reproduced by permission from Walsh et al. 2007a, b, American Chemical Society)

Choosing the dextran as a soft sacrificial template, Walsh et al. (2003) have developed a processing route for the fabrication of metals and metal oxides sponges without the requirement of any extraneous support materials. Self-supporting macroporous frameworks of silver, gold, copper and magnetic iron oxide, as well as silver/copper oxide or silver/titania composites can be prepared by decomposition of the metals salt containing dextran 70.000 gels shaped and patterned through the use of appropriate moulds, in the temperature range of 500–900°C. In each case, the expansion of the dextran matrix during thermal degradation gives rise to an open framework template together with associated spatial patterning of interconnected metal/metal oxide rods or filaments (with 1 to 20 µm thickness, depending on the calcination temperature).

A similar method was used in the synthesis of the high-temperature superconductor $YBa_2Cu_3O_7$ (Y123) sponges (Fig. 5.9a), obtained after a calcination treatment at 920°C (Walsh et al. 2007b). The semiconductor Y123 synthesized in the absence of the polysaccharide exhibits the typical polydispersity in terms of crystal size and morphology, while the Y123 dextran templated sponge (Fig. 5.9b) has a uniform, macroporous and opened architecture. The inclusion of silver or sodium metal ions into the dextran-based precursor gels improves the structural stability of the oxidic sponges (Fig. 5.9c).

Coral – like microcrystals of porous MgO nanoparticles, were also obtained by a single-step self-assembly synthesis of porous nanoparticles *via* a template process in the presence of dextran 40.000 (Niu et al. 2006). The morphologies of the final products are strongly dependent on the experimental conditions, for example the concentration of the raw materials. In the absence of the polysaccharide or to a lower concentration of dextran, MgO is formed either as irregular and imporous nanoparticles, or as a mixture of porous and imporous nanoplates. A high concentration of dextran obstructs the formation of pure MgO phase. On the other hand, the replacement of the nitrate salt of magnesium(II) with the chloride one determines the formation of a web-like morphology, with many polygonal pores and with diameters ranging from 250 to 700 nm. The proposed mechanism implies the formation of an inorganic polymer complex through the self-assembly behaviour of the hydrophilic groups of dextran (Walsh et al. 2003; Yang et al. 1998, 1999).

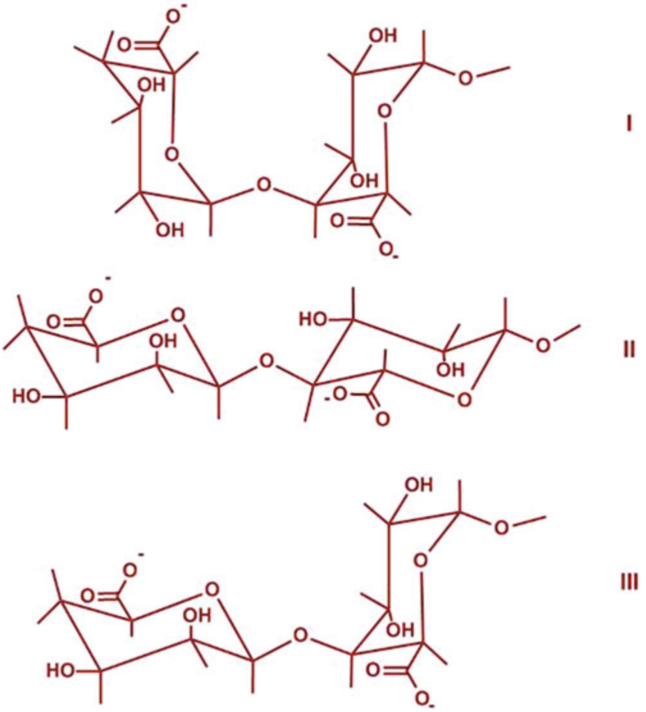


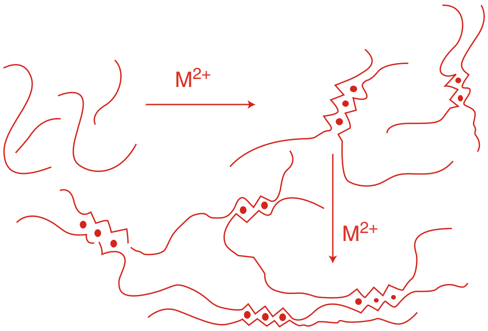
Fig. 5.10 Chemical structure of the repeating units of alginates: (I) L-guluronic acid (G); (II) D-mannuronic acid (M); (III) alternating L-guluronic and D-mannuronic acids (GM)

5.7 Alginate

The alginate, derived from alginic acid (extracted from marine alge or soil bacteria), is a linear anionic polysaccharide made-up from 1,4-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G), both in the pyranosic conformation, and arranged in a nonregular blockwise pattern with different ratios of GG, MG, and MM fragments (Smidsrød et al. 1966; Larsen et al. 1969; Haug et al. 1966, 1967, 1974; Fischer and Dőrfel 1955; Chanda et al. 1952) (Fig. 5.10).

The particular gel process formation resulted from the association of anionic alginate and metal cations is the key entrance of this polysaccharide in the materials synthesis domain. Alginates are able to adopt an ordered solution conformation through the dimerization of the poly-G sequences, in the presence of divalent/trivalent cations and that is one of the most interesting polysaccharide peculiarities (Smidsrød and Haug 1972; Grant et al. 1973; Nesterova et al. 2000; Finotelli et al. 2004; Nishio et al. 2004). The so-called "egg-box" model of ion binding means that the arrangement of the cations fits into the electronegative carbohydrate cavities as the eggs in an egg-box (Grant et al. 1973; Draget et al. 2002). The preferential binding of the metal cations to these confined regions of the G blocks brings some control over the

Scheme 5.3 The crosslinking of alginate induced by divalent metal cations



nanoparticles nucleation and growth processes, in a multi-stepped procedure. The terminal poly-M or mixed poly-MG chain sequences of the dimerized regions may be interconnected with neighboring chains promoting the gel network formation, the complete gelling process being resumed in Scheme 5.3.

An alginate with an increased amount of G sequences has a higher affinity for the cross-linking cationic agents than low G-containing one (Serp et al. 2000). The selective binding of the divalent/trivalent metal ions and the corresponding gel strength were found to increase following the order: MM block < MG block < GG block (Smidsrød and Haug 1968). A high G blocks content (with axial–axial linkage) develop a stiffer, more brittle, and more porous gel, which maintains the structure integrity for long periods of time. Since in the cation cross-linking the swelling and subsequent shrinking processes are not excessive, their form could be maintained in a better manner. In reverse, for the rich M (di-equatorially linked-alginates) the higher swelling degree during cations crosslinking (Grant et al. 1973), has led to less porous beads and fragile materials.

The properties of metals-containing gel depend also on the cations nature, their concentration and the reaction conditions (pH value) (Nava et al. 1994; Smidsrød 1973; Baskoutas et al. 2007).

5.7.1 (Co)-Precipitation Synthesis

One of the most available applications of alginate in oxides synthesis was in the precipitation methods. Several alginate-based precipitation procedures have been recently developed for the obtaining of magnetic iron oxide nanoparticles (Nishio et al. 2004; Llanes et al. 2000; Finotelli et al. 2004; Kroll et al. 1996; Shen et al. 2003).

(A) *in situ* synthesis, starting from ferrous salts;
(B) post synthesis coating, when ferrous/ferric salts have been used as raw materials;
(C) post synthesis coating, when ferric salts were used as precursors.

The oxidation of the ferrous hydroxide precipitate with O_2 or H_2O_2 is an indispensable step in A type methods, but brings one major synthetic drawback: multiple recycles to produce ca. 50% iron oxide, a higher control degree over the oxidation reactions being strongly required to achieve magnetic phases of iron oxides (Nishio et al. 2004). The B route is more efficient and affords higher content of Fe_3O_4 than in method A, the iron oxide having superior characteristics: a particle oxide-alginate core diameter of 5–10 nm, a hydrodynamic diameter of 193.8–483.2 nm, while the magnetization of saturation is 55 emu g^{-1} (Ma et al. 2007). The C method is based on the mild reducing alginate abilities as the temperature is rising, an illustrative example being gold nanodisks which have been obtained following this procedure (Gao et al. 2008b; Pal et al. 2005). The alginate-ferric salts combination forms a gel in which the metal ions are further reduced and the alginate-coated magnetite with a saturation magnetization value about 62.1 emu g^{-1} have been obtained (Gao et al. 2008b). The benefic role of alginate has been proved also carrying out a similar reaction in the absence of polysaccharides when final product was pure α-Fe_2O_3 (Gao et al. 2008b).

5.7.2 Gel-Template Synthesis

The very particular process of the gel formation builds ordered domains in which the polymer chain network defines confined spaces for cations binding, being a useful peculiarity of the polysaccharide for the controlled growth of oxides particles.

Monodispersed iron non magnetic oxides, α-Fe_2O_3, were obtained from alginate gels, after a heating treatment at 700°C (Nidhin et al. 2008; Sreeram et al. 2006). A pH value of 3.5 has favored the monodisperse character and lower particle sizes, while in a neutral or basic media the iron cations have been converted into iron hydroxide prior to their interaction with alginate.

Single-crystal superconductor nanowires of yttrium–barium–copper-oxide (YBCO) have been prepared using alginate as template (Schnepp et al. 2008). It is known that superconducting properties are strongly influenced by the morphology: a significant reduction of the superconducting properties occurs with the increase in either the polycrystallinity or as a result of the non-alignment of the grain boundaries (Klie et al. 2005). The cocooning effect of the alginate biopolymer has prevented the coalescence of the barium particles. The preorganization of barium ions within the polysaccharide matrix produces spatially separated barium carbonate nanoparticles that act themselves as sites for the subsequent catalytic outgrowth of YBCO superconducting nanowires at temperatures above 800°C. The growth of superconductor needles occurred radially from nucleation sites toward the surface of the polycrystalline aggregates. The material is made up from a complex microstructure of fibrous aggregates, up to several micrometres in thickness (Fig. 5.11a), with smooth surfaces and a circular cross section of 50–80 nm in diameter (Fig. 5.11b). Each fiber includes bundles of straight-sided nanowires, typically with 10 nm in diameter (Fig. 5.11c). The fibres were uniaxially aligned, with a preferred direction of growth (Fig. 5.11d), while the constituted nanowires have a critical temperature of 77 K, which is only slightly lower than the one, specific for YBCO, of 85–89 K.

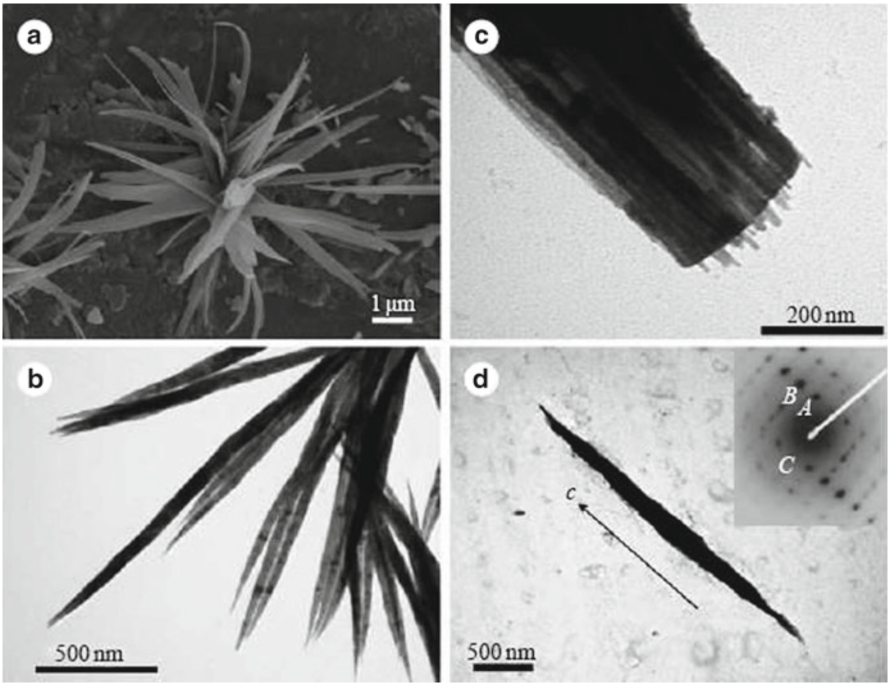


Fig. 5.11 (**a**) SEM image, (**b–d**) TEM images and corresponding single-crystal electron diffraction pattern (d inset) of YBCO nanowires (Reproduced by permission from Schnepp et al. © 2008, Wiley). SEM: scanning electron microscopy, TEM: transmission electron microscopy, YBCO: yttrium-barium-copper oxide

Nanocrystals of CuO, Co_3O_4 and NiO oxides aggregated in hollow millimetric spheres shape were obtained after a calcinations treatment at 500°C of the M(II)-alginate aerogels (Horga et al. 2007). The oxide preserves the spherical shape of the parent aerogel, but the size of the calcined spheres is nearly one third of the original size.

5.7.3 Hydrothermal Synthesis

Several interesting three-dimensional (3D) ZnO architectures – microspheres and other radial structures were obtained using alginate as soft template (Gao et al. 2006). The strategies rely on the one-dimensional ZnO nanorods self-assembly into hierarchical structures.

Two critical factors influence the self-assembly process of the hollow microspheres: the water-soluble alginate amount and pH value of solution (Fig. 5.12). In basic media (pH = 10.38) and in the absence of the polysaccharide, no internal hole is formed, the ZnO nanorods being rooted in one center and radially extended outward (Fig. 5.12a). In the presence of a certain amount of sodium alginate, the ZnO nanorods have built spherical architectures (Fig. 5.12b), while a five times dosage of polysaccharide has led to a different type of hierarchical superstructures, namely the hemispheric structures

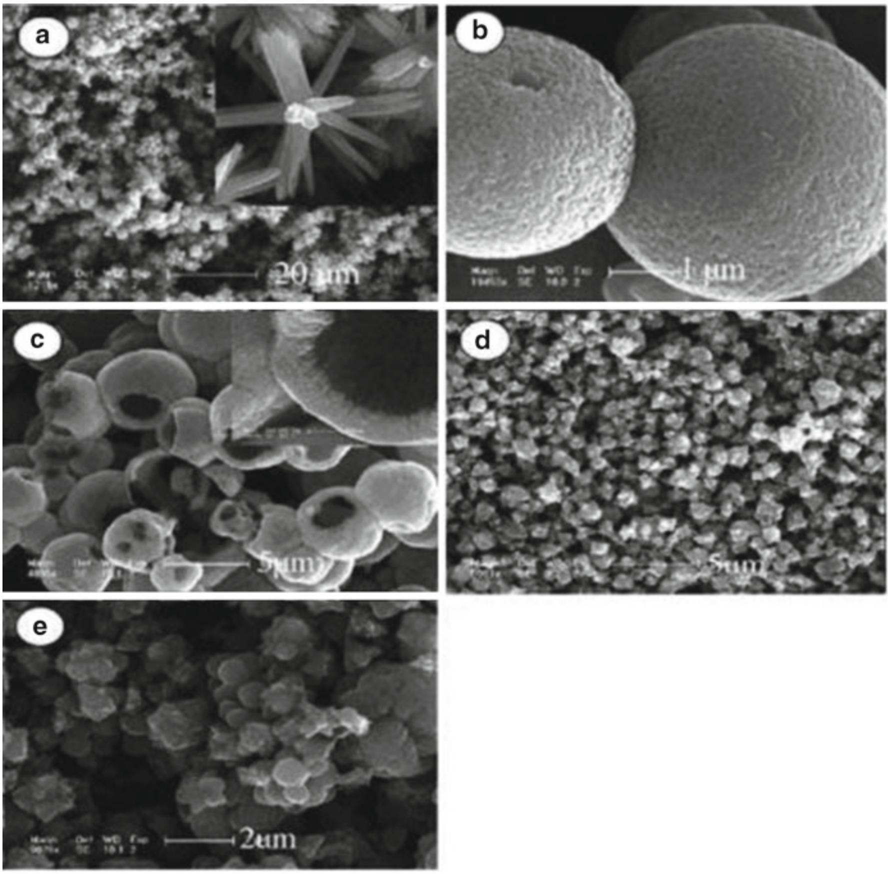


Fig. 5.12 Field emission scanning electron microscopy (FESEM) images of samples obtained from control experiments: (**a**) in the absence of sodium alginate (*SA*); (**b**) in the presence of SA under other identical conditions; (**c**) 5 times the dosage of SA under other identical conditions; (**d**) decreasing the pH value from 10.38 to 9.96; (**e**) and increasing the pH value from 10.38 to 10.48 (Reproduced by permission from Gao et al. © 2006 American Chemical Society)

(Fig. 5.12c). When the pH value was decreased to 9.96, the product has a flower-shaped structure (Fig. 5.12d) while for a value of 10.48 or higher, the structure has become to be nonuniform in terms of morphology and size (Fig. 5.12e).

5.8 Chitosan

Chitosan is a polyaminosaccharide obtained through the deacetylation of the natural chitosan. Structurally, is a linear copolymer assembled from glucosamine and *N*-acetylglucosamine [poly(N-acetyl-D-glucosamine-co-D-glucosamine)] units, having the chemical formula of $(C_6H_{11}NO_4)_m(C_8H_{13}NO_5)_n$ (Fig. 5.13).

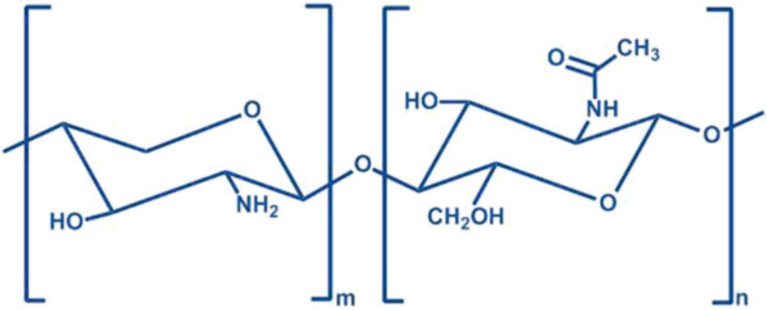


Fig. 5.13 Chemical structure of partially acetylated chitosan constituted by (m) glucosamine units and (n) N-acetylglucosamine units

Several of its physico-chemical features, namely excellent film-forming ability, good adhesion, biocompatibility, high mechanical strength and potentially high reactivity due to the constituent hydroxyl and amino functional groups (Yi et al. 2005; Ravi Kumar et al. 2004; Guibal 2004; Babel and Kurniawan 2003) makes it suitable as biomaterial (Muzarelli 1977; Cruz et al. 2000; Xu et al. 2001; Wei et al. 2002; Chung et al. 2005; Kim et al. 2009a; Yang et al. 2007; Li et al. 2008a). The degree of deacetylation and crystallinity are two of the most important characteristics of these materials (Guibal 2005) that influence the solubility in an aqueous medium, the acid-base properties (Sorlier et al. 2001) and the ability to form complexes (Hernández et al. 2008).

The bi-functional chitosan may capture transitional or post-transitional metal ions in aqueous solution (Ogawa et al. 1993) through coordination/chelation bonds to the hydroxo- and the more active amino-groups (Klepka et al. 2008; Bhati and Ravi 2003). The biopolymer is flexible, highly hydrophilic (due to the multiple polyol groups) and its structure integrity is kept up to 200°C (Bengisu and Yilmaz 2002). All these characteristics are very useful in elaborating successful oxides synthetic approaches.

The metal cations coordination to the chitosan is in fact a very complicated process and very sensible to the reaction media and polysaccharide characteristics. A higher degree of chitin deacetylation increases the amino-groups content and thus improved complexing/chelating chitosan abilities are observed. Several other factors influence the complexing/chelation of the metal cations: the physical state of the polysaccharide (powder, gel, fiber, film), the number of the polymer units (Rinaudo 2008) and some experimental parameters such as the nature of the transitional cation, the pH value and the chitosan/cation molar ratio (Neto et al. 2005; Wang et al. 2008; Varma et al. 2004; Zhu et al. 2009; Ng et al. 2002).

The chitosan selectivity for metal ions has been envisaged, by means of density functional theory, for copper(II) and nickel(II) cations which would preferentially coordinate to the amino functional group (Braier and Jishi 2000; Raíz et al. 2002). Several other complexing mechanisms for chitosan and its derivatives have been proposed and/or identified (Zhu et al. 2008, 2009). The coordination of iron(III) cation to chitosan is still an issue: some authors consider a lack of Fe^{3+} ion coordination to the chitosan based on some physical measurements (Sipos et al. 2003), others suggest the formation of an iron(III)-chitosan cluster without any effective link of the transitional trivalent cation (Gamblin et al. 1998). Evidences for the iron(III)-chitosan complex formation have been extracted from vibrational and magnetical data (Zhu et al. 2009), with a proposed penta- or hexacoordination of Fe^{3+} cation to the polysaccharide, which involves two nitrogen atoms from amino groups and two oxygen atoms from the hydroxyl groups. The transitional metal ion coordination sphere is completed with one/two water molecules. More detailed studies, including infrared spectra, thermal data and Mössbauer spectra, have revealed that two chitosan residues, three water molecule and one chloride anion have occupied the iron(III) coordination sites, after a direct reaction between the $FeCl_2$ and the polysaccharide.

Chitosan hydroxyl groups are usually involved in strong intra- and intermolecular hydrogen-bonds which diminishes the polysaccharide solubility in aqueous solutions, at neutral or basic pH. The chemical modifications on the chitosan structure (coupling the polysaccharide with ligands, biomolecules or blending with polymers, Nakajima 1995; Liang et al. 2007; Bhattarai et al. 2005; Park et al. 2003; Bahadur et al. 2009) has led to a new geometric arrangement of the polymer chains (Jiyoung and Leong 2006). The depolymerization of high-molecular weight chitosan (following a chemical treatment, enzymatic degradation, radiation degradation and fragmentation by ultrasonic irradiation, Allan and Peyron 1995; Nordtveit et al. 1994; Kasaai et al. 2008) is also viable and non-polluting solution to improve the polysaccharide water solubility in neutral media (Zhang et al. 2007; Tien et al. 2003).

A rigid and brittle skeleton of chitosan polymer represents a supplementary limitation of the polysaccharide in material synthesis that could be overcome by mixing the chitosan with polyanionic macromolecules (alginate, carboxymethyl cellulose or polyacrylic acid) to form interpolyelectrolyte complexes (Carlos et al. 2003; Yang et al. 2007).

The thermal behaviour of the chitosan is a critical factor to take into account for any wet procedure of the nanosized particles. Several decomposition steps were observed: a first degradation occurs in the temperature range 90–200°C and corresponds to the loss of the adsorbed and bound water (Li et al. 2008a; Hernández et al. 2008; Hu et al. 2004). The second step, in the 200–575°C temperature region, is complex and covers the dehydration, depolymerisation and decomposition of the acetylated and deacetylated units of the chitosan (Zainal et al. 2009; Peniche-Covas et al. 1993). The occurrence in the same temperature range of some thermal cross-linking reactions followed by the destruction of amino groups is also stipulated (Zubieta et al. 2008; Pawlak and Mucha 2003; Wanjun et al. 2005; Zhan et al. 2003; Zohuriaan and Shokrolahi 2004; Ding et al. 2003; Neto et al. 2005; Nieto et al. 1991; Qu et al. 2000).

5.8.1 (Co)-Precipitation Synthesis

The co-precipitation methods, *in situ* (Wang et al. 2008; Varma et al. 2004; Feng et al. 2009) or post-synthesis (Podzus et al. 2009; Zhu et al. 2008; Pan et al. 2009;

Dnekbas et al. 2008), are available and suitable routes to obtain hybrid magnetite (Fe_3O_4)-chitosan materials, and are by far the most investigated systems (Liang et al. 2007; Wang and Tan 2007; Zhao et al. 2006; Lin and Leu 2005; Hrbac et al. 2007; Zhang et al. 2007; Kaushik et al. 2008).

A mixed *in situ* co-precipitation and chitosan gelling procedure has been used to obtain spherical magnetite nanoparticles (Hernández et al. 2009). The chitosan concentration strongly influences the crystallization of the spinelic phase, 2 wt% polysaccharide concentrations being very favorable for the oxide nanoparticle development with an average size of 10 nm. The attempts with 3 wt% chitosan concentration were unsuccessful, leading to iron oxyhydroxides. One possible explanation is related to the lower viscosity of the less-chitosan solution, which increases the viscoelastic modulus and reinforce the polysaccharide hydrogel characteristics, assuring a good dispersion of the iron oxide particles within the polymeric matrix.

Zhang et al. (2010) have successfully developed a modified co-precipitation method *via* UV light irradiation, in an emulsifier-free aqueous system, obtaining magnetic Fe_3O_4–chitosan nanoparticles, with regular shape and a mean diameter of 41 nm. The nanoparticles have showed water swelling properties, having a 64 nm average diameter in aqueous solution, and a superparamagnetic behaviour, with a magnetization of saturation reaching 48.6 emu g^{-1}. The proposed mechanism is based on the magnetite particles ability to adsorb on their surface the chitosan molecules as well as the polysaccharide capacity to produce free radicals (a process initiated by the formed hydroxyl radicals which result from the H_2O_2 decomposition under the UV irradiation). The recombination of the chitosan free molecules has produced cross-linked structure and grafted the polysaccharide chains on the magnetite nanoparticle surface.

Several studies have been dedicated to the thermal behaviour of the iron-containing chitosan. Three degradation steps are observed instead of the two remarked for the starting chitosan (Pawlak and Mucha 2003). The chitosan-coated magnetites are relatively stable up to 300°C, the small recorded weight loss being assigned to the removal of the physically and chemically absorbed water (Zhang et al. 2010). At higher temperatures (300–500°C), a partial degradation of the chitosan has occured, the superior temperature values than in the single chitosan case indicating an increase of chitosan-iron oxide thermal stability. The last degradation step of the bound chitosan is registered in the 575–785°C range (Okuyama et al. 2000). A direct dependence of the thermal effects on the degree of deacetylation is identified (Hall 2006; Kittur et al. 2002).

Mesoporous aluminium and silicon oxides spheres with regular diameter of 1.0 mm were obtained through a simple precipitation methodology using the chitosan as template (Braga et al. 2009). Chitosan with higher polymerization degree will enhance the mechanical resistance of the spheres. The surface area of the materials obtained after calcination at 500°C ranges between 62 and 245 m^2 g^{-1}, the pore volume varies between 0.82 and 0.28 cm^3 g^{-1}, depending on the molar ratio of the organic and inorganic materials.

5.8.2 Hydrothermal Synthesis

The Nb_2O_3-chitosan composites, obtained through a hydrothermal method, were used to photocatalyse the degradation of indigo carmine dye in aqueous solution by UV irradiation (Torres et al. 2006). Whilst the thermal stabilities of the Nb_2O_3-chitosan composites were slightly lower than that of the pure biopolymer, the materials have shown high catalytic efficiencies that remained unaltered after 15 cycles of reuse.

5.8.3 Post Synthesis Procedures

The post synthesis chitosan-coating of various oxides is based on the chitosan affinity for metal cations and represents a facile and convenient strategy to obtain composite materials.

The TiO_2–chitosan composites present a combined effect of photodegradation–adsorption, the two inorganic-organic components being complementary and providing a comprehensive method in pollutants degradation. Thus, the photocatalytic degradation process mediated by TiO_2 is very efficient in the decomposition of various organic pollutants, while the polysaccharide is suitable for the metal elimination (Chen and Ray 2001). The literature mentions the removal of several dyes such as methyl orange, methylene blue and benzopurpurin in the presence/absence of metal cations (Li et al. 2008b; Zainal et al. 2009; Zubieta et al. 2008).

Chitosan-coated barium hexaferrite ($BaFe_{12}O_{19}$) is a potential magnetic support for hyperthermia applications, the low cytotoxicity and the high heating rate of the magnetic chitosan particles under an alternating magnetic field representing strong arguments (Park et al. 2005). The average particle sizes (0.2–1 mm) and the magnetization of saturation (31.5–45.8 emu g^{-1}) of the magnetic chitosan-coated particles depend on the barium hexaferrite/chitosan 1–10 ratio, while the coercivity (~3,800 Oe) remains almost constant.

ZnO quantum dots–chitosan folate carrier loaded with anticancer drug and prepared following a post synthesis method, has shown a drug loading efficiency of *ca.* 75% (Yuan et al. 2010). The hydrophobicity and the positive charged character of the chitosan have enhanced the stability of the quantum dots. An initial rapid drug release followed by a controlled process has been observed for anticancer drug-loaded ZnO quantum dots –chitosan folate carrier.

5.8.4 Gel-Template Synthesis

High-temperature superconductor nanowires have been obtained in a similar way as the alginate-assisted synthesis, the chitosan acting as gel-template (Schnepp et al. 2008). The polymer ability to capture and bind metal ions and thus to provide preferred nucleation and crystal growth sites allows the control of the high-temperature superconductor $YBa_2Cu_4O_8$ particles morphology and prevent the particles sintering during the heating treatment (Hall 2006).

5.9 Carrageenan

Carrageenan is a generic name for a family of cell-wall polysaccharides, obtained by extraction from certain species of Rhodophyta red seaweeds (Van De Velde et al. 2002).

Carrageenans are generally made-up of linear sulfated polysaccharides which includes a linear galactose skeleton build up from 1,3-glicosidically linked β-D-galactopyranose units and α-D-galactopyranose residues 1,4-connected through glicosidic bonds. The large family of the carrageenan includes polysaccharides with different compositions and conformations which gives a wide range of rheological and functional properties, the most popular being *ι*-, *κ*-, and λ- carrageenan (Fig. 5.14).

Carrageenans form nontoxic and hot water-soluble thermoreversible gels, often stabilized by alkali-metal cations and have been widely used as gelling agents in the food and pharmaceutical industries (Piculell 1995).

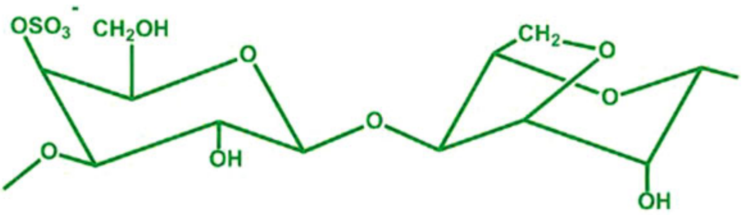
The gelling mechanism is based on the high flexibility of the carrageenans molecules: at higher polysaccharide concentration, the carrageenans chains are aggregated into double helices and stabilized through hydrogen-bonds, which further are aggregated (cross-linking points) into helices aggregates, the metal cations playing important roles in gel stabilization (Piculell 1995; Chheda et al. 2007; Rinaudo and Rochas 1981; Rochas et al. 1989, 1990).

Specific studies regarding the interaction of *κ*-carrageenan with several transition metal oxides have been carried out (Jones et al. 2000a, b).

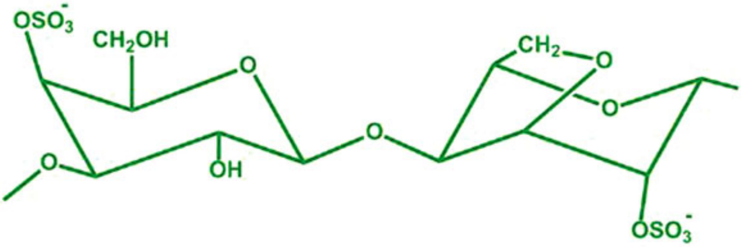
The proposed structural model for the biomineralization of iron oxides in the presence of this polysaccharide has highlighted that the coating *κ*-carrageenan build "cages" around the particles acting as a nanoreactor protecting and stabilizing the metal oxide nanoparticles (Jones et al. 2000a, b).

A possible mechanism for the formation and stabilization of iron oxyhydroxide (or magnetite) mineralized in κ-carrageenan has been proposed. The iron(II) or iron(III) cations are first coordinated to the functional sulfate group of the biopolymer, the *κ*- and *ι*-carrageenans being susceptibles to coordinate ferric ions to the hydroxyl groups also (Ciesielski 2004a, b, c) promoting the physical crosslinking of the biopolymer chains and the formation of a microgel at low pH (Jones et al. 2000a; Daniel-da-Silva et al. 2007). Carageenan self-capped iron oxide nanoparticles are gradually formed, with the increase of the pH value, while, within these superstructures, the iron cations start to detach from the polysaccharide sulfate groups to migrate toward the particle nucleation sites (Jones et al. 2000a). The cross-linked carbohydrate chains assembles protective layers and stabilize the formed iron oxyhydroxide particle, in basic solution (pH = 13) (Jones et al. 2000a), these localized areas becoming the growth sites of the oxide particles, the free polymer remaining in solution.

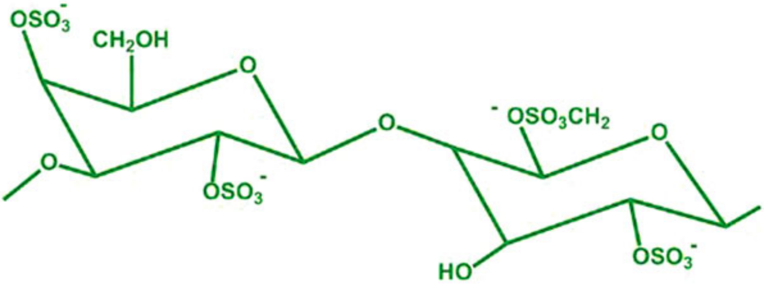
The polysaccharide has also the role to limit the particle sizes, the average dimensions depending on the nature (the particle size increase in the order $\iota > \kappa > \lambda$



κ–carrageenan



ι–carrageenan



λ–carrageenan

Fig. 5.14 Disaccharide repeating units of κ-, ι-, and λ-carrageenan

carrageenan-types) and concentration of the carrageenan: a rich carageenan synthesis generates smaller nanoparticles. The relative magnetite stability to oxidation in different carrageenan systems (ι>κ>λ types) is a result of a balance between two factors: (i) average particle size and (ii) the rheological state (sol or gel) of the resulting nanocomposite. In the case of κ-carrageenan, in spite of the smaller particle size, the chemical stability is enhanced by the stronger gels formed, compared to λ-carrageenan. Considering the above mentioned effects of the increased polysaccharide contents and that the magnetite oxidation follows a size dependent diffusion mechanism, it is suggested that small particle sizes accelerate oxidation while strong gels have opposite effect, as oxygen diffusion within the gel becomes more difficult (Daniel-da-Silva et al. 2007).

Repetition of the loading/neutralization steps of the reaction results in hybrid materials with iron contents much higher than the stoichiometric balance of iron and functional groups of the polymer (greater than 100% Fe/SO_4^{2-}) (Jones et al. 2000b). Moreover, since carrageenans form thermoreversible gels, the controlled release of magnetic particles or loaded drugs can be envisaged by both thermal and magnetic stimuli.

A nice example for a complex superstructure formation is the cobalt hydroxide/carrageenan hybrid. It is obtained at a pH value of 13, and was generated by the slow aggregation of the hydroxide particles, after the initial oxidation of the primary particles Co(II) to Co(III) (Jones et al. 2000b). The cobalt(III) hydroxide crystals (approx. 20 nm in radius) rearrange themselves into polygons (100–200 nm in radius) which, in turn, will further aggregate to form micrometersized (~10 µm in diameter) ball-like superstructures. The formation of ball-like spherical superstructures must be a product of energy minimization, in the lowering of the surface energy being balanced by the entropy loss upon aggregation.

5.10 Perspectives and Conclusions

The present review is the first deeper look, to our knowledge, into a new and a very promising research area: the polysaccharide-assisted synthesis of metal oxide nanoparticles. Last decades has enlighted the great potential of the polysaccharides in the chemistry of materials taking into account their increased and various industrial and biomedical applications. Their “migration” toward nanotechnology is viewed as a natural stepforward for this special family of carbohydrates. Their compatibility with solution-based approaches for the materials synthesis and with the restrictive demands of the non-polluting chemistry transform them into a beneficial input for nanoparticles area of research.

The present paper gather the most illustrative examples of the polysaccharide interferences in different solution methods to obtain oxide-based materials (or related composite materials), highlighting the multiple roles [coating, protecting, (bio)-template with structure-directing role, complexing, assembling, fuel, pores agent], the great versatility of carbohydrates in the already classical soft chemistry approaches [(co)-precipitation, sol-gel, combustion or hydrothermal synthesis] as well as some superior characteristics of the obtained nanosized metal oxides particles. An unknown and spectacular chemistry of polysaccharides has been unveiled and cleverly applied in materials sciences opening controlled pathways from molecular levels toward nanodimensions. Thus, one of the principal nanotechnology aims, small sizes of the oxide particles with large specific surface areas as well as tunable particles morphologies could be easily reached involving natural ingredients such as polysaccharides by means of highly available chemical synthetic methods.

The polysaccharide-based nanoparticles research domain is still in a pioneering age and there is still a lack of information concerning the mechanisms of nanoparticles formation in the presence of these biopolymers. In other words, the existing literature data shows only “the tip of the iceberg”, further systematic studies being necessary to clarify the adsorption, complexation or templating actions of polysaccharides which will improve our understanding about the growth mechanism of the nanoparticles. Another critical issue that needs a detailed investigation in the future is the relation between the coordination compound/gel properties and the final materials properties and also the thermal stability of the polysaccharide-metals precursors.

The information provided by the review here is a strong argument that polysaccharides represent a cheap, versatile, eco-friendly and available sources for the design of the future advanced materials, and could make sensitive the research community about one incontestable fact: the nature is the best tutor for any researcher, it offers him unexhausted resources and also it teach him how to wisely used it!

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Part II
Health Risk

Chapter 6
Environmental Fate of DDT Isomers and Metabolites

Mathias Ricking and Jan Schwarzbauer

Contents

Abstract It is known for decades that isomeric composition of organic pollutants can be influenced substantially by environmental processes such as biotransformation or transfer between compartments. This accounts also for the pesticide 2,2,-bis(4-chlorophenyl)-1,1,1-trichlorethane, better known as p,p′-DDT, and its accompanied substitution isomer 2-(2-chlorophenyl)-2-(4-chlorophenyl)-1,1,1-trichlorethane (o,p′-DDT). Therefore, for this literature review over 2000 recent literature citations were checked for information on the isomer ratios of DDT and its metabolites in the environment. Although many studies followed the environmental fate of DDT, only very few publications reported on quantitative data of both

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o,p′- and p,p′-isomers. However, this review revealed evidence for remarkable changes and shifts in o,p′-/p,p′-ratios of DDX. The application of isomer specific analysis remains dominantly on emission source apportionment, e.g. to differentiate DDT and dicofol emission.

Only very few studies linked observed isomer shifts to aspects of environmental processes, such as (i) volatility from soil to air, (ii) environmental stability in soil or (iii) bioaccumulation in fishes. Additionally, several studies failed to use isomer specific interpretation in order to obtain more detailed insight into environmental processes e.g. for observed isomer shifts during air-water fluxes.

Evaluating the comprehensive data set presented in this review a clear discrimination of o,p′-/p,p′-ratios of DDT, DDD and DDE is evident. The o,p′-/p,p′-ratios of DDT and DDD have been detected more or less on the same level, whereas the isomers of DDE were definitely depleted by the o,p′-isomer in all environmental compartments. This observation indicates a general isomer-specific differentiation during DDT metabolism.

Finally, the potential to follow the environmental fate of DDX via the isomer composition has not been realized accurately so far, and, consequently, has not been well established in the field of environmental chemistry yet.

Keywords DDT • Isomer-specific analysis • Isomeric ratio • Source identification

List of DDX Abbreviation

DDD	2,2-bis(chlorophenyl)-1,1-dichloroethane
DDE	2,2-bis(chlorophenyl)-1,1-dichloroethene
DDMS	2,2-bis(chlorophenyl)-1-chloroethane
DDMU	2,2-bis(chlorophenyl)-1-chloroethene
DDNU	2,2-bis(chlorophenyl)ethene
DDT	2,2-bis(chlorophenyl)-1,1,1-trichloroethane
DBP	dichlorobenzophenone
DDA	bis(chlorophenyl)acetic acid
DDCN	bis(chlorophenyl)acetonitril
DDM	bis(chlorophenyl)methane
DDX	sum of DDT and all of its metabolites

6.1 Introduction

The widespread application of the pesticide DDT (bis(chlorophenyl)-1,1,1-trichloroethane) began in the 1940s but DDT was banned in many countries in the early 1970s. During this time period the intensive and widespread usage combined with a high environmental stability and its tendency for geo- as well as bioaccumulation caused an ubiquitous contamination of nearly all environmental

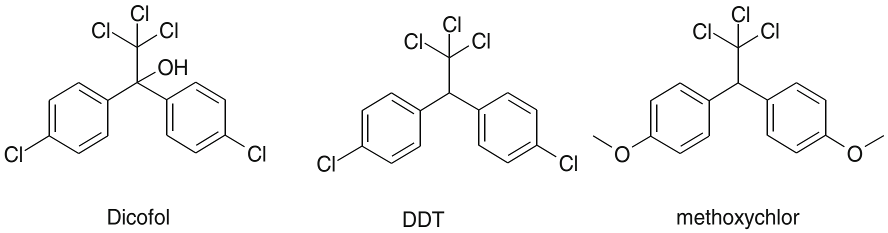

Fig. 6.1 Molecular structure of DDT, an organochlorine insecticide. High structural similarity exists to further pesticides like methoxychlor (insecticide) and dicofol (acaricide)

compartments. Consequently, DDT and its main metabolites have been subjects of numerous analytical studies.

First synthesized in 1874, DDTs insecticidal properties were discovered in 1939 by the Swiss chemist Paul Hermann Müller. The application during World War II was of great success in controlling malaria and typhus. After the war DDT was made available for use as an agricultural insecticide. Examples of trade names are Anofex, Cesarex, Clofenotane, p,p′-DDT, Dicophane, Gesarol, Guesarol, Gyron, Neocydol and Zerdane.

DDT crystals exhibit high hydrophobicity, are colorless, and offer a weak chemical odour. Due to its nonpolar molecular structure (see Fig. 6.1) it is good soluble in fat, oils and organic solvents, almost insoluble in water. The technical production was based on a double step Friedel-Crafts acylation using chlorobenzene (C_6H_5Cl) and chloral (CCl_3CHO) in the presence of sulfuric acid as catalyst.

Due to the relatively low substitution selectivity of Friedel-Crafts acylation reactions technical DDT consists of varying percentages of p,p′-DDT, 2,2-bis (4-chlorophenyl)-1,1,1-trichloroethane(upto80%),ando,p′-DDT,2-(2-chlorophenyl)-2-(4-chlorophenyl)-1,1,1-trichloroethane (up to 21%, see Table 6.1). No further of the six possible substitution isomers (o,p′-, p,p′-, m,p′-, o,m′-, m,m′- and o,o′-isomers) have been determined, with exception of m,p′-DDD mentioned by Lichtenstein et al. 1971 and Malins et al. (1984) as third isomer in their analysis – although no data were reported. However, beside the two major isomers commercial DDT is a mixture of several closely related compounds with p,p′-DDT as the major component, the o,p′-DDT beside the dechlorinated by-products o,p′- and p,p′-DDD as well as p,p′-DDE. Additionally, bis(p-chlorophenyl)sulfone has been detected in trace amounts (Buser and Müller 1995 and literature cited in there; Zitko 2003).

In the scientific literature information on composition of technical DDT is used, that is based dominantly on the publication by Haller et al. (1945). However, more recent analyses illustrate clear differences in composition (Buser and Müller 1995; Zitko 2003, see Table 6.2). For example, in technical DDT supplied by Dr. Ehrenstorfer (Germany) only o,p′-DDT and p,p′-DDT were detectable beside very small amounts of a third isomer not yet identified (see Fig. 6.2).

Beside its former extended application as pesticide some further application of DDT related formulations are still leading to environmental contaminations. Constant usage

Table 6.1 Composition of technical DDT formulations

o,o′-DDT	o,p′-DDT	p,p′-DDT	o,p′-DDD	p,p′-DDD	p,p′-DDE		Literature
–	≤30	85	–	–	–		WHO (2009)
0.1–1.0	8–21	63–77	–	–	–		WHO (1976)
–	15	77	–	–	–		Wikipedia (2010)
	17.5	79	0.35	1.2	0.2	Tris(4-chloro-phenyl)-methane	Buser and Müller (1995)
	15.6	79	0.6	2.1	0.2	Tris(4-chloro-phenyl)-methane	Buser and Müller (1995)
	19.0	66.7	–	0.3	–	Bis(4-chloro-phenyl)-sulfone (0.6)	Haller et al. (1945)
	11.9	72.7	0.044	0.17	–	Bis(4-chloro-phenyl)-sulfone (0.034)	Haller et al. (1945)

Table 6.2 Summary of some physico-chemical data of DDT, DDD and DDE according to Lee et al. (1994)

Compound	DDT	DDE	DDD
Molecular weight	354.5	318	320.1
Water solubility [ppb at 25°C]	5.5 (p,p′-DDT) 26.0 (o,p′-DDT)	14.0 (p,p′-DDE)	20.0 (p,p′-DDD)
Vapor pressure ($\times 10^{-1}$ Torr)	7.3 (p,p′-DDT) 55.0 (o,p′-DDT)	65.0 (p,p′-DDE) 62.0 (o,p′-DDE)	10.0 (p,p′-DDD) 19.0 (o,p′-DDD)
log K_{ow}	6.91	6.96	6.22
log BCF (Fish)	4.52 (Fathead Minnow) 4.58 Trout	4.71 (Fathead Minnow) 7.26 Trout	5.24 (Estimated)

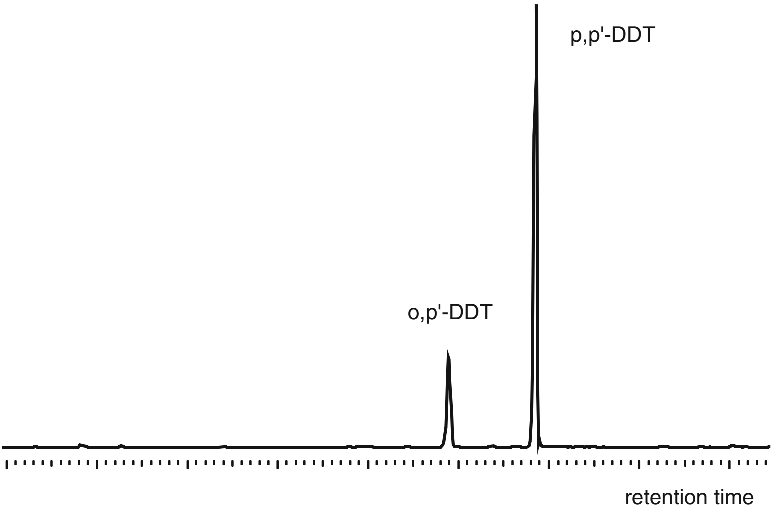

Fig. 6.2 Gas chromatogram of technical DDT as received from Dr. Ehrenstorfer

of DDT as vector control in Africa, China and Mexico (e.g. Karlsson et al. 2000) leads to current pollution in these regions. Secondly, DDT is also used in antifouling paints in China (Lin et al. 2009). Also the acaricide dicofol, a hydroxylated derivative of DDT, is under current usage in Europe, Trukey, Asia and USA. Dicofol is produced by hydroxylation of DDT and, consequently, its application leads to DDT pollution. Some further minor sources of DDT related emissions are also known. E.g. o,p′-DDD was produced and applied in human and veterinary medication as antineoplastic medicine (trade name: Lysodren).

Once released to the environment DDT is affected dominantly by biotic transformation. The principal degradation pathways under aerobic and anaerobic conditions have been intensively investigated and published (Wetterauer et al. 2011). Commonly 3-/4-letter abbreviations are used for the denotation of DDT metabolites. A detailed

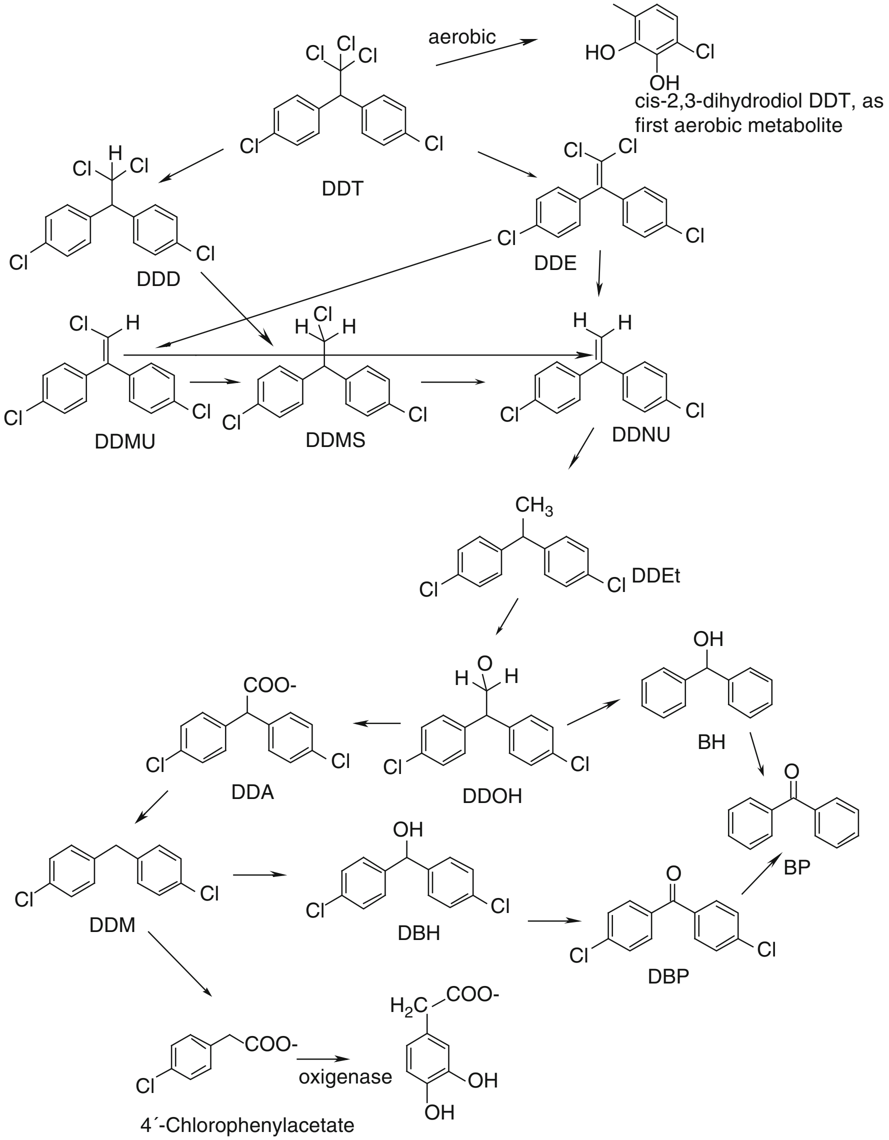

Fig. 6.3 Simplified anoxic degradation pathways of *p,p′*-DDT in aquatic systems (According to Sayles et al. 1998; Zeng and Venkatesan 1999; Eganhouse and Pontolillo 2008; Feng and Turnbull 2011; adapted by Wetterauer et al. 2011). The position of DDCN has only partially been enlightened through the direct pathway from DDT to DBP (Metcalfe 1973)

view on the anaerobic degradation pathway is depicted in Fig. 6.3 and can be easily summarized as follows:

- Initial transformation processes affect the aliphatic moiety of the molecule forming dehalogenated intermediates with or without double bonds (DDD, DDE, DDMS, DDNS, DDMU, DDNU).

- After dehalogenation a second group of metabolites are formed with functional groups at the position of the former trichloromethyl-group. These functional groups include hydroxyl-, carboxy- and nitrilo-moieties (DDA, DDOH, DDCN).
- Further on, biphenyl derivatives are formed by the loss of the 1-carbon atom forming either dichlorinated diphenylmethane (DDM) or dichlorinated benzophenone (DBP).

During all these anaerobic transformation processes the o,p′- or p,p′-substitution at the aromatic rings remain unaltered. The same accounts for the aerobic degradation pathway.

Since the amount and stability of metabolites depends on the generation and degradation rate, those metabolites with high formation rates but low degradation rates accumulate dominantly. Under anaerobic conditions the main metabolite is DDD, whereas under aerobic conditions DDE is the most representative metabolite.

For assessing the environmental mobility of DDT contaminations the knowledge on the physico-chemical properties of the metabolites are essential information. E.g. all metabolites of the initial transformation processes under anaerobic conditions are highly lipophilic and tend to accumulate in particulate matter. On the contrary, functionalized metabolites like DDA exhibit higher polarity and, therefore, higher water solubility. Consequently, DDA was observed as water relevant contaminant (Heberer and Dünnbier 1999; Frische et al. 2010). An overview on environmentally relevant properties of DDT and its main metabolites DDD and DDE are given in Table 6.2. However, such data has to be used carefully. Recently, a review by Pontolillo and Eganhouse (2001) revealed a variation of published log K_{OW} for p,p′-DDE in the range of 1–2 units.

Further information on DDT and its environmental behaviour as well as its ecotoxicological and toxicological effects have been summarized by Zitko (2003).

It is known for decades that isomeric composition can be influenced substantially by environmental processes, in particular by biotransformation and transfer between compartments. Hence, if the original isomer composition is known, the alteration of isomer ratios can be used to trace these environmental processes. In particular, for DDT not only the o,p′/p,p′-ratio itself, but also the modification of this parameter for the DDT metabolites exhibit a high potential to act as key parameters to follow the environmental fate of DDT contaminations. Although DDT analysis has been performed for more than 60 years and since the early 1980s capillary GC is available for isomer-specific analysis an isomer specific approach has not been used intensively. E.g., only very scarce information is available on differences in isomeric persistence (Lichtenstein et al. 1971; Fry and Toone 1981). Baczynski et al. (2010) reported that anaerobic biodegradation leads to different ratios of o,p′-/p,p′-DDT. The interconversion of isomers was early checked in the 2 possible directions from o,p′- to p,p′-DDX and vice versa (Abou-Donia and Menzel 1968; Cranmer 1972). Noteworthy, it was also demonstrated recently that ecotoxicological effects differ for the individual positional isomers of DDT. The o,p′-isomer exhibits stronger estrogenic effects as compared to the ,p,p′-DDT (Wetterauer et al. 2011). Further on, the data situation for reliable isomer specific log Kow-data is inadequate (Pontolillo and Eganhouse 2001).

Therefore, for this literature review over 2,000 literature citations were checked for information on the isomer ratios of DDT and its metabolites in the environment. Generally a lot of analyses included the o,p′-isomers, but unfortunately were not detected or not reported. In many cases only p,p′-isomers are reported or detected (n.d. of o,p′-isomers are very scarce reported, like Eganhouse et al. 2000; Eganhouse and Pontolillo 2008 in PVS, Gillis et al. 1995 in New Jersey Harbor). Hence, only some 50 more recent studies dealed with quantitative data on o,p′-/p,p′- isomers or corresponding isomer ratios, which were all used for this review. In principal, this review on DDT isomers is the only one as far as we know.

Noteworthy, also enantiomeric ratios have to be taken into account although only the o,p′-isomers are optical active (chiral) and may be used for environmental process analysis (relative biodegradation). Recently Buser and Müller (1997) identified (S)-(+)o,p′-DDT is responsible for the strong estrogenic effect (egg shell thinning) leading to the important differentiation between insecticidal and estrogenic action in the environment. Hence a short chapter concerning enantioselective detection of DDT related compounds is added to this review.

6.2 o,p′- and p,p′-DDX in the Atmosphere

Isomer specific data on DDT contamination in the atmosphere are limited. The most relevant investigations of the last 15 years are summarized in Table 6.3. Results obtained from a large-scale passive sampling campaign around south-east Asia has been published by Jaward et al. (2005). The corresponding o,p′-/p,p′-ratios ranged from 0.2 to 3.3 and differ significantly from those values known for technical DDT mixtures. In a more global survey Iwata et al. (1993) detected DDT in the air of different oceanic regions with o,p′-/p,p′-ratios between 0.09 and 2.3.

Interestingly, a major part of measurements were performed on the south-east Asia region. Noteworthy, especially in these regions elevated o,p′-/p,p′-ratios of up to 14 (see Table 6.3) have been reported as the result of an alternative emission source. Many authors suspected the intensive usage of dicofol to be the dominant source for DDT in these regions (Liu et al. 2009; Wang et al. 2010; Qiu and Zhu 2010). Li et al. (2008b), as well as Wang et al. (2010) used DDT isomer ratios to differentiate local DDT emissions from dicofol derived contamination in the Lhasa region and the Tibetan Plateau. The same approach was applied to air samples from Chinese cities by Li et al. (2007), Liu et al. (2009) and Zheng et al. (2010) monitoring the contribution of technical DDT and ‘dicofol-type’ DDT along the seasons (see Fig. 6.4). Louie and Sin (2003) missed to interpret their data accordingly. But in the highly populated area around Lake Taihu, China, dicofol contribution to the DDT contamination in the air was stated by Qiu et al. (2005). On the other hand, Zhang et al. (2008) interpreted elevated o,p′-/p,p′-ratios as the result of preferential mobilisation of o,p′-DDT from contaminated soils to air. The authors substantiate their conclusions not only with the absence of dicofol sources in the area investigated. They also pointed to a 7.5 time greater vapour pressure of the o,p′-isomer

Table 6.3 Literature compilation reporting on o,p′-/p,p′-ratios of DDX in the atmosphere

Atmosphere			DDT			DDE			DDD			
	Location	*Comments*	o,p-Isomer	p,p′-Isomer	o,p-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	Reference
Air concentration (pg/m^3)	China	n=32	4.7–472	2–928	**0.5–2.4**	1.2–75	2.8–380	**0.2–0.4**				Jaward et al. (2005)
	Singapore	n=10	1.3–53	1.9–16	**0.7–3.3**	0.3–4	1.5–10	**0.2–0.4**				
	Japan	n=15	1.4–70	4.4–146	**0.5–0.5**	0.4–10.4	1.62–544	**0.02–0.3**				
	South Korea	n=20	0.3–14	1.9–20	**0.2–0.7**	0.4–1.8	1.5–25	**0.07–0.3**				
Air concentration (pg/m^3)	Chukchi Sea	n=2	0.3–1.7	3.2–5.9	**0.09–0.29**							Iwata et al. (1993)
	Bering Sea	n=5	0.3–1.3	0.7–3.9	**0.33–0.43**							
	Gulf of Alaska	n=4	0.3–1.9	0.3–4.7	**0.4–1**							
	Northern north Pacific	n=14	0.3–14	0.4–27	**0.52–0.75**							
	North Pacific	n=9	0.9–17	0.8–16	**1.06–1.13**							
	Caribbean Sea	n=1	2.1	4.6	**0.46**							
	Gulf of Mexico	n=1	17	22	**0.77**							
	North Atlantic	n=4	0.9–3.1	1.1–9.6	**0.32–0.82**							
	Mediterranean Sea	n=2	3–4.4	2.9–5.3	**0.83–1.03**							
	Red Sea	n=1	3.5	6.8	**0.51**							
	East China Sea	n=3	1.3–20	1.5–15	**0.87–1.33**							
	South China Sea	n=5	8.6–39	3.7–46	**0.85–2.32**							
	Strait of Malacca	n=1	180	220	**0.82**							
	Celebes Sea	n=1	13	23	**0.57**							
	Java Sea	n=1	14	23	**0.61**							

(continued)

Table 6.3 (continued)

Atmosphere			DDT			DDE			DDD			
	Location	*Comments*	o,p-Isomer	p,p′-Isomer	o,p-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	Reference
	Bay of Bengal and Arabian Sea	n = 7	18–420	19–390	**0.95–1.08**							
	Eastern Indian Ocean	n = 5	0.5–2	0.8–3.9	**0.51–0.63**							
	Southern Ocean	n = 5	0.7–1.2	0.9–1.5	**0.78–0.8**							
Air concentration (pg/m^3)	South China Sea	n = 32	61–790	9–230	**1.4–11**							Zhang et al. (2007)
Air concentration (pg/m^3)	Kinngait		0.40	0.29	**1,4**							Li et al. (2008a)
	Tagish		0.65	0.22	**3.0**							
	Dunai		0.18	0.14	**1.3**							
	Mt Waliguan		18	4.4	**4.0**							
	Mt Everest		5.1	3.7	**1.4**							
	Taihu Lake, China		770	120	**6.2**							
	Guangzhou, China		910	720	**1.3**							
	Hong Kong, China		190	360	**0.53**							
	Lhasa	Two sites, (n = 20)	25–770	5–710	**0.5–10.3**							
Air concentration (pg/m^3) Passive sampling	Tibetan Plateau	n = 13	2.1–42	0.6–11	**0.4–6.2**	0.1–8.2	0.9–13	**0.25–2.2**				Wang et al. (2010)

Air concentration (pg/m^3) Passive sampling	Toronto	Urban-rural transect, 7 sites, 3 times, n = 21	2.6–99	2.7–156	**0.59–0.96**				Montelay-Massei et al. (2005)
Air concentration (pg/m^3) Passive sampling	Toronto	Urban-rural transect, n = 6	8–40	10–27	**0.7–0.9**				Harner et al. (2004)
Air concentration (pg/m^3)		Urban-rural transect, 6 sites , 2 times n = 12	11–710	8.6–650	**0.8–1.7**				Zheng et al. (2010)
Air concentration (pg/m^3)	Urban area	(n = 9)	23–620	2–250	**2.5–12**				Zhang et al. (2008)
	Rural area	(n = 6)	0–310	3–390	**0–0.8**				
	Wetlands	(n = 3)	0–78	9–45	**0–1.7**				
Passive sampling (pg/d)	Chinese cities	Winter	97–2,200	31–1,050	**0.21–14**				Liu et al. (2009)
		Spring	33–5,080	11–1,600	**0.16–7.1**				
		Summer	nd–6,620	nd–2,730	**0–5.4**				
	Autumn	Min	25–4,050	20–2,370	**0.37–3.6**				
Air-concentration (pg/m^3)	Hong Kong and Guangzhou	n = 69	<10–3,380	<10–4,530	**0.4–6.8**				Li et al. (2007)
Air-concentration (pg/m^3)	Lake Taihu	n = 21	80–2,750	34–390	**3.9–9.8**				Qiu et al. (2004)
Air concentration (pg/m^3)	Hong Kong	n = 3	22–71	24–29	**0.8–3.0**	34	25	**1.4**	Louie and Sin (2003)

(continued)

Table 6.3 (continued)

Atmosphere			DDT			DDE			DDD			
	Location	*Comments*	o,p-Isomer	p,p′-Isomer	o,p-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	Reference
Air concentration (pg/m^3) Passive and active sampling	Chennai, India	n = 17	17–527	10–77	**0.7–10.5**							Chakraborty et al. (2010)
	New Dehli	n = 15	2–322	10–95	**0.2–20**							
	Mumbai	n = 17	22–462	16–. 469	**0.1–8.2**							
	Kolkata	n = 19	61–823	8–186	**1.1–21.3**							
Air concentration (pg/m^3)	Lake Malawi South Africa	n = 28	<7–41	< 7–140	**0.29**[a]							Karlsson et al. (2000)
Air concentration (pg/m^3)	5 cm above soil	n = 18	120–3,400	100–5,000	**0.68–1.2**	20–380	290–6,900	**0.06–0.07**	25–360	30–880	**0.41–0.83**	Kurt-Karakus et al. (2006)
	20 cm above soil	n = 18	100–2,100	70–3,100	**0.68–1.43**	10–230	210–4,000	**0.05–0.06**	20–230	20–530	**0.43–1**	
	72 cm above soil	n = 18	70–910	40–1,400	**0.65–1.75**	6–120	140–1,700	**0.040.07**	10–110	10–280	**0.4–1**	
	200 cm above soil	n = 18	50–540	40–890	**0.61–1.25**	3–110	90–1,200	**0.03–0.09**	7–90	9–170	**0.53–0.7**	
	Background	n = 6	1.1–3.4	2.3–6.5	**0.48–0.52**							
Air concentration (pg/m^3)	Soil influenced	n = 40	12–164	19–534	**0.3–0.6**							Bidleman et al. (2006)
	Minimal soil influenced	n = 40	<10	<10–19								

[a] Calculated from maximum values

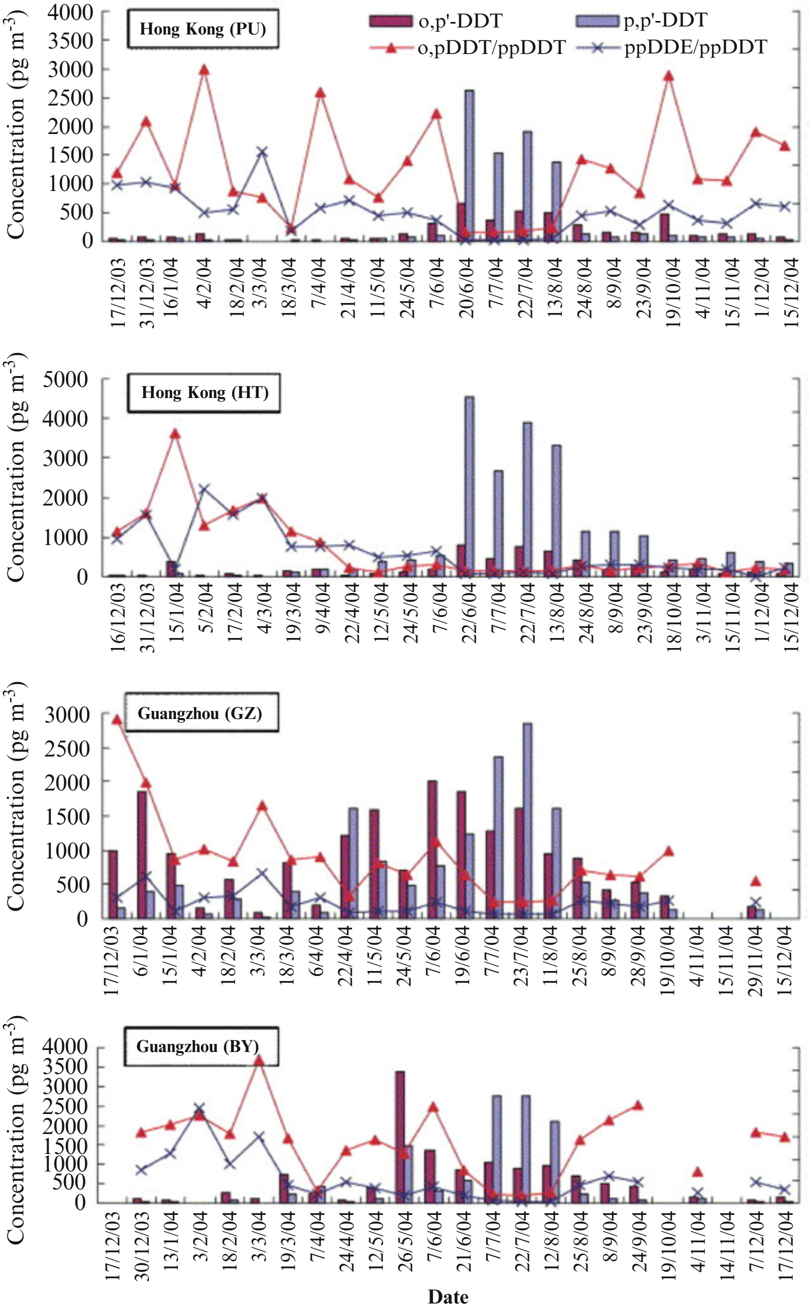

Fig. 6.4 The DDT isomer concentrations and ratios of o,p′-DDT/p,p′-DDT and p,p′-DDE/p,p′-DDT in urban and suburban areas of Hong Kong and Guangzhou, South China (Adapted from Li et al. 2007)

accompanied by a faster metabolism rate of the p,p′-isomer in tropical soils. This argument was also used by Chakraborty et al. (2010) to interpret their observed o,p′-/p,p′-DDT ratios between 0.1 and 21.3 in air samples from Indian cities.

Studies comparable to the approach of Liu et al. (2009) were performed by Harner et al. (2004) and Montelay-Massei et al. (2005). They investigated air samples along a transect from urban to rural areas at Toronto, Canada. The isomer specific data revealed a significant lower o,p′/p,p′-ratio with a lower variation as compared to the Chinese samples.

An overall aim of a couple of studies was to evaluate the DDT exchange rate at water/air or soil/air interfaces. An interesting approach was used by Kurt-Karakus et al. (2006) trying to calculate the tendency of DDT release from contaminated soils in Canada towards the atmosphere. Based on measurements of the concentration profile of DDT in different air layers and the resulting concentration gradient, they calculated soil-to-air fluxes between 90 and 660 ng/m^{2}h. Hence, soil can act as net source of atmospheric DDT contamination and a corresponding volatilization half-life of approx. 200 years for the top 5 cm of the soils has been deduced. This implies still a future problem for decades from agricultural soils. With respect to the isomer distribution no gradient of o,p′-/p,p′-ratios was observed in the soil contamination affected air layers (see Table 6.3). A simpler approach was used by Bidleman et al. (2006) comparing soil and corresponding air samples of agricultural soils from Canada without the measurement of gradients but with discriminating soil influenced from minimal soil influenced air samples. Unfortunately, they neglected an evaluation of isomer related interpretation of their data.

Air-water fluxes of DDT were studied at Lake Malawi, Southern Africa, by Karlsson et al. (2000), in the South China Sea by Zhang et al. (2007) and on a more global level by Iwata et al. (1993). All investigations pointed to a net flux of DDT towards the aquatic systems. Zhang et al. (2007) differentiated DDT air-water fluxes among geographical locations: from water to air close to land and vice-versa in remote marine regions. Further on, they stated a general air-water flux of p,p′-DDE from the water to air.

Although all air-water flux studies detected o,p′- and p,p′-DDT in water and air, the authors failed to compare the isomer ratios in the different compartments. Recalculating the data published by Zhang et al. (2007) as well as Iwata et al. (1993) indicates a clear trend to lower o,p′/p,p′-ratios in the water phase as compared to the atmosphere. It has not been investigated so far, whether this shift relates to the exchange processes at the marine water/air interface.

Beside DDT itself only two publications presented also data on the metabolites DDE and/or DDD. Kurt-Karakus et al. (2006) detected DDE and to a minor extend also DDD in air samples above DDT contaminated soils. In comparison to o,p′-/p,p′-ratios of DDT a similar data range was observed for DDD (0.4 to 1.0) but significantly lower values were detected for DDE in the range between 0.03 and 0.07. This observation was supported by the study of Jaward et al. (1995), in which DDE isomer ratios of 0.03–0.4 were reported, as well as the investigations by Wang et al. (2010) with lower o,p′-/p,p′-ratios for DDE as compared to DDT. Although significant differences in isomer distribution among DDT metabolites were obvious in these studies, no attempts have been made to interpret this phenomenon.

Generally, due to the lack of a comprehensive data set the knowledge on the isomer composition of DDT metabolites in the atmosphere remains very limited.

6.3 o,p′- and p,p′-DDX in Soils

Although the long time application of DDT as pesticides has led to an extensive contamination of soils, the knowledge on changes in isomer distribution is restricted too. Ten relevant references as presented in Table 6.4 address mostly surface soils, but two studies subdivided their work into top soil and subsurface soil. Only in two case studies the application of DDT (Martijn et al. 1993) and the sludge amendment (Meijer et al. 2001) was followed for more than a decade. Further on, no global study is available, but most of the reports focus on the USA/Canada and SE-Asia.

Investigations in Asia mostly used isomer ratio data for differentiating dicofol contributions to the overall DDT contamination. Hence, the data from Asia are influenced by more recent applications of dicofol and technical DDT as antifouling agent. DDT ratios are in the range of ND – 6.57 (n = 9), those for DDE and DDD are between ND – 1.09 (n = 4) and 0.16–1.07 (n = 2), respectively.

Qiu et al. (2005) have proposed the o,p′-/p,p′-DDT ratio as indicator for dicofol-type DDT pollution ranging from 1.3 to 9.0 (Di Muccio et al. 1988, Gillespie et al. 1994), cited in Qiu et al. (2005). Yang et al. (2008) revealed through analysis of cotton field soils in China a high residual contamination due to the application of dicofol. The o,p′- DDT and o,p′-DDE concentrations in top soils were significantly higher than in deeper soil layers (see Table 6.4). Calculating the o,p′-/p,p′-DDT ratio they deceived a historical DDT contamination although a contamination of the top soils by dicofol could not be ruled out. o,p′-DDD was not detected in any sample. Work by Li et al. (2008a, b) on soils in the Yangtze River area (China) indicates only for one soil in a vegetable field (nr. 4) a dicofol-based contamination (see Fig. 6.5).

Analyses of karst cave soil samples from China (Silvie and Shihua 2009) indicated fresh applications of dicofol as the main source of the contamination. Monitoring analyses of soils from the Wolong Nature Reserve, Sichuan, China (Chen et al. 2008) indicate the application of dicofol and atmospheric deposition on soils by o,p′-/p,p′-DDT ratios >1 up to an altitude of 4,600 m, noteworthy, with increasing concentrations at higher altitude. Furthermore, several studies detected o,p′- and p,p′-isomers but did not reveal any clear correlation of ratio changes with environmental processes or source pattern. Aigner et al. (1998) analysed surface soils from the corn belt region (USA) for past emissions with no clear trend in isomer-specific ratio and concentrations ranging from limit of quantitation to over 1,000 ng/g d.w. per individual isomer. Gaw et al. (2006) analysed soils in New Zealand and presented min/max/mean data. The isomer-specific ratios indicate an emission of technical DDT or pesticide formulation by ratios <1 for DDT, DDD and DDE.

Meijer et al. (2001) analysed soil residues in sludge amended and non-amended Luddington soils in GB. The depletion over time is not statistically significant. With the exception of 1944, levels of p,p′-DDE were higher than DDT, indicating

Table 6.4 Literature compilation reporting on o,p′-/p,p′-ratios of DDX in the soil

Soil			DDT			DDE			DDD			
	Location	*Comments*	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	Reference
Agricultural soil (ng/g) d.w	Broadbalk (UK) (1944–1986)	n = 5	0.07–0.88	0.56	**0.4–0.9**							Meijer et al. (2001)
Soil/slugde (ng/g) d.w	Luddington (1972–1990)	n = 10	0.4–1.2	0.14–1.3	**0.45–2.1**							
Surface soil (0–15 cm) (ng/g) d.w.	Ohio (USA)	n = 15	0.52–2,150	0.59–7,640	**0.1–0.9**							Aigner et al. (1998)
	Indiana	n = 3	0.7–45	1.5–106	**0.3–0.6**					0.88		
	Illinois	n = 4	0.7–2.1	0.5–12	**0.14–1.6**							
Soil cores (mg/kg) d.w.	Wageningen, (NL) (1969–1989) (0–60 cm)	n = 54	nd–13	nd–60	**nd–0.31**	nd–0.01	nd–0.51	**nd–0.02**				Martijn et al. (1993)
Surface soil (μg/kg) d.w.	Yangtze River Delta (China)	Range	1.1–16	1.3–102	**0.15–0.9**	0.6–25	0.6–184	0.13–1.0	0.3–5.6	0.3–27	**0.2–1.1**	Li et al. (2008a, b)
Surface soil (μg/kg) d.w.	Wolong Nature Reserve Sichuan	Range	0.07–0.4	0.02–0.4	**1–3.5**							Chen et al. (2008)
Cotton soil (ng/g) d.w.	Jangshua Province, China	Topsoil	nd–57	1.3–109	**nd–0.53**	nd–6.34	1.7–546	**nd–0.1**				Yang et al. (2008)
		Subsoil	nd–28	0.8–124	**nd–0.22**	nd–4	1.8–501	**nd–0.008**				
Vegetable soil (ng/g) d.w.		Topsoil	nd–4.6	1.4–7.6	**nd–0.6**	nd–1.6	2.2–13	**nd–0.12**				
		Subsoil	0.7–4.6	0.8–5.8	**0.8–0.9**	0.5–1	1.8–12	**0.08–0.28**				
Soil (ng/g) d.w.	Guilin, China		0.05–0.5	nd–0.09	**nd–5.1**							Silvie and Shihua (2009)
Cave soil (ng/g) d.w.	Dyan Cave		0.05–0.47	nd–0.09	**nd–6.57**							
Agricultural soil (ng/g) d.w.	Southern Ontario, (Canada)	2003	3,000	1,100	**2.7**	64	5,100	**0.01**	1,200	3,700	**0.3**	Kurt-Karakus et al. (2006)
		2006	3,200	1,100	**2.9**	90	3,100	**0.03**	400	1,200	**0.3**	

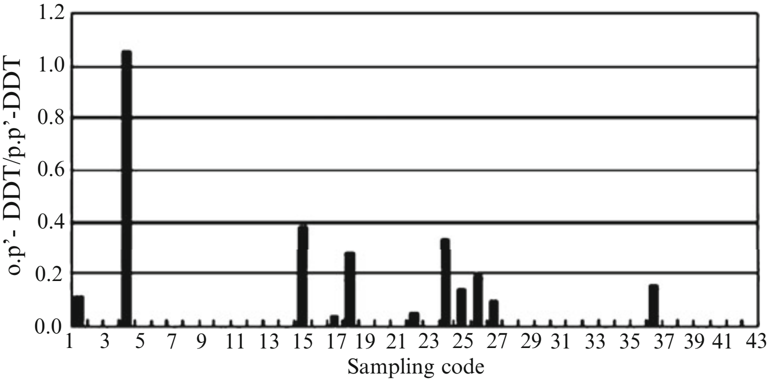

Fig. 6.5 o,p′-/p,p′- ratios in soils from the Yangtze River Area (Li et al. 2008b)

the recalcitrance of degradation at low concentrations. Differences in half-life between o,p′- and p,p′-DDT ranged between 14 and 12 years for o,p′-DDT and 11.8 and 10.5 years for p,p′-DDT in control soils and sludged soils, respectively. Hence, a slightly isomer specific degradation was observed in this study. Finally, the half-lives for p,p′-DDE were in the range of 40.9 and 17.2 years for control soils and sludge, respectively.

Martijn et al. (1993) analysed over a period of 15 years the residues of applied chemicals as long-term trial and checked for vertical distribution over time. Based upon their results the half-life of technical DDT in soils is approx. 20 years. Interestingly, the half-life time varied with isomers, for o,p′-DDT approx. 15 to 20 years and for p,p′-DDT around 20 years. Hence a higher stability for the p,p′-isomer was evident. Likewise, Lichtenstein et al. (1971) performed a 15 year long-term test. An agricultural soil was applied with DDT in 1954 and during the following 15 years at certain time intervals samples were analysed for DDT and metabolites (o,p′-DDT, p,p′-DDE). On the contrary, the results indicated that the o,p′-DDT isomer was slightly more persistent than the p,p′-isomer which correlates well with the study by Meijer et al. (2001) but contradicts the results of Martijn et al. (1993). During the 15 year time span only 75.2% of o,p′-DDT was lost relative to 84.5% of the p,p′-DDT.

Kurt-Karakus et al. (2006) investigated the soil-air flux in historically contaminated soils in Canada and calculated based upon their experiments a volatilization half-life of ~200 years for the top 5 cm of the soils representing still a future problem for decades from agricultural soils in Canada with different gradients for the DDT isomers (see Chap. 2), indicating differences in volatility between the o,p′- and p,p′-isomers. Furthermore, Menchai et al. (2008) revealed isomer-specific differences in uptake into SPMD from spiked soil samples and an aged sandy soil from 1962 (1,880 mg ΣDDT/kg d.w.). The results refer to still (bio)available fractions decades after application.

Table 6.5 o,p′-/p,p′-DDA concentrations (ng/L) and ratios in Teltow Canal and related groundwater

Sample	o,p′-DDA	p,p′-DDA	o,p′/p,p′-DDA ratio	Reference
Surface water Teltow Canal (n = 6)	30–110	33–760	0.2–0.4	Heberer and Dünnbier (1999)
Industrial contaminated groundwater near Teltow Canal (n = 9)	2,000–39,000	4,000–140,000	0.02–0.5	Frische et al. (2010)

In summary, isomer specific data of DDT in soils have been frequently used for pollution source apportionment and to differentiate DDT and dicofol contamination. But isomer analysis pointed also to environmental processes affecting the isomer ratios. o,p′-DDT seems to be more resistant against microbial degradation, and transfer processes appeared to be also responsible for isomer shifts in soil. Finally, although the formation of non-extractable residues (NER) of DDT in soils is very well known since the 1970s no isomer-specific data for bound DDX are available.

6.4 o,p′- and p,p′-DDX in Water

Since DDT and most of its metabolites exhibit low polarity and, consequently, are characterized as lipophilic compounds, they tend to accumulate in particulate matter rather than in water. The only more polar DDT metabolite is DDA. Hence, in Table 6.5 only five relevant studies are presented that dealt with isomer-specific analyses of water samples, subdivided into groundwater (one reference) and surface water. The o,p′/p,p′-ratios were for DDT in the range of 0.11–3 (n = 3) , for DDE at 0.11 (n = 1) and for DDD in the range of 0.02–0.91 (n = 2). Only at one location (Teltow Canal) further isomeric concentrations are reported for water and sediment samples.

Iwata et al. (1993) collected surface ocean water data for o,p′-/p,p′-DDT ratios worldwide, indicating a higher ratio close to recent dicofol sources in Asia. Zhang et al. (2007) analysed surface water samples from the South China Sea and postulated for three samples sources other than technical dicofol by their isomer ratios above 1.

Cotter et al. (1996) analysed pore water from a contaminated area in Huntsville Spring Branch – Indian Creek near Huntsville (USA) with no clear trend regarding the isomer ratios. Awofolu and Fatoki (2003) analysed water and sediment samples in the Eastern Cape Province (South Africa) for endocrine disruptors. The isomer-specific data for DDT and DDD (p,p′-DDE was not measured) indicate a recent application of DDT in the agricultural region. Also in this study the ratios indicated no clear trend of pesticide source, as the ratio is in the range of smaller/equal and higher than 1. Zeng et al. (2004) performed a monitoring analysis of water samples at three locations off the California coast (USA) by means of SPME revealing high variations of o,p′-/p,p′-DDE ratios without any systematic trend.

Analyses of groundwater samples at a former pesticide production site at Teltow Canal, Berlin (Germany), revealed high concentrations of DDT and its metabolites with no clear trend in isomer-specific ratios (Frische et al. 2010). However, it is assumed that a non aqueous phase liquid is responsible for the accumulation of non polar metabolites in the ground water as well. Accordingly, the surface water contaminated by the same source revealed only a very low DDD contamination with o,p′-/p,p′-isomer ratios up to 0.67. Former studies indicated a very low contamination in surface waters close to the Teltow Canal by non polar metabolites but a significant occurrence of the most polar and, therefore, best water soluble metabolite DDA (Heberer and Dünnbier 1999). Its o,p′-/p,p′-isomer ratios varied between 0.24 and 0.38, which fit very well the riverine DDA isomer data reported by Frische et al. (2010) (see Table 6.6).

6.5 o,p′- and p,p′-DDX in Aquatic Sediments

In the aquatic environment DDT contamination is dominantly associated to particulate matter due to the lipophilicity of the majority of DDT related compounds. Table 6.7 summarizes relevant studies performed on aquatic sediments that reported also on DDX isomer composition. The 12 references focus mainly on surface sediment samples, except 3 references dealing with subsurface sediments or sediment cores. No global study is available, but the dominant focus lays on USA/Canada/Europe and SE-Asia. In many cases the initial composition of the primary pollution is unknown. However, a highly variable composition depending on the production location is assumed (Lee et al. 1994). E.g., for two Superfund Sites in USA (Palos Verdes Shelf, California) and Germany (Teltow Canal, Berlin) the different production processes and the release of production waste into adjacent water bodies resulted in different contamination patterns over time spans of decades.

In summary, as presented in Table 6.7, the overall isomer-specific ratios are in the range of 0.01–1.2 (n = 8) for DDT, 0.1–1.03 (n = 12) for DDE and 0.01–1.21 (n = 12) for DDD. Beside the case studies at the Teltow Canal (Germany), where more than 20 congeners isomer-specifically were determined, only the six congeners routinely measured are reported.

In the marine environment several studies dealed with the DDX contamination, but only very few measured isomer specific data. Strandberg et al. (1998) analysed sediment trap samples and biota from the northern Baltic Sea with no clear regional trend. The isomer-specific ratios indicate aged applications of technical DDT/DDT-based pesticides. Analyses by Falandysz et al. (1999) on sediment samples from the Baltic South coast revealed technical DDT or formulations of DDT as source via the an o,p′-/p,p′-ratio well below one.

A lack of isomer specific data is also valid for the aquatic freshwater environment. Schwarzbauer et al. (2001) analysed in detail the isomer-specific distribution

Table 6.6 Literature compilation reporting on o,p′-/p,p′-ratios of DDX in water

Water			DDT			DDE			DDD			
	Location	*Comments*	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	Reference
Surface water (ng/l)	Berlin (Germany) Teltow Canal	n = 5							<5–50	<5–140	**0.25–0.7**	Heberer and Dünnbier (1999)
Surface water (pg/l)	Asia Chinese Sea	n = 9	4–278	21–844	**0.2–2.0**							Zhang et al. (2007)
Ground water (µg/l)	Berlin (Germany)	n = 3	<10–6,000	130–17,000	**0.2–0.55**				7–6,200	50–6,800	**0.02–0.91**	Frische et al. (2010)
Surface water (pg/l)	Chukchi Sea	n = 3	0.1	<0.1–0.10	**<1**							Iwata et al. (1993)
	Bering Sea	n = 4	<0.1	0.1	**<1**							
	Gulf of Alaska	n = 3	0.1–0.2	0.5–1.3	**0.15–0.2**							
	Northern North Pacific	n = 12	<0.1–1.6	0.3–2.5	**<0.3–0.6**							
	North Pacific	n = 8	0.2–0.5	0.1–1.3	**0.4–2**							
	Carribean Sea	n = 1	0.8	2.6	**0.31**							
	Gulf of Mexico	n = 1	0.6	1.4	**0.43**							
	North Atlantic	n = 4	0.1	0.2	**0.5**							
	Mediterranean	n = 2	0.3–0.5	0.8–0.9	**0.4–0.6**							
	Red Sea	n = 1	0.2	0.1	**2**							
	East China Sea	n = 3	0.3–14	0.7–19	**0.4–0.7**							
	South China Sea	n = 6	0.5–5.1	1.3–7.4	**0.4–0.7**							
	Strait of Malacca	n = 1	2.6	2.9	**0.9**							
	Celebes Sea	n = 1	0.5	1.1	**0.45**							
	Java Sa	n = 1	1.3	3.4	**0.38**							

	Bay of Bengal and Arabian Sea	n = 7	0.3–8.5	0.9–10	**0.3–0.9**							
	Eastern Indian Ocean	n = 5	0.3–1	<0.1–2.4	**<0.42–3**							
	Southern Ocean	n = 5	0.1–0.2	0.1–0.5	**0.4–1**							
Pore water (ng/ml)	Huntsville (USA)	n = 7				0.13–0.61	0.52–2.48	**0.19–0.27**	0.45–2.39	1.58–8.19	**0.22–0.47**	Cotter et al. (1996)

at the Teltow Canal and in the vicinity of the point source. Starting with a survey of surface sediments influenced by the point source and applications in the German Democratic Republic they focused on sediment cores close to the production effluents. In addition to the 6 standard congeners more than 24 congeners were quantified isomer-specifically. The data reveal no clear trend in ratios, indicating technical DDT or synthesis waste as the source of DDT. Even the most polar metabolite DDA was detected in sediment samples. The total concentrations ranged between a few ng/g up to several 100 μg DDX/g d.w.

De la Cal 2008 analysed fish and sediments from Cinca River, a tributary of Ebro River (Spain), indicating different bioaccessibility (see Table 6.7) with elevated o,p′-/p,p′-DDT ratios as dicofol-indicator. The changes between 1999 and 2002 are evident.

Ricking and Terytze 1999 detected isomers of DDD and DDE in sediment samples from the Bulgarian Danube without a clear trend. No DDT was detected in the samples. The isomer-specific ratios indicate past applications of DDT or technical DDT. Awofolu and Fatoki (2003) detected in riverine sediment samples from Eastern Cape (South Africa) DDT and its metabolites in isomer-specific analyses not matching the distribution in technical DDT or dicofol. Hu et al. 2010 analysed surface sediments from Baiyangdian Lake in North China but presented only ranges of the specific isomers and no data for calculation. The graphic presentation indicates a higher variability in isomer-specific contribution to the sum DDT.

Noteworthy, Hale et al. (2009) used isomer specific data to obtain information on environmental processes. They measured different partition and mass transfer coefficients for different isomers between water and sediment in sediments from the Lauritzen Canal (SF Bay, USA) via PED strips and applied modelling parameters for charcoal – pore water – sediment distributions. Clear differences in desorption have been obtained with respect to the o,p′- and p,p′-isomers of DDT and DDD (see Fig. 6.6) indicating an isomer specific partition behaviour.

However, most of the studies used o,p′-/p,p′-ratios for emission source apportionment and to differentiate dicofol from DDT pollution. Tao et al. (2007) analysed the distribution of DDT isomers in Tianjin Rivers (China) indicating quite different distribution patterns for isomers in water-suspended particulate matter -sediment systems. The o,p′-DDX compounds comprised usually up to 8% of the total DDTs, except for 2 SPM samples from Yongding River. In these two samples the percentage of o,p′-Isomers reached up to 75% due to the vicinity to Renmin Pesticide Factory where dicofol was manufactured. The o,p′-isomers in the products build up to one-third of the total DDT. Detailed isomer-specific analyses of surface sediments in fishing harbours in China (Lin et al. 2009) eventuated in a technical-DDT like pattern with p,p′-isomers dominating over o,p′-isomers. These analyses indicate antifouling paint as a source of DDT, keeping in mind that roughly 50% of the applied antifouling paint is DDT-based with high residues of Σ DDT in the range of 525–2,360 μg/g (Zhang et al. 2007 and SEPA GEF project 2008; cited in Lin et al. 2009).

Although the formation of bound DDT residues is known for decades for the soil compartment, this aspect has been neglected so far in isomer specific analysis as

Table 6.7 Literature compilation reporting on o,p′-/p,p′-ratios of DDX in aquatic sediments

Sediment			DDT			DDE			DDD			
	Location	*Comments*	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	Reference
Surface sediment (µg/kg) d.w.	Ebro River (Spain)	1999			**≤0.07**							De la Cal et al. (2008)
		2002			**≤0.26**							
Offshore and coastal surface sediments (ng/g) d.w.	Baltic Sea (Sweden)	n = 14 offshore	0.04–1.2	0.42–4.8	**0.01–0.25**	0.02–0.33	0.48–5.2	**0.02–0.06**	0.04–1.4	0.32–4.2	**0.03–0.82**	Strandberg et al. (1998)
Surface sediments (ng/g) d.w.	Danube River Bulgaria	n = 5				nd–1.4	nd–3.7	**nd–0.38**	0.6–4.2	1.5–10.2	**0.29–0.53**	Ricking and Terytze (1999)
	Lake Srebarna	n = 4				0.1–0.4	0.7–6.4	**0.05–0.36**				
Sediment core (µg/kg) d.w.	Teltow Canal Berlin (Germany)	n = 3				1–2	4–34	**0.03–0.25**				Kronimus et al. (2006)
Surface sediments (µg/kg) d.w.	Havel River (Germany)	n = 9				1–39	5–278	**0.01–0.19**	1–152	4–427	**0.01–0.36**	Schwarzbauer et al. (2001)
	Spree River	n = 5				1–4	3–71	**0.06–0.33**	1–16	1–82	**0.1–1**	
	Teltow Canal	n = 4				6–10	61–180	**0.04–0.13**	13–940	52–2,900	**0.25–0.32**	
Sediment core (µg/kg) d.w.	Teltow Canal Berlin (Germany)	Extractable fraction n = 4	5–4,200	5–9,700	**0.4–1.0**	360–3,700	3,500–13,000	**0.1–0.4**	5,200–50,000	9,500–130,000	**0.3–0.6**	Schwarzbauer et al. (2003)
		Bound fraction n = 4				<20–330	<20–500	**0.4–0.9**	<20–13,000	<20–38,000	**0.1–0.6**	
Surface sediments (µg/kg) d.w.	Lauritzen Canal (USA)	n = 21	nd–2,550	3–34,000	**0.02–0.14**	0.1–105	1–1,500	**0.05–0.25**	1–6,300	5–32,000	**0.13–0.33**	Lee et al. (1994)
Surface sediment (ng/g) d.w.	Baiyangdian Lake (China)					0.17–0.22	0.4–0.6	**0.33–0.43**	0.2–0.8	0.4–1.1	**0.5–0.73**	Hu et al. (2010)
	Fu River					0.2–2.4	0.4–13	**0.18–0.5**	0.2–4.5	0.4–16	**0.28–0.5**	

(continued)

Table 6.7 (continued)

Sediment			DDT			DDE			DDD			
	Location	*Comments*	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	Reference
Surface sediment (ng/g) d.w.	Baltic Coast		1.8	9.1	**0.2**				5	21	**0.23**	Falandysz et al. (1999)
Surface sediments Fishing Harbors (ng/g) d.w.	Sanya (China)		3.7–27	12–46	**0.31–6**	0.13–1.0	11.0–130.0	**0.008–0.01**	15–87	54–270	**0.28–0.32**	Lin et al. (2009)
	Maoming		34–140	67–180	**0.51–0.78**	0.3–1.3	20–96	**0.013–0.015**	50–210	190–830	**0.25–0.26**	
	Macao		29–530	65–1,200	**0.44–0.45**	1.3–1.5	170–420	**0.003–0.008**	130–760	520–2,900	**0.25–0.26**	
	Zhuhai		0.53–130	2.2–310	**0.24–0.42**	0.11–2.5	9.3–280	**0.009–0.01**	9.7–520	32–2,000	**0.26–0.3**	
	Hong Kong		4.3–1,500	9.4–2,300	**0.46–0.65**	0.2–3	20–300	**0.01**	8.7–650	34–2,600	**0.25–0.26**	
	Stenzhen		0.1–21	0.36–37	**0.28–0.57**	0.17–2	2–220	**0.01–0.09**	2.6–270	5.4–940	**0.29–0.48**	
	Guangzhou		3–12	3.6–10	**0.83–1.2**	nd–0.13	3.2–13	**nd–0.01**	2.4–6.7	9.5–27	**0.25**	
	Zhoushan		0.58–110	2.2–200	**0.26–0.55**	nd–0.36	1.6–91	**nd–0.004**	1.3–40	3.5–140	**0.28–0.37**	
	Quingdao		0.47–73	2.0–160	**0.24–0.46**	nd–0.49	1–46	**nd–0.01**	1.0–110	3.9–450	**0.24–0.26**	

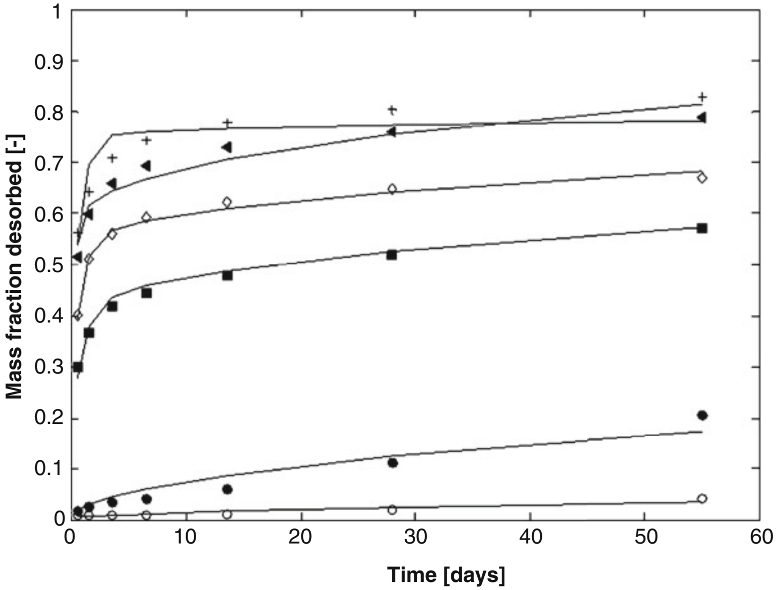

Fig. 6.6 Measured (*symbols*) and modelled (*lines*) mass fractions of DDT and its metabolites desorbed from untreated Lauritzen Channel sediment according to Hale et al. (2009). Data are shown for p,p′-DDT (●), o,p′-DDT (◦), p,p′-DDD (+), o,p′-DDD (◀), p,p′-DDE (■) and p,p′-DDMU (◊)

already mentioned in Chap. 3. However, DDT is forming non-extractable residues (NER) also in aquatic particulate matter and for these sediments a few isomer specific data are available for bound DDT residues. However, the studies published by Schwarzbauer et al. (2001, 2003) and Kronimus et al. (2006) are the only available reports so far. The concentrations were in the range of a few µg/g up to more than 100 µg/g d.w. in sum of extractable DDX and the same order of magnitude of DDT in the bound state. However, comparing the o,p′-/p,p′-ratios of all isomers in the free and bound fraction revealed no clear trend.

6.6 o,p′- and p,p′-DDT in Biota

Since biological samples cover a wide range of organisms, environmental analyses applied to biota are inhomogeneous and the corresponding data exhibit a high variety. Both facts hinder a reasonable comparison of environmental data on DDT residues in organisms. Regarding the substitution isomers of DDT and its metabolites, there are only a limited number of publications presenting individual concentration values or calculated o,p′-/p,p′-ratios as presented in Table 6.8.

Table 6.8 Literature compilation reporting on o,p′-/p,p′-ratios of DDX in biota

Organism			DDT			DDE			DDD			
	Comments		o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	Reference
Lichens, mosses, mango (ng/g dw)	Scandinavia		0.9	1.6	**0.6**							Calamari et al. (1991)
	New Delhi		11	78	**0.1**							
	Nepal		2.4	14	**0.2**							
	Nepal mountains		4	11	**0.4**							
	Everest		1.8	2.0	**0.9**							
	Guatemala		0.4	2.9	**0.1**							
	Mali-Guinea		4.3	37	**0.1**							
	Amaruco Delta		2.1	28	**0.1**							
	Benin-Burkina Faso		1	5.1	**0.2**							
	Suhurn, Ghana		0.8	2.4	**0.3**							
	Ivory Coast		0.7	3.3	**0.2**							
	Accra, Ghana		1.5	15	**0.1**							
	Amazonas		7.7	52	**0.2**							
	Mount Kenya		1	4	**0.3**							
	Mombasa, Kenya		5.7	14	**0.4**							
	Bolivia		0.4	1.2	**0.3**							
	Terra del Fuego		0.2	0.15	**1.3**							
Pine needles (ng/g dw)	Netherlands	n = 6	0.3–1.6	1.1–2.2	**0.5**^{a}	<0.1	1.1–1.8					Calamari et al., (1994)
	Slovakia	n = 6	<0.1–9.8	4.2–23	**0.3**^{a}	<0.1–2.4	7.9–79	**0.02**^{a}				
	Austria	n = 3	<0.1	0.9–2.0		<0.1–0.9	1.4–5.3	**0.2**^{a}				
	Italy	n = 18	0.3–14	2.6–79	**0.2**^{a}	<0.1–0.9	1.6–39	**0.04**^{a}				
	Greece	n = 3	1.8–2	2.8–6	**0.5**^{a}	<0.1	2.6–9.4					
Alligator eggs (ng/g)	Orange / Lochloosa	n = 19	1.0^b	0.8^b	**1.3**^{a}				0.8^b	2^b	**0.4**^{a}	Rauschenberger et al. (2007)
	Apopka	n = 23	11^b	9^b	**1.2**^{a}				5^b	42^b	**0.1**^{a}	

	Emeralda Marsh	n = 31	170[b]	12[b]	**14[a]**				37[b]	1300[b]	**0.03[a]**	
	Lake Griffin	n = 42	4[b]	5[b]	**0.8[a]**				1[b]	7[b]	**0.1[a]**	
Laysan albatross,fat	Pacific Ocean	n = 20	20–42	67–300	**0.1–0.3**	2.6–8.6	680–1,500	**0.004–0.006**	4.1–10	18–40	**0.2–03**	Muir et al. (2002)
Blackfooted albatross, fat		n = 6	70–120	510–940	**0.1**	9.4–27	2,200–4,600	**0.004–0.006**	11–30	90–140	**0.1–0.2**	
Blackfooted albatross, eggs (ng/g)		n = 2	3–9.7	13–83	**0.1–0.2**	0.5–1.5	140–330	**0.004–0.005**	1.4–2.6	1.4–4.4	**0.6–1.0**	
Rice field fish (ng/g dw)	Nashindi, Bangladesh		1.7–38	7.9–140	**0.2–0.3[c]**							Abdullah et al. (1997)
Eel (ng/g wet weight)	Scotland	n = 30	<1.0–10.5	<1.0–251	**0.06–0.2**							Macgregor et al. (2010)
Salmon (ng/g)	Strait of Georgia	n = 1	0.5	0.3	**1.9**	0.08	3.5	**0.02**	0.06	0.4	**0.2**	Cullon et al. (2009)
	Johnstone Strait	n = 6	0.07[b]	0.1[b]	**0.7[a]**	0.07[b]	0.9[b]	**0.08[a]**	0.07[b]	0.3[b]	**0.3[a]**	
	Lower Fraser River	n = 6	0.04[b]	0.2[b]	**0.2[a]**	0.04[b]	3.3[b]	**0.01[a]**	0.06[b]	0.6[b]	**0.1[a]**	
	Puget Sound,	n = 1	0.02	0.1	**0.2**	0.02	2.4	**0.008**	0.01	0.1	**0.08**	
	Duwanish River	n = 6	0.1[b]	0.4[b]	**0.3[a]**	0.1[b]	15[b]	**0.007[a]**	0.2[b]	2.9[b]	**0.07[a]**	
Barbel fish, muscle	Ebro River, Spain	n = 4			**0.8–3.0**							De la Cal et al. (2008)
Barbel fish, liver		n = 4			**0.3–5.5**							
Bleak fish (ng/g)		n = 4			**0.8–11**							
Largemouth bass fish (ng/g)	TombigBee River											Hinck et al. (2009)
	Childersburg	n = 10	0.1[b]	1.4[b]	**0.07[a]**	0.9[b]	60[b]	**0.02[a]**	0.2[b]	4.1[b]	**0.05[a]**	
	Eureka	n = 10	0.1[b]	1.7[b]	**0.06[a]**	3.1[b]	29[b]	**0.1[a]**	0.4[b]	3.5[b]	**0.1[a]**	
	Lavaca	n = 11	0.1[b]	2.2[b]	**0.05[a]**	1[b]	19[b]	**0.05[a]**	0.02[b]	3.7[b]	**0.005[a]**	

(continued)

Table 6.8 (continued)

Organism			DDT			DDE			DDD			
	Comments		o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	o,p′-Isomer	p,p′-Isomer	o,p′-/p,p′-ratio	Reference
	McIntosh	n = 4	560^b	380^b	**1.5**^{a}	1200^b	4700^b	**0.3**^{a}	780^b	1856^b	**0.4**^{a}	
	Bucks	n = 12	0.1^b	2.9^b	**0.03**^{a}	9.3^b	81^b	**0.1**^{a}	1.9^b	8.9^b	**0.2**^{a}	
Plankton	Baltic South Coast	n = 4				nd–1.6	110–130	**0.01**^{d}	22–55	100–130	**0.2–0.4**^{c}	Falandysz et al. (1999)
Blue mussel		n = 2	23–28	60–100	**0.28–0.38**^{c}				73–79	320–430	**0.2**^{c}	
Crab		n = 1	7	120	**0.06**				15	580	**0.03**	
Three-spined sticklerblack		n = 4	52–130	170–390	**0.3**^{c}	5–12	700–1,400	**0.007–0.008**^{c}	67–140	230–500	**0.3**^{c}	
Lesser sand-eel		n = 1	12	35	**0.3**	3.9	280	**0.01**	36	130	**0.3**	
Sand eel		n = 1	14	72	**0.2**	5.5	250	**0.02**	59	140	**0.4**	
Herring		n = 1	6.6	120	**0.0550**		590		22	470	**0.05**	
Lamprey		n = 2	11–12	77–120	**0.1–0.14**^{c}	1.4–1.8	590–750	**0.0020**^{c}	14–16	270–440	**0.04–0.05**^{c}	
Pikeperch		n = 1	26	180	**0.1**	9.3	720	**0.01**	51	750	**0.07**	
Eelpout		n = 1	17	180	**0.09**	22	3,700	**0.006**	40	640	**0.06**	
Cod		n = 1	8	36	**0.2**	4.8	780	**0.006**	36	320	**0.1**	
Round goby		n = 1		120		1.2	740	**0.002**	4.6	460	**0.01**	
Flounder		n = 3	18–22	58–92	**0.2–0.3**^{c}	5.8–16	590–700	**0.009–0.02**^{c}	46–120	560–750	**0.08–0.2**^{c}	
Perch		n = 2	12–18	80–120	**0.2**^{c}	3.9–8.3	740–800	**0.005–0.01**^{c}	36–51	400–440	**0.09–0.1**^{c}	
Harbor porpoise		n = 4	39–79	390–1,300	**0.06–0.1**^{c}	13–43	2,300–9,600	**0.004–0.006**^{c}	32–82	670–7,300	**0.01–0.05**^{c}	
Black commorant	Breast muscle	n = 3							nd–1.2	70–120	**0.01**^{d}	
	Liver	n = 3							1.1–2.2	120–190	**0.01**^{c}	
White tailed sea eagle	Breast muscle	n = 10				4.8–580	4,200–4,700,000	**0.001–0.0001**^{c}	nd–150	240–120,000	**0.001**^{d}	
	Liver	n = 3				20–440	67,000–11,000,000	**0.0003–0.00004**^{c}	nd–20	1,700–37,000	**0.0005**^{d}	

(ng/g Lipid weight)	Egg	n = 1				36	240,000	**0.0002**	28	22,000	**0.001**	
	Breast muscle	n = 3				4.7–40	2,400–350,000	**0.0001–0.002**[c]	20–32	520–5,000	**0.006–0.04**[c]	
	Liver	n = 3				4–22	2,100–180,000	**0.0001–0.002**[c]	14–53	400–8,400	**0.006–0.04**[c]	
	Adipose fat	n = 2	4.1–31	23–230	**0.1–0.2**[c]	10–18	3,600–4,400	**0.003–0.004**[c]	55–80	760–1,400	**0.06–0.07**[c]	
Human breast milk	Chinese women	n = 60	4.0–18	43–170	**0.08–0.2**							Fuji et al. (2011)
(ng/g Lipid)	Korean women	n = 60	1.4–1.8	6.5–21	**0.08–0.2**							
	Japanese women	n = 90	0.7–2.4	4.8–9.2	**0.1–0.2**							

[a] Calculated from average values

[b] Average values

[c] Calculated from minimum and maximum values

[d] Calculated from maximum values

There is a clear dominance of marine or even aquatic organism in which most of these data have been examined. However, a more global study analysed DDT isomers in lichens, mosses and mango in Europe, Africa, South America and Asia (Calamari et al. 1991). The detected o,p′-/p,p′-ratios ranged from 0.1 to 1.4. Further on, terrestrial samples investigated include European pine needles from five different countries. Calamari et al. (1994) detected DDT and DDE on low concentration levels of up to 80 ng/g d.w. for individual isomers. The observed o,p′-/p,p′-ratios were 0.2–0.5 for DDT, that is slightly in accordance with the technical formulation, but DDE isomers that were more dominated by the p,p′-isomer.

Animals with a close relationship to the aquatic environment are alligators. Eggs of alligators have been investigated by Rauschenberger et al. (2007). This study revealed low concentrations around 1–11 ng/g egg yolk wet weight for most areas investigated, but maximum values (170 ng/g) for egg samples from Emeralda Marsh. Interestingly, in particular these samples were strongly dominated by the o,p′-isomers resulting in o,p′-/p,p′-ratios around 14. On the contrary, this relation was conversed for the simultaneously detected DDD residues, for which a dominance of the p,p′-isomer was obvious (o,p′-/p,p′-ratio around 0.003). Also for lower contaminated samples a similar inverse isomeric distribution was observed, that changed from higher o,p′-/p,p′-ratios (0.8–1.3) for DDT to lower values (0.1–0.4) for DDD.

For Albatross birds Muir et al. (2002) published a comprehensive data set on DDT related compounds in fat tissue and eggs comprising not only DDT but also both main metabolites, DDE and DDD. These data revealed also significant differences in the relative isomer composition of the metabolites. DDT and DDD exhibited similar o,p′-/p,p′-ratios around 0.1–1.0, whereas the DDE isomers were much more dominated by the p,p′-isomers resulting in 100-fold lower o,p′-/p,p′-ratios (0.004–0.006).

Most isomer-specific data on DDT residues are published for fishes and other aquatic species (see Table 6.8). Nearly all studies detected non-metabolised DDT in different fish species (eels, salmon, barbell fish etc.) and presented o,p′-/p,p′-ratios between 0.06 and 11 (Abdullah et al. 1997; Macgregor et al. 2010; De la Cal et al. 2008; Hinck et al. 2009; Falandysz et al. 1999) . However, most values ranged around 0.2 reflecting more or less the composition of the technical mixtures. Three studies presented additionally isomer composition of DDD and DDE. Also for fish samples significant shifts of o,p′-/p,p′-ratios are visible. Cullon et al. (2009) reported slightly decreased ratios from DDT over DDD to DDE in salmon, whereas Hinck et al. (2009) reported isomer ratios in Largemouth Bass fish, that were only partially depleted by the o,p′-isomers of DDE and DDD. Noteworthy, the very comprehensive study by Falandysz et al. (1999) reported on data from DDT, DDE and DDD in numerous aquatic species, comprising fishes, mussels, crab and, additionally, tissue samples of Sea Eagles. On the other hand, for all biota investigated similar trends of isomer composition were obvious. The o,p′-/p,p′-ratios of DDT and DDD remained more or less on the same level, whereas the isomers of DDE were dramatically depleted by the o,p′-isomer leading to o,p′-/p,p′-ratios down to 0.00004, that is by 500-fold lower as compared to the composition in the technical mixtures.

Although many studies have dealed with the DDT contamination of human tissue, isomer specific data have been published only sporadically. Very recently, Fuji et al. (2011) reported on DDT concentrations in human breast milk of Asian women comprising individual o,p′- and p,p′-values. The isomer ratios ranged between 0.08 and 0.2 and were in the range of technical compositions. However, these ratios have been used by the author to differentiate dicofol contributions from other contamination sources and stated an only minor dicofol input.

Generally, all isomer-specific data of DDT related compounds in biota revealed major changes in the relative composition of o,p′- and p,p′-isomers for DDT and its different metabolites. No clear trend was observed regarding the type of organism, but a general trend is slightly evident for the individual metabolites as discussed. Noteworthy, the relative shifts of o,p′-/p,p′-ratios are exceeding by far statistical irrelevant variations and, therefore, point to a strong impact of transformation and transfer processes on DDT residues within the organisms affecting their isomeric composition.

6.7 Enantioselective Analysis on DDX

For molecules exhibiting chiral carbon atoms enantiomeric analysis as a special case of isomeric analysis demonstrate further insights into environmental behaviour of contaminants. It is very well known, that in particular biotic processes like biodegradation or penetration of biological membranes can affect heavily the relative composition of enantiomers. With respect to DDT and its metabolites solely the o,p′-isomer are chiral and, consequently, are subject to enantioselective analysis. Noteworthy, the application of enantioselective analysis of DDT contamination is very restricted. Most of these studies indicated no clear trend in specific enantiomeric preference.

Kurt-Karakus et al. (2005) analysed the enantiomer specific degradation of o,p′-DDT in global background soils revealing no significant correlation with organic matter content or ambient temperature. Changes in land use had an effect as reversals of the ratio did appear. Bidleman et al. (2006) analysed enantiomer factors (EFs) of o,p′-DDT in soils and air samples with individual samples illustrating the ambivalent nature of o,p′-DDT. The data indicate the preferential degradation of the (+) enantiomer. Meijer et al. (2001) analysed soil residues in sludge amended and non amended Luddington soils (see above). There is no statistically significant difference in EF between control soil and sludge amended indicating no enantioselective microbial degradation over time. The EFs are similar to agricultural soils from various locations in the USA. Wong et al. (2009) analysed EF in passive sampler air samples and stated a mix of racemic and non-racemic fractions, the nearly racemic ratio in southern Mexico indicates a more fresh input. At higher amounts of application a lack of enantioselective degradation is indicated.

Wiberg et al. (2002) revealed by enantiomer-specific analysis of salmon and grey seals from the Baltic Sea via M74-syndrome (a deviant physical and behavioural syndrome complex) a strong correlation of a poor health status with chemical contamination of the food. Wiberg et al. (2006) indicated differences in enantiomeric-ratios in different organs. Konwick et al. (2006) used chiral analysis to measure the bioaccumulation and biotransformation in juvenile rainbow trout (*Oncorhynchus mykiss*) to asses the fate of current-use pesticides. The accumulation was rapid and the following depuration indicated a non-selective biotransformation. Hence, the EFs of o,p′-DDT and o,p′-DDD in fish were not significant different from the food.

6.8 Conclusions and Implications

The isomeric composition of the pesticide DDT in environmental samples has not paid extensive attention so far. Although this review revealed evidence for remarkable changes and shifts in o,p′-/p,p′-ratios of DDT as well as of its metabolites DDD, DDE and to a minor extend for DDA, the application of isomer specific analysis remains dominantly on emission source apportionment. In particular, the differentiation of DDT and dicofol emission used intensively o,p′-/p,p′-ratios.

Only very few studies linked aspects of environmental processes to isomer shifts. Exemplary, differences in volatility of individual isomers from soil to air have been described (see Chap. 2). Also an isomer specific differentiation of environmental stability for DDT in soil was postulated (see Chap. 3). The bioaccumulation of DDT in fishes was also characterised as isomer-specific transfer process (see Chap. 6). Further on, several studies failed to use isomer specific interpretation of their results in order to obtain more detailed insight into environmental processes as illustrated for observed isomer shifts during air-water fluxes (see Chap. 2). Further on, evaluating the comprehensive data set presented in this review a clear discrimination of o,p′-/p,p′-ratios of DDT, DDD and DDE is evident. The o,p′-/p,p′-ratios of DDT and DDD have been detected more or less on the same level, whereas the isomers of DDE were definitely depleted by the o,p′-isomer in all environmental compartments. This observation indicates a general isomer-specific differentiation during DDT metabolism.

Finally, to our opinion the potential to follow the environmental fate of DDX via the isomer composition has not been realized accurately so far, and, consequently, has not been well established in the field of environmental chemistry yet.

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Chapter 7
Geochronology of Anthropogenic Contaminants in Aquatic Sediment Archives

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Contents

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Abstract *Sediment archives are mind of aquatic systems.*[1] We report historical trends of marine, limnic and fluvial sediment contamination. Over the last four decades, the increasing problems of environmental contamination induced a growing interest in the fate and sources of pollution. Environmental contaminants emitted by human activities can be stored ultimately in sediments which act under these circumstances as a sink. In this context, historical monitoring studies of aquatic sediment archives are used to assess the extent and effect of human inputs in the past towards the present. This review gives a summary of the available literature concerning definitive time trends of the contamination load determined in estuarine, fluvial and limnic sedimentary archives. It gathers information about main input sources and contamination pathways as well as the spectrum of anthropogenic contaminants in aquatic sediment deposits. In addition, special chapters point to (i) the prerequisites of the methodical approach, (ii) the spectrum of sediment contaminants, (iii) suitable sedimentary archives as well as (iv) the standard methods of sediment dating. Finally, this review highlights representative studies on pollution histories exemplifying the potential of geochronological investigations on common and modern pollutants.

Keywords Historical trends • Geochronology • Anthropogenic contaminants • Aquatic sediment archives • Emission histories • Common and modern contaminants

7.1 Introduction

The aim of this article is to review and assess current knowledge related to the historical input of organic and inorganic anthropogenic pollutants in the aquatic environment in general and in the fluvial environment in particular. The main aspects covered in this review are the inventory of discharged and accumulated contaminants (persistent organic pollutants and metals) within sedimentary archives, their sources and their transport pathways. Moreover, this review will show the benefit using correlated chronological and geochemical investigations, in order to evaluate the inventory and fate of persistent pollutants within the aquatic ecosystem over space and time. A further objective is to list the advantages and potentials of geochronological investigations and to characterise constraints and limits of this method. Furthermore, this chapter aims at assessing the minimal requirements

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[1] Following Klös and Schoch (1993a) "river sediments as a mind of a river".

necessary to make the method useful as a tool for the evaluation of the chemical status and risk assessment of pollutants in aquatic systems. Finally, management aspects and processes related to the protection of the environment, restrictions and ban of the discharge of ecotoxicological pollutants as well as the reflection of the effectiveness of environmental regulations are discussed. Based on numerous articles reported for marine (coastal and estuarine), limnic and fluvial aquatic systems this literature survey deals predominantly with the historical record, the combination of geochemical and chronological investigations of organic and inorganic contaminants determined in dated (aquatic) soil and sediment profiles.

7.1.1 Why Geochronology?

The increase in the concentrations of many anthropogenic contaminants (e.g. persistent organic pollutants, heavy metals) discharged into the environment by human activities is obvious, especially in river and coastal ecosystems during the last 200 years (Vink et al. 1999). Since the dawn of industrialization and a related growth of population, particularly rivers have been affected by anthropogenic activities and recorded different stages of water quality problems. Numerous studies have reported this impact as well as the harmful effects on the environment, and they have tried to predict variances in the chemical inventory over a broad time interval, mostly discharged in the last 100 years. Since the beginning of the 1970s and 1980s, a reduction of these negative impacts within the aquatic environment is of particular interest.

Various countries have started with joint efforts to reduce the emission load on a large-scale, regarding the (river) basin scale from the input up to the final sediment accumulation, the catchment to the river mouth, the estuarine and coastal zones. Besides, the determination of the emission sources and through different transportation pathways, fate and consequences of human activities should be reflected. For this purpose, national and international agreements have been initiated for the protection of the (aquatic) environment. For instance, the OSPAR-agreement (1999) is aimed at a significant reduction of environmental contaminants discharged by various point sources. Nowadays, environmental protection regulation programs (e.g. the EU-WRRL, initiated within the European Union 2000, EU 2001) pursue the goal of cutting the emission load for a selected group of pollutants to nearly zero or near background values, respectively.

Historical monitoring studies of aquatic sediment archives are used to assess the extent and effect of human inputs in the present and the past. Geochronological investigations of anthropogenic pollutants in aquatic sediment archives are a useful tool to predict variances in the contaminant inventory over a broad time interval. In addition, based on a catchment-wide assessment of the historical load of soil and sediment, this method is able to provide detailed information about the:

- spectrum of sediment contaminants, which can be classified according to their ecotoxicological relevance (priority pollutants/persistent pollutants and in water/sediment hazardous classes),

- sphere of direct or indirect influence of an emission source, regarding the specific conditions within the aquatic system (transport, flow, morphological and geological setting),
- classification of polluted areas, for instance in areas of low/high/significant pollution, and
- significance of regulatory intervention for the areas of high and significantly high contamination (areas of significant risk).

Finally, historical monitoring enables the measurement of the effectiveness of previous and present environmental regulations (Brandenberger et al. 2008; Vink et al. 1999). Based on historical contamination trends, it will be possible to predict the future course of sediment contamination. Moreover, the result can be used to point out the necessity of further restrictions, monitoring of accounted areas with significant emission risks (keyword: resuspension; Heise and Förstner 2006) or to call attention to specific effects of sources and pollutants concerning the environmental compartment.

7.1.2 Pollutants Associated with Aquatic Sedimentary Matter

The aquatic environment is composed of some considerable compartments of ecological importance: the water phase, suspended matter and the sediment phase. The influence of the latter two compartments, in case of accumulation and sediment deposits, is now being increasingly recognised (Westrich and Förstner 2007). The reason for this growing interest is the fact that many pollutants, because of their largely hydrophobic nature, are known to associate strongly with particulate matter or dissolved organic matter, respectively (Warren et al. 2003). Transport, transfer and transformation processes are the most important aspects which the occurrence of anthropogenic contaminants in aquatic sedimentary matter can be referred to. In this context, the partitioning processes between the polar water phase and the more lipophilic solid phase (suspended particulate matter or sediment matter) play a major role. They act as a determining factor deciding on the distribution and fate of organic contaminants. A quantitative approximation of the partitioning between water and sediment phase is given by the octanol-water partition coefficient (K_{ow}), a key factor to consider the fate of chemical compounds in the environment (Schwarzbauer 2010).

Hence, the fate of lipophilic pollutants (mainly those with $K_{ow} > 1$) is closely connected to the sediment phase, and therefore strongly associated with processes observed and determined by them. For instance, high concentrations of pesticides and heavy metals are frequently found in the sediment phase of freshwater deposits and in coastal marine sedimentary systems. Information on surface sediments as well as deep sediment deposits are used more and more to understand the complex causal relationship between contamination influx into the aquatic environmental and the fate of the pollutants within the different compartments. A brief introduction to the effects of micro-organic contaminants within the aquatic environment has been given by Warren et al. (2003). The article reviews and summarises the complexity of natural ecosystems and provides information on toxicological and ecological effects of (micro)-pollutants in freshwater environments, studies of sediment toxicity, as well as the adsorption and desorption process of organic compounds to sedimentary matter and dissolved organic matter. In addition, Schwarzbauer (2010) gives a brief overview on the occurrence and the molecular characterisation of organic matter in the aquatic environment. Principle transport and transformation processes affecting the molecular composition are discussed for instance by Breivik et al. (2004) and Lair et al. (2009).

In spite of the increasing number of lipophilic particle bound sediment contaminants, there are some criteria to use them for adequate historical trends:

- After accumulation on particulate matter and during compaction and diagenesis the pollutants must be insensitive to or resistant against environmental influences and should not undergo chemical or biological degradation or mobilisation.
- In order to avoid misinterpretation it is necessary to consider the natural emission levels, the so called “baseline values” or “background values” for pollutants.

Because of the fact that the majority of pollutants (organic and inorganic) also have natural biogeochemical cycles, their baseline values have to be established. Increasing concentration levels and the human impact on the environment have to be taken into consideration (Alderton 1985). It is needed to determine the concentration ranges of pollutants of natural appearance and those which are exclusively man-made; even though man-made pollution mostly superimposes the natural background. Alderton (1985) proposed a comparison of concentrations calculated by the ratio of the mean anthropogenic concentration and the background concentration, the “enrichment factor”. Xenobiotics such as polychlorinated biphenyls and chlorinated pesticides do not have a natural level; nevertheless some of them show an ubiquitous distribution. Because of their widespread previous use it is necessary to establish the concentration ranges as background data for them as well.

7.1.3 Essential Prerequisites for Geochronological Investigations

After the release of contaminants into the environment and incorporation in depositing sediments, a preservation of these past emissions can occur. In case of unaffected preservation, these sediments record the past pollution events and can be used for historical monitoring (see also previous review studies published by Alderton 1985; Warren et al. 2003). Preconditions for incorporation and permanent fixing of (anthropogenic) organic and inorganic pollutants are reducing anoxic conditions and non-turbulent environment (without physical disturbance or bioturbation).

In order to reconstruct load histories of preserved particle bound contaminants in aquatic sediment archives, some essential criteria concerning the sediment deposits must be taken into account. Suitable (aquatic) sediment archives reveal (Alderton 1985; Warren et al. 2003):

- undisturbed sedimentation of fine-grained particles (particulate matter such as clay minerals, organic matter) for contaminant adsorption during periodic or aperiodic/steady deposition,

- sediment profiles with sufficiently long sedimentation intervals, between 10 and 100 years,
- a complex environmental and scientific interest, which may also allow the consideration of different factors such as the evaluation of input sources or transport/transformation processes.

The number of suitable aquatic archives with ideal conditions is severely limited. This is the main reason why most of the published geochronological studies have been performed for lake and estuary sediments, which more often fulfil the requirements than river sediments. Physical mixing, resuspension and bioturbation, often down to depths of several centimetres, disturb the profiles and can lead to misinterpretation.

The main reasons for less effective results (Alderton 1985) are mechanisms like incorrect dating, natural production of contaminants, laboratory contamination and/or physical disturbance of the sediments or bioturbation. Without an adequate dating (a time-stratigraphy) of the sediment profile only a generally applicable statement about the emission trends can be made.

7.2 Anthropogenic Contaminants, Their Major Input Sources and Transport Pathways in the Aquatic Sediment Archives

Investigations of anthropogenic contaminants preserved in sediment cores may provide insights into the major sources and pathways by which contaminants are discharged into the aquatic system. In general, the major contamination sources include industrial and municipal discharges, surface and stormwater runoff, diagenetic processes in sediments, groundwater, and atmospheric deposition. Occurrence, extent and fate of environmental contamination are determined, as a result of their physico-chemical and biological behaviour, by the conditions and amounts of production and use, compound application and sometimes their specific input sources (e.g. Eganhouse 1997; Warren et al. 2003; Breivik et al. 2004; Schwarzbauer 2010).

Finally, the fate of compounds with relevance for the environmental system is affected by accumulation, alteration (degradation or metabolisation) and preservation processes. Thereby, the occurrence, distribution and increase in contaminant concentrations are not necessarily located close to a production area. Hence, transport pathways inside and outside the aquatic system play a major role. Rivers are particularly important for the supply of matter from land to ocean. Beside other forms of transport, for instance weathering, erosion and/or atmospheric particle transport, rivers are the major pathway of pollution within the global aquatic system, from man to the ocean (Eisenreich et al. 1989).

7.2.1 Input Sources and Transport Pathways

Breivik et al. (2004) distinguish between two principal classes of input sources, especially for persistent organic pollutants (POPs). In one group (i), the authors

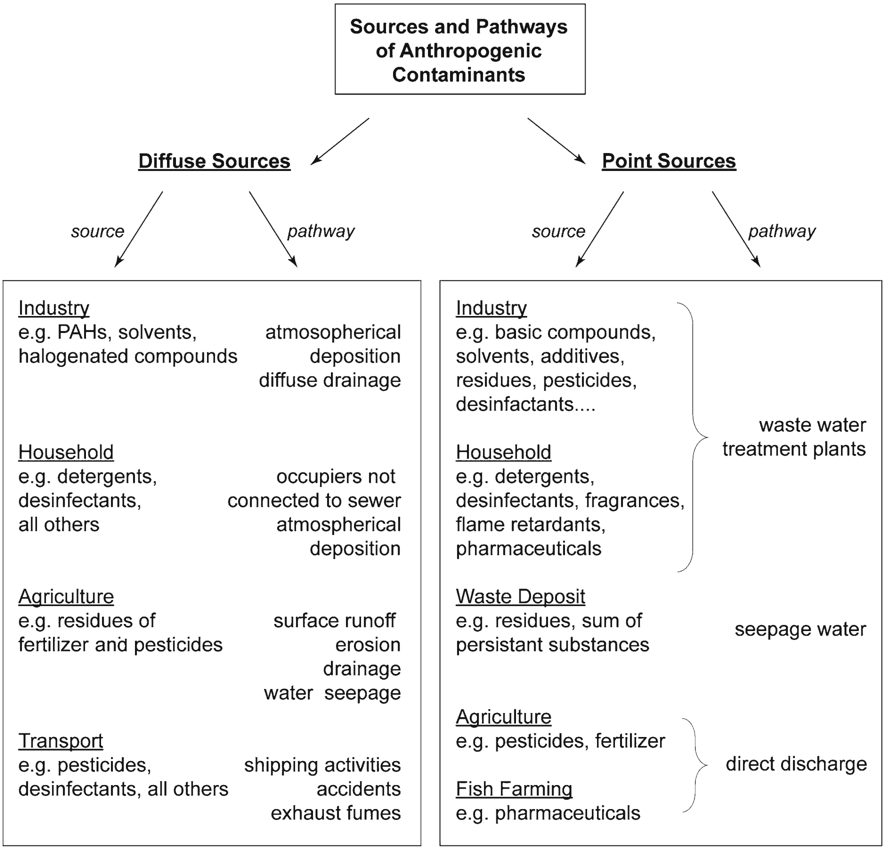

Fig. 7.1 Sources and pathways of anthropogenic contaminants (Heim 2005)

include chemical compounds which are intentionally produced for one reason or multiple purposes, and in another group (ii), they comprise those which are more or less accidentally formed as by-products in other (industrial) processes or by human activities. Besides this, a large number of substances emitted as pollutants are also produced naturally as a part of natural biogeochemical cycles (e.g. metals; Alderton 1985). Typical representatives of group one are POPs, (chlorinated) pesticides and industrial chemicals. The group of unconscious contaminants can be subdivided into the subgroup of combustion residues (PCDD/Fs and PAHs) and the subgroup of substances produced by chemical/industrial processes (Breivik et al. 2004). Beside the classification, some of these contaminants belong to more than one group, whereas a detailed source classification depends on the extent of the contamination and the contamination pathway.

The main input sources for anthropogenic pollutants are emitted from point sources or by diffuse source (Fig. 7.1).

Identification of the source of pollutants and their transport (emission) pathways are the main steps towards reducing the contamination levels in the environment (Breivik et al. 2004). The authors emphasize the necessity to identify the sources and pathways of the pollutants, equal to the analysis of usage and emission trends.

In general, identification of point sources seems to be obvious, in particular if the sampling site is nearby. Indication of diffuse input sources can be supposed, if no local point can be assigned as reference for the origin of a contamination. Besides this, some further information about the chemical composition or isotopic ratios can be used for source identification. In the following, some typical diffuse contamination pathways are listed:

Soil erosion and sediment transport:
The most important process of dispersion of sediment-associated contaminants within an aquatic system is the riverine sediment erosion and transport of suspended matter by river flow, as well as leaching and or soil erosion from (agricultural) fields.

Surface runoff and stormwater discharge:
Surface runoff and discharge of contaminants by stormwaters means the overflow from roadside and other urban surfaces (Larson et al. 1995) as well as field drains (Burgoa and Wauchope 1995) during heavy rainfall events. In case of hard surfacing and/or exceeding soil infiltration capacity particulate matter and soil can be eroded which contain notable amounts of associated contaminants. Typical constituents of street or field drainage water can be related to vehicle exhausts, motor fuel and oil spillages (petrogenic related products), such as saturated hydrocarbons and PAHs, PCBs, PCDD/Fs as well as heavy metals (e.g. Pirrone et al. 1998; Eisenreich 1999; Marvin et al. 2004a).

Atmospherically transported compounds, ubiquitous distribution:
The aerial deposition represents the particle associated distribution of micro-pollutants initiated by wind drift of particles, aerosols or spray drift from agricultural areas. This also includes a significant amount of organic micro-pollutants, notably PAHs which can be emitted by combustion processes of fossil fuels.

It has been suggested that persistent organic pollutants can be transported through the atmosphere by a general global transport (Wania and Mackay 1995). Volatilisation of pesticides and other contaminants, emitted far away from the point of usage are transported through the troposphere and deposited, among others at higher latitudes (Warren et al. 2003).

Transport processes of contaminants within the sediment; diffusion and slow contaminant release:
The movement of contaminants from the water column to bottom sediments, within the sediment bed, and from the bed back into the overlying water, is controlled by a variety of mechanisms. These include:

- diffusion down a concentration gradient in the porewater of the sediment,
- enhanced diffusion when attached to dissolved organic carbon (Warren et al. 2003),
- mass transport by which infiltering water may be exchanged with groundwater,

- redistribution as a result of the physical mixing of sediment (bioturbation),
- resuspension and mixing of bed sediments in the water column, and
- movement by association with clay colloids.

These mechanisms are obviously be influenced by the association of compounds with sediment particles, as well by degradation processes in the porewater or in a sorbed state.

Sediment contaminants and concentrations profiles within a sediment archive can be used as indicators for specific sources and transport pathways. A detailed review of biological, chemical and/or physical processes concerning the fate of pesticides within a sedimentary (freshwater) environment is given by Warren et al. (2003). The authors conclude that the following criteria are relevant for geochronological sediment analyses: occurrence, bioavailability and ecotoxicology as well as processes related to the fate of contaminants like degradation, diffusion in bed sediments and slow contaminant release.

7.2.2 Spectrum of Suitable Sediment Contaminants for Historical Time Trends

The spectrum of organic and inorganic pollutants discharged by different input sources will be supplemented by metabolites. These metabolites are formed during sewage treatment or physico-chemical and biological degradation until they reach their final destination and lead to a wide range of compounds delivered to rivers, lakes and coastal areas (Warren et al. 2003). Hence, investigations of point-source and diffuse contamination input must consider the original chemical compounds as well as products, built partially by exposition during wastewater treatment.

The outflow of domestic and industrial wastewater treatment plants (WWTPs) includes a wide spectrum of compounds determined by their numerous input sources, inclusive detergents and anionic surfactants such as:

- detergents (e.g. linear alkylbenzenesulphonates, LAS) and disinfectants,
- pharmaceuticals and personal care products, synthetic fragrances of perfumes and cosmetics,
- plasticiser, fire retardants and ingredients of paints,

and a huge range of other ingredients of chemical production (Reiser et al. 1997; Rimkus 1999; Cavalli et al. 2000; Breivik et al. 2004; Schwarzbauer 2010).

Typical representatives of these remaining contaminants, discharged after wastewater treatment, are for instance chlorinated hydrocarbons, pesticides (e.g. DDT and its metabolites), technical additives (PCB) and constituents of petrogenic and pyrolytic processes (PAHs, PCDD/Fs). Their occurrence in a complex mixture sometimes makes it impossible to reconstruct the original chemical composition or single chemical products. Additionally, the commercial formulations often also contain a mixture of active substances and by-products and therefore these ingredients show different affinities for sediments and different degradation ratios and rates.

7.2.3 General Emission Trends and Classification of Contaminants

Over the past century, anthropogenic activities have released large quantities of contaminants into the environment. Organic and metal contaminants are known to be readily sequestered by settling of contaminated particulate matter and removed from the water column (Nriagu et al. 1982; Eisenreich et al. 1989). As a result, a number of studies have utilized sediment cores in deriving contaminant loading histories (Edgington and Robbins 1976; Kemp et al. 1978). Sediment profiles (with and without adequate time-stratigraphy) reflect general trends of increased inputs of contaminants.

In this context, surface sediments always indicate the date of sampling and with increasing depth the contaminated sediments represent the emission input of a time range of the last decades and centuries. Regardless of the rate of sedimentation, the time correlated depth or the level of mixing, input trends represent the increasing sediment contamination with industrialisation during the nineteenth and the beginning of the twentieth century. Especially one group of contaminants (heavy metals, PAHs, PCBs etc.) show a general increase in emissions from the background level. Up to the recent decline, this trend is triggered by a growing awareness and sensitivity to the environment, beginning in the 1960s (Smith 2001).

A few studies differentiate between “older or common” and “modern or present-day” anthropogenic contaminants, especially for the group of organochlorine compounds and pesticides, respectively (Alderton 1985; Warren et al. 2003; Heim et al. 2003). The group of “older” sediment contaminants includes primary organochlorine compounds, pesticides like DDT, endrine, dieldrin, aldrine and lindane, PCBs, PCDD/Fs, chlorinated benzenes as well as PAHs or heavy metals. Many of them were phased out for legal use or their discharge or production and usage are restricted since the late 1970s (e.g. PCBs, DDT and others) and late 1990s in North America and Europe, but still used in some other countries. For most of these “older/common” contaminants their ecotoxicological potential (chemical, toxicological and biological behaviour) is well known and documented in numerous laboratory and field studies.

On the contrary, more modern contamination is reflected for instance by pharmaceuticals, detergents, biocides and flame retardants, which have been introduced in the technosphere in the late 1960s. Only a few monitoring studies are dealing with these “present day” contaminants within aquatic sediment archives (see Table 7.1). Miller et al. (2008) and Cantwell et al. (2010) published input trends of the modern bactericides triclosan and triclocarban determined in different marine-estuarine sedimentary archive of the South-East coast of the USA. Furthermore, the polymer additives mono- and dibutyl tin have been analysed in the riparian wetlands of the Lippe River (Germany, Heim et al. 2004; see Fig. 7.5). In addition, organotin compounds and synthetic musk fragrances have been detected in coastal sediments of the Southern-California bay, USA (Venkatesan et al. 1998; Peck et al. 2006).

Table 7.1 Compilation of geochronological studies (historical trends in anthropogenic emissions), determined for different aquatic sediment archives (published between 1980 and present)

Location	Reference	Time scale (year)	Pollutants/compounds
Marine deposition (costal and estuarine)			
North America			
Buffin Bay, CAN	Gustafsson et al. (2001)	170	Chlorinated compounds
Saguenay Fjord, CAN	Smith and Walton (1980), Smith and Levy (1990)	>100	PAHs
Puget Sound, NW-USA	Brandenberger et al. (2008)	>100	Heavy metals, lignin
St. Lawrence River, estuary, USA	Coakley et al. (1993)	<35	PAHs, PCBs
San Francisco Bay, USA	Hornberger et al. (1999)	>100	Heavy metals
	Fuller et al. (1999)	>50	Radionuclides
	Pereira et al. (1999)	>100	PAHs
S-California Bight, USA	Venkatesan et al. (1980/1998/1999)	50–100	DDX, Organotins
	Katz and Kaplan (1981)	–	Heavy metals
	Peck et al. (2006)	>50	Synthetic musk fragrances
NE-coast, USA	Gschwend and Hites (1981)	80	PAHs
Chesapeake Bay, USA	Nichols (1990)	20	Kepone
	Arzayus et al. (2002)	50	PAHs
Narragansett Bay, USA	Latimer and Quinn (1996)	80	PAHs, PCBs
	Bricker (1993, 1996)	20	Heavy metals
	Lima et al. (2003)	180	PAHs
Hudson River, USA	Bopp et al. (1982)	25	DDX, PCBs
Estuarys, Florida, USA	Alexander et al. (1993, 1999)	50–80	Heavy metals, pesticides
Sabine-Neches Estuary, USA	Ravichandran et al. (1995)	100	Trace metals
E-coast, estuary, USA	Miller et al. (2008)	Ca. 60	Biocides (triclosan)
	Cantwell et al. (2010)	100	Biocides (triclosan)
SE-coast, USA	Santschi et al. (2001)	>50	PAHs, PCBs, DDX, metals
Hudson Estuary, USA	Valette-Silver (1993)	100	DDT, PCB
South America			
Culiacan R. estuary; MX	Ruiz-Fernández et al. (2002, 2003)	>50	Heavy metals, nutrients
Salt marshes, CL	Barra et al. (2004)	>40	PCBs, HCHs

(continued)

Table 7.1 (continued)

Location	Reference	Time scale (year)	Pollutants/compounds
Europe			
United Kingdom			
South coast, UK	Sanders et al. (1992, 1993)	>60	HCB, DDT
Coastal wetlands UK, NL, PL	Callaway et al. (1998)	>100	Heavy metals
Mersey estuary, UK	Fox et al. (2001)	>50	BHC, DDT
Humber estuary, UK	Lee and Cundy (2001)	100	Heavy metals
Estuaries; ES/I/UK	Cundy et al. (1997/2003)	Ca. 40	Heavy metals
Tees estuary; UK	Plater and Appleby (2004)	>50	Heavy metals
Scandinavia			
Gulf of Finland, FI	Salo et al. (2008)	>50	PCDD/Fs, Hg
Baltic Proper, S	Kjeller and Rappe (1995)	>100	PCBs, PCDD/F
The Netherlands/Germany			
Harima Bay, JP; Baltic Sea, DE	Ricking and Terytze (1997)	>90	PCBs, PCDD/F
Scheldt estuary, NL	Van Zoest and Van Eck (1993)	>80	HCB, PCBs, PAHs
Ijselmeer, Rhine, NL	Winkels et al. (1993)	>60	PAHs, PCBs, metals
Mediterranean Sea/Southern Europe			
Mediterranean Sea	Lipiatou et al. (1997)	20–100	PAHs
Mediterranean Sea, ES	Diez et al. (2002)	Ca 15	Organotin compounds
Bay of Cádiz, ES	Ligero et al. (2002)	115	Heavy metals
Portuguese shelf (PT)	Mil-Homens et al. (2006)	>100	Heavy metals
Lagoon of Venice, I	Pavoni et al. (1987)	50	DDX, PCBs, PAHs
Lagoon of Venice, I	Secco et al. (2005)	>40	POPs
Russia			
White Sea, RUS	Savinov et al. (2000)	>100	PAHs
Asia/Australia/Africa			
China/Taiwan			
Yangtze estuary, CN	Liu et al. (2000)	>30	PAHs
Sai Kung Bay, CN	Fung and Lo (1997)	50	Heavy metals
Macao estuary, CN	Zhang et al. (1999)	>30	BHC, DDX
Pearl River estuary, CN	Ip et al. (2004)	>100	Heavy metals
	Liu et al. (2005)	120	PCDD/F
	Peng et al. (2008)	>70	PAHs
Deep Bay, S-China	Qiu et al. (2009)	50	PAHs
Nanliu River estuary, CN	Xia et al. (2011)	80	Heavy metals
Kaoping coast, TW	Hung and Hsu (2004)	250	Trace metals
Japan			
Kanto region, JP	Sakurai et al. (2002)	50	PCDD/Fs
Sendai Bay, JP	Okumara et al. (2004)	70	PCDD/Fs, CO-PCBs
Tokyo Bay, JP	Ishiwatari et al. (1983)	40	Alkylbenzenes
Osaka Bay estuary, JP	Yamazaki et al. (2008) Hosono et al. (2010)	Ca. 60	Heavy metals
Ariake Bay, JP	Kim et al. (2007)	>60	POPs

(continued)

Table 7.1 (continued)

Location	Reference	Time scale (year)	Pollutants/compounds
Thailand, Philippines			
Manila Bay, PH	Hosono et al. (2010)	20	Heavy metals
Gulf of Thailand, TH	Boonyatumanond et al. (2007)	60	PCBs, PAHs, LABs
New Zealand/Australia			
Pegasus Bay, estuary, NZ	Deely and Fergusson (1994)	>150	Heavy metals
Queensland, AUS	Gaus et al. (2001)	50	PCBs, PCDD/F
Africa			
Oualidia lagoon, MC	Zourarah et al. (2007)	50	Heavy metals
Fluvial archives			
North/South America			
Black River, USA	Gu et al. (2003)	Ca. 50	PAHs
St. Lawrence River, CAN	Delongchamp et al. (2009)	Ca. 30	Mercury
Europe			
Lippe River, DE	Klös and Schoch (1993a, b)	Ca. 50	PCBs, HCH, heavy metals
	Heim et al. 2003, 2004	80	Spectrum of contaminants
Wolga, Danube, Rhine EU	Winkels et al. (1998)	Ca. 50	PCBs, heavy metals
Havel, Spree, DE	Ricking et al. (2003)	>20	Spectrum of contaminants
Rhine River, DE	Heim et al. (2006)	30–50	Spectrum of contaminants
Elbe River, DE	Götz et al. (2007)	Ca. 50	PAHs, PCDD/F, DDX,
Teltow Canal, DE	Heim et al. (2005)	Ca. 10	DDX, chlorinated pesticides
River Ouse, UK	Labadie et al. (2007)	>50	Sterpodal estrogens
Lot River, FR	Audry et al. (2004)	Ca. 50	Heavy metals
Africa/Asia/Australia			
Wetland profiles, ZM	Von der Heyden and New (2004)	>100	Heavy metals
Karoo Upland, ZA	Foster et al. (2007)	70	Metals
Limnic archives			
North America			
Great Lakes	Nriagu et al. (1983)	>100	Heavy metals
	Evans et al. (1986)	–	Pb
	Graney et al. (1995)	150	Pb
	Kolak et al. (1998)	200	Heavy metals
	Pirrone et al. (1998)	>100	Hg
	Belzile et al. (2004)	>50	Trace metals
Lake Erie and Lake Ontario	Song et al. (2005)	>60	PCDD/F
	Peck et al. (2006)	>100	Fragrances

(continued)

Table 7.1 (continued)

Location	Reference	Time scale (year)	Pollutants/compounds
Lake Ontario	Eisenreich et al. (1989)	80	Chlorine. hydrocarbons
	Mayer and Johnson (1994)	>150	Heavy metals
	Wong et al. (1995)	90	Chlorinated hydrocarbons
	Pearson et al. (1997)	>70	Toxaphene, pesticides
	Kaminsky and Hites (1984)	>60	Octachlorstyrol
	Oliver et al. (1989)	Ca. 40	PCB, PAH, DDX
	Wong et al. (1995)	>90	DDX
Lake Michigan, USA	Christensen and Arora (2007)	70	PAHs
	Simcik et al. (1996)	>90	PAHs
	Schneider et al. (2001)	>25	PAHs, PCBs, Toxaphene
Green Bay, Lake Michigan	Zhang et al. (1993)	>100	PAHs
	Su et al. (1998)	40	PAH
Lake Yukon, CAN	Rawn et al. (2001)	>50	PCBs, DDX
Louisiana, USA	Catallo et al. (1995)	25	PAHs, DDX, Heavy metals
Lake Hartwell, USA	Magar et al. (2005)	45	PCBs
Different lakes, USA	Van Metre et al. (1997)	>60	PCBs, DDX
Different locations USA	Wakeham et al. (1980, 2004)	>25	PAHs
Californian lakes, USA	Sanders et al. (2008)	300	Hg
Western USA	Mast et al. (2010)	200	Hg, trace metals
Lirios Lake, MX	Piazza et al. (2009)	>80	PCBs
Lago Verde lake, MX	Ruiz-Fernández et al. (2007)	>60	Trace metals
South America			
Laja Lake, CL	Quiroz et al. (2005)	>50	PAHs
Andean lakes, CL	Pozo et al. (2007)	>60	PCBs
Europe			
United Kingdom			
Windermere, Priest Plot, UK	Cranwell and Koul (1989)	>100	Aliphatics (Norhopanes)
Coventry, UK	Winter et al. (2001)	>30	Heavy metals
Scotland, UK	Eades et al. (2002)	>100	Pb
Lochnagar Lake, UK	Yang et al. (2002)	>100	Trace metals
Lakes, IRL	O'Dwyer and Taylor (2009)	>100	PAH
Scandinavia			
Subarctic lakes, FIN	Vartiainen et al. (1997)	>100	PCDD/F, PCBs
Lakes, FIN	Kähkönen et al. (1998)	100	AOX, heavy metals

(continued)

Table 7.1 (continued)

Location	Reference	Time scale (year)	Pollutants/compounds
Germany/Switzerland/Alps			
Lake Constance, DE	Bollhöfer et al. (1994)	>80	Pb
Lake Constance, DE	Kober et al. (1999)	>150	Heavy metals
Eifel, DE	Regier (2003)	>50	Tensides
Alps, EU	Grimalt et al. (2004)	>60	HCH, DDX, PCBs
Lake Biel, CH	Reiser et al. (1997)	>50	Tensides
Greifensee, CH	Zennegg et al. (2007)	>10	PCBs, PCDD/F
Africa/Asia/Australia			
China/Taiwan			
Tanshui, TW	Chi et al. (2007)	Ca. 20	PCBs, POPs
Lake Suwa, JP	Ikenaka et al. (2005)	80	PCDD/Fs, PAHs
Yangtze region, CN	Zhang and Shan (2008)	50	nutrients
Wuhan, CN	Yang et al. (2009, 2010)	90	PCBs, PAHs
Qinghai Lake, Tibet (CN)	Wang et al. (2010)	>100	Hg, trace metals, PAH
Poyang Lake, CN	Yuan et al. (2011)	50	Heavy metals

7.3 From Contamination of Suspended Particles to the Formation of Sediment Archives

Investigations of sediment contamination, emitted into the aquatic system by human activities, pay specific attention to particulate matter and (undisturbed) sediment deposits of rivers, streams, canals and lakes, as well as adjacent areas like estuaries and coastal zones, fluvial floodplains and wetlands.

7.3.1 Sediment Deposits: Formation and Accumulation

Contaminated sediments play an important role in distribution and transport of pollutants within the environment, from the moment when pollutants have entered the aquatic environment and have associated with particulate matter (Warren et al. 2003). Within the water body transportation and deposition of suspended fine-grain particles are related to the water flow, tidal effects (in coastal areas and estuaries) as well as fluctuating water level caused by weather influence (e.g. flooding events).

Sediments, organic and inorganic material, reach the dynamic part of an aquatic system by weathering processes, mobilisation and erosion. Once in the river system, the particle matter is transported downstream by flowing water towards the river basin outflow. Different flow rates affect the settle down of sediments, for instance in low-energy areas, where the flow is reduced or in accumulation zones, where low current speed and low resuspension rates allow a more or less continuous sediment accumulation. Furthermore, in case of preferred transport, at the end of the river much of the sediments are deposited in the estuary and on the seabed of the coastal zone (Secco et al. 2005; Westrich and Förstner 2007).

The deposition process of suspended sedimentary matter within the river body is largely determined by water flow and water and wind borne undulation. Furthermore, suspended particulate matter can be transported and distributed outside adjacent areas, characterised as the terrestrial part of the river catchment. In general, this transport is caused by flooding events as a result of temporal stormwater or extraordinary undulation. It ensures a transfer from the water body, as (re)suspended particulate matter or from subaquatic accumulation zones, into the terrestrial zone of the river catchment, the wetlands and floodplains, whereas terrestrial sediment archives can be formed. In case of undisturbed periodical or aperiodical flood events slow growing accumulated sediment deposits can develop (Le Cloarec et al. 2007).

7.3.1.1 Sorption of Contaminants to Suspended Particulate Matter

Several studies report on the correlations between contaminants and fine-grain particulate matter and related transport processes (e.g. Kaiser et al. 1990; Zhou et al. 1999). Warren et al. (2003) give a brief overview at (1) effects of flow and sedimentation regimes on transport and concentration ranges of pollutants, (2) spatial and temporal variations in sediment-contamination concentrations, and (3) correlations between sediment organic matter and the concentration of accumulated pollutants. The authors compare the differences in the sorption behaviour of organic pollutants deposited and suspended sediments, which can be attributed to differences in the grain size distribution and other micro-structural characteristics of different sediment types.

In this context fluctuations in pollution load, especially a reduction of usage or release, must be excluded, otherwise the opposite effect can be observed (Kaiser et al. 1990). Because of differences in the release of pollutants in time, concentration differences between surface samples (or suspended particulate matter) and buried sediments may occur.

7.3.2 Variation in Contamination Levels

Contamination levels determined within aquatic sediments (surface sediments and sediment profiles) range from micro-pollution to pollutants on a high concentration level (Warren et al. 2003). Contaminants are referred as mirco-organic pollutants (MOPs) if they show an environmental occurrence in very small amounts but with a significant harm to the ecological systems and/or for humans.

In general the detected levels of sediment contaminants range between ng/kg for micro pollutants, and up to mg/kg for higher level contaminants. Fluctuating sediment contamination levels (spatial and temporal variations) occur because of (i) different sediment and flow regimes, as well as because of (ii) complex temporal and quantitative variations in the source discharging a specific contaminant (Warren et al. 2003).

These temporal and spatial variations are related to:

- seasonal and tidal effects: variations on different time scales (e.g. hours and months),
- fluctuation in contaminant load: source specific differences,
- down-core changes in sediment grain size: qualitative and quantitative aspects of fine-grained particles, changes in sediment composition,
- variations related to the specific sampling location,
- variation in contaminant composition: temporal/seasonal contamination load.

7.3.2.1 Influence of Different Flow Levels: Temporal and Spatial Variations

Temporal variations in the quantitative sediment load are caused by several flow-related aspects, (1) resuspension of contaminated sediment layers, (2) erosion of soil and sediments and (3) run-off from storm drain and flooding events. Besides this, variances in water column and quantity of suspended matter are related to tidal effects, as a further influence on the contamination content and quality of the sediment load (Warren et al. 2003).

High flow rates will give an increase in sediment erosion and transport which may result in dilution of suspended sediment contaminant concentrations. There are few studies investigating aspects of fluctuating contamination levels whereas some major correlations can be distinguished:

(i) quantitative variations of suspended matter in the water column (e.g. within estuarine zones, during tidal cycles) which may show highest sediment concentrations observed during low water (Nichols 1990),
(ii) increasing particle-bound contaminations correlated to increasing contents of (mean) organic carbon; this increase is detected in areas of low water levels and associated to the fine-grain fraction settling down in calm-water zones (Nichols 1990),
(iii) different pollutant concentrations related to differences in sediment grain-size distributions (Abarnou et al. 1987).

Long et al. (1998) describe temporal variations in non-tidal river sections as a result of changes in flow levels in different seasons, into and through the river. Within estuarine zones discharge variations can be attributed to both hourly and seasonal timescale in case of tidal effects. In addition, temporal variations can take place, if the pollution input is flow-related (in case of resuspension of contaminated particulate matter, as a result of flood events or storm runoff).

7.3.2.2 Contamination Levels and Contamination “Hot Spots”

An overall effect of high contamination levels in sediment deposits close to a source is not strictly required. Nichols (1990) reports increased concentration levels far away from direct contamination sources; in particular sediment deposited in accumulation zones which showed a much higher contaminant load than elsewhere. Hence, contamination “hot spots” can be determined for deposition areas close to the discharge of the contaminant. In these areas, in which geochronological studies are performed, a monitoring of fine-sediment accumulations could provide an early-warning system, especially for the contamination with organic micro-pollutants (Nichols 1990).

The effects of flow rate can also be very important in the transport of micro-pollutants (Warren et al. 2003). Whereas the analyses of bed and suspended sediments from low flowing rivers (Rivers Air and Calder, Yorkshire, UK; Long et al. 1998) have resulted in relatively high concentrations of pesticides, some investigations on fast flowing river showed only relatively low concentrations, even though the catchment of these rivers include heavy industrial discharge (rivers and estuarine systems in China, Wu et al. 1999).

These results show that for fast-flowing rivers or high-energy areas relatively high self-purification ability can be expected against pollution, in case of high water-discharge and sediment load. On the other hand, local points of high sediment contamination are not restricted to near-source zones, they can also be localised in accumulation zones far away from the source, caused by suspended-sediment transport processes (Warren et al. 2003).

Westrich and Förstner (2007) classify the present-day pollution of recent surface sediments as low level, covering older (higher level) contaminated sediment deposits in low-energy areas of the river basin. They postulated an increasing risk of resuspension of old contaminated sediment layers by transport of the particle-bound pollutants downstream in river systems due to the potential for increasing water discharge.

7.3.3 Historical Load of Persistent Pollutants in Undisturbed Aquatic Soil and Sediment Archives

Within the aquatic system it is of major importance to consider the sediment phase. As soon as contaminants are discharged into the aquatic environment, suspended particulate matter plays a significant role in their transport within the system. Dating of undisturbed, periodical or aperiodical deposited sediment profiles and geochemical analysis of the content and the amount of contamination reveals a detailed record of the historical load of preserved particle bound persistent contaminants (Alderton 1985; Valette-Silver 1993; Catallo et al. 1995; Kähkönen et al. 1998; Smith 2001).

In this context, geochronological investigations are used for the evaluation of the contamination spectrum and for trend correlations of specific anthropogenic contaminations (e.g. between different sampling sites). Time related differences in the concentration levels of a pollutant within a sediment profile can be used as a distinct information about the temporal differences in source strength and source origin (Vink et al. 1999).

There are three main depositional areas within an aquatic system relevant for historical monitoring:

- marine environment: lacustrine, coastal and estuarine archives,
- limnic environment: sediment archives in natural and artificial lakes and their floodplains,
- riverine environment: subaquatic undisturbed sediment deposits inside the riverbody and ancient terrestrial sediment archives like floodplains and wetlands.

Most of the time monitoring investigations have been performed for selected accumulation zones, regarding various input sources and influences of different contamination species induced over an expected period of time (Gocht et al. 2001). This includes indicating both the natural background levels (Hudson-Edwards and Taylor 2003) as well as sediment accumulations of persistent (organic of inorganic) pollutants.

Moreover, a correlation of time-related concentration profiles should helps to reflect the historical contamination load within the overall aquatic system (river basin scale) over time and space, allowing the identification of principal contamination pathways (e.g. Miller et al. 2008).

Sediment loadings are assumed to be regulated by factors including the magnitude and concentration of discharged effluents, as well as the physical and chemical characteristics of the receiving water bodies and sediments (Cantwell et al. 2010). Once deposited in sediments, contaminants accumulated on sediment particles (e.g. PAHs, PCBs, pesticides and others) are only slightly exposed to photochemical and biological oxidation and thus tend to persist for longer periods and to accumulate in high concentrations.

7.3.3.1 Marine Environment

Due to the fact that organic compounds tend to accumulate near to their input sources (Secco et al. 2005) aquatic sediments are very important in order to study physical, geochemical and biological processes in the environment. A large amount of organic matter within the suspended sediment facilitates the adsorption of hydrophobic organic pollutants from the water column (Karickhoff et al. 1979; Grathwohl 1990). In particular, marine sediments, from estuaries and lagoons, record the composition of the overlaying water column and the particle bound in case of accumulated and deposited pollutants (Secco et al. 2005) with time. They integrate contamination inputs of hydrophobic substances from the water into the sediment phase over seasonal of yearly time scales (Zhang et al. 1999).

The sedimentological record in dynamic marine (coastal and estuarine) environments is often distorted or obscured by sediment reworking as a result of biological activity or by depositional and erosion processes (Smith and Walton 1980; Alderton 1985; Smith and Levy 1990). Hydrodynamic phenomena such as wave action, storm surges, or seasonal variability in sediment rates and textures lead to discontinuities in the sedimentary sequence. Although sediment archives of coastal and estuarine areas are often influenced by mixing processes and the occurrence of undisturbed sediment archives are rather scarce (Gocht et al. 2001), a considerable number of emission histories within these sediments is available (see Table 7.1).

A main prerequisite of radiometric interpretation of vertical sediment profiles in this high-dynamic sedimentation regime is that a sediment deposition model can be developed which can resolve the sediment time-stratigraphy. Consequently, there is a need for correlation of different dating methods in order to ensure the accuracy of sediment accumulation rates and geochronologies for these sediments.

Estuarine Sediment Archives

In order to avoid misinterpretations of contamination flux and input and due to the fact of complex mixing processes within marine-estuarine sediment archives it is of major importance to determine the transport processes of sediment bound pollutants from rivers into the ocean (Warren et al. 2003). With regard to the flow regime of the river, this can be a main cause for variations in concentration profiles. There are correlations between the concentration of particle bound contaminants and freely-dissolved concentrations (at the time of sediment deposition) with the consequence of variation in the emission input without significant changes in the source of the pollutants.

Finally, it depends on factors that are known to complicate the use of excess ^{210}Pb for dating sediments in dynamic (estuarine/coastal) systems (Cantwell et al. 2010); such as:

- non-turbulent environments,
- sediment composition, with reducing (anaerobic) and steady deposition,
- grain size (fine-grained particles for contaminant adsorption), organic content and salinity changes,
- processes like physical mixing, episodic sediment deposition, or variability in sediment sources and sediment supply.

If sediment deposits show significant variations in contaminant concentrations, as a result of intensive mixing or reworking processes, this does not allow a model fitting. In this case an evaluation of contaminations levels correlated with general information on the (historical) scale of contamination can be obtained (Cundy et al. 2003).

Saltmarshes and Maritime Bays Sediments

A reconstruction of historical trends is possible, if the present sedimentological settings can act as an effective sink for contaminant-reactive fine sediments, and erosion processes, reworking, and bioturbation are limited (Cundy et al. 2003). Undisturbed saltmarshes as well as other coastal areas have been widely used to reconstruct input trends, as these provide a stable, vegetated substrate of predominantly fine sediments, and are less prone to erosion and reworking than adjacent mudflat areas.

For instance, Roychoudhury (2007) identifies diurnal tidal flushing, sediment mixing by bioturbation, as well as by vegetation pattern and degradation as the dominant influence on the trace metal content within sedimentary archives of saltmarshes. Comparative studies on the trace metal input within different saltmarshes have been used to identify these main influences and may explain variations (lateral heterogeneity) in the trace metal concentrations of the investigated saltmarshes (Sapelo Island, USA; Roychoudhury 2007). In addition, as essential prerequisites for historical monitoring in maritime bay-zones, some further aspects have to be taken into account:

- environmental bay configuration as a result of natural evolution conditioned by coastal dynamics,
- tidal influences, meteorological conditions, biological factors,
- human activities (e.g. various industries and the development of an urban area).

Ligero et al. 2002, use these aspects to ratify the results determined for the evolution of heavy metal concentration in dated sediment profiles of the Bay of Cadiz, Spain. For accurate sediment dating, dynamic conditions are of major importance in order to determine the accumulation and the sedimentation rate. In this context, the organic carbon contents and parameters linked to the sediment grain size are useful to classify the energetic conditions of the investigated environment. Geochronological investigations of estuarine sediment archives are available for the eastern and western coast of the USA, the east coast of Mexico and some estuaries in Europe, Asia and Africa, for details see also Table 7.1.

7.3.3.2 Limnic Environment

Lake sediments are described as most valuable archives of the catchment area, the fluvial system and the atmosphere over time (Kober et al. 1999). Documented sediment data reflect the temporal changes of the contamination sources, and of variations in the transport path regimes. Therefore, limnic sediments are widely used to reconstruct temporal changes (Giesey et al. 2006; Hites 2006; Kannan et al. 2006). The recorded data sometimes has considerable influence on shaping environmental assessments and regulatory actions. Furthermore, this information enables the study of effects of climate change on distinct metal fluxes (e.g. atmospherical Hg deposition, Outridge et al. 2005).

The interpretation of sedimentary metal profiles in most lakes as an unambiguous record of atmospheric metal deposition has been contested, due to the possibility of post-burial remobilization of metals resulting from diagenesis. Kober et al. (1999) reconstructed the Pb isotope distribution using them for the interpretation and complementation of pollution trends. Variations within the input trends underlie the differences during seasonal aeolian pollution (e.g. Hopper et al. 1991; Erel et al. 1997);

this has been confirmed by pollution time series recorded in snow and ice cores (e.g. Rosman et al. 1994) or by ombrotrophic peat bogs (e.g. Shotyk et al. 1998).

Most of the geochronological investigations on lake sediments have been performed for different sediment archives of the North American Great Lakes (see review by Alderton 1985, and references listed in Table 7.1, MacLeod and Mackay 2004); some further suitable sediment archives were found in:

- lakes in North America or remote lakes in the Arctic or in high altitude mountain regions (e.g. Yukon Lake),
- European lakes like Lake Constance and Alpine lakes (Lake Greifensee, Lake Biel), lakes in Northern Europe (Scotland, Wales and Scandinavia),
- Chinese/Taiwanese lakes and some studies on sediment cores taken from lakes in South America and Africa.

A few studies reveal that certain elements (Hg, Pb, Cd, Cu and Zn) display positive correlations (high enrichment factors and a high affinity) with organic carbon content, whereas others (Cr, Al, Co, Fe and Mn) display a negative correlation and no consistent enrichment in their total concentration on the surface. Bilalia et al. (2002) report that relative affinities for organic and mineral fractions play an important role in the distribution of trace metals during burial (and diagenesis) resulting in a specific patterns in their vertical profiles. Hence, degradation processes within the sediment profile have to be taken into account in order to interpret historical trends in sediment archives.

7.3.3.3 Fluvial Environment

Sediment bound contaminants in fluvial systems are derived from point (industrial and sewage discharge, spillages) or diffuse sources (e.g. remobilisation of contaminated alluvium, agricultural and street run-off) (Hudson-Edwards and Taylor 2003). Within several studies, the need of long-term geochemical (and geomorphological) monitoring for forecasting downstream contaminant dispersal rates and patterns are reported (e.g. Macklin et al. 2003).

In addition to the subaquatic accumulation and deposition of fine-grained sediments within the river body (e.g. in stagnant water zones of groynes areas and harbours, cut-off meander), particle-bound contaminants may leave the water body during flooding events or stormwaters and are deposited on the adjacent terrestrial areas, the floodplains and wetlands. Hudson-Edwards and Taylor (2003) name floodplains, channels, riparian wetlands and occasionally dammed reservoirs constructed on rivers as the most important sink for heavy metals, contaminants and nutrient deposition and storage in the fluvial environment.

Adjacent Areas: Floodplains, Wetlands and Riverbanks

River floodplains arise during the deposition of suspended sediments of flood events; they build up if particle-associated pollutants are deposited with the suspended sediments which can remain stored in alluvial environments for decades or centuries.

Hence, they are described as important long-term and large-scale sedimentological archives within a fluvial system, used to interpret sedimentation processes as well as to evaluate the surface and sub-surface distribution of anthropogenic pollutants (Zhao et al. 1999).

A few studies discuss the relationship between sediment particle size and the sediment-bound compound concentrations (e.g. for heavy metals). Although results contrary to this aspect are reported, there is a need for information concerning heavy metal content in the sediment archives of floodplains further downstream former mining sites, industrial and municipal-related sources for a better understanding of transportation and sedimentation processes of heavy metals carried by rivers (Zhao et al. 1999).

There is a limited number of studies on the historical record of anthropogenic contaminants derived from the analysis of lake, coastal and estuarine sediments, as reported before. Results of similar investigations on floodplains have been reported only scarcely (e. g. Gocht et al. 2001) and are mostly worked out for contaminants like PAHs, PCBs, pesticides and heavy metals. Monitoring of anthropogenic contaminants in fluvial systems is reported from different areas worldwide. Especially geochronological studies are available from:

- North and South America (PAHs in Black River sediment cores, Ohio, USA),
- Europe (heavy metals, PAHs., PCBs, pesticides and organotin compounds, as well as a broad spectrum of "modern" contaminants in the Rivers Elbe, Lahn, Lippe, Rhine, Teltow Canal),
- Asia (PAHs in Pearl River, CN),
- Africa (pesticides and PCBs in sediments of the Ouémé River, in the Republic of Bénin).

7.4 Methods

In order to perform historical trends, the sampling and processing of the sediment samples must be planned and carried out very accurately. In the following several methods are listed.

7.4.1 Sediment Sampling

The collection of intact profiles of non-compacted (soft) surface sediments without disturbing the stratigraphy/bedding is performed by an elaborate coring device. Typically the samples are taken with:

- piston and gravity corer, using a stainless steel core barrel with polybutyrate liner/diver-operated piston corer (e.g. Sansone et al. 1994; Hornberger et al. 1999),

- tube coring in combination with a deep-freeze core sampling technique (Veerschuren 2000; Ricking and Schulze 2003; Renberg and Hansson 2009).

Besides this, different gravity core techniques or sampling by hand coring, the deep-freeze sampling method (Ricking and Schulze 2003) seems to be an appropriate technology for core sampling. This method allows sampling of sediments in an undisturbed stratified way, covering the entire corn grain size from fine grain particulate matter to very coarse sand.

Surface sediments up to a sediment depth of approx. 2 m are taken by in-situ freezing of the sediment. A variety of freeze core devices have been used, from simple metal tubes filled with dry ice that are dropped into the sediment to high-tech samplers using for instance liquid nitrogen (Renberg and Hansson 2009). In order to take suitable core samples for geochronological investigations the coring device should not disturb the stratigraphy when penetrating into the sediment, guarantee a fixed and stable position during freezing and obtain and preserve adequate quantities of sediment (Veerschuren 2000).

7.4.2 Petrogenic Analytical Investigations

From the overall composition, the fine suspended-sediment particles, fine silty sediments with higher organic-carbon contents are of utmost interest, particularly with regard to long-term sedimentation and accumulation as well as to their properties of adsorption of lipophilic contaminants. Compared to coarse sandy sediments, they can be characterised by their higher surface area to volume ratio, which may result in higher concentrations of accumulated pollutants on a weight for weight basis (Warren et al. 2003).

For petrogenic analysis the following measurements are used for analysis:

- grain size measurements: laser granulometer (Audry et al. 2004; Zourarah et al. 2007),
- organic and inorganic carbon contents: e.g. determined by combustion (LECO analyser, e.g. Zourarah et al. 2007), alternatively the loss-on-ignition (LOI) and moisture can be determined,
- porosity: comparison of the weights of wet and dried sediment (Audry et al. 2004), and
- assessment of combined chemical and hydrodynamic effects (Westrich and Förstner 2007).

7.4.3 Sediment Dating

Various approaches for sediment dating are still utilised; particularly with regard to an adequate time-stratigaphic classification of the sediment archives (e.g. summarized by Alderton 1985). By now ^{210}Pb chronometric dating has become the most important technique. In this context Smith (2001) emphasises for ^{210}Pb geochronology the need to validate at least one independent tracer (for a tracer flux model) that separately provides an unambiguous time-stratigraphic horizon, such as ^{137}Cs. In order to confirm the accuracy of the model and to produce a precise time-stratigraphy in sediment horizons a correlation is necessary which can be performed by other (independent) chronological methods. Several other dating methods are used, for instance some further radiogenic markers and varve chronology, by exploiting variations in specific flora and fauna (e.g. pollen), chemical marker compounds or a site specific analysis.

A main criterion for accurate timing of sedimentation (and the emission of anthropogenic pollutants) is to consider the effect of physiological activities of benthic organisms (bioturbation) and other mixing processes. Furthermore some other conditions must be taken into account:

- Background correction: Heavy metal or PAH concentrations must be background corrected and compared to other rivers (Audry et al. 2004). For instance, bay watershed contains mineral deposits and ultramafic rocks that are naturally enriched in metals relative to the mean composition of the continental crust. Interpretation of human influences requires an understanding of this natural baseline of metal concentrations (Hornberger et al. 1999).
- Factors which may complicate or distort the CRS (constant flux) model are: short water residence time, bioturbation, discontinuous or disturbed sedimentation, sediment resuspension and shifts in sediment source (Oldfield and Appleby 1984)
- Down-core changes in sediment grain size and/or the composition (Plater and Appleby 2004)

A comprehensive summary and analysis of the result of a broad set of dating studies is given by Oldfield and Appleby (1984). The authors present advantages and disadvantages of ^{210}Pb dating models, possibly modification of the ^{210}Pb/CRS dating models to accommodate discontinuities in sedimentation, and the effects of bioturbation and sediment resuspension.

Christensen and Arora (2007) observe the PAH fluxes to obtain the total contaminant concentrations. With the culminate mass of sediments they transform the sedimentation rate into a time scale and estimate the original mixing depths, based on (near constant) ^{210}Pb activities and PAH concentrations. A correlation of both methods is used in order to take uncertainties in this estimation into account.

7.4.3.1 Radioisotopic Dating: Identification of Marker Horizons

Radioisotopic dating of soil, sediments and ice archives, represents the most important technology for geochronological investigations of different scientific issues, using e.g. ^{210}Pb, ^{137}Cs and ^{239}Pu + ^{240}Pu nuclides. Since 1950 the release of radionuclides into the environment has been used for dating purposes. Mainly caused by anthropogenic activities, for instance by nuclear weapon testing or as a result of a nuclear fall out (e. g. the Chernobyl event) in particular ^{137}Cs appears in measurable quantities in the environment. Thus, radionuclides act as indicators of the sedimentation rate of particles on which they are adsorbed (Edgington et al. 1991).

Several other dating techniques have been used (e.g. Allen et al. 1993 and references within, Alderton 1985):

- discrete marker horizons related to evident historical events,
  In this way an approximate time-frame can be established and the sediment deposition after this event (in case of constant sedimentation rate) can be estimated,
- annual lamination/bands or varve chronology (Renberg 1979; Wessels et al. 1995; Allen et al. 1993),
- dating of artefacts in a well-defined horizon within a sequence,
- inspection of dated topographic maps,
- pollen and/or diatom analysis (Smith and Walton 1980; Allen et al. 1993),

Dating by ^{210}Pb

The interest in the history of recent sedimentological events has also focused on applications of the naturally occurring radionuclides. In particular, ^{210}Pb is used as a geochemical tracer to determine sedimentation rates, predominantly in *lakes* (Krishnaswamy et al. 1971; Robbins and Edgington 1975; Robbins 1978; Kober et al. 1999) *estuaries* (Eisenreich et al. 1989; Venkatesan et al. 1998; Zhang et al. 1999; Miller et al. 2008) and *coastal* marine sediments (Zourarah et al. 2007). A few studies have been performed for fluvial sediment archives (e.g. Klös and Schoch 1993a, b; Winkels et al. 1993; Vink et al. 1999; Audry et al. 2004; Heim et al. 2004, 2005, 2006; Götz et al. 2007).

The method is based on the radioactive decomposition of ^{238}U through a series of steps to a stable form of lead (finally to ^{210}Pb and ^{206}Pb). During this decay ^{226}Ra is built in the soils and yields the gaseous nuclide ^{222}Rn. A portion of ^{222}Rn diffuses into the atmosphere where it subsequently decays rapidly into ^{210}Pb. Finally, this ^{210}Pb is deposited from the atmosphere and incorporated into the aquatic environment by adsorption onto sedimentary particles and hence consolidated into the sediment as “unsupported” ^{210}Pb. In addition, there is a so called “supported” part of ^{210}Pb, resulting from the decay of “in situ” produced from the decay of ^{226}Ra.

In a first step of determining of the sediment ages the conceptual model is based on the estimated initial activity, regarding the total activity of ^{210}Pb (as the sum of supported and unsupported ^{210}Pb). This requires a radioactive equilibrium within the sediment between the in situ ^{226}Ra and the (unsupported) ^{210}Pb content. Equilibrium conditions are present, if the decay products undergo transformation at the same rate they are produced, this depends on the relative lengths of the half-live of the radionuclides and their decay products. In case that the concentration of supported ^{210}Pb in the sediment remains constant, and a progressive decay of the excess (unsupported) ^{210}Pb, a concentration decrease in sediments (of unsupported ^{210}Pb) can be determined. Based on the assumption that the atmospheric influx of ^{210}Pb is constant, the age of sediment deposition can be calculated from the present-day content of "unsupported" ^{210}Pb and the known decay rate.

Finally, for calculation of sediment ages there are two modes used, regarding the variations in sedimentation rates. On the one hand, there is the model of "Constant Initial Concentration, CIC", (Alderton 1985) that assumes an annually uniform sedimentation, where each unit weight of sediment should have the same content of "unsupported" ^{210}Pb. This assumption considers the changes in the flux of sediment particles from the water column and mirrors changes in the amount of ^{210}Pb (removed from water to sediment). Otherwise, in case of variable concentration rates, the "Constant Rate of Supply, CRS" model (Appleby et al. 1979; Oldfield and Appleby 1984; Cantwell et al. 2010) is used. This approach assumes a constant flux of "unsupported" ^{210}Pb from the atmosphere to the sediment, which is independent of any changes in sedimentation rates. This takes varying sedimentation rates into account, by dilution of ^{210}Pb by a more rapid sedimentation or concentration increase, caused by slower sedimentation rates (Allen et al. 1993).

For a given half-live of 22.3 years of ^{210}Pb, this dating method is an excellent tool to determine the age of sediments and soils within an overall time interval of the last 100–150 years, the period of time during which appreciable environmental changes occurred due to industrialization (Alderton 1985; Krishnaswami et al. 1978; Ruiz-Fernández et al. 2007).

Dating by ^{137}Cs

Several authors use the ^{210}Pb dating techniques in conjunction with ^{137}Cs, in order to fit their models. Matching the sedimentation rate determined with the ^{210}Pb-CRS model fit ensures an adequate sediment geochronology. A few studies are reported using this correlation, for instance for *lake sediments* (Outridge et al. 2005); as well as for *marine/estuarine archives* (Plater and Appleby 2004; Cantwell et al. 2010); *fluvial archives*: (Benninger et al. 1998; Audry et al. 2004; Heim et al. 2004). It is important to note that estuarine systems generally receive both direct atmospheric radionuclide deposition and river-derived inputs from catchment soil erosion (Oldfield and Appleby 1984).

In general, ^{137}Cs enables some fixing of age with depth to be determined from the onset of ^{137}Cs. A first peak can be related to the first weapons testing in 1954, followed by a second maximum ^{137}Cs activity peak due to the fallout from atmospheric weapons testing in 1963 (see Fig. 7.2). Finally, a more recent increase was caused by the atmospheric fallout from the Chernobyl reactor in 1986 (Plater and Appleby 2004).

Activities of ^{137}Cs and ^{210}Pb radionuclides in sediment and soil cores are determined by α and γ- spectroscopy. A detailed description of the analytical/experimental setup is reported in Appleby and Oldfield 1978; Appleby et al. (1979, 1988), Allen et al. (1993), Bollhöfer et al. (1994).

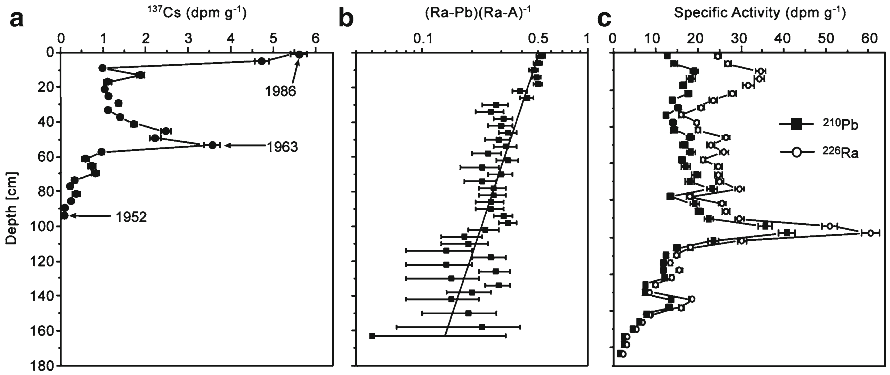

Fig. 7.2 (**a**) ^{137}Cs-profiles, determined in riparian wetland sediments of the Lippe River, (**b**) ^{210}Pb/^{226}Ra-profiles and (**c**) a ^{210}Pb/^{226}Ra resulting plot (Heim et al. 2004)

7.4.3.2 Dating by Using Annually Laminated Sediments: Varve Chronologies

Varve geochronology is an important method of sediment dating. This method is based on the concept of an annual rhythm of deposition, where sediment variation (lamination) in clastic, biological, and chemical sedimentary processes is caused by seasonal differences. Primarily used in marine and lacustrine depositional environments, this method relies on the fact that during the summer months a consequent deposition of coarser particles takes place (e.g. by increased ice melting), whereas during cold weather (winter) this is reduced, and sedimentation of finer particles can be observed. One year cycle consists of two horizons: one dark and fine-grained and one light-coloured and coarser. Differences in the colour of the sediments can be related to oxidising conditions during water turnover periods whereas the darker sediments are placed under reducing conditions as a result of water stratification (Renberg 1979).

The geochemical and the petrographical composition of the sediments deposited for instance in lake sediments closely follow the seasonal changes of water discharge. Undisturbed sediment profiles are reflected by a mm- to sub-mm lamination due to the seasonal changes in material and colour. Wessels et al. (1995) report that the laminated sediment layers in a sediment profile taken from Lake Constance contain some superimposing layers, which were generated by flood layers of historical high-water events. This additional lamination can be used for precise dating of sediment cores from the investigated lake sediments (Kober et al. 1999).

7.4.3.3 Other Dating Techniques

Usage of Organic Compounds (Molecular Markers) as Time Markers

A further method to determine the timing of the first occurrence of an environmental contaminant is to consider both chemical and physical characteristics such as natural discharge and size of drainage area. Organic biomarkers that trace land-cover changes by recording marked shifts in the source of terrestrial organic matter (TOM) are also used to reconstruct impacts of urbanization (Brandenberger et al. 2008).

Eganhouse (1997) states that molecular markers under appropriate circumstances can provide information about sources of organic material. The exposure of molecular markers, source specific (organic) compounds with a conservative environmental behaviour, are produced by humans either intentionally or inadvertently, and for some specific representatives a distinct time of first occurrence is given. Suitable compounds used for correlation of sediment dating are the biocides triclosan and triclocarban. Miller et al. (2008), correlate the first occurrence of both biocides in the 1960s with the announced patent date of the compounds. A similar correlation between the first occurrence as sediment contaminant and the documented increasing usage of a compound has been found for PCBs and its substitute Ugilec$^{(R)}$, as reported by Heim et al. (2004).

Dating by Using Variations in Specific Flora and Fauna

Deposition events related to variations in specific flora and fauna (also related to cultural eutrophication). Outridge et al. (2005) use varved sediments for a high-resolution record of metal accumulations in lakes of the Canadian High Arctic. Here the metal flux (Hg, Cd, Cu, Pb and Zn) since 1854 has been correlated with elements of predominantly local geological origin such as Ca, Al and La. In addition the authors correlate these data with the total diatom abundance over a long time interval, and then it was possible to interpret the increase in Hg-concentrations in Arctic and sub-Arctic lakes.

In this context, pollen studies are reported as a method of particular importance (Alderton 1985), used to reflect historical changes in vegetation. Monitoring studies of Great Lakes sediments show variations in the concentration levels (of PAH) caused by extensive forest clearance for agriculture by settlers.

Prior to geochemical analyses sediment samples used for monitoring studies are stored at low temperatures (in the dark) and sometimes freeze-dried. There are several analytical approaches used for qualitative and quantitative analyses. Regarding the variety of potential methods, this work will give some references to additional literature and materials. Qualitative and quantitative analysis is performed using standard methods, depending on the chemical character of investigated pollutant and the subordinate research interests.

7.5 Case Studies: Pollution Histories of Persistent Pollutants in Aquatic Sediment Archives

Since the late 1970s, when dating by radioisotopes made possible the reconstruction of the sedimentary contamination history, a large number of monitoring studies have been performed for the aquatic environment (an overview is given in Table 7.1).

Since chemical degradation of pollutants, physical and biological mixing processes or intermittent sedimentation are the main restrictions for the geochronological approach, most of the suitable sedimentary archives have been indentified within the marine and limnic environment. By contrast, geochronological investigations on fluvial sediment archives are rather limited.

First research focused on heavy metals, but nowadays geochronological investigations consider also a broad spectrum of organic contaminants (Alderton 1985; Valette-Silver 1993). Most of these studies combine the geochemical and geochronological data with geographical information, as well as with product specific data of the specific contaminant.

In this review, only a brief overview of historical trends of representative compound classes is given. Persistent organic pollutants (POPs), heavy metals and the more "modern" contaminants are chosen in order to illustrate the overall influence, extent and the input sources of anthropogenic activities on the sedimentary aquatic environments.

7.5.1 Heavy Metals and Their Long-Term Behaviour in Aquatic Sediment Profiles

The heavy metal input is a typical sediment contamination caused by extensive human activities. Input trends of a broad range of metals are documented in numerous studies for marine, limnic and fluvial sediment archives worldwide (e.g. Alderton 1985; Kolak, et al. 1998; Macklin et al. 2003; Walling et al. 2003). In most cases they are particle-associated and preferentially transported, deposited and eventually buried with fine grained sediments (Hart 1982; Hornberger et al. 1999; Peng et al. 2008).

7.5.1.1 Historical Trends in Anthropogenic Emission into Sediments of Lake Sediments

Lake sediments often act as sink for pollutants from a variety of sources. They provide detailed information on the historical record of particle bound contaminations which allow establishing a connection between the temporal evolution of the contaminant input and historical changes in its usage. As predominant input sources for metals mining activities, industrial usage or as petroleum additive have been identified. Sometimes these contamination trends have been used to reflect effects on environmental protections measurement like enhanced waste-treatment (Audry et al. 2004).

Heavy metals are among others the best characterised anthropogenic contaminants used for monitoring histories. Exemplary for their overall discharge, accumulation, "sequestration" and persistance, in particular input trends of lead and mercury into the archives of lake sediments are chosen for documentation. Based on appropriate natural accumulation, conditions of sediment trapping and deposition as well

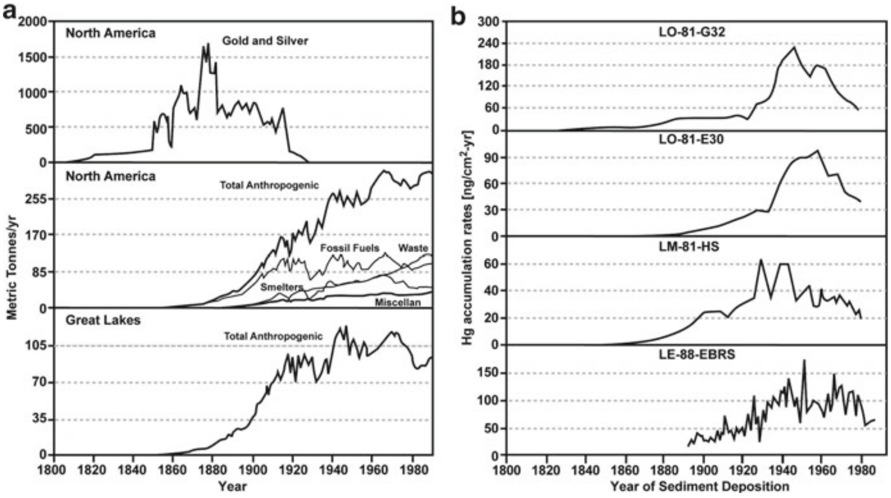

Fig. 7.3 (**a**) Hg emissions from different sources and (**b**) vertical profiles of Hg accumulation rates in Lake Ontario, Erie and Michigan (After Pironne et al. 1998)

as a broad spectrum of emission sources, limnic sediment archives are of major importance and interest (e.g. Hites 2006).

Mercury Emissions into Sedimentary Archives of the Great Lakes

Detailed and extensive work is given in order to determine the input trends and contamination histories of the anthropogenic mercury load. Several studies provide detailed information about the dominant input sources and pathways, input fluxes and methods in order to determine temporal and spatial variations in emission and pathways (Evans et al. 1981, 1986; Mayer et al. 1994; Graney et al. 1995; Kolak et al. 1998; Pirrone et al. 1998; Marvin et al. 2004a and b).

Mercury is a well known globally dispersed environmental contaminant that is found both naturally and as a result of anthropogenic activities. Although its potential for toxicity (USGS 2000), bioaccumulation and biomagnification in highly contaminated areas is well documented (Alderton 1985 and references within, Wang et al. (2010)), mercury can be a significant sediment contaminant; in particular if an environment is not obviously polluted by a local point source.

Main release of Hg into the environment of North, Central and South America is reported as industrial emission, in particular for the beginning of the last century due to intense gold and silver mining activities. In consideration of the absence of suitable local input sources within the Great Lakes area, increasing Hg sediment concentrations during the 1960s to 1980s are related to (increasing) atmospherical deposition (see Fig. 7.3; Pirrone et al. 1998; Marvin et al. 2004a and b).

This historical sediment load, far away from the input sources, suggests atmospheric deposition as a predominant emission source and input pathway for this time interval. Further emission sources, indicated by additional temporal and spatial increases in the particle bound Hg concentrations, reflect variations in the regional and local emissions of Hg. In this context, Marvin et al. (2004a and b) reported the highest sedimentary Hg levels for Lake Ontario and Lake Erie sediments. The input is related to historical point sources such as chlor-alkali production facilities during the 1940s and in the 1970s.

As a general assumption the spatial trends in mercury contamination may have been influenced by local industrial activities in the watersheds and along major tributaries (Marvin et al. 2004a). In addition to distinct (point) sources, the increase in sediment concentrations determined in nearly all sampling sites can be related to a general growth in the urban and industrial centres. Otherwise the most recent decreases in Hg concentrations can be linked with environmental protection measures (Alderton 1985).

7.5.1.2 Monitoring Studies in Lake Sediment in a Global Comparison: Historical Trend in Lead Emissions

Similarly, the historical record of environmental lead contamination indicates local and global effects of anthropogenic activities to the aquatic sedimentary environment. Deposition of lead in Europe, caused by metal production and smelting, can be described as the main input source until the twentieth century, when emissions from vehicles using alkyl-leaded petrol became dominant. Analyses of sediment archives from several regions in Europe suggest synchronous temporal changes in past pollution and point out some corresponding marks (*Scottish lakes*, Eades et al. 2002; *Lake Constance*, Müller et al. 1977*;* Bollhöfer et al. 1994; Wessels et al. 1995; Kober et al. 1999; Renberg et al. 2001). It became possible to distinguish between five distinct time steps of lead emissions due to variations in predominant input sources:

- initial anthropogenic lead pollution during and after the Roman period, marking the Medieval increase in mining, smelting and metal production in mainland Europe,
- coal consumption as predominant input source until 1820,
- emissions by the smelting of indigenous Pb ore and coal burning until the year 1900 and an increase in industrial activities at the beginning of the twentieth century (until 1930),
- Pb emissions, reflecting the rapid increase in traffic, using leaded gasoline after the Second World War and increasing industrial emissions related to a deposition maximum at about 1970,
- decline in Pb values as a consequence of a reduction in car-exhaust Pb-emissions between 1975 and 1985, due to the progressive uptake of unleaded petrol.

Figure 7.4 shows similarities of the temporal changes in Pb fluxes and ^{206}Pb/^{207}Pb ratios, determined for Scottish lakes and Great Lakes of North America.

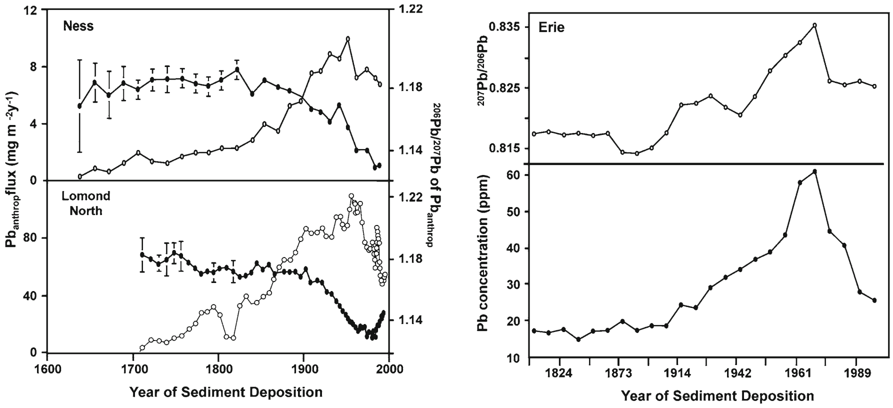

Fig. 7.4 (*left*) Temporal changes in fluxes (o) and ^{206}Pb/^{207}Pb ratios (•) of anthropogenic Pb deposited in the sediments of different Scottish lakes (After Eades et al. 2002) (*right*) Temporal changes in lead sediment concentrations from Lake Erie (After Graney et al. 1995)

As discussed for European lakes, long-term anthropogenic Pb contamination related to human activities are reported worldwide. For the Great Lakes close similarities in the monitored input history of Pb are obvious (Alderton 1985 and references within). The major pathway for lead into the limnic environment is correlated with atmospheric dust-transport and deposition (Wang et al. 2010) in conjunction with a general increase in traffic, local and supra-regional industrial activities as well as the urban growth.

7.5.2 Ubiquitous Persistent Organic Pollutants in Marine Sediment Archives

In order to determine historical trends of anthropogenic contaminants a group of most frequently investigated contaminants can be compiled (Vink et al. 1999). In addition to heavy metals, the group of persistent organic pollutants (POPs), especially chlorinated organic substances and polycyclic aromatic hydrocarbons (PAHs) are some of the ubiquitous contaminants of predominant anthropogenic origin within aquatic sediments. PAH are of major interest. Hereby POPs typically appear within the sediment profiles at much more recent times (in general since the year 1950), and therefore they are specific indicators for industrialisation and population growth (Venkatesan et al. 1980; Bopp et al. 1982; Alderton 1985; Valette-Silver 1993).

In the coastal or estuarine sediment profiles the monitored variations of sediment concentrations provide insights into local and global time trends of the past and present (Barra et al. 2004). For the marine environment a few research studies consider sediment deposits of deep basins, for instance the area of the southern California coast of the USA (see Table 7.1). These sedimentation zones show only minor bioturbation, rapid and varved sedimentation under anaerobic conditions and offer ideal conditions for preservation of particle bound contaminants. Furthermore the majority of geochronological investigations are performed for estuarine sediment archives, because they can often be readily related to particular input sources (Alderton 1985).

River discharge and atmospherical deposition are the major emission pathways for particle associated persistent pollutants within the marine ecosystem. As reported, regional/global (allochthonous) sources as well as some local point sources (autochthonous) are of great importance. In most cases, the level of contamination corresponds to the location of the study area. For some typical pollutants like PAHs high pollution levels are found in locations close to centres of human activities, while low concentrations occur in remote areas (Gschwend and Hites 1981).

In general, investigations of estuarine sediment archives provide significant information related to particular contamination sources, whereas investigations on coastal archives supply evidence of the long-range lateral transport and land-based contamination over larger areas (Alderton 1985).

7.5.2.1 PAHs Within the Estuarine Sedimentary Environment

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment and well-known sediment contaminants in marine sediment archives. They are predominantly emitted by anthropogenic activities, whereas specific background levels can be attributed to a distinct PAH input by natural forest and grass fires. The PAH load of sediment profiles has been investigated several times (Laflamme and Hites 1978; Wakeham et al. 1980; Gschwend and Hites 1981; Arzayus et al. 2002).

PAHs are produced during combustion processes of organic matter and accumulate on particulate matter via condensation from the vapour phase (Smith and Levy 1990). After entering the environment they are widely distributed on fluvial and aeolian pathways, and finally accumulated in soils and sediments. Once deposited, these compounds are less subject to photochemical and biological oxidation and thus tend to persist for longer periods and to accumulate in high concentrations (Liu et al. 2005). Time trends of sedimentary PAH concentrations indicate the increasing industrialisation and the related increase in combustion processes of fossil fuels over the last 200 years as the major anthropogenic emission sources in North America and Europe (Smith and Levy 1990; O’Dwyer and Taylor 2009).

In general, four distinct concentration maxima are detectable: a first and initial maximum prior to the beginning of the twentieth century, followed by a maximum PAH flux in the 1950s. Then, a third maximum is detectable in 1973, followed by decreasing ranges as a result of the oil embargo in this time, and finally an abrupt increase in PAH fluxes between 1996 and 1999. For the latter one, Lima et al. (2003) suggest that an increase in energy consumption (diesel fuel combustion and traffic) is the most probable explanation.

7.5.2.2 PCBs as (Non)Specific Marker Substance in Sediment Cores

Polychlorinated biphenyls (PCBs) are as well widely used, primarily as additives to oils and industrial fluids (Hites 2006; Norstrom et al. 2006). They are well known and ubiquitous distributed contaminants and show a high persistence, bioaccumulation, and toxicity to animals and humans (Takada and Eganhouse 1998). Depending on the degree of chlorination of PCBs, their physico-chemical properties (in flammability or electric conductivity; Hornbuckle et al. 2006) imply a wide field of applications into the environment. Relative large amounts of PCBs are released due to inappropriate disposal practices, accidents and leakages from industrial facilities. Even though PCBs have been restricted for use since decades, the usage of e.g. PCB-containing transformers (in some countries, for instance Chile) up to now is well-known (Barra et al. 2004).

Some monitoring studies use input trends in sedimentary PCB concentrations as an indicator for industrial influences due to their extended usage in hydraulic oils (Poppe et al. 1991). Klös and Schoch (1993a, b) and Heim et al. (2004) determined PCB concentration in riverine sediment archives and associate their emission with local mining activities. Within the investigated sediment cores a maximum in sediment contamination has been related to the beginning of the 1980s, followed by a distinct decrease up to the present. The authors correlate this reduction to a gradual substitution of PCBs by its substitute (tetrachlorobenzyltoluenes, TCBTs), whereas the TCBTs show a distinct increase in sediment contamination since 1980.

Moreover, a few monitoring studies report consistently a reduction of specific persistent toxics as a consequence of the implementation of a ban, in case of PCBs in the late 1970s (USA). Substantial reductions of PCBs determined in sediment cores are reported for different locations (e.g. Wong et al. 1995; Pearson et al. 1997; Heim et al. 2004). Some of the investigations show a reduction to nearly 70–80% correlated to a time period between 1960 and 1990 (Schneider et al. 2001; Marvin et al. 2004a and b).

In general two main sources of PCBs can be identified, on one hand emissions by the industrial production, for instance electric capacitor manufacturing facilities (Bopp et al. 1982) and secondly emission as by-product in combustion processes as thermodynamically stable compounds.

In particular these examples show the specific utilization of historical monitoring studies. Although PCBs are no specific marker compounds, due to their broad technical application and multiple emission sources, they can be used as well as specific marker compounds under (the reported) certain conditions (Heim et al. 2004).

7.5.2.3 Time Trends of Pesticides Within Aquatic Sediment Archives

Although the main occurrence and fate of pesticides in the environment is correlated to their agricultural application, they are still not remaining in the soil. A large amount is transported to rivers and groundwater by leaching, surface runoff from agricultural areas, atmospheric transport or soil erosion. However, chlororganic pesticides (e.g. γ-HCH, dieldrin, DDT) show mostly an ubiquitous distribution and diffuse emission sources (Marvin et al. 2004b).

For the time period since the 1950s organochlorine pesticides, in particular DDT and its metabolites (DDX) as well as γ-HCH (Lindane) are extensively used in agriculture. Despite the ban in most industrialized countries in the early 1970s, today residues of them are ubiquitous detectable in sediment and soils. Heim et al. (2005) report increased concentration levels of former affected environments as a result of sediment re-suspension. In general, monitoring studies dealing with concentration trends of DDX show only a very slow reduction in sediment concentrations, presumably because of the large amount of emitted DDT, remaining in the sediment.

Hence time trends determined in dated sediment core make possible not only a reconstruction of temporal variations within a sediment profile. This methodical approach reveals the influence of recently remaining emission sources, transmission and transportation processes of contaminated particulate matter. It enables an identification and also visualization of (highly) contaminated sediment horizons and their remaining contamination potential, especially within a river system. Hereby long-term effects on the ecosystem can be studied, which indicate the necessity for detailed and long-term monitoring studies of affected aquatic environments (Heim et al. 2005).

7.5.3 “Modern Contaminants”

The occurrence of common contaminants, like heavy metals, PAHs and PCBs, can be recorded within sediment profiles covering a long period of time, mostly in a range of 50 years up to more than 200 years. The group called as “modern contaminants” occur only in sediment layers representing a time period since the 1970s (Warren et al. 2003; Heim et al. 2004).

Whereas the most of the common contaminants show decreasing sediment concentrations up to now, especially since environmental protection has been implemented in the 1960s and later, most of the modern contaminants show maximum concentrations in the late 1980s. This time trend highlights the beginning of an efficient cleaning process, covering a broad spectrum of anthropogenic contaminants, as a result of a progressive sewage treatment technique.

However, the varied and intensive usage of detergents, consumer goods and personal care products with a huge inventory of a large number of different chemical substances is steadily increasing. Introduced into the environment by domestic wastewater, a wide range of substances are only partially removed during wastewater treatment (e.g. Miller et al. 2008; Cantwell et al. 2010).

In addition the group of modern contaminants show an increasing number of constituents. Typical representatives are biocides and antifouling paints (e.g. organotin compounds, organtriclosan/triclocarban), synthetic musk fragrances (e.g. galaxolide/tonalide) or technical flame retardants (e.g. tris-(chloropropyl) phosphates, polybrominated diphenyl ethers/PBDEs, tetrabromobisphenol A/TBBPA).

Interestingly most of these contaminants are determined in sediment archives of freshwater-environments, only a few studies have dealt dealing with these compounds within a truly marine environment, so far. In this context, Venkatesan et al. (1998) report that e.g. organotin compounds are determined in sediments and waters mainly on coastal areas and near centres of intense boat use or fish farms. The authors indicate the stability of organotins in a deeper marine basin suggesting the stability of organotin compounds on their long-range transport to offshore sites. Here butyltin contaminations detected in deep ocean waters and sediments range in the ultra-trace level.

The growth in demand of products with antimicrobial properties has resulted in the increased production and release. A typical example is for instance the biocide triclosan. Triclosan enters the aquatic environment primarily through discharge of municipal wastewater treatment plants; although in the process of wastewater treatment effective sequestration and partly biodegradation of biocides can cause a significant reduction (e.g. Kolpin et al. 2002).

Miller et al. (2008) report the occurrence of the biocides triclosan and triclocarban, tracing the time course of biocide usage and wastewater treatment strategies. Due to their significant lipophilicity triclosan and triclocarban tend to adsorb to abiotic particulate matter (Cantwell et al. 2010; Miller et al. 2008; Halden and Paull 2005). Within in the water phase, both biocides are removed from the water column through various physical, chemical and biological processes and find their final sink in aquatic sediments. Miller et al. (2008) report the first occurrence of both biocides in 1950 (triclocarban) and 1960 (triclosan), peaking in the late 1960 and late 1970, respectively. This time trend of the first appearance in the sediment cores near 1964, corresponds to the US patent issuance date of triclosan. Within this study discharge into the river system after wastewater treatment has been identified as the principal pathway of contamination.

Significant decline in triclosan and triclocarban concentrations within samples deposited since the mid 1980s was related to the WWTP (wastewater treatment plant) upgrade since end of 1970s, e.g. by the introduction of full activated sludge treatment or trickling filter (Miller et al. 2008; Singer et al. 2002). Temporal increase in concentration can reflect the influence of major combined sewer outflow events. The highest concentration amounts are related to >30 year old sediments, suggesting a very slow degradation rate.

Increasing or continuing high values of triclosan concentration are reported for limnic, fluvial and estuarine sediments for the last three decades (by Singer et al. 2002; Heim et al. 2006; Miller et al. 2008) reflecting the greater biocide usage since 1980s. The major issue concerning the fate of a pollutant like triclosan is the extent to which it is being preserved in aquatic sediments. The presence of triclosan in deep sediment horizons corresponds to its patent date and this compels evidence that it is being largely preserved. Uncertainty remains as to whether there is loss of a pollutant once it has been sequestered in the sediments (Cantwell et al. 2010).

Furthermore synthetic musk fragrances belong to this group of chemicals. They are extensively used in detergents, perfumes, shampoos, and other personal care products and the typical input pathway is related to municipal discharge of wastewater. Peck et al. (2006) estimate a significant increase in the consumption

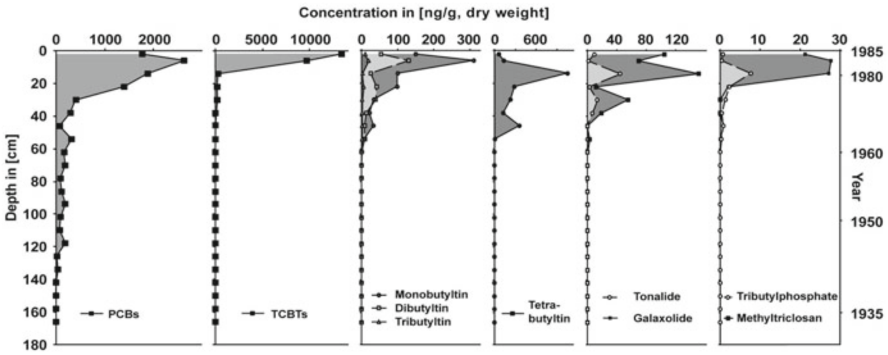

Fig. 7.5 Depth- and time-correlated concentration ranges of different common and modern sediment contaminants, determined in dated sediment cores of a Lippe River wetland (After Heim et al. 2004)

of different synthetic musk fragrances in the USA. The authors indicate an initial discovery of some of these compounds in Great Lakes sediment in the early 1960s. Since this time they are detected in waters, sewage sludge as well as in soil and (dated) sediments. In contrast to investigations in Japan and Germany where a ban/phase out of these compounds in the 1980s has been stated (Peck et al. 2006 and references within), a significant decrease in sediment concentrations has not been detected for all of these compounds. Instead, the input trends of some synthetic musk fragrances determined in different locations of the North American Great Lakes, show significant increases and maximum levels in the time period between 1990 and 2000. Besides this, possibly differences in the emission trends, responsible for the detected variations, may be the importance of local input sources (e.g. wastewater treatment outfall; Peck et al. 2006).

Finally, the determination of “modern contaminants” and their spatial and temporal occurrence within sediment (aquatic) archives has to be correlated with some further data (e.g. the introduction date of the contaminants). If this is possible, the observation of input trends within different sediment archives can be used to assess the status quo of an aquatic environment (e.g. a river system, see Fig. 7.5), regarding the long-term preservation and possibly the necessity of protection measures (Klös and Schoch 1993a, b; Heim et al. 2004; Cantwell et al. 2010).

7.6 Conclusion

The documentation of the human impact on aquatic environments over a long time range in the past is possible primarily by geochronological monitoring of pollution histories. This includes a reconstruction of concentration trends of anthropogenic derived sediment pollutants and their spatial distribution in a definitive time frame.

In most countries and for all aquatic environments the effort to reduce the emission load started in the late 1960s. The reconstruction of past input trends and temporal variation in sediment contamination is a very valuable way to support and evaluate the strategies used for contamination reduction. Although there are some preconditions that have to be fulfilled, the large number of published studies shows that suitable sediment archives are available within all aquatic environments (especially marine, coastal, estuarine and limnic sedimentary archives). Contrary to the previous statement of Alderton (1985) the published data indicated that also suitable sediment archives within the fluvial environment, both subaquatic and terrestrial (wetlands and floodplains), can be identified and used for geochronological studies. Nevertheless, this review also clearly indicates that geochronological investigations on fluvial environment are only scarce, and some further research work is obviously necessary.

An expansion of the spectrum of sediment contaminants and their corresponding long-term input trends, as well as the expected future concentration trends were clearly identified by geochronological investigations. In addition to the expanding spectra of contaminants, most of the reviewed studies indicated a distinct decrease in the concentrations of common anthropogenic contaminants for the last three decades. This suggests that environmental protection measures have been effective even though the growth of urban centres and population worldwide is increasing (dramatically). On the other hand, screening analyses of sediment contaminations show an increase in more "modern contaminants", which are determined with increasing concentrations since the 1970s. Their occurrence and the extent of these contaminants indicate a potentially future risk of this group of only recently unknown pollutants. Here as well the necessity of further research works is evident.

In summary geochronological investigations on aquatic sediment archives correlate information of several unique aquatic systems. They provide insights into the initial appearance of a contamination and its subsequent behaviour and fate in the aquatic system. In addition, this methodical approach reflects the sustained accumulation over time and the remaining contamination potential. Using further environmental information (geographical data, production and usage rates of compounds and input sources) it becomes possible to expand highly the knowledge on historical contaminations. This information is particularly valuable for assessing present and future potential risks of remaining sediment contaminations.

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Chapter 8

Organic Pollutants as Endocrine Disruptors: Organometallics, PAHs, Organochlorine, Organophosphate and Carbamate Insecticides, Phthalates, Dioxins, Phytoestrogens, Alkyl Phenols and Bisphenol A

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Abstract Several natural or anthropogenic substances have endocrine disrupting properties that can modify the endocrine system of living organisms. This has led to increasing concern of the public. Results from animal models, human clinical observations, and epidemiological studies incriminate endocrine disrupting substances as a significant concern to public health. Estimation of health impacts of endocrine disruptors is complicated because some of these chemicals contribute to the occurrence of common diseases of multifactorial etiology such as infertility, cancer and neurobehavioral deficits. The difficulty of assessing public health effects is increased by the fact that people are typically exposed to multiple endocrine disruptors simultaneously.

We review here natural and anthropogenic endocrine disrupting substances occurring in the environment. We discuss the potential effects of exposure to endocrine disruptors in humans and wildlife. This review focus on toxicity, environmental fate, ecological effects and metabolism of organometallic compounds, polycyclic aromatic hydrocarbons, organochlorine, organophosphate and carbamate insecticides, phthalates, dioxins, phytoestrogens, alkyl phenols and bisphenol A. Recent studies show that nonylphenol, bisphenol-A, flavonoids, isoflavonoids and some chlorinated pesticides modify thyroid hormone systems. Androgen mimicking chemicals in the environment can bioaccumulate and evolve through the food web. Exposure to androgenic substances can alter reproduction of all species including humans. Research should be focused on the identification of the life stages and species that are more vulnerable to the effects of endocrine disrupting compounds and how this mechanism of disruption affects populations and communities.

Keywords Organic pollutants • Endocrine disruptors • Imposex • Anti-estrogens • Androgen antagonists • Egg shell thinning • Breast cancer • Dioxins • Phthalates • Polycyclic aromatic hydrocarbons • Organochlorines • Organophosphates • Phytoestrogens • Organometallic compounds

8.1 Introduction

The endocrine system of the body has an indispensable role in the short-and long-term regulation of metabolic processes. Endocrine systems control behavioral, nutritional and reproductive processes including growth, functioning of gut, cardiovascular, and kidney, and responses to all kind of stress. It consists of glands such as the pituitary, the pancreas, the adrenals, and the testes which secrete carefully measured amounts of messenger chemicals called hormones into the bloodstream. Hormones pass through to different parts of the body and bind to specific receptors in order to control and regulate many life functions. Overactive and underactive hormone secretion associated with disorder of the endocrine function inevitably leads to results that are most often life-threatening. Compounds that interfere with natural hormone functions have many names: environmental estrogens, xenoestrogens, endocrine disrupters, endocrine modulators, and environmental hormones, to name the most common. Although all researchers do not accept one specific term, endocrine disrupters and endocrine disrupting chemicals are probably used most widely. As per United States Environment Protection Agency, an environmental endocrine or hormone disruptor may be defined as an exogenous agent that interferes with the synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior (USEPA 1997).

Endocrine disruptors differ in origin, size, potency, chemical life cycle, amount, and effects. Many are chemicals produced for specific purposes and are used in pesticides, plastics, cosmetics, electrical transformers and other products. Other substances are generated as a byproduct during manufacturing or are breakdown products of some other chemical. Some, like diethylstilbestrol and ethinylestradiol, are synthetic drugs, while others are natural plant compounds called phytoestrogens. Endocrine disrupters are compounds that alter normal hormone regulation in humans and wildlife. These could be either naturally occurring environmental chemicals and/or synthetic compounds from industrial products and wastes. Chemicals may bind to sex hormone receptors, activate them and thus lead to responses similar to endogenous oestrogens and androgens. They may also bind to hormone receptors without activating them. However, by this they block binding of endogenous hormones, which therefore cannot be active. Hormones play a crucial role in guiding normal cell differentiation in early life forms, and so exposure to endocrine disrupting substances in the egg or in the womb can alter the normal process of development. Mature animals can also be affected, but it is the developing organism that is especially vulnerable. Exposure at this sensitive time may cause effects that are not evident until later in life, such as effects on learning ability, behaviour, reproduction and increased susceptibility to cancer and other diseases. Endocrine disruptors comprise various classes of organic compounds that have emerged as a major environmental issue in the last decade (USEPA 1997). Domestic and industrial wastewaters are significant sources of endocrine disruptors s to receiving surface, coastal waters and regional environments (Ahel et al. 1996; Lee Ferguson et al. 2001; Ying et al. 2002a, b; Voutsa et al. 2006). Some of these chemicals have biological activity similar to that of endogenous 17-estradiol and are known to affect development, sexual maturation and reproduction of many wildlife species and humans. There is increasing evidence that some synthetic chemicals in our environment may interfere with our bodies' complex and carefully regulated hormonal messenger system. Chemicals can disrupt the endocrine system in several ways. They can mimic or block chemicals naturally found in the body, alter hormonal levels, and thus, affect functions that these hormones control. Less direct interferences involve alteration of the body's ability to, interference with the ways hormones travel through the body, and changes in numbers of receptors.

Suspected endocrine disrupting chemicals are found in insecticides, herbicides, fumigants, and fungicides and in industrial chemicals such as detergents, resins, plasticizers, and monomers in many plastics. Exposure to these chemicals occurs through direct contact in the workplace or at home, or through ingestion of contaminated water, food, or air. When these plastics, or other materials, are burned many unwanted byproducts that are endocrine disruptors or suspected endocrine disruptors are released into the air or water.

Most endocrine disrupting chemicals are fat-soluble and they do not get rapidly flushed out of the body, but rather are stored in fat tissues. Very low levels of a chemical in the air, water, or soil result in higher levels in plant life, still higher levels in herbivores, and even higher levels in carnivores. An individual will accumulate more of these chemicals throughout his/her lifetime. The major routes of removing these chemicals involve transfer from mother to child, through the placenta and in breast milk. Decreased reproductive capability in feral organisms may be considered as one of the most damaging effects of persistent pollutants released by man. A number of xenobiotics with widespread distribution in the environment are reported to have endocrine activity which might affect reproduction and thus might threaten the existence of susceptible species. Animals at high trophic levels, generally having limited reproduction rates, are likely to be the most vulnerable in this regard. This article reviews the literature on the endocrine effects of various organic pollutants and the metabolic and environmental fate of such endocrine disrupting chemicals.

8.2 Major Organic Pollutants

8.2.1 Organochlorine Insecticides

8.2.1.1 Background

Organochlorine compounds are widely used as pesticides and are substantial environmental pollutants and carcinogens due to their extensive environmental release. Many pesticides are now suspected of being endocrine disruptors – chemicals that can lead to an increase in birth defects, sexual abnormalities and reproductive failure. An example is formed by the indications that polychlorobiphenyl pollution

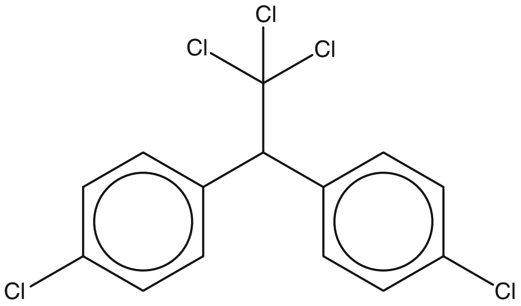

Fig. 8.1 Organochlorine insecticide Dichlorodiphenyltrichloroethane (DDT)

of Swedish waters is linked to uterine occlusions and stenoses in female ringed seal, resulting in reproductive failure and, consequently, a rapid decrease of the seal population (Helle et al. 1976a, b). The insecticide dichlorodiphenyltrichloroethane (Fig. 8.1) has been banned in the developed world for many years, though is in widespread use in the developing world. Various dichlorodiphenyltrichloroethane metabolites have endocrine effects, including blocking the action of male hormones. Dichlorodiphenyltrichloroethane is metabolized in the body to dichlorodiphenyldichloroethylene, and both these compounds persist in the body fat. It is interesting to note that body fat concentrations in the USA have reduced from 15 mg/kg in 1955 to less than 5 mg/kg in 1980, though this is pretty high, due to the ban in dichlorodiphenyltrichloroethane use (IEH 1995). Many hormone-related effects on wildlife have been ascribed to dichlorodiphenyltrichloroethane, including thinning of eggshells, damage to male reproductive ability and behavioral changes (Colborn 1995; LeBlanc 1995). The two major metabolites of dichlorodiphenyltrichloroethane, *p,p*- dichlorodiphenyldichloroethylene and *o,p*- dichlorodiphenyltrichloroethane, have been detected in adipose tissue, breast milk and serum of individuals with no past record of occupational exposure or were living in areas where dichlorodiphenyltrichloroethane has not been used for years. This raised questions concerning chronic exposure to dichlorodiphenyltrichloroethane through food, which could increase the hazard of developing estrogen dependent tumors such as breast cancer. Another widely used organochlorine insecticide Chlordane, on occasion, has been reported in breast milk, as oxychlordane, the stable metabolite.

Metabolism

Biotransformation of organochlorine pesticides was observed in the microsomal fractions and whole cells of Saccharomyces cerevisiae expressing human cytochrome P450 3A4. As per the observation of Mehmood et al. (1996), hexachlorobenzene and pentachlorobenzene were metabolised into pentachlorophenol which was further transformed into tetrachlorohydroquinone in both in vitro and in vivo studies.

Environmental Fate

There is particular concern about endocrine disrupting pesticides that are Lipophilic, resistant to metabolism, and able to bioconcentrate up the food chain. These substances become stored in body fats and can be transferred to the developing offspring via the placenta or via the egg. Animals feeding at the top of the food chain are at increased risk, particularly mammals because during breast feeding contaminants are again mobilized and transferred to the new born infant. Marine mammals may be most vulnerable, because not only do they carry large amounts of body fat, but also the oceans are the final sink for many persistent pollutants. Some persistent pollutants, including several pesticides, are carried in air and in water over several hundred miles, and so even wildlife and people living far away from where these substances are used are under significant threat. Some areas are especially vulnerable because these substances are redistributed to the colder northern regions in a process termed ‘global redistillation’ or the grasshopper effect. The United Nations Environment Programme Convention on persistent organic pollutants (2001) focused on 12 substances, including the following pesticides: aldrin, chlordane, dichlorodiphenyltrichloroethane, dieldrin, endrin, heptachlor, mirex, and toxaphene. Ecological magnification in organisms of the food chain appears to be the most harmful environmental effect resulting from the general usage of organochlorine pesticides. Bioconcentration clearly results from two important properties; their lipid solubility and water insolubility i.e. a large lipid/water partition coefficient, and their resistance to degradation by multi function oxygenase enzymes (Hamelink et al.1971).

Toxicity

Organochlorine pesticides act primarily by altering the movement of ions across the nerve cell membranes, thus changing the ability of the nerve to fire. Organochlorines introduced into the environment since the early 1940s could threaten the reproductive potential of baleen whales and other cetaceans. In a study conducted by Colborn and Smolen (1996) on the effects of dichlorodiphenyltrichloroethane and polychlorobiphenyl in humans, pinnipeds and other wildlife had shown that, the mechanisms of action of the organochlorines reveal their ability to affect developing organisms at very low concentrations during critical life stages: embryonic, fetal, and early postnatal. Exposure during early development can disrupt the organization of the endocrine, reproductive, immune and nervous systems, effecting irreversible damage that may not be expressed until the individuals reach adulthood. Administration of methoxychlor to the new born rat at a dose level of 0.5 μg/day caused accelerated puberty and accelerated loss of fertility. Similarly, new born female rats injected with 1 mg/day of o’p-dichlorodiphenyltrichloroethane on days 2–4 after birth had early onset of puberty and accelerated loss of fertility. Even doses as low as 1 μg/day of either of these substances, given to pregnant female mice on days 11–17 of pregnancy, causes effects on the territorial behaviour of male offspring. However, dichlorodiphenyldichloroethylene induced eggshell thinning, one of the most well known effects noted in wildlife, is now not thought to result from dichlorodiphenyldichloroethylene binding to a sex hormone receptor.

The recent discovery that human sperm count is declining worldwide at a rate of 1 × 10(6) sperm/(mL year) suggests common exposure to estrogen-like chemicals during prenatal and early postnatal development (Colborn and Smolen 1996). This raises concern for other top predator species that also share the same exposure. Recent years has expressed concern a propos the potential endocrine disruptive means of chemicals that persist in nature and build up in body tissues. Some chemicals are thought to act as estrogen mimics because they antagonize the effect of estradiol in vitro by interacting with the estrogen receptor and because their toxicity in vivo resembles the effects of premature estrogen exposure (Cooper and Kavlok 1997; Turner and Sharpe 1997). Accordingly, the developing male reproductive tract is a target for unfortunate xeno estrogen exposure that could lead to infertility later in adulthood. Moreover, wildlife studies representing damaged reproductive function in environments, where levels of xeno estrogens are high, have stirred up research into their endocrine disrupting effects (Bolger et al. 1998; Colborn et al. 1993; Ramamoorthy et al. 1997; Shekhar et al. 1997). Though in vitro and in vivo assays of estrogenicity have revealed that certain chemicals act as estrogens, the likelihood that some chemicals may wield their effects by interfering with the binding of androgens to the androgen receptor is still an 'orphan' issue that gained moderately petite consideration (Timothy et al. 2000). Grippingly *p,p*9- dichlorodiphenyldichloroethylene, one of the most abundant organochlorine compounds in the environment which is proved not to bind, or very poorly bind, to the estrogen receptor, has been observed to perform as an anti androgen (Kelce et al. 1995, 1997). Lindane is a persistent organochlorine pesticide, the oestrogenic properties of which have been demonstrated in several systems, including the production of vitellogenin (egg yolk protein) and zona radiata (egg shell protein) in primary hepatocyctes from Atlantic salmon *Salmo salar* (Celius et al. 1999). Lindane has also been shown to damage human spermatozoa at concentrations as low as those found in female genital tract secretions (Silvestroni and Palleschi 1999) and its presence in the breast milk has been observed (Lyons 1999).

Eggshell thinning due to dichlorodiphenyldichloroethylene has also affected populations of bald eagles (*Haliaeetus leucocephalusyr*). The mechanism for eggshell thinning although previously thought to be caused by the estrogenic effects of dichlorodiphenyldichloroethylene is now proposed to involve the inhibition of prostaglandin synthesis in the eggshell gland muscosa (Bowerman et al. 2000; Lundholm 1997). Additional reports of dichlorodiphenyltrichloroethane effects in birds include decreased egg hatchability in eastern bluebirds *(Sialia sialis)* (Bishop et al. 2000). Eggs from alligators from Lake Apopka in Florida are known to contain residues of organochlorine pesticides including toxaphene, dieldrin, dichlorodiphenyldichloroethylene and chlordane, as well as polychlorobiphenyls (Heinz et al. 1991). Several studies have described adverse reproductive effects to the alligator population on this lake including increased embryo mortality (Woodward et al. 1993) and morphological and endocrine abnormalities in juvenile alligators. (Guillette et al. 1994; Gross et al. 1995). Dichlorodiphenyldichloroethylene also has been shown to cause sex reversal in alligators and red-eared slider turtles *(Trachemys scripta elegans)* following the treatment of eggs at early embryonic stages and at incubation temperatures necessary for the production of male offspring.

Major ecological effects of organochlorine compounds include interference with reproductive success of organisms high on the food chain, especially fish eating birds (osprey, pelicans, falcons and eagles). Ortho and para isomers of dichlorodiphenyltrichloroethane have estrogenic effects and they compete with estradiol for binding to estrogen receptors in uterine cytosol. Estrogenic and enzyme inducing properties of dichlorodiphenyltrichloroethane cause changes in steroid metabolism. Organochlorine compounds also alter ability of birds to mobilize Ca to produce strong egg shells. Once the ecological impact of these pesticides was documented, they were banned from use in many countries. They are still used in some developing countries, though, because of their efficiency in controlling diseases an increasing food production. Examples of effects of dichlorodiphenyltrichloroethane contamination in marine mammals include low reproductive success and declining populations of harbor seals in the Dutch Wadden Sea (Reijnders 1980; 1986; 1990), premature pupping in California sea lions (Gilmartin et al. 1976), and immune and reproductive impairment in Baltic ringed and gray seals (Bergman and Olsson 1985; Roos et al. 1998). Concentrations of persistent organic pollutants in Arctic species reflect their position in the food web. For example, eggs of top prey species such as white tailed sea eagles had higher concentrations than did species lower in the food web. Studies of Canadian seabirds have shown that eiders, which overwinter in contaminated waters, have a higher contaminant load than do birds overwintering in clean waters. In mammals, concentrations in marine species are higher than in terrestrial species and highest in top predators at the end of long food chains, for example, in polar bears (de March et al. 1998).

8.2.2 Organometallic Compounds

The occurrence of heavy metals in the environment has obtained a great deal of awareness due to their high toxicity and the potential to get translocated through the food chain. Natural sources of Hg include volcanoes, geologic deposits of Hg, and volatilization from the ocean. The majority of environmental Hg exposure occurs through atmospheric deposition of Hg released from both natural and anthropogenic sources. Anthropogenic sources of mercury include those associated with its use in the chlor-alkali, paint, agriculture, pharmaceutical, and paper and pulp industries as disinfectants, catalysts, and fungicidal agents. The crisis called mercury pollution entered the focal point after the detection of high levels of methyl mercury in fish and shellfish in Minamata Bay, Japan, that resulted in 46 deaths (D'Itri 1972). In Sweden the use of phenyl mercuric acetate and methyl mercury in fungicidal agents in seed dressings resulted in a significant decrease in the populations of seed-feeding birds (Gavis and Ferguson 1972). High levels of methylmercury have also been detected in fish from the Great Lakes region of North America.

$$CH_3 \text{———} Hg^+ X^-$$

Fig. 8.2 Organomercury compound methyl mercury

8.2.2.1 Organomercury Compounds

Chemical Properties

Organomercury compounds are of three types. viz. elemental, organic, and mercury salts. Methyl mercury (Fig. 8.2) is a type of organic mercury which is highly neurotoxic and teratogenic and is formed by bacterial action in water. Methyl mercury is a persistent organic pollutant. Organo mercury compounds (also called alky l mercury compounds) are toxic by inhalation, ingestion and are easily absorbed through the skin. Organomercury compounds are typically colorless liquids with an unpleasant, faintly sweetish odor.

Metabolism

Methyl mercury in the diet is almost completely absorbed into the bloodstream (WHO 1976b). Methyl mercury is converted to inorganic mercury in mammals (WHO 1976b). The fraction of total mercury present in the tissues as methylmercury depends on the duration of exposure and the time after the end of exposure. Suda and Takahashi (1986) observed that macrophage cells, like those present in the spleen, convert methylmercury to inorganic mercury. The reaction may involve the production of oxygen free-radicals. The faecal pathway accounts for about 90% of the total elimination of mercury in man and other mammals after exposure to methylmercury (WHO 1976b). Faecal elimination process begins with the biliary secretion of both methylmercury and Hg^{++}, forming complex mostly with glutathione (Refsvik and Norseth 1975) or other sulfhydryl peptides (Norseth and Clarkson 1971; Ohsawa and Magos 1974). Inorganic mercury is weakly absorbed across the intestinal wall (WHO 1976b) so that about 90% of the inorganic mercury secreted in bile goes into the faeces. Methyl mercury secreted into the intestinal contents gets reabsorbed into the bloodstream and may afterward put in to biliary secretion, thereby forming a secretion-reabsorption cycle called enterohepatic circulation (Norseth and Clarkson 1971). This in turn increases the amount of methylmercury passing through the intestinal contents and thereby ensuring the constant availability of methylmercury for the intestinal microflora, to be used as substrate. These microorganisms are potent to convert methyl mercury to inorganic mercury (Rowland et al. 1980). Apparently about 10% of the inorganic mercury produced by the intestinal microflora is absorbed into the bloodstream and contributes to the inorganic mercury concentrations in tissues, plasma, bile, breast milk, and urine (IPCS 1990).

Environmental Fate

Mercury is a significant global pollutant. Mercury can travel long distances on air and water currents and in the bodies of migratory species (IPEN 2009). It causes harm to human health as well as to the ecosystems at locations far from where it was initially released. Once released to the atmosphere, mercury is distributed to the earth's surface including soils, wetlands, lakes, and oceans. Some studies have shown that mercury gather in sewer pipes which can lead to long-term releases of mercury to municipal wastewater that may persist even after the original source of release has been stopped. It undergoes various chemical transformations such as oxidation, reduction, methylation, and demethylation. Ultimately, bacteria may convert some of the deposited mercury to methyl mercury, which is taken up by organisms through ingestion and absorption. Almost all of the mercury found in animal tissues is in the form of methyl mercury (WHO 1989). Methylmercury accumulates in fish at levels that may harm the fish and the other animals of consequent trophic levels. Methylmercury has been found in eagles, otters, and endangered Florida panthers (USGS 2000).

Toxicity

Mercury is not only a grave threat to human health and the environment; it is fundamentally an issue of social and environmental justice. Mercury is highly poisonous, but it is most dangerous when bound by organic groups to form organo mercury compounds (Clarkson and Magos 2006). Methylmercury is 100 times more toxic than inorganic mercury and has been found to be mutagenic under experimental condition. The organic forms of mercury are generally more toxic to aquatic organisms and birds than the inorganic forms. Aquatic invertebrates broadly differ in their vulnerability to mercury. Larval stages of organisms, in general, are most sensitive to mercury (Boening 2000). Aquatic plants are affected by mercury in water at concentrations of 1 mg/l for inorganic mercury and at much lower concentrations of organic mercury (Boening 2000). Methyl mercury in fish is formed by bacterial methylation of inorganic mercury in the environment or in bacteria in fish. In aquatic milieu, mercury toxicity is influenced by temperature, dissolved oxygen, water hardness and salinity. There are five main endocrine-related mechanisms of Hg across these systems: accumulation in the endocrine system; specific cytotoxicity in endocrine tissues; changes in hormone concentrations; interactions with sex hormones; and up-regulation or down-regulation of enzymes within the steroidgenesis pathway (Tan et al. 2009) A wide variety of reproductive, biochemical and physiological abnormalities have been observed in fish exposed to sublethal concentrations of organomercury. Mercury, particularly methyl mercury, is highly toxic to humans. Human embryos, fetuses, infants, and children are particularly susceptible as mercury hinders with the development of nervous system (IPEN 2009). Exposure to mercury can reduce the child's cognitive and thinking abilities, memory, attention, language acquisition, fine motor skills and visual spatial skills (IPEN 2009).

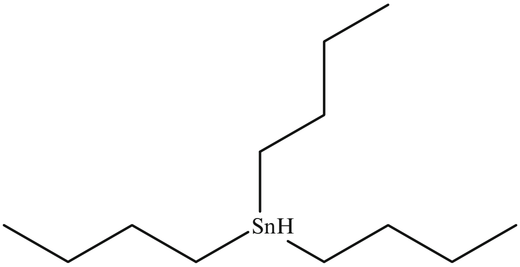

Fig. 8.3 Organotin compound tributyltin

The solubility of inorganic and organic mercury compounds in lipids as well as their binding to sulfhydryl groups of proteins in membranes and enzymes (Berlin 1986) account for their cytotoxicity.

It is clear that mercury has an affinity for the endocrine system. Pituitary gland, thyroid, and testes accumulate concentrations of mercury that were similar to the levels that accumulated in the kidney or liver (as reviewed by Tan et al. 2009). One possible rationale for this particular affinity can be the affinity of mercury for selenium, and therefore, for the selenoproteins (Tan et al. 2009). Potential abundance of selenoproteins functioning in the endocrine system, including in hormone metabolism can be the source of this affinity.

8.2.2.2 Organotin Compounds

Chemical Properties of Organotin Compounds

Organotin compounds differ in their chemical and biological properties. Organotins with four organic groups, e.g. tetrabutyltin, tetraoctyltin and tetraphenyltin, finds application as starting materials or catalysts. Organotins with three organic groups are highly effective fungicides and bactericides, depending on the organic group R. Tetraorganotins are stable, ineffective as biocides (substances that are capable of killing living organisms) and are relatively non-toxic. Triorganotin compounds are generally more toxic than organotins in other classes. Trialkyltins with linear organic groups cannot be used as agricultural biocides due to their high toxicity to plants. Antibacterial and toxic activity of diorganotins is low, except for their diphenyl derivatives. Monoorganotins have very low toxicity to mammals. Report by NPI, Australia, shows that triphenyltin acetate is insoluble and soluble in ether. Triphenyltin chloride reacts with water while triphenyltin hydroxide is insoluble. Azocyclotin is a triorganotin compound which has a less than 1 ppm solubility in water.

Metabolism of Organotin

Tributyltin (Fig. 8.3) and triphenyltin are metabolized by cytochrome P-450 system enzymes, and their metabolic fate may contribute to the toxicity of the chemicals.

Organotin degradation can involve the sequential removal of organic moieties to yield less toxic derivatives, e.g. debutylation of tributyltin compounds to di- and monobutylins. Such degradation is known to take place in bacteria, algae and fungi, and this provides one route for detoxification. In addition, microorganisms are capable of accumulating tributyltin compounds, and this is another mechanism of removal from solution. The high lipid solubility of organotins ensures cell penetration and association with intracellular sites, while cell wall components also play an important role (Gadd 2000).

Environmental Fate

Organotin compounds, particularly tributyltin which forms active ingredients of anti-fouling paints that are generally used on ship hulls, are well recognized endocrine disruptors causing sex changes in marine organisms. Organotin compounds are distributed far and wide in coastal waters and sediments worldwide. Organotins are more readily bioavailable due to the fast and reversible sorption/desorption behavior (Berg et al. 2001). Even though diffusion of organotins from deeper sediments to the surface will be quite slow, due to their readily desorption, any resuspension of contaminated sediments e.g., by the tide, storms or dredging activities, will lead to their increased concentrations in the overlaying water column.

Tributyltin oxide is an organotin compound chiefly used as a biocide (fungicide and molluscicide), especially a wood preservative. Tributyltin oxide's production and use in marine antifouling paints, cooling-water system slimicides, latex and other paints, plastics, and disinfectants may effect in its discharge to the environment through various waste streams. The use of tributyltin compounds in antifoulants is restricted because of their toxicity to aquatic organisms and the USEPA is cooperating in international efforts for a global phase-out (UNEP-FAO/RC/CRC 2005). In atmosphere, tributyltin oxide will exist in both the vapor and particulate phases. Vapor-phase tributyltin oxide will be degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals. Particulate-phase tributyltin oxide will be removed from the atmosphere by wet and dry deposition. In soil, tributyltin oxide will strongly bind to soil and will have low mobility. Volatilization from near-surface soil is not expected to be an important fate process. Biodegradation half-lives for tributyltin oxide range from 15 to 20 weeks in soil. If released to water, tributyltin oxide will exist mainly as tributyltin cation which will strongly bind to sediment. Tributyltin oxide may react with sulfides present in sediment which would lead to the formation of tributyltin sulfide. The photodegradation half-life of tributyltin oxide in water will be at least a few to several months. Biodegradation half-lives for tributyltin oxide range between 6 days and 35 weeks in water and water-sediment mixtures. Tributyltin oxide is likely to exist in the dissociated form in the environment and consequently volatilization from water surfaces is not expected to be an important fate process.

Toxicity

Organotin compounds such as tributyltin and triphenyltin have been adopted in industrial applications since their biocidal properties were revealed in early 1950s. They are used for various purposes such as molluscicides and disinfectants, but most importantly, organotins are applied globally as wood preservatives and anti-fouling paints (De Mora 1996). The ability of trialkyl organotins to cause the anomalous induction of male sex characteristics in female marine invertebrates leading to the phenomenon termed 'imposex' represents one of the finest examples of their endocrine disruption potential. The first reports of imposex on female gastropods surfaced (Blaber 1970) shortly after the introduction of organotins into the marine environment by large and wide. Field and laboratory research identified tributyril tin as the causative agent. Bioaccumulation of tributyril tin resulted in the reduced activity of P450 aromatase, the key step in conversion of androgens to estrogens, with a subsequent decrease in estrogen and increase in testosterone levels (Matthiessen and Gibbs 1998).

Imposex has been reported in more or less 150 gastropod species (Matthiessen et al. 1999). It has been reported for some species such as *Nassarius reticulates* and *Ilyanassa obsolata*, the reproductive activity of the imposex females appeared not to be affected, whilst for certain species like *Nucella lapillus* and *Thais clavigera* (Gibbs and Bryan 1986; Horiguchi et al. 1994), the developing vas deferens may block the oviduct opening (vulva), ultimately resulting in the sterilization of the females due to the malfunction in egg capsule release (Bryan et al. 1986). The latest observations and hypotheses in this regard are presented by Horiguchi et al. (2006), Hagger et al. (2006), Scott et al. (2006), Jobling et al. (2006), Hayes et al. (2006a), Veeramachaneni et al. (2006), and Hall et al. (2006). These case studies exemplify cause–effect relationships between chemical exposures and physiological function in diverse species.

Recent reports demonstrated that tributyril tin can also induce masculinization in fish species (McAllister and Kime 2003). The prime markers of organotin exposure in mammals include hepatic, neural, and immunotoxicity, with no effect on sex-ratio (Ogata et al. 2001; Boyer 1989). The mechanistic understanding of the endocrine-disrupting potential of organotins is based primarily on their actions on key steroid regulatory enzymes (e.g. aromatase activity) or general toxicity by damage to mitochondrial functions and following cellular stress responses (Cooke 2002; Gennari et. al. 2000; Philbert et al. 2000).

Situation in the northeastern waters of Hong Kong has been getting worst since 1996 that is probably associated with the rapid development of the cargo container port at Yantian in China. A study conducted by Leung et al. (2006) demonstrated that imposex indices were positively correlated with the body burden of organotins in the gastropods. Across all sites, the sex ratio (female: male) decreased significantly with increasing imposex levels or tissue burden of organotins, indicating that organotins can result in a male-biased population, potentially leading to local extinction in extreme cases. Tributyltin exposure to non-target aquatic organisms such as mussels, clams, and oysters, at low levels, may cause structural changes, growth retardation, and death. Imposex, the development of male characteristics in females,

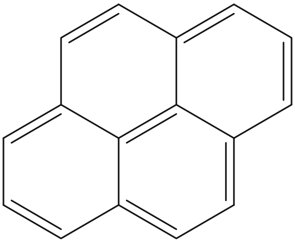

Fig. 8.4 Polycyclic aromatic hydrocarbon compound pyrene

has been initiated by tributyltin exposure in several snail species. In laboratory tests, reproduction was inhibited when female snails exposed to 0.05 ug/L of tributyltin developed male characteristics (USEPA 1985). Tributyltin is lipophilic and tends to accumulate in oysters, mussels, crustaceans, molluscs, fish, and algae. Juvenile chinook salmon accumulate tributyltin immediately upon exposure to low concentrations. Tributyltin and its metabolite, dibutyltin, were found in the salmon's muscle tissue (Short and Thrower 1986). Imposex, the development of male characteristics in females, has been initiated by tributyltin exposure in several snail species. In laboratory tests, reproduction was inhibited when female snails exposed to 0.05 ug/L of tributyltin developed male characteristics (USEPA 1985).

8.2.3 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons occur naturally as products of incomplete combustion of organic compounds and enter aquatic environments via oil spills, waste discharge, runoff, and dry or wet deposition. Even though they are biodegraded in soils and water within weeks to months, the metabolites are more toxic and may last for long. Vehicle exhaust, cigarette smoke, soot, and the burning of solid or hazardous waste usually contain polycyclic aromatic hydrocarbons. Natural incidence like volcano eruption and forest fires can also generate these contaminants. Polycyclic aromatic hydrocarbons are also present in a number of oil-based household products, including petroleum jelly, lipsticks, baby lotions, and cooking oils.

8.2.3.1 Metabolism

Wunder et al. (1994) studied on the metabolism of pyrene (Fig. 8.4), a polycyclic aromatic hydrocarbon, by *Aspergillus niger* and the metabolites formed were isolated and identified as 1-hydroxypyrene, 1,6- and 1,8-pyrenequinone, 1,6- and 1,8-dihydroxypyrene, 1-pyrenyl sulphate and 1-hydroxy-8-pyrenyl sulphate. This study is the first report of 1-hydroxy-8-pyrenyl as a metabolite in the microbial metabolism of pyrene. The results established that *A. niger* metabolizes pyrene by cytochrome P-450 monooxygenase enzyme systems. Heitkamp et al. (1988) isolated a pyrene-mineralizing bacterium (*Mycobacterium sp*) by the microbiological analyses of sediments located near a point source for petrogenic chemicals. This is the first milestone report of a bacterium able to extensively mineralize pyrene. The mycobacterium mineralized pyrene as well as other polycyclic aromatic hydrocarbons and alkyl- and nitro-substituted polycyclic aromatic hydrocarbons including naphthalene, phenanthrene, fluoranthene, 3-methylcholanthrene, 1-nitropyrene, and 6-nitrochrysene.

The preliminary step in the aerobic catabolism of a polycyclic aromatic hydrocarbon molecule by bacteria occurs by its oxidation to form a dihydrodiol by an enzyme system. Dihydroxylated intermediates may undergo either an ortho or meta cleavage type of pathway, leading to the production of intermediates such as protocatechuates and catechols, which are further converted to tricarboxylic acid cycle intermediates (Van der Meer et al. 1992). Weissenfels et al.(1991) documented the isolation of the soil microorganism *Alcaligenes denitrificans* strain WW1, which biodegraded fluoranthene at a rate of 0.3 mg/ml per day and which also cometabolized other polycyclic aromatic hydrocarbons, including pyrene and benz[*a*] anthracene· Kelley and Cerniglia (1991) showed that in mineral medium supplemented with organic nutrients, *Mycobacterium* sp. strain PYR-1 was capable of degrading greater than 95% of added fluoranthene within 24 h.

8.2.3.2 Environmental Fate

Polycyclic aromatic hydrocarbons can be introduced to the environment by residential wood burning, cooking foods, and combustion of fossil fuels, as well as discharges from industrial plants, waste water treatment plants, and escape from waste storage containers. Higher molecular weight polycyclic aromatic hydrocarbons bioaccumulate more effectively than the lower molecular weight ones do, except for some specific compounds like benzo(a)pyrene undergo metabolism in some aquatic organisms. Hydrolysis may not be a significant environmental fate process, since polycyclic aromatic hydrocarbons lack functional groups that hydrolyze under environmental conditions. The largest ever exposure to polycyclic aromatic hydrocarbons to the general population is via the intake of foods. Exposure can also arise from drinking water and inhalation of air containing fuel combustion exhausts or cigarette smoke.

Concern in the mechanisms of biodegradation and environmental fate of polycyclic aromatic hydrocarbons is impelled by their extensive distribution and potential to cause deleterious consequences on human healthiness. The microbial biodegradation of polycyclic aromatic hydrocarbons has been outstandingly reviewed by many workers. (Cerniglia 1984, 1992; Cerniglia and Heitkamp 1989; Shuttleworth and Cerniglia 1995; Sutherland et al. 1995) and the biodegradation of 3 ringed polycyclic aromatic hydrocarbons is well established. Kanali and Harayama (2000) reviewed the bacterial biodegradation of more than 3 ringed ‘high-molecular-weight’ polycyclic aromatic hydrocarbons. Chemical properties and the environmental fate of a polycyclic aromatic hydrocarbon molecule are dependent in part upon both molecular size, i.e., the number of aromatic rings, and molecule topology or the pattern of ring linkage. Stability and hydrophobicity of polycyclic aromatic hydrocarbons are two principal aspects that determine the persistence of high molecular weight polycyclic aromatic hydrocarbons in the environment. A study by Gennadiyev et al. (1996) showed that low molecular weight polycyclic aromatic hydrocarbons considerably accumulate, depending partly of natural origin, in subsurface and deep soil horizons according to the intensity of soil contamination, activity of soil biota and leaching of soil solution.

8.2.3.3 Toxicity

Effects of polycyclic aromatic hydrocarbons are wide-ranging within an organism and have been found in many types of organisms, including birds, invertebrates, plants, amphibians, fish, humans and other mammals. Due to their lipophilic nature, polycyclic aromatic hydrocarbons have a high potential for biomagnification through trophic transfers. They are also known to exert acutely toxic effects and/or possess mutagenic, teratogenic, or carcinogenic properties. Some polycyclic aromatic hydrocarbons are classified as priority pollutants by the United States Environmental Protection Agency (Keith and Telliard 1979; Smith et al. 1989). Their effects are varied and so it cannot be generalized. Mammals can absorb polycyclic aromatic hydrocarbons by inhalation, dermal contact, or ingestion (Eisler 1987b). Plants intake polycyclic aromatic hydrocarbons from soils through the root system, and transfer them to other parts of the body such as developing shoots. Uptake rates are generally governed by the concentration and physicochemical state of polycyclic aromatic hydrocarbons, their water solubility and soil type.

8.2.4 Organophosphorus and Carbamate Insecticides

8.2.4.1 Background

The organophosphate and carbamate insecticides were developed to replace the persistent organochlorine insecticides, due to their rapid breakdown and low environmental persistence. These two classes of insecticides have the same mechanism of action: inhibition of the enzyme acetylcholinesterase which hydrolyses the neurotransmitter substance acetylcholine at nerve synapses. Although the equations depicting the inhibition of acetylcholinesterase by a carbamate and organophosphorus ester are similar, there are distinct differences in the reaction between the enzyme and the two classes of compounds. First, while appropriate chemical reactivity is essential for high anticholinesterase activity for an organophosphorus ester, a good fit of the carbamate on the enzyme active site is essential for a high anticholinesterase activity by a carbamate ester. These insecticides have less of an ecological impact due to their quick breakdown after application. They are, however, much more toxic to birds and humans. They are classified as Class I pesticides (extremely hazardous) by World Health Organization based on their LD50 values while the organochlorine pesticides are generally belonging to Class II.

Organophosphorus Insecticides

A profile from 66 poison control centers in United States indicated that organophosphorus pesticides were involved in more poisonings than any other single class of pesticides (Litovitz et al. 1998). Individuals at greatest risk are those who most frequently handle these compounds including formulators, applicators, farmers and home gardeners. Though the primary toxicity is associated with organophosphorus exposure is cholinergic crisis resulting from acetylcholinesterase inhibition, these compounds has numerous other compound specific chronic effects including delayed polyneuropathy, immunotoxicity, developmental, reproductive and endocrine toxicity. Some organophosphates have been associated with decreased egg production and reduced serum luteinizing hormone in birds, and similarly, carbamates have been associated with a reduced number of eggs. Also, in the males of several animal species, certain organophosphates have been linked with effects on sperm. Some organophosphate pesticides have been suggested to cause abnormal menses, amenorrhea, and early menopause, and again these effects have been linked with a perturbation of luteinizing hormone release from the pituitary.

Metabolism

Organophosphorus insecticides are tertiary esters susceptible to hydrolytic degradation, resulting in detoxication products. Detoxication of an organophosphorus insecticide may take place in different ways. Cleavage of any bond attached to the phosphorus atom will lead to a detoxication product, e.g., by enzymatic or chemical hydrolysis (Eto 1974) Enzymatic hydrolysis is mediated by a number of different esterases which are hydrolases or phosphotriester hydrolases (Dauterman 1971). Metabolic degradation or detoxication may take place at a site away from the phosphorus center. The classical example of this is found in the carboxylesterase catalyzed hydrolysis of malathion to its non toxic carboxylic acid derivatives. Degradation of organophosphates varies as a function of microbial composition, pH, temperature, and availability of sunlight. Under laboratory conditions (25°C and pH 7) biodegradation is about one order of magnitude faster than chemical hydrolysis, which in turn is roughly ten times faster than photolysis (ValaRagnarsdottir 2000). Microbial biomass often needs a lengthy adaptation period in which soil bacteria mutate to be able to metabolize organophosphates. Biodegradation is thus in general an order of magnitude faster in soils that have had repeated applications of organophosphate pesticides compared to control soils which have never had organophosphates applications.

Environmental Fate

Organophosphate pesticides are generally regarded as safe for use on crops and animals due to their relatively fast degradation rates. As organophosphates are relatively soluble, they frequently penetrate surface and ground waters. In the ground water, organophosphates are primarily broken down through chemical hydrolysis, which is pH dependent. Hydrolysis half-life of an organophosphate pesticide of 10 days in the laboratory increases to 1 year if the pH of the water is 6 and the temperature 5°C, suggesting that organophosphates can persist in the environment for long periods of time. Certainly, organophosphates are detected in soils years after application. Why this environmental persistence occurs is not clear, but it may be due to sorption of the organophosphates to soil particles, making them unavailable for microbial metabolism. Available literature data show that conditions can occur in soil where organophosphates are preserved and transferred to humans through food. Evidence suggests that organophosphates are mutagenic and teratogenic and that a large number of modern-day diseases of the nervous and immune system of mammals can be linked to these pesticides (ValaRagnarsdottir 2000) which include mad cows disease, Gulf war syndrome, parkinson's disease and multiple sclerosis,

Toxicity

Some of the early organophosphates were developed as nerve poisons for human warfare. Their primary mode of action on insects and other animals is by phosphorylation of the acetylcholinesterase enzyme. This enzyme is necessary for controlling nerve impulse transmission between nerve fibers. A loss of this enzyme function results in an accumulation of acetylcholine, which causes unregulated nervous impulses. Higher levels of acetylcholine result in sensory and behavioral disturbances, lack of coordination and depressed motor function.

German Federal Environment Agency has listed Organophosphate insecticide chlorpyriphos, dimethoate and trichlorfon as potential endocrine disrupters, who report that it is (ENDS 1999). Organophosphate pesticides probably lead to reproductive effects by interfering with hormones of the pituitary-gonad-axis (WWF 1998). Chlorpyrifos is a neurotoxin, and exposure to low concentrations can affect brain development in rats (Johnson et al. 1998; Roy et al. 1998). It is also linked to male and female genital deformities. Chlorpyrifos has also been shown to affect the thyroid system in ewes, reducing blood thyroxine concentrations (Rawlings et al. 1998). Dimethoate cause testicular damage, damage to sperm production and reduction in testosterone levels when fed to adult male rats (Afifi et al. 1991). Dimethoate also resulted in decreased thyroxine concentrations in ewes (Rawlings et al. 1998) and affected thyroid metabolism in mice (Maiti and Kar 1997). Trichlorfon is reported to cause mammary gland tumours and affect sperm and egg production (ENDS 1999). A cluster of Down's syndrome children in Hungary was associated with consumption of fish from a local fish farm after the fish had become excessively contaminated by trichlorfon (Czeizel 1996). A degradation product of trichlorfon, dichlorvos, has been shown to damage immune system function in humans; trichlorfon itself damages immune function in Carp (Voccia et al. 1999). Some recent studies identified organophosphate fenitrothion (Fig. 8.5) as an androgen receptor antagonist (Curtis 2001). This study provided both in vitro and in vivo evidences, and more

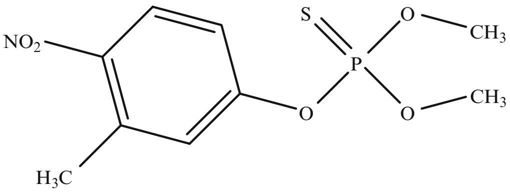

Fig. 8.5 Organophosphorus insecticide fenitrothion

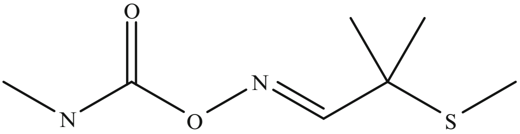

Fig. 8.6 Carbamate insecticide aldicarb

significantly in vivo evaluation of antiandrogenic activity was studied analogous with multiple measures of neurotoxicity. Fenitrothion competitively inhibited dihydrotestosterone dependent human androgen receptor activation and the potency of fenitrothion was 8 fold higher than that of *p,p'*- dichlorodiphenyldichloroethylene and about 50% of flutamide, a pharmaceutical anti androgen (Curtis 2001)

8.2.4.2 Carbamate Insecticide

Most carbamate insecticides are derivatives of methylcarbamic acid and, therefore, are referred to as methylcarbamates. Insecticidal methylcarbamates are esters of substituted phenols and oximes (Fukuto 1990). Methylcarbamates of substituted phenols and oximes with good complementary fit to the enzyme active site are generally strong inhibitors of acetylcholinesterase (Metcalf 1971) Oxime methylcarbamates, represented by aldicarb (Fig. 8.6) and methomyl are structurally similar to acetylcholine, good inhibitors of acetylcholinesterase, and also potent insecticides. Another important methylcarbamate insecticide, carbofuran, is structurally closely related to 2-isopropoxyphenyl methylcarbamate. Carbofuran is about tenfold more potent in inhibiting acetylcholinesterase than propoxur and is one of the most effective carbamate insecticides.

Metabolism

The principal route of metabolism of carbamate insecticides in animals is oxidative in nature and is generally associated with the multifunction oxygenases enzymes (Fukuto 1990). Typical oxygenation reactions in which an oxygen atom is introduced into the molecule include hydroxylation of aromatic rings, O-dealkylation of ethers, N-methyl hydroxylation and demethylation, oxidation of aliphatic side chains, and thio ether oxidation (Knack 1971; Fukuto 1972).

However, the metabolism of aldicarb to its sulfoxide is believed to be an activation reaction, since aldicarbsulfoxide is approximately tenfold more potent as an anticholinesterase than aldicarb. Methylcarbamate insecticides are also highly susceptible to alkaline hydrolysis but are relatively stable to neutral or acidic conditions (Aly and El-Dib 1972).

Environmental Fate

Carbamate pesticides hydrolyze rapidly over a range of pHs. Lyman and Lacoste (1975) investigated the half-lives for carbamate mancozeb in water at pH 5–9 as less than 1 day. The products of degradation and their relative amounts are also pH-dependent. This study identified the hydrolysis products ethylene bisisothiocyanate sulfide, ethylenethiourea and ethyleneurea. At pH 9, hydantoin was identified as additional product. One possible degradation route to form ethylene bisisothiocyanate sulfide is the oxidation of ethylene bisdithiocarbamate dianion to ethylenethiuram disulfide , which was subsequently decomposed into ethylene bisisothiocyanate sulfide (Aldridge and Magos 1978). Carbamate mancozeb undergo photolysis and possible degradation products include ethylenediamine and ethylene bisisothiocyanate. There was no measurable decrease in concentration over 30 days in dry soil. In wet soil, mancozeb degrades quickly due to its rapid hydrolysis as opposed to photolytic degradation.

Toxicity

Aldicarb, an extremely toxic systemic carbamate insecticide, is also suspected of being an endocrine disruptor. Likewise, exposure to carbaryl has been associated with adverse effects on human semen. Methylcarbamate insecticides are, on the whole, relatively toxic to mammals. One of the reasons for their high acute toxicity is that they are direct inhibitors of acetylcholinesterase, and metabolic activation is not required as in the case of many safe organophosphorus insecticides, for e.g. malathion (Fukuto 1990). Carbendazim is a broad spectrum and systemic methyl-2-benzimidazole carbamate fungicide for the control of molds, rots, and blights (Vettorazzi 1976). Prenatal administration of carbendazim to rats during pregnancy resulted in embryonic death, growth retardation, and developmental abnormalities such as exencephaly, microphthalmia and hydronephrosis in offspring (Cummings et al. 1990, 1992). Rehnberg et al. (1989) showed that treatment of male rats with carbendazim increased testosterone concentration and the levels of androgen binding protein in the interstitial and seminiferous tubule fluid, indicating an association between endocrine disruption and carbendazim toxicity. A toxicokinetic study showed that intraperitoneal or intratesticular administration of carbendazim to male rats produced a more positive correlation between testicular pesticide concentration and microtubule damage (Lim and Miller 1997b).

8.2.5 Phthalates

8.2.5.1 Background

Phthalates are diester derivatives of phthalic acid used mainly as plasticizers to make plastic products stretchier. Some plastics may be containing up to 40% phthalate by weight. Consumer products containing plastics include rainwear, imitation leather, upholstery, footwear, tablecloths, shower curtains, food packaging materials, children's toys, tubing, and containers for blood transfusions. The major phthalates used in commerce are the diethyl, dibutyl, dicyclohexyl, butyl, benzyl, di-2-ethylhexyl, di-*n*-octyl, diiso-nonyl, and di-isodecyl. These plasticizers are not a permanent chemically bonded fraction of the plastic matrix during the manufacturing and they can transfer from the plastic goods to environment under certain conditions. As a result, they have become ever-present in the environment, and people are frequently exposed to low levels of phthalate esters. Exposure of young children to phthalate esters orally by chewing on toys, teething rings, and pacifiers containing these plasticizers are of great concern (Steiner et al. 1999).

Metabolism

Entering the body, phthalates are rapidly metabolized to the equivalent monoester metabolite, which is then further metabolized or swiftly eliminated in the urine as its glucuronide conjugate. Reproductive effects of phthalates on adult males and development of male offspring has been of great concern recently. U.S. NHANES III (1988–1994) survey has measured the exposure to phthalates in 300 urine specimens collected from adults and it was inferred out that the phthalate monoesters with the highest urinary levels were monoethyl phthalate (95th percentile, 3,750 ppb; median, 305 ppb), monobutyl phthalate (95th percentile, 294 ppb; median, 41.0 ppb), and monobenzyl phthalate (95th percentile, 137 ppb; median, 21.2 ppb) which reflected the exposures to the respective parent compounds diethyl phthalate, dibutyl phthalate, and benzyl butyl phthalate (Blount et al. 2000a, b). Metabolites of the more Lipophilic phthalates, such as diethylhexyl phthalate, may be excreted via the bile and into the feces.

Environmental Fate

Phthalates are frequently detected in groundwater, rivers and drinking water due to their persistence in the environment (Jobling et al. 1995). Phthalate solubilities in water decrease with increasing molecular weight. Higher molecular weight phthalates are practically insoluble, making detection in the water column extremely difficult (Group Jr 1986). Phthalates are generally less soluble in salt water than in fresh water. Even the lower molecular weight phthalates are only slightly soluble.

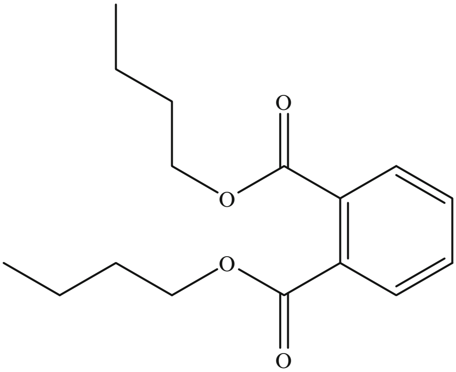

Fig. 8.7 Phthalate compound dibutylphthalate

The higher molecular weight phthalates are practically insoluble, with solubilities in the 0.1–1.2 mg/L range (Group Jr 1986) Dimethyl phthalate esters can easily be released into the environment from plastic products. As endocrine disruptors, dimethyl phthalate esters mimic estrogenic activities in animals and humans. The metabolites of DMPE are suspected to cause even more serious health problems. The dominant species of microorganisms utilizing individual dimethyl phthalate ester isomer as the sole carbon source were isolated and identified as facultative anaerobe *Thauera sp., Xanthobacter sp. and Agrobacterium sp.* for Dimethyl phthalate, dimethyl isophthalate and dimethyl terephthalate respectively (Cheung et al. 2007). The harmful dimethyl phthalate esters and their natural metabolites may well accumulate in the sulfate-reducing environment.

Toxicity

Phthalates are fat soluble, so tend to concentrate in materials such as butter, margarine and cheese. In addition, they are likely to accumulate in body fat. Several phthalates, particularly diethylhexyl phthalate, are testicular toxicants. Part of this toxicity is believed to involve depletion of testicular Zinc, and may include the death and disintegration of the testicular germ cells (Hoffmann 1991; Peters et al. 1997). Occupational exposure to high levels of phthalates has been reported to lead to miscarriages and other complications of pregnancy (IEH 1995).

Dibutylphthalate (Fig. 8.7) does damage the reproductive system of male rats at low exposures by disrupting the androgen system rather than imitating oestrogen (Foster 1997). Further research has established that dibutylphthalate cannot bind the androgen receptor, but does disrupt androgen-regulated male sexual differentiation (Mylchreest et al. 1999). Both dibutylphthalate and diethylhexylphthalate cause irregularities in male sexual differentiation when given to pregnant rats (Gray et al. 1999a, b). Diethylhexylphthalate caused testicular and epididymal abnormalities, while dibutylphthalate caused malfunctions including retained nipples and hypospadias.

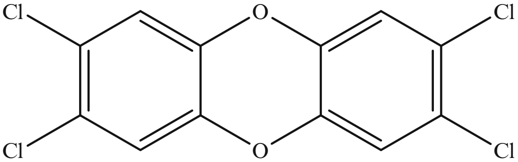

Fig. 8.8 Dioxin compound 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD)

8.2.6 Dioxins

Dioxins are persistent and bioaccumulative, and the most studied dioxin, 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (Fig. 8.8) is confirmed to cause cancer in humans (McGregor et al. 1998). Dioxins are also endocrine disrupters, and are able to modify the immune system (Grassman et al. 1998). The World Health Organization recommended safe limit for dioxins are 1–4 pg/kg/day. Research by the UK Ministry of Agriculture has shown that adults are already taking in enough dioxin (including dioxin-like polychloro biphenyls) in their food violating this new limit, and children are taking in even more quantities (ENDS 1998). Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, known collectively as dioxin like compounds, are by-products of a variety of industrial and thermal processes. Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans have 75 and 135 congeners respectively; however, only seven and ten respectively, are commonly found in humans. Unfortunately, these include the most toxic 2, 3, 7, 8-substituted congeners. Two chemical subclasses of PCBs, the non-*ortho*-chlorinated PCBs and the mono-*ortho* chlorinated PCBs, have toxicological properties similar to the polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans and are also discussed here. The ingestion of food containing trace levels of these chemicals is estimated to account for more than 90% of human background body burden. Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofuran levels are normally reported in various matrices as concentrations of individual polychlorinated dibenzo-p-dioxin / polychlorinated dibenzofurans congeners or as total dioxin concentration per gram of lipid in the sample calculations. WHO has established a tolerable daily intake for the whole group of dioxin like compounds of 1–4 pg TEQs/kg body weight/day (Van Leeuwen and Younes 2000).

8.2.6.1 Metabolism

Research of the dioxin kinetics following oral exposure have established that they are well absorbed and undergo extensive distribution throughout body tissues, with particular accumulation in the liver and adipose tissues (IPCS, 1989). Dioxins are not quickly eliminated and are highly stable, with a half-life of 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin in humans is approximately 7–12 years (ASTDR 1998). Due to the extensive distribution and persistence of absorbed dioxins there is a high potential for accumulation following repeated exposure. Relatively little is known about the metabolism of dioxins in humans, however, there is some evidence to suggest that absorbed 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin may be slowly converted to polar metabolites that are eliminated as glucuronates (COC 2001). P450 monooxygenase systems including CYP1A1 are greatly responsible for dioxin metabolism in vivo (Shinkyo et al. 2003). Huwe et al. (1996) performed studies on the metabolism of 1,4,7,8-tetrachlorodibenzo *p*-dioxin, a relatively nontoxic dioxin congener to get a better perceptive of dioxin metabolism in mammals, and the two major fecal metabolites detected were hydroxylated tetra- and trichlorodibenzo *p*-dioxins. Glucuronide and sulfate conjugates of these hydroxyl metabolites were found in the urine and bile. Minor metabolites observed included dichlorocatechol, dihydroxylated tetra- and trichlorodibenzo *p*-dioxins, and conjugates of these compounds.

8.2.6.2 Environmental Fate

The environmental fate of dioxins is not hitherto entirely understood, regardless of ever mounting literature from laboratory, field, and monitoring studies on their fate and distribution. Dioxins are mainly associated with particulate and organic matter because of their high lipophilicity and low water solubility. They show little potential for significant leaching or volatilization once absorbed to particulate matter. According to the available evidence, dioxins particularly the tetra- and higher chlorinated congeners, are exceptionally stable compounds under most environmental conditions, with their environmental persistence measured in decades (USEPA 1994). The only environmentally significant transformation process for these congeners is believed to be photodegradation of chemicals not bound to particles in the gaseous phase or at the soil- or water-air interface (USEPA 1994). Brominated congeners of dioxins undergo more readily photodegradation. Although some volatilization of dioxin-like compounds on soil does takes place, their principal fate is to persist next to the surface of undisturbed soil or to travel to reach aquatic systems as soil erodes. In the water column dioxins mainly undergo sedimentation. The apparent final environmental sink of dioxin compounds is supposed to be sediments of aquatic ecosystems. Since dioxin is lipophilic as well as hydrophobic, it tends to bioaccumulate and work its way up the food chain. This means that dioxin, when it settles on water bodies, will rapidly accumulate in organism's body tissues rather than remain in the water.

8.2.6.3 Toxicity

Dioxin is a general term that describes a group of hundreds of chemicals that are highly persistent in the environment. Polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and polychlorinated biphenyls are synthetic, toxic, and greatly persistent chemicals first produced in the twentieth century. They are now ever-present and go through the general population about exclusively from ingestion of food (Startin 1994; Beck et al. 1989; Birmingham et al. 1989; Theelen 1991;

Ministry of Agriculture, Fisheries, and Food, UK 1992). A draft report released for public comment in September 1994 by the US Environmental Protection Agency clearly describes dioxin as a serious public health threat. The public health impact of dioxin may rival the impact that dichlorodiphenyltrichloroethane had on public health in the 1960s. According to the USEPA report, not only does there appear to be no "safe" level of exposure to dioxin, but levels of dioxin and dioxin-like chemicals have been found in the general US population that are "at or near levels associated with adverse health effects. The most toxic compound is 2,3,7,8-tetrachlorodibenzo-p-dioxin. The toxicity of other dioxins and chemicals like PCBs that act like dioxin are measured in relation to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. The concept of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin toxic equivalency (TEQ) was developed in order to simplify risk assessment and regulatory control (Eadon et al. 1986). 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin also increase the metabolism of thyroid hormones, resulting in potential increases in thyroid neoplasms (Barter and Klaassen 1992). Many studies investigated the mechanism of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin -induced atrophy of thymus (reviewed by De Waal et al. 1997). The effect of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin on the thymus may be through an action on epithelial cells, although bone marrow prothymocytes have also been claimed to be targets for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin induced thymus toxicity (De Waal et al. 1997). Thymus atrophy through an effect on epithelial cells is indicated from in vitro studies on both cultured mouse and human epithelial cells as well as from in vivo data. These studies also established that the human thymus can be a target for the toxicity of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin with similar sensitivity to cells of a receptive mouse strain, confirming the significance of data on mice, for risk assessment to humans. .

Studies on the effects of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in birds have shown significant variation in sensitivity across species, with over 40-fold differences on embryo mortality (Peterson et al. 1993; Hoffman et al. 1996). For instance, doses of only 20–50 ppt of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in chicken eggs cause mortality and malformations, as opposed to 1,000–10,000 ppt in eggs of ring neck pheasants *(Phasianus colchinus)* and eastern bluebirds *(Sialia sialis)*. Chicken embryos are also much more susceptible to the teratogenic effects of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, predominantly to develop cardiovascular malformations.

Dioxin is formed as an unintentional by-product of many industrial processes involving chlorine such as waste incineration, chemical and pesticide manufacturing and pulp and paper bleaching. Dioxin was the primary toxic component of Agent Orange, was found at Love Canal in Niagara Falls, NY and was the basis for evacuations at Times Beach, MO and Seveso, Italy. In addition to cancer, exposure to dioxin can also cause severe reproductive and developmental problems (at levels 100 times lower than those associated with its cancer causing effects). Dioxin is well-known for its ability to damage the immune system and interfere with hormonal systems. Dioxin exposure has been linked to birth defects, inability to maintain pregnancy, decreased fertility, reduced sperm counts, endometriosis, diabetes, learning disabilities, immune system suppression, lung problems, skin disorders, lowered testosterone levels and much more.

The function of aryl hydrocarbon receptor (Ah receptor) in the animal body is to bind to many naturally occurring contaminants, e.g. benzene and other aromatic hydrocarbons, some plant toxins and all organochlorine compounds and thereby activating genes of DNA to produce cytochrome p-450 enzymes which break down the redundant molecules. Once the molecule is degraded, enzyme production is switched off; the molecule is no longer on the receptor to give the signal. The Ah receptor thus plays an important part in detoxifying the body. Many different molecules bind to the Ah receptor, but 2,3,7,8-tetrachlorodibenzo-*p*-dioxin binds extraordinarily well and it forms a stronger receptor-dioxin complex. The toxic actions of dioxins depend absolutely on the formation of this complex and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin has no effect on animal cells which have no Ah receptors. Once the dioxin-receptor complex is formed, it moves to the DNA where it activates genes which produce P450 enzymes. It also activates genes which generate substances that control the growth and division of cells. In this way dioxin behaves like a hormone. The toxicity of the different dioxin-like compounds depends on the strength of their bond with the Ah receptor; 2,3,7,8-tetrachlorodibenzo-*p*-dioxin is the dioxin that binds the most strongly. The Ah receptor has functions other than enzyme induction. It also controls cell functions those regulate the growth and differentiation of cells. Dioxin is similar to natural hormone molecules such as thyroxin which is produced by the thyroid gland and which regulates the general metabolism of the body; both are flat aromatic molecules. Dioxin's hormone-like activity may also indirectly modify the levels and action of hormones not instantly acted on by dioxin. For example, 2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin has been observed to decrease the number of oestrogen receptors in human cells thereby reducing the effects of oestrogen.

2,3,7,8-Tetrachlorodibenzo-*p*-dioxin by binding to the Ah receptor for too long, may produce a signal at the wrong time during organ formation. As a result, cells may become specialized too late, thus causing malformation. Although dioxins have been shown to act exclusively through the Ah receptor, knowledge is not complete, and it is possible that there are further undiscovered mechanisms, such as action through another receptor.

By binding to a cell's hormone receptor, dioxins literally modify the functioning and genetic mechanism of the cell, causing a wide range of effects, from cancer to reduced immunity to nervous system disorders to miscarriages and birth deformity. As it changes functions at genetic level, it can cause so-called genetic diseases to appear, and thereby can hinder with child development. There is no safe level dose - the smallest quantity can cause damage, and our bodies have no defense against it.

8.2.7 Phytoestrogens

8.2.7.1 Background

Phytoestrogens can be described as, any plant substance or metabolite that induces biological responses in vertebrates that mimic or modulate the actions of endogenous estrogens by binding to estrogen receptors (McClatchy et al. 1995). Phytoestrogens consist of more than 20 compounds and can be found in more than three hundreds of plants including herbs, grains, and fruits (Moon et al. 2006). Three main classes of compounds are currently recognized as phytoestrogens—the isoflavones, coumestans, and lignans (Moon et al. 2006). These types of phytochemicals are some of the most prevalent compounds found in fruits, vegetables, legumes, and tea and are generally concentrated in the fruit skin, bark, and flowers of plants.

They are present in low levels in many plants, and some are anti-oestrogens (IEH 1995). Phytoestrogens have also been detected in effluents from pulp mills, resulting in reproductive effects in certain fish species. Exposure to naturally occurring endocrine disruptors such as the phyto- and fungal estrogens, which are important components of some human and wildlife diets, occurs globally. The isoflavonoid phytoestrogens are found in soy and legumes, the lignanes are found in grains and several fruits and vegetables, and clover and alfalfa contain the coumestans. These phytoestrogens have relatively short half-lives in humans, and their metabolites can be detected in urine and feces. Diverse species of fungi produces low molecular weight metabolites called mycotoxins. Some mycotoxins have been shown to have estrogenic potential. The main course of general human exposure to mycotoxin is via the food chain while inhalation is the main route for occupational exposure.

Metabolism

Unlike the natural estrogens found in vertebrates, phytoestrogens tend to: have weaker effects than animal estrogens, are not stored in the body, and can be easily broken down and eliminated via normal metabolism. Isoflavones are mainly present as inactive glycosides and, after removal of the sugar residue in the gut by bacteria they become active compounds, taken up by enterocytes and entering the peripheral circulation (Branca and Lorenzetti 2005) They are reconjugated in the liver, following absorption to form glucuronic acid and to a smaller extent to form sulphuric acid (Shelnutt et al. 2002; Zhang et al. 2003). Genistein and daidzein metabolism in humans vary to a great extent, which has been accredited to varying individual intestinal flora and transportation time (Moutsatsou 2007) Some of the glycosidic conjugates of phytoestrogens contain further chemical modifications such as acetate, malonate, and 3-hydroxy-3-methylglutarate esters and 2,3-dihydroxysuccinate ether). In the gastrointestinal tract, the conjugates undergo enzyme catalyzed hydrolysis and also by gut bacteria. On entering the systemic circulation, the phytoestrogens may undergo extensive metabolism to other compounds through reactions involving demethylation, methylation, hydroxylation, chlorination, iodination, and nitration. In addition, all these compounds can undergo conjugation to form beta-glucuronides and sulfate esters (D'Alessandro et al. 2005).

Environmental Fate

Almost all phytoestrogens eaten daily by people were reported partly recovered in urine or feces, which can be regarded as one of the main sources of their occurrence

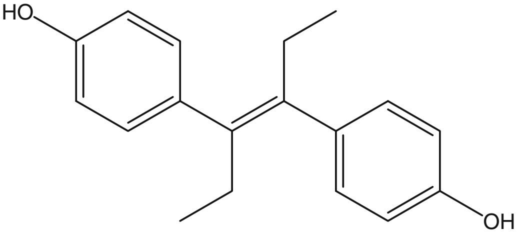

Fig. 8.9 Phytoestrogen compound diethylsilbestrol

in municipal wastewaters. There is a dearth of studies on the fate of phytoestrogens is both aquatic and terrestrial environment. A study on diethylstilbestrol, a common phytoestrogen it was reported that it strongly adsorbs to the soil. Volatilization from the soil surface would most likely be improbable. The scope of biodegradation in soil is not known, though diethylstilbestrol has been shown to be resistant to degradation in activated sludge. Diethylstilbestrol may bioconcentrate in aquatic organisms and strongly adsorbs to suspend solids and sediments. The extent of biodegradation in natural waters is not certain. Diethylstilbestrol vapors quickly oxidize when released to atmosphere, mainly by reaction with ozone.

Toxicity

Phytoestrogens are naturally occurring plant-derived phytochemicals, whose general biological roles are to safeguard plants from stress as part of a plant's defense mechanism. Although composed of a broad assembly of nonsteroidal compounds of varied structure, phytoestrogens have been shown to bind estrogen receptors and to perform as weak agonist/antagonist in both animals and humans (Mueller et al. 2004). Ecological functions of phytoestrogens are based on their abilities to bind to the endocrine disruptor. These receptors render animals vulnerability to plant estrogens. Receptors in animals allow plant phytoestrogens to disturb animal functions, particularly reproduction. Phytoestrogens are biologically active phenol compounds of plant origin that structurally mimic the principal mammalian estrogen 17β-estradiol (Sarah et al. 2008; Sirtori et al. 2005). Shared structures include a pair of hydroxyl groups and a phenolic ring, which is required for binding to the specific estrogen receptors known as Estrogen receptor -α and Estrogen receptor -β, and the position of these hydroxyl groups appears to be an important factor in determining their abilities to bind the estrogen receptors and activate transcription. (Le Bail et al. 1998).

Diethylstilbestrol (Fig. 8.9) induces persistent structural and functional alterations in the developing reproductive tract of males. Xenoestrogens other than diethylstilbestrol also modify sexual differentiation in males and account for the increasing occurrence of developmental disorders of the reproductive tract in men and wild animals. Clotfelte and Rodriguez (2006) investigated the behavioral effects of exposure to waterborne phytoestrogens genistein, equol, β-sitosterol, in male

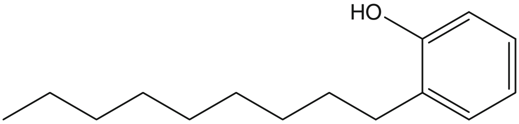

Fig. 8.10 Alkylphenol compound nonylphenol

fighter fish *Betta splendens*. Changes in spontaneous swimming activity, the latency to respond to the mirror, and nest size, and modest changes in the probability of constructing a nest were observed. These findings suggest that phytoestrogen contamination has the potential to significantly affect the behavior of free-living fishes.

Phytoestrogens (coumestans, isoflavonoids, flavonoids, and lignans) present in many edible plants are quantitatively the most important environmental estrogens when their hormonal potency is assessed in vitro (Santti et al. 1998). They exert their estrogenic activity by interacting with estrogen receptors in vitro. They may also act as antiestrogens by competing for the binding sites of estrogen receptors or the active site of the estrogen biosynthesizing and metabolizing enzymes, such as aromatase and estrogen-specific 17 beta-hydroxysteroid oxidoreductase. Phytoestrogens and structurally related compounds could harm the reproductive health of males also by acting as antiestrogens. Genistein, another phytoestrogen is derived from certain plant precursors by human metabolism of food containing soybeans and soy protein. At concentrations that are achieved from dietary soy exposures, genistein has been found to have both weak estrogenic and weak antiestrogenic effects. Genistein bind to both α and β- estrogen receptors, nevertheless they preferentially bind to and activate estrogen receptors β (Messina et al. 2006). For this reason, they are sometimes classified as selective estrogen receptor modulators. Phytoestrogens are mimics of estrogen and target similar receptors. Their concentration is lower in plants but they can concentrate in the body of animals.

8.2.8 Alkyl Phenols

Alkyl phenol ethoxylates are non-ionic surfactant components of industrial and domestic detergents, paints, cosmetics and pesticide formulations. Nonylphenol-polyethoxylates and octylphenol-polyethoxylates represent the greater part of all alkyl phenol ethoxylates. Biodegradation by sewage treatment process results in the formation of alkyl phenols such as nonylphenol (Fig. 8.10) and octylphenol (Gross et al. 2001). Nonylphenol and octylphenol are hydrophobic and lipophilic and thus can accumulate in sediment and fish adipose tissue. Both alkyl phenol ethoxylates and alkyl phenols are known to have estrogenic properties.

8.2.8.1 Metabolism

The complete metabolic pathway for alkylphenol ethoxylates has not hitherto been determined, and studies have been focusing on the detection of intermediates in bacterial culture media. It is probable that microbial degradation generally begins by an attack on the ethoxylate chain, rather than on the ring or the hydrophobic chain (Ball et al. 1989; Ahel et al. 1994b). Degradation of alkylphenol ethoxylates in wastewater treatment plants or in the natural environment results in persistent shorter-chain alkylphenol ethoxylates and alkylphenols such as nonylphenol, octylphenol and alkyl phenol mono- to triethoxylates (Ying et al. 2002a). Metabolites of alkylphenol ethoxylates bioaccumulate in food chain, bioconcentration factors varying according to the species, metabolite and organ. The metabolites of alkylphenol ethoxylates are generally more toxic than the original compounds. Alkylphenol ethoxylates have LC50s above about 1.5 mg l^{-1}, whereas nonylphenol LC50s are generally around 0.1 mg l^{-1}. Ahel et al. (1994c) have established that nonylphenol is vulnerable to photochemical degradation. Ahel et al. (1994a) have embarked on a comprehensive study of the fate of nonylphenols and their metabolites in 11 sewage works in Switzerland. It was concluded that only less than 40% of the effluent was subjected to final biodegradation, with 20% ending up absorbed onto the sludge, and 40–45% in the secondary effluent.

8.2.8.2 Environmental Fate

Alkylphenol ethoxylates are biodegraded by removal of ethoxy groups, producing less biodegradable products such as alkylphenol mono- and di-ethoxylates, alkylphenoxy acetic and alkyl phenoxy polyethoxy acetic acids, and alkylphenols. Anaerobic conditions generally lead to the accumulation of alkylphenols. Rivers in Switzerland have been found to contain concentrations of tens of μg l^{-1} of a wide range of alkylphenolic metabolites. Low levels have also been found in drinking water in the USA, with a total concentration of alkylphenolic compounds of almost 1 μg l^{-1}. A recent modelling study concluded that 83% of UK nonylphenol ethoxylate production enters the environment, with 37% entering the aquatic environment (CES 1993). It has been reported that chlorination of river water during the treatment of drinking water can produce brominated nonylphenols (Ventura et al. 1988; Ball et al. 1989). Ahel et al. (1993) observed a bioconcentration of nonylphenol roughly 7,000 times (dry weight) in the macrophytic algae at levels up to 38 mg kg^{-1}. In the higher trophic levels the bioconcentration may include biomagnification levels too, through the food chain, and the uptake of sediment containing higher levels adds to this (Ahel et al. 1993).

8.2.8.3 Toxicity

The toxicity of alkylphenols increases with the length of the hydrophobic chain (McLeese et al. 1981). Toxicity occurs by partition into lipid membranes in the organism. In mitochondrial membrane, partitioning can lead to the uncoupling of energy production (Argese et al. 1994). The most comprehensive study of the oestrogenic effects of alkylphenols, by White et al. (1994) has observed that alkylphenols were able to rouse vitellogenin gene expression in trout hepatocytes, gene transcription in transfected cells and the growth of breast cancer cell lines. This study employed a wide range of cell lines and receptors such as human breast cancer cell lines MCF7 and ZR- 75–1, chicken embryo fibroblasts, rainbow trout hepatocytes and a mouse oestrogen receptor. All these cell lines and receptors showed oestrogenic responses to alkylphenols, proving the response of oestrogen receptors to alkylphenols.

Male rainbow trout treated with alkyl phenol chemicals responded with significant increases in plasma vitellogenin concentrations, mostly after treatment with at least 3 ppb octylphenol (Jobling et al. 1996). Same study observed testicular growth inhibition with octylphenol recording the maximum inhibitory effect. Christianson et al. (1998) reported like effects in male eelpout, *Zoarces viviparous* exposed to nonylphenol. A significant raise in plasma vitellogenin levels with an associated decline in gonado-somatic index was observed in *Zoarces viviparous,* on 25 days prolonged exposure to 10–100 ppm of nonylphenol. Seminiferous lobules in exposed males were showing degeneration and a reduction in gonadotropin activity which is a marker for Sertoli cell function. Plasma vitellogenin induction was observed in male and immature female rainbow trout (Lech et al. 1996), male flounder (Christenson et al. 1999), male and female Atlantic salmon (Madsen et al. 1997; Arukwe et al. 2000), Japanese medaka (Shioda and Wakabayashi 2000) and immature channel catfish (Nimrod and Benson 1996) as a result of nonylphenol exposure.

On a post hatch day first to post hatch 6 months exposure to octylphenol, there was a significant decline in the courtship activity in adult Japanese medaka males (Gray et al. 1999a, 1999b). Transgenerational effects were observed in the form of increased incidence of fry developmental abnormalities, in the same study. Exposure to octylphenol and 4-tertoctylphenol has induced similar developmental toxicity effects in embryos and larvae of killifish *(Fundulus heteroclitus) (*Kelly and Di Giulio 2000). Disruption of sexual differentiation has been reported in common carp (Gimeno et al. 1997) and mosquitofish (Dreze et al. 2000) exposed to alkyl phenols. The potential ability of alkyl phenol to bind the endocrine receptors mediates their endocrine disrupting properties. Several in vitro bioassays have confirmed the estrogenic potentials of alkyl phenols, substituted at position 4, for example 4-nonylphenol (Flouriot et al. 1995; Jobling and Sumpter 1993; Soto et al. 1991). Likewise, p-substituted phenols, such as 4-t-pentylphenol (TPP), are amongst the most potent estrogens. (Jobling and Sumpter 1993; Smeets et al. 1999).Post-transcriptional regulation of vitellogenin mRNA processing can be involved with the activity of nonylphenol as confirmed by the studies by Ren et al. (1996). Advanced research has shown that alkyl phenols can bring on reproductive modifications by increasing the rate of apoptosis of sertoli cells, and eventually negatively affect the maturity and discharge of sperm (Raychoudhary et al. 1999).

8.2.9 Bisphenol-A

Bisphenol A (2,2-bis (4-hydroxyphenyl) propane) (Fig. 8.11) is one of the most widely used chemicals in the production of epoxy resins and polycarbonate plastics.

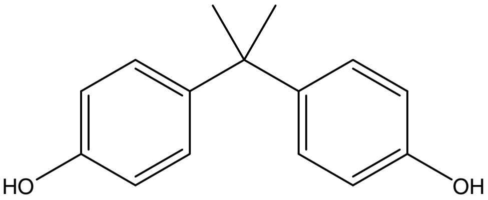

Fig. 8.11 Bisphenol A

These plastics find application in food and drink packaging, while the resins are generally used as lacquers to coat metal products such as food cans, bottle tops and water supply pipes (ENDS 1995). Le et al. (2008) found that bioactive BPA was liberated from both new and used polycarbonate drinking bottles and were migrated at a similar rate into water at room temperature. Bisphenol A is extensively used for all kind of products like computer housings, carpets, upholstery, for car paintings and flame retardants such as tetrabromobisphenol A. The liquid in some cans of tinned vegetables have been found to contain both bisphenol A, and the related chemical dimethyl Bisphenol A. The highest levels of bisphenol A were found in cans of peas, with an average of 23 μg per can (Brotons et al. 1995). As per United States Food and Drug administration research report, bisphenol A leaches into infant formulae, from the infant formula cans which contain them. (Biles et al. 1997). The levels of Bisphenol A detected in the infant formula food ranged between 0.1 and 13.2 ppb. Some polymers used in dental application also contain Bisphenol-A. Olea et al. (1996) has identified a sealant containing bisphenol A diglycidylether methacrylate as oestrogenic to MCF7 breast cancer cells. In 2004, the estimated production volume of BPA in the United States was ~2.3 billion pounds (CERHR 2007). Of the 1.9 billion pounds of BPA used in the US in 2003, nearly 3/4 was used to manufacture polycarbonate resins that were in turn used to manufacture various consumer products including polycarbonate containers for storage of foods and beverages (CERHR 2007).

8.2.9.1 Metabolism

Biological metabolites of Bisphenol A are 4,4′-dihydroxy-α-methylstilbene 2,2-bis(4-hydroxyphenyl)-1-propanol, 2,2-bis(4-hydroxyphenyl) propanoic acid, and 2-(3,4-dihydroxyphenyl)-2-(4-hydroxyphenyl)propane. Suzuki et al. (2004) has monitored the Bisphenol A and its metabolites in a river system using solid phase extraction and gas chromatography –mass spectrometry determination. This study found that, under the aerobic conditions in the river water, Bisphenol A disappeared within 8 days of incubation, but 2, 2-bis (4-hydroxyphenyl) propanoic acid, 2,2-bis(4-hydroxyphenyl)-1-propanol, and tetraol were remaining in the supernatant after 14 days. Bisphenol A is primarily metabolized through bacteria mediated oxidative rearrangement in the river water, and intermediate bisphenols are metabolized by minor metabolic pathways exist in river water (Suzuki et al. 2004).

8.2.9.2 Environmental Fate

The distribution of bisphenol A in the environment can be predicted by its physical properties. Bisphenol A is a solid with low volatility at ambient temperature conditions, water solubility of 120–300 mg l^{-1} and a greater solubility at alkaline pH values (Staples et al. 1998). Based on these properties, a simple equilibrium model predicts that about 50% of bisphenol A in the environment has the potential to bind to sediments or soils with the rest remaining in the water column. Bisphenol A was reported to degrade fairly rapidly in aerobic conditions in marine sediments and seawater but is likely to persist longer under anoxic conditions (Ying and Kookana 2003).

8.2.9.3 Toxicity

Dodds and Lawson (1938), in a study using ovariectomized rats, revealed for the first time that Bisphenol A to be oestrogenic. Later on, it was found to be oestrogenic in the MCF-7 human breast cancer cell culture assay in 1993 (Krishnan et al. 1993). The hormonal effects of Bisphenol A could be measured at concentrations as low as 2–5 ppb. Bisphenol-A is also proved to have anti-androgenic activity, hindering with the action of dihydrotestosterone in a yeast screen containing a human androgen receptor (Sohoni and Sumpter 1998) and it was more or less as powerful as flutamide, another well identified anti-androgenic compound. Once bound to androgen receptor (AR), the AR/BPA complex may prevent endogenous androgens from regulating androgen-dependent transcription. The specificity of AR–ligand interaction may be critical in eliciting adverse effects on male reproductive system. (Wetherill et al. 2007). However, there are disparities among different research groups on antiandrogenic property of BPA making this area of research requires more investigation. Studies by Lee et al. (2003) using in vitro yeast-based assays revealed that BPA exhibits strong anti-androgenic activity. Using ligand competition assays, it was demonstrated that BPA could compete with 5 α -dihydrotestosterone (DHT) for binding at the androgen receptor (AR) with an IC50 (the concentration of chemical required to reduce the specific DHT binding by 50%) value of 2.14 μM (Sun et al. 2006; Lee et al. 2003). A recent study by Xu et al. (2005) has confirmed that BPA can act as an anti-androgen in a mammalian system. In this study, BPA showed significant inhibitory effects on the transcriptional activity induced by 5α-dihydrotestosterone (DHT) with an IC50 value of ~0.8 μM; the highest anti-androgenic activity of any endocrine-disrupting compounds tested.

Bisphenol-A present in the liquor obtained from tinned vegetables has been found to be oestrogenic to human breast cancer cells. All liquors which contained bisphenol A were showing oestrogenic activity in a human breast cancer cell assay. Liquors devoid of detectable bisphenol A were not oestrogenic in action. The liquor from the most contaminated vegetables, the peas, produced 58% of the oestrogenic response generated by oestradiol (Brotons et al. 1995). More recent studies reported that in human cultured MCF-7 breast cancer cells, Bisphenol A increased cell numbers in a dose-dependent manner at concentrations from 10^{-7} to 10^{-5} M (Suzuki et al. 2004).

Steinmetz et al. (1998) observed that bisphenol-A produces identical effects to those produced by oestradiol on rat uterus and vagina, with vagina showing predominantly high sensitivity to the chemical. Exposure of male mice embryo in the womb, to Bisphenol-A has been reported to develop enlarged prostate glands. Bisphenol acts in the same way as female hormones in the developing rat brain which controls fertility and sexual behaviour (Anon 1998). Fisher et al. (1999) reported that, introduction of Bisphenol-A to new born male rats led to slight, but transient changes in the structure of the efferent ducts. Further research by Howdeshell et al. (1999) showed that female mice exposed in the womb to low doses of bisphenol A (2.4 μg kg^{-1} day^{-1} to the mother) had shown a significantly reduced delay between vaginal opening and first vaginal oestrus. This study also considered the information on litter position inside the womb. The females positioned between female litter mates were most affected by bisphenol A, while females located between males were least affected. The estrogenicity of bisphenol A has been confirmed by a number of in vitro assays (Sonnenschein and Soto 1998; Soto et al. 1995; Smeets et al. 1999; Krishnan et al. 1993; Olea et al. 1996; Gaido et al. 1997). Bisphenol A has been reported to bring on the synthesis of the egg yolk protein vitellogenin in liver slices of rainbow trout (Shilling and Williams 2000), vitellogenin mRNA in rainbow trout primary hepatocyte cultures and vitellogenin and zona radiata proteins in the primary hepatocytes of Atlantic salmon. Arukwe et al. (2000) observed a dose-dependent increase in plasma VTG and zona radiata proteins following a single intraperitoneal injection of bisphenol A. Bisphenol A is also known to cause significant declines in sperm production (VomSaal et al. 1998).

There are very little data on the concentration levels of bisphenol A in the aquatic environment, but studies have shown that even at very low concentrations, bisphenol A was observed to affect the sexual differentiation of frogs. Kloas et al. (1999) subjected the newly hatched tadpoles of *Xenopus laevis* to bisphenol A for 12 weeks and they were able to observe a significant increase in the number of females at an exposure level of 23 μg l^{-1}, while at a concentration of 2.3 μg l^{-1} a slighter, but not significant, increase in the number of females.

8.3 Endocrine-Disrupting Chemicals and Their Environmental Impacts

As endocrine disrupting chemicals are present everywhere, wildlife and humans face a continuous exposure of toxic chemicals. Exposure occurs in every stage of life, from development in egg or womb to adulthood, and any number of sources, including food, air, water, soil, household products, breast milk, and the womb. Though most endocrine disruptors are weaker than natural hormones, some have been related with reproductive and developmental problems in wildlife and laboratory animals. Many of the accused chemicals have distinct effects in different species and organs and at different developmental stages.

Endocrine disruptors can also disrupt signaling between organisms, though the effects are not completely understood. For example, legume plants, such beans, depend on special bacteria living in their roots to supply required nitrogen. These plants liberate specific chemicals into the soil that bind to the bacteria's receptors and commence the gene expression essential to locate its way to the plant. Dichlorodiphenyltrichloroethane and the herbicide 2, 4-D, are potent to block these signaling to various degrees and thereby obstructing recruitment of the vital partners (Fox 2004; Fox et al. 2004). Some other hormone signals such as the peptide hormones may also be susceptible. These less studied relationships influence most body regulatory processes, such as brain functions, appetite, immunity and metabolism. Physical factors, such as low oxygen conditions, can influence hormones, too. Light and electromagnetic fields may contribute to certain type of cancers by changing performance of the hormone melatonin, which controls human hormone production and sleep (Blask et al. 2005).

Most known facts about endocrine disruptors is how they impede with one or a combination of steroid hormones (the estrogens, androgens, progestins, and corticoids) and thyroid hormones, including thyroxine. Within this group, attention has been focused on the environmental estrogens – the synthetic and plant compounds that affect the natural estrogen hormones, chiefly the potent and widespread estradiol, which regulates reproduction. A wide range of invertebrates (coral, lobster, snails, and starfish) and all the vertebrates produce estradiol (Cheek et al. 1998). Altering this hormone could affect a large section of the Earth's organisms.

Concerns regarding exposure to these endocrine disruptors are due primarily to (1) adverse effects observed in certain wildlife, fish, and ecosystems; (2) the increased incidence of certain endocrine-related human diseases; and (3) endocrine disruption resulting from exposure to certain environmental chemicals observed in laboratory experimental animals. Several field and laboratory studies have shown that exposure to certain endocrine disruptors has contributed to adverse effects in some wildlife species and populations. These effects diverge from slight changes in the physiology and sexual behavior of species to permanently distorted sexual differentiation. Aquatic species are most affected, but effects have also been observed in terrestrial species. Some adverse effects observed in certain species are likely to be endocrine mediated, but in most cases, the contributory link involving exposure and endocrine disruption is imprecise.

Most of the research on endocrine disruptors has focused on impairments to reproductive potential, perhaps because this aspect is sensitive and also easily observable. Nevertheless, recent workers have raised the likelihood that endocrine disruptors also distress thyroid function and also they can have deep but subtle effects on memory and behaviour (Jahnke et al. 2004). Studies on a range of endocrine disruptors showed that each compound brought out its own range of modifications in the metabolism and function of thyroid hormone (Ishihara et al. 2003) while thyroxine binding to the transport protein transthyretin is an important target for plasticizers like nonylphenol, bisphenol-A and butyl benzyl phthalate (Harvey and Johnson 2002). Flavonoids and isoflavonoids are comparatively poorly absorbed and less fat-soluble unlike bisphenol A, and they may front less risk, even though they can also affect thyroid hormone metabolism in vitro (Waring and Haris 2005). The chlorinated pesticides such as polychlorobiphenyls are reported to upset the thyroid hormone homeostasis in animal studies. Hagmar (2003) and Winneke et al. (2002) reported some evidences strongly suggesting that polychlorobiphenyls cause developmental neurotoxicity in man. Vreugdenhil et al. (2004) had demonstrated that prenatal exposure to polychlorobiphenyls interrupt and delay the processing in the central nervous system in Dutch babies, as a forewarning of neurological damage that can occur.

Thyroid hormones such as thyroxine not only control metabolic rates but are also involved in regulation and differentiation of the developing central nervous system (Waring and Haris 2005). Lesser recognized, but just as important, are substances that hamper with thyroid and androgen hormones. Antiandrogens, like the fungicide vinclozolin, produce males with malformed organs and female characteristics. Opposite effects are seen in fish exposed to the growth steroid trenbolone and plant steroid compounds found in pulp and paper mill effluent. Both masculanize, producing females with male attributes. The reproductive and immune function in Baltic seals, were adversely affected on exposure to organochlorines ensuing in marked population declines. These seals exhibit a compromised endocrine system, but precise mechanisms of action remain unclear. Eggshell thinning and altered gonadal development have been observed in birds of prey exposed to dichlorodiphenyltrichloroethane, resulting in severe population declines. A syndrome of embryonic abnormalities known as GLEMEDS has been observed in fish-eating birds and can be directly related to polychlorobiphenyls exposure, but the precise linkage to endocrine function is uncertain. An alleged pesticide spill in lake Apopka (Florida, USA) provides a well-publicized example of potential effects of endocrine disruptors on population decline in alligators. An array of developmental abnormalities was observed that have been attributed to high levels of organochlorine compounds that upset endocrine homeostasis. There is extensive evidence that chemical constituents present in pulp and paper mill effluents and sewage treatment effluents can affect reproductive endocrine function and contribute to alteration in reproductive development of fishes. A variety of mechanisms (e.g., hormone–receptor interactions, interference with sex steroid biosynthesis, altered pituitary function) are involved, but precise modes of action or the causative chemicals are still poorly understood (International Programme on Chemical safety-WWF). Exposure of marine gastropods to tributyltin, a biocide used in antifouling paints, Masculinization of marine gastropods exposed to tributyltin provides the best example of an endocrine-mediated adverse effect caused by exposure to an environmental contaminant in invertebrates. The endocrine mechanism probably involves elevated androgen levels possibly through altered aromatase activity. The detection of chemicals in the environment with androgenic activity raises questions about the prospective for these substances to bioaccumulate and progress through the food chain. Androgenic hormones are vital for reproduction in all vertebrates. The biochemical and molecular mechanisms of hormone action are greatly conserved among the vertebrates (Norris 1996), therefore exposure to significant levels of androgenic substances could harmfully affect reproduction in all species, including humans.

8.4 Ecotoxicological Effects of Endocrine Disruptors

The effects that can be seen in an organism exposed to an endocrine disrupting chemical depend on which hormone system is targeted. In an organism exposed to sex hormone disrupting pesticides in the womb, effects on sexual behaviour, structural deformities of the reproductive tract, including intersex type conditions, eficits in sperm counts, and effects on sex ratios are mainly observed. If, primary action is on the thyroid hormones, then as these hormones are responsible for metabolism and normal brain development, exposure in the womb may cause effects on intelligence and growth. Laboratory tests have confirmed that endocrine disrupting chemicals do indeed cause such effects in exposed animals, but all the effects listed above have also been noted in wildlife or humans heavily exposed to endocrine disrupting pesticides or industrial chemicals. Some endocrine disruptors may exert their action by interfering with the brain's release of hormones, which in turn regulate the production of other hormones that control the growth and the activity of many other endocrine glands.

The Baltic Sea is one of the marine areas that have been most seriously polluted by dichlorodiphenyltrichloroethane and polychlorobiphenyls, due to the presence of highly industrialized communities within its drainage areas. Potential endocrine-mediated adverse effects have been observed in a number of species in the Baltic Sea. Examples include an increased prevalence of female salmon producing offspring with a low survival rate (Johansson and Ahlborg 1994); lowered reproductive capacity and eggshell thinning in white-tailed sea eagles (Stjernberg et al. 1990; Helander et al. 1998; Odsjö et al. 1997), razor bill (Andersson et al. 1988), and guillemot (Bignert et al. 1995), and immune and reproductive impairment in marine mammals (Simms and Ross 2001).

8.5 Organic Pollutants and Endocrine Disruptors: Future Prospects

Studies in wildlife have been proposed as sentinels of human exposure to endocrine disruptors. However, given the diversity of wildlife, caution must be taken in extrapolating the responses to endocrine disruptors, as research has focused primarily on only a few species of wildlife. Also, potential effects of endocrine disruptors on wildlife tend to focus on the individual, whereas ecological risk assessments focus on populations and communities. The significance of disturbances in reproductive output and viability of offspring on populations is difficult to quantify. Overall, the current scientific knowledge provides evidence that certain effects observed in wildlife can be attributed to chemicals that function as endocrine disruptors. However, in most cases, the evidence of a causal link is weak, and most effects have been observed in areas where chemical contamination is high.

Our understanding of hormonal actions and receptor sites is also remote from precision. In addition, there are many other hormones involved, including retinoids, progestins, and corticosteroids apart from the sex hormones and thyroid hormones. There is also involvement and interest of many other signaling processes besides hormone messengers. The fact that, although chemicals can be shown to bind to certain receptors in test tube experiments, it is occasionally not easy to elucidate whether the adverse effects that they cause in animals are in reality mediated mainly by the endocrine system, further complicates the situation. Wildlife will be particularly susceptible to the endocrine disrupting effects of pesticides, since these chemicals are intentionally released into the environment. Effects associated with endocrine disruption have been noted in invertebrates, reptiles, fish, birds, and mammals living in polluted areas, but although most are linked to exposure to organochlorines, it is always not easy to tie down particular causal agents with surety. Humans exposed occupationally are also at increased risk, and there are studies linking exposure to pesticides at work to impotence, reduced sperm counts, increased time to pregnancy, and increased rates of birth defects in offspring. Similarly, in the Yaqui children in Mexico, who are highly exposed to pesticides, developmental effects have been reported, and in women highly exposed to dichlorodiphenyltrichloroethane, shortened lactation has been noted (Lyons 1999).

There is some evidence on the transgenerational effects of endocrine disruptors. Research from the National Institute of Environmental Health Sciences (USA) has shown that the undesirable effects of pharmaceutical diethylstilbestrol in mice can be transferred to succeeding generations even though they were not directly exposed. The increased vulnerability for tumors was seen in subsequent generations of mice those were developmentally exposed to diethylstilbestrol (NTP 2011) Mechanisms involved in the transmission of malady were shown to involve epigenetic events. Their study also suggests that the endocrine disrupting compounds may have caused changes in the developing male germ cells and that endocrine disruptors might be capable to modify the expression of genes without mutating the DNA.

Human are exposed from residues in fruit and vegetables, and from contaminated meat, fish, and dairy produce, due to the buildup of persistent and bioaccumulating pesticides in the food chain. Yet, it is not only the effects due to any one particular spraying operation which give rise to distress, the foremost concern is with the possible interactive effects of the several hormone disrupting substances to which humans and wildlife are now continually exposed. Risk assessment procedures on single compounds will not reproduce the real world situation. It could definitely be envisaged that exposure to substances mimic estrogens, substances that are anti-androgenic, and substances inhibit the steroid synthesis could all result in an enhanced de-masculinising effect. Future research in various fields may answer issues that have been presented by researchers. These questions leave opportunities for future researchers and keep phytoestrogens and endocrine disruptors as current challenges in one aspect of chemical ecology. Earlier, for many years it has been assumed that genetic and chromosomal changes to the fetus are the reason for childhood cancers. Later workers demonstrated that environmental exposure to pesticides and industrial chemicals are also significant to reflect on. Understanding the interaction of genes and the environment, together with epigenetic processes, holds the key to our understanding of cancer incidence in a person's life.

8.6 Conclusion

This review summarized the past and present research carried out on the potential hazards of exposure to endocrine disruptors in humans and wildlife. In the past few years, the possibility of adverse health effects of endocrine disruption has received considerable public attention. The issue of endocrine disruption is a matter of interest, if not concern, to numerous industries such as plastics, food packaging, petroleum, pesticides, agricultural products, and chemicals. As discussed in greater detail forgoing, public concern over potential endocrine-disruptive chemicals led to congressional hearings and legislation. In view of the attention that the field has received, it is not surprising that endocrine disruption has been the topic of numerous books and articles in both the professional and the lay literature. The endocrine system is complex, involving processes that operate at the organ, tissue, cellular, and molecular levels. While the possibility that exposures to environmental substances can result in reproductive and developmental abnormalities is challenging, alarming, and credible, the biological complexity of the endocrine system is often underappreciated and biological mechanisms of endocrine disruption are oversimplified. This over generalization can lead to flawed conclusions about the grounds of adverse effects as well as improper public policy in dealing with possible ecological issues.

This review has revealed that despite of the high quality work carried out in the past years, our present understanding and knowledge of/on the effects of endocrine disruptors to wildlife and humans is incomplete. Recent studies revealing the crucial impact of high level exposure of these substances on both humans and wildlife signifies that this potential mechanism of toxicity by endocrine disruption calls for great attention. The potential effects posed by exposure to these chemicals become an obvious research concern, when the primary roles played by endocrine system in the maintenance of homeostasis and the still continuing ambiguity over the probable impacts of long term, low level exposure to innumerable chemicals are considered. It is necessary to identify life stages and species that are more susceptible to the impacts of endocrine disruptors and to know how this mechanism of toxicity may impinge on populations and communities.

We need to expand basic knowledge about endocrine systems in humans and wildlife and the biology underlying endocrine-mediated effects. The range of mechanisms by which endocrine disruption may interfere with reproductive/population success, immune function, Neuro behavior, and development of cancer, at all levels of biological organization and at key stages of life cycles needs to be elucidated as well. It is required to develop enhanced methodologies for assessing dose–response relationships at environmentally relevant concentrations. We need to develop more precise and sensitive biomarkers for detecting endocrine-mediated effects in individuals and populations.

To achieve ample availability of baseline data on population status, long-term monitoring of wildlife has to be conducted. Improving global collaboration and cooperative research to evaluate the exposure and consequences of endocrine disruptors on natural world populations on a more international basis can be more beneficial. We need to constantly identify persistent and non persistent, naturally occurring and anthropogenic chemicals that are the most probable candidates to effect populations at environmentally significant concentrations. Identification of hot spots for exposure or effects deserves particular concern. Populations or subgroups most likely to be susceptible to endocrine disruptors deserve special focus. The role of endocrine disruptors on the fitness of populations relative to other environmental stressors needs to be particularly investigated. Development of global data base on the status and trends of environmental contamination, exposure, and health outcomes is a priority target. Successful accomplishment of these objectives will depend on the upgrading of international synchronization for sharing of information on effects caused by endocrine disruption.

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Chapter 9
Heavy Metals in Seafood Mussels. Risks for Human Health

Slavka Stankovic, Mihajlo Jovic, Ana R. Stankovic, and Lynne Katsikas

Contents

Abstract Life on earth is threatened both by environmental pollution and overpopulation. Natural phenomena contributing to pollution have always existed but anthropogenic activities are increasing contamination of air, soil and water. Waters are especially polluted by metals. The main threats to life from toxic metals are associated with exposure to Pb, Cd, Hg and As, which accumulate in organisms. Overpopulation means more food is required but the amount of arable land is declining

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due to human requirements. One way of overcoming these consequences of overpopulation is to exploit seas and oceans. Thus, the consumption of seafood has increased in recent years, especially in coastal regions. However, as many traditional fishing grounds have been over-fished, aquaculture seems a viable solution to these problems. Marine mussels are an excellent candidate for aquaculture. However mussels accumulate a wide range of metals in their soft tissue. Thus, the determination of the concentrations of potentially toxic substances in mussels is essential because of their usage as seafood and the potential adverse effects of their consumption on human health. Moreover, as contamination by metal pollutants continues and is even increasing in some parts of the world, particularly in less developed countries, it is also important to determine the level of pollution in the marine environment, especially in regions where aquaculture is foreseen and where the local population consumes large amounts of mussels.

In this review, these issues are presented and discussed using the Mediterranean mussel *Mytilus galloprovincialis* as an example. When this mussel is in its best condition, the meat weight can approach 50% of the total wet weight, i.e., *M. galloprovincialis* is very efficient at converting low value victuals into high quality animal protein. For all these reasons, *M. galloprovincialis* is an ideal candidate in attempts to alleviate famine through aquaculture. Mussel farming is a relatively "clean" operation because no pollutants are released into the environment. The mussels remove suspended materials from the water column, thereby improving the local water quality. However mussels accumulate metals. Metal concentrations in *M. galloprovincialis* are valuable indicators of contamination of coastal and estuarine ecosystems. "Mussel Watch", introduced in 1975, is the longest continuous contaminant monitoring program of coastal waters for assessing spatial and temporal trends in coastal contamination, providing a baseline for assessing the impacts of anthropogenic and natural events and identifying contamination hot spots.

In Europe, the production of cultivated mussels is almost five times higher than wild collected mussels. Recently, the production of *M. galloprovincialis* in Europe has been increasing rapidly in Greece and Turkey but Spain is still the largest producer of mussels in Europe. The production of the mussel *M. galloprovincialis* in Spain is about 25% to the total world production, over 200,000 t y^{-1}. Only China has a larger production of these mussels than Spain, about 600,000 t y^{-1}. However, the bioaccumulation of toxic contaminents, mainly Cd, Pb, Hg and As, remains an issue concerning the consumption of mussels. A review of literature data revealed large variations in the Cd, Pb, Hg and As concentrations in *M. galloprovincialis* from their endemic areas, e.g., Mediterranean, Adriatic and Black Sea and that the concentrations of these toxic metals were generally in the following order: As > Pb > Cd > Hg. The levels of Cd, Pb and Hg were the lowest in mussels from the Aegean Sea, compared to the others investigated Seas, but a very high level of As was found.

The guidelines on the trace elements for seafood safety set by different countries and associations are reviewed. The defined legal limits on permissible concentrations of non-essential elements that are toxic in traces, such as Cd, Pb, Hg and As, in mussels on a wet weight basis in mg/kg are in the ranges: for Cd from 0.1 to 4.0; for

Pb from 1.0 to 6.0; for Hg from 0.05 to 10 mg/kg and for As from 0.5 to 86 mg/kg. The reviewed Provisional Tolerable Weekly Intake values appear to support the conclusion that risk to human health from dietary exposure to the investigated elements from Mediterranean mussels is relatively low. Comparison of the published data with European legislation showed that the levels of Cd, Pb and Hg generally did not exceed the existing limits in all the mussels analyzed, excluding mussels from hot spots, such as lagoons and harbors in the Mediteranean, Adriatic and Black Sea.

Overall, the assessment that the investigated toxic elements may pose a health risk to heavy mussel consumers, especially related to the levels of Pb and Cd in *M. galloprovincialis* from hot spots in the all investigated Seas. Although consumption of these mussels provides proteins, essential minerals and vitamins, and thus, some protection from certain diseases, the risks and benefits of their consumption are still hard to assess because of the metals bioacumulated from the marine environment, with their reviewed toxicity. The final conclusion of this review is that *M. galloprovincialis* is an excellent candidate for aquaculture but that extreme care must be taken when choosing the location of farms. Care should also be taken by coastal populations when consuming wild mussels from contamination hot spots.

Keywords Mediterranean mussel • Seafood • Toxic elements • Risks • Human health

List of Abbreviations

AQ	Aquaculture
AsB	Arsenobetanine
BC	Before Christ
CIESM	Commission Internationale pour l'Exploration Scientifique de la Mer Mediterranee
CLOC	Consumption Level of Concern
DOM	Dissolved Organic Matter
d.w.	Dry weight
EC	European Commission
EEC	European Economic Community
Eh	Soil Redox potential
EQS	Environmental Quality Standards
EU	European Union
FAO	Food and Agriculture Organization of the United Nations
FSANZ	Food Standards, Australia New Zealand
iAs	inorganic Arsenic
LOC	Level of Concern
Me-Hg	Methylmercury
MED POL	Marine pollution assessment and control component of MAP
MMW	Mediterranean Mussel Watch

MPHT	Ministry of Public Health Thailand
NW	Northwest
PTWI	Provisional Tolerable Weekly Intake
RINBIO	Biological Network Integrators, Réseau Intégrateur Biologique
RNO	National Network for the Observation of Marine Environment Quality, French Mussel Watch
RQ	Risk Quotient
RQ_{bcs}	Risk Quotient for the best scenario
RQ_{mcs}	Risk Quotient for the median scenario
RQ_{wcs}	Risk Quotient for the worst case scenario
RSC	Rate of Shellfish Consumption
t	Tonne
TDI	Tolerable Daily Intake
$t\ y^{-1}$	Tonne per year
UK	United Kingdom
UNEP/MAP	United Nations Environment Programme/Mediterranean Action Plan
USA, US	United States of America, United States
USFDA	Food and Drug Administration of the United States
WB	Weight Basis
WHO	World Health Organization
WMW	World Mussel Watch
wt	Weight
w.w.	Wet weight
y	Year

9.1 Introduction

The world population has increased almost three times in the last 60 years. The population is increasing rapidly, which means simply greater food production and more jobs are required. Although, vegetable production is enough for the present population and is likely to be for the future population, the intake of animal protein is insufficient in spite of the attempts made during the last 60 years, Culha et al. (2008).The world population is estimated to increase from about six billion currently to 8.3 billion by 2025, Bowen and Crumbley (1999). Presently, 60% of the world's population is estimated to live in coastal areas and the present population of coastal areas exceeds the global population of just 50 years ago, Bowen and Crumbley (1999). Over two billion people worldwide rely on seafood as the major source of protein in their diet, and seafood consumption continues to increase worldwide, FAO (2006). Additionally, the sustainability of remote coastal populations depends on a source of uncontaminated seafood. Natural stocks of seafood have been supplemented by the aquaculture industry, Bowen and Crumbley (1999).

Aquaculture commenced primarily in Asia but has now spread to all continents, Subasinghe et al. (2009). From an activity that was family-based and non-commercial, aquaculture now includes large-scale commercial and industrial production of a range of high-value aquatic species that are traded at national, regional and international levels, Holmyard (1997), although production remains predominantly Asian, Subasinghe et al. (2009). Worldwide, aquaculture has shown an average annual world growth rate of 8.8% per year since 1970, which is higher than that of any other animal food-production sector Dias et al. (2009). Aquaculture plays an important role in global efforts to eliminate hunger and malnutrition by supplying aquatic products rich in protein, essential fatty acids, vitamins and minerals, Subasinghe et al. (2009). In addition, through its development, expansion and intensification, aquaculture makes significant contributions to development by improving incomes, providing employment opportunities and increasing the returns on resource use.

Mollusks are among the most successfully cultured and commercially important types of shellfish and a large variety of different mollusk species are cultured throughout the world. Seafood, notably fish, shrimp and mussels, is of value for both local consumption and export revenue, Culha et al. (2008). In recent years, the consumption of seafood has increased, Kalogeropoulos et al. (2004), Perugini et al. (2007) and marine mussels are commercially important seafood species worldwide, Phillips (1980), Widdows (1985), Farrington et al. (1987), Holmyard (1997), Prou and Goulletquer (2002), Smaal (2002), Nesto et al. (2007), Culha et al. (2008) and their production is increasing worldwide, FAO (2006). Mussel (*Mytilus* spp.) production is one of the most economically important aspects of global aquaculture. The farming of mussel (*Mytilus* spp.) is without doubt the most efficient way to convert the organic matter produced by marine organisms in the first link of the food chain, phytoplankton and the remains thereof, into palatable and nutritious human food, Culha et al. (2008). According to data from 2002, the annual world production of mussels *Mytilus galloprovincialis* was 1.690.835 t, Ozden et al. (2010). In Europe, production is known to consist of *M. galloprovincialis*, *M. edulis* and a third, less profitable species *M. trossulus,* but only in the Baltic Sea, Dias et al. (2009). Mussels are important for the mariculture industry in Europe and the annual production exceeds 800,000 t, Smaal (2002).

The Mediterranean mussel, *M. galloprovincialis*, is endemic to the Mediterranean, Black and Adriatic Sea and the Atlantic Ocean from Ireland to Morocco, Gosling (1992). The mussel species *M. galloprovincialis* is raised mainly in the Mediterranean and farming of this species is common along the coastlines of a number of countries in the region: France, Spain, Italy, Sicily, Greece and Tunisia, Smaal (2002). The culture of *M. galloprovincialis* in the Black Sea region has recently been developing but is not yet widespread. However, there are mussel farms in the Marmara and Aegean Sea in Turkey, Karayücel et al. (2010).

The Mediterranean mussel is an invasive, warm-water species frequently transported by human activities. It is highly invasive where it has been introduced, including in Australia, Asia, California and the Puget Sound in the United States, Gosling (1992), Geller et al. (1994) and Anderson et al. (2002). This species has also been successfully introduced in South Africa, where it now dominates over other locally farmed species, Gangnery et al. (2004).

Mussel farming is a relatively "clean" operation. As filter feeders, mussels tend to remove suspended materials from the water column, thereby improving the local water quality. Regardless of the technology employed, the culturing of mussels does not involve the application of feed or the release of pollutants in any other way. *M. galloprovincialis* is a filter feeding animal, which depends on phytoplankton, organic detritus, bacteria and, probably, dissolved organic matter in the water as sources of food. It is well-known that through feeding, mussels accumulate a wide range of metals from water. Metal concentrations in the mussel *M. galloprovincialis* can provide a measure of the effects of potential pollutants in marine environments, Goldberg and Bertine (2000), Pergent-Martini and Pergent (2000), Romeo et al. (2003a, b, 2005), Morillo et al. (2005), Usero et al. (2005), Gorbi et al. (2008), Deudero et al. (2009), Stankovic et al. (2005, 2006, 2008), Fernández et al. (2010), Bartolomé et al. (2010b), Jovic et al. (2011), and information of direct ecological significance, Costas-Rodríguez et al. (2010), Tsangaris, et al. (2010) and potential relevance to human health, Culha et al. (2008). Seafood is a major source of animal protein and very rich sources of mineral components, Fuentes et al. (2009), Ozden et al. (2010).The health benefits associated with the consumption of seafood products are particularly important for the prevention of heart-related diseases and for many vulnerable groups, such as pregnant and lactating women, infants and children, Cozzolino et al. (2001), Christophoridis et al. (2009).

The distribution of metals within aquatic environments is governed by complex processes of material exchange affected by various anthropogenic activities or natural processes, including reverine or atmospheric inputs, coastal and seafloor erosion, biological activities, water drainage and discharge of urban and industrial wastewaters. The sources of pollutant metals in the marine environment are mainly from industrial processes and discharge of metal-containing waste, landfill leachates and secondary precipitation of polluted airborne matter. As pollutant metals are widely distributed in coastal environments, due to both natural geological processes and anthropogenic activities, the determination of the level of potentially toxic substances in mussels is important because of their negative effect on human health, Giusti and Zhang (2002), Kwoczek et al. (2006), Sivaperumal et al. (2007), Kayhan et al. (2007), Turkmen and Ciminli (2007), Çevik et al. (2008), Baeyens et al. (2009), Ozden et al. (2010).

Mussels have proven themselves to be useful for biomonitoring chemical contamination and, therefore, have been used for indicating levels of trace metal concentrations in the marine environment, Conti and Cecchetti (2003). Mussels of the genus *Mytilus* have been employed extensively in Mussels Watch Programs to establish current trace metal levels in coastal environments, e.g., in the USA, the UK, Australia, Hong Kong and France, Przytarska et al. (2010). Mussels Watch Programs are considered efficient tools to study environmental trace metal levels and they have been adopted in many countries, Hellou and Law (2003). To safeguard public health, maximum acceptable concentrations of toxic contaminants have been established in various countries. Thus, in the framework of numerous legislative measures, many monitoring programs have been performed to investigate the health quality of marine species used as human seafood, including mollusks, in European and Asian regions, Franco et al. (2002), Marcotrigiano and Storelli (2003), Liang et al. (2004), Yap et al. (2004), Kwoczek et al. (2006), Kljakovic-Gaspic et al. (2007), Marti-Cid et al. (2007), Nesto et al. (2007), Sivaperumal et al. (2007), Amirad et al. (2008), Sloth and Julshaman (2008), Metain et al. (2009), Whyte et al. (2009), Jovic et al. (2009, 2010), Ozden et al. (2010), Dahl et al. (2010). Thus, balancing the risks and benefits of seafood consumption is clearly a topic of interest. Much has been realized in the case of fish, Gochfeld and Burger (2005), but risk assessment is not so well developed in the case of shellfish, Amiard et al. (2008).

The interactions between the seas and human health are increasing, in part, due to the increasing numbers of humans living within close proximity of the world's seas. The consequences of this are: higher usage of sea resources as food and the greater possibility of contamination of the coasts. The necessity for monitoring metal pollution of coastal waters is therefore important worldwide from the commercial and resource sustainability points of view.

9.2 Mediterranean Mussel – *Mytilus galloprovincialis*

9.2.1 Distribution

Three *Mytilus* mussel taxa are present in European coastal sea waters: *Mytilus galloprovincialis* (Mediterranean mussel), *Mytilus edulis* (Blue mussel), and *Mytilus trossulus* (Baltic mussel), Gosling (1992), Śmietanka et al. (2004). The Mediterranean mussel *M. galloprovincialis* is a temperate, warm-water mussel, occurring in more exposed locations which do not experience pronounced salinity variations and also in southern areas such as the Black Sea, the Mediterranean and the Iberian Atlantic coast. *M. edulis* is a temperate, cold-water mussel, which can live in brackish water and predominates in central and northern Europe. *M. trossulus*, a cold-water species that can tolerate low salinities, occurs in the Baltic Sea and presumably some areas in northern Europe, Kijewski et al. (2009).

The Mediterranean mussel, *M. galloprovincialis*, is endemic to the Mediterranean Sea, the Adriatic Sea and the Atlantic Ocean from Ireland to Morocco, Gosling (1992). Due in part to its capacity to tolerate warm-water conditions, the Mediterranean mussel is a warm-water invasive species, Branch and Steffani (2004), frequently transported by human activities, Geller et al.(1994), Anderson et al. (2002). From its source in the Mediterranean, *M. galloprovincialis* has colonized the sea waters of Hong Kong, Japan, Korea, southeast Australia, Hawaii, Mexico, California, the west and east coast of Canada and perhaps Britain and Ireland and arrived accidentally in South Africa in the mid-1970s, Branch and Steffani (2004), since when its geographic range has extended at about 115 km year^{-1}, Kijewski et al.

(2009). It is not known whether the expansion of its range in the Atlantic and Pacific Oceans is due to climate change or human activity but is probably a mixture of the both, Braby and Somero (2006), Coghlan and Gosling (2007) Wonham (2004), Zardi et al. (2007).

It is known that *M. galloprovincialis* is able to out compete and displace native mussels and has become the dominant mussel species in certain localities. This was case with the native mussel *Perna,* Branch and Stephanni (2004). This is because *M. galloprovincialis* may grow faster than native mussels, be more tolerant to air exposure and have a reproductive output of between 20% and 200% greater than that of indigenous species, Branch and Stephanni (2004). Thus, *M. galloprovincialis* is both ecologically invasive and a source of 'genetic pollution' that may threaten the genetic integrity of a native mussel species over much of its geographic range, Hilbish et al. (2010).

M. galloprovincialis, *M. edulis* and *M. trossulus* are closely related species, the identification of which has long been controversial. More accurate species identification is now possible using genetic methods, Inoue et al. (1995), Gosling et al. (2008), Dias et al. (2009). The three species are known to hybridize wherever their geographic ranges overlap, Zardi et al. (2007), Dias et al. (2009). Well-studied hybrid zones of *M. galloprovincialis* include the areas between southwest France and the Scottish coasts between *M. galloprovincialis* and *M. edulis*, Skibinski et al. (1983), Gosling (1992) and Hilbish et al. (2002); on the west coasts of North America between *M. trossulus, M. galloprovincialis* and *M. edulis*, Braby and Somero (2006), Johnson and Geller (2006) Shields et al. (2008). There remains debate about the true taxonomic status of these two "species" because wherever their distributions overlap they can hybridize and their hybrids are fertile, Dias et al. (2009). Its occurrence in Britain and Ireland is still an open question: whether its occurrence there due to introduction or is simply an expansion of its natural range in the Mediterranean, Branch and Steffani (2004). In Scotland, small numbers of *M. galloprovincialis* and its possible hybrids were identified, *M. trossulus* (37%) was found to be more common than *M. edulis* (30%) and 23% of the sampled mussels were *M. trossulus* and *M. edulis* hybrids, Dias et al. (2009). Identification of *M. galloprovincialis* and *M. edulis* (and any hybrids) based on shell shape is usually uncertain because of the extreme plasticity of shape exhibited by the mussels under environmental variation. Since 1995, a DNA-based genetic method that seems truly diagnostic for European populations of these species has become available, Inoue et al. (1995) and Wood et al. (2003).

However, no large scale studies have yet been carried out to characterize the mosaic of populations of *Mytilus* spp. and their hybrids. Up to the early 1990s, all mussels from Western Europe were considered to be *M. edulis*. Now, it is known that the mussels from southern Brittany (France) to the Mediterranean Sea are *M. galloprovincialis*. The knowledge of the distribution of mussel species around Europe, as was assessed in 1992, is given in Fig. 9.1, Gosling (1992).

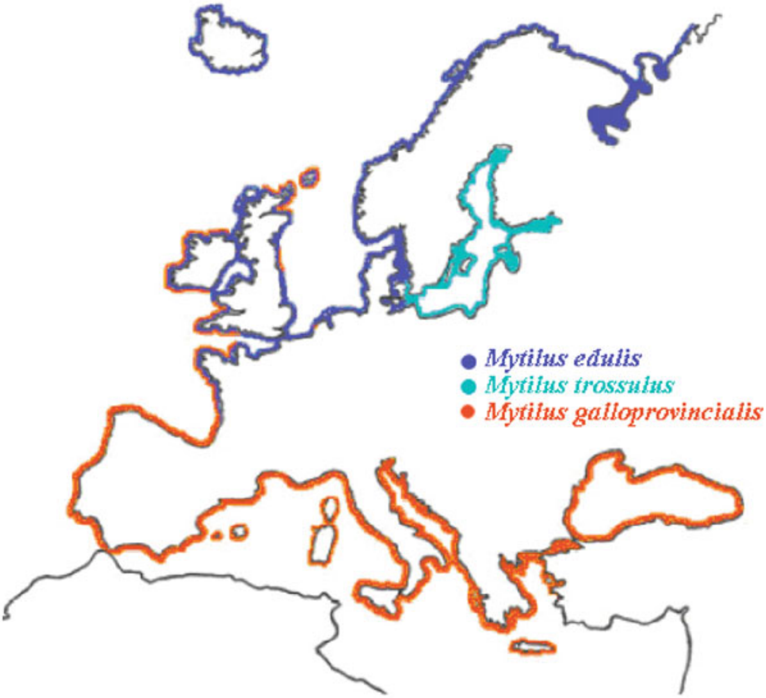


Fig. 9.1 Approximate distributions of *M. galloprovincialis*, *M. edulis* and *M. trossulus* in Europe, Gosling (1992). It would appear that *M. galloprovincialis* prefers slightly warmer water than the other two European *Mytilus* species but, due to its invasive nature, has spread from the Mediteranean region to the slightly warmer waters of northern Europe

9.2.2 Biology

M. galloprovincialis is an endemic Mediterranean species, the exact distribution range of which is not well defined due to the confusion with the very similar congener *M. edulis*. The Mediterranean mussel *M. galloprovincialis* is known from classical texts of Greek antiquity and their use in diet and medicine by humans in the Mediterranean coastal areas, Voultsiadou et al. (2010). It is dark blue or brown to almost black, Fig. 9.2. The two shells are equal in size and nearly quadratic. The outside is black-violet colored; on one side the rim of the shell ends with a pointed and slightly bent umbo, while the other side is rounded, although the shell shape varies by region.

In its native range, *M. galloprovincialis* can be found from exposed rocky outer coasts to sandy bottoms. It is an intertidal species extending down to a depth of 40 m and it may be found on all European coasts with hard substrata. It lives attached

Fig. 9.2 The Mediterranean mussel *M. galloprovincialis*

by byssus threads to rocks, piers and ropes within sheltered embayment, harbors, estuaries and on open rocky shores, while it may also form dense mussel beds directly on sandy-muddy bottoms in favorable sites. Unlike the other 26 Asian and Atlantic mollusks introduced into Pacific regions, only the Mediterranean mussel as an introduced species occurs on open coasts; all the remaining species are restricted to bays and estuaries, Carlton (1992). The invaders typically require rocky coastlines with a high rate of water flow.

The Mediterranean mussel tends to grow larger than its cousins, up to 15 cm, although typically only 5–8 cm. Intertidal specimens often remain small, rarely exceeding 6 cm, while deep-water individuals often attain a length of 9 cm and occasionally may even reach 15 cm. A 5 cm-long mussel can filter 5 l water/h. While mussels grow to optimum size in sea water of temperature 15–25°C, their biological activities are decreased over 25°C. They are resistant to 5–40% salinity, but the optimal degree of salinity is between 20% and 35%, Braby and Somero (2006). The continuous upwelling of cold nutrient-rich water during heavy rains probably stimulates an abundance of phytoplankton. The mean density in the most crowded beds may reach 24,000 mussels/m², Voultsiadou et al. (2010). Greece together with Italy and Spain are the Mediterranean countries with the largest catches of *M. galloprovincialis* FAO (2007).

Mussels are bivalve mollusks and much is known of their biology mainly because they have been an easy marine organism to collect and study, Gosling (1992). The two shells are equal in size and nearly quadratic. The outside is black-violet colored; on one side the rim of the shell ends with a pointed and slightly bent umbo, while the other side is rounded, although the shell shape varies by region. The two valves of the shell are held tightly closed by a large posterior adductor muscle when the mussel is exposed to air. Feeding and respiration are realized *via* currents of water directed across the gills. Digestion occurs in the digestion gland, brown-greenish in color, situated in the centre of the body. Mussels feed on phytoplankton and organic matter. Food particles are trapped by cilia on the gills and carried in mucous strings to the mouth, but this is a selective process and some particles are rejected before entering the gut, Beaumont et al. (2007).

Mussels can move with the aid of a foot. The foot of a mussel is an important organ because it enables the mussel to attach itself by byssus threads to a solid substrate. The threads can be broken and replaced at will, allowing mussels to re-orientate themselves within clumps or in rock cracks or crevices. Byssal attachment is an important, sometimes critical, factor in mussel aquaculture, Beaumont et al. (2007).

The reproductive cycle of *M. galloprovincialis* varies greatly according to geographic region and is characterized by one or two major spawning events per year and a more or less long resting period after spawning events, Gangnery et al. (2004). Maturation of eggs and sperm occurs in the gonad tissue that develops within the folds of the mantle and, depending on environmental temperature and food availability, mussels may spawn just once or several times each year, Beaumont et al. (2007). In Galicia, Spain, *M. galloprovincialis* reproduction may occur at any time of the year. The two main reproductive peaks of the year are in spring and autumn. Immediately after the reproduction process, a mussel can lose up to 70% of its soft tissue, Cossa (1989). The sexes are separate in mussels, but there are no morphological differences between males and females. Even in ripe mussels where the mantle is packed with gametes, eggs or sperm, the mantle color is not always a reliable guide to the sex of an individual because the eggs can range in color from white to orange/pink. Two days after fertilization, the embryos develop into planktonic larvae that are dispersed by sea and ocean currents, Beaumont et al. (2007). The larvae settle after 4–8 weeks at a size of 250–300 microns shell length and may have a secondary post-larval dispersal phase by “byssus drifts” up to a size of 2 mm shell length Beaumont et al. (2007). Due to their high fecundity, their extensive larval and post-larval dispersal capability, their ability to attach by byssus threads to non-specific substrates and also to one another and their fast growth, mussels are often a very significant and abundant element of the ecology of many inter-tidal and sub-tidal habitats, Gosling (1992).

Factors such as water temperature, nutrient availability and the reproduction cycle of mussels can influence meat yield, microbiological characteristics and biochemical composition of these mussels, Vernocchi et al. (2007). The overall quality of mussels is the result of biological, chemical and organoleptic characteristics, such as the aspect of the shells, meat aspect and yield, typical taste and flavor, Vernocchi et al. (2007). Meat weights can approach 50% of the total wet weight when the mussels are in their best condition. When a large percentage of the mussels are close to spawning or just past spawning, harvesting should be postponed until they are in better condition. Production extends over 17–18 months for seeding in summer and over 22 months for seeding in mid-winter, Gangnery et al. (2004).

In conclusion, *M. galloprovincialis* is an endemic Mediterranean species. *M. galloprovincialis* can be found from exposed rocky outer coasts to sandy bottoms and typically grows to 8 cm. They are filter-feeders with mostly two reproductive cycles per year. When this mussel is in its best condition, the meat weight can approach 50% of the total wet weight. The main factors which influence meat weight and yield of *M. galloprovincialis* are water temperature, nutrient availability and the reproduction cycle.

9.2.3 Ecology

Measuring and monitoring pollutant levels in organisms, i.e., bio-monitoring these levels, represents the only method that takes into account and integrates all the changes in the water quality which may influence the accumulation of pollutants in seafood and, ultimately, their possible transfer to mankind *via* seafood consumption, Rodriguez y Baena and Thébault (2006). Mussel Watch programs have been used to assess coastal environmental pollution as a framework to put national data into a global context. Therefore, monitoring programs were historically conceived to control the quality of the marine environment without special emphasis on how contamination of the media could potentially impact the health of edible organisms and mankind. Most of the reports were based on quantifying contamination, but some of the oldest were on the nutritional use of oysters in the treatment of anemia. Results for the trace elements Cr, Ni, Cu, Zn, As, Se, Ag, Cd, Sn, Sb, Hg, Ti, and Pb in mussels and oysters were entered into four files to create the World Mussel Watch data base.

However, during the past few decades there has been increasing evidence of the existence of a deep, mutual relationship between the health of the environment and that of mankind. Strict environmental monitoring activities have thus adopted an ecosystem-based approach, and Mussel Watch programs have been developed following this innovative concept. Nowadays, WMW data are results from two long-term Mussel Watch Programs: the Reseau National d'Observation de la Qualite du Mulieu – Marin Mussel Watch in France and National Status and Trends – Program in the United States, Cantillo (1998).

The first Mussel Watch program was implemented in the USA during the mid 1970s by Goldberg (1975) in order to monitor levels of pollutant trace elements and organochlorines, and more recently those of several biochemical parameters in marine coastal waters. The US Mussel Watch is coordinated by the National Oceanic and Atmospheric Administration and was extended to Latin America in the early '90s. The bivalve species used to biomonitor these regions are the blue mussel *M. edulis* and the Californian mussel *M. californianus* along the North Atlantic and the Pacific coasts, and the American oyster *Crassostrea virginica* in the Gulf of Mexico and Southern Atlantic, Cantillo (1998).

Several European countries have implemented similar national Mussel Watch programs, e.g. France, Italy and Spain. For instance, in France the French Research Institute for Exploitation of the Sea developed the "Réseau National d'Observation" in 1974 to assess the levels of metals and organochlorines along the French coastlines. Biota, the mussels *M. edulis* and *M. galloprovincialis* and the oyster *C. gigas*, are collected twice a year at about 100 sampling sites, passive biomonitoring in the RNO program. In the second phase, the "Réseau Intégrateur Biologique" was implemented in 1996 to monitor the concentrations of chemicals and radiochemicals in organisms caged for several weeks prior to collection, active biomonitoring by the RINBIO program, Andral et al. (2004). Despite the presence of several ongoing national programs, no large-scale Mussel Watch network was coordinated at the Mediterranean level until 2002, when the "Commission Internationale pour l'Exploration Scientifique de la Mer Mediterranee" launched a program called the Mediterranean Mussel Watch, designing a regional program for the detection of radionuclides and trace contaminants in sentinel organisms. The CIESM developed and implemented a regional MMW program using the mussel *M. galloprovincialis* as the bioindicator species to document reliable baseline levels of radionuclides and pollutant metals in the coastal waters of the Mediterranean and Black Sea, Rodriguez y Baena and Thébault (2006).

Ever since Goldberg et al. (1978) proposed the application of the 'Mussel Watch' concept, based on the suitability of mussels as bio indicators of contamination, most national and international monitoring programs of marine pollution have adopted this concept and the MMW started with limited sampling sites in each country, Sunlu (2006), Catsiki and Florou (2006). For example, studies of trace metal levels in *M. galloprovincialis* from Turkish sea coasts have been comparatively few and little data has been published in the scientific literature, Sunlu (2006).

International monitoring programs have established some standards for sampling and sample preparation procedures to reduce sources of variation, other than the metal content itself, in the contamination levels in mussels. These include, among others, sampling depth and season and the size of the individuals. Mussels are known to have a high capacity for metal accumulation, as reported in various mussel watch programs, Goldberg et al. (1978), making them potentially very dangerous for consumers. Therefore, strict metal controls are required in order to guarantee the safety of the product. The potential hazard of metals has long been recognized.

As mussels feed by filtering large amounts of water, whereby they bioaccumulate tremendous amounts of contaminants, they are valuable indicators of contamination of coastal and estuarine ecosystems. "Mussel Watch", introduced by Goldberg in 1975, is the longest continuous contaminant monitoring program of coastal waters. Since the introduction of the "Mussel Watch" approach, mussels have been widely chosen as ideal bio-monitors for regular National and Regional monitoring programs. These monitoring activities are designed to quantify and assess spatial and temporal trends in coastal contamination, and to provide a baseline to assess the impacts of anthropogenic and natural events.

9.3 Mediterranean Mussel as a Seafood

9.3.1 World Mussel Production

The population is increasing rapidly, which means simply more food production and more jobs are required. Although, vegetable production is sufficient for the present population and is likely to be for the future population, the intake of animal protein is inadequate in spite of attempts made during the last 60 years. This gap has not yet been closed. For this reason, the world aquaculture production has grown tremendously over the past 50 years from a production of less than one million tonnes in the early 1950s to 48.1 million tonnes in 2005, an average annual growth rate of 8.8% (Fig. 9.3a,b), Subasinghe et al. (2009). Of this production, 32.4 million tonnes (or 67.3%) was produced in China and 22.3% in the rest of the Asia–Pacific region. Western Europe contributed 4.2% with 2.0 million tonnes, while Central and Eastern Europe contributed 270 000 t or 0.6%. Latin America and the Caribbean, and North America contributed 2.9% and 1.3%, respectively. Finally, production from the Near East and North Africa, accounted for 1.2% and 0.2%, respectively, of the global total for 2005, Subasinghe et al. (2009).

In the recent years, the consumption of seafood has increased, Perugini et al. (2007), Kalogeropoulos et al. (2004), and marine mussels are a commercially important seafood product worldwide Phillips (1980), Farrington et al. (1987), Widdows (1985). The world production of mussels, including both, aquaculture and wild harvest production, is given in Fig. 9.4, FAO (2006).

The area of the world with the highest mussel's production is China. Denmark is the only country that still produces very large quantities of wild harvest mussels, but producers there are now investing seriously in increasing the capacity to culture mussels. Spain and Denmark lead the world in the production of canned products, FAO (2006).

In the last several decades, producers have been switching away from wild harvests toward a variety of culturing techniques. Hickman (1998) refers to marine mussels as an "ideal candidate for aquaculture," having characteristics such as rapid growth rates, high productivity on almost any substrate, relatively straightforward husbandry and ability to filter plankton and take up nutrients, and resilience to disease. Most of the world's production of mussels is canned, nearly 65%, or frozen nearly 35%; most international trade in the residual (<1%) is of high-valued premium fresh or chilled products, FAO (2006). European Union shellfish sanitation regulations limit imports of the fresh product from extra-EU sources; however, much of the international trade in fresh mussels occurs among EU countries. The Netherlands leads among the producers of fresh or chilled products for the European market.

According to the reviewed literature data, the world production of all mussel species still includes wild harvested mussels as well as aquacultured ones. In the last 20 years the world production of cultivated mussels has been almost 100% higher than that of wild harvested mussels. China is the largest producer of mussels, including aquacultured and wild harvested mussels, in the world.

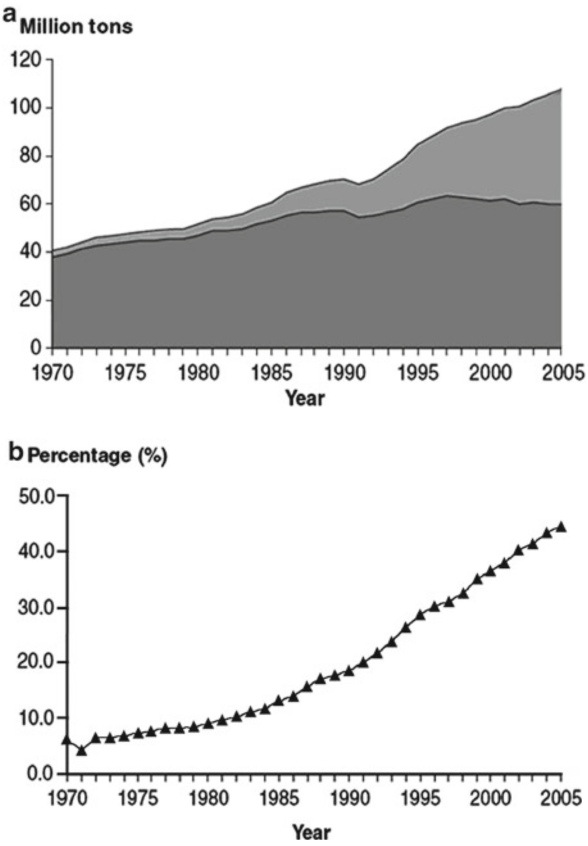


Fig. 9.3 (**a**) Contribution to seafood supply: aquacultured – *light gray*; captured – *dark gray*. In the last 40 years, the world production of aquacultured mussels has increased and nowadays aquacultured mussel production is almost double that of wild harvested mussels. (**b**) The world aquacultured seafood production has grown tremendously over the past 40 years. Mussel production was less than 10% of the total seefood production in the early 1970s but attained 45% in 2005, with an average annual growth rate of 8.8%

9.3.2 *Mytilus galloprovincialis Production*

The Mediterranean mussel *M. galloprovincialis* is mainly cultured in coastal waters from NW Spain to the northern shores of the Mediterranean Sea. The production of this mussel has also been reported from some southern Mediterranean countries, the Russian Federation, Ukraine, South Africa and also China, Lutz et al. (1991), Gosling (2003).

Cultured and harvested mussels date back to historic times in many countries, such as in Italy >2,000 years ago, France >700 years ago and the Netherlands >100 years ago. In Spain, mussel harvesting was already described in 400 BC, but the actual

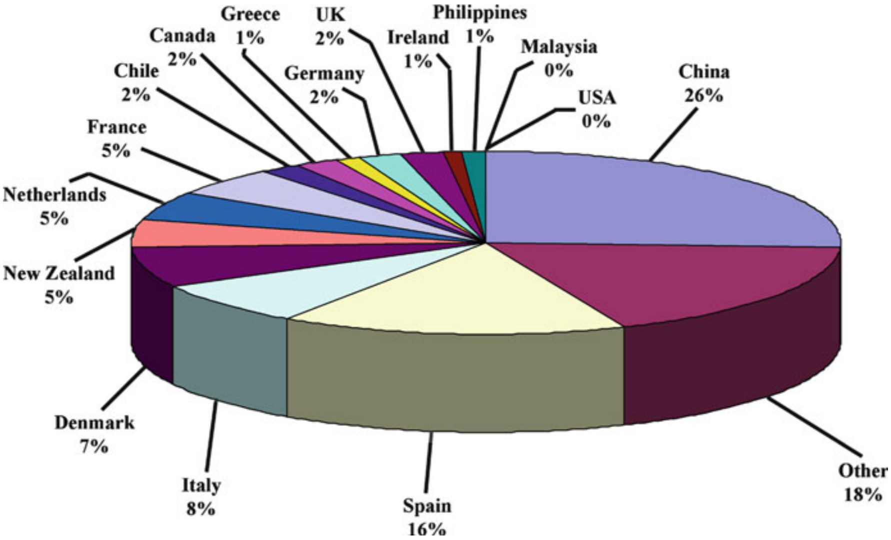


Fig. 9.4 Share of world production of mussels of all species, including both aquacultured and wild harvested production. The area of the world with the largest mussel production is China. Denmark is the only country that still harvests very large quantities of wild mussels. The shares are calculated as the average for each country during 1997–2001, FAO (2006)

Galician raft culture emerged only after 1945. Mediterranean mussel culture is now developing in Greece and Turkey, although the main yields are still produced in the traditional areas, Smaal (2002).

The exploitation of mussels as a food source in Europe consists of *M. edulis*, along the Atlantic and North Sea coasts and *M. galloprovincialis* in the Mediterranean, Adriatic and Black Sea, and in the Rias, Northwest Spain, (Fig. 9.1). Mussels are important for the mariculture industry in Europe and annual production exceeds 800,000 t and Europe produces around 50% of the annual world production of mussels, consisting of *M. galloprovincialis* and *M. edulis*, Smaal (2002). Most of the current production in Europe originates from the historically large producers: Spain, France and the Netherlands, followed by a marked increase in production in the UK, Ireland and Norway, Smaal (2002).

M. galloprovincialis and *M. edulis* are the most important mussel production species in Europe and the total European tonnage for the culture and capture of these two kinds of mussels from 1950 to 2004 are given in Fig. 9.5. It should be noted that the statistics provided by FAO (2006) treat mussels from the Atlantic coast of Spain as *M. edulis*, but, as the distribution map shows in Fig. 9.1, the species in this region is *M. galloprovincialis*.

European aquaculture of mussels relies on natural spatfall and there are three main methods of culturing these spat up to market size: bottom cultivation, *bouchot* culture and the suspended rope method, Spencer (2002). Spain is by far the greatest producer of mussels by aquaculture in Europe; greater than the combined total of the other important mussel producing countries, such as the Netherlands, France, Italy,

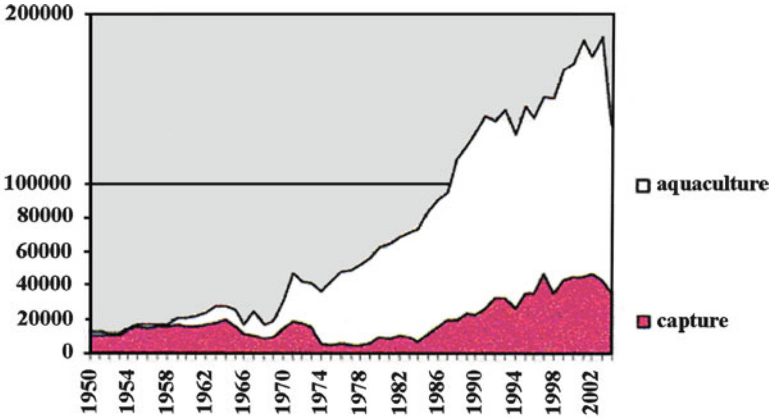


Fig. 9.5 Total mussel tonnage in Europe: aquaculture and capture, 1950–2004, FAO (2006). In Europe, the production of cultivated mussels in the last 20 years is more than five times higher than that of wild harvested mussels. In 2007, 52% of the EU aquaculture production was primarily mussels and oysters, but the contribution of European countries to the total world production of mussels has decreased

Ireland and the UK, FAO (2006). The production of the mussel *M. galloprovincialis* in Galicia (Northwest of Spain) contributes approximately 25% to the total world production (over 200,000 t y^{-1}); only China has a greater production (about 600,000 t y^{-1}), Costas-Rodríguez et al. (2010).

European countries produced 38% of the world production of mussels in 2003, FAO (2006). In 2007, 52% of the EU aquaculture production was primarily mussels and oysters and 48% of fish species. Mussel farming has an important economic impact in many European countries. The main yields of Atlantic mussels are from Spain, while the Mediterranean production predominantly comes from Italy. In Spain, mussel is the principal seafood product, while in Italy this mussel is harvested in an amount higher than 170,000 t, which represents more than 75% of the total shellfish production in Italy, Vernocchi et al. (2007).

Mussel production in France involves the two common species: *M. edulis* is widely distributed along the English Channel to the southwest coastline of France and *M. galloprovincialis* is mainly distributed on the Mediterranean shores. *M. galloprovincialis* has been cultivated since 1925 in French Mediterranean lagoons. The French mussel industry produces around 60,000 t on a yearly basis, with 13% from Mediterranean coast, Prou and Goulletquer (2002). Although a public mussel fishery still exists in France, most of the production is based upon 3 culture techniques: the bouchot-type culture, developed in the thirteenth century; on-bottom culture, a traditional activity, and harvests from longline culture, which have significantly increased in the last 10 years.

European aquaculture of mussels relies on natural spatfall and these three main methods of culturing the spat up to market size: bottom cultivation, *bouchot* culture and the suspended rope method Spencer (2002).This last technique allows development offshore, far away from any pollutant source, Prou and Goulletquer (2002).

Mussel production in these traditional areas of Europe has been stabile since the 1970s, but the contribution of European countries to the total world production has decreased due to increased production outside Europe. In these traditional mussel culture areas, new functions have developed, such as recreation and nature conservation, and therefore extension of mussel culture is now also space limited, Smaal (2002). Expansion of *M. galloprovincialis* mariculture in the Mediterranean occurs in areas of Greece and Turkey, i.e. in areas of the Aegean Sea, and also Marmara and the Black Sea, Karayucel et al. (2010).

Marine aquaculture in Greece is now well-established and Greek production from intensive mariculture represents almost 47% of the total intensive mariculture in the eastern Mediterranean region; the production increased from 5,800 t in 1990 to 28,100 t in the year 2000, UNEP/MAP/MED POL (2004). The North Aegean Sea is one of the most significant areas in the eastern Mediterranean Sea for bivalve production concerning both fishing and culture activities. More than 80% of the total Hellenic *M. galloprovincialis* production is derived from this area, Kalaitzi et al. (2007). Mussel farming is one of the most dynamic sectors of Hellenic aquaculture and the number of mussel farms in Greece has increased rapidly from five in 1980 to more than 550 in 2005, Voultsiadou et al. (2010). In Turkey, the total aquaculture production reached 139,873 t in 2007, while *M. galloprovincialis* culture was only 1,100 or 5,000 t, depending on the published data, Karayucel et al. (2010) or Ozden et al. (2010). The culture of *M. galloprovincialis* in the south region of the Black Sea is a relatively recent development and not yet widespread, but prospects for mussel culture in the Black Sea are quite high due to the favorable salinity, temperature, topography, food availability and socio-economic conditions in the area, Karayucel et al. (2010).

Mussels produced in Europe are predominantly consumed within Europe, and the major internal trade occurs between neighboring countries, Smaal (2002). Mussel markets are changing. For example in Spain, at the beginning of mussel farming, the national consumption was limited but has now exceeded 100,000 t annually, mainly as fresh mussels. The distribution of mussels was approximately 40% for the fresh market, 50% for canning and 10% for freezing. In the past decade, about 60% of the mussels were for the fresh market and 40% for canning. Exports are mainly to Italy, France and Germany.

In Europe, the production of cultivated mussels is almost five times higher than wild collected mussels. In the last 20 years, the contribution of European countries to the total world production of mussels has decreased due to: (1) increased production outside Europe and (2) space limited extension of mussel culture in traditional areas of Europe. Recently, the production of *M. galloprovincialis* in Europe has been increasing rapidly in Greece and Turkey. Spain is still the largest producer of mussels in Europe. The production of the mussel *M. galloprovincialis* in Spain is about 25% to the total world production, over 200,000 t y^{-1}. Only China has a larger production of these mussels than Spain, about 600,000 t y^{-1}.

9.3.3 Regulations

The oceans and seas are prime sources of food for mankind. Contamination of seafood by toxic contaminants represents a serious threat to human health and is a major economic concern. In order to protect the health of seafood consumers, many countries have set guidelines for the maximum permissible levels of toxic pollutants in seafood, EC (2006). Although such guidelines are essential for public health protection, problems can arise when guidelines are not met, which may lead to dramatic economic impacts on people and companies making their living out of sea resources. It is therefore of prime importance to monitor the levels of key contaminants in the coastal zone, where most fishery and farming activities are realized.

Most European countries have environmental quality standards, EQS, for marine aquaculture, mainly in relation to water quality and nutrient output and in the most European countries, marine aquaculture is monitored but the type and extent of seafood monitoring varies from country to country, Smaal (2002). Mussel culture is regulated by EU directives with regard to quality for the consumer in terms of pathogenic bacteria, biotoxins and chemical contaminants. The water quality of shellfish culture areas is under EU regulation: contaminant levels, EU directive 79/923/EEC; biotoxins and pathogenic bacteria, EU directive 91/492/EEC. In all European production areas, there are EU and national standards for product quality and for the environment where seafood is cultured or fished, Smaal (2002) and Prou and Goulletquer (2002). The sanitary quality and level of contaminants are monitored according to national rules, based on EU directives, but not in all countries. EU classifications of shellfish harvesting areas are given by the Shellfish Hygiene Directive 91/492/EEC. Different countries and world associations defined legal limits on permissible concentrations of non-essential elements that are toxic in traces, such as Cd, Pb, Hg and As in mussels, on a dry or wet weight basis, the values of which are given in Table 9.1.

The control of hazards for mussels is conducted according to the relevant EU legislation (EU Directive 1881/2006 – EC (2006)). The controls include parameters such as marine biotoxins, microbiological indicators, radionuclides, organohalogenated substances and pollutant metals. It should also be emphasized that every movement of mussels (for processing or sale) requires the approval of a Competent Veterinary authority, which takes into account the analysis results of the above-mentioned parameters. This approval is recorded on the mussel registration forms, which are actually the “passport” of mussels for their marketing.

In the near future, the mussel industry will face several challenges since it might be less costly than other protein products and a comparative evaluation of the environmental costs could be useful for making decisions on the development options and improved management, including all necessary regulations, such as increased sanitary regulations too, Prou and Goulletquer (2002). This could result in further off-shore development of mussel cultures, which might lead to space conflicts with other users, such as tourism and fisheries, Smaal (2002), Prou and Goulletquer (2002).

Table 9.1 Guidelines on pollutant trace elements for seafood safety set by different countries and associations

Locations	WB	Cd (mg/kg)	Pb (mg/kg)	Hg (mg/kg)	As (mg/kg)
EC (2006). EU Commision Regulation	Wet	1.0	1.5	0.5	/
UUSFDA/CFSAN & ISSC (2007). Food and Drug Administration of the jUnited States	Wet	4.0	1.7	1.0	86
FAO/WHO (2004). The ranges of maximum permissible concentrations for diff. countries	Wet	2.0	1–6	0.05–1	1.0–3.5
FSANZ (2003). Food Standards, Australia New Zealand, The 20th Australian Total Survey, A total diet survey of pesticide and contaminants, Canberra Wellington	Wet	2.0	2.5	0.5	1.0
Permissible limits set by the *Malaysian* Food Regulation (1985) (µg/g), Yap et al. (2004)	Wet	1.0	2.0	0.5	1.0
Croatian Regulatory Act (2007), Maximum Permissible Levels of metals in shellfish, Kljakovic-Gaspic et al. (2007)	Wet	1.0	1.0	1.0	8.0
Permissible limits set by the Ministry of Public Health, *Thailand* (MPHT 1986), Yap et al. (2005)	Wet	/	1.0	0.5	2.0
Permissible limits by the *Montenegrin* Food regulation, Jovic et al. (2010)	Wet	1.0	1.0	1.0	4.0
Maximum permissible levels, *Brazilian* Ministry of Health (ABIA, 1991), Yap et al. (2005)	Dry	5.0	10.0	/	/
Permissible limits set by the *Hong Kong* Government (1989), Yap et al. (2005)	Dry Wet	2.0 /	6.0 /	/ 10	/ /
Maximum permissible levels, *Turkish* Food Codex Regulation (1997), Ozden et al. (2010)	Wet	0.1	1.0	0.5	0.5

WB weight basis

The guidelines on the trace elements for seafood safety set by different countries and associations were reviewed. The defined legal limits on permissible concentrations of non-essential elements that are toxic in traces, such as Cd, Pb, Hg and As, in mussels on a wet weight basis in mg/kg are in the ranges: for Cd from 0.1 to 4.0; for Pb from 1.0 to 6.0; for Hg from 0.05 to 10 mg/kg and for As from 0.5 to 86 mg/kg.

9.4 Pollutant Trace Elements

Metals toxic in the trace have been used by humans for thousands of years. They are natural components of the earth's crust and cannot be destroyed. Although there are many elements that are classified as metals toxic in the trace, the ones of most concern, with respect to their biotoxic effects and presence in food are Cd, Pb, Hg and inorganic As. These metals are very toxic and their absorption and toxicity depends on dose and, among other diet constituents, on the intake of essential metals through diet. These elements have no known bio-importance in human biochemistry and physiology and their consumption, even at very low concentrations, can cause toxic effects, because they tend to accumulate in the human body over time. The major routes of exposure of the general population to Pb, Cd, Hg and As are through air, water and diet Järup (2003).

Pollutant trace elements can be present in food either naturally or as a result of human activities, such as mining, irrigation, energy extraction, agricultural practices, incineration, industrial emissions and car exhausts. The contamination chain of pollutant trace elements almost always follows the cyclic order: industry, atmosphere, soil, water, fish, and humans, Suseno et al. (2010). Pollutant trace elements have the ability to bioconcentrate in organisms directly from the water, bioaccumulate and biomagnify in the food chain, causing higher trophic organisms to become contaminated with high concentrations of chemical contaminants, Suseno et al. (2010). They tend to undergo interactions and transformation in sea water, sediments and marine biota, due to physical, chemical, microbial or light-mediated mechanisms. The variability of metal concentrations in marine organisms depends on many factors, either environmental, such as metal concentrations in sea water, temperature, salinity, dissolved oxygen, pH or purely biological i.e., species, tissues, organs, feeding conditions, Sunlu (2006). They may also originate from contamination during manufacture, processing and storage, or from direct addition. They are stable elements and persist for long periods in the environment. There is evidence to suggest that the levels of As and Cd in mussels are decreased by processing or freezing, Devesa et al. (2008), Dahl et al. (2010) and Metian et al. (2009), and Cd and Pb are increased by canned storage, Waheed et al. (2003). However, for example, methyl mercury, Me-Hg, can be found in canned fish that has undergone severe thermal treatment, Lawley et al. (2008).

Bioaccumulation phenomena in marine organisms may result from food-chain biomagnification processes or from concentration of pollutants by filter feeders. Metal concentrations in the mussels *M. galloprovincialis* are used as an indicator of marine pollution. In addition, toxic metals may be accumulated in marine organisms up to levels which may affect the mussels directly, e.g., by killing their larvae or damaging shell growth, thus affecting their quantity and quality. Moreover, because the pollutant trace elements are potentially detrimental to human health, their presence can limit the quantity of mussels humans can consume, Andersen et al. (1996).

Cd, Pb, Hg and As are stable elements and persist for long periods in the environment. The mussel *M. galloprovincialis* as a filter feeders have the potential to accumulate high levels of these toxic elements from their environment up to levels which may affect the mussels directly or bioaccumulate in mussels, and lead to their unsuitability as food for humans.

9.4.1 Properties and Sources of the Toxic Elements

Metals fall into one of two categories, essential and non-essential. Essential metal micronutrients, such as Cu, Zn, Fe, Mn, Co, Cr and Se, are required in small quantities, a few mg or µg per day, for the optimal functioning of biological and biochemical processes in humans, Verplanck (2003). Essential metal micronutrients, such as Ca, Mg, Na, P and S, are also required for similar biochemical processes, but in larger quantities, 100 mg or more per day, Verplanck (2003). Non-essential elements, such as Cd, Pb, Hg and As, have no known biological function in organisms and exert their toxicity by competing with essential metals for active enzyme or membrane protein sites. Moreover, *Mytilus* species are able to synthesize the metal-binding protein, metallothionein, for metal detoxification, Kohler and Riisgard (1982).

Regardless of the class of a metal, it is the dose that makes a poison. Exposure to either an excess or deficient amount of metal causes various toxic effects within an organism. These effects vary, depending upon whether the exposure is chronic or acute, and whether they are mutagenic, carcinogenic or teratogenic, developmental defects, in nature. In general, pollutant metals produce their toxicity by forming complexes or ligands with organic compounds. Such modified biological molecules lose their ability to function properly and can result in malfunctioning or death of the affected cells. The most usual elements involved in ligand formation are oxygen, sulfur and nitrogen, Merian (1991). The following sections contain information on the mode of action and routes of uptake and elimination of the four pollutant metals present in this mussel: Cd, Pb, Hg and As.

9.4.1.1 Cadmium (Cd)

Cd is non-essential element commonly used in the electroplating industry, as a paint stabilizer, color pigment fixer in plastics and in agriculture fertilizers. In non-polluted freshwaters, it has a concentration lower than 1 µg/L while in seawater the concentration ranges from 0.04 to 3.0 µg/L, Chang (1996).

Cereals, fruit and vegetables are the main source of Cd in the diet, making up about 66% of the mean Cd intake. The other sources include meat and fish, with liver, kidney, crustaceans, mollusks and cephalopods containing comparatively higher Cd levels. The main routes of aqueous Cd uptake in aquatic organisms are *via* the gills or gut; subsequently, it binds to low molecular weight proteins metal-lothioneins and accumulates in the liver and kidneys, making Cd difficult to extract, Widmeyer et al. (2004).

9.4.1.2 Lead (Pb)

Pb is a non-essential element commonly used by the battery industry, as a gasoline additive, and in the pigment/paint and metal alloy industries. The concentrations in freshwater vary considerably with values ranging from 34 to 300 μg/L, while in seawater they range from 0.3 to 20 μg/L, Chang (1996). None of the most commonly consumed foods were found to be high in Pb. The most common uptake routes are *via* the lungs or gills, as it is not commonly absorbed by the tract/gut. The general population is exposed to Pb through food, water and air. Exposure to Pb from the air is higher in the urban population. Hazards from these sources have gradually diminished due to the exclusion of Pb from gasoline. Absorption of Pb from ingested food and water greatly depends on the levels of other element present in the diet, such as calcium, iron, and zinc. It was shown that dietary deficiencies in these essential elements enhance Pb absorption, Goyer (1995).

9.4.1.3 Mercury (Hg)

Elemental Hg naturally occurs in lakes and streams, but emissions from industrial and mining processes and the burning of fossil fuels concentrate elemental Hg in the environment. The form of Hg hazardous in drinking water is the inorganic form, which can easily be converted to the organic Me-Hg form by the action of bacteria present in marine and freshwater sediments. It is this form that eventually enters the food chain, Selin (2009). In non-polluted freshwaters, it has a concentration lower than 1 μg/L, while in seawater the concentration is lower than 4 μg/L, Fitzgerald and Clarkson (1991). Once in the environment, microorganisms within the lakes and streams convert elemental Hg to Me-Hg, which travels from the oceans to phytoplankton and seafood. However, the study of Me-Hg uptake by phytoplankton and its transfer through the various components of trophic webs is a challenging issue for a better understanding of its bioaccumulation and biomagnification processes in marine seafood.

The main source of Hg in the diet is fish. Fruit, dried fruit, mushrooms and vegetables are other sources of Hg. Hg accumulated in the tissues of seafood usually takes the form of Me-Hg, which is largely responsible for the accumulation of Hg in organisms i.e., bioaccumulations, and the transfer of Hg from one trophic level to another i.e., biomagnifications. Bioaccumulated organic Hg is more toxic to higher organisms, including humans, than inorganic Hg. Hg can affect productivity, reproduction and survival of coastal and marine organisms and the population living near the coast and on islands runs a greater risk of ingesting this highly toxic substance, Kehrig et al. (2006).

In *Mytilus* species , metals are likely to be absorbed from water and from ingested phytoplankton and other suspended particles and a Me-Hg to total Hg ratio of about 40% in the Mediterranean mussel was reported, Mikac et al. (1996). The soft tissues of all specimens of common mussels from two estuaries in the State of Rio de Janeiro showed percentages of Me-Hg ranging from 31.9% to 64.5%, with an average of 53.2%, Kehrig et al. (2006). These results are similar to other data reported for marine mollusks, Kehrig et al. (2001, 2002) Joiris et al. (2000), Odzäk et al. (2000) and Claisse et al. (2001). Furthermore, a study of Pastor et al. (1994) in which a different suite of metals was measured in the mussel *M. galloprovincialis* from a polluted area in the western Mediterranean, Spain, showed on average similar total Hg and Me-Hg concentrations.

The digestive gland of the Mediterranean mussel *M. galloprovincialis* is the preferential organ for the accumulation of Hg, while Me-Hg is mostly accumulated in the soft edible tissue, Boening (2000) and Odzäk et al. (2000).

Mussels showed a higher capacity for the accumulation of Hg compared to other mollusk species, such as oyster and clam, Kehrig et al. (2006). Even though the feeding habits of the mollusks are similar; mussels presented higher Hg and Me-Hg concentrations in their soft tissues than oysters, Kehrig et al. (2006). Filter-feeding bivalves, such as mussels and oysters, accumulate less Me-Hg than fish and hence apparently present a smaller risk to human consumers, Claisse et al. (2001). This is possibly related to their capacity to select particle size and composition of the ingested food they assimilate, and also reflects on the greater ability of mussels to concentrate and excrete Me-Hg and also on their environmental conditions.

The routes of Hg accumulation, including the relative importance of different Hg species, inorganic and organic, and exposure pathways, aqueous vs. dietary, are not yet well understood. Most field studies examined the trophic transfer of Hg by collecting various abiotic compartments, such as water and sediment, and biotic compartments, such as phytoplankton, zooplankton, mussels and fish, to analyze the respective Hg concentrations. On other hand, in estuarine and coastal environments, various environmental factors, including pollutant input, salinity, temperature, and food availability, can vary widely. These external factors are known to influence metal bioaccumulation in organisms by changing either the bioavailability of the dissolved and particulate metals in the water or the physiological attributes of organisms, Suseno et al. (2010).

A recent publication showed that marine organisms might accumulate Hg both by ingestion of contaminated food and direct adsorption from the water column, Wang and Fisher (1996). They can assimilate Hg from ingesting suspended particulate material, but the trace metal assimilation efficiencies depend on the inorganic and organic chemical composition of the particulate material, Gagnon and Fisher (1997). The bioavailability and the chemical species, especially as free ions, influence the toxicity of trace metals and their bioaccumulation by organisms in an estuarine environment. Hg and Me-Hg bioaccumulation is different from that of other metals because the uptake of free metal ions *via* facilitated transport is not the only important mechanism, suggesting that Hg and Me-Hg accumulation in the presence of large organic compounds occurs through other uptake mechanisms in addition to passive diffusion, Wright and Mason (2000). Dissolved organic matter interacts very strongly with Hg, affecting its speciation, solubility, mobility and toxicity in aquatic ecosystems. DOM reduces the bioavailability of both inorganic and Me-Hg in that the bioaccumulation factors decrease with increasing organic content of the exposure medium, Ravichandran (2004) and Wright and Mason (2000).

9.4.1.4 Arsenic (As)

As is an element which occurs naturally in seawater and rocks of the Earth, is notoriously poisonous and is commonly used in pesticides, herbicides and insecticides. As in the soil, originating from air emissions in coal-fired power plants, waste recycling, pesticides and treated wood is increasing at a rate to suggest potential public health risks, Luong and Rabkin (2009).

In some areas, the concentration of As in water can attain levels of 1 mg/L, in non-polluted freshwaters it has a concentration lower than 10 μg/L, while in seawater, the concentration ranges from 2.0 to 4.0 μg/L, Devesa et al. (2008). These high concentrations are either due to the presence of As-rich rocks and minerals in aquifers of Taiwan, Bengal, Mexico, Chile, Argentina, Mongolia, Finland, Hungary and the west of the United States, or to anthropogenic contributions, Devesa et al. (2008). In water, As occurs in both inorganic and organic forms, in dissolved and gaseous states. The form of As in water depends on *Eh*, pH, organic content, suspended solids, dissolved oxygen and other variables. The inorganic forms of As are the most toxic, whereas most organic forms are considered non-toxic, Sloth and Julshamn (2008). Both organic and inorganic As compounds are absorbed almost completely in the gastro-intestinal tract and predominately eliminated from the body *via* the kidneys as urine, Sloth and Julshamn (2008).

Once As reaches water and soil, its transmission through the food chain is imminent, Suner et al. (1999). It is bioaccumulated by various land and water organisms, although more so by aquatic animals, but there is no evidence of magnification along the aquatic food chain, Suner et al. (1999). As is one of the most toxic elements found and it is present in food in organic or inorganic forms. Additionally, inorganic As(III) salts are more toxic than As(V) salts. The International Agency for Research on Cancer classifies As as a carcinogenic agent for humans – category 1, Sirot et al. (2009).

The levels of As in most foods are very low, with the exception of seafood. Seafood is known to be the most significant source of As in the diet and, consequently, the total human intake of As depends on the quantity of seafood consumed, Suner et al. (1999). As is found in seafood in different chemical forms, differing in their degree of toxicity and the pathologies that they generate, Shiomi (1994). However, the majority of As in seafood is present in the organic, less toxic form, Shiomi (1994). Provided by Munoz et al. (1999), the percentages of inorganic As in seafood are 1–5%, while in bivalve mollusks, they are 1.9–6.5%. Mussels contain a relatively high content of inorganic As compounds, approximately 1–2%, Sloth et al. (2005). The part of inorganic As in foodstuffs has been calculated according to the estimations proposed by the WHO: 75% in meat and dairy products, 65% in poultry and cereals, 10% in fruits and 5% in vegetables, drinking water and other beverages; it was assumed that the As was 100% inorganic, Sirot et al. (2009).

Most of the As accumulated in marine organisms is in the organic, water-soluble form; arsenobetanine which is considered non-hazardous and totally safe for human consumption, Sloth et al. (2003). The ability of marine phytoplankton to accumulate high concentrations of inorganic arsenicals and transform them into methylated arsenicals, which are later efficiently transferred to the food chain, is well documented, Shiomi (1994). The great majority of the As in marine organisms exists as water-soluble and lipid-soluble organoarsenicals that include arsenolipids, arsenosugars, arsenocholine, arsenobetaine, monomethyl arsonate, and demethyl arsinate, as well as other forms, Cao et al. (2009). For most marine species, however, there is general agreement that As exists primarily as AsB, a water soluble organoarsenical that has been identified in the tissues of many marine species, including mussels, Shiomi (1994). The potential risks associated with the consumption of AsB containing seafood seem to be minor: it was neither toxic nor mutagenic, had no effect on metabolic inhibition and showed no synergism or antagonism on the action of other contaminants, it was rapidly absorbed from the gastrointestinal tract and rapidly excreted in urine without metabolism, Sloth et al. (2003, 2005), Sloth and Julshamn (2008).

As does not significantly bioaccumulate in the body, Jones (2007). In humans, arsenate As(V) is first reduced to arsenite As(III), methylated into methylarsonic and dimethylarsinic acids, most of which are than excreted *via* the renal pathway; excretion *via* feces, nails and hair is minor, Sirot et al. (2009). The literature results indicate that AsB and As(V) are the dominate species in dry seafood products, while all other As species are present in relatively low concentrations, Cao et al. (2009).

Marine organisms naturally accumulate considerable quantities of organic As compounds, AsB, which are mainly non-toxic, and a very small percentage of inorganic As, arsenite and arsenate, which are very toxic forms. As concentrations in tissues of marine biota show a wide range of values, being the highest in lipids, liver, and muscle tissues, and varying with the age of the organism, geographic location and proximity to anthropogenic activities; in general, tissues with high lipid content contain high levels of As, Eisler (1994).

In *Mytilus* species, toxic elements such as Cd, Pb, Hg and As can be absorbed from water and from ingested phytoplankton and other suspended particles. These toxic metals can accumulate with time, becoming an ever greater toxic threat as their concentrations increase, but it should be noted that for some toxic elements, such as Cd and Hg, *Mytilus* species are able to synthesize the metal-binding protein for their own detoxification, metallothionein, neutralising the harmful influences of exposure to them.

9.4.2 The Bioaccumulation of the Toxic Elements in Mussels

Intertidal areas are the natural habitats of marine mussels and they are usually close to estuaries. Therefore, the chance of exposure to many contaminants from land-based activities through the reverine systems as well as sea-based sources is high, and one of its attributes is the possible usage of mussels as a biomonitoring agent for the estimation of pollutant metal concentrations in a sea environment. Among the environmental pollutants, trace metals represent natural constituents in tissues of marine organisms and their basal levels can be affected by marked seasonal fluctuations. Several environmental and biological factors mutually compete to determine such variations, Fattorini et al. (2008). Mussels are sedentary organisms, long-lived, easily identified and sampled, reasonably abundant and available throughout the year, tolerant of natural environmental fluctuations and pollution. Due to their biological and ecological characteristics, mussels have been commonly applied in more than 50 nations during the last 40 years, to provide a time-integrated picture of local contamination, Cantillo (1998).

The importance of bivalves in pollution impact studies is shown by the concept of the International Mussel Watch Program, Goldberg (1975), which has continued to maintain its momentum until today, Rainbow (1995), Sericano (2000) and Kavun et al. (2002). Mussels are well known to accumulate a wide range of metals in their soft tissues. Since it is edible and marketed commercially, the determination of pollutant metals levels in mussel species provides a means of assessing the possible toxicant risk to public health. As pollutant metals are widely distributed in coastal environments, from both natural geological processes and anthropogenic activities, determination of pollutant metals in mussels is important because of their effects on human health, Yap et al. (2004), Sivaperumal et al. (2007), Kljakovic-Gaspic et al. (2007), Turkmen and Ciminli (2007), and these metals are readily accumulated in the soft tissues of the mussel *M. galloprovincialis*. Some metals, such as Cd and Pb, have long been known to accumulate within the aquatic food chain.

Mussels are nutritional by ensuring the intake of essential minerals, necessary for the maintenance of good health; on the other hand, they can be toxic because certain metals, such as Pb, Cd, As and Hg, are detrimental to health, Szefer (2002) and Sivaperumal et al. (2007). From the toxicological point of view, excessive consumption of metal-contaminated mussel may result in toxicity to humans. Since pollutant metals are inorganic chemicals that are non-biodegradable, cannot be metabolized and do not break down into harmless forms, Kromhout et al. (1985), the measurement of metal levels in the soft tissue of mussels has becoming more significant. Mussels can simply accumulate metals through time, Mubiana and Blust (2007), becoming more and more of a toxic threat as the concentration levels increase. Mussels are used as sentinel organisms and bioindicators to evaluate the toxic effects of chemical pollutants in marine organisms, especially pollutant metals, representing an important tool for biomonitoring environmental pollution in coastal areas. The reliability of mussels as biomonitors of pollutant metal contaminations has been demonstrated by a number of researchers. Levels of metals above the permissible limits would certainly create notorious food image from the public health point of view.

The mussel is a good bioindicator for Cd, Pb, Hg and As, Szefer (2002). The distribution of contaminants in mussel organs is known to vary as a result of the differing affinities of pollutants for binding sites and the different rates of pollutant accumulation in and excretion from tissues, Fernández et al. (2010). It has been reported that metals such as Hg, Cd and Pb accumulate in mussels more rapidly and to a greater extent in the gills than in tissues, such as the mantle, muscle or digestive gland, while the digestive gland and mantle tissues accumulate higher levels of organic pollutants than gills, Fernández et al. (2010). In addition, the spawning season of the mussels and environmental factors may contribute to the wide variability of pollutant metal concentrations in the total soft tissues of mussels, Yap et al. (2006).

9.4.2.1 The Content Cd, Pb, As and Hg in the Soft Tissues of the Mediterranean Mussel

Several studies demonstrated the presence of significant seasonal and spatial variations of the content of toxic elements in the total soft tissue of the Mediterranean mussels. The Cd, Pb, As and Hg concentrations determined in the soft tissues of Mediterranean mussels, *M. galloprovincialis*, mainly in last decade all over the world where exist given in Fig. 9.6. and in Tables 9.2–9.6, together with the sites and the years of sampling with the corresponding bibliographical references.

Some concentrations were determined over several years and others result from several samples in a single year. Metal concentrations are given in mg/kg dry wt. However, some metal concentrations are given with respect to the fresh weight in the original references, Sunlu (2006), Klaric et al. (2004), Ünlü et al. (2008), Özden et al. (2010). The data from the period 1991 to 2009 are grouped by countries and seas in order to enable the easiest comparison of the concentrations of the toxic metals. Since *M. galloprovincialis* are aqua cultured and collected from the Mediterranean and Atlantic coast of Spain and France, from Italy- Adriatic and Mediterranean, Adriatic, Greece and in the last 10 years from Turkish coasts, the concentrations of Cd, Pb, Hg and As are primarily compared for these regions, Tables 9.2–9.4.

Some large variations in the Cd, Pb, Hg and As concentrations in *M. galloprovincialis* from this extensive analyzed region were observed due to the different ages, feeding behaviors and different geographical areas with different natural and anthropological impacts. Important factors which modulate the bioavailability and tissue burden of these pollutant metals include fluctuations of temperature, phytoplanktonic blooms and organic matter, the presence of nutrients, waters fluxes and circulation, up-welling phenomena, freshwater inputs, and also intrinsic species-specific features, such as the phase of reproductive cycle and the associated changes in the relative tissue composition, Fattorini et al. (2008).

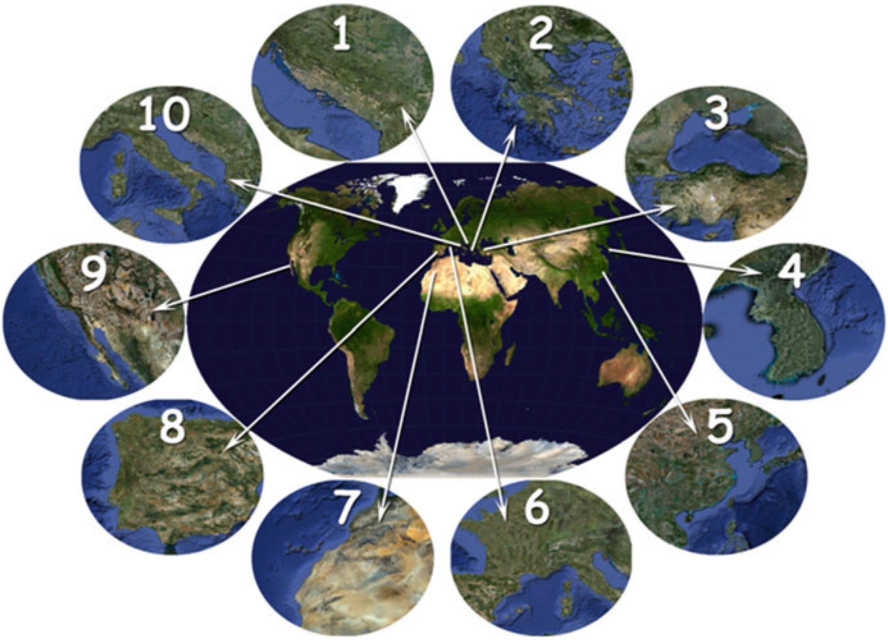


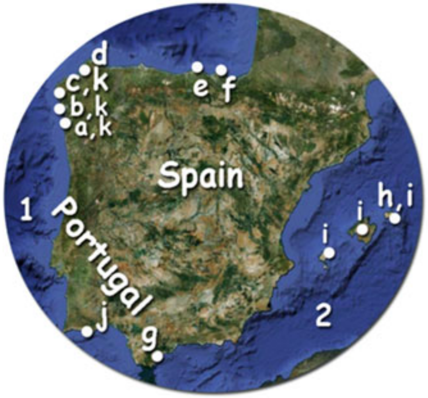
Fig. 9.6 Distribution of the Mediterranean blue mussel over the world: *1*. Slovenia, Croatia, Montenegro; *2*. Greece; *3*. Turkey, Romania; *4*. South Korea; *5*. China; *6*.France; *7*. Marocco; *8*. Spain, Portugal; *9*. California, USA, *10*. Italy

Broadly speaking, it can be said that most of the results for the concentrations of pollutant metals, Cd, Pb and Hg, in the investigated mussels were of the same order of magnitude in the case of the Spanish Atlantic and the Mediterranean coast, but significantly higher concentrations were observed in the case of As, especially in Galicia, Cantabria, and the Basque Country, as well as in mussels from Spanish Mediterranean coast, Bartolomé et al. (2010b) and Fernández et al. (2010). The temporal variation had no specific trend and the concentrations were quite constant over a wide range of sites and during time on both sides of the Spanish coastline. The highest mean concentrations were found for As, between 13 and 25.6 mg/kg d.w., in the mussel from both Spanish coastlines, the Atlantic and the Mediterranean. Lower mean concentrations were found for Pb, mainly between 2.0 and 5.0 mg/kg d.w., and Cd, between 0.4 and 2.0 mg/kg d.w., and the lowest were found for Hg, between 0.05 and 0.35 mg/g d.w, Bartolomé et al. (2010b) and Fernández et al. (2010).

Significant downward trends were observed for the concentrations of Pb and Hg in mussels from a large number of sampling stations along the coast of Spain, while the Cd concentrations in the mussels showed upward trends Benedicto et al. (2003). The mean concentrations of Pb in mussels were lower than those determined in previous studies that were performed in the same area. The distribution of Pb in a

Table 9.2 The toxic metal concentrations in *M. galloprovincialis* (in mg/kg d.w.) from the published data for Spain, Portugal and France

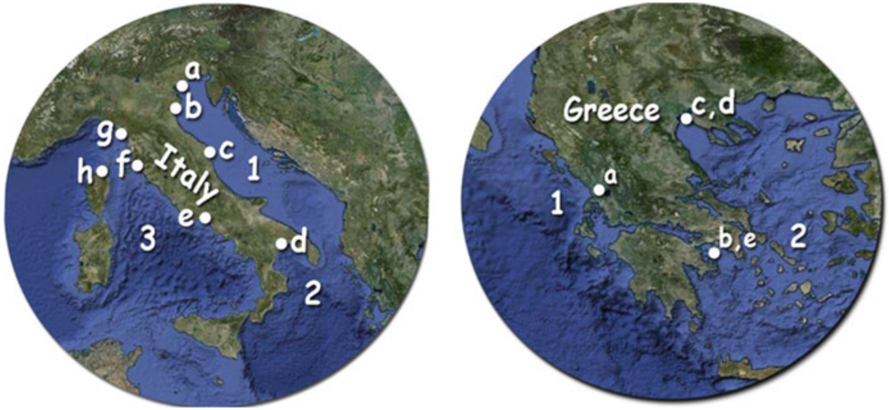
Country				Year		Cd	Pb	Hg	As	Reference
Spain										
	1	**Atlantic ocean**								
		a-f	Atlantic coast	1991–1999	d.w.	0.36–2.84	0.52–8.22	0.08–0.88		Besada et al. (2002)
		k	Galicia	1909	d.w.	0.20–0.77	0.3–6.1	0.10–0.6.3	7.1–13.7	Beiras et al. (2003)
			Atlantic coast	2005	d.w.	0.41–1.57	0.87–16.41	0.037–0.536		Besada et al. (2011)
			Bilbao estuary	2002–2004	d.w.	3.1–11.2	5.7–25.2	0.1–0.2	17.4–22.6	Bartolomé et al. (2010a)
			Atlantic coast	2004–2006	d.w.	0.4–2.3	1.1–13.3	0.07–0.5	14.6–20.0	Bartolomé et al. (2010b)
	2	**Mediterranean sea**								
			Basque region	1990–2000	d.w.	0.70–1.33	1.12–5.83	0.28–0.70	1.33–2.45	Franco et al. (2002)
			Andulusian coast	1991–2003	d.w.	0.20–1.25	0.50–11.20	0.05–1.80		Benedicto et al. (2003)
		h	Menorca	1991–2005	d.w.	0.25–1.70	3.3–18.6	0.13–2.21	0.8–11.0	Deudero et al. (2007)
		i	Balearic Islands	2005	d.w.	1.57–3.37	1.82–3.34	0.16–0.26	6.02–11.56	Deudero et al. (2009)
		g	Algeciras Bay	2005	d.w.		1.4–10.2	0.03–0.21	11.1–21.7	Guerra-Garcia et al. (2010)
			Mediterranean coast	2003–2005	d.w.	0.28–1.67	1.82–57.83	0.09–0.78	12.9–82.6	Fernandez et al. (2010)
Portugal										
	1	**Atlantic ocean**								
			South Portugal	2001	d.w.	0.36–0.69	0.84–2.89			Morgado and Bebianno (2005)
		j	South coast	2005	d.w.	0.22–2.92	0.13–19.2			Cravo et al. (2009)



France								
1	**Mediterranean sea**							
	Mediterranean coast	2000	d.w.	0.35–5.80	0.50–5.40	0.05–0.35	10.0–68.0	Andral et al. (2004)
a	Mediterranean coast		d.w.	0.03–36.2	0.1–83.2	0.02–1.24		Deudero et al. (2007)
b	Canari, Corsica		d.w.	1.77–1.87	1.08–1.26	0.09		Lafabrie et al. (2007)
2	**Atlantic ocean**							
c	Atlantic France		d.w.	0.011–11.70	0.15–13.3	0.01–0.83		Deudero et al. (2007)

Table 9.3 The toxic metal concentrations in *M. galloprovincialis* (in mg/kg d.w.) from the published data for Italy and Greece

Country				Year		Cd	Pb	Hg	As	Reference
Italy										
	1	**Adriatic sea**								
		a	Murano, Venice	1999	d.w		2.5–3.9		12.0–18.0	Giusti and Zhang (2002)
		b	Goro Bay		d.w	3.7–4.3	15.8–29	0.167–0.231		Locatelli (2003)
			Portonovo	2001–2005	d.w	0.41–1.60	0.29–2.95	0.022–0.186	7.83–37.6	Fattorini et al. (2008)
		c	Marche Region	2007–08	d.w	1.0–1.2	0.8–2.4	<1.0		Desideri et al. (2010)
	2	**Ionian sea**								
		d	Taranto Gulf	1999–2000	d.w.	0.21–0.98	0.81–4.44		0.18–5.40	Cardellicchio et al. (2008)
	3	**Tyrrhenian sea**								
		g	La Spezia		d.w.	2.0–6.8	13.9–44.6	0.15–0.38		Capeli et al. (1978)
		e	Gulf of Gaeta	2000	d.w.	0.23–0.59	1.26–3.10			Conti and Cecchetti (2003)
		f	Livorno, Toscana		d.w.	1.08–1.18	0.98–1.16	0.11–0.13		Lafabrie et al. (2007)
		h	Porto-Torres, Sardinia		d.w.	1.65–1.89	1.24–1.62	0.09–0.11		Lafabrie et al. (2007)



Greece										
	1	**Ionian sea**								
		a	Amvrakikos Gulf	1996–1998	d.w.	2.0–2.9				Tsangaris et al. (2010)
	2	**Aegean sea**								
		b	Saronikos Gulf	2001–2002	d.w.	0.21–1.40		0.06–0.16		Tsangaris et al. (2004)
		c	Thermaikos Gulf	1999	d.w.	0.7–1.37	0.59–3.26			Catsiki et al. (2004)
		d	Thermaikos Gulf		d.w.				8.7–13.1	Schaeffer et al. (2005)
		e	Saronikos Gulf		d.w.				32.2–36.0	Schaeffer et al. (2005)

Table 9.4 The toxic metal concentrations in *M. galloprovincialis* (in mg/kg d.w.) from the published data for Slovenia, Croatia, Montenegro, Turkey and Romania

Country				Year		Cd	Pb	Hg	As	Reference
Slovenia										
	1	**Adriatic sea**								
		a	Dockyard Izola	2001–2002	d.w.	0.52–0.65	3.0–11.8			Scancar et al. (2007)
		b	Marina Portoroz	2001–2002	d.w.	0.43–0.61	0.76–2.0			Scancar et al. (2007)
		c	Bay of Mesecev zaliv	2001–2002	d.w.	0.92–1.12	1.5–1.7			Scancar et al. (2007)
		d	Mariculture Secovlje	2001–2002	d.w.	0.65–0.69	2.0–2.2			Scancar et al. (2007)
Croatia										
	1	**Adriatic sea**								
		e	Rijeka Bay	1998–1999	w.w.				1.87–23.83	Klaric et al. (2004)
		f	Middle Adriatic	2003–2005	d.w.		2–7		4.0–30.0	Orescanin et al. (2006)
		g	Kastela Bay	2000–2001	d.w.			0.14–0.32		Kljakovic-Gaspic et al. (2006a)
			Eastern Adriatic coast	2001–2003	d.w.	0.2–2.0	0.9–15.1	0.04–8.58		Kljakovic-Gaspie et al. (2006b)
		h	Mali Ston Bay	1998–2005	d.w.	0.4–2.4	0.24–3.7	0.08–0.28		Kljakovic-Gaspic et al. (2007)
Montenegro										
	1	**Adriatic sea**								
			South East Adriatic	2005–2009	d.w.	1.73–2.14	4.0–11.5	0.11–1.06	4.0–11.5	Jovic et al. (2010)
		i	Boka Kotor Bay	2005	d.w.	0.3–3.5	6.0–15.0		23.0–42.7	Stankovic et al. (2006)

Turkey										
	1	**Aegean sea**								
		a	Turkish Aegean Sea coast	2002–2003	w.w.	0.04–0.52	0.49–1.72			Sunlu (2006)
	2	**Marmara sea**								
		b	Northern Marmara Sea	2000	d.w.	1.23–2.91	0.1–5.7			Topcuoglu (2004)
		c	Marmara Sea	2006–2007	d.w.	0.29–1.11	0.19–1.12	0.018–0.748	0.07–1.22	Ozden et al. (2010)
		d	Gulf of Gemlik	2004	d.w.	2.3–2.5	0.4–0.6			Ünlü et al. (2008)
		e	Bosphorus European side	2002–2004	d.w.			0.14–2.86		Kayhan (2007)
		f	Bosphorus Asian side	2002–2004	d.w.			1.03–2.94		Kayhan (2007)
		e	Bosphorus European side	2003–2004	d.w.	0.18–10.68	0.06–11.55			Kayhan et al. (2007)
		f	Bosphorus Asian side	2003–2004	d.w.	0.01–8.95	0.54–8.76			Kayhan et al. (2007)
	3	**Black sea**								
		g	Black Sea coast	1997–1998	d.w.	1.8–6.4	0.3–2.6			Topcuoglu (2000)
		h	Eastern Black Sea		d.w.	1.9–4.2	2.9–22.0			Çevik et al. (2008)
		i	Southeastern coast	2006	d.w	0.83–1.33	0.75-1.03	0.035–0.043	6.48–11.92	Ergul et al (2007)
Romania										
	3	**Black sea**								
		j	Romanian Black Sea coast	2001–2002	d.w.	0.76–1.91		0.023–0.029		Romeo et al. (2005)

Table 9.5 The toxic metal concentrations in *M. galloprovincialis* (in mg/kg d.w.) from the published data for Marocco and USA

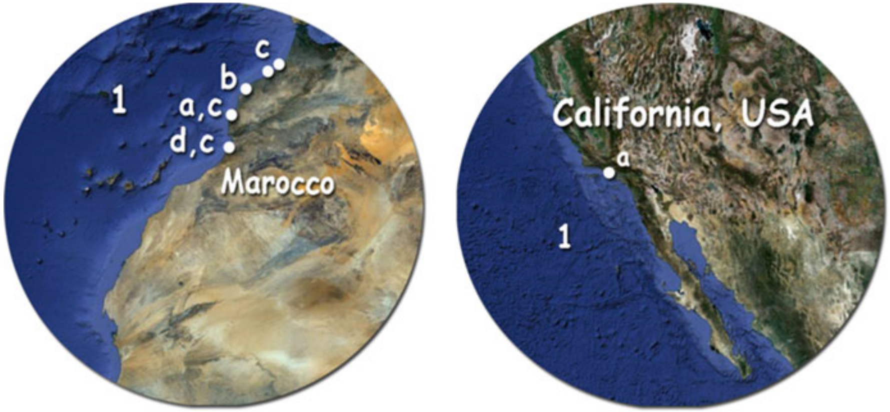
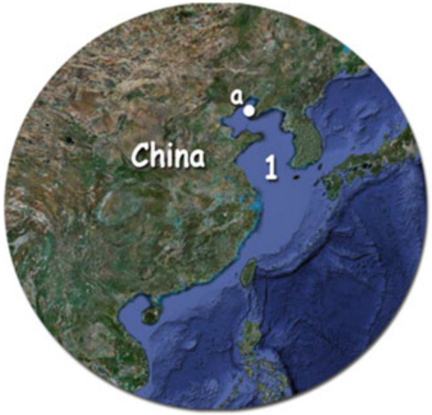
Country			Year		Cd	Pb	Hg	As	Reference
Marocco									
	1	**Atlantic ocean**							
	a	Safi	2004–2005	d.w.	2.12–34.71	0.1–26.45	0.01–2.31		Maanan (2007)
	b	El Jadida	2004–2005	d.w.	1.33–25.30	0.50–34.2	0.02–2.30		Maanan (2008)
	c	Atlantic coast	1993–1997	d.w.	0.4–8.0				Chafik et al. (2001)
	d	Jorf Lasfar	1995	d.w.	1.00–6.25				Kaimoussi et al. (2001)
 									
California, USA									
	1	**Pacific ocean**							
	a	Mugu Lagoon	1995	d.w.	0.86–0.94	0.4–1.2		0.9–4.7	Cohen et al. (2001)

Table 9.6 The toxic metal concentrations in *M. galloprovincialis* (in mg/kg d.w.) from the published data for China and South Korea

Country			Year		Cd	Pb	Hg	As	Reference
China									
	1	**Yellow sea**							
	a	Da Lian	2001	d.w.	0.86–1.20	0.52–1.74			Blackmore and Wang (2003)
  									
South Korea									
	1	**South sea**							
	a	Masan Bay	1998–1999	d.w.	0.06–2.36	0.01–1.89	0.02–0.07		Szefer et al. (2004)
	b	Ulsan Bay	1998–1999	d.w.	0.73–18.6	3.62–52.7	0.04–1.41		Szefer et al. (2004)

marine environment is controlled by atmospheric deposition; the concentration of excess Pb in marine organisms is directly linked to human activities, Besada et al. (2002). A study of the spatial distribution of chemical contaminants realized using mussels allowed the identification of clear hot spots along the Spanish coastline, Fattorini et al. (2008).

Along the French Mediterranean coast, the Cd concentrations were in the same order of magnitude as in the open sea and in lagoons (mean value: 1.1 mg/kg), with the exception of one lagoon with concentrations of up to 4.5 mg/kg. The Hg background level was stable and below 0.1 mg/kg with high levels in some lagoons (0.15 mg/kg), Andral et al. (2004). High concentrations of Hg were also observed in the mussels of Toulon waters (0.25 mg/kg). The Pb background level was 1.13 mg/kg, with extreme values in one lagoon (4.86 mg/kg) and in the coastal waters of large urban areas (3.5 mg/kg), but the mean As value was 20 mg/kg, Andral et al. (2004). It is oblivious that the concentrations of As, Pb, Cd and Hg in *M. galloprovincialis* from the Mediterranean part of Spain were higher on average than those in the mussels from the Mediterranean coast of France. However, the mussels along the Spanish Mediterranean coast were collected in May–June 2003, in the pre-spawning period, Fernández et al. (2010), while those from the French Mediterranean coast after the spawning period, in July 2000, Andral et al. (2004). In the case of Atlantic coast, the mussels from Spanish and French waters contained similar concentrations of these metals, Table 9.2. It is interesting to note that the mean concentrations of As, Cd and Hg were generally higher in mussels from the Mediterranean coast, but the Pb concentration was lower than in the mussels from the Atlantic coast. Exceptions were mussels from some "hot spots" on the Mediterranean coast, in which very high concentrations of Pb were found, whether they were from the French or Spanish coast, 83.2 and 57.83 mg/kg d.w., respectively. The overall trends observed along the French coasts for 1979–1999 confirmed decreasing values for Cd and Pb, while for Hg the local decreases were about twice, Regoli (1998) and Fattorini et al. (2008). In both cases, on the French and Spanish coastal areas, the pollutant metal concentrations in the mussel *M. galloprovincialis* were in the order: As > Pb > Cd > Hg.

In Tables 9.2–9.4, the results for the pollutant metal concentrations in the whole edible soft tissues of mussels from the Spanish and French regions are also compared with the results of studies from different locations of the Mediterranean Sea, such as Italian, Hellenic and Turkish coastal regions, since they are producers of this mussel. The mean concentration of Pb in mussels from the Ionian Sea, Italy, was higher than in mussels from the Tyrrhenian Sea in Italy, but the opposite was true for the Cd concentrations, Cardellicchio et al. (2008), Lafabrie et al. (2007). In the last decade, the Cd, Pb and Hg concentrations were much lower than in previous studies realized with mussels from the Tyrrhenian Sea, Capeli et al. (1978). For Pb, this decrease could be the result of a decrease of the Pb concentrations in gasoline. In the early 1970s, very high Hg concentrations were observed in some coastal areas, in 'hot spots', near harbors and industrial areas, Mikac and Picer (1985). Results from the northern Adriatic Sea in Italy showed higher levels of Cd, Pb, Locatelli (2003), and As, Giusti and Zhang (2002), when compared with studies from the Ionian Sea and Tyrrhenian Sea, Lafabrie et al. (2007) and Cardellicchio et al. (2008). Mussels from the Italian Adriatic coast have higher Cd and Pb levels, 3.7–4.3 and 15.8–29.0 mg/kg d.w, respectively, than mussels from the eastern part of the Adriatic Sea, 0.4–2.4 and 0.9–15.1 mg/kg d.w, respectively, at hot spots. The highest concentrations of As, Pb and Cd in mussels from the northern Adriatic Sea are correlated to the industrial development of the Venetian region over the last 20 years and the impact of the River Po, Licata et al. (2004). From 1986 to 2003, the Italian National Mussel Watch showed national decreasing trends of the Cd concentrations in mussels, but other trace metals exhibited only local or regional variations with trends in the concentrations in bivalves more or less evenly split between increases and decreases, Fattorini et al. (2008).

Quite limited data are available for the As concentrations in Mediterranean mussels, normally obtained in specific periods or in different seasons of a single year. The results obtained in these investigations generally indicated higher values of As in Adriatic mussels, Stankovic et al. (2006, 2008) and Jovic et al. (2011), than in organisms from unpolluted sites of the French and Spanish Mediterranean coast, Andral et al. (2004) and Fernández et al. (2010), and the Tyrrhenian coasts, Fattorini et al. (2008), Bartolomé et al. (2010a,b) and Fernández et al. (2010), except two hot spot locations with 82.6 and 60.0 mg/kg d.w. levels of As on the Mediterranean Spanish and French coast, respectively. Overall, these results confirm the general distribution of As compounds in mussels which, with a few exceptions, tend to exhibit their basal content of this element mostly as organic, non-toxic molecules. Factors controlling the bioavailability of this element in the marine environment are complex to recognize and may include, e.g., redox conditions, iron and manganese oxides, acid-volatile sapphires and total organic carbon, Fattorini et al. (2008).

Basal levels of trace elements in mussel can also exhibit geographical differences, such as those related to site-specific geological or environmental features. Well known examples include the Hg anomaly in the Tyrrhenian Sea, which is responsible for the elevated bioavailability of this element, Fattorini et al. (2008). The total Hg values in the Mediterranean and the Marmara Sea (Bosphorus) species were generally higher than those found in the Atlantic, Tables 9.2–9.4. The levels Hg in mussel from the French and Spanish Mediterranean coast, including hot spots, are in the range 0.02–1.24 and 0.03–2.21 mg/kg d.w., respectively, while in the Atlantic and Adriatic Sea, they are in the range 0.01–0.88 and 0.02–0.32 mg/kg d.w, respectively. Only on the eastern Adriatic coast, there were two hot spots with high levels of Hg in the mussels: 8.58 and 1.06 mg/kg d.w., in Croatia, Kastela Bay, and in Montenegro the harbor Bar, respectively, Kljakovic-Gaspic et al. (2006a) and Stankovic et al. (2008), Jovic et al. (2010). In the Marmara Sea, *M. galloprovincialis* from Bosphorus Asian and European side had very high levels of Hg: 1.03–2.94 and 0.14–2.86 mg/kg, Kayhan (2007). The higher Hg levels are deemed to be the result of the region being in the Mediterranean – Himalayan mercuriferous belt, Shoham-Frider et al. (2002).

The highest measured As levels are in the mussel from the Adriatic and Aegean Sea, Fattorini et al. (2008), Orescanin et al. (2006), Stankovic et al. (2006), Jovic et al. (2010) and Schaeffer et al. (2005), Table 9.2. It was the lowest in the mussel from the Marmara and Black Sea, Özden et al. (2010) and Ergul et al. (2007). The high level of As in the mussels of the eastern Adriatic could be explain by the exhibited high concentrations of As (1–19 mg/kg) found in the sediments of the southern Adriatic, Dolenc et al. (1998). A better knowledge of the natural variability of the concentrations of trace metals in mussels from the Adriatic Sea is of special interest due to the different geographical characteristics and human activities which could have an impact on this basin and the relative lack of appropriate reference values available for pollutant metals, which are required when monitoring various anthropogenic pressures, i.e., dredging operations, coastal management and off-shore activities to cite just a few, Fattorini et al. (2008).

The Mediterranean Mussel Watch program suggests a dominant source of metal contamination from urban and industrial activities and less important inputs from continental and agricultural origins, Sunlu (2006). The levels of trace metal concentrations in the soft tissues of mussels indicate that the inner part of the Izmir Bay is the most contaminated area along the Turkish Aegean Sea coast. Traffic is very important along the Turkish Aegean Sea coast and it could be a major source of Pb pollution of the coastal seawater. Location is the primary factor along the Turkish Aegean Sea coast and metal levels vary only depending on the location. There is no indication of a seasonal variation in the metal levels, Sunlu (2006). Consequently, hot spot areas are especially near large urban and industrial centers, notably the Izmir and Candarli Bay. However, localities relatively far from anthropogenic sources, e.g., the Sigacik and Gulluk Bay, have a considerably high potential for aquaculture, since they are affected very little by pollutant metal contamination, Sunlu (2006). Cd and Pb are considerably lower compared with the values obtained in large-scale research into the pollutant metal levels in mussels on the Atlantic coast and in countries around the Mediterranean Sea, Tables 9.2–9.4.

If the data of pollutant metals in mussels from the Turkish seas are analyzed, the highest levels of Cd and Hg were found in mussels from the Bosphorus, Kayhan et al. (2007). Concentrations of Cd in the soft tissue of *M. galloprovincialis* from the Bosphorus were high and in general displayed significant variation from station to station, Kayhan et al. (2007). From Bosphorus European and Asian side, there were very high concentrations of Cd up to 8.95–10.68 mg/kg d.w, Kayhan et al. (2007), which are similar to the Cd levels in mussels from the French Atlantic coast, up to 11.70 mg/kg d.w., Deudero et al. (2007). Along the Turkish coastline, the highest Pb concentrations were found in mussels from the eastern Black Sea, up to 22.0 mg/kg, Çevik et al. (2008).

From Tables 9.2–9.4, it could be concluded that the highest concentrations of Cd and Pb were found in mussels from hot spots on the French and Spanish Mediterranean coast, up to 36.2 mg/kg d.w. and 83.2 mg/kg d.w., respectively. Mussels from the Adriatic Sea, Croatia, had the highest concentrations of Hg, up to 8.58 mg/kg d.w, than mussels from the Atlantic coast, Mediterranean and Black Sea, but again at hot spots. Generally, the levels of Cd, Pb and Hg were the lowest in mussels from the Aegean Sea, compared to the others investigated seas, Tsangaris et al. (2004) and Catsiki et al. (2004), but a very high level of As was found, Schaeffer et al. (2005).

Generally, Hg was present in low concentrations; higher average Hg levels were observed in *M. galloprovincialis* from the Marmara Sea, Bosphorous, Kayhan et al. (2007), but the results for As indicated that a large proportion of As was in the organic form, Marcotrigiano and Storelli (2003). In Mediterranean mussel from the all investigates Seas, the concentrations of these pollutant metals were in the following order: As > Pb > Cd > Hg.

Despite the considerable seasonal and inter-annual variations, data on trace metal concentrations presented in this work are generally within the range of mean values more recently reported for Mediterranean mussels sampled or translocated in unpolluted sites of the French coast, Andral et al. (2004), the NW Mediterranean, Roméo et al. (2003a), the Spanish Mediterranean coast, Benedicto et al. (2003), the North Tyrrhenian Sea, Nigro et al. (2006), the North Aegean Sea, Catsiki and Florou (2006), the Turkish Aegean Sea, Sunlu (2006), the Black Sea, Çevik et al. (2008) and the Croatian coast, Kljakovic-Gaspic et al. (2007), if the hot spots would be excluded. Most of the examined metals showed a seasonal decrease in July and the highest values in February and April. A similar seasonal trend was described by other authors, Nesto et al. (2007). Bioaccumulation values were generally much lower than the threshold metal limits established for mollusk consumption by the EC (2006), Table 9.1, and were generally similar to previous values obtained for the same species sampled at various sites, Nesto et al. (2007), Fattorini et al. (2008), Vidal-Linan et al. (2010), Desideri et al. (2010).

Since Cd, Pb, Hg and As are non-biodegradable chemicals which cannot be metabolized and do not break down into harmless forms, measurement of their concentration in mussel soft tissue, as a seafood, has become significant. A review of literature data related to the concentrations of Cd, Pb, Hg and As in *M. galloprovincialis* from their endemic areas, e.g., Mediterranean, Adriatic and Black Sea, revealed that the concentrations of these toxic metals were in the following order: As > Pb > Cd > Hg. The levels of Cd, Pb and Hg were the lowest in mussels from the Aegean Sea, compared to the others investigated Seas, but a very high level of As was found.Some large variations in the Cd, Pb, Hg and As concentrations in *M. galloprovincialis* from their endemic regions were observed probably due to different: age, feeding behavior, natural impacts, anthropological impacts and geographical areas, as well as factors which modulate the bioavailability of these toxic metals: temperature fluctuation, waters fluxes and circulation, freshwater input, phytoplanktonic blooms and organic matter, the presence of nutrients and the phase of reproductive cycle.

9.4.3 Dietary Exposure Assessment

It is well-known that the intake of food contaminated with chemicals can lead to intoxication episodes that can be described as acute or, when the disease appears after a latent period of time, chronic. The chemicals producing the latter tend to accumulate in the body during long periods of time, producing illness when the levels reach critical values in certain tissues. Ingestion of contaminated food is the principal way of human exposure to these compounds, accounting for >90%, if compared to other ways, such as inhalation and dermal contact. Due to their persistence and lipophilic character, they tend to concentrate in the food chain and are particularly associated with fat, foodstuffs of animal origin being one of the main sources, Bordajandi et al. (2004).

The consumption of fish and fishery products in the European Union countries, such as France (29.7 kg year^{-1} per capita), Germany (12.2 kg year^{-1} per capita), Greece (22.7 kg year^{-1} per capita), Italy (23.1 kg year^{-1} per capita), Portugal (57.4 kg year^{-1} per capita), Norway (50.0 kg year^{-1} per capita) and Poland (9.6 kg year^{-1} per capita), is still low, Kwoczek et al. (2006). As there is no data on the average national Rate of Shellfish Consumption, the Provisional Tolerable Weekly Intake and the Tolerable Daily Intake were employed as standards for calculating the metal concentration levels of concern associated with mussel consumption. According to FAO/WHO (2004), *PTWI* is defined as µg of metal per kg of body weight, µg/kg body weight/week, or mg of metal per adult, where an adult is assumed to weigh 60 kg. According to the FAO/WHO, the average weekly intake for adults was estimated to be 1.5 mg for Pb ($PTWI_{Pb}=25$ µg/kg body weight/week), 0.42 mg for Cd ($PTWI_{Cd}=7$ µg/kg body weight/week), 0.9 mg for As ($PTWI_{As}=15$ µg/kg body weight/week) and 0.3 mg for Hg ($PTWI_{Hg}=5$ µg/kg body weight/week) The *PTWI* for Me-Hg was set at 1.6 µg/kg of body wt/week. In this study, a consumption rate of 28.6 g/person/day was used to calculate the level of concern for the low mussel consumption group, assumed by taking 200 g/person/week as the one mussel meal, to calculate the Tolerable Daily Intake (µg/person/day) for the each element, Table 9.7.

In this study, the environmental health risk was assessed by a comparison between the environmental status, as represented by the concentrations of the metals in mussels, and threshold values likely to cause adverse effects in human consumers. In this context, a risk quotient can be calculated as follows:

$$\text{Risk Quotient} = \frac{\text{Concentration of metal X in mussels}}{\text{Level of concern for metal X}}$$

The Risk Quotient was calculated as the ratio between the concentration of a trace metal in the mussels and the level of concern for that metal, Fung et al. (2004), Kljakovic-Gaspic et al. (2007). The Level of Concern is the “threshold concentration” of a metal above which a hazard to human health may exist, and it can be calculated as follows:

$$\text{Level of Concern} = \frac{\text{Tolerable Daily Intake}}{\text{Rate of Shellfish Consumption}}$$

Table 9.7 Provisional Tolerable Weekly Intake (*PTWI*) and calculated Tolerable Daily Intake (*TDI*) for mussel consumption

	Cd	Pb	THg[a]	iAs[b]
***PTWI* (μg/kg b.w./week)**	7.0	25.0	5.0	15
***TDI*[c] (μg/person/day)**	60	214.3	42.86	128.6

[a] *THg* total Hg

[b] i*As* inorganic As

[c] *TDI* calculated from the *PTWI* for 60 kg human weight

Results of the evaluation of the risks to human health associated with the consumption of Mediterranean mussel containing pollutant metals are summarized in Table 9.8. The Risk Quotient was calculated for the best, median and worst-case scenario, RQ_{bcs}, RQ_{mcs} and RQ_{wcs}, respectively. In the present case, Risk Quotient for the best scenario was calculated for the minimum concentrations, Risk Quotient for the median and RQ_{wcs} for the maximum concentrations of the metals (mg/kg wet weight) found in the investigated mussels to estimate the potential exposure levels of humans related to mussel consumption. For cases where $RQ < 1$, the chemicals involved are unlikely to cause harm to human consumers, Fung et al. (2004), Kljakovic-Gaspic et al. (2007).

The concentration ranges and median of pollutant metals present in the Mediterranean mussel were converted into the wet weight, Yap et al. (2004) and Kwoczek et al. (2006) and used to estimate the potential exposure levels of pollutant metals related to the consumption of mussels, Table 9.8. It is noteworthy that the RQ_{wcs} values were higher than one for As (Mediterranean Sea, Adriatic Sea and Atlantic coast), for Cd and Pb (Mediterranean Sea) and Hg (Adriatic Sea) suggesting that probable health associated problems might be encountered in pollutant shellfish consumers. It is related to mussels from hot spots, such as urban areas, near the mouth of rivers, harbors and lagoons. Of particular concern were the Cd, Pb and As concentrations in mussels from the hot spots in the Mediterranean Sea because the values of RQ_{wcs} were 3.45, 2.22 and 3.67, respectively, Table 9.8. The risk quotients in the best case scenario, RQ_{bcs}, for Cd, Pb, Hg and As indicated that these metals are probably not of great health concern for mussels consumers, Table 9.8. The RQ_{mcs} values for As for consumers of mussel from the Mediterranean Sea, Atlantic coast and Adriatic Sea indicate that this metal could be of health concern, but it should be noted that the As present in mussels is mostly in the organic form, which is relatively non-toxic to humans and readily excreted.

Thus, As is unlikely to represent a significant risk to human health, since in the mussels, the maximum level of the more toxic, inorganic form of As is less than 5%, Sloth et al. (2005). Overall, the assessment indicates that metals may pose a health risk to pollutant seafood consumers, especially related to the levels of Pb and Cd in mussels from hot spots. In the case of the risk quotient values for Hg, it should be born in mind that the toxic Me-Hg in mussels participates by about 40–50% to the total Hg. All the risk quotient values for As and Hg in this study were calculated related to the total concentrations of Hg and As.

It should be emphasized that the consumption data used in this study are based on one meal of 200 g of Mediterranean mussel per week. As seafood, and particularly

Table 9.8 Risk analysis for the minimum, median and maximum concentrations of metals present in the Mediterranean mussel samples

Metal		Range (ug/g)	Median (ug/g)	*RSC* (g/p/d)	*TDI* (μg/p/d)	*LOC* (μg/g)	*CLOC* (g/p/d)	RQ_{bcs}	RQ_{mcs}	RQ_{wcs}
Cd	Adriatic sea	0.20–4.30	1.0	28.6	60	2.10	13.97	0.02	0.1	0.41
	Mediterranean sea	0.03–36.20	0.75				1.66	0.002	0.07	3.45
	Atlantic ocean	0.01–11.70	0.72				5.13	0.002	0.07	1.11
	Black and Marmara sea	0.01–10.68	0.60				5.62	0.002	0.06	1.02
Pb	Adriatic sea	0.24–29.00	1.5	28.6	214.3	7.49	7.39	0.006	0.04	0.77
	Mediterranean sea	0.10–83.20	2.5				2.57	0.002	0.07	2.22
	Atlantic ocean	0.13–25.20	4.0				8.50	0.004	0.11	0.67
	Black and Marmara sea	0.06–22.00	0.80				9.74	0.002	0.02	0.59
Hg	Adriatic sea	0.02–8.58	0.25	28.6	42.9	1.50	5.00	0.002	0.03	1.14
	Mediterranean sea	0.02–2.21	0.12				19.41	0.002	0.02	0.29
	Atlantic ocean	0.01–0.88	0.30				48.75	0.002	0.04	0.12
	Black and Marmara sea	0.02–2.94	0.35				14.59	0.002	0.05	0.39
As	Adriatic sea	1.87–37.60	15.0	28.6	128.6	4.50	3.42	0.08	0.67	1.67
	Mediterranean sea	0.18–82.6	18.0				1.59	0.01	0.8	3.67
	Atlantic ocean	7.10–22.60	17.0				5.69	0.32	0.76	1.02
	Black and Marmara sea	0.07–11.92	0.60				10.80	0.004	0.03	0.53

PTWI (μg/kg of body) FAO/WHO – Cd (7.0), Pb (25.0), Hg (5.0), As (15)
RSC Rate of Shellfish Consumption (g/person/day) – 28.6 g/person/day
LOC Level of concern (in μg/g) (*TDI*/*RSC*)
CLOC Consumption Level of Concern (in g/person/day) (*RSC* × *LOC*/*MAX*)
RQ_{bcs} Risk Quotient for the best case scenario (X_{min}/LOC)
RQ_{mcs} Risk Quotient for median case scenario (X_{med}/LOC)
RQ_{wcs} Risk Quotient for the worst case scenario (X_{max}/LOC)
TDI Tolerable Daily Intake (in μg/person/day) $TDI = \frac{PTWI \times 60\text{kg}}{7\text{day}}$

TDI (μg/person/day) – Cd (60), Pb (214.3), Hg (42.9), As (128.6) mussels, consumption rates can vary greatly between countries and among specific sections of a community; these standards should only be used for screening purposes. For example, if the consumption of two 200 g meals of the mussels per week is considered, the risk quotient values would be two times higher but related to the health of mussels consumers, the pollutant metals would still not be a health concern for the consumers of *M. galloprovincialis*, excluding the mussels with maximum concentrations found or with $RQ_{\mathrm{wcs}} > 1$ from the hot spots. Generally, if the consumption of mussels from hot spots is excluded, it is safe to consume Mediterranean mussel.

The *PTWI* values appear to support the conclusion that risk to human health from dietary exposure to pollutant metals from mussels is relatively low. Based on typical Cd concentrations of 0.7 and 0.1 mg/kg in Italy and France, respectively, a 70 kg adult would need to consume ≈1.0 kg and ≈7.0 kg of mussel flesh per week to exceed the *PTWI* value in Italy and France, respectively, Falcó et al. (2006). Dietary intake of mussels must be even larger than 7.0 kg to exceed the *PTWI* values for the other pollutant metals tested. However, the calculations are based on the current *PTWI* values and it is unknown whether these are sufficient to mitigate lifelong dietary exposure to pollutant metals, Falcó et al. (2006). Permissible values change over time, a value that is assumed to be innocuous at present may be considered dangerous in the future. For this reason, values below the current *PTWI* values should not automatically be considered 'low-risk' to consumers and values that are close to the current limits should be taken seriously. In addition, individual susceptibility to toxins in humans is variable, meaning that even concentrations below the current 'permissible' values may lead to toxic effects in people with high sensitivity. Consequently, it is hard to assess the human health impacts of exposure to pollutant metals through diet. For some people with a low dietary tolerance, the metals might result in toxic effects. For example, especially Maori with a low dietary tolerance, increase their risk of toxic effects because of a higher consumption of shellfish than the general public, Whyte et al. (2009).

Further information on the type, amount and frequency of shellfish consumption is required to adequately assess the possible health risk associated with pollutant metals ingestion. The intake of As, Cd, Hg and Pb in Spain from the consumption of 14 marine species, including shellfish and fish, were estimated and the *PTWI* for most of the population was within acceptable limits, although the Me-Hg concentrations for boys were excessive, Falcó et al. (2006). This study highlights the particular risk of pollutant metal accumulation in children who, because of their smaller body weight, require less seafood to exceed regulatory limits. Consumption of Cd and As contaminated seafood was found to pose a potential health risk to fisherman in Taiwan, Whyte et al. (2009), again highlighting the increased risk of pollutant metal accumulation in sectors of the population that consume more seafood than 'average', Whyte et al. (2009).

To prevent health risk from the pollutant metals exposure, the European Commission, EC (2006), Das et al. (2009), established in the past years maximum levels permitted in seafood and recently proposed target and action plans in order to reduce their presence in different food items. People consuming large amounts of contaminated seafood may have elevated concentrations of pollutants in their tissues compared to the general population, Han et al. (2000).

Comparison of the published data with European legislation, Table 9.1, showed that the levels of Cd, Pb and Hg usually did not exceed the existing limits in all the mussels analyzed, excluding mussels from hot spots such as lagoons and harbors, Andral et al. (2004), Nesto et al. (2007) and Jovic et al. (2010). In EC (2006), the Maximum Permissible Limits in edible tissues of mussels are 0.5 mg/kg for Hg, 1 mg/kg for Cd and 1.5 mg/kg for Pb related to fresh weight, Nesto et al. (2007), Amiard et al. (2008), Das et al. (2009). Contaminants in mussels were examined from the standpoint of food safety in the Mediterranean and Black Sea basins. In mussels from some locations, the levels of Pb and Cd exceeded the health standards, i.e., mussels from the Adriatic Sea, Giusti and Zhang (2002) and Kljakovic-Gaspic et al. (2007), but in mussels from the Taranto Gulf (Ionian Sea, Southern Italy), the Pb and Cd concentrations were always below the levels recommended by the European Community, Cardellicchio et al. (2008). Concentrations found for Cd and Pb indicate that the mollusk populations under investigation pose no health risk to seafood consumers, because their metal contents were within the permissible range established for safe human consumption, Cardellicchio et al. (2008).

The mean concentrations of pollutant metals determined in the mussel *M. galloprovincialis* from Istanbul fish markets and the eastern Black Sea showed that the contents of Cd and Pb were below the *MPL* for fish proposed by EC (2006) and the Turkish Food Codex from 2002, Ozden et al. (2010). The levels of Hg and As were found to be above the *MPL* in mussels from the eastern Black Sea, Cevik et al. 2008; Ozden et al. (2010) and Das et al. (2009). Mussels from the Marmara Sea are safe regarding the Cd and Hg concentrations but may contain Pb above the permissible limits, Mol and Alakavuk (2010). The levels of trace metal concentrations in the soft tissues of mussels indicate that the inner part of the Izmir Bay is the most contaminated area along the Turkish Aegean Sea coast. The levels of the pollutant metals in *M. galloprovincialis* from the North Aegean Sea are characterized, in general, as being below the *MPL* values and comparable to those from other non-polluted Mediterranean areas, Catsiki and Florou (2006).

The *PTWI* values appear to support the conclusion that risk to human health from dietary exposure to the investigated elements from Mediterranean mussels is relatively low. People consuming large amounts of contaminated mussels may have elevated concentrations of the pollutant trace elements in their tissues compared to the general population. To prevent health risk from exposure to pollutant trace elements, the European Commission established in the past years maximum levels permitted for Cd, Pb and Hg in seafood. Comparison of the published data with European legislation showed that the levels of Cd, Pb and Hg generally did not exceed the existing limits in all the mussels analyzed, excluding mussels from hot spots, such as lagoons and harbors in Mediteranean, Adriatic and Black Sea. Overall, the assessment in this work indicates that the investigated toxic elements may pose a health risk to pollutant mussel consumers, especially related to the levels of Pb and Cd in *M. galloprovincialis* from hot spots in the all investigated Seas.

9.4.4 Impact of Mussel Consumption to Human Health

9.4.4.1 Beneficial Effects If Mussel Consumption

By 2002, fish fisheries and aquaculture products contributed 12% to the total protein for human consumption, although there are no detailed global statistics on the provision of other essential minerals and components, FAO (2006). The total content of minerals in raw marine fish and invertebrates is in the range of 0.6–1.5% wet weight, Ozden et al. (2010). An epidemiological study in Japan showed that seafood was the largest source of vitamin B6 (16–23% of the total intake) and B12 (77–84%) in the diet, Yoshino et al. (2005). Many species of fish and shellfish are rich sources of Omega 3 fatty acids, Ackman et al. (2000) and the health benefits associated with the consumption of seafood products are particularly important for the prevention of heart-related diseases and for many vulnerable groups, such as infants and children, and pregnant and lactating women, Cozzolino et al. (2001), Christophoridis et al. (2009) and the positive impact of seafood consumption on bone mineral density has also been reported, Zalloua et al. (2007). Meeting nutritional requirements of antioxidants, particularly Zn, to defend human beings against xenobiotic-induced oxidative stress and associated toxic hepatitis could be improved through zinc-rich seafood consumption, Stehbens (2003).

In *M. galloprovincialis*, proteins contribute about 60% to the dry weight of the soft tissues, Karaycel et al. (2003). Mussels are very important for marine ecology and for the human diet, since they are a cheap source of protein for human consumption, Yap et al. (2004), Amiard et al. (2008). Consumption of these bivalve mollusks provides an inexpensive source of protein of a high biological value, essential minerals and vitamins, Fuentes et al. (2009), Ozden et al. (2010). From the nutritional point of view, mussel is an important food source for supplying essential elements, e.g., Ca and Fe, and also certain vitamins, such as niacin, thiamine and riboflavin, Yap et al. (2004), Amiard et al. (2008). Minerals and trace elements are very important components in human diets as both their deficiency and excess may cause serious health problems. Trace metals can be divided into essential elements and non essential elements. The effects of deficiency of essential trace elements are the most severe during development and growth and they are especially important for infants and children, Cozzolino et al. (2001).

9.4.4.2 Risks of Mussel Consumption

On the other hand, the toxicity effect of pollutant metals in living marine organisms was recognized as early as the early decades of the twentieth century, although it received little attention in the past. This effect was considered of secondary importance. However, all metals are potential toxins at some concentration and the non-essential elements, e.g., Hg, Pb, Cd and As, are particularly toxic at relatively low concentrations, Bat et al. (1999), Çevik et al. (2008). Lately, however, there was a growing concern regarding toxic contaminants, in general, and toxic pollutant metals in seawater, in particular. This awareness occurred in the wake of the tragic events of the Minamata and Itai-itai Hg and Cd poisoning cases, respectively, which erupted in Japan around the middle of the twentieth century, Fleming et al. (2006) and Malik et al. (2010). Ever since, the disease caused by poisoning human beings with Hg-contaminated seafood was named Minamata after the Japanese Bay where it was first recognized and the name itai-itai was given to the disease caused by poisoning humans with seafood contaminated with Cd, Fleming et al. (2006) and Malik et al. (2010).

In Minamata Bay, the Hg had come from industrial discharges into the bay. Eating fish that had accumulated Hg in Minimata Village between the years 1953 and 1960 poisoned hundreds of individuals. Soon after this tragedy, the other Itai-itai tragedy erupted, also in Japan, when eating fish contaminated with Cd metal this time, poisoned a lot more humans. The disease was named after the characteristic screams, known as the itai screams, which was a cry common to all poisoned casualties. These tragic Japanese incidents flared a vivid awareness of the problem of bioaccumulation of metals by marine organisms and spurred research on the fate and impact of metals in marine environments and their negative effects on human health.

Seafood products in general also pose carcinogenic and other adverse effects on human health due to biomagnifications over time. For example, cancer and damage to the nervous system, etc. have all been documented in human beings as a result of metal consumption.

Many pollutant metals accumulated in mussels can also be accumulated in the food chain. These non-essential elements, such as Cd, Pb, Hg and As, are non-biodegradable chemicals which do not have any positive effects on organisms and are harmful already at low doses. They cannot be metabolized into harmless forms and accumulate with time in the human body and might act alone or together over time to cause the disease, as well as other health problems. Thus, people consuming mussels could be exposed to these potentially dangerous to health metals, Han et al. (2000), Giusti and Zhang (2002), Clarkson (2002), Yap et al. (2004), Kwoczek et al. (2006), Kljakovic-Gaspic et al. (2006b), Türkmen and Ciminli (2007), Sivaperumal et al. (2007), Çevik et al. (2008).

Cd, a metal with high toxic effects, which is strongly bioaccumulated in mussels, has an elimination half-life of 10–30 years and accumulates in the human body, particularly the kidney, Amiard, et al. (2008). Cd may act as an acute and chronic type of poison. In chronic exposure, the first sign is kidney damage, usually diagnosed by increased excretion of low molecular weight proteins, Widmeyer et al. (2004). Over time, Cd can accelerate osteoporotic process, since a high calcium dose can inhibit Cd absorption. The reverse situation – the inhibition of calcium absorption by Cd – has also been reported. This interaction is of special importance because of the suggested role of Cd in the development of bone softening due to decalcification, a characteristic of ltai-itai disease, Han et al. (2000).

Absorbed Pb is bound to erythrocytes in the blood and initially distributed to the liver, kidney and heart, where it preferentially binds to cell membranes and mitochondria, Widmeyer et al. (2004). Most forms of Pb are then distributed and stored in the bones. The primary root of elimination is *via* the feces (90%) and the remaining *via* the urine (10%), Gilbert (2004). Pb is known to cause both acute and chronic adverse effects in the hematopoietic, nervous, gastrointestinal and renal systems, Widmeyer et al. (2004). Acute poisoning causes gastrointestinal colic, often resulting in mortality, while chronic poisoning causes anemia due to a decrease in the hemoglobin levels leading to organ damage in one or all of the four above-mentioned systems, Gilbert (2004), but Pb is not-carcinogenic, Chang (1996).

Hg is highly toxic and extremely damaging to cellular and tissue function, Crinnion (2000) and Fleisher (2001). Hg exposure reduces the mucosal entry of sugars and amino acids to 80–90% of the control levels in the small intestine cells within several minutes and blocks intestinal nutrient transport by interacting directly with the brush border membrane transport proteins. Both Me-Hg and elemental Hg, once absorbed, can cross the blood-brain and placental barriers, Crinnion (2000) and Fleisher (2001). Both forms of Hg are immunotoxic, although they differ quantitatively and qualitatively in their effects on the immune system. Me-Hg accumulates mainly in the kidneys, liver, and brain, Fleisher (2001). Elemental Hg may accumulate in the brain, lungs, fatty tissues, kidney, liver and digestive tract. Over time, Hg accumulates and is slowly converted into inorganic Hg, Crinnion (2000). As inorganic Hg, it binds to sulfur-containing molecules, such as hemoglobin in the blood and the powerful antioxidant glutathione, thus depleting their levels. The increased danger associated with Me-Hg is that it can also have a direct effect on cells without being converted into the inorganic Hg form. Both forms of Hg affect the following systems: nervous system, cardiovascular system, immune system and reproductive system, Crinnion (2000) and Fleisher (2001).

Hg is highly toxic and extremely damaging to cellular and tissue function. It is important that everyone but especially those most at risk, such as pregnant women, is aware of the Hg toxicity of fish. Fetal development is the most dangerous time for Hg toxicity.

The effects of As, mainly caused by inorganic As, may produce inhibition of growth, skin discoloration, respiratory problems or even death, Eisler (1994). Illnesses associated with excessive inorganic As intake include skin, lung and heart conditions, gastrointestinal diseases and possible carcinogenic effects. As(III) compounds are bound by red blood cells and affect the activity of many enzymes, particularly those involved in the respiratory process, Eisler (1994). There are a number of potential mechanisms by which As affects tissues that might lead to cell death, but intracellular calcium or enzyme systems regulated by calcium may alter the toxicity of arsenate, Luong and Rabkin (2009). Organic As neither causes cancer, nor is it thought to damage DNA, but exposure to high doses may result in nerve injury and stomach problems, Eisler (1994).

It is emphasized in the literature that the metabolism and toxicity of As vary greatly between species, and that the effects are significantly altered by numerous physical, chemical, and biological modifiers. Adverse health effects, for example, may involve the respiratory, gastrointestinal, cardiovascular, and hematopoietic systems, and may range from reversible effects to cancer and death, depending partly on the physical and chemical forms, Luong and Rabkin (2009).

Since pollutant metals are non-biodegradable inorganic chemicals which cannot be metabolized and do not break down into harmless forms, Kromhout et al. (1985), the measurement of their concentration in mussel soft tissue has become increasingly significant. Accumulation of toxic metals to above permissible limits in *M. galloprovincialis* would certainly create a notorious food image from the public health point of view, as it is well known that chronic exposure to pollutant metals, such as Cu, Pb and Zn, is associated with Parkinson's disease and the metals might act alone or together over time to cause the disease, as well as other health problems, Gorell et al. (1997). Zn appears to have a protective effect against the toxicities of Cd and Pb and its toxicity is rare, Sivaperumal et al. (2007). As(V) causes damage to the heart and blood vessels cells, Luong and Rabkin (2009). A link between traditional food sources high in Cd and diabetes has been postulated in Australian Aborigines, Satarug et al. (2003), and high Cd concentrations have also been associated with prostate cancer, Vinceti et al. (2007), while high Hg and low Zn concentrations have been linked to autism, Yorbik et al. (2004). Although previous studies found a link between shellfish consumption and protection from certain diseases, e.g., myocardial infarction, Yuan et al. (2001), the relative risks and benefits of seafood consumption are hard to assess Whyte et al. (2009) and Yuan et al. (2001).

Although the consumption of these mussels provides proteins, essential minerals and vitamins, and thus, some protection from certain diseases, the risks and benefits of their consumption are still hard to assess, since mussels as filter-feeders are known to bioacumulate Cd, Pb, Hg and As from their surrounding environment. Toxic elements accumulated in mussels can also be accumulated in the food chain. Cd and Pb have long been known to accumulate with time in the human body from different sources, causing health problems.

All metals are potential toxins at some concentration for humans, but Cd, Pb, Hg and inorganic As are particularly toxic at relatively low doses. People consuming very frequently mussels with a high accumulation of one or more of these considered toxicants could be exposed to health risks. These toxic metals accumulated in the human body with time, might act alone or together over time causing different health problems or diseases.

9.5 Conclusion

Mussel production and consumption has been increasing worldwide. There is a growing demand for bivalves, not only in historically developed countries, but also in developing regions. The prospects for expansion of the bivalve industry in developing countries will depend on their ability to build reliable monitoring and inspection programs and implement sustainable farming practices. The global outlook suggests a need for a 50% increase in world food production within next 30–40 years. This is a tremendous challenge in itself, also bearing in mind that food production is a key driver in the degradation of the environment and natural resources.

The metal load is higher in inshore waters and, consequently, in the mussels inhabiting them, owing to the elevated levels of elements in the coastal zone. Mussels as filter feeders accumulate trace metals from food, from suspended matter, or directly from seawater, whether or not these metals are essential to their metabolism. Mussels may even take up certain metals to a level above that in the surrounding waters; hence the degree to which they are accumulated is very much species-specific.

For monitoring programs, in which the Mediterranean mussels are used as bioindicator organisms, some criteria should be adopted in the mussel sampling phase. Mussels should be taken in the same period and at the end of the reproductive cycle, when the percentage of metal concentration obtains its highest value, late winter. Otherwise, comparisons between mussels at different stages of the reproductive cycle would show different concentrations of metals, which could simply be a function of the seasonality in the reproductive cycle. Furthermore, mussels should be of the same size and be sampled from the same depth. Only by following these instructions is it possible to obtain, in different geographical areas, homogeneous data that can be easily compared to each other.

The highest producers of cultivated *M. galloprovincialis* as seafood are Spain, Italy, France, Greece and Turkey. The levels of pollutant metals in the mussel from these countries depend upon the geographical region, hydrological impact and the period of sampling. Levels of Pb, Cd, Hg and As in the Mediterranean mussel are of the same order of magnitude in the Atlantic, Mediterranean, the Adriatic, Aegean and Black Sea regions. The highest values of pollutant metals in *M. galloprovincials* were in the hot spots of the urban areas, near the mouth of rivers, harbors and lagoons of the Mediterranean and Atlantic coast, such as in the Bosphorus European and Asian side and the Izmir Bay in the Aegean Sea. If the mussels from the hot spots are excluded, in this whole native region of *M. galloprovincials*, all the investigated metals were not of great health concern, including As, which is present in mussels mostly in the organic form, which is not toxic to humans.

As the Black Sea and the Mediterranean Basin will potentially be the largest producers of the Mediterranean mussels in the future, health of the mussels consumers will depend on integrated management of the land and near-shore components of the coastal zone. Human health impacts caused by the consumption of contaminated seafood were nearly always related to the quality of the environment where the aquaculture products were produced. For this reason, it is important to provide sustainable management of shellfish harvesting waters and, simultaneously, maintain public health. The production and management of cultivated mussels also require integrated work between health, environmental and food regulators and the commercial and casual exploiters of mussel resources.

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Chapter 10
Persistent Organic Pollutants (POPs) in Sediments and Biota in Coastal Environments of India

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Abstract Persistent organic pollutants (POPs) are semivolatile organic compounds of special concern because of their toxicity, persistence, long-range transport and bioaccumulation potential. They are present in the marine environment, notably in coastal areas affected by municipal sewage, agricultural and aquaculture effluents, industry and shipping traffic. The 7,555 km-length coastal region of India is the most vulnerable zone facing frequent geohazards, e.g. tsunami and flooding. It is contaminated from direct discharge of wastes from the densely populated coastal areas, runoff of fertilizers, dumping by vessels, oil spills, deforestation and ill-planned river basin developments. This chapter summarizes the knowlegde on residues of 5 classes of persistent organic pollutants (POPs) such as dichlorodiphenyltrichloroethane and its metabolites (DDTs), hexachlorocyclohexane and its isomers (HCHs), polycyclic aromatic hydrocarbon and its congeners (PAHs), polychorinated biphenyl and its congeners (PCBs) and polybrominated diphenyl ether and its congeners (PBDEs) in the sediments and in selective biota: bivalve mollusks, fishes and marine mammals. Their potential ecotoxicological impacts on biota have also been assessed based on the sediment quality guidelines (SQG) specified by USEPA (The incidence and severity of sediment contamination in surface waters of the United States, vol 1, National sediment quality survey. EPA 823-R-97-006, Washington, DC, 1997a: Environmental protection agency, National Sediment Quality Survey, App D, Washington DC, 1997b) and by Canadian Council of Ministers of the Environment (CCME, Canadian quality guidelines for the protection of aquatic life-summary tables. Available from. http://www.ccme.ca/assets/pdf/sed summary_table.pdf, 2002).

Contribution of DDT and its metabolites, DDT, DDD and DDE residues, varied in different Indian coastal regions predominated by pp′-DDT and pp′-DDD. The measured concentrations of HCHs were lower than DDTs in sediments. HCH and DDT residues in fish from coastal regions of India were lower than those in temperate countries indicating a lower accumulation in tropical fish, which might be ascribed to rapid volatilization of this insecticide in the tropical environment. Distribution of congener profiles of PCBs, PAHs and PBDEs reflects moderate to very low concentrations closely in conformity to other Asian coastal environment. Predominance of highly chlorinated PCB congeners was evident in comparison to lightly chlorinated PCBs, which are less persistent, have lower $log_{ko}w$ and are more volatile than the former. The prevalence of 4–6 aromatic ring PAHs and cross plots of specific isomer ratios such as phenanthrene/anthracene, fluoranthene/pyrene and methylphenanthrene/phenanthrene suggest the predominance of wood and coal combustion sources, where the atmospheric deposition and surface runoff are the the major transport pathways. In case of PBDEs the nature of lesser-brominated congeners may be due to the extensive use of penta-BDE technical mixture or as a result of environmental debromination of higher brominated BDEs. The east coast of India, on an average, is found to be much more contaminated than the western counterpart which might be attributed to residues with their behavior, fate and bioaccumulation in the different trophic levels should be planned. An alarming situation has already emerged due to the presence of pesticide residues in the human breast milk as well as in the blubber of the endangered gangetic dolphin (*Platanista gangetica*) inhabiting both riverine and estuarine regions of the Ganga River. Hence authors suggest that a regular monitoring, assessment and reporting machineries should be implemented in accordance with appropriate environmental policies, laws and regulations to guarantee health of environment and human.

Keywords Organochlorine pesticides • PCBs • PAHs • PBDEs • Sediments • Biomagnification • Ecotoxicological risk • India

List of Abbreviations

BCF	Bioconcentration factor
BDE	Bromo diphenyl ether
BDEs	Bromo diphenyl ether isomers
BMP	Best Management Practice
CB	Chlorinated biphenyl
CCME	Canadian Council of Ministers of the Environment
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DDTs	Dichlorodiphenyltrichloroethane isomers
ERL	Effects Range Low
ERM	Effects Range Median
HCH	Hexachlorocyclohexane
HCHs	Hexachlorocyclohexane isomers
HMW	High Molecular Weight
LMW	Low Molecular Weight
OCP	Organochlorine Pesticide
OCs	Organochlorines
op′-DDD	op′-dichlorodiphenyldichloroethane
op′-DDE	op′-dichlorodiphenyldichloroethylene
op′-DDT	op′-dichlorodiphenyltrichloroethane
pp′-DDE	pp′dichlorodiphenyldichloroethylene
PAH	Polycyclic Aromatic Hydrocarbon
PAHs	Polycyclic Aromatic Hydrocarbon isomers
PBDE	Polybrominated diphenyl ether
PBDEs	Polybrominated diphenyl ether isomers
PCB	Polychlorinated biphenyl
PCBs	Polychlorinated biphenyl isomers
PCDD	Polychlorinated dibenzodioxins
PCDD/Fs	Polychlorinated dibenzo-p-dioxins and dibenzofurans

PEL	Probable Effects Level
POP	Persistent Organic Pollutant
POPs	Persistent Organic Pollutant isomers
pp′-DDD	pp′-dichlorodiphenyldichloroethane
pp′-DDE	pp′-dichlorodiphenyldichloroethylene
pp′-DDT	pp′-dichlorodiphenyltrichloroethane
SQG	Sediment Quality Guideline
TEL	Threshold Effects Level
UNEP	United Nations Environment Program
USEPA	US Environment Protection Agency

10.1 Introduction

Persistent organic pollutants (POPs), a group of xenobiotic lipophilic pollutants, are semivolatile, bioaccumulative, persistent and toxic (Jones and de Voogt 1999). Organochlorines (OCs) such as PCBs and chlorinated pesticides (such as HCHs and DDTs), PAHs and PBDEs represent an important group of POPs that have caused worldwide concern as toxic environmental contaminants. In 2001, the Stockholm Convention on POPs acknowledged these as global problems. Although the occurrence of POPs at elevated levels is of great environmental concern at contaminated hot spots, the regional and global significance of the problem has received increased attention in the last decades (UNECE 1998; UNEP 2001). They have been reported to cause variety of effects including immunologic, teratogenic, carcinogenic, reproductive and neurological problems in organisms (Kodavanti et al. 1998) and are of considerable concern to human and environmental health. In addition, some congeners have shown some effects on the endocrine system such as reducing serum concentrations of the thyroid hormones like thyroxine and triiodothyronine (Koopman-Esseboom et al. 1994). The liphophilic nature, hydrophobicity and low chemical and biological degradation rates of these xenobiotics have led to their accumulation in biological tissues and a subsequent magnification of concentrations in organisms progressing up the food chain. Individual POPs have characteristic patterns of distribution depending on regional patterns of usage and their physicochemical properties. Considering the global distribution of POPs it is important to understand their transport mechanism and to identify any hot spots where regulatory and remediation efforts are required. To evaluate the effectiveness of the regulations and remediation, monitoring of POPs is essential and the importance of global monitoring of POPs was emphasized at the Stockholm Convention (Secretariat of the Stockholm Convention).

India is one of the few remaining countries still engaged in the large scale manufacture, use and export of some of the toxic chlorinated pesticides, such as DDT), hexachlorocyclohexane (HCH) and pentachlorophenol (PCP). Even in the

1990s more than 70% of the gross tonnage of pesticides used in agricultural applications in India consisted of formulations which are banned or severely restricted in the east and west (Gupta 1989, 1986, 1985; Shetty 2001; Subramanian et al. 2007). According to a Green Peace Report, India is now producing 90,000 metric tons of pesticides as the largest industry in the whole of Asia and twelfth largest in the entire world (http://www.greenpeaceindia.org.nopesti.htm). The cumulative consumption of the pesticide, HCHs in India until 1985 was 5,75,000 tons and since then about 45,000 tons of HCHs has been used annually. The usage of DDT and HCH continued till recently. Apart from the US, India is the only country which has applied more than 1,00,000 tons of DDTs since its formulation, mainly in its agricultural and malarial control programs until it was banned for agricultural use in 1989. Even though usage of technical HCH was finally banned completely in 1977, the Government of India is encouraging its replacement with Lindane (γ-HCH), an isomer which has all the hazardous properties of HCH. Even though DDT has been banned for agricultural use, India has sought exemption under Stockholm Convention for use of 10,000 tons of DDT for restricted use in the public health sector (Lallas 2001). The national malaria program (NAMP) used 3,750 tons of DDT in the year 2001, in rural and peri-urban areas for residual spraying (Gupta 2004).

India has a coastline of about 7,555 km, of which about 5,400 km belong to peninsular India and the remaining to the Andaman, Nicobar and Lakshadweep Island. With less than 0.25% of the world coastline, India houses 63 million people, approximately 11% of global population living in low lying coastal areas. The coast also includes 77 cities, including some of the largest and most dense urban agglomerations – Mumbai, Kolkata, Chennai, Kochi and Visakhapatnam (Fig. 10.1). India's coastal zone is endowed with a wide range of mangroves, coral reefs, sea grasses, salt marshes, sand dunes, estuaries, lagoons, and unique marine and terrestrial wildlife. The abundant coastal and offshore marine ecosystems include 6,740 km of mangrove belts, including part of the Sundarban (West Bengal) and the Bhitarkanika (Orissa), which are among the largest mangroves in the world. Rapid urban-industrialization, maritime transport, marine fishing, tourism, coastal and sea bed mining, offshore oil and natural gas production and aquaculture cause severe environmental degradation. A significant ecological change is pronounced in this coastal region due to contamination of inorganic and organic pollutants originated from huge discharge of domestic and industrial effluents carried by the rivers, disposal of contaminated mud from harbor dredging, intense shipping activities, agricultural runoffs, oil spills, deforestation, ill-planned river basin developments as well as atmospheric depositions. The present chapter attempts to elucidate the distribution, behavior and fate of these compounds in Indian coastal regions which are characteristically different in geomorphological and hydrological set up with varying anthropogenic stresses. The Arabian Sea and the Bay of Bengal (Fig. 10.1) are subject to semidiurnal tides and are also influenced by biannual reversal of the monsoon winds. These two factors result in the flushing of Indian coastal regions which help in dispersing pollutants.

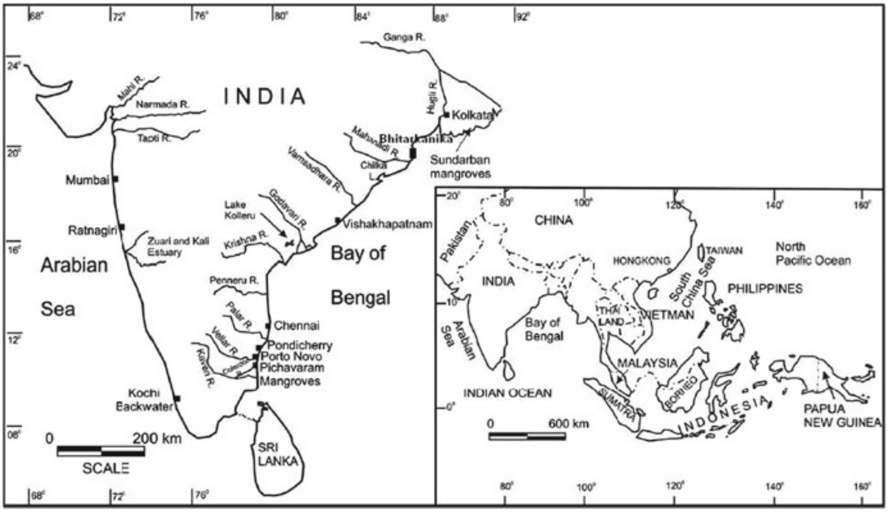

Fig. 10.1 Map showing the distribution of major rivers, important coastal cities and mangrove areas in the east and west coast of peninsular India. The map of southeast Asia shows important locations as referred in the text

10.2 Data Sources and the Objectives of This Article

The authors have extracted data from different departments, published literature in research journals and national reports of POPs in the coastal regions of India. The sampling and analysis methods were described in details in the cited documents. Due emphasis has been given on the coastal regions of Sundarban mangrove wetland along with the lower stretch of Hugli River (Ganges) in the article as these have been sufficiently explored in the context of POP contaminations in sediments and biota.

This article summarizes the data available to review the contamination status of DDTs, HCHs, PAHs, PCBs, and PBDEs in the sediments and representative biota in Indian context. The objectives are as followed: firstly, to examine the contamination profiles of these POPs in sediments and biota; secondly, to apportion their sources; lastly, to compare their concentrations with the reverse effect thresholds to evaluate their ecological risks aiming at safeguarding the environmental and human health.

10.3 Characteristic Features of the Persistent Organic Compounds

India is a generics giant (Dave 1996). It is one the few remaining countries still engaged in the large scale manufacture, use and export of some of the toxic chlorinated pesticides (e.g., DDT, HCH etc.). Even in the 1990s more than 70% of the gross tonnage of pesticides used in agricultural applications in India consisted of formulations which are banned or severely restricted in the east and west (Iyer 1993; Gupta 2004). According to a Green Peace report, India is now producing 90,000 metric tons of pesticides as the largest industry in the whole of Asia and the 12th largest in the entire world (http://www.greenpeaceindia.org/nopesti.htm); the cumulative consumption of the pesticide, HCHs, in India until 1985 was 5,75,000 ton and since then about 45,000 ton of HCHs has been used annually (Kannan et al. 1995); the usage of DDTs and HCHs continued until recently (Gupta 2004). Apart from the US, India is the only country which has applied more than 100 000 ton of DDTs per year since its formulation, mainly in its agricultural and malarial control programs until it was banned for agricultural use in 1989 (Anon 1991; Kannan et al. 1995; Voldner and Li 1995). Even though usage of technical HCHs was finally banned completely in 1997 (Anon 1997), the Government of India is encouraging its replacement with Lindane (γ-HCH), an isomer which has all the hazardous properties of HCHs. Even though DDT has been banned for agricultural use, India has sought exemption under Stockholm Convention for use of 10,000 ton of DDT for restricted use in the public health sector. The National Malarial Program (NAMP) used 3,750 ton of DDT in the year 2001, in rural and peri-urban areas for residual spraying (Gupta 2004). PCBs have been banned in transformers and capacitors in India from the year 1997. A 1996 World Bank Study estimated that approximately 2,000–4,000 ton of PCBs existed in India at that time. Much of the old machinery that contain PCBs is 20–30 years old and are expected to be decommissioned in the near future – increasing the need for their regulated disposal and effective PCBs identification in the environment.

Organochlorine pesticides are persistent, bioaccumulative in fatty tissues and are found distributed in different compartments in marine environments as a result of transfer by wind from long distances and from domestic and industrial discharges. They are effective pest control chemicals, used in agriculture and public health activities (malaria eradication, etc.) worldwide for the past several decades and are still in use in many developing countries. Though complete ban on DDTs was imposed in many developed nations, in India it was banned only for agricultural use, but still used for malaria control, and HCH is also not completely banned (still used for agriculture). While the bulk of HCH used today is in the form of the I isomer of the compound, there is concern that this isomer can be transformed into other isomers that exhibit greater persistence and have potentially more deleterious effects on humans and wildlife (Walker et al. 1999).

Polychlorinated biphenyls (PCBs) are among the most important industrial contaminants in marine ecosystems estimating more than 1.5 × 106 ton as world production (excluding the former USSR and China) between 1929 and 1988 (Koppe and Keys 2002). PCBs are a group of synthetic halogenated aromatic hydrocarbons that has been linked to a number of environmental and public health concern. Despite their ban or restricted use (UNEP 2003a, b), PCBs and organochlorine pesticides are among the most prevalent environmental pollutants and can be found in various abiotic (air, water, sediments, soil) and biotic (from plankton to humans) compartments (de Voogt et al. 1990; Jones and de Voogt 1999; de Boer et al. 2000, 2001).

Theoretically, there are 209 PCB congeners with one to ten chlorine atoms bound to the phenyl rings. They are very resistant to decomposition and have an excellent insulating property as well as a high heat absorbed capacity. Their properties have led to many industrial applications but also make PCBs one of the major environmental pollutant classes. The commonly considered key representatives of the industrial pollutants, PCBs are extensively used in electrical transformers and capacitors as heat transfer fluids and in consumer products (Eduljee 1988; Harrad et al. 1994). They enter the environment through dispersion from their identifiable and specific place of use or from incineration and landfill sites.

About 31 banned or restricted pesticides in other countries are still in use in India and about 350,000 ton were used since 1985 and 7,000 ton of DDT were used during 2001–2002 (http://www.cseindia.org/, 2002). Presence of PCBs and chlorinated pesticides were reported in harbors, near shore sediments and Bays all over the globe (Iwata et al. 1994; Hong et al. 1995; Strandberg et al. 1998; de Mora et al. 2001; Zhou et al. 2001; Barakat et al. 2002; Fillmann et al. 2002; Hong et al. 2003). Earlier studies in Indian marine environment showed that PCBs and organochlorine pesticide residues are comparable with other developing countries, but predicted an increase in future due to continuous usage of organochlorine pesticides in agriculture and vector control measures.

Distribution of organochlorine pesticides in Indian marine environment has been reported by several authors (Babu Rajendran et al. 1999; Sarkar et al. 1997a, b; Tanabe 2000), but PCBs in Indian marine environment was scarcely reported (Tanabe 2000). An extensive study on organochlorines both from east and west coasts of India was done mainly in biota of different trophic levels (e.g., mussel (bivalve mollusk), fish, birds and mammals) by Tanabe (2000). Findings on chlorinated pesticides were only limited to seashore sediments (Pandit et al. 2001), except a couple of reports from the offshore sediments (Sarkar and Sen Gupta 1988a, b, c; Sarkar et al. 1997a, b).

Polycyclic aromatic hydrocarbons (PAH) are a class of ubiquitous organic compounds with two to seven condensed aromatic rings. Overall 16 PAHs are considered by the USEPA as priority micropollutants because of their carcinogenic and mutagenic properties. PAHs are derived mainly from anthropogenic inputs and they are products of incomplete combustion. Natural and anthropogenic sources contribute significantly to the PAH concentrations in the environments. Anthropogenic sources include combustion of fossil fuels, waste incineration and production of coke, carbon black, coal tar pitch, asphalt and petroleum cracking (Mc Cready et. al. 2000). Likewise, spillage of fossil fuel (e.g., huge oil spill at Mumbai-Raigad coast, western part of India occurred on 11th August, 2010) is another common anthropogenic source of PAHs. Pyrolytic and petrogenic sources are known to generate substantially different PAH assemblages. PAHs can be introduced in the environment by various processes (Neff 1979; McElroy et al. 1989): (a) incomplete combustion at higher temperatures of recent and fossil organic matter (pyrolytic origin), (b) slow maturation of organic matter under the geochemical gradient conditions (petrogenic origin) and (c) short-term diagenetic degradation of biogenic precursors (diagenesis).

Identificaiton of PAHs is difficult for their origins in sedimentary medium, owing to the possible co-existence of several sources (various pyrolytic sources, petrogenic contamination and early diagenesis). In addition, physical and chemical properties of some PAH, like chemical reactivity (photooxidation, oxidation), can contribute to modify the original distribution pattern of the emission sources (Butler and Crossley 1981). In marine ecosystems, PAHs can undergo degradation by photo-oxidation in the superficial water layer (and by microbial activities into the sediments (Ceniglia and Heitkamp 1989). However, PAH ubiquity in the sediments indicates that the accumulation phenomenon dominates the degradation processes in sedimentary matrices (Smith and Levy 1990), so, some PAHs could exhibit comparable evolution kinetics. Molecular indices based on PAH physical and chemical behavior covariability were developed to access the various origins of these pollutants (Soclo 1986; Baumard et al. 1998). The determination of PAHs is possible as they are attached to the molecule indices simultaneously to the hydrocarbons to the studied matrices (Lake et al. 1979; Neff 1979; Budzinski et al. 1997).

Polybrominated diphenyl ethers (PBDEs), one of the most important groups of brominated flame retardants (BFR), are used commercially as non-covalent additives in plastics and textiles, building materials, carpets, and automobiles and aircraft (Sellström et al. 1993; Pijnenburg et al. 1995) with a half-live of 2–10 years (Hooper and McDonald, 2000). PBDEs are structurally similar to PCBs and DDTs and their chemical properties, persistence and distribution in the environment follow similar patterns. In computers, these compounds are commonly used in printed circuit boards, components such as connectors, cables, plastic covers and parts of keyboards and monitors. Only three different commercial mixtures (penta-, octa- and deca-BDE) are in use, a small number of 209 possible BDEs are found in aquatic and terrestrial ecosystems worldwide. The presence of high levels of these compounds in samples from remote areas suggests that they may now have been distributed worldwide as a result of long range atmospheric transport (Jansson et al. 1987; Sellström 1996; Corsolini et al. 2006). Although several data sets are available on PBDE levels in biotic and abiotic matrices from American and European aquatic ecosystems (Covaci et al. 2006; de Boer et al. 2003; Eljarrat et al. 2004; Oros et al. 2005), Martin et al. (2004) remarked the urgent need to determine PBDE distribution in Asian coastal environments, particularly in regions with heavy industrialization. Mostly undocumented reports of major deposits of plastics and electronic parts in China and India lead to the speculation of an important source of PBDEs in the region. China, India and Pakistan have long been suspected of receiving and disposing the bulk of the world's obsolete computers and electronic components (Martin et al. 2004).

10.4 POPs in Coastal Sediments

Coastal sediments are recognized to be excellent temporary or long-term sinks for many classes of anthropogenic contaminants. Their study is an important step in mapping the possible pollution sources and exposure pathways which facilitate

POPs bioavailability to sediment dwelling organisms. Moreover, they provide a chronological record of micropollutants extending over a long period of time. Sediments thus offer the prospect of serving as a chemical museum in which the history of industrial activity is preserved in a stable profile. Contamination of soil and sediments of coastal areas with persistent organochlorine compounds could be related to point sources, e.g., industrial discharges and domestic sewage. In the case of pesticide pollution, it can also be attributed to precipitation, agricultural runoff, surface run-off and leaching. Hence the bottom sediments represent an integrated measure of particle-bound contaminants that have deposited over a longer period of time.

10.4.1 Levels of DDT and HCH in Sediments

The data on the accumulation of pesticides in marine sediments is limited, especially considering the length of India’s coastline. We have chosen Sundarban mangrove wetland, which is located in the estuarine part of Hugli River, as an example to demonstrate the pollution status of Indian coastal systems with these contaminants. Guzzella et al. (2005) documented distribution of various organochlorine pesticides in the surface sediments (<63 μm particle size) along the stretch of the Ganges (Hugli) estuary including Sundarban mangrove wetland, eastern coastal part of India (Fig. 10.2). The results revealed a wide range of spatial variations. The range of concentrations of HCH, HCB, DDT and PCBs in the sediments were 0.11–0.40, <0.05–0.98, 0.18–1.93 and 0.18–2.33 ng g^{-1} dry wt, respectively. The presence of HCH isomers and DDT and its metabolites can be attributed to the use of these insecticides in agriculture as well as anti-malaria sanitary activities carried out throughout the country due to their cost benefits, bioefficacy potential, and popularity among the farmers (Pandit et al. 2002). HCH pesticide has been used for agricultural purposes to control insects in cotton, rice, and vegetable crops and is still used in some of the developing countries around the tropical belt (Doong et al. 2002). The concentration of four important isomers of HCHs (α, β, γ and δ) reveals a heterogenic nature of distribution. The composition of HCH isomers α- and γ-HCH (lindane) was detected in all the samples, whereas β- and δ-HCH were below the detection limits in majority of the cases (the limit of detection was 0.02 μg l^{-1} for each PCBs, 0.2 μg l^{-1} for each HCH insecticide and 0.05 μg l^{-1} for each DDT). This may be relative to isomerization of HCHs during the process of transport and transformation in a marine ecosystem (Iwata et al. 1994; Dou and Zhao 1998). The α-isomer was the predominant one followed by γ – isomer, reflecting the use of a technical mixture of HCHs (Kannan et al. 1995). α – HCH has higher values (0.26 ng g^{-1} dry wt) of Henry’s law constant and vapor pressure than β--HCH and γ -HCH, indicating greater efficiency by atmospheric transport of α -isomer than other isomers (Iwata et al. 1994) favoring existence of the isomer in all the samples. The ratios of α – to γ -isomer were well below those in the technical mixture (i.e., 4–7). The low HCH ratio in the sediment sample implies the use of lindane in this region. HCH contamination might have occurred through atmospheric transport

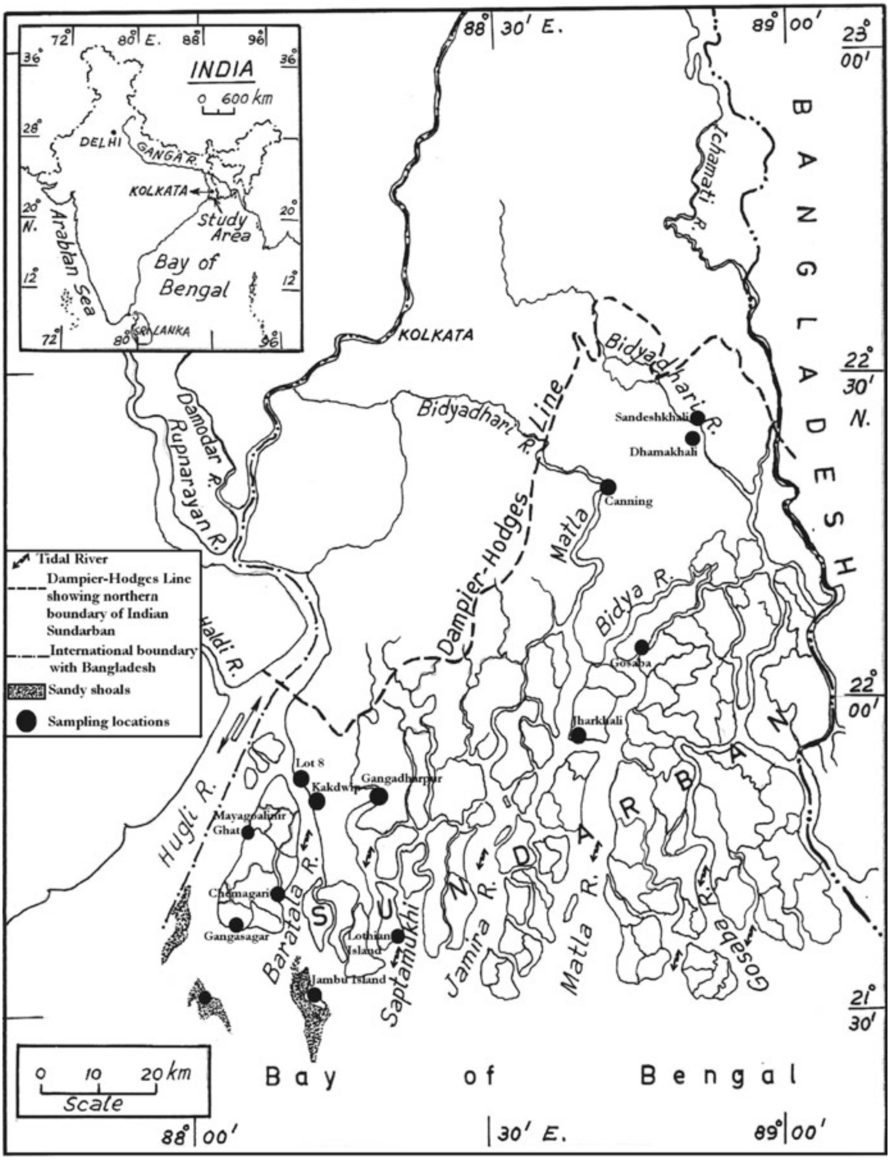

Fig. 10.2 Map showing the sampling locations in the lower stretch of the Hugli estuary and Indian Sundarban mangrove delta

from others parts of India where a large amount of technical HCHs is still being used and high concentrations were found in biota (Ramesh et al. 1992). Recently, Sarkar et al. (2008) reported the first comprehensive account of the organochlorine pesticide residues (HCHs, DDTs etc.,) in core sediments (<63 μm particle size) from the mudflat of Sundarban wetland, which revealed an erratic pattern, either top to bottom or vice versa, reflecting non-homogenous input of these compounds. DDTs were detected in all sediment samples, but the contribution of individual metabolites showed differences. pp'-DDT and op'-DDT were found to be much more significant than DDE and DDD. The occurrence of DDT isomers is predominant in the following order: pp′-DDT > pp′-DDD > pp′-DDE > op′-DDT > op′-DDD > op′-DDE. The dominance of DDTs in the sediment compared to DDT metabolites was also reported by Pandit et al. (2002) from the coastal marine environment of Mumbai, western part of India. This may be attributed to the slow degradation of DDTs or recent input of DDTs in this environment (Tavares et al. 1999; Yuan et al. 2001). The dominance of either pp′-DDT or both pp′-DDT and pp′-DDE in sediments was also recorded by Guruge and Tanabe (2001) from the west coast of India and by Booij et al. (2001) from the northwest coast of Java, Indonesia.

According to Strandberg et al. (1998), the ratio of pp′-DDT/ pp′-DDE provides a useful index to know whether the DDT input at a given site is recent or happened in the past, a value <0.33 generally indicates an aged input and an overall value of >0.33 was found in majority of sediment samples along the east coast of India, indicates recent inputs of DDT. The contribution of pp′-DDT over 50% of the total DDT along the coast seems to be associated with vegetable growing activities. The use of pesticides in agriculture and aquaculture has generally been increasing due to rising population and demand for more agrochemicals at these sites. The Hugli (Ganga) River passes through relatively dense industrial and residential areas (Fig. 10.2) where pesticides are sprayed during the public health campaign against malaria and also for other purposes. The relative concentration of the parent DDT compared to its biological metabolites, DDD and DDE can be used as indicative indices for assessing the possible pollution sources. The high percentage composition of op′-DDT and pp′-DDT with respect to total DDT clearly illustrates that DDT usage has not been eradicated yet in the country, and there might be fresh input of DDT to the coastal estuary, which was also observed by Babu Rajendran et al. (2005) in sediments of Chennai harbor and Cuddalore fishing harbors, south east coast of India. India is ranked the biggest consumer and manufacturer of HCH and DDT in the world (Mehrotra 1993) as these are cheap as well as effective chemicals (Bashkin 2003). Sarkar and Sen Gupta (1987) measured the pesticide residues in sediments along the west-central coast of India in the Arabian Sea showing the following decreasing order: HCH > pp′-DDE > pp′-DDT > op′-DDE > pp′-DDD. Among the metabolites of DDT, residues of pp′-DDE and op′-DDE are known to be much more significant than DDD in the marine environment. In the east and west coast of India, Pandit et al. (2001) observed that HCH isomers and DDT and its metabolites are the predominantly identified compounds in majority of the surface sediment samples. The predominance of α- and β-HCH reflects the use of technical grade HCH in India. An overall low level of DDT, DDD and DDE residues in sediments were recorded in sediments where DDE followed by DDT constituted the bulk portion. Comparable residue levels of these pesticides have earlier been reported in the Indian marine environment (Sarkar and Sen Gupta 1987; Sarkar and Sen Gupta 1988a, b, c). They attributed that the significant concentrations of DDE in the coastal sediments to the presence of various kinds of marine benthic organisms, which

Table 10.1 Comparison of organochlorine concentrations in sediments from coastal regions in Asia (ng g^{-1} dry weight, n.d = not detectable)

Location	Year	DDTs	HCH	Reference
Mason Bay, Korea	1997	0.2–80.2	nd–1.3	Hong et al. (2003)
Ulsan Bay, Korea	2001	0.02–41.9	0.02–4.55	Khim et al. (2001)
Wu–Shi estuary, Taiwan	2002	nd–11.4		Doong et al. (2002)
Daya Bay, China	1999	0.10–20.3	0.3–4.2	Zhou et al. (2001)
Minijiang River Estuary, China	1999	1.6–13.1	3–16.2	Zhang et al. (2003)
Yangtze Estuary, China	2001	nd–0.6		Liu et al. (2003)
Singapore coast	2003	2.2–11.9	3.3–46.2	Wurl and Obbard (2005)
West coast of India	1995–1997	nd–364	1.5–1053	Pandit et al. (2001)

accelerates the biodegradation process and the alkaline nature of marine systems which is highly favorable for such types of transformations (Pandit et al. 2001). To evaluate the relative degrees of OCP contamination in coastal sediments in India, a comparison has made against the available data in Asian context as shown in Table 10.1. The comparison study is compromised by the fact that different studies considered different DDT metabolites and it is still important to evaluate the OC contamination to get a sense of regional similarity. It is evident that the Indian coastal regions present low to moderate OC contamination in sediments. The highest values for both, total DDT and total HCH, in Indian coastal environments are higher than in other Asian countries referring to Table 10.1. Sarkar et al. (1997a, b) found higher mean concentration of ∑DDT and dieldrin (by factors of 1.7 and 2.4 respectively) in estuarine sediments of the Arabian Sea areas compared to offshore sediments while mean concentrations of ∑HCH, aldrin, and endrin were similar for both offshore and estuarine samples. In both offshore and estuarine sediments, α-HCH was the most dominant isomer and for the DDTs, pp’-DDE was the most predominant metabolite except near Cannanore and Murmugao (west coast of India) where op’-DDE and pp’-DDT were significant in offshore samples. Their overall assessment revealed that Zuari and Kali estuaries, west coast of India, are the most susceptible to DDT as compared to other estuaries. Sarkar and Sen Gupta (1988a, b) determined residues of organochlorine pesticides in sediments from the Bay of Bengal. The compounds and concentrations detected were aldrin at 20–530 ng g^{-1} (all sample weights expressed as ww), γ-HCH at 10–210 ng g^{-1}, dieldrin at 50–510 ng g^{-1} (Sarkar and Sen Gupta 1988a, b), and ∑DDT at 20–790 μg g^{-1} (Sarkar and Sen Gupta 1988a, b). The total DDT concentration in offshore sediments of Chennai, southeastern part of India, ranged between 0.3 and 1.18 ng g−1, the maximum concentration was 670–103 times lower than the highest concentration reported by Sarkar and Sen Gupta (1988a, b, c) This reveals that, during the 10 year period the DDT burden in the marine environment has drastically declined, clearly indicating that DDT usage in India has decreased and the restrictions imposed by Indian government is effective in containing use of POPs. A decreasing trend of DDT in coastal atmospheric air from east coast of India has been reported earlier by Babu Rajendran et al. (1999). Similarly, Monirith et al. (2000) also reported an obvious decline of HCHs and DDTs concentrations in the green mussel *Perna viridis*, bivalve mollusca, from the east coast of India during 1988–1989, 1994–1995 and 1998.

The variability in pesticide residue concentrations is attributed to the presence of numerous rivers along the east coast of India, which includes the Hugli, Mahanadi, Vamsodhara, Godavari, Krishna, Pennar and Palar Rivers, (Fig. 10.1). All these rivers bring copious amount of agricultural discharges containing persistent organic pollutants including organochlorine pesticides and drains into the Bay of Bengal. Among the metabolites of DDT, both pp′-DDE and op′-DDE were consistently found along the east coast of India, which is attributed to the degradation of DDT to DDE in the coastal sediments. Sarkar and Sen Gupta (1988a, b) suggested that the following phenomenon, either individually or in combination, are responsible for the degradation of DDT to DDE: the alkaline nature of the marine system the presence of chemical constituents and their characteristics, e.g. salinity, clay mineral concentration, major elements and the presence and concentration of organic matter; and stored thermal energy in ocean waters, DDT isomers and their metabolites were detected in the sediments of coastal Bay of Bengal in the following order: op′-DDE > pp′-DDE > pp′-DDT > op′-DDD > pp′-DDD > op′-DDT.

Concentration of DDT was in the range of 1.8–25.8 ng g^{-1} ww and HCH in the range of 0.4–7.1 ng g^{-1} dw in sediment samples of Vellar Estuary as reported by Venugopalan and Rajendran (1984). The higher concentration of residues, especially $\sum$DDT, in the Bay of Bengal is attributed to the rapid transportation by rivers of their high-suspended sediment load (about 8.1 mg l^{-1}) compared to the rivers draining into the Arabian Sea, where suspended particulate loads are 1.6 mg l^{-1} (Shailaja and Sarkar 1992). Several studies have measured the pesticide concentration of sediment of Indian rivers, which includes the Vellar, Ganges, Cauveri and Mahanadi. Ramesh et al. (1991) found higher sediment loads of DDTs and HCHs in the Vellar River during the wet season (3, 4 and 12.4 ng g^{-1} dw, respectively) compared to dry season (1.0–2.3 ng g^{-1} dw, respectively). Senthilkumar et al. (1999) found mean sediment concentrations in the Ganges of 5.6 and 2.6 ng g^{-1} dw DDT and HCH, respectively. Chlorinated pesticide residues in surface sediments from the River Cauvery, in the southeastern coast of India were reported by Babu Rajendran and Subramanian (1999). Total DDT was low and showed no wide variations among sampling sites, which reflect its ban on the use of agriculture to mosquitoes control use. The concentrations of HCHs (39.4–158.4 ng g^{-1} dw) at various collection sites reflected its agricultural use, with peak values affirming the application of HCH for paddy crops during the monsoon and subsequently to grams during the post-monsoon season. Iwata et al. (1994) analyzed air, river, water, and sediment samples from eastern and southern Asia (India, Thailand, Vietnam, Malaysia and Indonesia) and Oceania (Papua, New Guinea and the Solomon Islands) for the presence of OC pesticides to elucidate their geographical distribution (Fig. 10.1). The distribution patterns in sediments showed smaller spatial variations on global terms, indicating that OCs released in the tropical environment are dissipated rapidly through air and water and retained less in sediments. They noted that the atmospheric and hydrospheric concentrations of HCHs and DDTs in the tropical developing countries were higher than those observed in the developed nations. There are only a few studies on the fate and behavior of OP pesticides in the marine sediments (Sarkar and Sen Gupta 1985, 1986; Sujatha and Chacko 1991) from Indian waters. The low stability of these pesticides in sea sediments indicates that the presence of major element cations have reduced the toxic effects of these pesticides in marine environment (Sarkar and Banerjee 1987). It is known that OCs are relatively stable in marine sediments. DDT and DDE were even detected in the Arabian deep sea to which they were transferred with sinking particles. There is a striking contrast in pesticide residue concentrations in sediments of the east and west coasts of India. Sediment samples of the east coast contain pesticide residue concentrations in magnitude higher than samples from off the west coast of India the cause of which might be attributed to several factors. All the major Indian rivers flow towards east and drain through fertile agricultural lands and thus receive a considerable input of pesticides, and carry their sediment loads to marine waters on the coast. Also, the use pattern of pesticides shows a predominance of pesticides to lands bordering the eastern coast. The significant role of the sediment quality characteristics (e.g., texture and total organic matter) controlling the leaching process in sediments was emphasized by James and Ramesh (2002). In general, fine grained sediments inhibit pesticide leaching, because of low permeability or higher surface area and enhance the adsorption of pesticides. They established correlation between grain size and organic matter in surface sediments of a river basin of south India. They had also observed a relatively high concentration of γ-HCH near the agricultural non-point source area and β-HCH was always higher than gamma- HCH confirming the characteristic feature of β HCH as stable and resistant to microbial degradation (Rajendran and Subramanian 1997). Recently, Sarkar et al. (2008) established negative correlations for all the organochlorines (HCH, DDT etc.,) with sand in core sediments from the Indian Sundarban wetland which reveals that the coarse particles have less adsorption capacity for OCs.

10.4.2 Levels of PCBs in Sediments

Polychlorinated biphenyls (PCBs) are persistent organic pollutants with significant bioaccumulation potentials in environmental systems (UNEP 2003a, b). These compounds are frequently detected in a wide variety of environmental matrices such as sediments, soils, biota, water and air, in both industrial and nonindustrial areas (Iwata et al. 1995; Floch et al. 1996; Bodin et al. 2004). The synthesis of PCBs was first described in 1881 (Schmidt and Schultz 1881). The presence of PCBs in the environment was first identified in biological samples in 1966 (Jensen 1966). PCBs have long been identified as harmful substances due to their toxicity (Safe 1992; Persson et al. 2005; Sprovieri et al. 2007; Juang et al. 2009a, b).

Distribution of POPs in sediment cores from the intertidal mudflat of Sundarban wetland did not follow any uniform trend as recorded in case of OCs. This is probably due to the hydrological characteristics of the Sunderban Wetlands being severely influenced by the southeast monsoon and the mesomacrotidal regime (Goodbred 2003), as well as the non-homogeneous inputs from point and non-point sources of these chemicals. The dispersion process is also influenced by estuarine the mixing and resuspension processes in this typical mesomacrotidal environment.

In the sediment core samples from Sundarban revealed that the textural characters indicate a variable mixture of sand, silt and clay, with an overall size range from sandy to clayey. Levels of $\sum_{12}$ PCBs measured at seven sampling sites from Sundarban mangrove wetland range between 0.23 and 31.4 ng g^{-1} with a mean concentration of 5.4 ng g^{-1}. Marked variations in relative contribution of individual congeners together with sharp spatial heterogeneity recorded. This might be due to the differences in local inputs of PCB along the Hugli estuary and the relative mechanisms of dispersion and accumulation. Concerning the PCB congeners, tri-chlorinated biphenyls (tri-CB) to octa-CB were detected in the sediment samples. An overall decreasing order of seven dominant PCB congeners contributing to the total load was CB 138 > 153 > 149 > 101 > 118 > 141 > 151 (Binelli et al. 2008). This order can be explained since the lightly chlorinated PCBs are less persistent and more volatile than the heavily Chlorinated PCBs. Therefore, the heavily chlorinated PCBs get accumulated in the sediments, whereas lightly chlorinated PCBs are degraded and volatilized more than the others (Toan et al. 2007).

Sarkar et al. (1997a, b) reported the concentration of total DDT in sediments from the Arabian Sea along the west coast of India in the range of 1.14–17.59 ng g^{-1} and pp′-DDE as the most detected metabolite. It could be inferred from the literature that China and India are the largest pesticide consumers in Asia.

The observation of fairly high concentration of PCB at upstream of Hugli River is related to the high density of multifarious industries along the upstream side of the estuary (Fig. 10.2) including refining, chemical production, waste treatment and disposal facilities. Likewise higher concentration of PCBs near industrialized areas was also recorded by other workers (Hong et al. 2005; Wurl and Obbard 2005; Howell 2007). In addition, the presence of fine-grained particles, dominated by silt fractions bearing large surface area, facilitates the absorption of the compounds. The three stations (Babughat, Bajbaj, Nurpur) belong morphologically to the intertidal mudflat of a mesotidal setting of the Hugli River Estuary (Fig. 10.2) and showed a general homogeneity with silty clay to clayey materials. The moderately high values at these sites are attributed to the huge discharge of untreated or semi-treated industrial waters from the upstream part of the estuary. In addition, intense shipping activities, dredging operations, sewage discharges, dumping of industrial wastes and atmospheric depositions, further aggravate the PCB pollution. Other important sources of PCBs in this wetland include volatilization from previously contaminated sediments, followed by atmospheric transport and deposition (Galassi et al. 1992; Kallenborn et al. 1998).

Trichlorinated to octachlorinated biphenyls were detected and they were in the following decreasing order: CB 118>CB 194>CB 18>CB 28>CB 149>CB 31>CB 153. Differences in PCB congener concentrations may be attributed to a decline in the proportion of less chlorinated PCBs (lower log K_{ow}) that are more susceptible to losses through volatilization, sedimentation and possibly microbial degradation (Brown et al. 1987; MacDonald et al. 1992; Quensen et al. 1988). Moderately and higher chlorinated PCBs may therefore remain at relatively constant levels in the aquatic environment because they are less volatile, more soluble in lipids, adsorb more readily to sediments and are more resistant to microbial degradation (Shiu and Mackay 1986; Tyler and Millward 1996).

In a marine environment with intense shipping and trawling activities (such as Hugli estuary), with multifarious sources of PCB inputs, it is rather hard to pinpoint precisely a specific source-occurrence relationship. Furthermore, the sediment resuspension from tidal movement in the estuary may promote dechlorination dependent on different transport further masking source-concentration matches (Tyler and Millward 1996). Again, the hydrological characteristics of the Hugli River estuary, such as macrotidal effect and seasonal fluctuation in flow-rate due to performed impact of southwest monsoon (annual rainfall 1,600 mm), can influence the distribution of these compounds in sediments.

10.4.3 Levels of PAHs in Sediments

The PAH study in the coastal environments is of great importance as these areas are biologically important and productive system possesses high socioeconomic values. They receive considerable pollutant inputs from land-based sources via coastal discharges, thus potentially threatening the biological resources, among other negative effects. In general, the spatial distribution of PAHs in surface sediments is controlled by the hydrodynamic conditions of the wetland, including the following factors: (i) textural composition and depositional rate of sediments (ii) input rate of PAHs (iii) differential resuspension and redeposition of sedimentary PAHs (iv) vertical mixing due to physical or biological processes, and (v) microbial degradation of PAHs (Boonyatumanond et. al. 2006). There are very scarce information about the status of PAH contamination in sediment in coastal regions of India, preliminary work has been carried out in quantification and source identification of PAHs in surface sediments from the lower stretch of Hugli estuary by Guzzella et al. (2005) and in core sediments from Sundarban wetland by Dominguez et al. (2010).

Guzella et al. (2005) recorded low to moderate PAHs contamination where $\sum_{19}$ PAHs ranged from 2.5 to 1,081 ng g^{-1} in surface sediments considering 10 sampling stations along the lower stretch of Hugli river. The total concentration of PAH revealed an overall gradual decreasing trend from upper to lower stretch of the river where the maximum value was recorded at the site Babughat ($\sum_{17}$1081 ng g^{-1}). This is also observed that 4-ring PAHs fluoranthene, chrysene, pyrene and benzo(a) anthracene were dominant congeners in sediments.

For core sediments, elevated level of $\sum_{16}$ PAHs (2,938 ng g^{-1} at 12–16 cm) were recorded at Lothian, an offshore island of Sundarban wetland, indicating a situation where tidal recycling of sediments works at the mouth of Saptamukhi River (in Fig. 10.2). The local resuspension and recycling processes may account for the higher concentration of most of the components. In addition, the fine sediment particle size (silty clay together with high organic matter content (1.20%) facilitate the absorption and accumulation of PAHs in this location.

The depth profiles of individual PAHs are complex and did not follow any consistent trend, as it was also found in the region for other organic and inorganic pollutants like PBDEs (Binelli et al. 2007) and heavy metals (Chatterjee et al. 2007). However, an overall decreasing trend of total PAHs from top to lower levels of the core seems to occur and this is more evident in the case of 3-ring PAHs, which attain their maximum values at 20–30 cm depth. Perylene was present at all levels of the core samples, showing a more uniform profile, probably associated to its diagenetic origin.

The prevalent erratic vertical distribution of PAHs might be mainly related to the non-homogenous textural composition of the different sediment core layers resultant from the particular hydrological conditions of the Hugli estuary and adjoining Sundarban wetland situated under a meso-macrotidal setting and seasonal flow rate fluctuations. The PAH accumulation patterns and *in situ* degradation or metabolism by benthic communities could also have contributed to the dispersion of the profiles.

10.4.4 Levels of Polybrominated Diphenyl Ethers (PBDEs) in Sediments

The concentration of PBDEs was analyzed from core sediments collected from seven sampling sites in Sundarban during winter months of 2006. The levels of Σ_{12} PBDEs measured at intertidal sediments from Sundarban mangrove wetland ranged between 0.08 and 29.0 ng g^{-1} (Binelli et al. 2007). An overall enrichment for majority of the congeners was observed at Canning and Dhamakhali sites, with a maximum level of $\sum_{12}$ PBDEs (29.0 ng g^{-1}) at 0–4 cm sediment layer. Stations Lot 8, Kakdwip, Mayagoyalinir Ghat and Sandeshkhali (the locations are shown in Fig. 10.2) showed uniform trends of very low PBDE concentrations. The fairly elevated concentrations measured at Canning and Dhamakhali is due to the dense population and comparatively poor seawater exchange at these two sites. The huge discharge of municipal wastewater along with local industries contributes to these elevated values, as well as the presence of several textile plants along the upper stretch of Hugli (Ganges) estuary (Fig. 10.2) might point out a local use of PBDE formulates for textile production (Hale et al. 2006). Tanabe (2002) has also suggested that the burning of electronic wastes in municipal dump sites in Asia, under such conditions, often generates as much of these chemicals as seen in industrialized countries. The elevated concentrations (~18 ng g^{-1} dry wt) found at Canning, where high values of trace elements were also encountered in surface sediments (Sarkar et al. 2004), may be attributed to the extensive siltation in this area, where pollutants have the tendency to retain for a longer time due to weak ebb flow. No uniform temporal trend on PBDE levels between the seven sampling stations was noticed probably due to the particular hydrological characteristics of

Sundarban wetland which are severely influenced by southeast monsoons and the meso-macrotidal regime (Goodbred 2003; Bhattacharya and Sarkar 2003). Fluctuations in PBDE levels may also arise from non-homogeneous inputs from point and non-point sources for these chemicals.

Distribution patterns of BDE (brominated diphenyl ether) congeners recorded in sediments from the mudflat of Sundarban wetland did not follow any uniform trend of distribution from top to bottom profile (in core sediments) for each congener. Tetrabromodiphenyl ether BDE- 47 was found in all samples, followed by hexabromodiphenyl ether BDE-154 (95% of sediment layers) but they did not seem to be the dominant congeners. The general order of decreasing congener distribution of the total load was: BDE 47>99>100>154, similar to the distribution worldwide. However, different distribution pattern is observed at the site located on the main flow of Hugli River (Fig. 10.2), where BDE-47 was dominant, followed by BDE-85 and BDE-99. On the contrary, distribution patterns observed in many other sediments collected worldwide are in the following order: BDE- 47>99>100>154>183>153 (Voorspoels et al. 2003, 2004; Song et al. 2004; Liu et al. 2005), even if several recent studies pointed out the major presence of the decabrominated ether (BDE-209) in western countries (Sawal et al. 2004; Voorspoels et al. 2004; Schlabach et al. 2004; Eljarrat et al. 2004). Relative contribution of tri and tetra-congeners recorded at Sundarban mangrove wetland was very similar to that of the moderately and heavily substituted BDEs. The ubiquitous nature of lesser-brominated congeners is due to the extensive use of penta-BDE technical mixture (e.g. Bromkal 70-5DE), characterized by about 43% of BDE- 47 (La Guardia et al. 2006), or as result of environmental debromination of higher brominated BDEs (Ikonomou et al. 2002). The possible presence of low degree brominated congeners (such as di- BDEs and tri-BDEs) in marine and river sediment samples was demonstrated by Lacorte et al. (2003), indicating the possible degradation of commercial mixtures to less brominated congeners.

10.5 Accumulation of POPs in Biota

The interest in using organisms to monitor pollution arose from the fact that some bivalve and gastropod molluscs might accumulate and “record” the contaminants present in water column and/or in sediments, whereas the contaminants in the water column may not be recorded in the sediments. Besides, analysis of bivalve tissues gives an indication of the bioavailable fraction of environmental contamination and of direct exposure to chemicals. By virtue of their wide geographic distribution, sufficiently long-lived and of a reasonable size, marine bivalves have been used as essential organisms in many countries for marine pollution monitoring, e.g., in ‘Mussel Watch Programmes’, since the late 1970s. Hence the report especially concentrates on bioaccumulation of POPs by this specific macrozoobenthos considering the following species: *Sanguinolaria acuminata* (clam) (Family Psammobiidae), *Meretrix meretrix* (clam) (Family Veneridae), *Macoma birmanica* (mussel) (Family Tellinidae), *Perna viridis* (green mussel) (Family Mytilidae).

10.5.1 Organochlorine (OC) Residues in Marine Shellfishes, Finfishes and Mammals

The distribution of chemical species in a multiphase system is governed by physical and chemical properties such as vapor pressure, water solubility, octanol-water partition coefficients and bioconcentration factor (BCF). Despite the higher quantity of consumption levels, HCH and DDT residues in fish in India were lower than those in the temperate countries suggesting a lower accumulation in tropical fish. In finfishes and shellfishes from east and west part of India, Pandit et al. (2001) reported dominance of γ-HCH and α-HCH in the muscle tissues, which is due to the use of technical HCH in India. The similar trend of concentration of HCH isomers was also observed in west coast of India by Pandit et al. (2002). An obvious decline of HCHs and DDTs concentrations in green mussel, *P. viridis* from the east coast of India during 1988–1989, 1994–1995 and 1998 with 18 ± 15, 11 ± 10 and 4.4 ± 3.4 ng g^{-1} wet wt, and 7.5 ± 3.6, 5.8 ± 3 and 2 ± 1.8 ng g^{-1} wet wt, respectively (Monirith et al. 2000). The high temperature in the tropics also enhances the elimination rate of chemicals in fish as the biological half-lives of semi-volatile compounds such as DDT are short at high temperatures (Pandit et al. 2001). Pesticide residues in fish samples from Vellar estuary of southern part of India were studied by Venugopalan and Rajendran (1984) and observed that *pp'*-DDE was the dominant degradation product. The data on the distribution of OCPs in fishes is important not only for ecological research, but also because of their impact on human health.

Marine mammals especially cetaceans are considered to be particularly sensitive to the effects of contaminant that are exposed because they have a long life spans and feed high in the food chain. As a result, they are exposed to relatively high contaminant levels and can accumulate high concentrations in their tissues, and act as representative animals to illustrate global pollution. However, very scarce information is available regarding the OC contamination status in the tissues of this group from Indian coastal waters. A detailed report was contributed by Karuppiah et al. (2005) illustrating the level of OC residues in three odontocete species from the Bay of Bengal, southeast coast of India. They had considered blubber from bottle-nose dolphins *Tursiops truncates*, spinner dolphins *Stenella longirostris* and humpback dolphin *Sousa chinensis* and recorded considerable levels of three chemical classes (HCHs, DDTs and PCBs), where HCHs was in the range of 95–765 ng g^{-1}; DDT in the range of 3,330–23,330 ng g^{-1} and PCBs in the range of 210–1,220 ng g^{-1} (wet weight basis).

An extensive account of organochlorine pesticide concentration was first worked out by Kannan et al. (2005) in the smallest cetacean, Irrawaddy dolphin (*Orcaella brevirostris*) from Chilika lake, a Ramsar site, located in the east coast of India in the Mahanadi River delta (Fig. 10.1). DDTs were the predominant contaminants (maximum concentration 10,000 ng g^{-1}) followed by HCHs (maximum in 1,200 ng g^{-1}) in the blubber the dolphin tissues. DDT concentrations in *O. brevirostris* were threefold to tenfold less than what was reported for *T. truncates* and *S. longirostris* from the Bay of Bengal which may be related to a difference in their trophic status in the marine food chain.

10.5.2 PCBs in Marine Mammals

High accumulation of POPs, such as PCBs, in aquatic mammals has been linked to adverse health effects (Jepson et al. 2005; Ylitalo 2005). Because of their high trophic level in the food chain and relatively low activities of drug-metabolizing enzymes, aquatic mammals such as river dolphins, the world's most seriously endangered species, accumulate increased concentrations of POPs (Tanabe et al. 1988). Dolphins inhabiting riverine and estuarine ecosystems are particularly vulnerable to the activities of humans because of the restricted confinement of their habitat, which is in close proximity to point sources of pollution.

In *O. brevirostris*, Kannan et al. (2005) recorded 10–100-fold lower PCBs (ranging 28–390 ng g^{-1}) than the concentrations reported in three dolphins, namely, *P. gangetica* (Senthilkumar et al. 1999), *T. truncates* and *S. longirostris* from the Bay of Bengal (Karuppiah et al. 2005) and from other Asian coasts (Minh et al. 2000). The comparative lower concentration is might be attributed as the lake (lagoon) watershed is agricultural rather than urban and industrial in nature.

10.5.3 PAH Congener Residues in Bivalve Mollusc

The congener residues of PAHs in three intertidal bivalve mollusks of Sundarban wetland were studied by Zuloaga et al. (2009) collected from three sites of Sundarban, namely, deposit-feeder *M. meretrix* from Canning, *M. birmanica* from Chemagari and *S. acuminata* from Gangasagar, the later two are suspension-feeders. The individual tissue burden of total PAHs in the three bivalves differs widely, lower in shell of the suspension-feeder bivalve mollusc *M. birmanica* (21.3 ng g^{-1} dry wt) and higher in visceral mass of ng g^{-1} (5,919 ng g^{-1} dry wt) denoting the organisms' different selectivity for a range of PAH congeners. An overall enrichment of PAH concentration was observed in *S. acuminata* when comparing different organs. The pronounced variations might be related to the following factors: (i) variable capacities of the bivalves to metabolize them (ii) different degrees of bioavailability of the compounds and (iii) biotransformation capacities of the organism (Kennish 1997). Moreover, fluctuation in PAH levels arise from non-homogenous inputs from point and non-point sources of these compounds that are related to the results observed. A preferential low molecular weight (LMW) and high molecular weight (HMW) PAHs were evident both in hard (shell) and soft tissues (mantle, gill, podium, visceral mass etc.,) of *S. acuminata.* In contrast, comparative low values were recorded in *M. meretrix* and *M. birmanica*, exhibiting an overall similar trend of distribution of PAHs in bivalves and sediments. Small variations of total PAHs in these two sites could be produced by different physiological conditions in the mussel population (Guinan et al. 2001). In the case of bivalve mollusks exposed to both particulate and dissolved contaminants, mussels still preferentially accumulated the LMW

Table 10.2 Summary of PAH concentration levels (ng g^{-1} dry wt) detected in bivalve mollusk from different parts of the world

Location and year	Range of PAH in ng g^{-1}	References
East Coast, China, 2001	456.8–3,496.0 in mussel	Fung et al. (2004)
Pearl River Estuary, China, 2003	27.8–1,041.0 in shellfish	Wei et al. (2006)
Northern Irish Sea-loughs, Ireland	95–184 in mussel	Guinan et al. (2001)
Guanabara Bay, Brazil	60–6,000 in mussel	Fracioni et al. (2007)
Meditereanean Sea	25–337 in mussel	Baumard et al. (1998)

compounds tri- and tetra-aromatics), but in the turbid area at Gangasagar, the HMW compounds (penta- and hexa-aromatics) were accumulated to a moderately greater extent than the rest. The site experiences high turbidity throughout the year due to dual effects of wave swash and backwash from the open sea and tidal current of macrotidal amplitude.

As evidenced from Fig. 10.2, the site Gangasagar lies in close vicinity to an international shipping line and in direct influence to pollution sources throughout the year. Concentration of individual PAH congeners in the organs of bivalves revealed a wide range of variations. Interestingly, maximum values of all the 16 congeners (except for naphthalene) were recorded in S. acuminate inhabiting close to pollution sources (e.g., Baumard et al. 1999).The abundance of HMW PAHs present in the species was also typically encountered in atmospheric particles and urban aerosols (Muel and Saguem 1985; Sicre et al. 1987), due to their low water solubility, low microbial degradation rate (Readman et al. 1982), and high particulate affinity, compared with LMW PAHs.

Fluoranthene was the most abundant compound in soft tissues of all the three bivalves and adjacent sediments. Fluoranthene and pyrene fluctuated in three bivalves, with an over enrichment in *S. acuminata* collected from the mouth of Hugli estuary. This may be explained by the mixing of marine and riverine sediments mainly due to tidal flushing, together with additional inputs(e.g., exhausts of the trawlers used for fishing, leakage of crude oil and petroleum products from the oil terminals in the upstream of Hugli estuary) from various parts of the estuary. Among the tri-aromatics (phenanthrene and anthracene), all the bivalves accumulated preferentially phenanthrene, which reached a maximum value in visceral mass of *S. acuminata*, as well as in the adjacent sediments at Gangasagar. Chrysene, an aromatic compound of natural origin, is the best-accumulated congener in all the tissues of the bivalves and reached a maximum value of 537 ng g^{-1} in the visceral mass of *S. acuminata*. Chrysenes are more resistant to degradation than naphthalenes, dibenzothiophenes, phenanthrenes, and fluoranthenes (Wang et al. 1998) and bear higher K_{ow}s (octanol/water partitioning coefficients), which may favor bioaccumulation (Francioni et al. 2007).

To evaluate the relative degrees of PAH contaminations in marine bivalve mollusks, we compared the data against the available data reported elsewhere (Table 10.2). Although we recognize that the direct compatibility is somewhat compromised by the fact that different studies consider different PAH congeners, there are also regional differences due to the absence or presence of major polluters such as oil refineries, still it is important to evaluate the quantitative patterns of PAH contamination to get a send of regional similarity. Moreover, there is a complete lack of data on the accumulation of PAHs in individual organs of marine bivalves. The levels of PAHs recorded in Indian Sundarban wetland are comparable to those reported in bivalves from Pearl River Estuary (27.8–1,041 ng g^{-1} by Wei et al. 2006), but lower than those reported in mussel in Guanabara Bay, Brazil (60–6,000 ng g^{-1} by Francioni et al. 2005). A comprehensive monitoring survey for PAHs utilizing green mussels (*Perna viridis*) as sentinel organisms was conducted in south and southeast Asia as a part of Asian Mussel Watch Project. Based on categorization of PAH concentrations in mussels proposed by Baumard et al. (1998), PAHs concentrations in south and southeast Asia can be classified as low (0–100 ng g^{-1}) to moderate (100–1,000 ng g^{-1}).

10.5.4 PBDEs in Marine Mammals

PBDEs are structurally similar to PCBs and DDTs and, therefore, their chemical properties, persistence and distribution in the environment follow the same pattern. They have been found to bioaccumulate and there are concerns over the health effects in animals from exposure to PBDEs. An extensive information pertaining to the bioaccumulation of this compound in small cetacean mammals, namely, spinner dolphin (*Stenella longirostris)* and humpback dolphin (*S. chinensis)*, from Asian waters by Kajiwara et al. (2006). They established that PBDE profiles in cetaceans are species-specific and independent of exposure amount and/or body burdens. Concentrations of PBDEs ranged from a low value of 6.0 ng g^{-1} lipid wt. in *S. longirostris* from India to a high value of 6,000 ng g^{-1} lipid wt. in *S. chinensis* from Hong Kong and thus revealing different contamination sources. Kannan et al. (2005) observed maximum PBDEs levels of 0.98–18 ng g^{-1} in the blubber of *O. brevirostris* from Chilika lake and the compound was also found in muscle, liver and kidney tissues of this dolphin. An overall low PBDEs concentration was present in this species than the concentrations reported for other cetaceans in the coastal and riverine waters of Asia.

10.6 Ecotoxicological Concerns

The sediment quality guidelines (SQG) specified by USEPA (USEPA 1997a, b), Canadian Council of Ministers of the Environment (CCME 2002) and by Long et al. (1995) were used to assess the potential ecotoxicological impacts of organic contaminants measured in surface sediments of India. Effects range low (ERL) and effects range median (ERM) values are used to predict potential impacts of contaminants in sediments, whereas ERL values correspond to the lower 10 percentile and

Table 10.3 Minimum and maximum concentrations (C) of major organochlorine contaminants (ng g^{-1}) present in sediments of Sundarban along with the corresponding sediment quality criteria

OC pesticides	C min	C max	ER-L	% above ER-L	ER-M	% above ER-M	TEL	% above TEL	PEL	% above PEL
pp′DDT	<0.10	8.48	1	7.14	7	2.38	1.19	4.76	4.77	2.38
pp′DDD	<0.05	0.59	2	0.00	20	0.00	1.22	0.00	7.18	0.00
pp′DDE	<0.05	2.29	2.2	2.38	27	0.00	2.07	2.38	374.17	0.00
ΣDDT	0.05	11.47	0.5	64.28	6	2.38	2.26	21.43	4.79	2.38
Y-HCH	<0.05	2.75	–	–	–	–	0.32	66.67	0.99	40.48
ΣPCB	0.47	26.84	22.7	4.80	180	0.00	21.6	7.10	188.8	0.00

Note: *ER-L* effect range-low value, *ER-M* effect range-medium value, *% above ER-L/ER-M* percentage of sample above ER-L/ER-M, *TEL* threshold effect level, *PEL* probable effect level

ERM values to median values, when the chemical concentration of a contaminant in marine sediments are sorted according to the degree of their effects levels. ERL represents the value at which toxicity may begin to be observed in sensitive marine species, whereas ERM represents the concentration below which adverse effects are expected to occur only rarely. Besides the Threshold effect level (TEL), the probable effect level (PEL) is used as the criterion for the prediction of toxicity, and corresponds to a level above which adverse effects are frequently expected. From these assessments, it can be stated that the levels of the xenobiotic compounds in Indian marine environment are not alarming. Contamination by PCB in the Bay of Bengal, India is negligible/relatively very low and may not cause any toxicological effects in the marine species inhabiting the coastal Bay of Bengal. The minimum and maximum concentrations of major organochlorine contaminants (ng g^{-1} dry wt) present in sediments of Sundarban along with the corresponding sediment quality criteria (ER-L, ER-M, TEL, PEL) have been given in Table 10.3. Contamination by OC pesticides (DDT and γ-HCH), do exist to some extent in some specific regions of southern coastal regions of India, namely, Chennai, Pondicherry and Cuddalore, that may have some impact on resident organisms via a long-term chronic exposure.

10.7 Conclusion and Recommendations

The review summarizes and synthesizes the significant amount of data pertaining to persistent organic pollutants (POPs) in biotic and abiotic compartments in coastal regions of peninsular India. This reveals a better understanding of the current levels and spatiotemporal trends of contaminants. The east coast of India seems to be much more contaminated that the west coast, which is due to the greater quantum of residues carried by the major rivers along the former coast. The most significant observations which connote an urgent need for attention that organochlorine pesticide residues were also present in human blood (Subramaniam and Solomon 2006), mother's milk (Someya et al. 2010) and blubber of endangered gangetic dolphin (*Platanista gangetica*) (Tanabe et al. 1993) in various parts of India.

Keeping in view of the present grave scenario, authors strongly recommend the following programme:

(a) a multidisciplinary integrated approach involving toxicology, epidemiology, physioliogy and behavioral sciences to assess the hazards and plan the preventive strategies need to be developed.
(b) strict implementation of various legislation, standards and code of conducts for regulation of manufacturing, distribution, handling and application of pesticides. New legislation for the banning of illegal use of POPs should be introduced and education of the public implementation of such measures
(c) an extensive awareness scheme for safe use of pesticides through all possible forms of media, i.e., radio, television, newspapers etc., The government and other allied agencies should educate farmers and agriculture managers on best management practices (BMP) as well as integrated pest management (IPM) for sustainable use of pesticide in agriculture.
(d) establish a reliable monitoring programe for POPs including organochlorines, so that any mass fractions exceeding environmental quality standards can be detected for taking appropriate remedial action.
(e) studies to quantify the subtle effects of POPs on humans and wildlife, including molecular modeling for biodegradation, transformation and toxicity mechanisms
(f) a shift from detailed studies on the more ‘traditional’ POPs (i.e. PCBs, PCDD/Fs) to metabolites and ‘newer’ classes of POPs (eg. PBDE, chlorinated paraffins, toxaphene) and perhaps more polar persistent compounds may be focused.

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