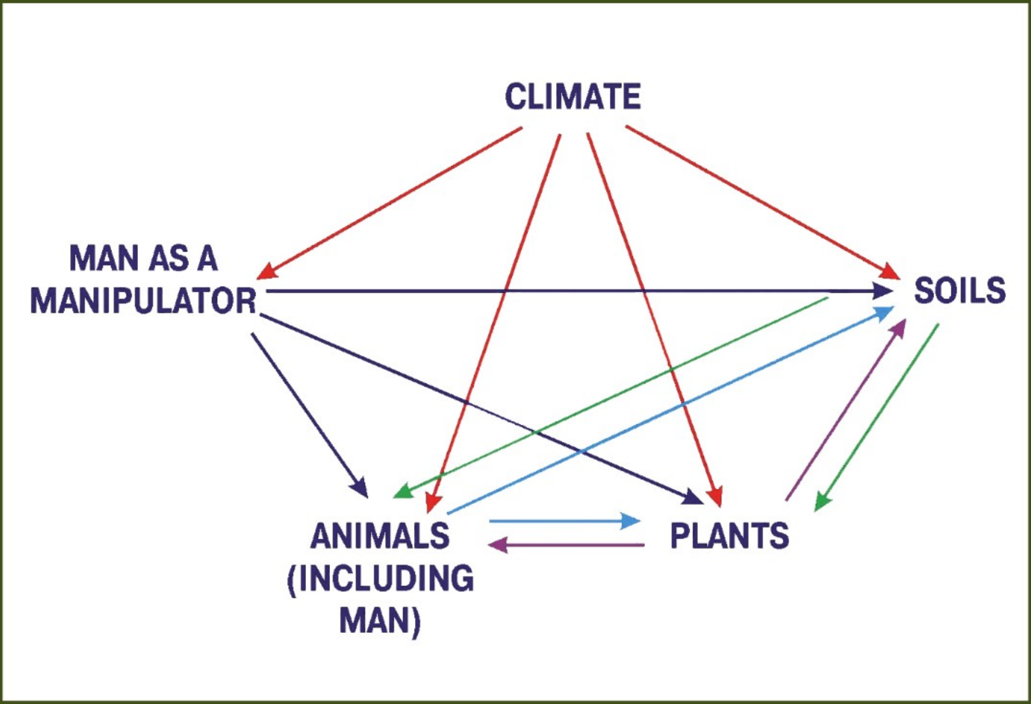
Modern Biogeochemistry: Second Edition

Environmental Risk Assessment

by

Vladimir N. Bashkin



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Springer

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Vladimir N. Bashkin was born in 1949 in the town of Dobrinka, Lipetsk region, Russia. He graduated from the Biology-Soil department of Moscow State University in 1971, where in 1975 he was awarded a PhD, and in 1987, a Doctor of Science degree. His scientific career began at the Pushchino Biological Center of the Russian Academy of Sciences in 1971. For many years Vladimir Bashkin delivered lectures in various universities such as Cornell University, USA, Seoul National University, Korea, and King Mangkut's University of Technology, Thailand. At present he is a professor of biogeochemistry and risk assessment at Moscow State University, and the principal researcher at the Gazprom company and Institute of Basic Biological Problems RAS. His main research is related to environmental risk assessment, biogeochemistry, urban ecology, and trans-boundary pollution. Professor Bashkin is the author of 22 books, including Modern Biogeochemistry and Environmental Chemistry: Asian Lessons (published by Kluwer), and more than 100 papers. Under his supervision more than 20 PhD and DrSc dissertations have been presented in various countries and universities. He is a member of the board of five international journals in the field of environmental pollution. During a five year period he was selected as vice-chairman of the Working Group of Effects (scientific committee) of the UN/EC Long-Range Trans-boundary Air Pollution Convention.

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PREFACE

The techniques of risk assessment are used in a wide range of professions and academic subjects. Engineers "risk assess" bridges to determine the likelihood and effect of failure of components, and social welfare workers "risk assess" their clients to determine the likelihood of reoccurrence of anti-social behavior. Risk assessment has become a commonly used approach in examining environmental problems. It is used to examine risks of very different natures. For instance, the approach is used to assess the environmental risks posed by Genetically Modified Organisms (GMOs), chemicals, ionizing radiation and specific industrial plants. Definitions in risk assessment are all-important because of the wide range of uses of the approach, and different meanings of terms used by different groups of experts and practitioners.

The concept of Environmental Risk Assessment (ERA) is based on the biogeochemical principles of sustainability of natural and technogenic ecosystems and applies the methods of biogeochemistry, geoecology, human physiology, applied mathematics and theory of probabilities and uncertainty, economics, statistics, sociology, toxicology, environmental chemistry and other disciplines. The quantitative estimate of ecological risk can be the principal link in the chain of ecological safety factor for the whole of society. Taking into account the modern regional and global statistics of technogenic accidents and catastrophes as well as environmental pollution, in many developed and developing countries the ERA calculations are of great importance and interest for governmental and private institutions.

At present quantitative ecological risk assessment is widely used in different settings, however very often without an understanding of the natural mechanisms that drive the processes of environmental and human risk and complicated by a high uncertainty of risk values. On the other hand, the sustainability of modern technoecosystems is known, based on their natural biogeochemical cycling that is transformed to various extents by anthropogenic activities. Accordingly an understanding of the principal mechanisms driving the biogeochemical food webs allows us to describe the quantitative ecological risk assessment and to propose technological solutions for ERA management in various contents. The same is true for insurance of ecological risks that is the powerful mechanism of a protection of responsibility rights and a management of ecological damage owing to natural and anthropogenic accidents and catastrophes.

This book is aimed at generalizing the modern ideas of both biogeochemical and environmental risk assessment during recent years. Only a few books are available for readers in this interdisciplinary area, however, as most books deal mainly with various technical aspects of ERA description and calculations. This text aims at supplementing the existing books by providing a modern understanding of mechanisms that are responsible for ecological risks for human beings and ecosystems.

This book is to a certain extent a summary of both scientific results of various authors and of classes in biogeochemistry and ERA, which were given to students by the author during recent years in different universities. So I would like to thank the many students of the Universities of Cornell, Moscow, Pushchino, Seoul, and Bangkok, who explored this subject initially without a textbook. The critical discussion and comments during these classes have provided me the possibility of presenting this book.

I am also thankful to my international colleagues whose various cooperative results were used in this text, Prof. R.W. Howarth, Prof. N. Kasimov, Prof. E. Evstafyeva, Prof. H.-D. Gregor, Prof. J.-P. Hettelingh, Mr S. Dutchak, Prof. S-U. Park, Dr. S. Tartowski, Dr. A. Kazak, Dr. R. Galiulin, Dr. I. Priputina, Dr. M. Kozlov, Dr. G. Vasilieva, Dr. D. Savin, Dr. O. Demidova, Dr. I. Ilyin, Dr. E. Mantseva, Dr. V. Shatalov, Dr. S. Towprayoon and many others.

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PART I

BIOGEOCHEMICAL CYCLING AND POLLUTANTS EXPOSURE

CHAPTER 1

ASSESSMENT OF ECOSYSTEMS RISKS

Over the last decades direct and indirect environmental effects of human activities has become a focus of special attention of the general public, state authorities, and international organizations. A number of approaches to predict, evaluate, and mitigate human-induced alterations in the biophysical environment have emerged including environmental impact assessment (EIA). EIA has become a powerful tool to prevent and mitigate environmental impacts of proposed economic developments.

In the current EIA practice, impacts on natural systems (ecological effects) are often given less attention than they deserve (Treweek, 1999). One of the key reasons is a great deal of uncertainty associated with ecological impact studies.

Meanwhile, there has arisen a well established methodology for assessing developments in the face of a high degree of uncertainty and establishing the potentially high significance of impacts, we call this methodology *risk assessment* (*RA*) including *environmental risk assessment* (*ERA*). Recent interest in "tools integration" (Sheate, 2002) is related to growing debate on the benefits of integrating RA into EIA procedures in terms of improving treatment of impacts of concern (see, e.g., Andrews, 1990; Arquiaga et al., 1992; NATO/CCMS, 1997; Poborski, 1999). A number of procedural and methodological frameworks for EIA–RA integration has already been proposed and many researchers believe that RA should be used extensively in assessment s for many types of impacts including impacts on ecosystems (Lackey, 1997).

Ecological impact assessment induced by various human activities is a focal point of improving methodology for environmental impact assessment. Although there is an established methodology for assessing EIA, it is applied mainly in an *ad hoc* manner (Eduljee, 1999). Moreover, there is a vocal critique on applicability of ERA methodology to studies of ecosystem effects of proposed development (Lackey, 1997). The state-of-art ecological risk assessment (EcoRA) has established tools and techniques for and provides credible findings at species level investigations. Recent developments in ERA methodology allowed the researcher to move to population and even community level assessments (see Smrchek and Zeeman (1998) for details). At the same time, formal EcoRA is sometimes focused on effects on groups of organisms, and not an ecosystem as a whole. RA at ecosystem level is usually comparative and qualitative (Lohani et al., 1997).

Meanwhile, a quantitative approach to assessing pollution effects on ecosystems has already been developed. A Critical Load and Level (CLL) concept has been used for defining emission reduction strategies under the UNECE Convention on

Long-range Transboundary Air Pollution (LRTAP). Over time, the critical load approach has been defined not only at international but also at regional and local levels (Posch et al., 1993, 1997, 1999, 2001, 2003; Bashkin, 1997, 2002).

Accordingly, this chapter discusses the incorporation of the CLL concept into EIA for assessment and management of risks for natural ecosystems. The authors aimed at providing insights on applying this effect-oriented approach within a legally established procedure for assessing proposed economic developments. The proponents are encouraged to consider the CLL methodology as a promising tool for cost-effective impact assessment and mitigation (Posch et al., 1996).

The first section explains the concepts of EIA and RA and the existing approaches to their integration. This is followed by an analysis of the current situation with ecological input into EIA and discussion on how the formal EcoRA framework provides for site-specific ecosystem risk assessment. The subsequent section reviews the CLL approach and its applicability for assessing ecological effects in EIA. Finally, a model for assessment of ecosystem risks within EIA using the CLL approach is proposed.

1. CONCEPTS OF ENVIRONMENTAL IMPACT ASSESSMENT AND RISK ASSESSMENT AND APPOACHES TO THEIR INTEGRATION

The technique of risk assessment is used in a wide range of professions and academic subjects. Accordingly, in this introductory section some basic definitions are necessary.

Hazard is commonly defined as “the potential to cause harm”. A hazard can be defined as “a property or situation that in particular circumstances could lead to harm” (Smith et al., 1988). Risk is a more difficult concept to define. The term risk is used in everyday language to mean “chance of disaster”. When used in the process of risk assessment it has specific definitions, the most commonly accepted being “The combination of the probability, or frequency, of occurrence of a defined hazard and the magnitude of the consequences of the occurrence” (Smith et al., 1988).

The distinction between hazard and risk can be made clearer by the use of a simple example. A large number of chemicals have hazardous properties. Acids may be corrosive or irritating to human beings for instance. The same acid is only a risk to human health if humans are exposed to it. The degree of harm caused by the exposure will depend on the specific exposure scenario. If a human only comes into contact with the acid after it has been heavily diluted, the risk of harm will be minimal but the hazardous property of the chemical will remain unchanged.

There has been a gradual move in environmental policy and regulation from hazard-based to risk-based approaches. This is partly due to the recognition that for many environmental issues a level of zero risk is unobtainable or simply not necessary for human and environmental protection and that a certain level of risk in a given scenario is deemed “acceptable” after considering the benefits.

Risk assessment is the procedure in which the risks posed by inherent hazards involved in processes or situations are estimated either quantitatively or qualitatively. In the life cycle of a chemical for instance, risks can arise during manufacture, distribution, in use, or the disposal process. Risk assessment of the chemical involves identification of the inherent hazards at every stage and an estimation of the risks posed by these hazards. Risk is estimated by incorporating a measure of the likelihood of the hazard actually causing harm and a measure of the severity of harm in terms of the consequences to people or the environment.

Risk assessments vary widely in scope and application. Some look at single risks in a range of exposure scenarios such as the IPCS Environmental Health Criteria Document series, others are site-specific and look at the range of risks posed by an installation.

In broad terms risk assessments are carried out to examine the effects of an agent on humans (Health Risk Assessment) and ecosystems (Ecological Risk Assessment). Environmental Risk Assessment (ERA) is the examination of risks resulting from technology that threaten ecosystems, animals and people. It includes human health risk assessments, ecological or ecotoxicological risk assessments, and specific industrial applications of risk assessment that examine end-points in people, biota or ecosystems.

Many organizations are now actively involved in ERA, developing methodologies and techniques to improve this environmental management tool. Such organisations include OECD, WHO and ECETOC. One of the major difficulties concerning the use of risk assessment is the availability of data and the data that are available are often loaded with uncertainty.

The risk assessment may include an evaluation of what the risks mean in practice to those effected. This will depend heavily on how the risk is perceived. Risk perception involves peoples' beliefs, attitudes, judgements and feelings, as well as the wider social or cultural values that people adopt towards hazards and their benefits. The way in which people perceive risk is vital in the process of assessing and managing risk. Risk perception will be a major determinant in whether a risk is deemed to be "acceptable" and whether the risk management measures imposed are seen to resolve the problem.

Risk assessment is carried out to enable a risk management decision to be made. It has been argued that the scientific risk assessment process should be separated from the policy risk management process but it is now widely recognised that this is not possible. The two are intimately linked.

Risk management is the decision-making process through which choices can be made between a range of options that achieve the "required outcome". The "required outcome" may be specified by legislation using environmental standards, may be determined by a formalized risk–cost–benefit analysis or may be determined by another process for instance "industry norms" or "good practice". It should result in risks being reduced to an "acceptable" level within the constraints of the available resources.

Risks can be managed in many ways. They can be eliminated, transferred, retained or reduced. Risk reduction activities reduce the risk to an "acceptable" level, derived after taking into account a selection of factors such as government policy, industry norms, and economic, social and cultural factors.

It is important to note that although risk assessment is used extensively in environmental policy and regulation it is not without controversy. This is also true for risk management.

2. BIOGEOCHEMICAL APPROACHES TO ENVIRONMENTAL RISK ASSESSMENT

It is well known that biogeochemical cycling is a universal feature of the biosphere, which provides its sustainability against anthropogenic loads, including acid forming compounds. Using biogeochemical principles, the concept of *critical loads* (CL) has been firstly developed in order to calculate the deposition levels at which effects of acidifying air pollutants start to occur. A UN/ECE (United Nations/Economic Committee of Europe) working Group on Sulfur and Nitrogen Oxides under Long-Range Transboundary Air Pollution (LRTAP) Convention has defined the critical load on an ecosystem as: "*A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge*" (Nilsson and Grennfelt, 1988). These critical load values may be also characterized as "*the maximum input of pollutants (sulfur, nitrogen, heavy metals, POPs, etc.), which will not introduce harmful alterations in biogeochemical structure and function of ecosystems in the long-term, i.e., 50–100 years*" (Bashkin, 1999).

The term *critical load* refers only to the deposition of pollutants. Threshold gaseous concentration exposures are termed *critical levels* and are defined as "*concentrations in the atmosphere above which direct adverse effects on receptors such as plants, ecosystems or materials, may occur according to present knowledge*".

Correspondingly, transboundary, regional or local assessments of critical loads are of concern for optimizing abatement strategy for emission of polutants and their transport (Figure 1).

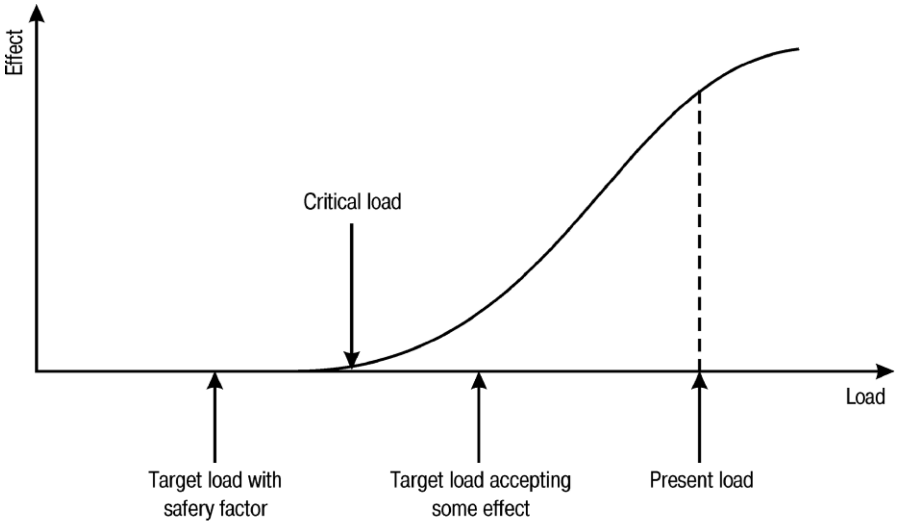

Figure 1. Illustration of critical load and target load concepts.

The critical load concept is intended to achieve the maximum economic benefit from the reduction of pollutant emissions since it takes into account the estimates of differing sensitivity of various ecosystems to acid deposition. Thus, this concept is considered to be an alternative to the more expensive BAT (Best Available Technologies) concept (Posch et al., 1996). Critical load calculations and mapping allow the creation of ecological–economic optimization models with a corresponding assessment of minimum financial investments for achieving maximum environmental protection.

In accordance with the above-mentioned definition, a critical load is an indicator for sustainability of an ecosystem, in that it provides a value for the maximum permissible load of a pollutant at which risk of damage to the biogeochemical cycling and structure of ecosystem is reduced. By measuring or estimating certain links of biogeochemical cycles of sulfur, nitrogen, base cations, heavy metals, various organic species and some other relevant elements, sensitivity both biogeochemical cycling and ecosystem structure as a whole to pollutant inputs can be calculated, and a "critical load of pollutant", or the level of input, which affects the sustainability of biogeochemical cycling in the ecosystem, can be identified.

3. INTEGRATION OF RISK ASSESSMENT AND ENVIRONMENTAL IMPACT ASSESSMENT FOR IMPROVED TREATMENT OF ECOLOGICAL IMPLICATIONS

EIA is a process of systematic analysis and evaluation of environmental impacts of planned activities and using the results of this analysis in planning, authorizing and implementation of these activities. Incorporation of environmental considerations into project planning and decision-making has become a response to growing public concern of potential environmental implications of economic activities. Over the last decades EIA has become a legally defined environmental management tool implemented in more than 100 countries worldwide (Canter, 1996).

A generic model of the EIA process includes such distinct stages as screening, scoping, impact prediction and evaluation, mitigation, reporting, decision-making, and post-project monitoring and evaluation (EIA follow-up) with public participation and consideration of alternatives potentially incorporated at all stages of the process (Wood, 1995; Canter, 1996; Lee and George, 2000).

A special assessment procedure that aims at tackling uncertain consequences of human activities is called risk assessment (RA). The main objective of risk assessment is to use the best available information and knowledge for identifying hazards, estimating the risks and making recommendations for *risk management* (World Bank, 1997).

Traditionally, RA has been focused on threats to humans posed by industrial pollutants. In recent times there has been a shift to other types of hazards and affected objects (Carpenter, 1996). Ecological risk assessment (EcoRA) has already evolved into separate methodology under the general RA framework.

When applied to a particular site and/or project, RA procedures include several generic steps such as *hazard identification, hazard assessment, risk estimation* and *risk evaluation*.

Often contrasted in conceptual terms, EIA and RA have a common ultimate goal — "the rational reform of policy-making" (Andrews 1990). Both assessment tools are intended to provide reasoned predictions of possible consequences of planned decisions to facilitate wiser choices among the alternatives. To link risk assessment and impact assessment paradigms one can suggest a definition of *environmental impact* as any change in the level of risk undergone by receptors of concern that are reasonably attributable to a proposed project (Demidova, 2002).

The following reasons for integrating EIA and RA are frequently distinguished. On one hand, it has been presumed that EIA can benefit from utilizing RA approaches, in particular in order to improve the treatment of human health issues and uncertain impacts. It has been argued that RA could make impact prediction and evaluation more rigorous and scientifically defendable. Beyond impact analysis, RA can facilitate analysis of alternatives and impact mitigation strategies. Apart from obvious benefit for impact assessors this would provide for "greater clarity and transparency in decision making" (Eduljee, 1999) and help manage risks at the project implementation stage. On the other hand, the integration might help to institutionalize the RA procedure in the framework of such a widely used decision-support tool as EIA. It may also enhance RA with public participation and consultation elements borrowed from EIA.

Few jurisdictions have mandatory legal provisions for RA application within EIA (e.g., Canada, USA (Smrchek and Zeeman, 1998; Byrd and Cothern, 2000)). There is no universally agreed methodological and procedural framework to integrate RA into EIA and only a limited number of practical recommendations for improvements in the EIA process that would facilitate such integration. Nevertheless, many researchers linked comprehensive impact assessment with using "scientifically based" risk assessment methods (see, e.g., Andrews, 1990; Arquiaga et al., 1992; Canter, 1996; Lackey, 1997).

Moreover, a number of approaches for EIA–RA integration have already been proposed (see, e.g., Arquiaga et al., 1992; NATO/CCMS, 1997; Eduljee, 1999; Poborski, 1999). Most of them follow the widely accepted idea of "embedding" risk assessment into EIA and incorporating RA methods and techniques into EIA methodology; they are organized according to the sequence of generic EIA stages discussed above (see Demidova (2002) for in-depth discussion). A general model for integrating RA into EIA, which summarizes many of them, is presented in Demidova and Cherp (2004).

4. ASSESSMENT OF ECOSYSTEM EFFECTS IN EIA: METHODOLOGICAL PROMISES AND CHALLENGES

Any changes in the environment resulting from the proposed projects including impacts on ecosystems are under the EIA scope. At the same time, the traditional focus of EIA is the quality of environmental media: ambient and indoor air, water, soil parameters of human biophysical environment. According to reviews of EIA practice, potential impacts of proposed developments on biota and natural ecosystems has often been assessed superficially and even neglected (see, e.g., Treweek et al., 1993; Treweek, 1995; Treweek, 1996; Thompson et al., 1997; Byron et al., 2000).

Firstly, this situation can be linked with a relatively strong anthropocentric tradition in environmental management and a utilitarian approach to natural resource use. Since scoping of impacts and differentiating among significant and insignificant impacts at an early stage of the assessment process is among key EIA features, an assessor can potentially overlook the importance of ecosystem change, rank these effects as insignificant and not include them in EIA ToR for detailed investigation.

Secondly, internal complexity of natural systems makes prediction of changes in the ecosystem functioning an extremely difficult task. The higher the natural system, the higher the complexity and lower predictability of its response to influence of stressors. Many existing impact prediction methods (including simulation modeling) imply a number of simplifications that generate high uncertainty, which undermines credibility of the findings. In addition, modeling of processes in living systems (from an organism to an ecosystem) requires collecting comprehensive input datasets. It may take a lot of resources to compile such a database (either by desk or field studies). However, the output of this hard work may be of little value due to high data and/or decision uncertainty. Lack of scientific evidence is a key reason to avoid conducting quantitative assessments of ecological impacts and even considering these issues in EIA.

Meanwhile, failure to quantify ecological impacts is among key shortcomings of ecological impact assessment (Treweek, 1999). In current practice quantification usually stops at defining the level of predicted concentration of pollutants in the environmental media and few assessors go further to assess actual effects on biological receptors—organisms, populations, communities, and ecosystems (Arquiaga et al., 1992; Treweek, 1996, 1999). At the same time many projects, especially greenfield developments, are associated with impacts on the natural ecosystems that are of high significance (e.g., if a protected area is to be potentially affected) that requires rigorous ecological impact assessment.

A number of EIA theorists believe in incorporating formal RA methods into EIA as a way to cope with uncertainties, especially in impact prediction where a formal framework for ecological risk assessment (EcoRA) is already developed. It includes three generic phases: *problem formulation*, *analysis*, and *risk characterization* followed by *risk management.* The analysis phase includes an *exposure assessment* and an *ecological effects assessment* (see, e.g., US EPA (1998)).

Despite rapid development of EcoRA guidance and wide support for the idea of tools integration, ecological risk assessment is rather an exclusion in EIA practice. In fact, the formal risk assessment follows the "bottom–up" approach to assessing ecosystem-level effects. The assessor depends mainly on findings of laboratory toxicity testing that are extrapolated to higher levels of natural system hierarchy (from organisms to communities and even ecosystems) using various factors (Smrchek and Zeeman, 1998). Meanwhile, too many assumptions put a burden of high uncertainty on final quantitative risk estimates. Moreover, ecosystem risk assessments of this type are rather experiments than established practice. High costs and lack of required data are among key reasons for avoiding this approach by practitioners.

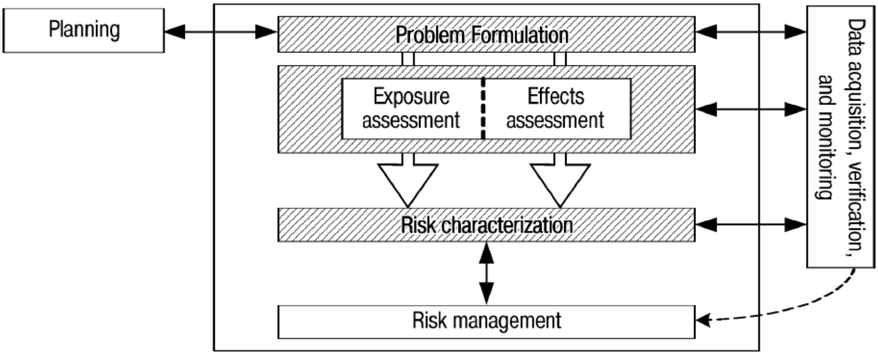

Figure 2. The framework for ecological risk assessment (from U.S. EPA, 1998).

As a result, an EIA practitioner faces considerable difficulties while assessing impacts on ecosystems. On one hand, there are legal requirements to assess fully ecological effects and best practice recommendations to undertake quantitative assessments where possible. On the other hand, many assessors lack tools and techniques to undertake estimations with a high degree of confidence and prove them to be scientifically defensive. Of importance, there are formal RA techniques for tackling the uncertainty[1] (first, data uncertainty) in a clear and explicit manner and its quantification, to increase impact predictability.

As to assessment of ecosystem impacts, the proposed integration model implies using formal EcoRA methodology. The general EcoRA framework suggested by the US Environmental Protection Agency is depicted in Figure 2. It is similar to schemes followed by other counties.

Ecological risk assessment in EIA is to evaluate the probability that adverse ecological effects will occur as a result of exposure to stressors[2] related to a proposed development and the magnitude of these adverse effects (Smrchek and Zeeman, 1998; US EPA, 1998; Demidova, 2002). A lion's share of site-specific EcoRAs were concerned with chemical stressors—industrial chemicals and pesticides.

In formal EcoRA framework three phases of risk analysis are identified: *problem formulation*, *analysis*, and *risk characterization* followed by *risk management.* The analysis phase includes an *exposure assessment* and an *ecological effects assessment* (see Figure 2).

The purpose of *problem formulation* is to define the rationale scope, and feasibility of a planned assessment process. The key implication for EcoRA is a concern that

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[1] The two most widely known are sensitivity analysis and Monte Carlo error analysis (see De Jongh (1990) for in-depth discussion).

[2] *Stressor* is a chemical, physical or biological agent that can cause adverse effects in non-human ecological components ranging from organisms, populations, and communities, to ecosystems (Smrchek and Zeeman, 1998).

something is or will be wrong with the environment. In response to this suspected problem, available information on stressors, effects, and receptors is analyzed to select risk assessment endpoints (assessment and measurement endpoints) and possible conceptual models. In addition, policy and regulatory requirements, available budget and an acceptability level of uncertainty are considered to develop a plan for EcoRA (analogous to EIA ToR) to determine which key factors to explore. The latter is a point where risk assessors and managers should interact closely to ensure the success of assessment process and final decision-making (Byrd and Cothern, 2000; Smrchek and Zeeman, 1998).

In the analysis phase, risk assessors examine exposure to selected stressors and resulting effects in receptors (including ecosystems or environmental compartments). An *exposure assessment* aims at identifying and quantifying stressors that are causing the problem by examining physical and chemical measurements and observing biotic indices. The *ecological effects assessment* links the degree of exposure (e.g., concentrations of contaminants in exposure media) to adverse changes in the state of receptors. First, data on effects of a stressor are categorized using toxicity testing known as the "dose–response" curve. Second, the evidence is weighted if the identified hazard is of practical significance (Smrchek and Zeeman, 1998).

In the final phase of risk analysis—*risk characterization*—one integrates outputs of effects and exposure assessments. Risk is expressed in qualitative or quantitative estimates by comparison with reference values (e.g., hazard quotient). The severity of potential or actual damage should be characterized with the degree of uncertainty of risk estimates. Assumptions, data uncertainties and limitations of analyses are to be described clearly and reflected in the conclusions. The final product is a report that communicates to the affected and interested parties the analysis findings (Byrd and Cothern, 2000).

Risk characterization provides a basis for discussions of *risk management* between risk assessors and risk managers (US EPA 1998). These discussions are held to ensure that results of risk analysis are presented completely and clearly for decision makers, thus allowing any necessary mitigation measures (e.g., monitoring, collecting additional data to reduce uncertainty, etc.).

At present conducting EcoRA is rather an exclusion in EIA practice. The reason is a dramatic discrepancy between the practical needs of project appraisal and features of formal EcoRA methodology.

The formal EcoRA focuses on relatively manageable and observable biological units (individual animals or plants or small populations of these organisms) rather than on the ecosystems. In turn, EIA is mostly concerned with ecosystem protection and with cases of endangered species that can potentially be affected.

In this framework hazard assessment is mainly based on toxicity testing in clean laboratory conditions. Findings of laboratory studies are then extrapolated to higher levels of natural system hierarchy (from organisms to communities and even ecosystems) using various factors (Smrchek and Zeeman, 1998).

For this "bottom–up" approach to ecosystem assessment a methodological framework has been rapidly developed: for a number of chemical and test organisms, substantive databases on species toxicity are already established, safety and uncertainty factors has been determined; testing schemes, exposure models, and algorithms for risk estimation and evaluation has been elaborated.

However, applicability of the bottom–up approach is limited primarily by cost implications: to conduct ecosystem risk assessment following accurately the formal U.S. EPA procedure, an assessor must spent huge amounts of time and money on collecting necessary input data, data processing and interpreting the outputs. Of importance, very specific data are often required that cannot be easily obtained with the help of standard environmental monitoring studies.

The "top–down" approach to ecosystem assessment that considers an elementary ecosystem as a receptor for evaluating toxic effects is currently in the making and remains difficult to carry out. One can identify the following key problem spots in methodology for ecosystem risk assessment:

- selecting appropriate assessment endpoints (at present, a number of them are already proposed including ecosystem integrity, biodiversity, resilience, sustainability (Lohani et al., 1997); however, many of these concepts are hardly applied to practical needs);
- deriving numerical criteria assessing state and effects on ecosystems (measurement endpoints);
- developing predictive tools (firstly biogeochemical models) for describing ecosystems behavior and their validation;
- establishing the assessment benchmarks ("unpolluted" ecosystems of particular type);
- establishing and justifying risk mitigation strategies (defining a threshold values for stressor impacts).

Due to lack of established, user-friendly, and cost effective quantitative approaches to ecosystem risk assessment in EcoRA, in the current EIA practice of project appraisal ecosystem risk assessment (if conducted) is usually comparative or qualitative (see, e.g., Lohani et al. (1997) for in-depth discussion).

Qualitative findings of ecosystem risk assessments are of low utility for risk management. They cannot be compared with quantitative estimates of other risks; this compromises the ability of risk ranking to provide insights to setting priorities. It is particularly difficult to convert them into a format applicable for cost–benefit analysis, which is a key tool that any proponent uses in decision-making on a proposed project.

The authors believe there is an obvious need for improving methodology for assessing ecosystem risks. It seems reasonable to review existing approaches to quantitative assessment of ecological effects, which are not usually included in the EcoRA domain. One promising solution may be the Critical Load and Level (CLL) methodology. Its key features and potential applicability to ecosystem risk assessment are discussed in the following section.

5. CRITICAL LOAD AND LEVEL (CLL) APPROACH FOR ASSESSMENT OF ECOSYSTEM RISKS

As has been mentioned above, the CLL concept was introduced initially for emission control at an international scale under the UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP). From the beginning it has been applied for regional and local assessments of ecological effects (see, e.g., Bashkin et al., 2002; Ignatova, 2003; Priputina and Mikhailov, 2003). The latest advances and trends in developing the CLL concept encouraged researchers to consider if critical loads and their exceedances could be applied in EIA for assessing effects on ecosystems.

Critical loads and levels are measurable quantitative estimates showing the degree of tolerable exposure of receptors to one or more pollutants. According to present knowledge, when this exposure remains below the critical load and level thresholds, significant harmful effects on specified receptors do not occur (Gregor, 2003). They serve as reference points against which pollution levels can be compared and potential risks to environmental components can be estimated.

The most common shortcomings include:

- failure to analyze impacts beyond development site boundaries,
- failure to quantify ecological impacts (vague descriptive predictions are the norm),
- failure to identify or measure cumulative ecological effects,
- failure to mitigate important ecological impacts (proposed mitigation measures are inappropriate and implementation is not mandatory),
- lack of monitoring or follow-up (actual outcomes are not known and no corrective action can be taken, e.g., in the event of mitigation failure).

The critical Load and Level (CLL) concept is an important element for emission control policies in Europe. It has become the internationally agreed scientific underpinning for setting targets in controlling SO_2, NO_x, and NH_3 emissions; development of critical loads and levels and similar pollution abatement strategies for heavy metals and persistent organic pollutants (POPs) is currently in the making (Bashkin, 2002).

Initially, the United Nations Economic Commission for Europe (UNECE) introduced the CLL approach into the control of transboundary air pollution under the Convention on Long-Range Transboundary Air Pollution (CLRTAP). In 1994, critical loads of acidity served as inputs to the second Sulphur Protocol. More recently, European critical load maps were central to the development of the Gothenburg Protocol on acidification, eutrophication and ground level ozone adopted by the Executive Body of the UNECE CLRTAP in November 1999. Critical load calculating and mapping has been currently undertaken worldwide at national levels including countries, which are not bound with CLRTAP obligations, e.g., India, China, Thailand (Bashkin and Park, 1998; Bashkin, 2002, 2003; Satsangi et al., 2003; Ye et al., 2002).

Over time, there has been growing interest in defining critical loads at a regional level to define sensitivity of particular areas to inputs of pollutants and to set specific threshold exposure values (see, e.g., Lien et al., 1995; Henriksen et al., 2002; Craenen et al., 2000; Helliwell and Kernan, 2004). Most of the research on critical loads and levels is concentrated in regions sensitive to sulfur and nitrogen pollution to generate input data for mapping critical loads and levels following common methodology developed under the Convention framework.

More and more research publications on critical loads of acidity for specific lakes, their catchments, or forest ecosystems within defined boundaries are appearing. However, local studies to provide comprehensive input data on biogeochemical parameters for CLL estimations are not being undertaken in countries where environmental monitoring network is rare. For example, Bashkin et al. (2002) proposed an approach to defining critical loads and their exceedances of nitrogen, sulfur and heavy metals for ecosystems adjacent to the Yamal-Zapad gas pipeline located in the North of European Russia (see Bashkin et al. (2002), and Chapter 20 of this book). Ignatova (2003) discussed findings of calculating and mapping critical loads and levels of acidifying pollutants for a small catchment and three monitoring sites in Bulgaria. Priputina and Mikhailov (2003) applied the CCL approach to calculating critical loads for heavy metals for forest ecosystems in European Russia.

The latest advances and trends in developing the CLL concept, which has been constantly validated and progressively improved since its international authorization in 1988 (Cresser, 2000), have encouraged the author to consider if critical loads and their exceedances could be used in EIA for assessing effects on ecosystems.

The following strengths of the CLL approach in the context of EcoRA/EIA are summarized below.

Quantitative nature of the CLL approach. Numerical tolerable exposure levels for pollutants of concern are defined to establish quantitative thresholds for risk characterization; therefore the CLL approach provides a basis for quantitative ecosystem risk and damage assessment.

Scope of the CLL approach. Critical loads and levels can be calculated for various specified “sensitive elements of the environment” (UNECE CLRTAP 2004, V-1). However, terrestrial and aquatic ecosystems are most frequently referred to as receptors in this effect-based approach. In addition, specific parts of ecosystems (e.g., populations of most valuable species) or ecosystem characteristics can be defined as receptors as well (UNECE CLRTAP, 2004). Such flexibility and established provisions for ecosystem assessment makes the CLL concept a promising solution for ecosystem risk assessment and a potential substitute for site-specific chemical RA following the bottom–up approach.

CLL approach and ecosystem, risk analysis. This approach provides insights on assessment and measurement endpoints for ecosystem-level EcoRA since it has a set of environmental criteria to detect the state of ecosystems; critical load itself can be treated as a criterion for ecosystem sustainability (Bashkin, 2002). Moreover, one can derive “spatial” ecosystem risk estimates based on the percentage of ecosystems protected/potentially at risk under the current and predicted level of pollutant loads.

CLL approach and EIA baselines studies. While calculating and mapping critical loads, an assessor reviews and systematize most of the data on current state of environment in the site vicinity; the clear and illustrative picture of receptors and their sensitivity to potential impacts is an output of this process.

CLL approach and impact mitigation. Critical loads are particularly useful for elaborating more focused and impact-oriented environmental monitoring programs; mapping critical loads and their exceedances highlights ecosystems (or areas) being damaged by actual or potential pollutant loads giving hints on siting environmental monitoring locations. In turn, critical levels provide a basis for defining maximum permissible emissions to substantiate the development of mitigation measures.

CLL mapping is extremely useful in *communicating* findings of environmental impact studies both for general public and decision-makers.

Input data requirements. Critical loads and levels are estimated with help of biogeochemical models that require a great deal of input data on parameters of biogeochemical turnover and pollutant cycling in ecosystems. Ideally, an assessor should use findings of field studies aimed at measuring all necessary parameters with appropriate extent of accuracy and at appropriate scale. For regions with underdeveloped networks of environmental monitoring (like vast areas of the Russian Federation or China), lack of required data would be a key obstacle for applying CLL within EIA. At the same time, simplified algorithms for CLL calculation have already been elaborated. One of these methods allows for defining critical loads through internal ecosystem characteristics and derived environmental criteria including soil properties, vegetation type, climatic data (Bashkin et al., 1995, see also Chapter 2). Therefore, an assessor is able to select a CL algorithm among those available bearing in mind input data availability (both empirical, modeled, and literature data) and selected highest degree of uncertainty.

Credibility of the CLL approach is relatively high: today the CLL approach is a widely-known internationally agreed effect-oriented methodology applied worldwide; this aspect is meaningful in communicating research findings on effects and making decisions on risk management.

Progressive update and improvement. Even those who criticize the theoretical soundness of this approach (Skeffington, 1999; Cresser, 2000) acknowledge efforts to validate and improve the CLL concept for increasing degree of confidence of critical loads and levels. UNECE CLRTAP provided an organizational and scientific framework for CLL elaboration having established a program dealing with collecting input data for the CLL calculation (EMEP), and a number of programs under the Working Group of Effects (WGE) focused on processing collected data while calculating CLL for specific receptors (forest ecosystems, aquatic ecosystems, human health, materials) as well as respective International Cooperative Programs (ICPs). In addition, there are ICPs engaged in developing methodologies and improving practice of mapping and modeling and environmental monitoring (Gregor, 2003). The recent trend in developing CLL methodology is introducing a dynamic approach into modeling (see Chapter 6 of Modelling and Mapping Manual (2004) for details).

Usability of CLL. There are plenty of practical guidelines on calculating critical loads and levels including the constantly updated Manual on Methodologies and Criteria for Modeling and Mapping Critical Loads & Levels and Air Pollution Effects, Risks and Trends (Modelling and Mapping Manual, 2004)[3]. Moreover, many research groups engaged in biogeochemical model development make them available as "freeware". Annual reports published by the National Focal Centers of the LRTAP Convention as provides insights on methodologies and partially input data for the CLL calculations.

The key shortcoming of the CLL approach from an EIA practitioner's perspective is data uncertainty—a "sore subject" for any predictive exercise. This is especially true for a simplified algorithm for critical load calculation (see above). Both assessors and reviewers will ask the following questions:

- Do critical loads really protect ecosystem health?
- Do applied models provide scientifically defensive results?
- Are current models capable of acceptive relevant data?

The uncertainty analysis that is a part of formal EcoRA methodology is designed to ensure adequate estimation of ecological effects based on a state-of-the-art scientific basis. Moreover, if applied on a local scale for site-specific assessments, with the use of empirical input data as biogeochemical parameters, the CLL approach is likely to provide results with a higher degree of confidence than the formal EcoRA model.

In the authors' opinion, even if imperfect, the CLL approach is preferable to apply for ecosystem risk assessment than a qualitative EcoRA based mainly on expert judgment.

In response to the need for more consistent treatment of ecological effects resulting from development projects, the current paper proposes a structured framework for introducing the CLL concept as an approach to ecosystem risk assessment into EIA. The model of the "integrated" process depicted in Figure 3 represents the widely accepted idea of "embedding" risk assessment into EIA (Arquiaga et al., 1992; NATO/CCMS 1997; Poborski, 1999; Demidova and Cherp, 2004). It is organized according to the sequence of generic EIA stages: *screening, scoping, impact prediction and evaluation, mitigation, reporting, decision-making*, and *post-project monitoring and evaluation (EIA follow-up)* with *public participation* and *consideration of alternatives* potentially incorporated at all stages of the process (Wood, 1995; Canter, 1996; Lee and George, 2000). The CLL methodology is considered as a quantitative approach to assessing ecological effects. Proposed CLL inputs into the EIA process are discussed below.

In the proposed model project, appraisal starts with addressing two questions at the screening stage:

- Is EIA necessary? and
- Is EcoRA within EIA necessary?

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[3] The Mapping Manual is available via Internet at www.icpmodelling.org.

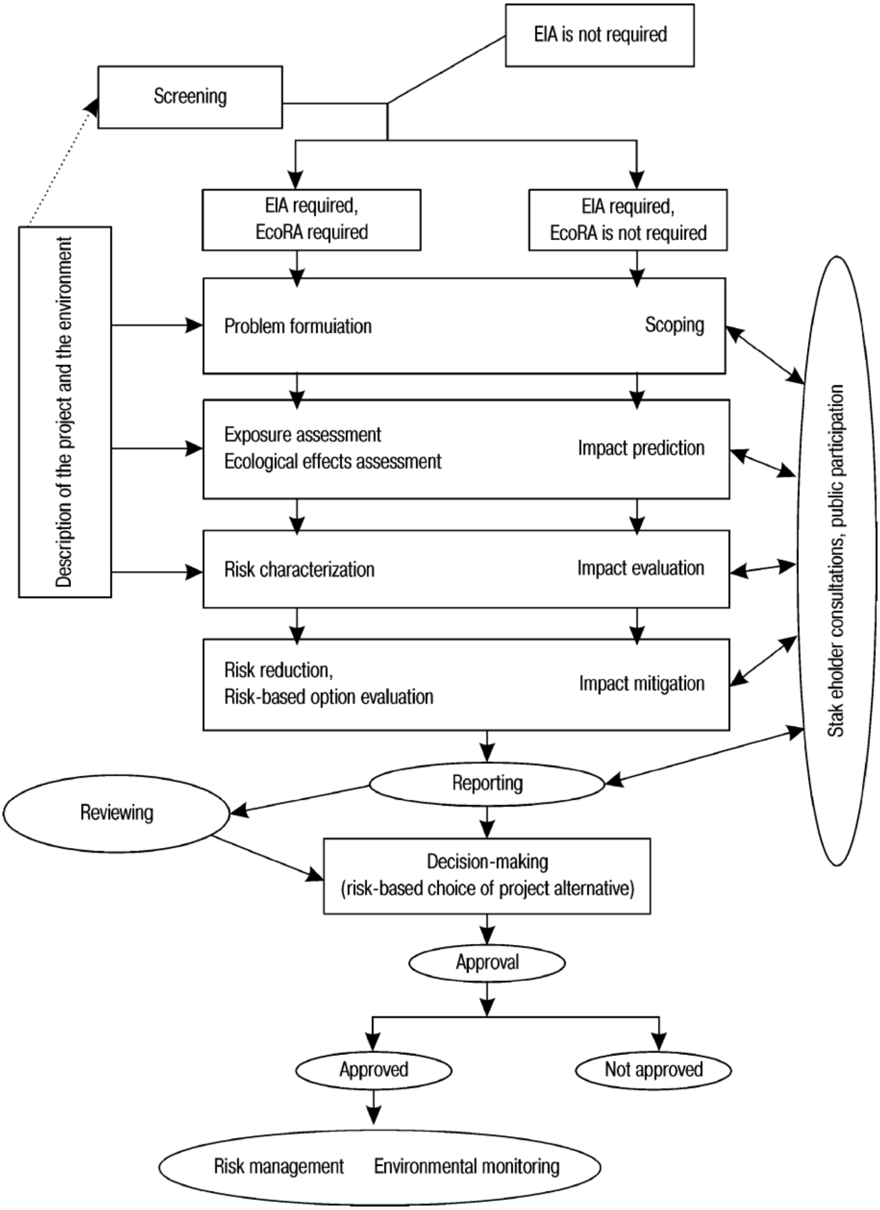


Figure 3. The model for assessment of ecosystem risks in the EIA for projects with significant ecological implications.

It is the responsibility of the appointed environmental consultants to undertake preliminary investigations and decide if a proposed development may result in significant ecological effects. Data on "risk agents" including ecosystem stressors associated with the project and their potential impacts on the environment underpin screening decisions.

Scoping should include defining project alternatives, compiling the list of project impacts, which should be subject to comprehensive impact assessment and planning the further steps of the assessment process. In the formal EcoRA framework this step is related to problem formulation. A separate task of this stage is to select methods and procedures for dealing with particular impacts. For ecosystem effects available information on stressors, effects, and receptors is analyzed to define risk assessment endpoints (assessment and measurement endpoints) and possible conceptual models. In addition, policy and regulatory requirements, available budget and an acceptable level of uncertainty are considered in developing a plan for EcoRA. Here the assessment team may consider applicability of the CLL concept to project ecological effects and develop a plan of specific studies for calculating and mapping critical loads. The outcome of the scoping is to be an EIA Terms of Reference (ToR) referring to all abovementioned issues.

The next step is impact prediction that requires detailed quantitative information about the sources of risk agents, exposure models, the receptors and possible changes in the state of these receptors caused by the defined agents. If the CLL concept was selected for assessment ecosystem effects it should firstly be utilized for impact baseline studies or assessing the "do-nothing" scenario. In this context CLL calculation includes the following steps (Bashkin, 2002):

- characterizing receptors that are potentially affected by the proposed development,
- defining environmental quality criteria,
- collecting input data for CLL calculations,
- calculating critical loads (CLs),
- comparing CLs with actual loads to calculate the exceedances.

When the environmental baseline is established one can proceed with predicting the magnitude of potential impacts onto receptors at risk for *exposure assessment* in EcoRA terms. This includes:

- quantifying emissions of pollutants of concern,
- modeling their transport in the environmental media,
- estimating the predicted exposure levels,
- estimating predicted loads.

Under the CLL approach, *ecosystem effect assessment* means comparing critical loads with predicted loads of pollutants. Of importance, this may be limited to an ecosystem as a whole without further evaluating adverse effects on specific ecosystem components. CL mapping with help of GIS is especially useful for this purpose.

Impact prediction should cover all project alternatives selected at scoping (either spatial or technological) and project phases (construction, operation, closure and post-closure are the main subdivisions). Moreover, exposure assessment should cover both normal operation and accidental conditions.

Significance of the predicted impacts should be assessed in the process of impact evaluation or interpretation. At this stage the health risk estimates (quantitative and qualitative) are analyzed in terms of their acceptability against relevant regulatory and/or technical criteria: environmental quality standards or exposure limits.

Critical load exceedances may serve as the basis for interpreting ecological impacts as ecological risks (or rather changes in the level of current risk to "ecosystem health"). This would refer to the process of ecological risk characterization.

There are a number of approaches to measuring risks depending on assessment and measurement endpoints selected. At ecosystem level, one can propose a percentage of the affected area with CLs exceeded as an acceptable quantitative parameter for ecosystem risk magnitude. In pristine areas, actual state of the environment may be taken as a reference point for risk characterization.

As to risk significance, the degree of alteration in the current environment should be amended with qualitative and semi-qualitative criteria. Ecological impact significance should be considered in terms of:

- ecosystem resilience to particular impacts,
- principal reversibility of potential ecosystem damage,
- threats to valuable ecosystem components, etc.

The estimation of accuracy of quantitative predictions and the degree of uncertainty of the assessment findings should be attempted as well.

The results of impact prediction and evaluation are used for designing impact mitigation measures that aim to prevent or reduce the adverse effects associated with the projects and restore or compensate the predicted damage to the environment. Impact mitigation should firstly involve risk reduction measures: (1) control of the source of risk agents; (2) control of the exposure; (3) administrative/managerial improvements; (4) risk communication allowing for more comprehensive risk perception. The selection of appropriate mitigation measured would benefit from using risk–benefit analysis (with formal quantification of residual risks for every option if applicable).

Following the logic of the CLL approach, impact mitigation in EIA is to derive critical limits of exposure (concentrations of pollutants in exposure media) and based on these values calculating maximum permissible emissions that ecosystems in the site vicinity would sustain during the life-time of the proposed facility. Therefore, any technology that allows for not exceeding CLs for potentially affected ecosystems should be acceptable from the environmental viewpoint, not exclusively the Best Available Technology (BAT) as often recommended.

6. UNCERTAINTY IN IRA AND ERA CALCULATIONS

One can identify two major categories of uncertainty in EIA: data (scientific) uncertainty inherited in input data (e.g., incomplete or irrelevant baseline information, project characteristics, the misidentification of sources of impacts, as well as secondary, and cumulative impacts) and in impact prediction based on these data (lack of scientific evidence on the nature of affected objects and impacts, the misidentification of source–pathway–receptor relationships, model errors, misuse of proxy data from the analogous contexts); and decision (societal) uncertainty resulting from, e.g., inadequate scoping of impacts, imperfection of impact evaluation (e.g., insufficient provisions for public participation), “human factor” in formal decision-making (e.g., subjectivity, bias, any kind of pressure on a decision-maker), lack of strategic plans and policies and possible implications of nearby developments (Demidova, 2002).

Some consequences of increased pollution of air, water and soil occur abruptly or over a short period of time. Such is the case, for instance, with the outbreak of pollution-induced diseases, or the collapse of an ecosystem as one of its links ceases to perform. Avoiding or preparing for such catastrophes is particularly difficult when occurrence conditions involve uncertainty.

In spite of almost global attraction of the critical load concept, the quantitative assessment of critical load values is connected till now with some uncertainties. The phrase “significant harmful effects” in the definition of critical load is of course susceptible to interpretation, depending on the kind of effects considered and the amount of harm accepted (De Vries and Bakker, 1998a, 1998b). Regarding the effects considered in terrestrial ecosystems, a distinction can be made in effects on:

- soil microorganisms and soil fauna responsible for biogeochemical cycling in soil (e.g., decreased biodiversity);
- vascular plants including crops in agricultural soils and trees in forest soils (e.g., bioproductivity losses);
- terrestrial fauna such as animals and birds (e.g., reproduction decrease);
- human beings as a final consumer in biogeochemical food webs (e.g., increasing migration of heavy metals due to soil acidification with exceeding acceptable human daily intake, etc.).

In aquatic ecosystems, it is necessary to consider the whole biogeochemical structure of these communities and a distinction can be made accounting for the diversity of food webs:

- aquatic and benthic organisms (decreased productivity and biodiversity);
- aquatic plants (e.g., decreased biodiversity, eutrophication);

- human beings who consume fish or drinking water (surface water) contaminated with mobile forms of heavy metals due to acidification processes (e.g., poisoning and death).

7. BENEFITS OF APPLYING CCL IN EIA

Therefore, the CLL concept is a valuable methodology for ecological impact and risk assessment and is easily adjusted to the formal EIA procedure. The proposed framework could be applied to EIAs of development projects with high ecological implications that can potentially affect the environment both on local and regional scales. The model may be applicable to developments that involve releases of acidifying and eutrofying compounds, heavy metals and POPs into the environment in areas with high ecosystem vulnerability and/or pristine areas.

Ecological effects are often treated inadequately in the assessment of environmental impacts of proposed developments, while lack of quantitative ecological impact predictions is mentioned among key drawbacks of the current EIA practice. The idea of integrating RA into EIA for improving the quality of EI studies has been supported by many EIA practitioners. At the same time, formal ecological risk assessment has significant limitations for assessing ecosystems risks related to proposed developments.

To improve addressing ecological implications of human activities, the author has attempted to incorporate the Critical Load and Level (CLL) approach, an established methodology for assessing effects of industrial pollution on ecosystems and their sensitive components, into the EIA process. Benefits of and obstacles to applying that approach to assessing ecosystem effects within EIA were analyzed. Finally, a structured framework for CLL application for ecosystem risk assessment in EIA aimed at integrating three assessment tools was presented and key CLL inputs into impact assessment stages were discussed.

The proposed model of integrated assessment process is suggested for testing in EIAs for development projects with high ecological implications: those associated with releases of pollutants covered by current CLL calculating and mapping methodology and located in areas particularly sensitive to the selected indicator chemicals.

CHAPTER 2

BIOGEOCHEMICAL STRUCTURE OF ECOSYSTEMS

The biogeochemical structure of natural ecosystems resulted from the co-evolution of the geosphere and the biosphere (Degens, 1989; Schlesinger, 1997; Bashkin, 2002). During this co-evolution each elementary geochemical unit (the smallest unit of the Earth's surface organization) has corresponded to a specific ecosystem with regular biogeochemical food webs. In turn, these food webs have been adapted to the specific parameters of migration and accumulation of different chemical species in the biosphere.

1. CHARACTERIZATION OF SOIL-BIOGEOCHEMICAL CONDITIONS IN THE WORLD'S TERRESTRIAL ECOSYSTEMS

The biogeochemical cycling in different ecosystems is to a large extent determined by biota, especially by the primary production of plants and by microbial decomposition. At present we recognize the development of the intensive biogeochemical investigations of a large number of ecosystems in North America, Europe, Asia and South America.

The biogeochemical cycling picture is designed to summarize the circulation features in various components of ecosystems such as soil, surface and ground water, bottom sediments, biota and atmosphere (Figure 1).

Ecosystem and soil regionalization can be a basis for biogeochemical mapping (Fortescue, 1980; Glazovskaya, 1984; Ermakov, 1993). The combination of this mapping with the quantitative assessments of biological, geochemical and hydrochemical turnover gives an opportunity to calculate the rates of biogeochemical cycling and coefficients of biogeochemical uptake, C_{b}, for different ecosystems (Bashkin, 2002). In addition to the coefficient of biogeochemical uptake, we can also apply the active temperature, C_{t}, and relative biogeochemical, C_{br}, coefficients. The application of these coefficients for the characterization of soil-biogeochemical conditions in various ecosystems is based on the following hypothesis:

(a) For northern areas the real duration of any processes (biochemical, microbiological, geochemical, biogeochemical) must be taken into account because they are depressed annually for 6–10 months and the influence of acid forming compounds,

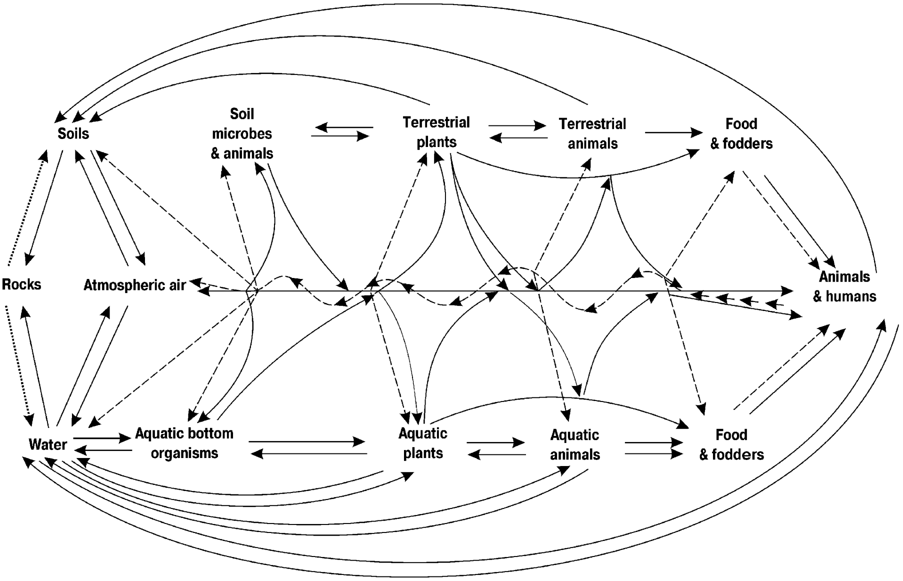


Figure 1. The general scheme of biogeochemical food webs in the terrestrial ecosystems.

as well as any other pollutant, occurs during summer. A process duration term has been derived as the active temperature coefficient, C_t, which is the duration of active temperatures >5°C relative to the total sum.

(b) The relative biogeochemical, C_{br}, coefficient is the multiplication of the first two coefficients. This may characterize the influence of temperature on the rates of biogeochemical cycling in various ecosystems. The relative biogeochemical, C_{br}, coefficient is applied as a correction to C_b values.

Table 1 shows the combinations of soil-biogeochemical and temperature conditions in various geographical regions of the World. The given combination of factors is represented by ecosystem types, FAO main soil types, biogeochemical, C_b, active temperature, C_t, and relative biogeochemical, C_{br}, coefficients. The subdivision of ecosystem types is based on various parameters, including vegetation and soil types, and main climate characteristics like temperature and ratio of precipitation-to-evapotranspiration.

The corresponding values of active temperature coefficients ranged in accordance with the main climatic belts are shown in Table 2.

The values of C_{br} for each geographical area were ranged to determine the type of biogeochemical cycling and these ranks are shown in Table 3. Five types of biogeochemical cycling are divided: very intensive, intensive, moderate, depressive and very depressive.

Using the above-mentioned approaches, we may describe the peculiarities of biogeochemical structure for the main global ecosystems in various continents. Detailed

Table 1. The values of biogeochemical cycling (C_b), active temperature (C_t) and relative biogeochemival (C_{br}) coefficients in various soil-ecosystem geographical regions of the World (Bashkin and Kozlov, 1999).

Ecosystems	Main FAO soil types	Geographical region	C_b	C_t	C_{br}
Arctic Deserts and Primitive Tundra	Litosols, Regosols	North American	10.0	0.06	0.6
		Eurasian	10.0	0.06	0.6
Tundra	Cryic Gleysols, Histosols, Humic Podzols	North American	18.0	0.15	2.7
		Eurasian	18.0	0.15	2.7
Boreal Taiga Forest	Podzols, Podsoluvisols, Spodi-Distric, Cambisols, Albi-Gleyic Luvisols, Gelic and Distric Histosols, Rendzinas and Gelic Rendzinas, Andosols, Gleysols	Alaskan-Cordillera	10.0	0.28	4.2
		Laurentian	8.5	0.35	3.0
		North Atlantic	5.5	0.55	3.0
		North European	8.0	0.45	3.6
		European–West-Siberian	8.5	0.35	3.0
		North Siberian	9.5	0.25	2.4
		Central Siberian	9.3	0.30	2.8
		East Siberian	7.5	0.20	1.5
		Kamchatka–Aleutian	5.0	0.25	1.7
Taiga Meadow-Steppe	Planosols	Central Yakutian	10.0	0.35	3.5
		Central Canadian	10.0	0.32	3.2

(*Conti.*)

Table 1. (Continued)

Ecosystems	Main FAO soil types	Geographical region	C_b	C_t	C_{br}
Subboreal Forest	Podzols, Dystric and Eutric Cambisols, Umbric Leptosols, Podsoluvisols	Eastern North American	2.0	0.65	1.3
		West European	1.5	0.83	1.2
		East European	2.0	0.60	1.2
		Hercian Alpine	2.5	0.72	1.8
		East Asian	2.6	0.67	1.7
		East Chinese	1.5	0.81	1.2
		Coastal Pacific	1.6	0.67	1.1
		New Zealand	1.2	0.78	0.9
		South Chilean	1.2	0.75	0.9
Forest Meadow Steppe	Luvic	Carpathian–North Caucasian	1.2	0.75	0.9
	Fhaeozems, Cambisols, Chernozems	Central Russian	1.4	0.65	0.7
Steppe		West Siberian	1.5	0.47	0.8
		South Siberian	2.0	0.42	1.0
		Amur–Manchurian	1.5	0.65	0.8
		Central Cordillera	1.1	0.70	0.8
		South Canadian	1.3	0.60	0.8
		Central Plain	1.1	0.71	0.8

South American Meadow Steppe	Chernozems, Vertisols	Eastern Pampa	0.8	0.95	0.8
Steppe	Chernozems, Kastanozems Solonetzes	European Kazakhstan	0.7	0.57	0.4
		Mongolo–Chinese	0.8	0.61	0.5
		Central Plains	0.7	0.70	0.5
Mountain	Vertisols, Eutric Cambisols	Mediterranean	0.9	0.87	0.8
Depression Forest, Bush and Steppe		North African	0.8	0.95	0.8
		Texas	0.8	0.95	0.8
		South East African	0.9	0.95	0.9
Desert-Steppe and Desert	Xerosols, Regosols, Arenosols, Yermosols, Solonetzes, Solonchaks	Central Asian	0.4	0.70	0.3
		Pamiro–Tibetan	0.6	0.62	0.4
		Middle Asian	0.5	0.77	0.4
		Preasiatic	0.3	0.89	0.3
		Hindukush–Alai	0.4	0.86	0.3
		Tien Shan	0.6	0.60	0.4
		West American	0.4	0.70	0.3
		Mexican–Californian	0.3	0.95	0.3
		Saharan	0.2	1.00	0.2
		Arabian	0.2	1.00	0.2

(*Conti.*)

Table 1. (Continued)

Ecosystems	Main FAO soil types	Geographical region	C_b	C_t	C_{br}
		South African	0.3	0.80	0.3
		Andean	0.4	1.00	0.4
		Patogonian	0.5	0.71	0.4
		Central Australian	0.2	1.00	0.2
Savanna, Tropical Forest	Livi-Plinticic Ferrasols, Luvisols, Vertisols, Subtropical Rendzinas, Ferralitic Cambisols, Nitosols, Ferralitic Arenosols, Subtropical Solonchaks	South Asian	0.3	1.00	0.3
		Caribbean	0.3	1.00	0.3
		Brazilian	0.2	1.00	0.2
		East Brazilian	0.3	1.00	0.3
		Cis–Andean	0.3	0.98	0.3
		Somalian–Yemenian	0.3	1.00	0.3
		Sudan–Guinean	0.4	1.00	0.4
		East African	0.3	1.00	0.3
		Angolo-Zimbabwean	0.3	1.00	0.3
		North Australian	0.2	1.00	0.2
		East Australian	0.3	1.00	0.3
		South Australian	0.4	1.00	0.4
		West Australian	0.3	1.00	0.3

Subtropical and Tropical Wet Forest	Ferrasols, Eutric Subtropical Histosols, Gleyic Subtropical Podzols, Plinthic Gleysols, Nitosols	South East Asian	0.2	1.00	0.2
		Himalayan	0.4	0.80	0.3
		Andean–Equatorial	0.3	1.00	0.3
		Central American	0.1	1.00	0.1
		Malaysian–New Guinean	0.1	1.00	0.1
		Brazilian–Atlantic	0.15	0.98	0.1
		Amazonian	0.1	1.00	0.1
		Congo–Guinean	0.1	1.00	0.1
		South East Latin American	0.1	1.00	0.1
		East Australian	0.1	1.00	0.1

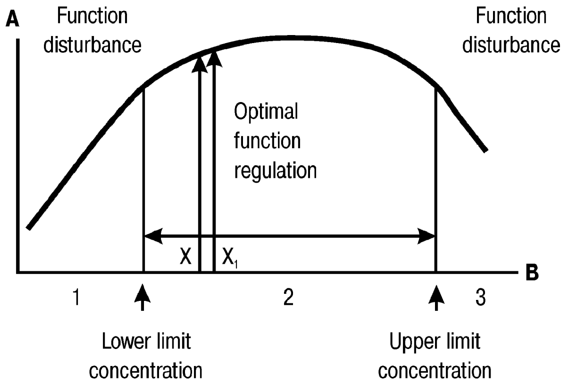


Figure 2. Dependence of biochemical and physiological processes in organisms on the content of essential chemical elements in the biogeochemical food webs as a physiological adaptation curve. 1—lower (deficient) content; 2—optimum content; 3—excessive (upper) content.

descriptions are given in the additional references (see Glazovskaya, 1984; Bailey, 1998; Bashkin, 2002).

2. BIOGEOCHEMICAL CLASSIFICATION AND SIMULATION OF BIOSPHERE ORGANIZATION

2.1. Biogeochemical Classification of the Biosphere

Biogeochemical mapping is the scientific method for understanding biosphere structure. This method is based on the co-evolution of geological and biological parameters of the biosphere and deals with the quantification of the interrelations between biota and the environment in consequent biogeochemical food webs. The fundamentals of biogeochemical mapping have been intensively developed during the twentieth century in Russia and other countries. Biogeochemical mapping combines the definitions of soil zones (Dokuchaev, 1948) and provinces (Prasolov, 1939), geochemical provinces (Fersman, 1931), biogeochemical provinces (Vinogradov, 1938),

Table 2. The ranges attached to temperature regime data to assess the duration of active biogeochemical reactions.

Ranks	Temperature regime	Active temperature coefficient, C_t
1	Arctic	<0.25
2	Boreal	0.26–0.50
3	Sub-boreal	0.51–0.80
4	Mediterranean	0.81–0.99
5	Subtropical and tropical	1.00

Table 3. The ranges attached to biogeochemical cycling data to assess the migration capacity of soil-ecosystem types.

Ranks	Biogeochemical cycling	Biogeochemical cycling coefficient, C_{br}
1	Very intensive	<0.4
2	Intensive	0.5–1.4
3	Moderate	1.5–2.5
4	Depressive	2.6–4.9
5	Very depressive	>5.0

climatic zones (Berg, 1938), geochemical landscapes (Polynov, 1946), biogeocenoses (Sukachev, 1964), ecosystems (Odum, 1975), and geochemical ecology (Kovalsky, 1980).

Using these approaches, biosphere mapping is accomplished over such units as region, sub-region and biogeochemical province.

Regions of biosphere are the first-order units for mapping of the global biosphere. These regions have the geographic features of soil-climate zones and their combinations. However, the predominant parameters are connected with general qualitative and quantitative conditions of biogeochemical food webs (biogeochemical cycles) and prevalent biological reactions of organisms to the natural chemical composition of the environment. These reactions include the alteration of chemical composition of organisms, element and energy exchange, physiological sensitivity to deficient or excessive content of different chemical species, endemic disease, etc. Every region of the biosphere is subdivided into sub-regions of biosphere.

Sub-regions of biosphere are the second-order mapping units. There are two main groups of sub-regions:

1. Sub-regions of biosphere with typical combinations of characteristic features of a given region, such as the limit concentrations of essential elements, its biochemical and physiological relationships and possible biological reactions;
2. Sub-regions of biosphere with features that do not correspond to the general characteristics of the region. These sub-regions occupy areas over the ore deposits, in depressions with no runoff, in zones of active volcanic activity, and territories of anthropogenic pollution.

Biogeochemical provinces are the third order units of biosphere. These are areas whose organisms exhibit permanent characteristic biological reactions to excesses or deficiencies of essential nutrients in the region's biogeochemical food webs. The typical forms of these reactions are endemic diseases. There are two types of biogeochemical provinces:

1. The first type is a natural biogeochemical area where the contents of various chemical species in the food webs do not confirm to the indexes that are characteristic

for the surrounding sub-region of biosphere. The development of these natural biogeochemical provinces occurs over the long-term co-evolution of geosphere and biosphere.

2. The second type is an anthropogenic biogeochemical area where the excessive content of many chemical species is due to industrial or agricultural human activities, like ore explorations, intensive emission of pollutants, application of fertilizers, improper irrigation, etc.

The first step in subdividing the biogeochemical provinces is to establish the existence of a correlation between the frequency of the endemic diseases and excessive or deficient content of essential elements in their respective food webs. However, we should also understand the biochemical and physiological mechanisms that drive the given correlation. Four additional notions should be applied:

(a) *physiological adaptation curve;*

(b) *lower limit concentration;*

(c) *optimum concentration;* and

(d) *upper limit concentration.*

Physiological adaptation curves depict the relationships between physiological and biochemical functions of organisms and the content of essential elements in biogeochemical food webs. The lower limit concentrations are those that induce abnormal development of organisms due to deficiency of essential chemical species, and upper limit concentrations are related to those that cause abnormal development of organisms owing to excessive content of elements. Thus, the limit concentrations show the interval of optimum physiological and biochemical development of organisms in connection with the geochemical conditions (Figure 2).

Physiological and biochemical studies are a necessary step in biogeochemical mapping. Together with geochemical monitoring of essential chemical elements in various environmental media, this can highlight the quantitative aspects of biogeochemical cycling in different biogeochemical provinces. For carrying out biogeochemical mapping we should analyze the content of essential macro-nutrients and trace elements in soil, surface and ground waters, river and lake sediments, vegetation, fodder crops, animals, food, drinking water and human and animal excretions. Using GIS technologies, these data are mapped with various overlapping layers and create a complete map of the biogeochemical province, where the endemic diseases correlates to the deficient or excessive content of essential elements in food webs.

2.2. Methodology of Biogeochemical Cycling Simulation for Biosphere Mapping

The simulation of biogeochemical cycles of chemical species is the basis for modeling the biogeochemical structure of the Earth's ecosystems and biogeochemical mapping.

The general scheme of an algorithm for simulation of biogeochemical cycles of various chemical species is shown in Figure 3.

We will consider this scheme in detail. Each system will be described as a combination of biogeochemical food webs and relationships between them.

System 1. soil-forming rock (I); waters (II); atmosphere (III); soil (IV). This system would not be active without living matter.

System 5. soil-forming rock (I); soil, soil waters and air (IV); soil microbes (bacteria, fungi, actinomicetes, algae) (V); atmospheric air (III, 25). The activity of this system depends on the activity of living soil biota (V). We can refer to Vernadsky (1932) here: "There is no other relation with the environment, i.e., abiotic bodies, except the biogenic migration of atoms, in the living bodies of our planet". During the consideration of the system organization of the biogenic cycle of a chemical species, the relationship between various links (I, II, V) and the subsequent mechanisms of causal dependence are estimated. Most attention should be paid to the biogeochemistry of soil complex compounds, which include the trace metals. The organic substances exuded to the environment by living organisms are of the most importance. The chemical substances from decomposed dead matter play minor role in biogeochemical migration of chemical species. The vital synthesis and excretion of metabolites, bioligands, is the main process of including chemical species from geological rocks into biogeochemical cycle. When trace elements are input into a cell in ionic form, the formation of metal–organic compounds inside the cell is the first step in the biogeochemical cycles. Ferments, metal–ferment complexes, vitamins, and hormones stimulate the cell biochemical processes. After extraction of metabolites into soil, the formation of soil metal–organic complexes proceeds. These complexes are subjected to further biogeochemical migration.

System 7. soil–soil waters, air (IV); atmosphere air (III, 26); roots–rizosphere microbes (VII); microbiological reactions—metabolisms (VII). The root exudates and microbes of the rizosphere provide organic compounds for the extra-cellular synthesis of metal–organic compounds. Plants can selectively uptake these compounds, thus determining the specificity of biogenic migration. This specificity was formulated during plant evolution in specific biogeochemical soil conditions.

System 7, 9, 10. roots–rizosphere (VII); plants (VIII); their biological reactions—metabolism (VIII); soil–soil solution, air (IV); aerosols—atmospheric air (26, 28). In this system, the influence of metal–organic complexes on the plant development and their metabolism is considered. Under deficient or excessive contents of some chemical species, the metabolism may be destroyed (see Figure 2).

System 6. soil–soil solution, air (IV); atmospheric air (III, 27); soil animals (VI); biological reactions of organisms, metabolism, exudates, including microbial exudates (VI); into soils (VI → IV); into waters (II, 4b); into air as aerosols

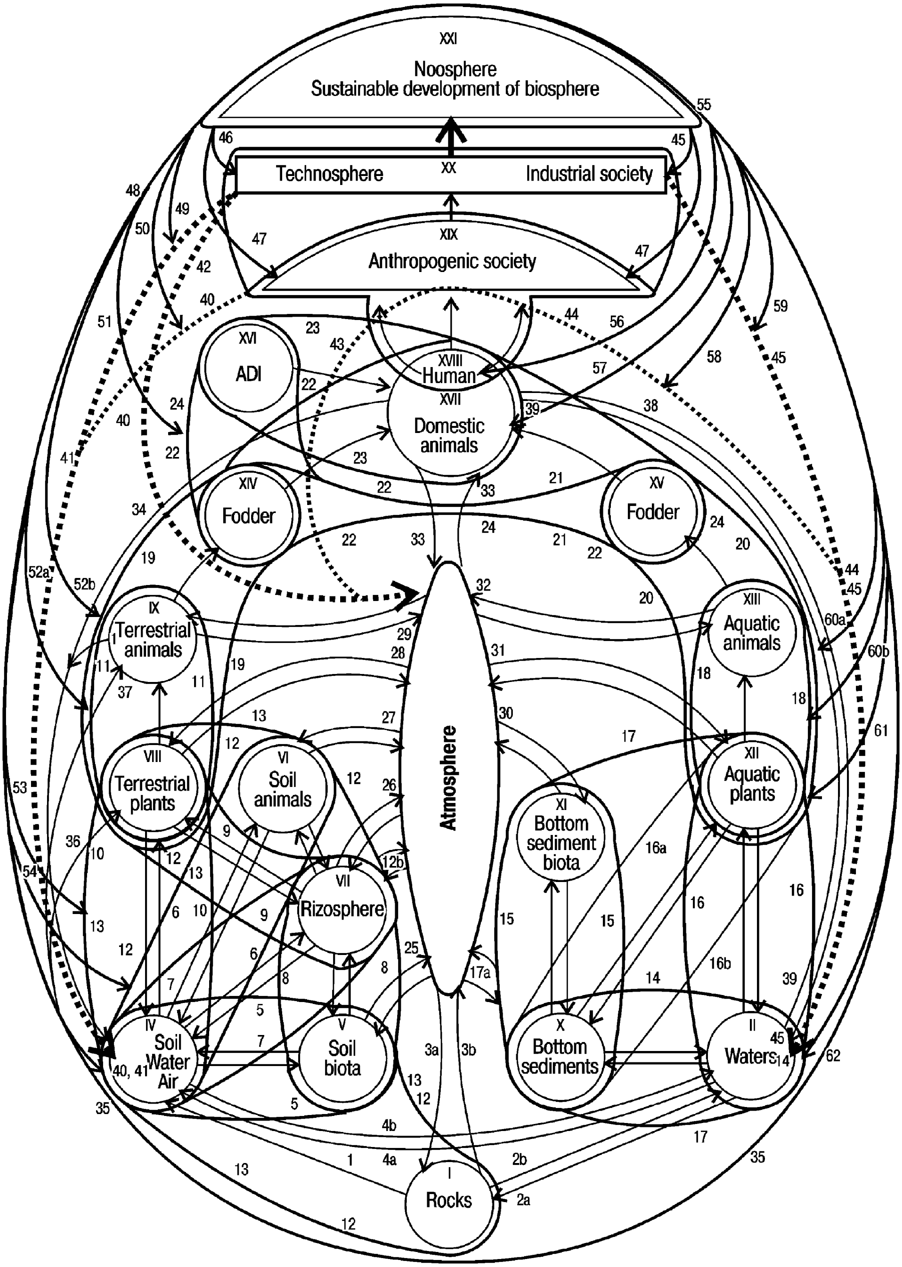


Figure 3. General model of biogeochemical cycles in the Earth's ecosystems. The left part is biogeochemical cycling in terrestrial ecosystems, the right part is aquatic ecosystems and the central part is connected with the atmosphere. The fine solid lines show the biogeochemical food webs (the Latin numbers I–XXI) and directed and reverse relationships between these

(III, 27). This system is very important for biogeochemical mapping but until now it has not been understood quantitatively.

System 12, soil cycle. soil-forming geological rocks (I); soil (dynamic microbial pattern) (IV); soil solution, air (IV); atmospheric air (III) (aerosols—3a, 3b, 12a, 25, 26, 27); soil organisms, their reactions, and metabolism (V, VI, VII). We should consider the content of essential trace elements in the atmospheric aerosols, both gaseous and particulate forms. These aerosols originate both from natural processes, like soil and rock deflation, sea salt formation, forest burning, volcanic eruption and from human activities, like biomass combustion, industrial and transport emissions. The processes are complicated because of the existence of metal absorption from air and desorption (re-emission) from plant leaves. The first process was studied in more detail. But the second process has not been understood quantitatively and even qualitatively at present. The experimental data in vitro with plant leaves showed the emission of radioisotopes of zinc, mercury, copper, manganese and some other metals. The rates of re-emission are very small, however the fluxes may be significant due to much greater size of leaf surface areas in comparison with soil surface area. For instance, the leaf area of alfalfa exceeds the soil surface 85 times, and that for tree leaves is greater by $n \times 10\text{–}10^2$ times. Furthermore, the animals and human beings can also absorb trace metals from air as well as exhale them.

System 10. soil (IV); plants (VIII); their biological reactions, endemic diseases (VIII); atmospheric air, aerosols (III, 28). During consideration of System 7–9–10, we have discussed the influence of the lower and upper limits of concentrations on plant metabolisms, including endemic disease. The study of link (VIII) should start with the correct selection of characteristic plant species. The following steps should include the different research levels, from floristic description up to biochemical metabolism.

System 13. soil–plant cycle: soil-forming geological rocks (I); soil (IV); soil living matter (community of soil organisms) (V, VI, VII); aerosols, atmosphere air (12a, III); plants (VIII); their biological reactions, endemic diseases (VIII). In the complex system 13, the inner relationships and biochemical and biogeochemical mechanisms are shown for natural and agroecosystems. The system 11 and link IX show the ways for interrelation of system 13 with terrestrial animals.

Figure 3. (Continued) webs; the thick solid lines show the primary systems of biogenic cycling organization, usually joining two links of a biogeochemical food web, for instance, 7, 11, 18, etc., and secondary more complicated complexes of primary systems, for instance, counters 12, 13, 19, 17, 20, etc.; fine dotted lines show the stage of initial environmental pollution, for instance, soils, 40, waters, 44, air, 43, due to anthropogenic activities; the thick dotted lines show the distribution of technogenic and agricultural raw materials, goods and wastes in biosphere, for instance, in soils, 41, in air, 42, in waters, 45, leading to the formation of technogenic biogeochemical provinces; the different arrows show the social stages of human activity, from human being up to the noosphere (After Kovalsky, 1981; Bashkin, 2002).

System 11. terrestrial plant (VIII); wild terrestrial animal (IX); aerosols, atmosphere air (28, 29); biological reactions (VIII, IX). System 7–9–10 considers the biological reactions of terrestrial plants on deficient or excessive content of essential elements. System 11 includes the new link of biogeochemical migration, terrestrial animal (IX). The terrestrial plants play the most important role in this biogeochemical food web, linking plant chemical composition with the physiological functions and adaptation of herbivorous animals. The links between herbivorous and carnivorous animals should be also set in the given systems 11. The inner relations between content of elements in fodder crops and their bioconcentration in herbivorous animals are connected with the formation of digestible species in the intestine–stomach tract, penetration through the tissue membranes (suction) with further deposit and participation in metabolism as metal–ferment complexes. The accumulated amount will finely depend on the processes of subsequent extraction from the organisms through kidney (urea), liver (bile), and intestine walls (excrements). These processes depend on both the limit concentrations of elements in animal organism and cellular and tissue metabolic reactions. The development of pathological alterations and endemic diseases are related to the combination of metabolism reaction and element exchange. We should again refer to Figure 2 for the explanation of how to determine the relationships between environmental concentrations and regulatory processes in animal organisms. Between lower and upper limits of concentrations, the adaptation is normal, however the resistance of adaptation increases with an approximation to both limit values. Some organisms of population may already show disturbance of metabolism and development of endemic diseases, but the alterations of the whole population will be statistically significant only when the concentrations of chemical species achieve the limits. Under optimal concentrations, there is no requirement in improving the element intake.

System 19. soil (IV); terrestrial plants (VIII); terrestrial animal (IX); forage with including the technological pre-treatments (XIV). This system shows the dependence of essential element contents from environmental conditions.

System 21. composition and quantity of crops and forage: food and crops of terrestrial origin including technological treatments (XIV); food and crops of aquatic origin including technological treatments (XV). In many countries, the daily intake standards have been set for humans and animals (see Radojevic and Bashkin, 1999).

Sub-systems 21^1. foodstuffs of terrestrial origin (XIV) + foodstuffs of aquatic origin (XV); drinking water (39); balanced essential trace element daily intake for domestic animals (XVI).

System 22^1. foodstuffs of terrestrial origin (XIV) + foodstuffs of aquatic origin (XV); drinking water (39); balanced essential trace element daily intake for humans (XVI).

System 23. balanced intake of various essential elements (XVI); atmosphere air (33); domestic animals—their productivity and biological reactions, endemic diseases (XVII); human, biological reactions (XVIII). The recommendations for balanced essential trace element daily intake for humans are under development in various countries.

System 24^1. feeding of domestic animals, forage (XIV, XV); balanced essential trace element daily intake (XVI); domestic animals (XVII). The additions of requirement trace elements should be applied for forage in various biogeochemical provinces.

System 24^2. human nutrition, foodstuffs (XIV); balanced essential trace element daily intake for humans (XVI); human health (XVIII). Research should be carried out on the endemic diseases induced by deficient or excessive content in the biogeochemical food webs of different essential elements, like N, Cu, Se, I, F, Mo, Sr, Zn, etc.

System 14. geological rocks (1, 2a, 2b); waters (II); bottom sediments (X). The chemical composition and formation of natural waters and bottom sediments depend strongly on the geochemical composition of rocks.

System 15. bottom sediments (X); sediment organisms and their biological reactions (XI). The invertebrates of bottom sediment are important in biogeochemical migration of many chemical species in aquatic ecosystems.

System 17. bottom sediments (X); sediment organisms and their biological reactions (XI); waters (II); aquatic plants and their biological reactions (XII); atmosphere air (17a, 30, 31). The chemical interactions between aquatic and gaseous phases play an extremely important role in the composition of both water and air. These interactions determine the development of aquatic ecosystems. The example of oxygen content in the water is the most characteristic one.

System 18. aquatic plants and their biological reactions, endemic diseases (XII); aquatic animals, including bentos, plankton, bottom sediment invertebrates, fishes, amphibians, mammals, vertebrates, their biological reactions and endemic diseases (VIII). Bioconcentration is the most typical and important consequence of biogeochemical migration of many chemical species in aquatic ecosystems.

System 20. aquatic plants—bentos, plankton, coastal aquatic plants (XII); aquatic animals including bottom sediment invertebrates, fishes, amphibians, mammals, vertebrates, their biological reactions and endemic diseases (VIII); aerosols, atmospheric air (31, 32)—foodstuffs, forages (XV). Human poisoning through consumption of fish and other aquatic foodstuffs with excessive bioaccumulation of pollutants is the most typical example of biogeochemical migration and its consequences.

System XVIII, XIX; human being (XVIII); human society (XIX). development of agriculture, industry and transport (XIX); accumulation of wastes in soil (40), air (43) and natural waters (44). Increasing accumulation of pollutants in the environment. We have to remember here that from a biogeochemical point of view, pollution is the destruction of natural biogeochemical cycles of different elements. For more details see Chapter 8 “Environmental Biogeochemistry” (Bashkin, 2002).

System XX, modern industrialized “throwing out” society. intensive industrial and agricultural development, demographic flush—pollutant inputs into soil (41), atmosphere (42), natural waters (45) up to the exceeding the upper limit concentrations. Development of human and ecosystem endemic diseases on local, regional and global scales. Deforestation, desertification, ozone depletion, biodiversity changes, water resources deterioration, air pollution are only a few examples of the destruction of biogeochemical cycles in the biosphere. These consequences were predicted by Vladimir Vernadsky at the beginning of the 1940s. He suggested a new structure of biosphere and technosphere organization, the noosphere.

System XXI. noosphere—organization of meaningful utilization of the biosphere on the basis of clear understanding of biogeochemical cycling and management of biogeochemical structure. The Kingdom of Intellect: re-structuring, conservation and optimization of all terrestrial ecosystems using the natural structure of biogeochemical turnover. We cite for example the re-cycling of wastes in technological processes and biogeochemical cycles (46, 48, 49, 50, 52a, 52b, 53, 54, 55, 56, 57, 58, 59, 60a, 61, 62), development of regional and global international conventions, like the Montreal Convention on Ozone Layer Conservation, the Geneva Convention on Long-Range Trans-boundary Air Pollution, etc., forwarding the juridical regulation of industrial, agricultural and transport pollution (47), protection of soil and atmosphere (42) as well as natural waters (45) from anthropogenic emissions (41).

Field monitoring and experimental simulation allow the researcher to study the variability of different links of biogeochemical food webs and to carry out the biogeochemical mapping of biosphere in accordance with above-mentioned classification: regions of biosphere, sub-regions of biosphere and biogeochemical provinces.

3. BIOGEOCHEMICAL MAPPING FOR ENVIRONMENTAL RISK ASSESSMENT IN CONTINENTAL, REGIONAL AND LOCAL SCALES

In this section we will present a few examples of different scale biogeochemical mappings on the Eurasian continent. This continent was studied extensively by various Russian and Chinese scientists during the 20th century. We should remember the names of Russian biogeochemists V. Vernadsky, A. Vinogradov, V. Kovaslky, V. Kovda, V. Ermakov, M. Glazovskaya and many others as well as Chinese biogeochemists J. Luo, J. Li, R. Shandxue, J. Hao, etc. The most extensive mapping has been carried out in the Laboratory of Biogeochemistry, which was founded by V. Vernadsky in 1932 and during the 1950s–1980s was led by Prof. V. Kovalsky.

3.1. Methods of Biogeochemical Mapping

Biogeochemical mapping is based on the quantitative characterization of all possible links of biogeochemical food webs, including the chemical composition of soil-forming geological rocks, soils, surface and ground waters, plant species, animals, and physiological excreta of humans, like excretions, urea, and hairs. These food webs include also fodder and foodstuffs. The biochemical products of metabolism of living organisms, activity of ferments and accumulation of chemical elements in various organs should be studied too.

The subsequent paths of biogeochemical migration of elements in local, regional, continental, and global scales can be figured in series of maps with quantitative information on content of chemical elements in rocks, soils, natural waters, plants, forage crops, foodstuffs, in plant and animal organisms. The distribution of biological reactions of people to the environmental conditions should be also shown. The geological, soil, climate, hydrological, and geobotanic maps can be considered as the basics for the complex biogeochemical mapping of the different areas. The resultant maps are the biogeochemical maps at various scales. The application of statistical information on land use, crop and animal productivity, population density, average regional chemical composition of foodstuffs and fodder crops, and medical statistics on endemic diseases, will be very helpful.

These mean that biogeochemical mapping requires a complex team of various researchers in fields of biogeochemistry, geography, soil science, agrochemistry, biochemistry, hydrochemistry, geobotany, zoology, human and veterinary medicine, GIS technology, etc.

According to the purpose required, biogeochemical maps can be drawn for different areas, from a few km^2 (for instance, 20–30 km^2 for the mapping of Mo biogeochemical province in mountain valley in Armenia) up to many thousands of km^2, like boron biogeochemical region in Kazakhstan. The biogeochemical maps can be widespread up to level of continent or the whole global area. The scale of these maps can vary from 1:50,000–1:200,000 for large scale mapping of biogeochemical provinces, to 1:1,000,000 for the mapping of sub-regions of biosphere, and up to 1: 10,000,000–1:15,000,000 for the continental and global scale.

The large scale mapping of biogeochemical provinces and sub-regions is quite expensive and to reduce the work expenses, the key sites and routes should be selected on a basis of careful estimation of available information on soil, geological, geobotanic, hydrological, etc., mapping. Remote sensing approaches are useful for many regions of the World.

The correct selection of chemical elements is very important for successful biogeochemical mapping. The first priority is the mapping of sub-regions and biogeochemical provinces with excessive or deficient content of the chemical species, which are known as physiological and biochemical elements. These elements are N, P, Ca, Mg, Fe, Cu, Co, Zn, Mo, Mn, Sr, I, F, Se, B, and Li. In different biogeochemical provinces, the role of chemical elements will vary. The leading elements should be selected according to the endemic diseases and the full scale monitoring of these elements should be carried out. Other chemical species can be studied in laboratory

Table 4. Description of regions of biosphere, sub-regions of biosphere and biogeochemical provinces in the area of Northern Eurasia.

Chemical elements	Distribution of sub-regions and biogeochemical provinces	Content of elements in biogeochemical food webs	Biological reactions of organisms and endemic diseases
		Taiga forest region of biosphere	
Co deficit	Everywhere	Low content of Co in Podsoluvisols, Podzols, Arenosols and Histosols. The average Co content in plant species is ≤ 5 ppb	The decrease of Co content in tissues; decrease of vitamin B_{12} in liver (tr.—130 ppm), in tissue (tr.—0.05 ppm), in milk (tr.—3 ppm). Synthesis of vitamin B_{12} and protein is weakened. Cobalt-deficiency and B_{12} vitamin-deficiency. The number of animal diseases is decreasing in raw: sheep → cattle → pigs and horses. Low meat and wool productivity and reproduction
Cu deficit	Everywhere, but especially in Histosols	Low content of Cu in Podsoluvisols, Podzols, Arenosols and Histosols. The 30% of forage samples contents $Cu \leq 3$ ppm.	The 3-fold reduction of Cu content in blood, 30–40-fold, in liver; $n \times 10$-fold increase of Fe in liver. The synthesis of oxidation ferments is depressed. The anemia of sheep and cattle was shown
$Cu + Co$ deficit	Especially in Swamp ecosystems	Low content of Cu and Co in Podsoluvisols, Podzols, Arenosols and Histosols. Declining contents of Cu and Co in forage species (Cu from 3 to 0.7 ppm, $Co \leq 5$ ppb)	Depressed synthesis of B_{12} vitamin and oxidation ferments. Cobalt-deficiency and B_{12} vitamin-deficiency complicated by Cu deficiency. The prevalent diseases of sheep and cattle
I deficit	Everywhere	75% of Podsoluvisols, Podzols, Arenosols and Histosols contain $I < 1$ ppm, 40% of natural waters contains I from 3 till 0.06 ppb. Low content of I in food and forage stuffs; 75% of forage crops contain $I < 80$ ppb	Disturbance of I exchange and synthesis of I-containing amino acids and tiroxine by thyroid gland, decreasing protein synthesis. Endemic increase of thyroid gland, endemic goiter. All domestic animals

Co + I deficit	In the Upper Volga regions	Co + I deficit in Podsoluvisols and Arenosols. The reduced content of both I and Co in foodstuffs and forage	The disturbance of I exchange and tiroxine synthesis is decreased by Co deficit. Endemic increase of thyroid gland and endemic goiter is often monitored in sheep and humans
I deficit, Mn excess	In the Middle Volga regions	Decreased I and increased Mn content in Podsoluvisols and Arenosols	Disturbance of I exchange due to its deficit is enhanced by Mn excess. Endemic increase of thyroid gland and endemic goiter
Ca deficit, Sr excess	South of East Siberia and the Tuva region, mainly in river valleys	Deficit of Ca, P, I, Cu, Co, excess of Sr and Ba, reduced Ca:Sr ratio in Podsoluvisols, Arenosols and Histosols. In forage, Ca content is decreased and that of Sr is increased, reducing Ca:Sr ratio	Disturbance of Ca, P, and S exchanges in cartilage tissues; disturbed growth and formation of bones (midget growth). Reducing Ca:Sr ratio in bones. Urov's diseases are often monitored in humans and domestic animals; wild animals suffer in young age
Forest Steppe and Steppe region of biosphere			
Content of chemical elements and their ratios are close to optimum	Phaerozems, Chernozems and Kastanozems. I deficiency is common in river valleys	Content of many nutrients is optimal in soils and forage crops; in some places, the I deficiency of P, K, Mn, and I occurs	Endemic increase of thyroid gland and endemic goiter take place in Phaerozems and Floodplain soils
Dry Steppe, Semi-Desert and Desert region of biosphere			
Cu deficit, excess of Mo and SO_4^{2-}	Pre-Caucasian plain, Caspian low plain, West Siberian Steppe ecosystems	Meadow-Steppe, Eustric Chernozems, Solonchaks, Arenosols	The reducing Cu content in the central nervous systems, depressed function of oxidation ferments and activation of catalase, demielinization of the central nervous systems, disturbance of motion, convulsions. Endemic ataxia. Lamb disease is predominant

(*Conti.*)

Table 4. (Continued)

Chemical elements	Distribution of sub-regions and biogeochemical provinces	Content of elements in biogeochemical food webs	Biological reactions of organisms and endemic diseases
B excess	Aral-Caspian low plain, Kazakhstan	Brunozems, Solonetses, and Solonchaks are enriched in B, up to 280 ppm. The increased content of B in forage species, up to 0.15% by dry weight	Accumulation of B in animal organisms leads to the disturbance of B excretion function of liver, reducing activity of amilase and, partly, of proteinase of the intestine tract in human and sheep. Endemic boron enterites sometimes accomplished by pneumonia. Human, sheep and camel morbidity
$NaNO_3$ excess	Central Asia deserts	Excess of nitrates in forages	Endemic methemoglobinemia
Mountain regions of biosphere			
I, Co, Cu deficit	Various mountain regions: Carpathian, Caucasian, Crimea, Tien-Shan, etc	Mountain soils	Endemic increase of thyroid gland and endemic goiter, Cobalt-deficiency and B_{12} vitamin-deficiency
Azonal sub-regions and biogeochemical provinces, which features differ from the typical features of regions of biosphere			
Co excess	North Azerbaijan	Co enrichment of Kastanozems and Brunozems, and forage pasture species	Excessive synthesis of B_{12} vitamin
Cu excess	South Ural and Bashkortostan	Cu enrichment of Chernozems, Kastanozems of Steppe ecosystems and Podsoluvisols of Forest ecosystems. High Cu content in food and forage stuffs	Excessive accumulation of Cu in all organs. Progressive exhaustion. Endemic anemia and hepatitis. Sheep diseases. Human endemic anemia and hepatitis

Ni excess	South Ural and North Kazakhstan	Kastanozems, Solonetses with Ni-enriched soil-forming rocks. 20-fold increase of Ni content in forage pasture species	Increasing content of Ni in all tissues, especially in epidermal tissues. Excessive accumulation in eye cornea, up to 0.4 ppm. Skin illnesses, Cattle osteodistrophia, lamb and calf diseases
Mo excess, Cu deficit or optimum	Armenia	Increasing Mo:Cu ratio in Mountain Kastanozems and Forest Brunozems. High content of Mo (9 ppm) and low content of Cu (1 ppm) in forage species, high Mo:Cu ratio	Increasing Mo content in tissues, increasing synthesis of xantinoxidase; 2–4-fold level of urine acid. Endemic disturbance of purine exchange in sheep and cattle. Endemic molybdenum gout in humans
Pb excess	Armenia	25-fold increasing Pb content in Mountain Kastanozems and Forest Brunozems (50–1,700 ppm). 7-fold increase of Pb content in plant species (0.5–11.6 ppm). 2–10-fold increase of Pb in foodstuffs	Daily human food intake of Pb is 0.7–1.0 mg/day. Pb accumulation leads to endemic diseases of central nervous system
F excess	Baltic Sea States, Belarus, Moldova, Central Yakutia, Kazakstan	Excessive content of F in natural waters, > 1.0–1.5 ppm. Low content of F in soil and plants	Tooth enamel dystrophy. Fluorosis and spotted teeth of human and animals
F deficit	Biogeochemical provinces in different regions of biosphere	Content of F in natural waters < 0.5–0.7 ppm	Reducing content of F in tooth enamel. Endemic tooth carious in humans and animals
Mn deficit	Biogeochemical provinces in different regions of biosphere	Lowering content of Mn in soils and plant species	Reducing Mn content in bones. Decreasing activity of phosphatase, phosphorilase, and isocitric dehydrogenase
Se deficit	Baltic Sea States, Northwestern Russia, middle Volga regions, south of East Siberia	Low Se content in forage plants, 0.01–0.1 ppm	Depressed glutationperoxidase activity. White-colored muscles

(*Conti.*)

Table 4. (Continued)

Chemical elements	Distribution of sub-regions and biogeochemical provinces	Content of elements in biogeochemical food webs	Biological reactions of organisms and endemic diseases
Se excess	Tuva region	Increasing Se content in sandy Dystrict Kastanozems, up to 2–4 ppm. Increasing Se content in plants, up to 13 ppm	Deformation of hoofs, wool cover losses, hypochromic anemia. Selenium toxicity in sheep and cattle
U excess	Issyk-Kul valley, Kirgizia	Increasing U content in soils, plants, food and fodder stuffs	Morphological alterations in plant species, which accumulate this element
Zn deficit	Foothills of Turkmenistan and Zerafshan ranges, Uzbekistan and Tajikistan	1.5–2 times reducing Zn content in all Serozem sub-types. The plant content is < 7.5 ppm	The reducing Zn content in blood (up to 1.8 ppm) and wool of sheep. Lowering activity of Zn-containing ferments. Endemic parakeratosis
Li excess	Middle and low flow of Zerafshan, Uzbekistan	High content of Li in Serozems and Brunozems. 2.5–3.0-fold increase of Li in plant species	Morphological alterations of plant species
Mn excess	Georgia	Excessive content of Mn in all biogeochemical food webs	Plant endemic diseases
Ni, Mg, Sr excess Co, Mn deficit	South Ural	Unbalanced ratio of essential elements in all biogeochemical food webs	Endemic osteodystrophy in humans and animals
Cu excess	Deserts, Uzbekistan	Serozems	Disturbance of Cu exchange, endemic intero-hemoglobinuria

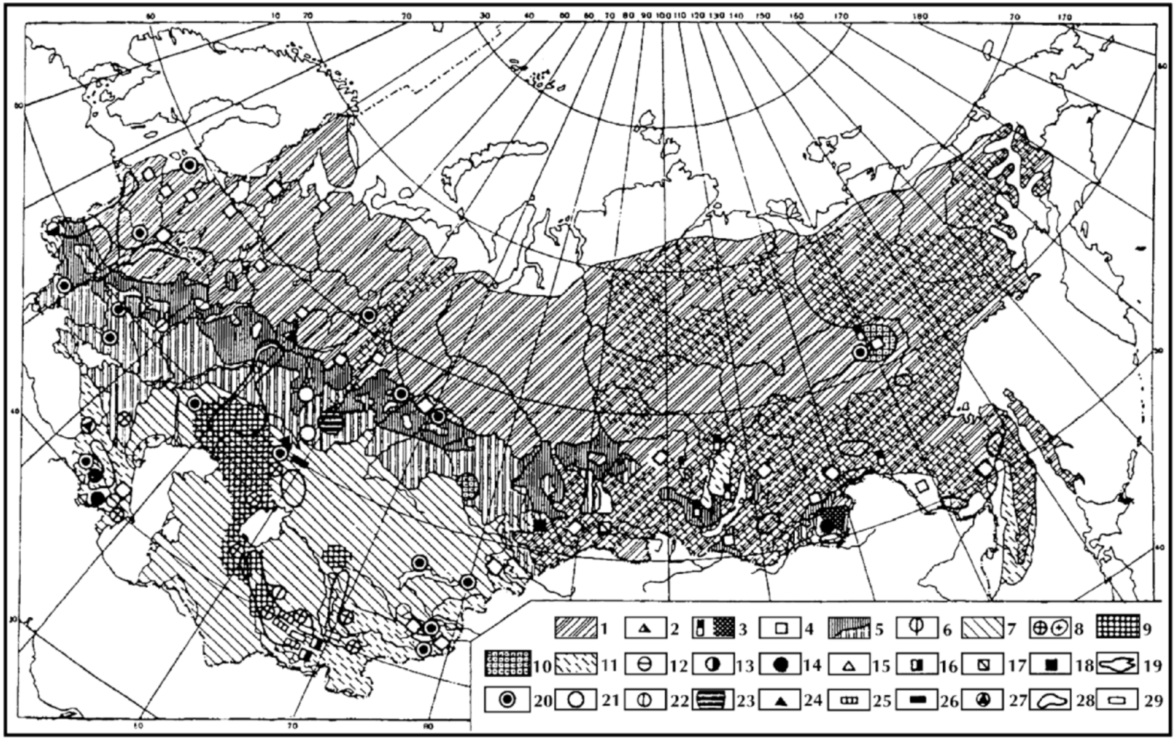


Figure 4. *Biogeochemical mapping of North Eurasia. 1–11. Zonal biogeochemical regions, sub-regions and biogeochemical provinces. 1–4—Taiga Forest region of biosphere. Biogeochemical provinces: 1—Co deficit, Cu deficit, Co + Cu deficit, Ca + P deficit; 2—I + Co deficit; 3—Ca deficit and Sr excess; 4—Se deficit. 5–6—Forest Steppe and Steppe region of biosphere. Biogeochemical provinces: 5—I deficit in floodplain soils; 6—disturbed ratio of Ca:P. 7–10—Dry Steppe, Semi-Desert and Desert region of biosphere. Biogeochemical provinces: 7—Cu deficit; 8—Cu deficit, Mo and sulfate excess; 9—B excess; 10—Co and Cu deficit, Mo and B excess. 11—Mountain region of Biosphere. 12–29. Azonal biogeochemical provinces 12—Co excess; 13—I and Mn deficit; 14—Pb excess; 15—Mo excess; 16—Ca and Sr excess; 17—Se excess; 18—unbalanced Cu:Mo:Pb ratios; 19—U excess; 20—F excess; 21—Cu excess; 22—disturbed Cu exchange; 23—Ni, Mg, Sr excess and Co, Mn deficit; 24—Ni excess; 25—Li excess; 26—Cr excess; 27—Mn excess; 28—F deficit; 29—Zn deficit.*

conditions using simulation approaches. The main attention should be given to the analyses of biochemical mechanisms driven by the given element and its active forms.

Using GIS technology we can compare the different layers of information with spatial distribution of endemic diseases. For subdividing sub-regions of the biosphere into biogeochemical provinces we must study the permanent biological reactions, endemic diseases and the areas with different chemical composition of plant and animal species. We can also foresee the potential areas of technogenic biogeochemical provinces due to chemical pollution of various regions. The comparison of geochemical background with chemical composition of organisms can give sufficient basis for mapping of biogeochemical provinces.

Biogeochemical provinces with pronounced excessive or deficient content of chemical species are strongly correlated with similar variations of biochemical processes in living organisms. This gives rise to various alterations in adaptation of morphological, physiological and biochemical processes. Finally this will lead to the formation of new biological species.

The problems related to biogeochemical mapping are complicated by the technogenic transformation of natural ecosystems and relevant primary biogeochemical provinces and their transition to secondary biogeochemical provinces. During biogeochemical mapping we must analyze carefully the sources of chemical elements to differentiate the natural factors from the anthropogenic ones. For more details see Chapter 8 “Environmental Biogeochemistry” (Bashkin, 2002).

Application of the above-mentioned approaches to biogeochemical mapping will be highlighted below on the examples from North Eurasia.

3.2. Regional Biogeochemical Mapping of North Eurasia

The first-order units of biogeochemical mapping are the regions of the biosphere. In Northern Eurasia, the regions of biosphere represent the differences of chemical macro- and trace elements in soils, plant species and corresponding endemic diseases. These regions are structural parts of the biosphere with a high level of ecosystem organization and similar typical peculiarities of ecosystem development. Furthermore, the regions of the biosphere are subdivided into sub-regions and biogeochemical provinces (Table 4).

On a basis of data, presented in Table 4, a biogeochemical map of Northern Eurasia (the former USSR area) has been created (Figure 4).

CHAPTER 3

BIOGEOCHEMICAL STANDARDS

From the biogeochemical point of view, the environmental pollution is a process of reversible and/or irreversible disturbance of biogeochemical structure of both terrestrial and aquatic ecosystems. To prevent this disturbance, the anthropogenic loads of pollutants must be decreased significantly. There are different approaches in environmental chemistry and ecotoxicology aiming to set various criteria, threshold levels, and standards to control the pollution of various biosphere compartments and decrease the rate of human and animal diseases. These methods are generally based on experimental modeling with various animals and there are many uncertainties in the implication of the results for real environmental conditions.

This chapter deals with the application of biogeochemical standards as the critical loads impacting the reduction of pollutant inputs to terrestrial and aquatic ecosystems.

1. CRITICAL LOAD AS BIOGEOCHEMICAL STANDARDS FOR ACID-FORMING CHEMICAL SPECIES

In accordance with its definition, a critical load is an indicator for sustainability of an ecosystem, in that it provides a value for the maximum permissible load of a pollutant at which risk of damage to the biogeochemical cycling and structure of an ecosystem is reduced. By measuring or estimating certain links of biogeochemical cycles of sulfur, nitrogen, base cations and some other relevant elements, sensitivity of both biogeochemical cycling and ecosystem structure as a whole to acidic deposition and/or eutrophication deposition can be calculated, and a "critical load of acidity", or the level of acidic deposition, which affects the sustainability of biogeochemical cycling in the ecosystem, can be identified, as well as "critical nutrient load", which affects the biodiversity of species within ecosystems. According to the political and economic requirements of the UN/ECE LRTAP Convention protocols for reduction of N and S emissions and deposition, as well as the parameters of subsequent optimizing models, the definitions of critical loads are given separately for sulfur, nitrogen and for total acidity, which is induced by both sulfur and nitrogen compounds. Hence, critical loads (biogeochemical standards) for acidity can be determined as the maximum input of S and N before significant harmful acidifying effects occur. When assessing the individual influences of sulfur and nitrogen, it is necessary to take into account the acidifying effects induced by these elements and the eutrophication effect caused only by nitrogen. In this case, the critical load (biogeochemical standards) for nitrogen can be determined as the maximum input of nitrogen into ecosystem, below which neither significant harmful eutrophication effects nor acidifying effects together with sulfur occur over long-term period (de Vries, 1989, 1994).

1.1. General Approaches for Calculating Critical Loads

In spite of almost global attraction of the critical load concept, the quantitative assessment of critical load values as biogeochemical standards has been accomplished with some uncertainties. The phrase "significant harmful effects" in the definition of critical load is of course susceptible to interpretation, depending on the kind of effects considered and the amount of harm accepted (de Vries and Bakker, 1998a, 1998b). Regarding the effects considered in terrestrial ecosystems, a distinction can be made in effects on:

(i) soil microorganisms and soil fauna responsible for biogeochemical cycling in soil (e.g., decreased biodiversity);

(ii) vascular plants including crops in agricultural soils and trees in forest soils (e.g., bioproductivity losses);

(iii) terrestrial fauna such as animals and birds (e.g., reproduction decrease);

(iv) human beings as a final consumer in biogeochemical food webs (e.g., increasing migration of heavy metals due to soil acidification with exceeding acceptable human daily intake, etc.).

In aquatic ecosystems, it is necessary to consider the whole biogeochemical structure of these communities and a distinction can be made accounting for the diversity of food webs:

(i) aquatic and benthic organisms (decreased productivity and biodiversity);

(ii) aquatic plants (e.g., decreased biodiversity, eutrophication);

(iii) human beings that consume fish or drinking water (surface water) contaminated with mobile forms of heavy metals due to acidification processes (e.g., poisoning and depth).

The possible impact of a certain load on soil and surface water quality can be estimated by determining:

- the difference between actual load and critical load;
- the difference between the steady-state concentration (that will occur, when the actual load is allowed to continue Maximum Permissible Concentration, MPC) and increasing levels of pollutant concentration in soil or surface water under permanent pollutant input.

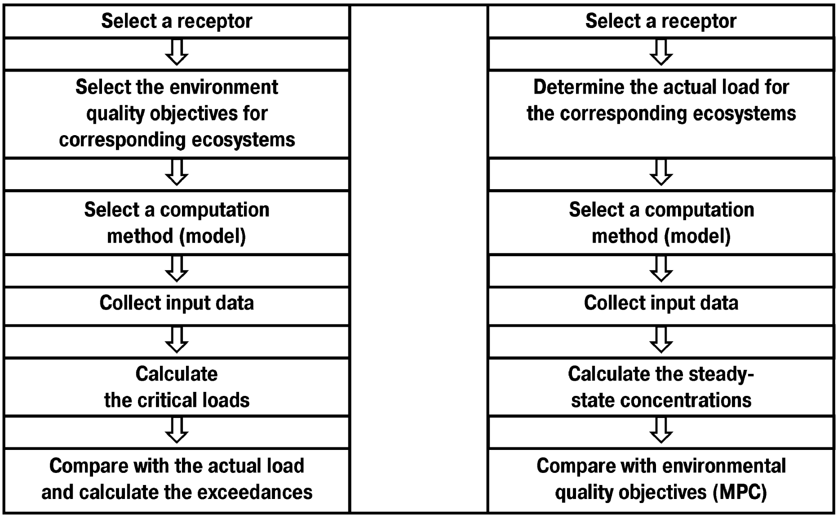


Figure 1. Flowchart for calculating critical loads (left) or steady-state concentrations (right) of acid-forming and eutrophication S and N compounds.

In the first, critical load, approach, the single quality objective is used to calculate a critical load. The second, steady state, allows comparison with various quality objectives. Both approaches, which are the reverse applications of the same model (Figure 1), have their advantages and disadvantages.

One can see that both algorithms are similar, but steady-state approaches based on MPC values do not practically take into account either ecosystem characteristics or their geographic situation. Furthermore, there are many known drawbacks of traditional approaches applying MPC (Bashkin et al., 1993; van de Plassche et al., 1997). Since the steps in the steady-state approach are similar but in reverse order, they will not be further elaborated and only the various steps of the critical load approach are summarized below.

1. *Select a receptor.* A receptor is defined as an ecosystem of interest that is potentially polluted by a certain load of acid forming or eutrophication compounds of sulfur and nitrogen. A receptor is thus characterized as a specific combination of land use (e.g., forest type, agricultural crops), climate, biogeochemical regionalization and soil type or as an aquatic ecosystem, such as a lake, a river or a sea, taking account of their trophical status and hydrochemistry. Regarding terrestrial ecosystems, one should consider information (environmental quality criteria, methods and data) for both agricultural soils (grassland, arable land) and non-agricultural (forest, bush) soils, where the atmospheric deposition is the only input to the system. Similar information has to be collected for aquatic ecosystems.

2. *Select the environmental quality objectives.* Quality objectives should be based on insight into the relation between the chemical status of the soil or the surface water and the response of a biological indicator (an organism or population). According

to the definition, the critical load equals the load that will not cause the irreversible changes in biogeochemical cycling of elements in ecosystems, thus preventing "significant harmful effects on specific sensitive elements of the environment". Consequently, the selection of quality objectives is a step of major importance in deriving a critical load.

3. *Select a computation method (model).* In this context, it is important to make a clear distinction between steady state and dynamic models. Steady-state models are particularly useful to derive critical loads. These models predict the long-range changes in biogeochemical structure of both terrestrial and aquatic ecosystems under the influence of acid deposition such as the weathering rates, base cation depletion, nutrient leaching etc. either in soils or surface waters. Dynamic models are particularly useful to predict time periods before these changes will occur. These models are necessary to determine an optimal emission scenario, based on temporal change of pollutant status.

4. *Collect input data.* This includes soil, vegetation, water (surface and ground), geology, land use, etc. data, influencing acidification and eutrophication processes in the considered ecosystem. For application on a regional scale it also includes the distribution and area of receptor properties (using available digitized information in geographic information systems, GIS).

5. *Calculate the critical load.* This step includes the calculation of critical loads of sulfur, nitrogen and the total acidity in a steady-state situation for the receptors of choice or for all receptors in all cells of EMEP or LoLa grid (150 $\times$ 150 km; 50 $\times$ 50 km; 25 $\times$ 25 km; 1 $\times$ 1°, 10 $\times$ 10$'$, etc.) of a region using a GIS (to produce critical load maps).

6. *Compare with actual load.* The amount by which critical loads are exceeded and the area in which they are exceeded (using a GIS) can be also included in the calculation when the actual loads (for example, atmospheric deposition data in case of forest) are known. Furthermore, these exceedance values are used for ecological-economic optimization scenario of emission reduction.

1.2. Biogeochemical Model Profile for Calculation of Critical Loads of Acidity

The biogeochemical model PROFILE has been developed as a tool for calculation of critical loads on the basis of steady-state principles. The steady-state approach implies the following assumptions:

(a) the magnitude of capacity factors such as mineral abundance and cation exchange capacity is constant;

(b) long-range average values for precipitation, uptake, water requirement and temperature must be used as input;

(c) the effect of occasional variations in input variables such as soil carbon dioxide, nitrification rate and soil moisture content can not be addressed;

(d) the rate of change in soil chemistry over time can not be taken into account.

The application of these assumptions allows the researchers to use the PROFILE model for calculation of critical loads in Europe (Posch et al., 1993, 1997, 1999) and Asia (World Bank, 1994; Shindo et al., 1995; Lin, 1998; Hao et al., 1998; Bashkin and Park, 1998). In spite of visible limitations connected with the numerated assumptions, a run of the PROFILE model can give comparable results for different ecosystems in regional and continental scales.

Since the biogeochemical model PROFILE includes such important characteristics as mineral abundance, another model UPPSALA has been created that allows the researcher to calculate the soil mineralogical composition on the basis of total element content. The combination of these models (PROFILE and UPPSALA) gives the possibility to use existing soil and ecosystem databases for calculating critical loads of acidity in broad-scale regions.

Both ratio of base cations to aluminum, and the aluminum concentrations, are used as indicators for steady-state geochemical and biogeochemical processes. By assigning established critical loads to these indicators (for example, the concentrations of aluminum in soil solution should not exceed 0.2 meq/L and the base cations to aluminum ratio should not be less than 1), it is possible to compute the allowable acidification for each ecosystem. An extensive overview of critical values for the ratio of base cations to aluminum for a large variety of plants and trees can be found in Prof. Sverdrup's papers (for example, Sverdrup et al., 1995; Warfvinge et al., 1992, 1993).

Model Characterization

PROFILE is a biogeochemical model developed specially to calculate the influence of acid depositions on soil as a part of an ecosystem. The sets of chemical and biogeochemical reactions implemented in this model are: (1) soil solution equilibrium, (2) mineral weathering, (3) nitrification and (4) nutrient uptake. Other biogeochemical processes affect soil chemistry via boundary conditions. However, there are many important physical soil processes and site conditions such as convective transport of solutes through the soil profile, the almost total absence of radial water flux (down through the soil profile) in mountain soils, the absence of radial runoff from the profile in soils with permafrost, etc., which are not implemented in the model and have to be taken into account in other ways.

1. *Soil solution equilibrium.* Soil solution equilibrium is based on the quantification of acid-neutralizing capacity, ANC, which has been defined as:

$$[\mathrm{ANC}] = [\mathrm{OH}^-] + [\mathrm{HCO}_3^-] + 2[\mathrm{CO}_3^{2-}] + [\mathrm{R}^-] - [\mathrm{H}^+] - \sum_{m=1}^{3} m\left[\mathrm{Al(OH)}_{3-m}^{m+}\right],$$

where $[\mathrm{R}^-]$ are organic acid anions.

With the ambient CO_2 pressure (4×10^{-4} atm) and no dissolved organic carbon (DOC) present, the ANC attains the value 0 at pH values in the range 4.6–5.6 and may thus attain positive or negative values, alkalinity or acidity, correspondingly. With the other [DOC] and P_{CO_2} values the ANC–pH dependence is much more complicated.

2. *Mineral weathering*. Chemical weathering is calculated on a basis of the equation

$$R_w = \sum_{i=1}^{\text{horizons}} * \sum_{i=1}^{\text{minerals}} \times r_i \times A_{\exp} \times c_i \times q \times z,$$

where r_i is mineral weathering rate for every i mineral (keq/m^2/s),$A_{\exp}$ is exposed mineral surface area (m^2/m^3), c_i is part of i mineral in total mineral mass (%), q is volumetric water content (m^3/m^3), z is soil layer thickness (m).

3. *Nitrification*. The nitrogen reactions in the PROFILE model are very simple, since only nitrification and uptake are included explicitly.

4. *Nutrient uptake*. Nutrient uptake includes base cation uptake (BC_u) and nitrogen uptake (N_u). BC uptake assigns annual average uptake of Ca^{2+}, Mg^{2+} and K^+. The data represent an annual net uptake in keq/ha/yr and storage in stems and branches calculated over rotation. This includes the nutrients in the biomass compartments that are expected to be removed from the site at harvest.

It should be stressed that PROFILE needs the nutrient uptake limited to PROFILE-acceptable layer (0.5–1 m depth) for simplicity, whereas the real nutrient uptake takes place down to the 3–5–7–10 m depth corresponding to the distribution of tree roots. So, the nutrient uptake in a PROFILE-acceptable layer is always less than the whole nutrient uptake. This might be a source of uncertainty in critical load calculations.

5. *Critical leaching of Acid-neutralizing Capacity of soil solution—$ANC_{le(crit)}$.* The second most important output parameter in the calculation of the critical acid load by PROFILE is the ANC in water leached from the soil system. This parameter characterizes the difference between basic and acidic compounds (between base cation and strong acidic anion contents or alternatively between OH^-, HCO_3^-, CO_3^{2-}, R^- and $H^+ + Al^{3+}$ contents) in soil solution. Thus, positive ANC is called alkalinity and the negative ANC is called acidity. Critical ANC (μeq/L) was calculated on the basis of critical molar BC/Al ratio equal to 1. A high amount of cations may alleviate Al toxicity or low cations may aggravate its toxicity. The molar ratio of Ca/Al or (Ca + Mg + K)/Al is an important index to calculate critical loads. Warfvinge and Sverdrup (1992) proposed a critical point of 1.0 for calculating critical loads, expressed as the molar ratio of (Ca + Mg + K)/Al that was mainly from the data of European species. Kohno et al. (1998) have shown also the applicability of this ratio for Asian conditions in the experimental studies with Japanese species and soils. Below BC/Al ratio = 1, irreversible changes in ecosystem functioning can happen.

1.3. Deriving Biogeochemical Parameters for Critical Loads of Acidity

The calculation and mapping of CLs of acidity, sulfur and nitrogen form a basis for assessing the effects of changes in emission and deposition of S and N compounds. So far, these assessments have focused on the relationships between emission reductions of sulfur and nitrogen and the effects of the resulting deposition levels on terrestrial and aquatic ecosystems.

General Models for Critical Load Calculation

Critical loads of sulfur and nitrogen, as well as their exceedances are derived with a set of simple steady-state mass balance (SSMB) equations. The first word indicates that the description of the biogeochemical processes involved is simplified, which is necessary when considering the large-scale application (the whole of Europe or even large individual countries like Russia, Poland or Ukraine) and the lack of adequate input data. The second word of the SSMB acronym indicates that only steady-state conditions are taken into account, and this leads to considerable simplification. These models include the following equations.

The maximum critical load of sulfur, CLmaxS

$$\mathrm{CLmaxS} = \mathrm{BC}_{\mathrm{dep}} - \mathrm{Cl}_{\mathrm{dep}} + \mathrm{BC}_{\mathrm{w}} - \mathrm{BC}_{\mathrm{u}} - \mathrm{ANC}_{\mathrm{le(crit)}}$$

where $\mathrm{BC}_{\mathrm{dep}}$ is base cation deposition, $\mathrm{Cl}_{\mathrm{dep}}$ is correction for sea-salt deposition, BC_{w} is base cation weathering, BC_{u} is base cation uptake by plants, $\mathrm{ANC}_{\mathrm{le(crit)}}$ is critical leaching of acid-neutralizing capacity of soil.

This equation equals the net input of (sea-salt corrected) base cations minus a critical leaching of acid-neutralizing capacity.

The minimum critical load of nitrogen, CLminN

$$\mathrm{CLminN} = \mathrm{N}_{\mathrm{u}} + \mathrm{N}_{\mathrm{i}}$$

where N_{u} is net nitrogen uptake, N_{i} is nitrogen immobilization in soil organic matter.

As long as the deposition of both oxidized and reduced nitrogen species, $\mathrm{N}_{\mathrm{dep}}$, stays below the minimum critical load of nitrogen, i.e.,

$$\mathrm{N}_{\mathrm{dep}} \leq \mathrm{CLminN} = \mathrm{N}_{\mathrm{u}} + \mathrm{N}_{\mathrm{i}}.$$

All deposited N is consumed by sinks of nitrogen (immobilization and uptake), and only in this case CLmaxS is equivalent to a critical load of acidity.

The maximum critical load of nitrogen, CLmaxN

$$\mathrm{CLmaxN} = \mathrm{CLminN} + \mathrm{CLmaxS}/(1 - f_{\mathrm{de}})$$

where f_{de} is the denitrification fraction.

The maximum critical load for nitrogen acidity represents a case of no S deposition. The value of CLmaxN not only takes into account the nitrogen sinks summarized as CLminN, but consider also deposition-dependent denitrification as a denitrification fraction f_{de}. Both sulfur and nitrogen contribute to acidification, but one equivalent of S contributes, in general, more to excess acidity than one equivalent of N, since nitrogen is also an important nutrient, which is deficient in the most natural ecosystems.

Critical load of nutrient nitrogen, CLnutN

$$\mathrm{CLnutN} = \mathrm{CLminN} + \mathrm{N}_{\mathrm{le(acc)}}/(1 - f_{\mathrm{de}})$$

where $\mathrm{N}_{\mathrm{le(acc)}}$ is acceptable leaching of nitrogen from terrestrial ecosystem.

Excess nitrogen deposition contributes not only to acidification, but can also lead to the eutrophication of soils and surface waters.

The CL calculation algorithm is described in detail below.

Critical Load Calculation Algorithm

The quality of CL calculations depends greatly on the available Data Base. These DB should allow the researcher to calculate CL values using the inner ecosystem parameters such as soil type, its chemical and physical characteristics, vegetation type, climate indices, etc. As a basis, the following algorithm is applied (Bashkin, 2002).

The values of sulfur maximal critical loads (CLmaxS) are calculated using the equation:

$$\mathrm{CLmax(S)} = C_{\mathrm{t}} \times (\mathrm{BC}_{\mathrm{w}} - \mathrm{ANC}_{1)}) + (\mathrm{BC}_{\mathrm{dep}} - \mathrm{BC}_{\mathrm{u}}) \tag{1}$$

where C_{t} is the hydrothermal coefficient characterizing the ratio between the sum of $T > 5\ ^{\circ}\mathrm{C}$ and the total annual sum of absolute values of air temperature.

The values of nitrogen minimal critical loads (CLminN) are calculated using the equation:

$$\mathrm{CLmin(N)} = (\mathrm{N}_{\mathrm{i}}^{*} + \mathrm{N}_{\mathrm{u}}^{*}) \times 71.4, \tag{2}$$

where index * means that these values are related to the atmospheric N deposition.

The values of nutrient nitrogen critical loads (CLnutrS) are calculated using the equation:

$$\mathrm{CLnutr(N)} = \mathrm{CLmin(N)} + \mathrm{N}_{1} + \mathrm{N}_{\mathrm{de}}^{*}. \tag{3}$$

For the quantitative estimation of the values of equations (1)–(3), the following approaches are used.

Base cation uptake, BC_u

$$\mathrm{BC_u} = \mathrm{N_u^*} \times \mathrm{N/BC}, \tag{4}$$

where N/BC is the ratio between N and BC in plant biomass. This value depends on soil and vegetation (ecosystem) type.

Base cation weathering, BC_w

$$\mathrm{BC_w} = W_\mathrm{r} \times D, \tag{5}$$

where W_r determines the soil weathering ability, and D is the plant active root depth.

Plant uptake of soil nitrogen, N_u

$$\mathrm{N_u} = (\mathrm{NMC} - \mathrm{N_i} - \mathrm{N_{de}}) \times C_\mathrm{t}, \tag{6}$$

where NMC is nitrogen mineralizing capacity (Bashkin, 1987), $\mathrm{N_i}$ is soil N immobilization, $\mathrm{N_{de}}$ is soil N denitrification.

Plant uptake of atmospheric deposition nitrogen, N_u^*

$$\mathrm{N_u^*} = \mathrm{N_{upt}} - \mathrm{N_u}, \tag{7}$$

where $\mathrm{N_{upt}}$ is the annual plant uptake, which is calculated based on the condition:

$$N_\mathrm{upt} = K_1 \times \begin{cases} N_\mathrm{upt} \times \left(1 - \dfrac{1}{C_\mathrm{b}}\right), & \text{if } C_\mathrm{b} < 1 \\ N_\mathrm{upt} \times \dfrac{1}{C_\mathrm{b}}, & \text{if } C_\mathrm{b} \geq 1 \end{cases}, \tag{8}$$

where C_b is the biogeochemical cycling coefficient, and the relative K_1 coefficient depends on soil type.

Soil N immobilization, N_i

$$\mathrm{N_i} = K_2 \times \mathrm{NMC}/C_\mathrm{b}. \tag{9}$$

The K_2 coefficient is found from the following condition:

$$K_2 = \begin{cases} 0.15, & \text{if C:N} < 10, \\ 0.25, & \text{if } 10 \leq \text{C:N} < 14, \\ 0.30, & \text{if } 14 \leq \text{C:N} < 20, \\ 0.35, & \text{if C:N} \geq 20, \end{cases} \tag{10}$$

where C:N is the ratio between carbon and nitrogen content in the organic soil pool.

Immobilization of atmospheric deposition nitrogen, N_i^*

$$\mathrm{N}_\mathrm{i}^* = K_2 \times \mathrm{N}_\mathrm{td} \times C_\mathrm{t}/C_\mathrm{b}, \tag{11}$$

where N_td is the total atmospheric deposition nitrogen (monitoring data), and the K_2 coefficient is calculated based on the condition (10).

Soil N denitrification, N_{de}

$$\mathrm{N}_\mathrm{de} = K_3 \times \mathrm{AMC} + K_4, \tag{12}$$

where coefficient K_3 is assumed to be equal to 0.145 (Bashkin, 1987), and K_4 coefficient is found based on the condition:

$$K_4 = \begin{cases} 0.605, & \text{if } 10 \le \mathrm{AMC} \le 60, \\ 0.9, & \text{if } \mathrm{AMC} < 10, \\ 6.477, & \text{if } \mathrm{AMC} > 60. \end{cases} \tag{13}$$

Denitrification of atmospheric deposition nitrogen, N_{de}^*

$$\mathrm{N}_\mathrm{de}^* = \mathrm{N}_\mathrm{td} \times C_\mathrm{t} \times \mathrm{N}_\mathrm{de}/\mathrm{AMC}. \tag{14}$$

Accordingly, nitrogen minimal critical loads: $\mathrm{CLmin(N)} = (\mathrm{N}_\mathrm{i}^* + \mathrm{N}_\mathrm{u}^*)$; nutrient nitrogen critical loads: $\mathrm{CLnut(N)} = \mathrm{CLmin(N)} + \mathrm{N}_\mathrm{l} + \mathrm{N}_\mathrm{de}^*$; sulfur maximal critical loads: $\mathrm{CLmax(S)} = C_\mathrm{t} \times (\mathrm{BC}_\mathrm{w} - \mathrm{ANC}_\mathrm{l}) + (\mathrm{BC}_\mathrm{d} - \mathrm{BC}_\mathrm{u})$; nitrogen maximal critical loads: $\mathrm{CLmax(N)} = \mathrm{CLmax(S)} + \mathrm{CLmin(N)}$.

Therefore, no unique acidity critical load can be defined, but the combinations of N_dep and S_dep not causing "harmful effects" lie on the so-called *critical load function of the ecosystem* defined by three critical loads, such as CLmaxS, CLminN, and CLmaxN. In addition, the critical loads of nutrient nitrogen should be also included, CLnutrN. An example of such a trapezoid-shaped critical load function is shown in Figure 2.

These four CL values have been calculated for all available natural Forest, Steppe and Heath terrestrial ecosystems for the whole European area. In the European integrated assessment modeling efforts, one deposition value for nitrogen and sulfur, respectively, is given for each 150 × 150 km^2 EMEP grid cell. In a single grid cell, however, many (up to 100,000 in some cases) critical loads for various ecosystems, mostly forest soils, have been calculated. These critical loads are sorted according to magnitude, taking into account the area of the ecosystem they represent, and the so-called *cumulative distribution function (CDF)* is constructed (see Posch et al.,

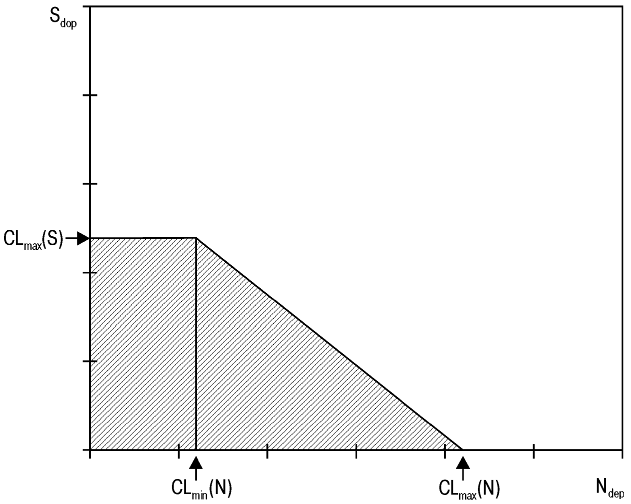


Figure 2. Example of a critical load function for S and N defined by the CLmaxS, CLminN, CLmaxN and CLnutN. Every point of the grey-shaded area below the critical load function represents depositions of N and S, which do not lead to the exceedance of critical loads (UBA, 1996; Modelling and Mapping Manual, 2004).

(1999) for the description of this statistical procedure). From this CDF, percentiles are calculated which can directly compared with deposition values. The application of 5-percentile value shows the protection of 95% ecosystems in grid cell, 3-percentile, 97%, 1-percentile, 99%, etc.

Critical Load Exceedance

If only one pollutant contributes to an effect, e.g., nitrogen to eutrophication or sulfur to acidification, a unique critical load (CL) can be calculated and compared with deposition (D_{ep}). The difference is termed *the exceedance of the critical loads*: Ex = D_{ep} − CL.

In the case of two pollutants no unique exceedance exists, as illustrated in Figure 3.

But for a given deposition of N and S an exceedance has been defined as the sum of the N and S deposition reductions required to achieve non-exceedance by taking the shortest path to the critical load function (see Figure 3). Within a grid cell, these exceedances are multiplied by the respective ecosystem area and summed to yield the so-called *accumulated exceedance* (*AE*) for that grid cell. In addition, *the average accumulated exceedance* (*AAE*) is defined by dividing the AE by the total ecosystem area of the grid cell, and which has thus the dimension of a deposition (for detailed explanations see Posch et al. (1999)).

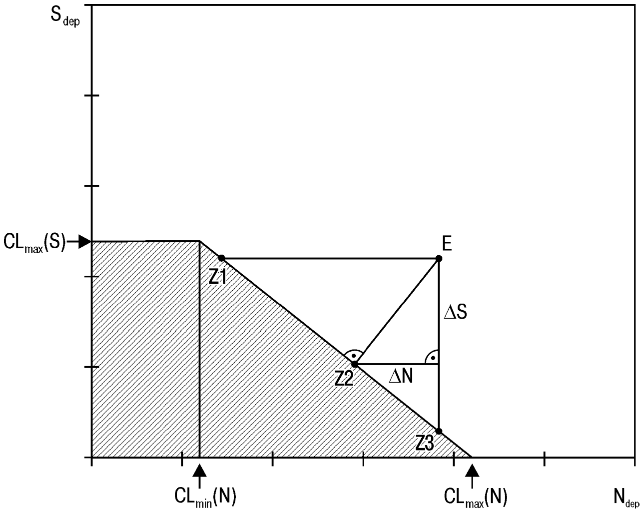


Figure 3. Critical load function for S and acidifying N. It shows that no unique exceedance exists. Let the point E denote the current deposition of N and S. Reducing N_{dep} substantially one reaches point Z1 and thus non-exceedance without reducing S_{dep}; but non-exceedance can also be achieved by reducing S_{dep} only (by a smaller amount) until reaching Z3. However, an exceedance has been defined as the sum of N_{dep} and S_{dep} reductions ($\Delta N + \Delta S$), which are needed to reach the critical load function on the shortest path (point Z2) (Posch et al., 1999).

2. CRITICAL LOAD AS BIOGEOCHEMICAL STANDARDS FOR HEAVY METALS

We have shown already that anthropogenic loading changed significantly the natural biogeochemical cycles of many heavy metals (HM), especially those like mercury or lead (see Chapter 11). In order to make adequate environmental policies concerning reduction of HM loading to the environment, efforts for assessment of the effects of such pollutants and describe identification of those loads of heavy metals below which harmful effects no longer occur, the so-called critical loads, are needed. Accordingly, we will provide how these critical loads at terrestrial and aquatic ecosystems can be calculated and show how to estimate the environmental standards based on biogeochemical food web estimates. Here we will also present different calculation methods to quantify the risk of inputs of several heavy metals, i.e., lead, cadmium, copper, zinc, nickel, chromium, and mercury.

Contrary to the critical loads for acidity, the critical loads for heavy metals refer to a single metal only. Accordingly, *the critical loads equal the load causing a concentration in a compartment (soil, soil solution, groundwater, plant, animal and human organisms, etc.), that does not exceed the critical limits set for heavy metals, thus preventing significant harmful effects on specified sensitive elements of the biogeochemical food web.*

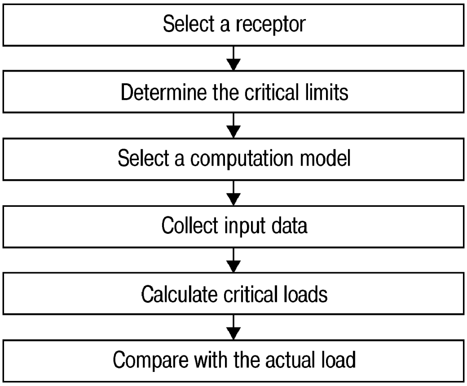


Figure 4. Flowchart for calculating critical loads of heavy metals.

2.1. General Approaches for Calculating Critical Loads of Heavy Metals

Discussing the problems related to the critical load calculation, an attention should be paid to (i) selection of a receptor of concern, (ii) critical limits, (iii) possible calculation methods, (iv) the necessary input data and (v) the various sources of error and uncertainty (de Vries and Bakker, 1998a, 1998b).

The following flowchart is useful for calculation of critical loads of heavy metals for both terrestrial and aquatic ecosystems (Figure 4).

2.2. Deriving Biogeochemical Parameters for Critical Loads of Heavy Metals

Selection of a Receptor of Concern

In general terms, *a receptor is defined as an ecosystem of interest that is potentially polluted by a certain load of heavy metal.*

Selection of a receptor is the first step in the flowchart for calculating critical loads (see Figure 4). When selecting a receptor in view of the different effects of heavy metals, the crucial question is related to what we want to protect. With respect to risks on terrestrial ecosystems, a major distinction can be made in risks/effects on humans that use ground water for drinking or that consume crops that are grown on the soil (human ecotoxicological risks) and ecosystems (ecotoxicological risks). In order to judge the ecotoxicological risks associated with elevated heavy metal contents in terrestrial ecosystems, a further distinction should be made in the following receptors:

1. Soil microbes. Effects include reduced microbial biomass and/or species diversity, thus affecting microbial processes such as enzyme synthesis and activity, litter decomposition, associated with carbon and nitrogen mineralization, and soil respiration;
2. Soil fauna, including invertebrates, like nematodes and earthworms. Effects are connected with biodiversity, productivity and biomass changes;

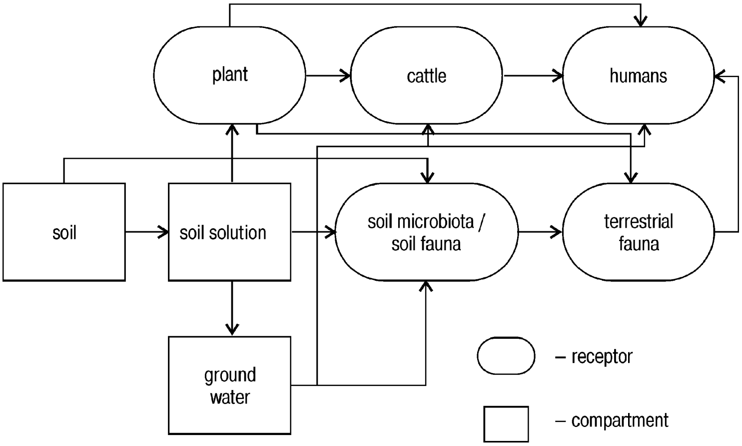


Figure 5. A simplified biogeochemical food web in the terrestrial ecosystems.

3. Vascular plants including trees. Effects are related to HM toxicity, such as the reduced growth of roots and shoots, elevated concentrations of starch and total sugar and decreased nutrient contents in foliar tissues and depressed biochemical activity;
4. Terrestrial fauna, such as birds, mammals, or domestic animals. Effects are heavy metals accumulation followed by possible disturbance of physiological and biochemical reactions and metabolisms. Bioaccumulation of Cd, Hg and Cu in the food web is the most important concern.

A simplified biogeochemical food web of heavy metals in the terrestrial ecosystems, including the most important receptors (biogeochemical links) is shown in Figure 5.

With respect to soils, a receptor is thus characterized as a specific combination of land use (e.g., Forest ecosystem types, agricultural crops) and soil type. The critical loads can be calculated for both agricultural soils (grassland, arable land) with HM inputs with deposition, fertilizers, and wastes, and non-agricultural (forest and steppe) soils, where atmospheric deposition is the only input to the system.

The receptors that one may consider in both types of ecosystems are presented in Table 1.

Possible effects on soil life, plants (phytotoxicity) and on ground water are of concern in all types of ecosystems. Food quality criteria are, however, of relevance for arable land only, whereas possible secondary poisoning effects on domestic animals or terrestrial fauna are relevant in grassland and non-agricultural land. A final critical limit can be based on the most sensitive receptor. Even though effects vary for each metal, soil microbes and soil fauna are generally most sensitive.

Table 1. Possible receptors in three main types of terrestrial ecosystems.

Receptor	Ecosystem types Non-agricultural land use	 Grassland and pasture	 Arable land
Soil microbes	+	+	+
Plants			
Phytotoxicity	+	+	+
Crop quality	–	–	+
Terrestrial fauna	+	–	–
Domestic animals	–	+	–
Ground water	+	+	+

When selecting a receptor in aquatic ecosystems, this may be the aquatic organisms, the benthic organisms or the fauna (birds and mammals) or human beings that consume fish (Figure 6).

With respect to aquatic ecosystems, a receptor is thus characterized as a like, a river or a sea. The major receptor that we will consider here is a lake, including catchment (see small catchment studies in Chapter 18). The reason is that the suggested models are all relatively simple and based on the assumption that the water compartment is homogeneously mixed. Much more complicated models are necessary to calculate

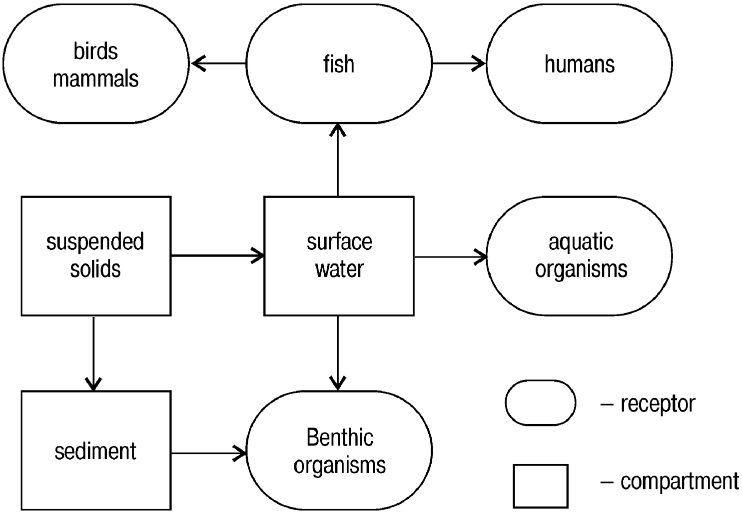


Figure 6. A simplified biogeochemical food web in the aquatic ecosystems.

critical loads for seawater or a large lake with horizontal currents and/or thermal stratification.

Critical Limits

The assessment of a critical limit for the receptor of concern is a second step in the flowchart for calculating critical loads of heavy metals (see Figure 4). Since critical loads of heavy metals are related to the concentration of a single metal in any link of a biogeochemical food web, the correct selection of critical limits is a step of major importance in deriving the critical loads. Those critical limits, which depend on the kind of effects considered and the amount of harm accepted, constitute the basis of the critical load calculation and determine their magnitudes.

Effect-based critical limits for soils and ground water have been derived or are under development in various countries for multiple purposes (Radojevic and Bashkin, 1999). These criteria can be used to assess the environmental quality of a site or area, to set priorities in control measures and to derive emission reduction goals. Most of the values are derived from comparable starting points such as protecting terrestrial population, water supply, food quality, and finally, animal and human health.

For most of the receptors (see Figures 5 and 6), critical limits have been defined related to ecotoxicological or human-toxicological risks, such as

(a) *Soil*. Relation to direct and indirect effects on soil microbes and fauna, plants, terrestrial fauna and humans. The typical values are given in mg/kg or ppm;

(b) *Ground water*. Relation to direct and indirect effects on animal and human health when this water is used as drinking water, μg/L or ppb;

(c) *Surface water*. Critical limits or maximum permissible concentrations (MPC) are related to direct effects on organisms in surface water or on human and animal health as drinking water, μg/L or ppb;

(d) *Mammals–birds–fish*. Maximum permissible concentrations (MPC) in target organs are related to direct (toxic) effects, or food critical limits in the human and animal food webs;

(e) *Plants, cattle, terrestrial fauna*. Critical limits in plant tissue or target organs are related to direct toxic effects, or food chemical limits related to indirect effects by animal and human consumption, mg/kg or ppm;

(f) *Humans*. These values are connected with acceptable daily intake or ADI, in μg/kg of body weight per day. This dose is the quantity of a compound to which man can be orally exposed, on the basis of body weight, without experiencing adverse effects on human health.

Below we will consider the critical limits applied for different purposes in Europe and North America. Examples are given for multifunctional soil and water use, differentiation in land use types and bioconcentration in food web.

Table 2. Critical limits for heavy metals in soil of various countries, related to multifunctional uses.

	Critical limits, ppm						
Country	Pb	Cd	Hg	Cu	Zn	Ni	Cr
Denmark	40	0.3	0.1	30	100	10	50
Sweden	30	—	0.2	—	—	—	—
Finland	38	0.3	0.2	32	90	40	80
Netherlands	85	0.8	0.3	36	140	35	100
Germany	40	0.4	0.1	20	60	15	30
Switzerland	50	0.9	0.8	50	200	50	75
Czech Republic	70	0.4	0.4	70	150	60	130
Russia	32	2	2.1	55	100	85	90
Ireland	50	1	1	50	150	30	100
Canada	25	0.5	0.1	30	50	20	20

Multifunctional soil use

In various countries, critical limits for soil have been derived to assure multifunctional soil use (Table 2).

The concentrations shown in Table 2 are in relatively limited range, i.e., 25–100 for Pb, 0.3–2 for Cd, 0.1–1.0 for Hg, 30–70 for Cu, 50–200 for Zn, 10–85 for Ni, and 20–130 for Cr. This indicates the similar ecotoxicological approaches that have been used for setting the critical limits in various countries.

Multifunctional water use

Hygienic standards for dissolved concentrations of heavy metals in surface water are shown in Table 3.

The range in critical limits for dissolved species of heavy metals in surface waters is large, especially for zinc and nickel. In general, values used by Denmark and the Czech Republic are much higher than for other countries, except for Zn and Ni. For these elements, Canada and the USA also use much higher values. These limits may refer to action values.

Differentiation in land use

In some countries, critical loads for heavy metals have been derived as a function of land use. An example of such a differentiation suggested in Germany (Table 4) indicates a strong increase in critical limits going from multifunctional land use to industrial areas.

Table 3. Critical limits for heavy metals in surface waters of various countries, related to multifunctional uses.

	Critical limits, ppb						
Country	Pb	Cd	Hg	Cu	Zn	Ni	Cr
Sweden	1.2	0.09	—	2.1	9	9	1
Denmark	3.2	5	—	12	110	160	10
Norway	0.6	0.05	—	1.1	4.5	1.5	0.45
UK	10	—	—	5	10	5	5
Netherlands	11	0.34	0.23	1.1	6.6	1.8	8.5
Germany	5	1	0.1	—	—	—	—
Czech Republic	50	5	1	100	50	150	50
Russia	1.0	5	0.01	1	10	10	1
Canada	1.0	0.2	0.1	2	30	25	2
USA	3.2	1.1	0.01	1.2	110	160	11
WHO	10	3	1	—	—	20	50

Methods to derive effect-based critical limits

Here we will describe the methods that are used to derive critical limits for soil, based on direct ecotoxicological effects on microorganisms and plants. The indirect approaches (food web models) to derive critical limits for soil based on critical limits for terrestrial fauna such as MPC values for target organisms will be also considered.

Table 4. Critical limits for heavy metals in Germany as a function of land use.

	Critical limits, ppm						
Land use	Pb	Cd	Hg	Cu	Zn	Ni	Cr
Multifunctional	100	1	0.5	50	150	40	50
Children's playgrounds	200	2	0.5	50	300	40	50
Domestic gardens	300	2	2	50	300	80	100
Agricultural areas	500	2	10	50	300	100	200
Recreational areas	500	4	5	200	1000	100	150
Industrial areas	1000	10	10	300	1000	200	200

Direct Effects on Soil Organisms and Plants

MPC's values for soils are derived using extrapolation methods that are based on ecotoxicological information. In this context, a distinction is made in acute toxicity data based on short-term ecotoxicological experiments (<1 day) and chronic toxicity data, based on long-term ecotoxicological experiments (1 day–1 month). *Acute toxicity is defined by the LC_{50} value, which is equal to the concentration at which 50% of the considered population are dead (LC_{50} with LC = lethal concentration). Chronic toxicity is defined by No Observed Effect Concentrations (NOECs), sometimes referred as No Observed Effect Levels (NOELs), of several species in an ecosystem.* The organisms or taxonomic groups that are considered in deriving LC_{50} values or NOEC data are microbes or microbe-mediated soil processes (enzymatic activity), earthworms, arthropods and plants. If only (i) acute toxicity data or a Quantitative Structure Activity Relationships (QSAR) or (ii) chronic toxicity data for a few different taxonomic groups (microbes, enzymes, earthworms, arthropods or plants) are available, the modified Environmental Protection Agency (EPA) method is applied.

The fixed safety factors are applied in this EPA method. The safety factors used are based on arbitrary extrapolation values of 10 going from (i) the laboratory (single species) to the field (whole ecosystem) situation and (ii) acute to chronic toxicity data. A similar approach is used to derive critical limits for surface water.

Indirect Effects on Higher Organisms

Biomagnification, which is the phenomenon that a chemical accumulates in species through different trophic levels in a food web, may cause toxic effects on mammals and birds as a secondary poisoning. Next to direct effects on soil organisms (see above), these indirect effects cam be considered in deriving critical limits for soil, by the use of simple food web models.

To indicate the transfer of chemicals in a biogeochemical food web, both bioaccumulation factors (BAFs) and bioconcentration factors (BCFs) are used. The following definitions can be applied (de Vries and Bakker, 1998a, 1998b):

BAF: defined as the ratio of the test chemical concentration in (a part of) an organism (e.g., bird, mammal or fish) to the concentration in its food (e.g., laboratory fodder, plants, invertebrates, birds, mammals) at steady state. BAFs are generally used for accumulation by birds, mammals and fish and are expressed on a weight basis.

BCF: defined as the ratio of the test chemical concentration in (a part of) an organism (e.g., plant, earthworm) to the concentration in a medium (e.g., water, soil) at steady state.

The food of top predators generally comprises small birds and/or mammals. Bioaccumulation of chemicals from soil to small birds and mammals takes place in at least two steps, namely a BCF from soil to food (plants and/or invertebrates), followed by a BAF to small birds and mammals.

A similar description is used for water ecosystems with fish species.

Terrestrial ecosystems. The simplest model used in terrestrial ecosystems is based on the simplified food chain:

$$\text{soil} \to \text{soil invertebrates} \to \text{mammals/birds.}$$

Assuming that the mammal or bird feeds on soil invertebrates (e.g., worm-eating birds or mammals), the simplest model to calculate an MPC based on this food web is

$$\mathrm{MPC}_{\mathrm{soil}} = \mathrm{NOEC}_{\mathrm{species\ of\ concern}}/\mathrm{BCF}_{\mathrm{food\ species\ of\ concern}}$$

where $\mathrm{MPC}_{\mathrm{soil}}$ is Maximum Permissible Concentration of a chemical in soil, ppm; $\mathrm{NOEC}_{\mathrm{species\ of\ concern}}$ is No Observed Effect Concentration of the food (invertebrate) corrected for the species of concern (mammals or bird, ppm); $\mathrm{BCF}_{\mathrm{food\ species\ of\ concern}}$ is Bioconcentration factor, representing the ratio between the concentration in the invertebrate, being the food of species of concern, and the concentration in soil, ppm.

Aquatic ecosystems. The simplest model used in aquatic ecosystems is based on the simplified food chain:

$$\text{water} \to \text{fish or mussel} \to \text{fish or mussel eating birds/mammals.}$$

Assuming that the mammal or bird feeds on fish or mussels, the simplest model to calculate an MPC based on this food web is

$$\mathrm{MPC}_{\mathrm{water}} = \mathrm{NOEC}_{\mathrm{species\ of\ concern}}/\mathrm{BCF}_{\mathrm{food\ species\ of\ concern}}$$

where $\mathrm{MPC}_{\mathrm{water}}$ is Maximum Permissible concentration of a chemical in soil, ppb; $\mathrm{NOEC}_{\mathrm{species\ of\ concern}}$ is No Observed Effect Concentration of the food (invertebrate) corrected for the species of concern (mammals or bird, ppm); $\mathrm{BCF}_{\mathrm{food\ species\ of\ concern}}$ is Bioconcentration factor, representing the ratio between the concentration in the invertebrate, being the food of species of concern, and the concentration in water, ppb.

A more detailed biogeochemical food web model is shown in Figure 7.

As shown in Figure 7, there are four possible main routes going from soil to birds or beasts of prey (soil–plant–bird, soil–invertebrate–bird, soil–plant–mammals, and soil–invertebrate–mammal). This number increases exponentially when different plant parts and invertebrate groups are distinguished as quantitatively important food items for small birds and mammals. For plants a distinction can, for example, be made between leaves, seeds, fruits and tubers. The group of invertebrates may comprise earthworms, gastropods, larvae of insects, caterpillars, insects, isopods and spiders. An additional distinction can be made between leaves and seeds with respect to plants and between worms and insects with respect to invertebrates, thus leading to a total of 16 routes going from soil to both beasts and beasts of prey.

Using these routs, we can estimate the MPC values for cadmium in soil (Table 5).

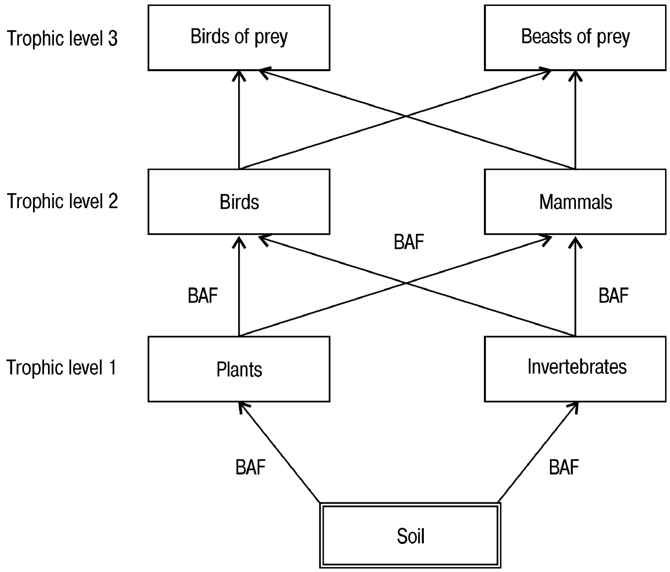


Figure 7. *Scheme of a terrestrial food web use for modeling bioaccumulation. The compartment's plants and invertebrates can be split up in several groups, depending on the availability and variation among bioaccumulation data (de Vries and Bakker, 1998a).*

Results show that for Cd (i) birds of prey are always more sensitive that beasts of prey and (ii) bioaccumulation is lowest in the food chain: Soil → worm → bird/mammal. The latter food chain to birds of prey is by far the most critical pathway for Cd exposure, leading to very low critical limits for soils (approximately 0.1 ppm,

Table 5. *MPC values for Cd in soil, based on 16 different exposure pathways (After de Vries and Bakker, 1998a).*

	Critical limit of Cd in soil, ppm	
Food chain	Beast of prey	Birds of prey
Soil → leaf → bird	37	2.3
Soil → seed → bird	7.2	0.44
Soil → worm → bird	1.5	0.08
Soil → insect → bird	6.4	0.40
Soil → leaf → mammal	48	3.6
Soil → seed → mammal	9.4	0.68
Soil → worm → mammal	1.9	0.12
Soil → insect → mammal	8.3	0.61

compare with Table 10.10). When one aims to protect the most sensitive species, the latter limit seems appropriate.

2.3. Calculation Methods for Critical Loads of Heavy Metals

The selection of a computation method or model is the third step in the flowchart for calculating critical loads of heavy metals (Figure 4). There are different models that can be used to calculate critical loads for terrestrial and aquatic ecosystems, based on receptor properties and on certain critical limits. Relevant aspects in relation to the selection of a calculation method are

(i) the choice of steady-state and dynamic models in calculating critical loads,
(ii) the choice of critical limits in relation to what we want to protect,
(iii) the required model complexity (simplicity) in view of the regional applicability of the calculation method.

These aspects are shortly summarized below.

In selecting a computation model, it is important to make a clear distinction between steady-state and dynamic models. For instance, steady-state soil models, predicting metal concentrations at the soil's solid phase and in the soil solution at steady state, are particularly useful to derive critical loads based on an infinite time perspective. Dynamic models, predicting changes in heavy metal chemistry in both soil and soil solution in response to changes in metal loading, are particularly useful to predict the time period before a critical limit is exceeded (if ever) for a given input scenario. A dynamic model may, however, also be used to calculate target loads. Unlike critical loads, target loads include a definite time target (e.g., 50 or 100 years) in relation to what is considered an acceptable input for the time.

As we have discussed earlier, the critical limit to be used depends on what we want to protect. In terrestrial ecosystems this can be soil fauna, the soil vegetation or the human beings that use ground water for drinking water or that consume crops that are grown on the soil. In aquatic ecosystems, the critical limits are connected with concentration of dissolved species in water.

The choice of a model for the calculation of critical loads not only depends on the question of "which time period" (steady state or dynamic) and "what to protect" (which critical limit) but also on the amount of detail required. Depending on the aim, one must chose a model with an appropriate level of detail in describing the processes in the terrestrial or aquatic ecosystems. A disadvantage of relatively complex mechanical models is that input data for their application on a regional scale is generally incomplete and values can only be roughly estimated. Even if the model structure is correct (or at least adequately representing current knowledge), the uncertainty of the output of complex models may thus still be large because of the uncertainty of input data. Simpler empirical models have the advantage of a smaller need for input data but the theoretical basis, which is needed to establish confidence in the predictions, is small, which limits the application of such models for different situations. There is thus a trade off between model complexity (reliability) and regional applicability.

When the aim of the model is to calculate critical loads on a regional scale consisting of receptors with different properties, it seems most rational to use a relatively simple model with aggregated description of processes in the total considered compartment. In choosing the model, one should be aware of the consequences of simplifications, such as ignoring certain processes (complexation, metal cycling, etc.) and making certain assumptions (steady state, homogenous mixing, equilibrium partitioning).

In order to gain insight into the consequences of the choice of a certain model and limits, one could perform critical load calculations with different models (complex dynamic models versus simple steady-state models) using various limits and compare the results. In this way, one also gets insight into (i) the differences in vulnerability of the various environmental compartments and related organisms and (ii) the relevance of the different processes in the systems and of the different ways of parameterizing certain processes.

As examples, the steady-state mass balance equations will be shown for terrestrial and aquatic ecosystems.

Terrestrial Ecosystems

The soil is the estimated compartment for terrestrial ecosystems. Using the assumptions (see above), a complete steady-state mass balance of a certain heavy metal, M, in a soil layer equals (see also Figure 5):

$$\mathrm{fM_{tl}} = \mathrm{fM_{fu}} - \mathrm{fM_{lf}} + \mathrm{fM_{ru}} - \mathrm{fM_{we}} + \mathrm{fM_{le}}$$

where all terms relate to biogeochemical fluxes of heavy metal M (in g/ha/yr or $\mathrm{mg/m^2/yr}$): $\mathrm{fM_{tl}}$ is the total load by deposition and other loads (e.g., fertilizers); $\mathrm{fM_{tl}}$ is foliar uptake or retention; $\mathrm{fM_{lf}}$ is litterfall; $\mathrm{fM_{ru}}$ is root uptake; $\mathrm{fM_{we}}$ is weathering; $\mathrm{fM_{le}}$ is leaching.

In this equation, no distinction has been made between various oxidation states of the metals. The approach implicitly lumps all the various metal species in the soil. With respect to Pb, Cd, Cu, Zn and Ni, it is assumed that the metal only persists as a divalent cation, which is a valid assumption for these metals in soil. This assumption, however, seriously limits the application of this model to calculate critical loads for Cr and Hg.

With respect to Cr a distinction should be made between Cr(III), which is the common oxidation state in the soils, being rather immobile and so toxic, and Cr(VI), which is very mobile and very toxic. With respect to Hg, the situation is even more complex, due to the occurrence of mercuric mercury ($\mathrm{Hg^{2+}}$), mercurous mercury ($\mathrm{Hg_2^{2+}}$), elemental mercury ($\mathrm{Hg^0}$) and organic mercury species, such as methyl mercury, $\mathrm{(CH_3)_2Hg}$ (see Section 18.5). Furthermore, volatilization of elemental mercury and organic mercury species is common. A description of these

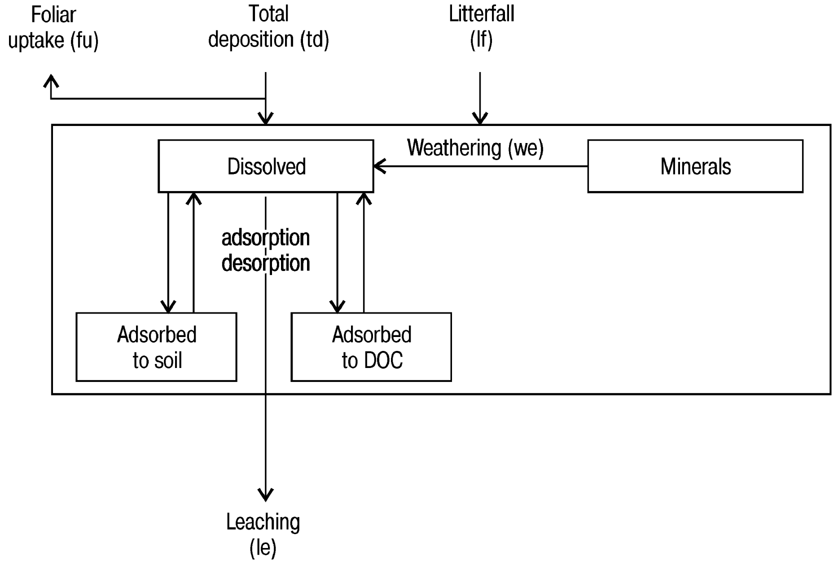


Figure 8. Schematic representation of the mass balance for heavy metals in soils of non-agricultural ecosystems.

processes, in combination with other interactions of Hg in soil, such as reduction, absorption and complexation, is extremely difficult and the approach can only be considered as very approximate for mercury. This also holds to a lesser extent for chromium.

In soils of non-agricultural ecosystems, above ground biomass (foliar uptake) and metal cycling is considered important (see Figure 8), due to large impact on the metal distribution in the humus layer and mineral soil profile. Especially in soils of Forest ecosystems, it may affect the accumulation in the humus layer, which is considered a very relevant compartment regarding the calculation of a critical load. In these soils, however, a steady-state element cycle is assumed, which implies that mineralization, M_{mi}, equals litterfall, M_{lf}.

In soils of agroecosystems, above ground biomass (foliar) uptake and metal cycling by mineralization and total root uptake can be lumped into a net removal term due to harvest (indicated as growth uptake, M_{gu}) when the critical load is calculated for the root zone, e.g., for upper 20–30 cm. In this situation we can calculate root uptake as a function of the growth uptake, whereas the net effect of litterfall and foliar uptake is assumed to be negligible.

Thus, the mass balance of heavy metals in soils of agroecosystems is

$$fM_{tl} = fM_{gu} - fM_{we} + fM_{le}$$

where fM_{gu} is the flux of heavy metal M by growth uptake.

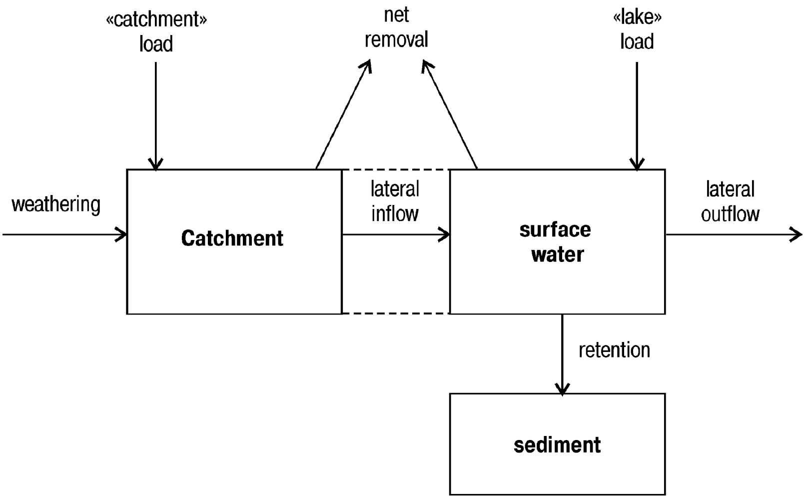


Figure 9. Schematic representation of mass balance for heavy metals in a catchment.

The critical metal leaching rate depends on critical dissolved metal concentrations, which can be derived in different ways, for instance as a critical limit for soil solution (see above).

Aquatic Ecosystem

The steady-state calculation method for surface water is based on the mass balance schematically shown in Figure 9.

Figure 9 gives the simplified mass balance for heavy metals in a catchment, including both a soil compartment in the catchment area and the aquatic system with water and sediment compartments. A complete steady-state mass balance of heavy metals for a catchment equals:

$$\mathrm{fM_{tl}} = \mathrm{fM_{up}} - \mathrm{fM_{we}} + (\mathrm{fM_{sed}} - \mathrm{fM_{res}} + \mathrm{fM_{ex}}) \times A_t/A_c + \mathrm{fM_{lo}}$$

where all terms relate to biogeochemical fluxes of heavy metal M (in g/ha/yr or mg/m^2/yr) and area (ha or m^2): $\mathrm{fM_{tl}}$ is the total load by deposition and other loads (e.g., fertilizers); $\mathrm{fM_{up}}$ is metal flux by net uptake in the catchment and the lake; $\mathrm{fM_{we}}$ is metal flux by weathering in the catchment; $\mathrm{fM_{lo}}$ is metal flux by lateral outflow of water; $\mathrm{fM_{sed}}$ is metal flux from water compartment to the sediment compartment by sedimentation; $\mathrm{fM_{res}}$ is metal flux from sediment compartment to the water compartment by resuspension; $\mathrm{fM_{ex}}$ is metal flux from sediment compartment to the water compartment or vise versa caused by exchange processes near the sediment water interface; A_c is the surface area of the catchment; A_t is the surface area of the lake (lowest water system) in the catchment area.

Table 6. The influence of location, land use and soil type on input data (+ effect; – no effect).

Input data	Location	Land use	Soil type
Precipitation	+	–	–
Deposition	+	+	–
Evapotranspiration	+	+	+
Litterfall	+	+	+
Foliar uptake	+	+	–
Root uptake	+	+	+
Weathering	–	–	+
Adsorption	–	–	+
Complexation	–	–	+

Table 7. Data acquisition approach for input data.

Input data	Data acquisition approach
Deposition	Estimate per unit area using emission/deposition matrices, corrected for forest filtering
Precipitation	Estimate per unit area based on data of weather stations or monitoring site
Forest canopy interception	Derivation of a relationship with precipitation amount and land use
Transpiration	Calculation as a function of climate, land use and soil type
Litterfall/foliar uptake	Derivation of a relationship with deposition and land use
Root uptake	Derivation of a relationship with deposition and land use
Absorption	Derivation of a relationship with soil characteristics such as pH, organic matter content, clay content and CEC
Complexation	Literature data; derivation of a relationship with pH

Similar to terrestrial ecosystems, no distinction is made between various oxidation states of the metals. This assumption seriously limits the application of the model to calculate critical loads for mercury.

Net uptake of heavy metals is due to the removal of heavy metals in crops or trees in the catchment and/or in aquatic plants and fish in a lake. Weathering relates to the release of HM from primary minerals in the catchment. Sedimentation is the result of the setting of suspended particles in the lake. As a result of this process, the pollutant absorbed to the suspended particles is transported from the water compartment to the sediment compartment. Resuspension of sediment particles is the results of the turbulence at water-sediment interface. As a result of this process, the pollutant absorbed to the sediment particles is transported from the sediment compartment to the water compartment. The exchange processes at the sediment water interface include advection or infiltration, molecular diffusion, and bioturbation and bioirrigation (the latter are the transport of HM resulting from the ventilation of tubes and burrows in the sediments by benthic organisms). To scale these processes to the catchment, the sedimentation and resuspension rates are multiplied by the ratio of the lake area and the catchment.

Input Data

Collecting input data is the forth step in the flowchart for calculating critical loads for heavy metals. It includes the assessment of hydrological data, vegetation data and soil data influencing the heavy metal fluxes in the considered ecosystems. For application on a regional scale it also includes the distribution and area of receptor properties using available digitized information and GIS technologies.

Input data for the most detailed soil model include parameters describing atmospheric deposition, precipitation, evapotranspiration, litterfall, foliar uptake, root uptake, weathering, adsorption and complexation of Pb, Cd, Cu, Zn, Ni, Cr and Hg. The input data mentioned above vary as a function of location (receptor area) and receptor (the combination of land and soil type) as shown in Table 6.

The receptors of interest are soils of agricultural (arable lands, grasslands) and non-agricultural (forests, steppes, heath lands, savanna, etc.) ecosystems. In non-agricultural ecosystems, the atmospheric deposition is the only input of heavy metals. Regarding the Forest ecosystems, a distinction should at least be made between Coniferous and Deciduous Forest ecosystems. When detailed information on the areal distribution of various tree species (e.g., pine, fir, spruce, oak, beech and birch) is available, this should be used since tree species influence the deposition and uptake of heavy metals and the precipitation excess. On a world scale, soil types can be best distinguished on the basis of the FAO–UNESCO Soil Map of the World, climate and ecosystem data from NASA database (1989).

In order to obtain for all receptors within all receptor areas (grids), a first good approach is to interpret and extrapolate data by deriving relationships (transfer functions) between the data mentioned before and basic land and climate characteristics, such as land use, soil type, elevation, precipitation, temperature, etc. A summarizing overview of the data acquisition approach is given in Table 7.

CHAPTER 4

BIOGEOCHEMICAL APPROACHES TO ECOSYSTEM ENDPOINTS

Under both national and international agreements, the process of quantitatively predicting the probability of an adverse response in ecosystem health due to exposure to one or more pollutants is collectively known as Environmental Risk Assessment, ERA (US EPA, 1992).

In accordance with this definition, an environmental risk assessment process is used especially in cases when the probability component arises during the calculation of various parameters which can be due to many reasons: uncertainty of input information; uncertainties in applying an algorithm due to lack of knowledge, insufficient knowledge and/or simplification of input information; uncertainties in the defined geographic boundaries of pollutant influence; uncertainties in both computer calculations and management operations based on these calculations.

1. ENVIRONMENTAL RISK ASSESSMENT UNDER CRITICAL LOAD CALCULATIONS

1.1. Suggested ERA Frameworks and Endpoints for Development of Acidification Oriented Projects

ERA in general is a process, as is EIA (Environmental Impact Assessment), and not the occasional report or document that is published at various steps. The framework for the orderly process, which has been developed for various environmentally sound projects can be applied also for acidification oriented projects and especially for an evaluation of ecosystem sensitivity to acid deposition and critical load calculations. Central management of the process is an essential feature.

The principal scheme of environmental risk assessment, ERA, is shown in Figure 1.

The analysis of this principal scheme of ERA is so defined that the quantitative risk assessment is valid only when based on a complete operational flowchart.

Hazard identification is akin to the qualitative prediction of impacts in EIA and is largely accomplished when the EIA is performed independently of, or prior to, an ERA. The potentially significant risks are often identified because of experience elsewhere with similar materials, processes, ecosystems, and conditions. This step is immediately useful to management and helps to sharpen the question posed in the

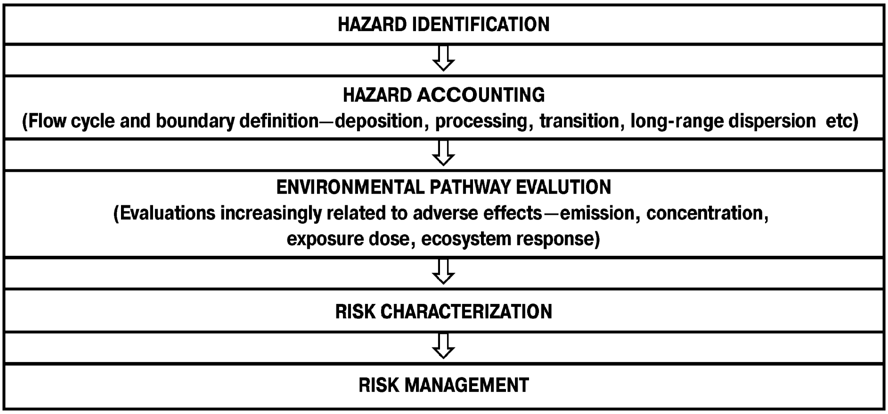


Figure 1. Recommended environmental risk assessment framework (Smith et al., 1988).

further stages, for example, in the stage Term Of Reference, TOR, for the ERA (ADB, 1991).

Hazard accounting considers the total system of which the acidification influence is a part and sets practical boundaries for the assessment. For example, Figure 2 shows the acidification and eutrophication processes identification in both terrestrial and aquatic ecosystems of concern in any of its critical points. These two steps are the basis for writing TOR for the ERA to be performed.

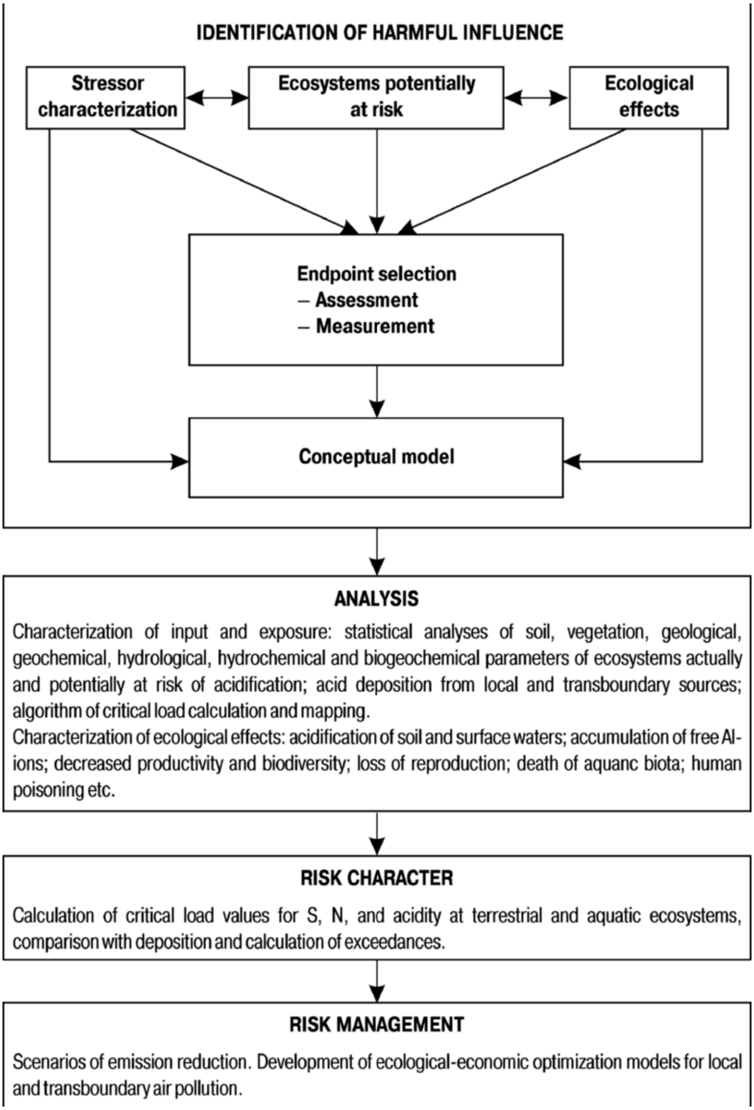
The environmental pathway evaluation considers various routes by which ecosystems could be exposed to acid deposition (Figure 2).

Associated with this step is a determination of the degree to which measurements of the hazardous acidification and/or eutrophication effects can be directly related to ecosystem/human health.

Risk characterization estimates the frequency and severity of adverse events and presents the results in a form useful to management, for example, in the form of various scenarios for emission abatement strategy on local or regional scale.

Risk management is the selection and implementation of risk-reduction actions. If the recommendations and findings of the ERA leave important questions unanswered, an iteration of hazard accounting can change the boundaries of analysis and refine the assessment. Although risk management is the use of assessment, it must be integrated to guide the process efficiently.

The purpose of providing risk information to managers who is responsible for investment decisions is to improve decision-making about development of acidification reduction strategy. These decisions are not just go or no-go statements about a project proposal, because financing agency is usually fully involved in the design of most projects. EIA and ERA advise of unwanted consequences to the environment. If the lender is not comfortable with predictions, there are opportunities to change the project plans such as different sites, alternative technologies, risk reduction measures,



ANALYSIS

Characterization of input and exposure: statistical analyses of soil, vegetation, geological, geochemical, hydrological, hydrochemical and biogeochemical parameters of ecosystems actually and potentially at risk of acidification; acid deposition from local and transboundary sources; algorithm of critical load calculation and mapping.

Characterization of ecological effects: acidification of soil and surface waters; accumulation of free Al-ions; decreased productivity and biodiversity; loss of reproduction; death of aquanc biota; human poisoning etc.

RISK CHARACTER

Calculation of critical load values for S, N, and acidity at terrestrial and aquatic ecosystems, comparison with deposition and calculation of exceedances.

RISK MANAGEMENT

Scenarios of emission reduction. Development of ecological-economic optimization models for local and transboundary air pollution.

Figure 2. Comparative application of CL and ERA analysis of acidification loading at ecosystem.

and emergency responses. The changes may be made a condition for loan approval or a covenant in the loan.

So, regarding the ecosystem acidification effect assessment, risk management is the evaluation of alternative emission reduction measures and implementation of those that appear cost-effective. Management concerns that arise because of substantial

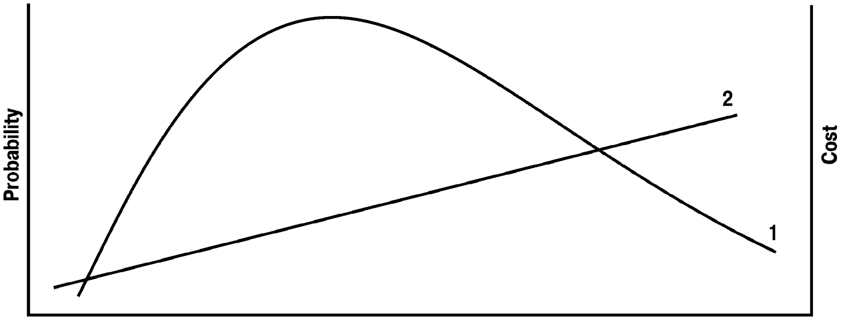


Figure 3. Scheme of comparative analysis of probability distribution function of critical load values of acidity at ecosystems and cost of emission reduction: (1) probability distribution function of critical load values; (2) cost of emission reduction.

uncertainties about major environmental consequences determine the scope of detailed risk assessment. Projects are undertaken for obvious and direct benefits of economic growth, employment, and exploitation of natural resources in various countries of the World, but ecosystem sensitivity is one of the main environmental concerns of many projects. Achievement of these benefits always entails risk, but the risk must be acceptable to the funding agency and the country. Reduction of risk costs money but so does incurring the unwanted impacts (Figure 3).

Avoiding one risk may create a new risk; net risk is always a consideration. Thus, the risk assessment analyses trade-off in risk, compares risk levels, and evaluates cost-effectiveness of risk reduction alternatives.

The inquiry into the presence of hazards is also part of the preliminary assessment for the EIA. It is by the explicit identification of significant uncertainties that the need to extend an EIA to include the ERA is determined. Of course, if uncertainties can be resolved by readily acquiring more information, then the assessor should proceed to do so.

The ecosystem acidification and critical load calculation processes are only partly scientific exercises, being connected closely with economic development of all countries. So, in different projects the hazards of concern include ecosystem damage due to acidification and eutrophication processes (e.g., decreased productivity and biodiversity, soil erosion, drinking water quality, reproduction losses, etc.), firstly, in local scale and, secondly, in regional scale that may lead to transboundary pollution. For more details see Figure 2.

Under critical loads calculations the uncertainties arise from:

- lack of understanding of important cause-effect relationships, lack of scientific theory (e.g., biogeochemical cycling of elements; bioaccumulation of toxic chemicals in food chain, reaction of trees and crops to air pollutants);
- models that do not correspond to reality because they must be simplified and because of lack of understanding (see above);

- weakness of available data due to sampling and/or measurement problems, insufficient time-series of data, lack of replication;
- data gaps such as no measurements on baseline environmental conditions at a study site;
- toxicological data that are extrapolated from high dose experiments to relatively low exposure;
- natural variations in environmental parameters due to weather, climate, stochastic events.

Consequently, risk assessment process is the obligatory continuation of the process of quantitative calculation and mapping of critical loads of sulfur, nitrogen and acidity at various natural and agricultural ecosystems. This is connected with numerous uncertainties *a priori* included in the computer algorithm for CL calculations:

- at *the receptor selection* step the uncertainty is related to the determination of the most sensitive receptor, which protection will definitely protect other, less sensitive, ecosystems;
- at *the select environmental quality criteria* step the uncertainty is connected with an assessment of biogeochemical structure of ecosystems and quantitative characterization of biogeochemical cycles of individual elements;
- at *the select computer method (model)* step the uncertainty is related to the applicability of steady-state models to dynamic systems requiring the definite simplification of these systems;
- at *the calculate critical loads* step the uncertainty is usually minimum and related mainly to the possibilities of modern computer pools;
- at *the compare with actual load* step the uncertainty is connected with an assessment of modern deposition and their spatial and temporal conjugation with definite ecosystems at the selected resolution scale.

1.2. Comparative Analysis of CL and ERA Calculations of Acidification Loading at Ecosystems

The existing uncertainty at all steps of an algorithm for critical load calculation and mapping influences the probabilistic character of these values and arise the necessary to combine both approaches. This is illustrated in Figure 2. In the maximum degree the given conjugation is required at *the risk management* step in the ERA flowchart. The probabilistic approach to the critical loads of acid forming compounds allows us to apply the set of emission reduction scenarios to minimizing the financial investments for ecosystem protection (see Figure 3).

Within the defined areas, critical loads are calculated for all major combinations of tree species and soil types (receptors) in the case of terrestrial ecosystems, or water biota (including fish species) and water types in case of freshwater ecosystems.

These combinations include the great variety of different ecosystems, the sensitivity of which to both acidification and eutrophication inputs by atmospheric pollutants differs greatly, determining the necessary reduction needs when CLs are exceeded by modern deposition levels.

This information on ecosystem sensitivity can be compared with a pollutant deposition map, to determine, which areas currently receive deposition levels, which exceed the area's CL. The areas of "exceedance" indicate where present levels of pollutant deposition increase the risk of damage to ecosystems.

2. BIOGEOCHEMICAL ENDPOINT IN CRITICAL LOADS CALCULATIONS FOR HEAVY METALS

At present, the calculation and mapping of critical loads for heavy metals is only at the beginning and in Europe there are only a few examples of application of methods described in Section 3.2. We will refer to case studies from Germany and Russia as the most characteristic research in this direction. The typical endpoints in these calculations refer to critical concentrations of different heavy metals in the ecosystems. The determination of the given critical concentrations is still uncertain and the relevant risk assessment calculated as an exceedance of critical loads should be based on selecting values of critical concentrations (see 3.2.2).

2.1. Calculation and Mapping of Critical Loads for HM in Germany

We have seen that heavy metals can cause toxic effects to living organisms when critical limits are exceeded. Present deposition rates may cause the long-term accumulation of heavy metals in the soil, especially in the forest humus layers and bottom sediments. Calculations based on comprehensive models show the long-range transport of various heavy metals in regional and continental scale. In addition to atmospheric deposition, in agroecosystems the input of HMs is connected with phosphorus fertilizers and application of wastewater effluents. Under increasing acidification of the forest ecosystems, many heavy metals accelerate aqueous migration in the biogeochemical food web. The known example is related to Cd and Cu. The accumulation of pollutants in various terrestrial and aquatic ecosystems of Germany is almost nonreversible. That is why we will consider the precautionary measures based on critical load calculations of HM. The case study in Germany may give the best example of such an approach (Schutze, 2004).

Methods of Critical Load Calculations for Heavy Metals

The approach, similar to that described in Section 3.2 was applied for the calculation of critical loads of HM s for German soils.

Critical concentrations as ecosystems endpoints

According to the heavy metals' effects, the soil microbes, crops and ground waters as a source of drinking water, are the most important receptors. During migration in the food web, the heavy metals, especially Cd and Hg, can affect also higher organisms, including people. After consideration of different pathways, the most sensitive links of food webs should be chosen for establishing the critical concentration in the soil's solution (critical limit) to protect all other pathways at this concentration.

The Critical concentrations with respect to the soil organisms should be related to a low effect level on the most sensitive species. The effects on the process of metabolism and other processes within the organisms should be considered and also the diversity of the species, which is most sensitive to the heavy metals, has to be accounted. Critical limits must refer to the chronic or accumulated effects. For assessment of the critical concentrations in crops and in drinking water, human-toxicological information is required. In general, for establishing critical loads we should also account the additive effects of the different metals and combination effect between the acidification and biogeochemical mobilization of the heavy metals in soils and bottom sediments.

The environmental standards based on total heavy metal concentration in the soil solution seem the most important criterion for the exposition of further compartments of the environment. The additional effects connected with metal speciation and complexations were not considered in the study.

A Monte Carlo simulation is proposed to appreciate the uncertainty in the process of establishing the critical concentrations of heavy metals in the soil solution.

Models

In this case study, steady-state mass balance models are applied for critical loads calculation for the heavy metals.

$$\mathrm{SM_V} + \mathrm{SM_{Dep}} + \mathrm{SM_D} + \mathrm{SM_{Abf}} = \mathrm{SM_E} + \mathrm{SM_{Aw}} + \mathrm{SM_{Er}} + \mathrm{SM_G} + \Delta\mathrm{SM_{Vorr}}.$$

where $\mathrm{SM_V}$ is release by weathering; $\mathrm{SM_{Dep}}$ is input by the atmospheric deposition; $\mathrm{SM_D}$ is input by "usual" fertilising; $\mathrm{SM_{Abf}}$ is input by the use of waste; $\mathrm{SM_E}$ is output by harvest; $\mathrm{SM_{Aw}}$ is output by leaching; $\mathrm{SM_{Er}}$ is output by erosion of the soil's parts; $\mathrm{SM_G}$ is output by degassing; $\Delta\mathrm{SM_{Vorr}}$ is changes of the heavy metal pool in soil.

This mass balance presents the possible links in the biogeochemical food web for various heavy metals. Some items may be neglected, like degassing of Pb, Cd, Cu and Zn metals. However, this process is of crucial importance for mercury (see Section 3.2). The output of the heavy metals with soil erosion may also be neglected. After elimination of these processes, the simplified following equation is workable. The sum of inputs by deposition, fertilizing, and waste and rubbish as fertilizer stands as the term Critical Load'.

Thus, critical loads of any heavy metals may be calculated as follows:

$$\mathrm{CL_{SM}} = \mathrm{SM_E} + \mathrm{SM_{Aw}} - \mathrm{SM_V} + \Delta\mathrm{SM_{Vorr}}.$$

The mass balance model for calculation of critical loads for heavy metals includes the weathering process, the net removal through the crop biomass harvest, leaching, and also leaf uptake and litterfall. Using the simple dynamic way, the distribution between adsorbed and dissolved phases was accounted.

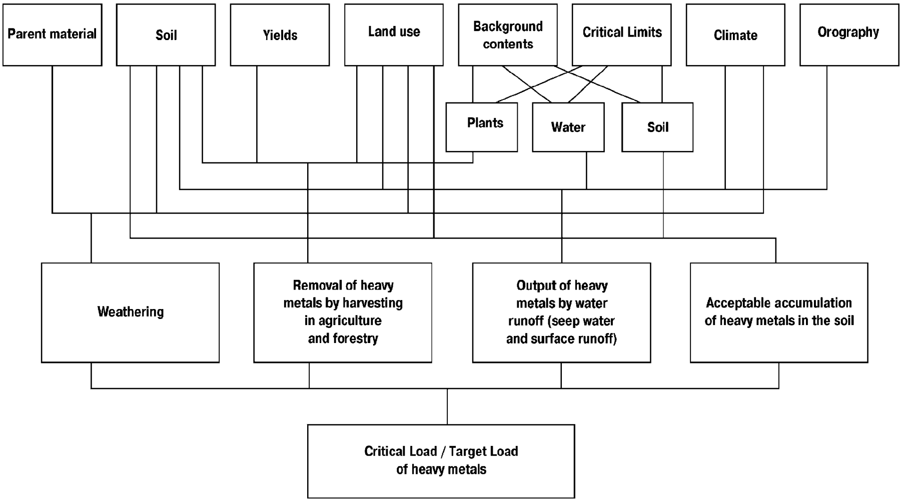


Figure 4. Database for initial information for calculation of HM critical loads in Germany (Bashkin and Gregor, 1999).

The uncertainties in the model inputs were elaborated using the statistic distribution functions for the initial parameters and also the Monte Carlo simulation.

The available information for calculation of critical loads of HMs in Germany is shown in Figure 4. This figure shows also the schematic algorithms for CL calculations.

The application of CL model and initial information allowed the researchers to map the critical loads of various heavy metals for different ecosystems.

2.2. Calculation and Mapping of Critical Loads for Cd and Pb in the European part of Russia

Biogeochemistry of heavy metals has been extensively studied in the former Soviet Union due to a widespread environmental pollution. The numerous results on ecosystem sustainability or sensitivity to metal inputs have been accumulated.

The assessment of ecosystem sustainability to the heavy metal loading includes primarily the estimation of soil compartment (Solntseva, 1982; Elpatievsky, 1994; Glazovskaya, 1997). These researches as well as literature data from other countries showed that the processes of metal accumulation and transformation in soil and further migration in biogeochemical food webs, like metal uptake by plants and metal leaching from the soils, are mainly dependent on geochemical properties of the soils. The following soil parameters were shown as the most important: pH, organic matter composition (mainly the humic and fulvic acids ratio), redox reaction, and soil granulometric composition (Davies, 1980; Sanders, 1982; Kabata-Pendias, Pendias, 1984, 1992; Adriano, 1986; Balsberg-Pahlsson, 1989; Bowen, 1989; Temminghof et al., 1997).

Glazovskaya (1997) applied an analysis of geochemical conditions in different soils and developed principles for assessing quantitatively the sustainability of ecosystems under the technogenic impact of heavy metals. The soils of the main natural zones distinguished on the East European plain area were combined into 6 groups according to their ecological-geochemical sustainability under HM loading (from "very sensitive" to "insensitive"). As shown in this research, most of the soils of the East European plain area have medium or weak sustainability under metal exposure. But quantitative parameters of HM impacts on the soil (including the permissible levels of metal depositions) were not considered in this classification.

The quantitative assessment of biogeochemical mass–balances of the metals in various natural, urban and agricultural ecosystems were carried out in the different regions of the Russian Federation (Bashkin et al., 1992; Elpatievsky, 1994; Kasimov et al., 1995; Priputina et al., 1999, 2002, 2004a, 2004b). Methodologically, these researches are similar to the general approach used for calculations of HM critical loads in Europe (de Vries et al., 1998a, 1998b). However, the results of these local researches could not be directly used for calculations of HM critical loads for the whole area of the East European plain due to scarcity of the data needed for computation according to the steady-state mass balance equation (see Section 3.2). Nevertheless, these data were used for estimating and mapping of HM critical loads for the European Russia area (Priputina et al., 1999; Bashkin, 2002).

Preliminary calculating and mapping of critical loads for heavy metals (Pb and Cd) in the forest ecosystems of European Russia have been accomplished using a simplified version of the steady-state mass balance model (Priputina et al., 2002). For present study *effect-based critical loads* evaluated in accordance to the Guidance (de Vries et al., 2002) have been derived using critical limits of heavy metals concentration in the soil solution (0.6–1.0 mg m^{-3} and 6–10 mg m^{-3} for Cd and Pb, respectively). Input data applied for preliminary estimations of ERA endpoints included the parameters required for computing root uptake, leaching and weathering of heavy metals in different soil types (Priputina et al., 2003). The calculations of critical loads for lead and cadmium have been accomplished for the forest ecosystems of several key plots located in various natural conditions of the European part of Russia; background areas from north taiga to deciduous forests zone have been taken for these evaluations (Figure 5).

Calculation Methods and Critical Limits

In this study two different endpoints have been selected: *human health aspects* (critical limits based on drinking water quality) and *ecotoxicological effects on biota* (critical limits based on free metal ions concentration) (Priputina et al., 2004b).

Two metal fluxes (net uptake in harvestable parts of plant biomass and leaching from the considered soil layer) are included in the *mass balance equation* (M&M Manual, 2004):

$$\mathrm{CL(M)} = \mathrm{M_u} + \mathrm{M_{le(crit)}}. \tag{1}$$

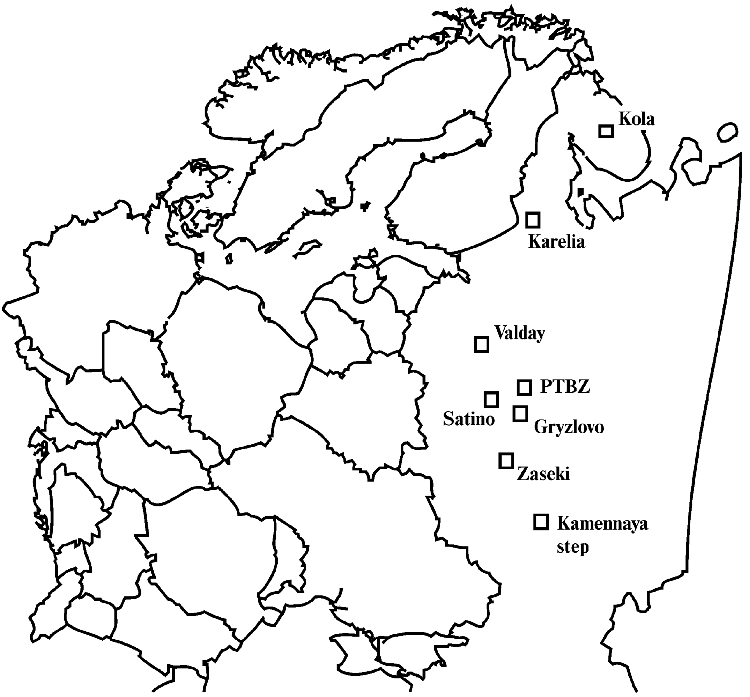


Figure 5. Location of case study ecosystems used in test of critical loads calculation in the European part of Russia.

In forest ecosystems these symbols stand for: CL(M) is critical load of a heavy metal (g ha^{-1} a^{-1}); M_u is metal net uptake in wood biomass under critical loads conditions (g ha^{-1} a^{-1}); $M_{le(crit)}$ is critical leaching flux of metal with drainage water (from the uppermost 10 cm soil layer) (g ha^{-1} a^{-1}).

In one's turn, *metal removal from the soil because of biomass uptake* is accounted in the following way:

$$M_u = \mathbf{f}_{Mu} * Y_{ha} * [M]_{ha} \tag{2}$$

where Y_{ha} is yield of harvestable biomass (wood biomass net production) under critical load conditions (kg dw ha^{-1} a^{-1}); $[M]_{ha}$ is content of the metal in the wood (g kg^{-1} dw); $\mathbf{f}_{Mu}$ is the fraction of metal net uptake within the considered soil depth (z_b or z); root uptake factor, f_{Mu}, is assumed to be equal to 1.

The critical leaching flux of HM can be calculated by the equation:

$$\mathbf{M}_{le(crit)} = \mathbf{c}_{le} * \mathbf{Q}_{le} * \mathbf{M}_{ss(crit)} \tag{3}$$

where $\mathbf{Q}_{le,zb}$ is leaching flux of water from the topsoil (the uppermost 10 cm soil layer) (m a^{-1}); $[\mathbf{M}]_{ss(crit)}$ is critical limit for metal concentration in the percolating soil solution (mg m^{-3}); $\mathbf{c}_{le}$ is 10 g mg^{-1} m^2 ha^{-1}, factor for appropriate conversion of flux units.

The annual mean *water percolation* $\mathbf{Q}_{le,zb}$ is determined by the long-term mean annual temperature (mainly determining the potential evapotranspiration, E_{pot}) and precipitation (mainly influencing the actual evapotranspiration, E_{act}) according to

$$\mathbf{Q}_{le,zb} = \mathbf{P}_m - \mathbf{f}_{E,zb} \cdot (\mathbf{P}_m^{-2} + (e^{(0.063 \cdot T_m)} \cdot \mathbf{E}_{m,pot})^{-2})^{-1/2} \tag{4}$$

where $\mathbf{P}_m$ is annual mean precipitation (m a^{-1}); T_m is annual mean air temperature (°C); $\mathbf{E}_{m,pot}$ is annual mean potential evapotranspiration in humid areas at $T_m = 0\,^\circ C$; $E_{m,pot} \approx 0.35$ m a^{-1} in forests, possibly less in other terrestrial ecosystems; $\mathbf{f}_{E,zb}$ is the fraction of total annual mean evapotranspiration above z_b $(\cdot)$; $f_{E,zb} \approx 0.8$ for the organic top soil layer of forests.

Critical concentrations of HMs in the soil solution, $[\mathbf{M}]_{ss(crit)}$, depend on the target to be protected (ERA endpoints). These values have to be derived from critical limits. Parameters of critical limits used in the calculations are presented in Table 1.

Input Data

The values of output metal fluxes mentioned above vary as a function of spatial distributed parameters including climate, soil and forest-type data. As a basis for computing critical loads, an overlay of three maps was made:

- FAO soil map;
- Runoff data map;
- Forest-types map generalized from Land use map.

Table 1. Overview of critical limits used for calculating critical loads in case study plots.

Endpoints	Indicator/critical limit	Pb, mg m^{-3}	Cd, mg m^{-3}
Human health effects	Total HM concentration in soil water below root zones (*aiming at ground water protection*)	10	3
Ecosystem functioning	Free metal ion concentration in soil solution re-calculated to total dissolved metal concentration in soil drainage water (*in view of effects on soil microorganisms, plants and invertebrates*)	1.7–20.4*	1.3–3.2*

**Values accounted using Look-up tables (Modelling and Mapping Manual, 2004)*

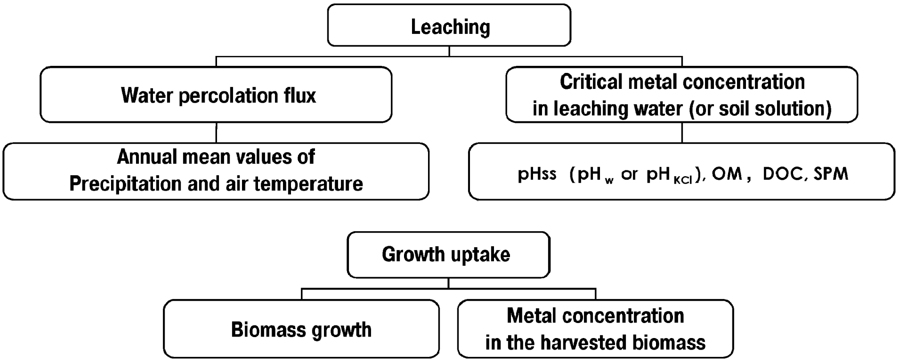


Figure 6. Diagram of metal fluxes and input data included in calculation methods.

Soil-related data (HM and BC content in soil parent materials) were included in calculations to account the values of HM weathering. Also we considered the influence of soil types on forest biomass productivity. Runoff data (at scale 0.5′ × 0.5′) were directly used to get input data on drainage water fluxes, $\mathbf{Q}_{\mathrm{le}}$. Forest-type-related data (wood biomass growth and HM content in wood biomass) inserted into our database were subdivided depending on either coniferous, deciduous or mixed forests.

Structure of the database and input data needed for inclusion in the present database are shown in (Figure 6).

Data on water leaching fluxes have been calculated using iteration approaches (Priputina, 2004). Water percolation parameters have been accounted (Manual, 2004). Annual mean air temperature and precipitation data have been obtained from IWMI World Water and Climate Atlas (2002). Two iteration versions of the map of water leaching parameters are shown in Figure 7.

The data needed for estimating *metal removal with harvestable part of wood biomass* have been obtained from literature as well as from sampling and simulating studies. As a rule, data on yields of forests can be accounted either from forest service statistics or using special calculations when forest potential growth is estimated as a function of climate, soil and tree type characteristics (Reinds et al., 2001). However forest statistical data are not spatially distributed in most areas of Russia. Also, there are many uncertainties in estimating potential bioproductivity of the forests. That is why we used simulation procedures to account annual mean growth of wood biomass in the forests of case study plots (Table 2).

Model EFIMOD (Chertov, Komarov, 1997) has been applied to compute data on annual increase of wood stock in stems and large branches of main tree types widespread in the forests of the European part of Russia. We assume that these data after some improving and completing could be applied in the national database. As a cartographic layer a generalized version of the map of forest tree dominants is used (Figure 8).

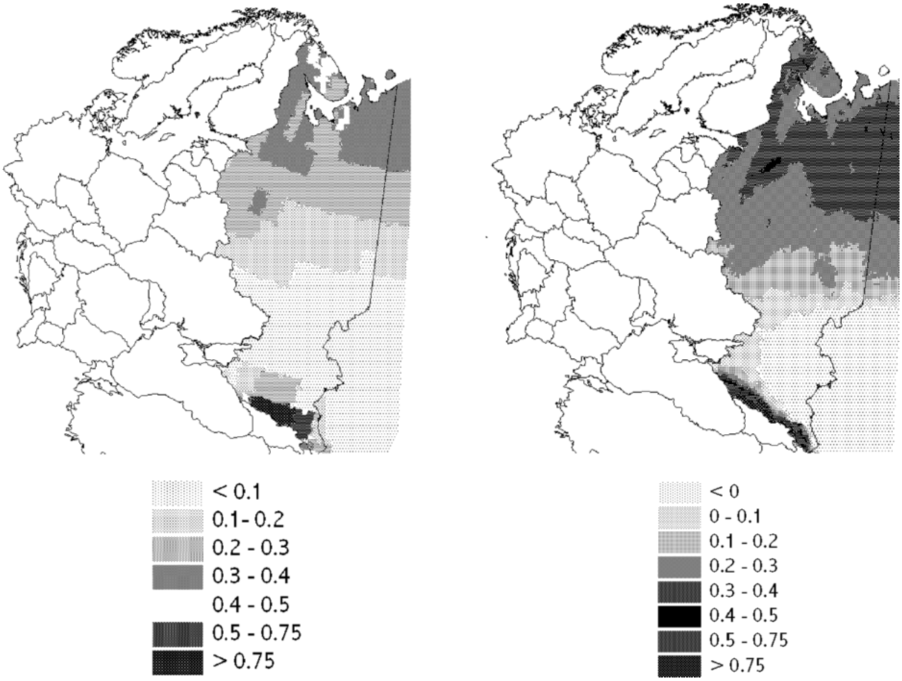


Figure 7. Spatial distribution of the data used for estimating water leaching fluxes (m a^{-1}*): on the left—runoff data only (iteration I), on the right—data calculated from climate parameters (iteration II).*

Table 2. Parameters of wood biomass growth for main tree types in the forests of European Russia; results of simulating based on EFIMOD (Chertov, Komarov, 1997).

		Wood biomass growth, kg m^{-2} (dw)		
Type	Location	*Stem*	*Branches*	*Total*
Pine (Pinus silvestris)	Northern regions	0.35–0.38	0.06–0.08	0.4–0.45
	Central regions	0.35–0.4	0.08–0.1	0.45–0.5
Spruce (Picea abies)	Northern regions	0.15–0.16	0.03–0.04	0.18–0.2
	Central regions	0.5–0.52	0.08–0.1	0.6–0.62
Birch (Betula pendula)	Northern regions	0.1–0.12	0.01–0.02	0.11–0.15
	Central regions	0.3–0.35	0.03–0.04	0.35–0.4
Oak (Quercus robur)	Central regions	0.25–0.26	0.05–0.06	0.3–0.32
	Southern regions	0.25–0.3	0.05–0.8	0.3–0.4

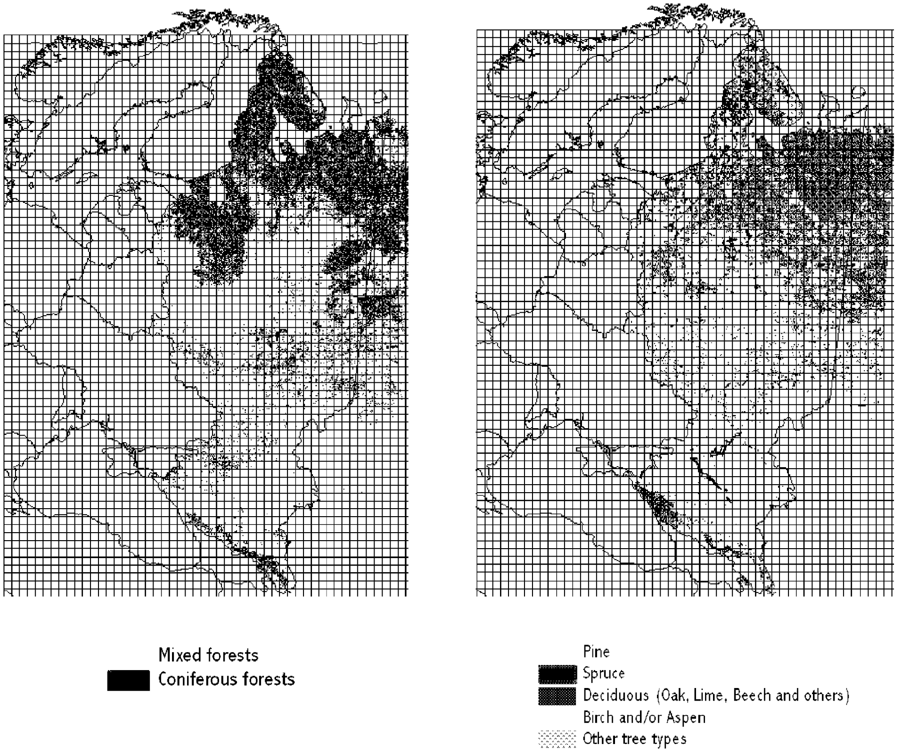


Figure 8. Forest-type-related cartographic data: on the left—Land use map (IGBP Map of EDC DAAC, 1997, see de Vries et al., 2002) applied in calculations'2002; on the right—fragment of the map of forest tree dominants (National Atlas, 2003, see Priputina, 2004b).

Since reference national data on Pb and Cd content in the harvestable part of forest biomass (stems and branches) are very rare, sampling of stem wood has been carried out in the background forested areas of European Russia. The results are presented in Table 3. The whole set of data from this table illustrates median values of Pb content in wood biomass for all tree types, which are lower than 1.0 mg/kg (dry weight). Minimal values of average concentrations were revealed in Pine tree (*Pinus silvestris*). In the same regions (sampling plots) average values of Pb accumulation in spruce species (*Picea abies*) are higher than in pine trees. But, conjugated analysis of distribution of Pb content values in the wood of both Spruce and Pine trees did not reveal evident differences between two groups of coniferous trees (Figure 9). Median (average) values of Pb concentrations in deciduous trees are higher in comparison with coniferous ones.

Maximum values of average Cd concentrations are revealed in stem wood of the Aspen tree (*Populus tremula*). Median values of Cd content in other types of both deciduous and coniferous trees are lower than 0.2 mg/kg (Table 3, Figure 10).

Table 3. Pb and Cd content in stem wood of main tree types. Overview of the data from relatively unpolluted areas of European Russia (Priputina et al., 2004a, 2004b).

Type	Number of samples (tested plots)	Pb, mg kg^{-1} (dw)	Cd,mg kg^{-1} (dw)
Spruce (*Picea abies*)	26 (3)	0.35* 0.1–1.6	0.2 0.07–0.7
Pine (*Pinus silvestris*)	62 (6)	0.1 0.01–1.1	0.13 0.01–0.42
Oak (*Quercus robur L.*)	20 (2)	0.45 0.03–1.3	0.05 0.01–0.4
Lime (*Tilia cordata)*	24 (3)	0.65 0.15–1.7	0.1 0.03–0.3
Birch (*Betula pendula*)	38 (4)	0.35 0.01–1.0	0.1 0.01–0.65
Aspen (*Populus tremula*)	24 (2)	0.6 0.25–1.8	0.35 0.15–0.65

*Median values in numerator, minimum–maximum values in denominator

As one can see from distribution of Cd concentration values in deciduous trees, there are three "separate" sections in this line. The first one "amalgamates" most wood samples, excepting Aspen tree samples. The second and third parts of the distribution line consist mostly the Aspen tree samples taken from two different

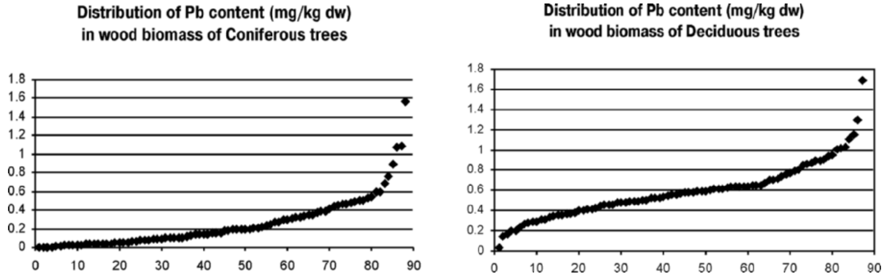


Figure 9. Distribution of lead concentrations in stem wood of coniferous (on the left) and deciduous (on the right) trees; value (X) axis—samples number.

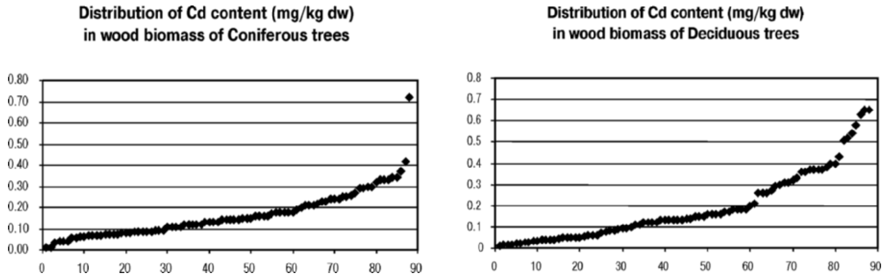


Figure 10. Distribution of cadmium concentrations in stem wood of the forest trees: on the left—coniferous, on the right—deciduous, value (X) axis—samples number.

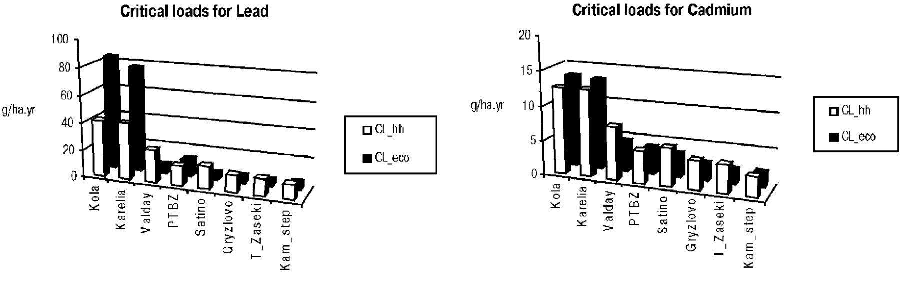


Figure 11. Ranges in critical loads of Pb and Cd: CL_hh—in view of human health effects; CL_eco—in view of ecotoxicological effects.

plots, correspondingly. These data on Pb and Cd content in harvestable parts of the forest biomass are naturally incomplete for their spreading all over the European part of Russia and can be considered as very relative. However preliminary analyses of these data allow us to conclude that present background parameters of heavy metals accumulation in the forests of European Russia are generally lower than in Central Europe.

The parameters related to *soil-related data* (to define soil solution status such as pHss, DOM or DOC, SPM) influences on HM toxicity for biota. These data should be either measured (in a few plots only) or simulated since this information is mainly not perennially monitored for forested areas of Russia. Soil pH data (water or KCl extraction) are more available parameters as depending on soil type. The same FAO soil map with added attributive tables containing soil pH values can be used for this purpose.

Critical Loads of Heavy Metals Depending on ERA Endpoints

The ecosystem characteristics of case study plots in various natural forests of the European part of Russia are shown in Table 4. Critical loads in an occasion of *human health* and *ecotoxicological effects on biota* (endpoints) have been accounted. Corresponding critical limits of HM concentration in soil drainage waters are presented in Table 1.

Critical metal concentrations in soil drainage water have been estimated for upper soil layer either organic or humus (depending on soil type). Look-up tables based on the data from WHAM model (Tipping et al., 2003) have been used for endpoint estimation in view of *ecotoxicological effects*. High values of the total critical Pb concentration (19–20 m kg l^{-1}) have been derived for two plots, Kola and Karelia, where organic layers of corresponding soils are characterized by low pH parameters and high content of organic matter. Simultaneously, maximal values of water leaching flux have been accounted for the same regions due to high precipitation excess. As a result, critical leaching flux of Pb for these northern forests has been computed to equal about 80 g ha^{-1} per year, which appears overstated. For other plots, critical Pb concentration in drainage water is estimated to equal 2–9 m kg l^{-1}; critical leaching

Table 4. Main characteristics of case study ecosystems.

Plot "nickname"	Annual mean temperature, °C	Precipitation, mm	Forest-type tree dominants	Soil type	Considered organic/ humus horizon
Kola	−0.5	550	Coniferous/*Pinus silvestris*	Al-Fe-h Podzols	O
Karelia	0.5	550	Coniferous/*Pinus silvestris*	il-Fe Podzols	O
Valday	3.5	740	Coniferous/*Picea abies*	Podzoluvisols	A0A1
PTBZ	4.2	560	Coniferous/*Pinus silvestris*	Podzoluvisols	A0A1
Satino	4.0	570	Mixed/*Picea abies*	Podzoluvisols	A1
Gryzlovo	4.3	520	Mixed/*Populus trem.*	Luvisols	A1
T_Zaseki	4.5	525	Deciduos/*Quercus robur*	Greyzems	A1
Kamennaya steppe	5.0	415	Deciduos/*Quercus robur*	Chernozems	A1

flux ranges from 2 to 12 g ha^{-1} per year. For all ecosystems included in the study, the calculated values of Pb removal with annual growth of wood biomass are considerably lower than Pb leaching flux that deals with low concentrations of HM in the wood of all tree types that was mentioned above. The computed critical loads for Pb are shown in Figure 11.

In the northern ecosystems where calculated critical concentrations of Pb in soil drainage water exceed "human health" critical limits 10 m kg l^{-1} the accounted critical loads of Pb related to ecotoxicological effects are higher than the ones related to human health effects. Critical loads for Cd range from 2 to 13 g ha^{-1} per year. Maximum value is also computed for Kola and Karelia ecosystems. Critical Cd loads aimed at both ground water protection and effects on biota have close values but the ranges computed illustrate that critical loads for Cd based on ecotoxicological limits are more stringent than those based on human health effects.

CHAPTER 5

BIOGEOCHEMICAL APPROACHES TO HUMAN EXPOSURE ASSESSMENT

For understanding the quantitative mechanisms of human risk assessment, the researcher has to know the interrelations between biogeochemical cycling and human risk endpoints. In the previous chapters we have considered the natural biogeochemical cycles of various chemical elements and their alterations under anthropogenic activity. We can conclude that at present the alteration of biogeochemical cycling under the influence of humans is undoubtedly accompanied by changes in food webs. This leads to the reversible and/or irreversible transformation of human health both at the individual and population levels. For the understanding of the interactions between changes in natural biogeochemical cycling and human health risk, one should take into account the numerous data on the migration of essential and non-essential elements in biogeochemical food webs and estimate the correlation with biochemical and physiological indexes of human organisms as the endpoints.

1. BIOGEOCHEMICAL AND PHYSIOLOGICAL PECULIARITIES OF HUMAN POPULATION HEALTH

The geochemical heterogeneity of biosphere and co-evolution of biosphere and geosphere have led to the formation of various biogeochemical provinces with different food webs and definite sustainability or sensitivity of living organisms, including human, to physiological disturbance and diseases (see Chapter 2).

V. Vernadsky has initiated the study of the interactions between chemical heterogeneity of biosphere and human health in his Biogeochemical laboratory in 1928. The main tasks of this laboratory were related to the study of living organisms and their origin depending upon geographic, geological and biological characteristic of the permanent environmental media. In 1932 the researchers have began to monitor the geochemical areas with different disease caused by the peculiarities of chemical composition of soil, waters, plant and animal species, or in other words, by biogeochemical food webs.

In 1938 A. Vinogradov published the book “Biogeochemical provinces and human endemic diseases”. He has analyzed the relationships of organisms and populations with geochemical structure of the biosphere. This book initiated the biogeochemical mapping of North Eurasia in 1940s–1980s headed by Kovalsky (see detail in Chapter 2).

In the USSR Kovalsky showed that productivity in cattle can be correlated to the excess or deficiency of boron, cobalt, copper, molybdenum and selenium in animal feed. Similar studies were carried out in England and Ireland by Webb (Webb, 1964; Webb et al., 1966) and in USA, by Ebens (Ebens and Schaclette, 1982).

As has been reported, the levels of trace metals in drinking water and foodstuffs of local production can affect human health. The Canadian biogeochemist Warren (1961) showed the relationships between thyroid gland malfunction and iodine deficiency in North America. Shacklette (1970) related the level of trace metals in soil and plants to the incidence of cardiovascular diseases in Georgia, USA. The Finnish geochemist Salmi (1963) reported a correlation between the concentration of lead in rocks and the incidence of multiple sclerosis. Dobrovolsky (1967) developed the method of geochemical mapping for hygienic and prophylactic health management.

Biogeochemical mapping brings together the biological reactions of living organisms and their adaptation to the environmental conditions with chemical composition of geological rocks, soils, natural waters, feed and food. The most important feature of biogeochemical mapping is the estimation of the upper and lower limits of essential elements in biogeochemical food webs, for instance in soils, waters, crops, feed and food daily intake. The limit concentrations are the values, lower or upper of which the regulatory mechanisms of exchange processes in living organisms (plant, animals and humans) will be disturbed. Tables 1 and 2 show the example of limit concentrations of some essential micronutrients in soil and forage crops.

Using similar data the biogeochemical mapping of North Eurasia was carried out (see Chapter 2, Figure 4).

Table 1. The lower, optimum and upper limit concentrations of essential trace nutrients in soils of North Eurasia.

		Limit concentrations, ppm		
Trace nutrient	Number of samples	Deficit/lower	Optimum	Excess/upper
Co	2,400	<7	7–30	>30
Cu	3,194	<15	15–60	>60
Mn	1,629	<400	400–3,000	>3,000
Zn	1,927	<30	30–70	>70
Mo	1,216	<1.5	1.5–4	>4
B	879	<6	6–30	>30
Sr	1,269	<600	600–1,000	>1,000
J	491	<5	5–40	>40

Table 2. The lower, optimum, and upper limit concentrations of essential trace nutrients in forage crops for domestic animals in North Eurasia.

			Limit concentrations, ppm		
Trace nutrient	Number of samples	Mean content in pasture crops	Lower (deficit)	Optimum for animal organisms	Upper (excess)
Mn	819	73.0	<20	20–30	>30
Zn	519	21.0	<20	20–60	>60
Cu	937	6.4	<3	3–12	>12
Mo	537	1.25	>0.2	0.2–2.5	>2.5
Co	859	0.32	<0.25	0.25–1.0	>1.0
I	397	0.18	<0.07	0.07–1.2	>1.2

According to the specific characteristics of North Eurasian biogeochemical provinces, the alterations of the biogeochemical food webs were studied for I (endemic goiter), Si (the Urov disease), B (endemic enteritis), Se (endemic myopathia), and Mo (endemic gout). On a basis of these results, the recommendations have been produced for correction of daily intake of essential elements.

1.1. Biogeochemical Structure of Ecosystems and Cancer Endpoints

During the last decades researches in human health risk and biogeochemistry were concerned to the cancer development in various regions of the World. It has been shown that the most human cancer diseases are related to environmental conditions such as the content of various macro- and microelements in biogeochemical food webs.

In accordance with existing knowledge, the inorganic and organic species of Ni, Be, Pt, Cd, Pb, Co, Zn, Mn, Fe, Ti and Hg are suspected carcinogens or procarcinogens (see Box 1. for classification of carcinogens).

Box 1. Biogeochemistry of Carcinogens (after Manahan, 1994)

Cancer is a condition characterized by the uncontrolled replication and growth of the body's own cells (somatic cells). Carcinogenic agents may be categorized as follows:

1. Chemical agents, such as many chemical organic and inorganic compounds;
2. Biological agents, such as hepadnaviruses or retroviruses;
3. Ionizing radiation, such as X-rays;
4. Genetic factors, such as selective breeding.

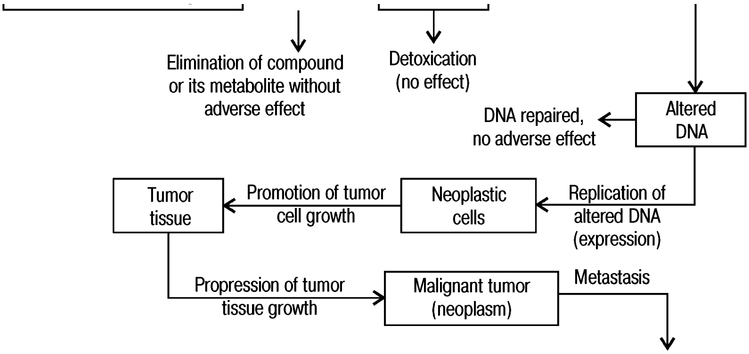


Figure 1. Outline of the process of carcinogenesis (Manahan, 2000).

Clearly, in many cases, cancer is the result of the action of synthetic and naturally occurring chemical species. The role of chemicals in causing cancer is called chemical carcinogenesis. It is often regarded as the single most important facet of toxicology and clearly the one that receives the most publicity.

Large expenditures of time and money on the subject in recent years have yielded a much better understanding of the biochemical bases of chemical carcinogenesis. The overall process for the induction of cancer may be quite complex, involving numerous steps. However, it is generally recognized that there are two major steps in carcinogenesis: an initiation stage followed by a promotional state. These steps are further subdivided as shown in Figure 1.

Initiation of carcinogenesis may occur be reaction of a DNA-reactive species with DNA or by the action of an epigenetic carcinogen that does not react with DNA and is carcinogenic by some other mechanism. Most DNA-reactive species are genotoxic carcinogens because they are also mutagens. These substances react irreversibly with DNA. They are either electrophilic or, more commonly, metabolitically activated to form electrophilic species, as is the case with electophilic $^+CH_3$ generated from dimethylnitrosoamine. Cancer-causing substances that require metabolic activation are called procarcinogens. The metabolic species actually responsible for carcinogenesis is termed an ultimate carcinogen. Some species that are intermediate metabolites between procarcinogenes and ultimate carcinogens are called proximate carcinogens. Carcinogens that do not require biochemical activation are categorized as primary or direct-acting carcinogens. Most substances classified as epigenetic carcinogens are promoters that act after initiation. Manifestations of promotion include increased number of tumor cells and decreased length of time for tumors to develop or by other words, shortened latency period.

Most metals, for which compounds are carcinogenic, are from IV group of Periodic Table of Elements. In biological systems, carcinogenic metals can form stable complexes and biological availability of these complexes determines the carcinogenic potential of various metal compounds.

The carcinogenicity of many metals, like As, Cd, Ni, Be, Cr, Pb, Co, Mn, Fe and Zn, depends on their concentrations in the food webs. These concentrations are the sum of natural content and input awed to pollution. In natural and technogenic biogeochemical provinces, the content of pollutants depends on both geochemical background and anthropogenic inputs. The understanding of relationships between concentrations of carcinogenic metal compounds in food webs and cancer mortality is very important. However, the role of other strong factors like smoking and professional work activity should be also accounted for.

During biogeochemical and physiological studies of cancer diseases, we should take into account also the combined influence of various carcinogens, for instance asbestos, PAH, PAN, metals, agrochemicals, etc. The combined action may change the risk of cancer due to synergetic, additive or antagonistic effects. For instance, the combinations of benzo(a)pyrene and Ni_3S_2, benzo(a)pyrene and chromates, benzo(a)pyrene and As_2O_3, are synergetic for the development of lung cancer in rats. The carcinogenic actions of nitrosoamines and Ni and Cd compounds are additive.

The antagonistic influence on cancer development due to organic carcinogens may be induced by chemical species of Se, As, Al, Co, Cu, Zn and Mo. We should note that the antagonistic effects of the latter metals depend strongly on their concentrations (see above on limit concentrations). Similar interactions are characteristic for the combinations of metals in biogeochemical food webs of various biogeochemical provinces.

1.2. Cancer Risk Endpoints in Different Biogeochemical Provinces

Extensive biogeochemical studies of cancer illnesses have been carried out in different biogeochemical provinces of North Eurasia.

Carpathian Region

The influence of various trace elements has been studied during the 1980s–1990s in the Forest Steppe and Mountain regions of the biosphere, in Ukraine. Three natural biogeochemical provinces, Carpathian, Pre-Carpathian and Forest Steppe, have been monitored for the migration of trace elements in food webs and human cancer distribution (Table 3).

We can see that the aborigines of Carpathian and Pre-Carpathian biogeochemical provinces are relatively seldom ill with lung and stomach cancer compared to those of Forest Steppe province. These differences are related to the chemical composition of soils and ground waters in various provinces. For instance, in the Carpathian biogeochemical province with Brownsols and Podsoluvisols enriched in titanium and depleted in vanadium, strontium and manganese, predominant human diseases are strong leukemia, hemorrhagic vasculitis, Fe-deficit anemia, and thrombosis. Lung or stomach cancer seldom occurs.

Table 3. Lung and stomach cancer distribution and average content of trace elements in soils and drinking waters of various biogeochemical provinces.

Province	Average content of trace elements, ppm								Rank of cancer morbidity
	Ti	V	Cr	Mn	Cu	Sr	Ba	Pb	
Soils, dry weight									
Carpathian	1.490	123	61	482	14	36	74	21	Low
Pre-Carpathian	1.297	110	62	690	15	49	99	21	Low
Forest Steppe	1.216	110	66	955	14	42	116	23	High
Ground waters, ppm per dry salt content									
Carpathian	—	53	16	1.714	23	6.992	69	5	Low
Pre-Carpathian	—	18	16	1.107	27	1.422	41	5	Low
Forest Steppe	—	14	16	754	18	2.927	12	6	High

In the Pre-Carpathian biogeochemical province with prevalent Eutric Podsoluvisols, enriched in lead and barium and depleted in chromium and vanadium, the predominant diseases are mieloleukemia, chronic lymphatic leukemia, hemorrhagic vasculitis, hypoanemia with a relatively low number of sharp leukemia, lung and stomach cancer.

In Forest Steppe biogeochemical province with Eutric Phaerozems and Distric Chernozems, enriched in all trace metals, such illnesses as lung and stomach cancer, tumor of cerebrum and spinal cord, and nephritis are predominant, whereas the Addison-Bearmer anemia, progressive myopia and glaucoma are relatively seldom.

Middle Volga Silicon Region

Similar biogeochemical studies of cancer development have been carried out in the biosphere of the Middle Volga silicon sub-region (Kovalsky and Suslikov, 1980; Ermakov, 1993). The biogeochemical map of this sub-region is shown in Figure 2.

In the Chuvash administrative region of the Middle Volga drainage basin, three sub-regions of biosphere (Pre-Kubnozivilsk, Pre-Sura, and Pre-Volga), and three natural biogeochemical provinces (silicon, nitrate and fluorine) have been mapped. We will consider the biogeochemical food webs and typical endemic diseases in these sub-regions and provinces.

Pre-Kubnozivilsk sub-region of biosphere

This sub-region is in the central and east part of the Chuvash administrative region. Most of the sub-region is occupied by Steppe ecosystems with some small spots of Broad-Leafed Forest ecosystems. The predominant soils are Phaerozems. The biogeochemical food web of this sub-region is presented in Figure 3.

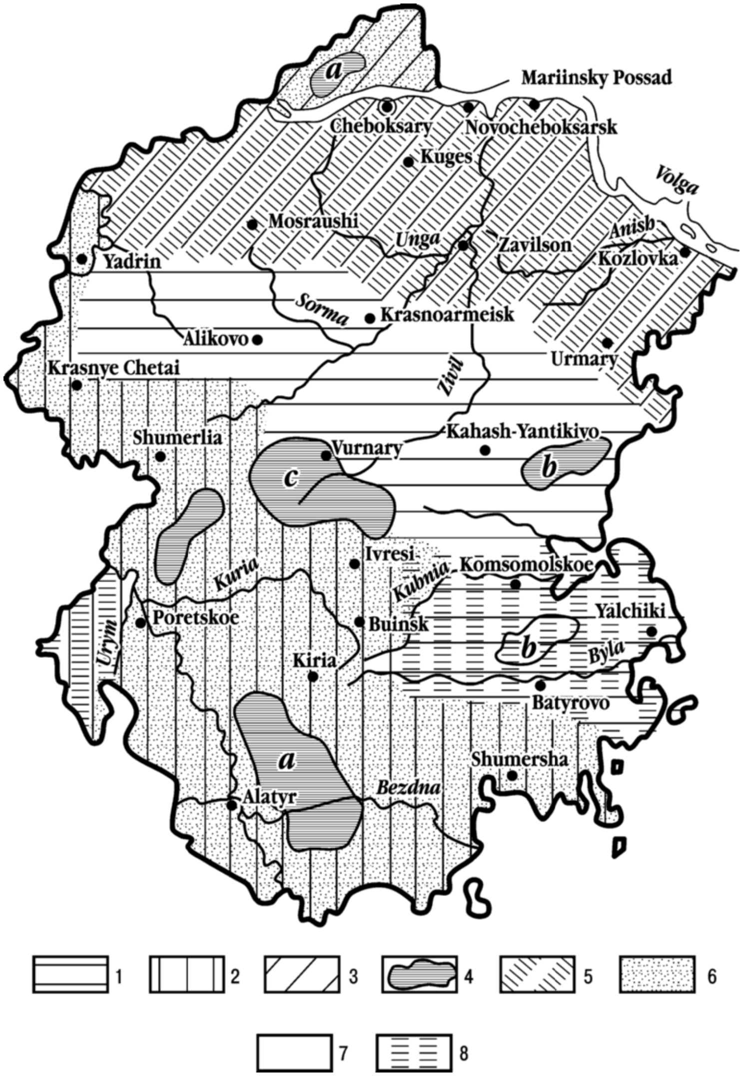


Figure 2. Biogeochemical mapping of the Chuvash administration region, Russia. Biogeochemical regions: 1—Pre-Kubnozivilsk, 2—Pre-Sura, 3—Pre-Volga, 4—Biogeochemical provinces—(a) silicon; (b) fluorine, and (c) nitrate, Soils: 5—Podzoluvisols, 6—Phaerozems, 7—Chernozems, 8—Arenosols.

We can see from Figure 3 that the moderate deficit of I, Co, Zn, Cu, Mo, B, and Mn with optimal ratios of trace metals to I and Si, is characteristic for all links of a biogeochemical food web. These biogeochemical peculiarities favor the optimal physiological regulation of exchange processes in animal and human organisms. However, a moderate deficit of essential trace nutrients weakens the human immune

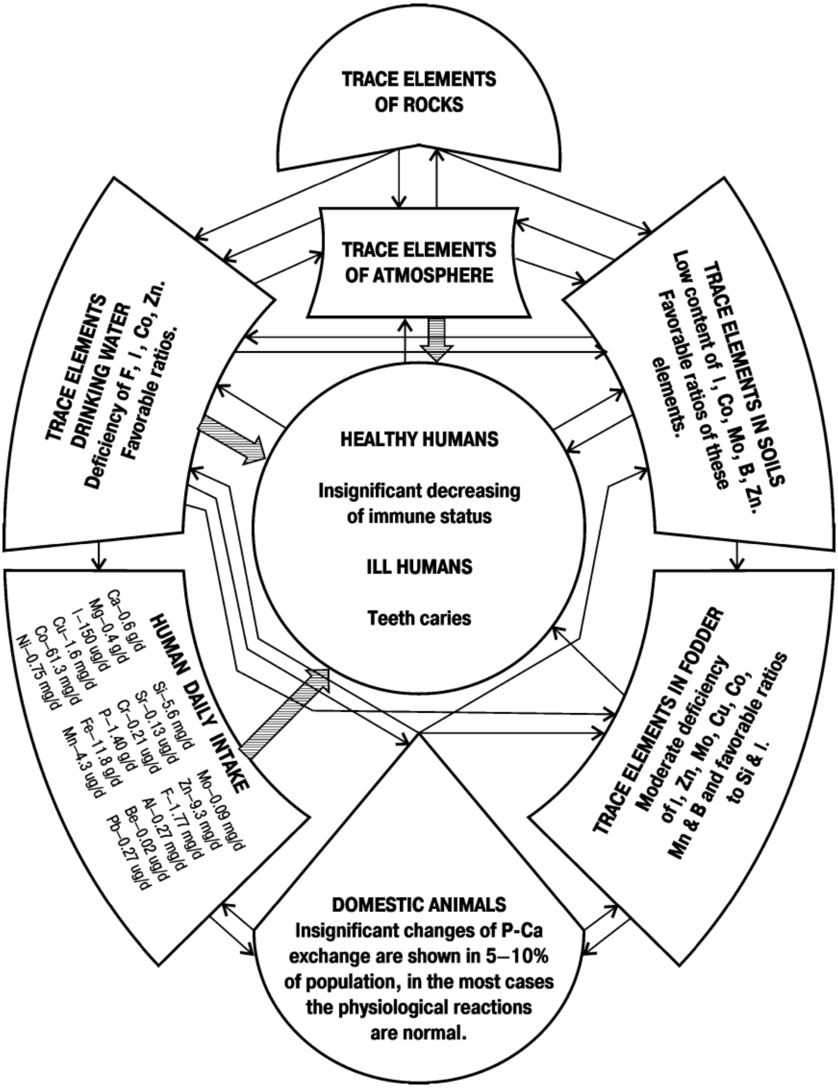


Figure 3. Biogeochemical food web in Pre-Kubnozivilsk sub-region of biosphere.

system. In spite of the latter point, this sub-region can be considered as a control natural biogeochemical area for understanding the endemic diseases of humans and animals.

Pre-Volga sub-region of biosphere

This sub-region of biosphere occupies the northern part of the Chuvash administrative region with predominance of Broad-Leafed Forest and Meadow Steppe natural

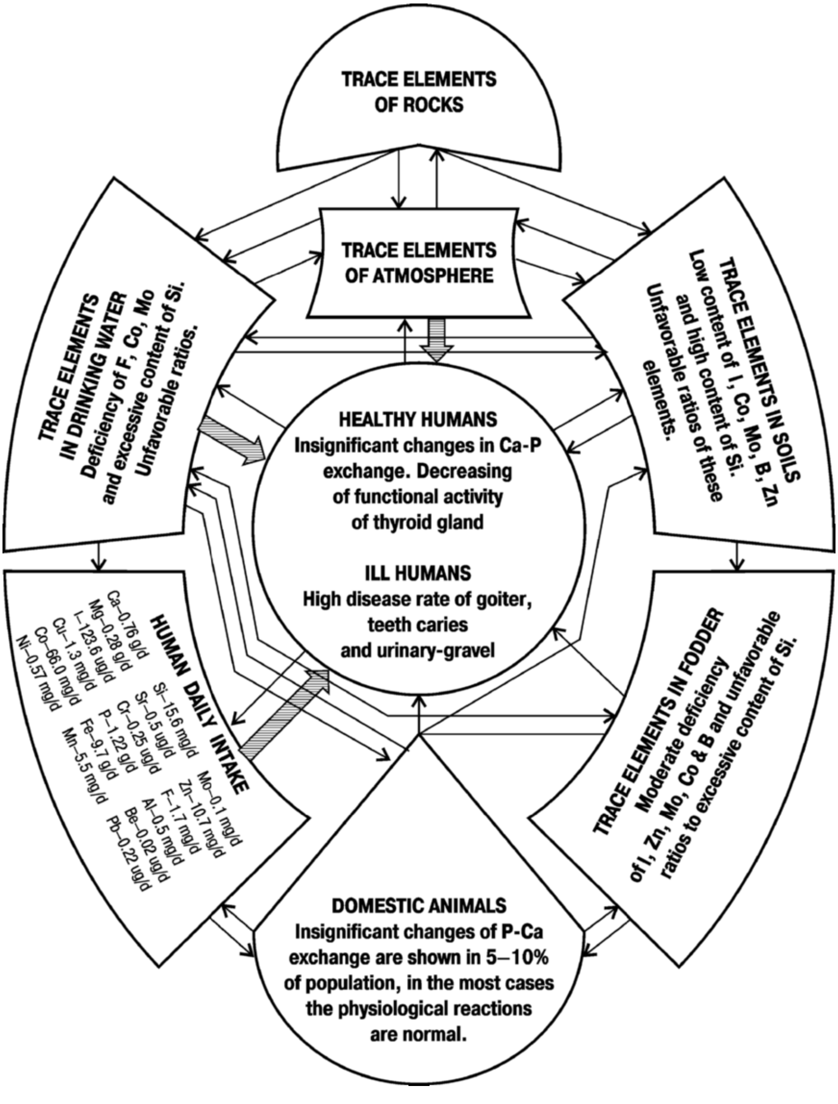


Figure 4. Biogeochemical food web in Pre-Volga sub-region of biosphere.

ecosystems and agroecosystems. The prevalent soils are Podsoluvisols. The scheme of its biogeochemical food web is shown in Figure 4.

The deficit of I, Co, Mn, and Zn, moderate excess of Si and disturbed ratios of trace metals to I and Si are characteristic features of the biogeochemical food web of this Pre-Volga sub-region of biosphere. Most of its natural water sources have a decreased content of fluorine. These peculiarities of biogeochemical food web favor the occurrence of tooth decay (caries) and endemic goiter.

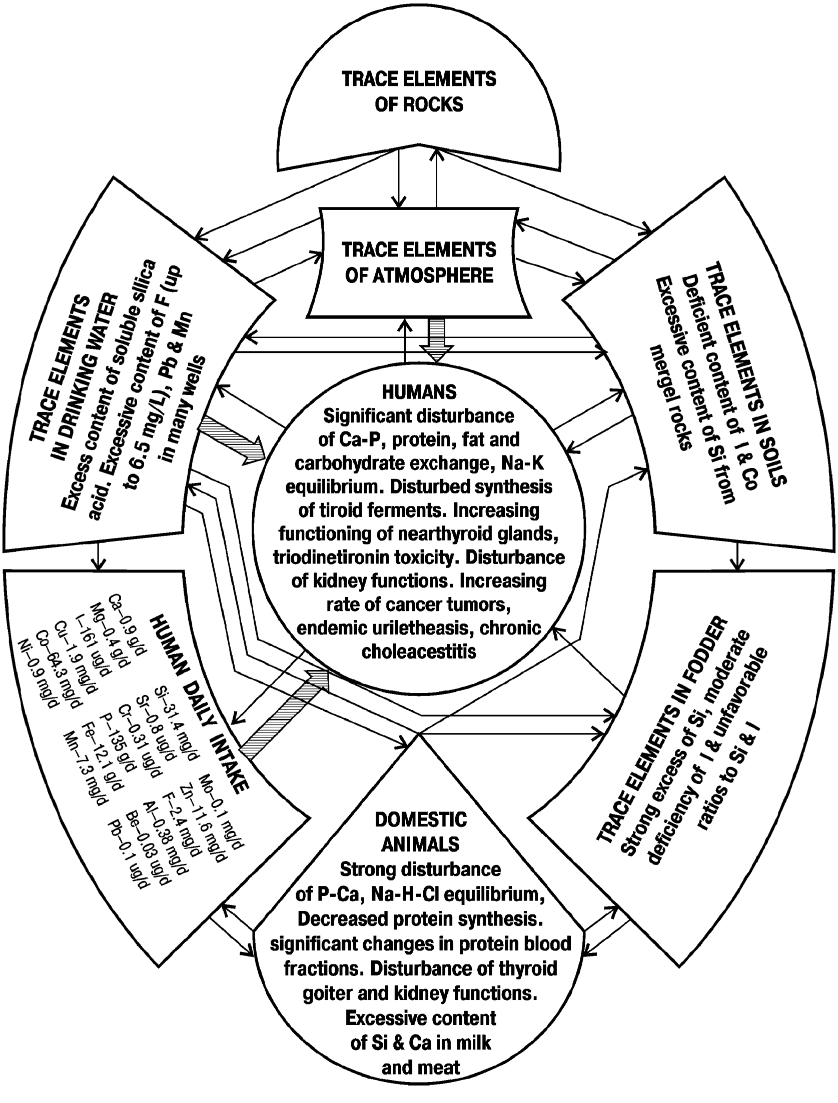


Figure 5. Biogeochemical food web in Pre-Sura sub-region of biosphere.

Pre-Sura sub-region of biosphere

This sub-region is found in southwestern and southern parts of the Chuvash administration region, Russia (see Figure 2). Most of its ecosystems are Coniferous Forests with Arenosols and Podsoluvisols. There is some silicon ore (trepels) in this area and silicon-enriched geological rocks are typical as soil-forming materials. Both soils and river waters are enriched in silicon and this has led to a specific form of biogeochemical migration, which can be called a silicon biogeochemical food web (Figure 5).

We can see that in all links of the biogeochemical food web in the Pre-Sura sub-region of biosphere, the large excess of silicon, moderate deficit of iodine and cobalt, and unfavorable ratios of essential trace elements to silicon are characteristic features. These peculiarities of biogeochemical migration of elements lead to the disturbance of phosphorus–calcium and protein exchange in the human and animal organisms and to the development of endemic goiter, urolithiasis and other endocrine illnesses.

In addition to these three sub-regions, we can see three biogeochemical provinces: (a) silicon; (b) fluorine, and (c) nitrate. The origin and development of these provinces are connected with local geological and agricultural conditions. The silicon and fluorine provinces were developed over dispersed areas of silicon and apatite ores. The nitrate biogeochemical province is related to the intensive application of nitrogen fertilizers in agroecosystems (Figure 2). The technogenic nitrate biogeochemical province (agrogeochemical province) occupies some places inside of the Pre-Sura silicon sub-region of biosphere. The increased rates of methemoglobinemia and stomach cancer have been monitored in the latter province.

Medical statistics indicate that in the Pre-Sura silicon sub-region, the number of malignant tumor formations is 3 times higher than in the control Pre-Kubnozivilsk sub-region. A significant increase of cancer has been registered in young women. For instance, in the silicon sub-region, the different types of uretheral cancer were from 0.117 to 2.63 cases per 1000 women, whereas these diseases were not detected at all in the control sub-region. The clinical monitoring of chemical blood composition showed increasing content of K ion in 88.64%, Ca ion, in 70.05%, and phosphorus, in 57.2% of monitored people above physiological optimal limits. The average content of K^+ in blood of people from the silicon sub-region was 2-fold, Ca^{2+} 1.14-fold, and phosphorus 1.45-fold higher than that of people from the control biogeochemical sub-region.

In this biogeochemical sub-region the rate of carcinogenecisis was also correlated with the drinking water hardness. Water hardness is connected with the content of Ca, Mg and Fe compounds (Table 4).

The minimum cancer number was monitored at content of Ca^{2+} 4.5–4.8 meq/L, Mg^{2+}, 2.5 meq/L, Ca:Mg ratio, 1.65–1.90 and water alkalinity, 6.0 meq/L.

From the physiological point of view the development of excessive cancer rates and various endemic diseases in silicon biogeochemical sub-region and especially in

Table 4. Correlation between water hardness and cancer rates in silicon sub-region.

Hardness, meq/L	Percent from monitored drinking water sources	Rank of cancer illnesses
<7	27	Low
8–14	62	Medium
15–29	11	High

silicon biogeochemical province can be explained by transmission from the norm to a pathological state through a pre-pathology state due to the long-term influence of small intensity factors on the human organisms. The human heath risk assessment showed that about 50% of local population are living in conditions of prelithiasis, or in other words, in conditions of the initiation stage of carcinogenesis.

Boron Biogeochemical Region

The influence of natural biogeochemical factors and technogenic pollution can be exemplified by the boron sub-region of biosphere. This sub-region occupies a vast area in the Caspian low plain, the watershed areas between the lower Volga and lower Ural rivers of Russia, the Ustyurt plateau and Syr–Daria River and Amu–Daria River watershed areas in north western Kazakhstan (Figure 6).

The natural biogeochemical peculiarities favor the development of endemic diseases as well as being complicated by anthropogenic activity (Bashkin, 2002). In the area of the Volga–Ural watershed and the Ustyurt plateau, this activity is connected with oil exploration and the oil-chemical industry. The watershed of the Amu–Daria and Syr–Daria rivers is an agricultural area with an intensive irrigated cotton production requiring application of heavy rates of pesticides and fertilizers.

Historical epidemiological statistics have been connected with the oil exploration and oil treatment that were initiated more than 100 years ago. For a long time, the cancer diseases (mostly, esophageal cancer) were more prevalent in Russian people, whose professions were in the oil industries, than in aboriginal Kazakh people. The disturbance of environmental media and social conditions of the Kazakh population from the beginning of the 1930s have led to a sharp increase of cancer rates among aborigines. The statistics of cancer rates and environmental pollution are shown in Tables 5–8.

We will consider the development of cancer in two administration regions: (a) the Guriev region with technogenic pollution by oil and oil products and (b) the Kzyl–Orda region with agricultural pollution by nitrogen fertilizers and pesticides. Both regions belong to the boron biogeochemical sub-region of the biosphere.

The results of Tables 7 and 8 show two peaks of cancer diseases in both regions. The first peak was in the 1950s as a consequence of environmental and social disturbances in the 1930s–1940s and the second peak was observed in the late 1980s to the earlier 1990s as a result of the strong environmental pollution and formation of technogenic and agrogenic biogeochemical provinces.

There is a correlation between content of carcinogens in various links of biogeochemical food webs and frequency of stomach cancer. The most significant correlation was monitored in the agrogenic biogeochemical nitrate province of the Kzyl–Orda administrative region. Multiple increases in the application of different agrochemicals, such as fertilizers, pesticides, and defoliants, induced the development of carcinogenecisis. The rate of cancer increased from 80.1 in 1955 to 213.8 in 1995. For a short time (1982–1987) the lung cancer rates were increased by 4 times and liver cancer rates, by 2 times.

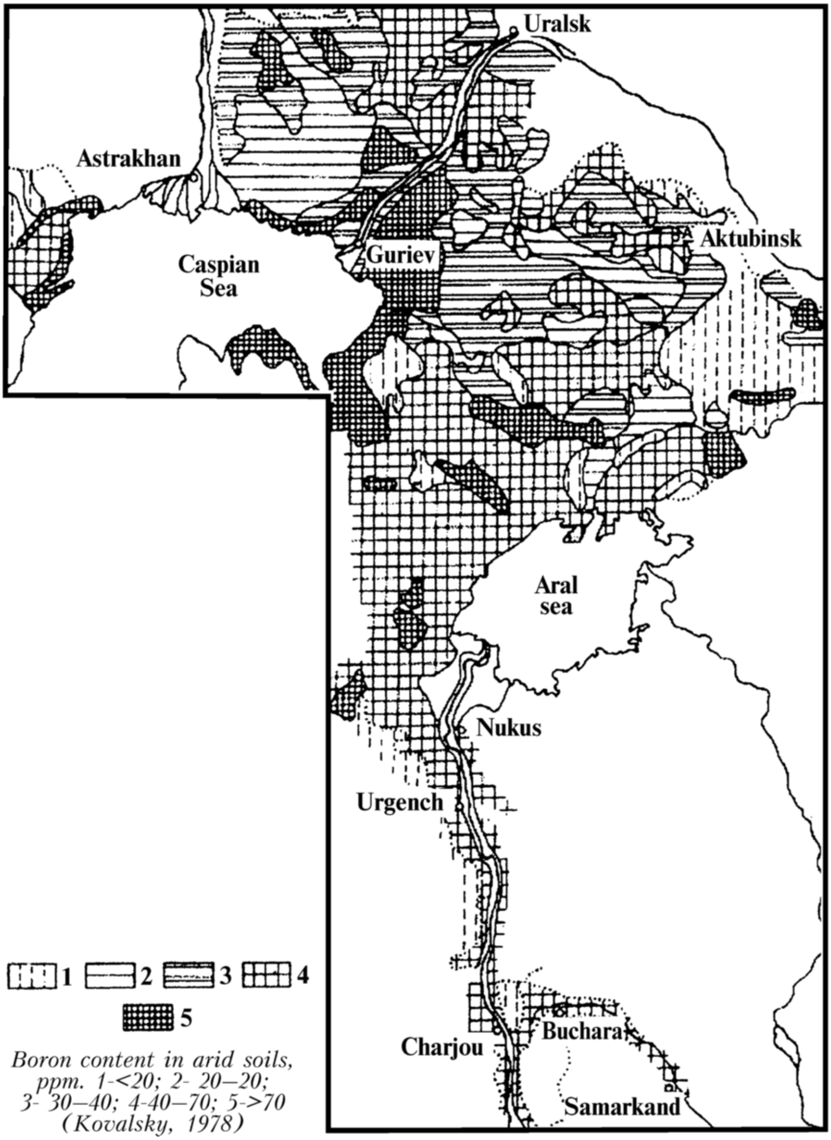


Figure 6. Boron biogeochemical sub-region of biosphere in Russia and Kazakhstan.

We should stress the role of natural biogeochemical and climate conditions in the development of various cancer diseases in the boron sub-region of biosphere, especially esophageal cancer. The average rates of esophagal cancer in developed countries are about 5 per 100,000 individuals. The traditional reasons, highlighted in the news media, are smoking and strong alcohol drinking. However, there are some

Table 5. Alteration of chemical composition of the Syr–Daria river water used for drinking by aborigines.

Chemical species	Content in river water, ppm	
	1956	1985
Nitrate	1.1	66.0
Nitrite	0.0	5.6
Chloride	40.0	480.0
Sulfate	141.0	900.0

Table 6. Concentration of chlourorganic pesticides in the Syr–Daria river water used for drinking by aborigines, μg/L.

Sampling point	DDT	DDE	HCH
Middle flow	0.026–0.095	0.001–0.012	0.068–0.14
Kzyl-Orda city	0.04–0.09	0.009–0.06	0.065–0.14
Kazalinsk city	0.03–0.11	0.00–0.012	0.05–0.09
Delta, Aral Sea	0.068	0.116	0.140

countries, like China, Kazakhstan, Iran, Pakistan, etc., with moderate/low smoking and drinking, where the rate of esophageal cancer exceeds 100 per 100,000 individuals. We can assume that in this Central Asian biogeochemical region with Dry Steppe and Semi-Arid and Arid Desert ecosystems, the environmental conditions favor cancer development.

Table 7. Dynamics of cancer diseases in the Kzyl–Orda administrative region (Syr-Daria drainage area).

	Cancer case per 100,000 individuals							
Malignant tumors	1955	1960	1965	1970	1975	1980	1985	1995
All tumors	80.1	91.7	186.8	117.6	137.7	140.0	130.2	213.8
Stomach cancer	—	12.4	32.6	23.6	19.7	12.1	19.1	32.7
Esophagal cancer	—	28.1	86.1	51.8	56.3	52.9	49.6	69.5
Lung cancer	—	4.1	9.5	8.1	9.1	7.9	13.0	21.4

Table 8. Growth of cancer diseases in Kazakhstan in 1970–1990, % of 1970 rate.

Administrative region	Lung cancer	Breast cancer	Skin cancer	Intestinal cancer	Lim-phomas
Guriev	143	257	209	54	26
Kzyl–Orda	100	285	—	275	113
Semipalatinsk	130	91	25	129	96
Chimkent	71	90	13	—	3
Dzhambul	166	96	93	133	285

This is an area of strong continental climate with dry and hot summer and severe winter with strong winds that transport dust at short and long distance, for instance "yellow sand" phenomenon in northwest China. During air transport these soil particles absorb numerous pollutants–carcinogens, like benzo(a)pyrene and heavy metals (Ni, Cd, Co, Zn, Pb, As) both from industrial emissions into the atmosphere and waste landfill sites.

These atmospheric particles inhaled through the respiratory tract may damage human health. Relatively large particles are likely to be retained in the nasal cavity and in the pharynx, whereas very small particles are likely to reach the lungs and be retained by them. The respiratory system possesses mechanisms for the expulsion of inhaled particles. In the ciliated region of the respiratory system, particles are carried as far as the entrance to the esophagus and gastro-intestinal tract by a flow of mucus. Macrophages in the non-ciliated pulmonary regions carry particles to the ciliated region.

The respiratory system may be damaged directly by particulate matter that enters the blood systems or lymph system through the lungs. In addition, the particulate material or soluble components of it, heavy metals, for instance, may be transported to organs. Particles cleared from the respiratory tract are to a large extent swallowed into the gastrointestinal tract.

Nitrate Biogeochemical Provinces and Cancer Diseases

Nitrogen species, such as nitrate and nitrite, are known to be confirmed procarcinogens. The excessive input of these nitrogen compounds with food and drinking water in the presence of tertiary amines, for instance, from medicines, can lead to the formation of carcinogenic N-nitrosoamines.

At present the extensive application of nitrogen fertilizers in many agricultural regions of the World has led to the formation of agrogenic nitrogen biogeochemical provinces. The characteristic feature of these provinces is the accumulation of nitrate and other nitrogen species in soils and drinking water. This accumulation accompanies an excessive input of nitrate in food webs (see Box 2).

Box 2. Nitrates in Food and Drinking Water (after Radojevic and Bashkin, 1999, and Bunce, 1994)

The nitrate (NO_3^-) content in crops is one of the most important indicators of farm production quality. Nitrate content in food is strictly regulated because of its toxicity, especially in young children. The actual toxin is not the nitrate ion itself but rather the nitrite ion (NO_2^-), which is formed when nitrate is reduced by intestinal bacteria, notably *Escherichia coli*. In adults, nitrate is absorbed high in the digestive tract before reduction can take place. In infants, whose stomachs are less acidic, *E. coli* can colonize higher up the digestive tract and therefore reduce the NO_3^- to NO_2^- before it is absorbed.

The nitrite ion is toxic because it can combine with hemoglobin with the resulting formation of methemoglobin. The association constant for methemoglobin formation is larger than that for oxyhemoglobin complex formation. Thus, the nitrite ion binds with hemoglobin, depriving the tissues of oxygen. Severe cases of disease called methemoglobinemia can result in mental retardation of the infant and even a death from asphyxiation.

At stomach pH, nitrite is also converted to $H_2NO_2^+$, which is capable of nitrosating secondary amines and secondary amides. The resulting N-nitrosoamines may be carcinogenic. For example, N-nitrosodimethylamine (or dimethylnitrosoamine) is carcinogenic in many experimental animals, although it is not a confirmed human carcinogen. Dimethylnitrosoamine can also contaminate drinking water supplies, both as a result of industrial activity and also because the compounds may be present in the discharge waters of sewage treatment plants, where it is formed by the microbial degradation of proteinaceous materials.

The average human daily intake of nitrate/nitrite is 95 mg/day in adults. Estimates of the relative contributions of nitrate from drinking water and food to the daily intake vary considerably, depending on how they are calculated. Nevertheless, they show that between 50% and 90% of nitrates in human intake may originate from vegetables, conserved meat (sausages, canned meat, smoked meat, etc.) and even milk products. Vegetables tend to concentrate nitrate ions, especially if they are grown using high rates of nitrogen fertilizers. The concentration of nitrate in vegetables can vary extensively. Lettuce, spinach, cabbage, celery, radish and beetroot can contain as much as 3,000–4,000 mg/kg of fresh weight. These levels could have potential health effects. The problem of nitrate accumulation seems to be especially severe in leafy vegetables grown in greenhouses under winter conditions, owing to intensive application of nitrogen fertilizers and low light intensity, which retard nitrate metabolism in crops.

Another source of nitrate and nitrite accumulation in food is their use as food additives. Nitrate and nitrite salts ($NaNO_2$, $NaNO_3$, KNO_2, KNO_3) are added to meats and other food products as a curing salt, color fixative (preventing the meat turning brown) and as food preservative to prevent the growth of the dangerous bacterium *Clostridium botulinum*, which produces the highly poisonous botulism toxin.

Cured meats, bacon, ham, smoked sausages, beef, canned meat, pork pies, smoked fish, frozen pizza and some cheeses contain nitrate and nitrite additives, typically at levels of 120 mg/kg. Although without them there would certainly be many deaths due to growth of toxic microbes in meat, excessive intakes of these salts may cause gastroenteritis, vomiting, abdominal pain, vertigo, muscular weakness and an irregular pulse. Long-term exposure to small amounts of nitrates and nitrites may cause anemia and kidney disorders. The level of these additives is strictly controlled (for example, 500 mg/kg as $NaNO_3$ in the UK), and the addition of nitrates and nitrites in baby food is now banned in many countries. The acceptable daily intake (ADI) for $NaNO_3$ is 0–5 mg/kg body weight. For KNO_2 and $NaNO_2$the ADI is 0 0.2 (temporary), while for KNO_3 is not specified. The value of ADI is zero for baby food. The WHO sets the ADI at 220 mg an adult.

Since vegetables are a major source of ingested nitrates, the most rational way of reducing the problem is to grow crops with safe levels of nitrates. Most counties do not have actual standards but some kinds of guideline or criteria value based on the ADI. Criteria values of nitrate content in the same kind of vegetable may vary broadly from country to country owing to differences in vegetable consumption and in vegetable production practices. For instance, the nitrate level (mg/kg of wet weight) in spinach in different countries is: USA, 3,600; Switzerland, 3,000; the Netherlands, 4,000; Czech Republic, 730; Russia, 2,100.

Nitrate content is also one of the indicators of fodder quality. Numerous cases of cattle poisoning by nitrates present in fodder have been reported in various countries, and many heads of cattle were lost from affected herds. Feed beetroot, cabbage, mustard, sunflower, oat, as well as various types of ensilage used as green fodder may contain potentially toxic levels of nitrate. The toxic level of nitrate for animals is 0.7 mg/kg of body weight. Among farm animals, cattle and young pigs are the most sensitive to nitrates, while sheep are more resistant. Also, consumption of nitrates at sub-toxic levels by cattle has been reported as a cause of reduced milk production and weight gain, vitamin A deficiency, abortions, stillbirths, cystic ovaries, etc.. Nitrate-N concentrations of 0.21% in the feed are considered to be toxic to farm animals.

Agriculture is usually the major source of nitrate ion in drinking water. Through manure seepage from feedlots, seepage from the holding tanks used to contain liquid manure from intensive hog production, and excessive use of fertilizers are important. The higher crop yields obtained today compared with 20–40 years ago are largely due to increased use of chemical fertilizers. However, low crop prices combined with high land and machinery cost encourage farmers to cultivate fields up to their margins, thus promoting runoff from fields to water bodies and ground waters. The accumulation of nitrates in ground water has become an issue of great concern in many European countries and many States of USA.

In 1945, H. H. Comly first estimated the correlation between nitrates in drinking water and the incidence of methemoglobinemia. Research shortly afterwards showed that no cases of methemoglobinemia had been reported in any area of the United States where the water supply contained less than 45 ppm of nitrate ion. This value has become accepted in USA as the upper limit for the nitrate concentration in drinking water. At present the WHO limit is also 45 ppm of nitrate but the value of 22 ppm of nitrate has been set for EC countries.

Table 9. Perennial concentrations of nitrogen species in food web of nitrate biogeochemical province of the Desert region of biosphere, Uzbekistan.

Links of food web	Nitrate	Nitrite
Surface water, ppm	2.03–12.10	0.03–0.42
Drinking water, ppm	3.62–150.80	0–0.09
Vegetables, ppm of wet weight	500–8,600	12.4–328.3

The main reasons for nitrate accumulation are the increasing application of nitrogen fertilizers and increasing generation of nitrogen-containing municipal wastes.

Let us consider in brief the nitrate biogeochemical provinces, where a significant growth of cancer incidents has been observed. It is known that the absorption of nitrate and nitrite from water in the intestinal tract is 2 times as much as from food products. This means that the accumulation of nitrate in drinking water sources should be of special concern during consideration of food webs in any relevant biogeochemical province.

As an example, we will consider the formation of nitrate biogeochemical provinces in the Desert region of biosphere in Zerafshan river watershed that occupies most of the Samarkand administrative region of Uzbekistan. This is an agricultural area with irrigation production of cotton and some other crops like cereals, vegetables and fruits. The natural biogeochemical provinces are characterized by iodine, copper, and zinc deficiency and lithium excess.

The concentration of nitrogen species in various links of biogeochemical food webs of this province is shown in Table 9.

We can see that the concentrations of both nitrate and nitrite in drinking water and vegetables are excessive. The accumulation of nitrate in food web of this biogeochemical province was accompanied with a high content of residual pesticides in soils of agroecosystems (Table 10).

Table 10. The residual content of persistent organochorine compounds in soils of nitrate biogeochemical province of the Desert region of biosphere, Uzbekistan, ppb.

	Cotton		Tobacco		Orchards	
Xenobiotic	Mean	Limits	Mean	Limits	Mean	Limits
DDT	8.3	tr–47.5	27.2	tr–157.7	24.7	tr–70.9
$\sum$DDT*	113.4	tr–970.0	282.7	tr–1715.0	19.9	tr–432.5
$\sum$PCB	28.0	2.3–100.6	121.1	28.4–425.8	24.9	9.2–67.5

Note: $\sum$DDT − DDT + DDE + DDD; the corresponding standard for DDT content in soil is 100 ppb, and temporary criterion for PCB is 60 ppb

Table 11. Growth of liver and stomach cancer rates in the Samarkand nitrate biogeochemical province of the Desert region of biosphere, Uzbekistan, cases per 100,000 individuals.

Period	Liver cancer	Stomach cancer
1950–1955	1.4	12.5
1956–1960	1.5	17.8
1961–1965	2.4	18.9
1966–1970	2.9	23.2
1971–1975	3.9	25.3
1980–1985	4.7	27.8
1985–1990	5.3	32.6
1990–1995	6.0	34.6

The accumulation of pesticides is connected with their long-term application in heavy rates, 15 kg/ha in average during 1970–1980s. The elevated concentrations of PCB are related to the irrigation by polluted waters from the Zerafshan River (Galiulin and Bashkin, 1996). The mean content of residual DDT and its metabolites DDE and DDD is higher than the corresponding standard in soils of Cotton and Tobacco agroecosystems. The mean content of total amount of PCB is also higher than the standard in soils of Tobacco agroecosystems.

Thus, the combination of natural biogeochemical features of the food web (deficiency of I, Zn, and Co with excess of Li) with anthropogenic pollution has led to increased cancer rates (Table 11).

2. HUMAN HEALTH ENDPOINTS IN TECHNOGENIC AND AGROGENIC BIOGEOCHEMICAL PROVINCES

2.1. Physiological Endpoints for Human Biogeochemical Studies

Traditionally, an assessment of population health is based on medico-demographic statistical rates of mortality, morbidity, and life period expectance. Among these parameters, the morbidity is the most informative one. The known toxicological and hygienic data describe physiological mechanisms of trace metals, pesticides and nitrate action at cellular, organ and systemic levels. Depending on chemical structure of these pollutants, the molecular mechanisms are variable (Blain, 1992; Trachtenberg, 1994). However, the generalization of these data allows us to reach the conclusion that a common link of function failure is hypoxia. This physiological phenomenon is an oxygen starvation of tissues (Evstafyeva, 1996). At long-term action of small doses of pollutants, the systems that required more oxygen will start suffering in the first turn. Amongst them the central nervous system, myocardium, and reproductive system should be noted. The metabolic transformation and excretion of chemical substances from an organism is one of the physiological mechanisms neutralizing the toxic action of pollutants, and the liver and kidneys should be also considered as indicator organs and systems.

Recent experimental data show that the chronic influence of pollutants in low doses produces a nonspecific action on the human organism resulting in different forms of pathology of all organs and systems. In turn, for a selection of the indicating forms, we should recognize the nosological profiles (morbidity specification) of population in various technogenic and agrogenic biogeochemical provinces and correlate these profiles with the technogenic loading. An example of such a correlation is shown in Table 12.

To test this hypothesis, different biogeochemical regions of biosphere in the territory of Ukraine were selected:

(1) The Western Forest Steppe region of biosphere with predominant agricultural activities, including the Lvov, Ivano-Frankovsk, Vinnitsa, Ternopol and Khmelnitsky administrative regions;

(2) The Eastern Steppe region of biosphere with strong industrial loading, including the Kharkov, Donetsk, Dnepropetrovsk and Zaporozhye administrative regions;

(3) The Crimean Dry Steppe region of biosphere with mixed industrial, agricultural and recreational activities.

In division into zones, the maps of an ecological situation in the Ukraine were applied. These zones are considerably different in biogeochemical food webs and in the manifestation of technogenic or agrogenic loading. The nosological profiles of population living in these regions of biosphere have been calculated on a basis of the National Report of the Ukrainian Ministry of Statistics on the rate of morbidity in 1994 (Table 12). The standardized values of average morbidity for these regions in 27 groups of nosologies encompassing the main diseases were counted. They were normalized concerning the mean value over all the Ukraine, using the formula

$$Z_{\mathrm{i}} = (X_{\mathrm{i}} - X_{\mathrm{m}})/s,$$

where Z_{i} is the standardized deviations; X_{i} is the values of morbidity in estimated region; X_{m} is the average morbidity for the whole Ukraine area; and s is number of observations.

The application of this approach can eradicate the difference in the morbidity rates of different nosologies and estimate an extent of a deviation of parameters from an average for the given disease over the country as a whole. The results showed that in the selected zones of the country, there are remarkable deviations of morbidity rates from the average values overall the Ukraine. For instance, in the industrial zone a significant increase of the morbidity rate of the respiratory system ($R^2 = 0.83$)

Table 12. The statistical estimation of the morbidity in different regions of biosphere, Ukraine, using the deviations from normalized mean values of morbidity (σ-values) (after Evstafyeva et al., 1999).

Diseases	Crimean Dry Steppe region	South-eastern Steppe region under strong industrial pollution	Western Forest Steppe region under agricultural influence
Infectious and parasitic	+2.40	−0.23	−0.55
Neoplasm	+1.53	+0.37	−0.83
Endocrine and immune	−0.82	−0.05	+0.49
Thyroid gland	−0.73	−0.91	+1.09
Blood and hemophoietic organs	−0.55	−0.54	+1.41
Nervous system and organs of sense	−0.89	+0.28	+0.10
Cardiovascular systems	−0.78	−0.20	−0.19
Peripheric nervous system	−1.64	−0.49	+0.63
Systems of the blood circulation	+3.43	−0.26	−0.23
Chronic rheumatic heart disease	−0.70	−1.30	+0.68
Hypertension	+0.66	−0.01	−0.43
Ischemia heart disease	−0.36	−0.60	+0.04
Acute infarct	+2.22	+0.76	−0.66
Stenocardia	+1.14	−0.06	−0.01
Cerebral-vascular distresses	+1.34	+0.60	−0.94
Insulite	−0.26	+0.01	−0.36
Respiration systems	−0.25	+0.83	+0.27
Digestion systems	−1.39	−0.62	+0.55
Stomach and duodenal ulcer	−0.75	+0.28	−0.57
Chronic hepatite	−0.89	−0.38	+0.83
Gallstone disease	+0.26	−0.62	+0.50
Urological disease	−0.73	+0.01	+0.19
Chronic pyelonephritis	+1.15	+0.52	−0.21
Skin disease	+0.78	+0.88	−0.61
Bone and muscular system	−1.06	−0.10	−0.05
Arthrosis	−0.27	+0.32	+0.43

was marked, while in other zones the level of significance for the morbidity of the respiratory system was lower than average in Ukraine. The excess over the average Ukrainian level took place in the cases of dermal diseases (on 0.88*s*), diseases of an excretory system (on 0.52*s*), cerebro-vascular distresses (on 0.60*s*), on 0.76*s* — acute infarction, on 0.37*s* — neoplasms. At the same time, in the agricultural zone the average Ukrainian level of the morbidity rate was exceeded in such forms of nosologies as a total morbidity of digestive system (0.55*s*), chronic hepatitis (0.83*s*), cholelithiasis (0.50*s*), disease of a peripheric nervous system (0.63*s*), disease of blood and hemophoietic organs (1.41*s*), thyroid gland (1.09*s*), chronic rhematoid diseases of heart (0.68*s*), and deforming arthrosis (0.42*s*). An extremely unfavorable situation occurred in the Crimea, where the infection and parasitogenic diseases are higher than the average Ukrainian level as much as 2.41 times, the acute infarction takes place more often as much as 2.22 times, tumors on 1.53*s*, the attacks of a stenocardia on 1.15*s*, chronic pyelonephritis on 1.15*s*, dermal diseases on 0.78*s*, hypertonia on 0.66 are higher 1.53*s*, and cerebro-vascular distresses as much as 1.34 times higher.

Thus the nosological profiles of the reviewed regions are variable. The distinctive feature of an industrial zone is the high morbidity of the respiratory system and dermal diseases, tumors, and also negative influence on excretory and cardiovascular systems, including vascular distresses of the brain. This generally corresponds to known susceptibility of an organism systems to an action of atmosphere pollutants of industrial zone. In agricultural zone the diseases of an alimentary system dominate, that is clear, because the inflow of pollutants with food and water through this system predominates in the rural areas. Besides this, the lesions of a peripheric nervous system take place here, which can be connected with the specific exposing of action of pesticides on an organism in professional contacts, which is in high usage in agriculture. As to the Crimea, the pattern of morbidity is characterized not only by the highest level of series of pathologies, but also the amplitude of these deflections is maximal in the whole Ukraine. It is known the Crimea is characterized by a big diversification of natural biogeochemical conditions, as well as technogenic loading. Probably, in this case we are dealing with a consequence of this diversification.

However, these results are not sufficient to estimate quantitative dependence on a level of the particular pollutants in the environment. The second working hypothesis on the relationship between pollutants loading and morbidity dynamics in the whole area of North Eurasia has been considered. This hypothesis was estimated using a complicated statistical treatment (Box 3). The considered pollutants were fertilizers, heavy metals, pesticides, radionuclides, oil products, and polycyclic aromatic hydrocarbons, PAH.

Box 3. Statistical assessment of morbidity in technogenic and agrogenic biogeochemical provinces of North Eurasia (after Evstafyeva et al., 1999)

The correlation between the indicator forms of diseases for both heavy metals and pesticides was estimated using the results on morbidity in Russia for a 10-years period of observation in the 1980s–1990s. The estimated pollutants were fertilizers, heavy metals, pesticides, radionuclides, oil products, and polycyclic aromatic hydrocarbons, PAH. The pollutant loading was estimated for different biogeochemical regions of biosphere in North Eurasia. According to these data, the rank assessment on each kind of pollution, and then summary mark with taking into consideration of the suspected danger of each factor was introduced. In the assessment of land pollution by heavy metals in rural areas, three levels (increased, mean and low) were established. The gradations for city soils of four categories were introduced separately: extremely dangerous, dangerous, moderately dangerous, and moderate. In pesticides loading, the extent of the danger of contamination of arable lands of four degrees and summary index of pesticides loading on arable lands of three levels were determined. The data file of morbidity by bronchitis, nasopharyngities, pneumonia, asthma was analyzed, and also the ulcer of a stomach and duodenum, gastritis, cholecystitis (incidents per 100,000 residents) for the period from 1982 until 1991. To compare the level of morbidity on various territorial regions (administrative and territorial units) preliminary analysis of the data was made. All the massif of observations (5,110 values) was divided into two 5-year's sets (1982–1986 and 1987–1991). Inside these sets, each parameter was ranged over 10 levels. Then the received ranging was converted in 2 ranks: low (-1) and high ($+1$) levels of morbidity with value of initial ranks with 1 on 5 and with 6 on 10 correspondingly. Thus, each administrative unit was described by nonparametric 2 level parameter of morbidity (-1, $+1$) on all nosologies for each year with 1982 on 1991. To characterize the territorial zones on definite nosologies, the average parameters for all 10-year's period was used. Received values characterize level of morbidity on studied territories on scale from -1 (low) up to $+1$ (high) and do not depend on the size of the chosen territories, which is recommended for a similar type of studies. The statistical treating of results was done on the basis of a computer system SAS on IBM PC-AT by a method of correlation analysis with calculation of standard, rank and signed correlation.

Let us consider the results of this biogeochemical study. The total morbidity for gastrointestinal and respiratory systems did not find a reliable connection with a total anthropogenic loading determined as the sum of scores for each pollutant. But the separate nosologies discovered such a connection. For instance, the pneumonia and asthma morbidity was correlated with total soil pollution. The level of total morbidity of alimentary and respiratory systems was connected with content of petroleum, PAH, and heavy metals in urban soils. Asthma was discovered to inter-couple with most considered pollutants. Apparently, large susceptibility of a respiratory system to negative influence of soil pollution can be explained by correlation of the last index with air pollution in large cities. Here the inhalation of chemical pollutants is prevalent. In rural areas, the main route of pollutants is via food chains and the interaction with morbidity of a digestive system was shown with the highest correlation to pesticides content in soil. We can note that about 40% of variations in asthma morbidity is related to soil pollutants ($R^2 = 0.378$; $n = 70$) and this is compounded with the similar regional epidemiological studies (Gryaznova et al., 1989; Diakovich et al., 1989; Zhakashov, 1990).

Thus the total soil pollution was connected with a respiratory system and a digestive tract. Both systems were also sensitive to such urban pollutants as heavy metals and PAH. For radionuclides the correlation with the given nosologies was not revealed. The asthma morbidity was mostly connected with soil pollution rates. This circumstance, apparently, can be related to nonspecific action of pollutants on a human organism, because the etiology of asthma is connected with the human immune defense system and allergy state (Roite, 1991). The last was shown for pesticides (Nikolaev et al., 1988) and heavy metals (Drouet et al., 1990). The sensitized immune system is, apparently, responsible for chronic toxic effects of other pollutants at low doses (Sidorenko et al., 1991; Novak and Magnussen, 1993).

2.2. *Case Study of Interactions Between Human Health Endpoints and Pollution in Crimea Dry Steppe Region of the Biosphere*

As we have seen the morbidity cases of respiratory and alimentary systems highlight the inter-correlation between biogeochemical food web, pollution loading and human health. However, the physiological response of central nervous and cardiovascular systems to heavy metals and pesticides is also known and the relevant analysis of morbidity of cardiovascular systems and psychological distresses was carried out in 1991–1997 in the industrial area of Crimea — Armyansk city, Ukraine (Evstafyeva et al., 1999). The correlation between morbidity of a respiratory system and pollutants emissions was found (Figure 7).

Simultaneously during these years the progressive increase of morbidity of cardiovascular systems and psychological distresses was noted (Figure 8).

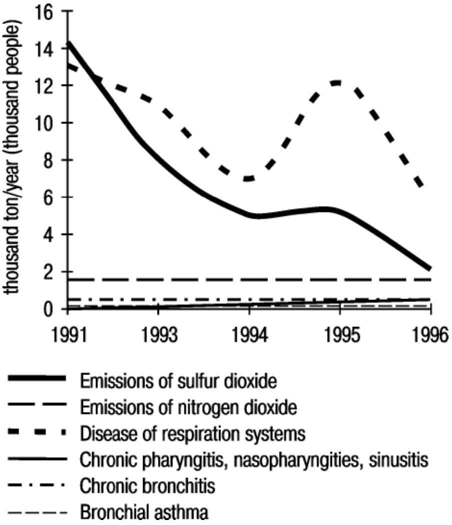


Figure 7. The dynamic patterns of SO_2 and NO_x emissions and the rates of respiratory morbidity over a period of 1991–1996 in Armyansk City, Ukraine.

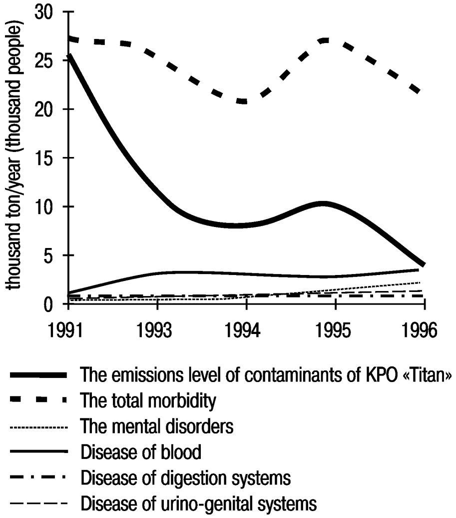


Figure 8. The dynamic patterns of SO_2 *and* NO_x *emissions and the rates of total morbidity over a period of 1991–1996 in Armyansk City, Ukraine.*

However, the specific weight of social factors in an etiology of these diseases was predominant during the observation period. Probably, the assessment of the state of these systems as an indicator can be more justified if we utilize preventive methods of an evaluation, namely, to determine functional parameters describing pre-morbidity states and adaptation to the environment. There are functional methods for pre-morbidity diagnostics, which have been tested in monitoring of the selected population groups. However, for wide screening these methods seem very expensive. Accordingly, a monitoring of population health can be based on the clinical examination data, which allowing the researcher to reveal physiological parameters, most reactive to various types of technogenic pollution. These data showed that radionuclide pollution, industrial loading, and pesticides rates are the most significant factors. In turn, physiological parameters related to the red blood and oxygen-supplying tissues were the most sensitive. This may be explained by hypoxic action of the most common pollutants.

Furthermore, it is necessary to evaluate the isolated and complex physiological effects of some toxic and essential metals on such endpoints (biomarkers) as the neurobehavioral and psycho-physiological parameters and also cardiovascular and immune parameters. The effect depends on metals content in the human body. Moreover, it depends on physiological effects, not only the daily intake.

The results of the investigation of 58 adult persons who live on industry territory of North Crimea and 60 male teenagers at age 15 years and 84 children (2–14 years) in the Simferopol city showed that the children are more sensitive to the relatively low level of heavy metal concentrations than the adult (Evstafyeva et al., 2002). It is known that many toxic metals have neurotoxic effects (Arezzo et al., 1985). It was also shown that the effects of central and autonomous nervous systems of different

Table 13. Metal content in hair of different aged people groups (Evstafyeva et al., 2004).

	Concentration in the hair (m kg/g)			
Element	Min	Max	$X \pm S_x$	Norm
Pb (1) 12 years ($n = 18$)	0.39	13.56	2.97 ± 0.79	0–5
(2) 15 years ($n = 25$)	1.3	7.4	3.9 ± 2.01	
(3) 18 years ($n = 33$)	0	8.88	1.58 ± 0.34	
Cd (1)	0	0.28	0.10 ± 0.02	0–2.7
(2)	0.79	4.75	2.59 ± 0.68	
(3)	0	0.17	0.06 ± 0.008	
As (1)	0	1.20	0.31 ± 0.11	0–2.5
(2)	0	2.87	0.96 ± 0.20	
(3)	0	1.18	0.26 ± 0.06	
Sr (1)	0.52	14.0	5.10 ± 0.94	0–3
(2)	1.12	6.10	2.27 ± 0.22	
(3)	0.39	5.74	1.53 ± 0.20	
Cu(1)	5.55	26.98	9.80 ± 1.18	9–40
(2)	5.93	194.08	25.92 ± 8.68	
(3)	5.11	14.02	8.26 ± 0.31	
Zn (1)	72.14	157.85	116.08 ± 6.01	115–250
(2)	85.42	177.56	136.92 ± 4.09	
(3)	89.9	168.45	120.35 ± 3.29	
Ca (1)	126.93	1,727.73	661.59 ± 130.22	500–1,500
(2)	93.75	483.53	273.79 ± 18.34	
(3)	93.67	954.95	334.99 ± 35.56	

age children groups were related to content of toxic and essential heavy metals in human hair (Evstafyeva et al., 2004).

Examination of the central nervous system was carried out on a basis of recording 30 indices of electroencephalograms (EEG) and evoked potentials (EP). This method has been earlier described in detail (Pavlenko et al., 2000). The state of autonomous nervous system was assessed by variability of cardio intervals (Vein, 1991).

The content of heavy metals in human hair was defined by the Roentgen-fluorescent method (non-toxic metals) in the laboratory of analytical chemistry and toxic substances at Institute of the Occupational Medicine of Scientific Medical Academy of Ukraine.

The results have been statistically processed by means of Spearman's non-parametrical correlation analysis and by multiple regression analysis to assess the complex effects induced by toxic and essential elements (Evstafyeva, Slusarenko, 2003; Evstafyeva et al., 2004).

Results of heavy metal content determination in the hair are shown in Table 13. They indicate that the average meanings for all toxic metals were within the maximal permissible limits excepting Sr in the 12-year age group. For cadmium and lead the norms (Valcovic, 1988) were exceeded in some cases; zinc, calcium and copper elements showed deficits, a calcium deficit was practically totally exposed.

Physiological influence of metals was assumed from the value and significance of correlation coefficients that are shown in Table 14.

These data allow us to conclude that the analyzed metals have significantly different importance and certain physiological specificity at concentrations that are considered permissible for toxic metals. So, the most significant correlations among toxic metals was found for Pb, then for Cd, Sr and for As only in one case (θ-rhythm on the left when the eyes are open). At the same time the influence of essential elements was also significant for electrophysiological parameters, in particular Zn. It correlated with the same characteristics of EEG in different groups. It is of interest that in some cases we have received significant correlation with Pb, As and Cd in decision of logical, space and mathematical tasks in a group of 12 old-year children ($0.48 < r < 0.67; 0.002 < p < 0.04$).

There is no significant correlation between the investigated toxic and essential metals content and the autonomous nervous system tone but some tendencies are shown for separate cardiovascular system parameters: mode of cardio intervals and Cd, $p = 0.09$; VPR (vegetative parameters of rhythm by (Vein, 1991) and Pb, $p = 0.06$).

These results are similar to the literature data concerning the separate toxic and essential metals effects (Araki et al., 1987; Araki, 1992; Arezzo et al., 1985; Baranski, 1986; Brockel and Cory-Slechta, 1999; Lilis et al., 1985; Trombley et al., 2000). But it is important to take in account simultaneously the influence of toxic and essential metals in particular if they are physiological antagonists or synergists and if an increase of toxic metals is accompanied by a deficit of the essential elements as it has been shown in this study.

The multiple regression analyses of electrophysiological indicators in 3 groups of children at different age 12, 15 and 18 years showed that the multiple regression coefficients were very high in the middle-age group ($R = 0.99$), but at p-level $0.04 < p < 0.09$. A low- (δ-, θ-) and high- (β-) frequency of the EEG-rhythms were related to the complex influence of the studied elements. In the senior group essential multiple regression was discovered for amplitude N1 ($R = 0.65; p < 0.05$). The most relative contribution in complex influence was given by Pb, Sr and As. In the junior group a significant complex influence of elements was determined for α-rhythm amplitude at eyes closed and α-rhythm reaction at eyes opened ($P = 0.82$; $p < 0.1$). A considerable contribution to the joint influence has been made by Zn and Sr (Table 15).

It is known that zinc and cooper play an important role in immune system functioning (Kelley et al., 1995; Skalny and Rudakov, 2004; Zinc, 2001). Deficiency of these metals causes immune system dysfunctions. Recently these dysfunctions are seen to be widely distributed, especially in children. It is known also that sensitivity of the immune system to external influences differs in different age periods and it was found (Evstafyeva et al., 2002) that the influence of toxic metals is more significant in 7–11-year-old urbanized children. At the same time zinc and cooper deficiency was found in 1–6-year-old children, zinc deficiency and copper lowered contents, in

Table 14. Relationships between the metal content in hair and electrophysiological parameters of the electroencephalogram and evoked potentials (Evstafyeva et al., 2004).

Parameters	Sr	Pb	Cd	As	Cu	Zn	Ca
α-Rhythm on the left (the eyes are closed)					−(2)	−−(1)	
α-Rhythm on the right (the eyes are closed)						−−(1)	
α-Rhythm on the right (the eyes are closed)	+(1)				−−(2)	−−(1)	+(1)
α-Rhythm on the right (the eyes are open)	+++(1)				−−(2)		++(1)
β-Rhythm on the left (the eyes are closed)		−−(1) −(3)	−(3)			−−(1) −(2)	
β-Rhythm on the left (the eyes are open)						−−(1) −−(2)	
β-Rhythm on the right (the eyes are closed)		−(3)	−(3)			−−(1) −(2)	
β-Rhythm on the right (the eyes are open)	+(1)					−−(1) −(2)	++(1)
θ-Rhythm on the right (the eyes are closed)			−(3)		−−(2)	−−(1) − − −(2)	
						−−−(1)	
θ-Rhythm on the left (the eyes are open)				−−−(3)	−−(2)	−−(1)	
θ-Rhythm on the right (the eyes are open)	+(1)				−(2)	−−−(1)	
γ-Rhythm on the right (the eyes are closed)		++(2)	+(2)			−(1)	
γ-Rhythm on the right (the eyes are open)		++(2)	+(2)				
γ-Rhythm on the left (the eyes are open)		++(2)				−(1)	
δ-Rhythm on the left (the eyes are closed)			−−(2)		−(2)	−−−(1) −−(2)	
δ-Rhythm on the right (the eyes are closed)					−−(2)		
δ-Rhythm on the left (the eyes are open)						−−(1) −(2)	

Table 14. (Continued)

Parameters	Sr	Pb	Cd	As	Cu	Zn	Ca
δ-Rhythm on the right (the eyes are open)						−−(1)	
P1 latency (on the left)						−−(3)	
P2 latency (on the left)						−−(3)	
P2 latency (on the right)		++++ (2)	+(2)				
P2 latency (on the left)		+(2)					
P300 latency (on the left)	−−(3)	+(2)					−−(3)
P300 amplitude (on the left)		−(3)		−−(3)		++(3)	
P300 amplitude (on the right)		−−−(3)		−−(2)		+(3)	
N1 amplitude (on the left)				++(3)			
N2 amplitude (on the left)		++(3)					
N2 amplitude (on the right)		+(3)					
UNV (on the left)		++(2)	+++(3)				
UNV (on the right)			+++(3)			−(3)	−−(3)

Note: "+" or "−" means presence of positive or negative correlation at level of probability: "+" ("−") −−− 92–94%, "++" ("−") −−−95–97%; "+++" ("−−−") −−−98–99%; "++++" ("−−−−") −−− 99–99.9%. P1, P2, P300, N1, N2, UNV −−− the evoked potentials characteristics:

(1) a group 12 age;
(2) a group 15 age;
(3) a group 18 age.

7–11-year-old children and coming nearer to the bottom border of norm contents of metals was found in 12–15-year-old children. Multiple regression analysis of immune parameters with the contents of zinc, copper, and also toxic elements as mercury, lead and cadmium, in this work has revealed the greatest number of correlations in 1–6-year-old children, and the lowest ones for 12–15-year-old children. No significance was shown for toxic Cd and Pb, and essential Cu and Zn.

Thus, the content of toxic and essential metals in children's hair on urbanized territory is characterized mainly by an insignificant tendency to exceed the toxic

Table 15. Multiple regression analysis of the immune system parameters and metal contents in hair (Evstafyeva et al.*, 2004).*

Parameters	Multiple regression coefficient	Regression coefficients for separate metals				
		Pb	Cd	Zn	Cu	Hg
1–6-year-old children						
O-Lymphocytes (%)	∗				−−−−	
CD3 (abs)	∗					+++
CD3 (%)	∗∗∗∗				++++	+++
CD4 (abs)	∗					+++
CD4 (%)	∗	+++				
CD8 (abs)	∗					++
CD8 (%)	∗∗∗		−−		++++	
Leucocytes	∗∗∗∗					++++
IgM	∗	++				
Stab neutrophils	∗		+++			
7–11-year-old children						
O-Lymphocytes (abs)	∗∗∗∗					
Lymphocytes (abs)	∗∗		−−		−−−	
CD3 (abs)	∗∗∗		−−		−−−	
CD4 (abs)	∗∗		−−		−−−	
CD8 (abs)	∗		−−		−−	
CD25 (abs)	∗∗					
B-Lymphocytes (abs)	∗∗∗∗				− − −−	− − −
Leucocytes	∗					− − −
Monocytes	∗				+ + +	++
12–15-year-old children						
O-Lymphocytes (abs)	∗∗∗∗	+ + ++		− − −−		

Note: “∗”, “+” or “−” means presence the multiple regression, positive or negative correlations accordingly at statistical significance “+” ”(“−”) − − − 92–94%; “++” (“−−”) − − −95–97%; “+ + +” (“− − −”) − − − 98–99%; “+ + ++” (“− − −−”) − − −99–99.9%.

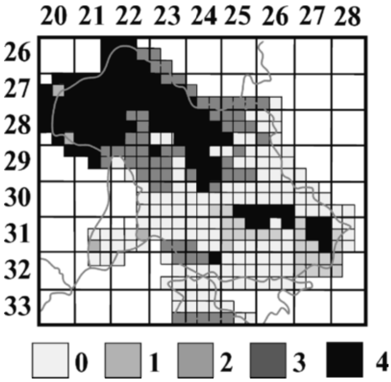


Figure 9. Exceedances of critical loads for terrestrial ecosystems of Ukraine for 1992 deposition.

metals, the physiological and hygienic norms and the more significant decrease of the essential elements. Nevertheless both groups of metals turned out to be essential for EEG and evoked-potentials characteristics. Complex effects of the toxic and essential metals on the nervous and immune systems, estimated by means of multiple regression analysis, were revealed. It was more significant, as a rule, than the isolated influence of separate elements in accordance with the data of correlation analysis and the more sensitive groups were the youngest and middle age children. The children have not shown any significant influence from the exposure of separate metals on the central nervous system functional state, but have shown important reactions to the complex impact of unbalanced element intake in cases where the immune status was assessed.

It is also known that the level of pollution may be also estimated using critical loads of pollutants as biogeochemical standards (see Chapter 3 for more details).

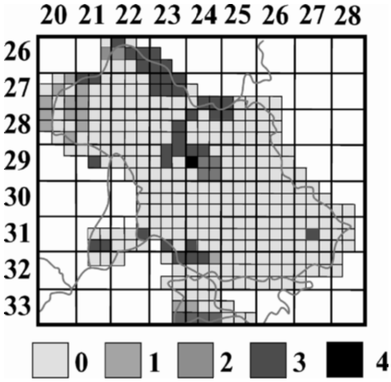


Figure 10. Exceedances of critical loads for terrestrial ecosystems of Ukraine for 1996 deposition.

For the calculation of critical loads of various pollutants on the human and ecosystem health, the following working hypothesis has been considered. This hypothesis is connected to the assessment of sensitivity of various human physiological parameters to environmental biogeochemical factors. In this case interaction may be established by statistical exploration of the dependence between loading and various types of morbidity. The critical loads of sulfur and nitrogen at various ecosystems and their exceedances during 1992–1996 were compared with human respiratory system morbidity both in the Crimea and the whole of Ukraine. In Ukraine, the respiratory cases were correlated with the exceedances of critical loads (Figures 9 and 10, Table 12).

PART II

NATURAL BIOGEOCHEMICAL PECULIARITIES OF EXPOSURE ASSESSMENT

The general characteristics of biogeochemical cycling shown in the previous chapters can provide us only with an integrated pattern of the biogeochemical structure of the biosphere, which is differentiated by many features and especially regarding quantitative parameterization of exposure assessment in various ecosystem types. In accordance with climate, geology, soil, vegetation, hydrology, and relief, we can subdivide the global ecosystem into different ecoregions and ecozones (see, for instance, Bailey, 1998) or climatic zones. Even a priori, based on knowledge of the organization of the World's ecosystem, we can suggest the existence of many peculiarities of biogeochemical cycling of various elements in natural terrestrial and aquatic ecosystems and accordingly, different characteristic features of human and ecosystem exposure to various pollutants via direct or indirect impact.

CHAPTER 6

ARCTIC AND TUNDRA CLIMATIC ZONE

1. GEOGRAPHICAL PECULIARITIES OF BIOGEOCHEMICAL CYCLING AND POLLUTANT EXPOSURE

In the Northern Hemisphere the area of arctic and tundra landscapes with plant species' ecosystems is 3,756,000 km^2. In the Southern Hemisphere similar landscapes are completely absent. Most of these landscapes occur in northern Eurasia (Russia, Fennoscandia), Greenland, Alaska, and Canada.

The climate conditions of Arctic and Tundra ecosystems are the main factor influencing many peculiarities of biogeochemical cycling. Because of the severity of the climate the vegetation season is very short. During the arctic summer the temporary melted soil layer is less than 40–45 cm and the deeper layers of ground are permanently frozen. These permanently frozen grounds are called permafrost. The existence of permafrost mainly determines the qualitative and quantitative parameterization of biogeochemical cycles of all elements. We can say that the biological and biogeochemical cycles are restricted both temporally and spatially in Arctic ecosystems.

The major restricting factor is the ocean. Both continental coastal areas and areas of islands are exposed to cold oceanic currents. The Arctic oceanic basin is separated from the warm influence of the currents from the Atlantic and Pacific Oceans owing to the existence of both narrow channels like the Bering Strait and submarine ranges. The average precipitation is from 100–200 mm (North American areas) to 400 mm (Spitzbergen Island) and the average temperature of January is between -30 °C and -38 °C (Figure 1).

The low precipitation and freezing water stage during 10–11 months per annum have led to the development of arid polar and tundra landscapes. The characteristic features of these landscapes are the alkaline soil reaction (pH 7.5–8.0) and even the occurrence of modern carbonate formations.

1.1. Landscape and Vegetation Impacts

In accordance with the local maximum of precipitation and the relative low winter temperatures, the most favorable climate conditions for biogeochemical processes and pollutant exposure are in the western part of Spitzbergen Island. Three types of landscapes with corresponding ecosystems are widespread (Dobrovolsky, 1994).

On the wide shore terraces of fjords and on the slopes of hills and low mountains, the Arctic Tundra ecosystems occur. The mosses and lichens are predominant with

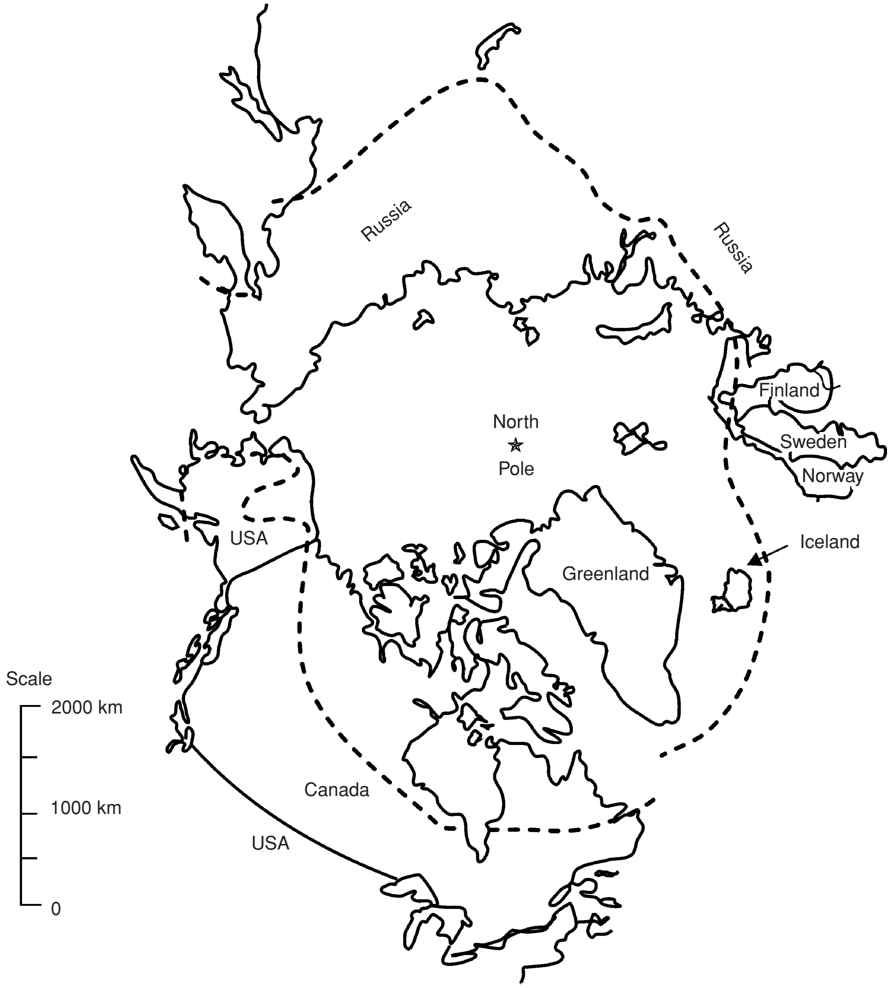


Figure 1. Polar and Tundra ecosystem area in the Northern Hemisphere.

the twigs of willow (*Salix polaris*), varieties of rockfoils (*Saxifraga oppositifoila, S. polaris, S. caespitosa*, etc.), dryad (*Dryas octopetala*), specimens of arctic poppies, buttercups, cinquefoils, various tufted rushes (*Juncus*) and grasses. In some areas the vegetation forms a continuous covering and in others it is confined to depressions enclosing cryogenic polygons. The plant mat covers the soil surface. Most soils are Brown Arctic Tundra soils having only A and C genetic horizons.

The vegetation becomes sparse at the high plateau over 400–500 m above sea level (a.s.l.). The surface coverage is mainly less than 10%. The short grown mosses are predominant. They occupy the depressions with shallow soil accumulation. Lichens

Table 1. Chemical composition of different plant species in Spitzbergen island ecosystems (after Dobrovolsky, 1994).

	Content, ppm by dry plant weight								
Plants	Ca	K	Na	Fe	Mn	Zn	Cu	Pb	Ni
Lichen	1,170	2,000	633	137	6.2	10.0	2.5	7.8	<1.5
Moss	758	2,170	867	1,240	13.9	8.3	5.2	5.8	1.7
Rockfoils	1,460	10,000	1,833	1,751	44.3	50.8	8.8	<1.5	2.6
Arctic willow	1,375	6,670	658	401	87.8	176.2	8.0	3.7	3.7
Cotton grass	683	20,000	442	Nil	Nil	90.0	7.3	2.5	2.5
Rush	400	667	2,000	1,380	286.0	63.5	5.8	1.5	4.3
Alpine sorrel	1,550	8,330	2,000	3,480	172.0	24.5	8.9	1.8	16.7
Heather	9,580	22,500	10,500	1,659	106.2	35.6	10.5	1.5	3.7
Laminaria	6,000	4,330	2,033	203	15.0	16.6	3.7	1.5	1.5

grow on mosses and large rock fragments. Only separate specimens of rushes and rockfoil occur. The soils are of the Arctic coarse skeleton type.

The rank *Hyphnum* and *Sphagnum* mosses are mainly represented on the flat variously waterlogged bottoms of glacial valleys. Cassiopes (*Cassiope tetragona*), tufted grasses and rushes grow in the relatively dry sites of these valleys. The given conditions favor peat formation; however, the permafrost layer restricted this process and the peat layer is mainly less than 40 cm. The small thermokarts lakes place in the wide valley and they are bordered by sedges (*Carex nordina, C. rupestis*), cottongrass (*Eriophorum*) and nappy plant species.

The ash of peat forming plant species contains a predominant amount of silicon. This element is particularly abundant in the *Sphagnum,* where its content achieves 36% by ash weight. Iron and aluminum are the next abundant. The first is accumulated during the peat formation process. The accumulation of calcium and potash is more pronounced than sodium, and the sulfur content is also remarkable. A large amount of mechanically admixed mineral particles (40–80% by ash weight) is found in mosses. This is due to the deposition of fine dispersed mineral material from snowmelting waters and atmosphere dust deposition (Table 1).

1.2. Pollutant Exposure and Chemical Composition of Plants

Let us consider the influence of various exposure factors on the chemical composition of plant species in the arctic islands. It seems the most influential factor is the distance from the ocean shore. For example, in arctic willow growing a few meters from the tide line, the content of Zn, Cu, Pb, and Ni was higher than that of the same plant

Table 2. The trace element composition of the Spitzbergen snowmelting water, ppb (Evseyev, 1988).

Trace metal	Fe	Mn	Zn	Cu	Pb	Ni	Co
Content	27.5	0.80	31.1	1.7	0.9	0.3	0.3

species growing about 1 km from the coast line and sheltered from the sea by a morain hill. The coastal plants contain also more sea salt cations like Na, Ca, K, and Mg.

The enrichment effect of the ocean is mainly related to the chemical composition of aerosols, which determine the chemical composition of snow. For the northern areas of the Eurasian continent and the western areas of Spitzbergen Island we can estimate the average values of sea salt deposition in snow from 3,000 to 5,000 kg/km^2. The predominant chemical species in the snow water are chlorides (anions) and sodium and calcium (cations). The content of trace elements (heavy metals) is negligible. Their origin is connected with long-range trans-boundary air pollution from industrial centers of North America, Russia and Europe. This was shown for the Greenland glaciers, where the statistically significant growth of zinc and lead in the recent probes in a comparison with ancient ice cores has been attributed to the environmental pollution (Bashkin, 2002).

The role of air aerosols in the biogeochemical cycle of various nutrients in the Arctic ecosystems has been studied in Spitzbergen Island. The supply of oceanic aerosols is very important in these conditions since the interaction between plant roots and soil or mineral substrates is depressed during a long part of the year. According to the monitoring data the following results are typical for the Spitzbergen snow melting water (Table 2).

For a comparison, the mobile forms of trace metals were extracted from the local geological rocks, as water-soluble and 1.0 N HCl-soluble forms. The results are shown in Table 3.

We can see that the content of trace metals in water extraction is very low. This means that the direct involvement of these metals in biogeochemical cycles is very restricted. The significant increase of metal contents in acid-soluble form was shown only for Fe, Mn and, partly, for Zn. These data testify the importance of atmospheric deposition for the Arctic ecosystems as a source of nutrients.

The supply of sea salts and trace metals via precipitation appears to contribute to the elevated content of water-soluble forms of alkaline and earth–alkaline elements and trace metals in the uppermost soil layer.

1.3. Influence of Soil on Pollutants Exposure

A high amount of various nutrients and trace metals is retained in peat and dead plant residues and thus temporarily eliminated from the biogeochemical cycles and pollutants exposure to human and ecosystem health. The period of this elimination depends on the solubility of these metals. It has been shown (Dobrovolsky, 1994) that

Table 3. Content of mobile forms of trace elements in rocks of Spitzbergen Island, number of rocks = 10 (after Dobrovolsky, 1994).

Statistics	Trace metal content, ppb						
	Fe	Mn	Zn	Cu	Pb	Ni	Co
Extractant—water							
M	5.71	0.54	0.53	0.11	0.05	0.07	0.03
σ	4.64	0.28	0.21	0.08	0.02	0.08	0.03
V, %	81	52	40	73	40	107	100
Extractant—1.0 N HCl							
M	1,266.6	408.8	7.41	4.64	4.23	0.83	1.04
σ	949.3	148.0	2.40	2.46	2.23	1.07	0.45
V, %	75	36	32	53	53	129	43

the soluble forms of such metals as iron and zinc accounted for about 70% and 50% of the total contents of these metals in solution, correspondingly, in the upper peat layer with living plants. In the underlying peat layer, the percentage of soluble forms tended to decrease. A similar tendency was recorded for soluble forms of carbon: on leaching from upper to lower peat layer, the concentration of soluble form decreases twice as much in the terrace and still greater, in waterlogged depression.

Electrodialysis of the soluble forms of iron has revealed the predominance of electroneutral forms. A similar distribution has been shown for carbon. The hypothesis that the organic iron-containing complexes are responsible for water-soluble forms of iron in polar peat ecosystems seems logical. Amongst the soluble zinc forms, the percentage of electroneutral forms is somewhat lower that that of charged forms, with the anions present in a larger amount in the upper peat layer.

However, only the smallest part of soluble metals is involved in the biological cycle. Most of these are either lost to water runoff, or retained in the peat organic matter. The latter is the source of gradual remobilization but the whole mineralization may last up to 50 years or even more. The total accumulated retained amount of macro- or trace metals in organic matter of peat is tens and hundreds of time higher than the concentration of annually released soluble forms, which are available for plants.

2. BIOGEOCHEMICAL CYCLES AND EXPOSURE ASSESSMENT IN POLAR ZONES

2.1. Biogeochemical Cycles

The different metal uptake by plants is accompanied by a different involvement of these trace metals and macronutrients in the biogeochemical cycles. A comparison of

Table 4. Airborne input of various trace metals in the Spitzbergen island ecosystems, mg/yr per 100 mm of precipitation (after Dobrovolsky, 1994).

Trace metals	Fe	Mn	Zn	Cu	Ni
Input	27,500	800	31,100	900	300

the metal concentrations in plant tissues and the metal concentrations in the aqueous extracts from soil-forming geological rocks shows that iron and manganese are the most actively absorbed by plants. The plant to soil metal ratio can be an indicator of this absorption. These values for Fe and Mn are in a range of $n \times 10^2$ to $n \times 10^3$. This ratio is about $n \quad \times 10^1$ for Zn, Cu, and Ni. It is noteworthy that the high concentrations of iron and manganese tend to even increase in the dead organic matter of peat.

The systematic removal of elements by runoff and the reimmobilization from solution by organic matter are continuously counterbalanced by the new input of chemical species, which maintain both biological and biogeochemical cycles. The main sources of water-soluble elements are oceanic aerosols deposited on the land surface and the weathering of rocks. The airborne input of the trace metals may be ranked as follows for the Spitzbergen island ecosystems (Table 4).

We can compare these values with those characterizing the fluxes of trace metals in biogeochemical cycles. The biological productivity of the Polar Tundra ecosystem grown on the low terrace in the region of Barentsberg, Spitzbergen Island, is shown in Table 5.

To be noted for comparison, the annual growth increase for arctic willow (*Salex arctica*) in Cornwallis Island in the Canadian Arctic Archipelago, 75°N, is a mere 0.03 ton/ha (Warren, 1957). The corresponded trace metal fluxes are shown in Table 6.

2.2. Exposure to Airborne and Ground Pollutants

We can see that for iron and manganese the annual fluxes of trace metals are an order of magnitude higher than airborne input. For copper this input is sufficient to supply the annual uptake, and for zinc is even in excess. All these trace metals are essential elements and their input with deposition can be considered as positive for

Table 5. The biological productivity of the Polar Tundra Low Terrace ecosystem.

Productivity	Ton, ha
Total mass of living plants	2.9
Mass of dead plant matter	9.6
Annual net primary productivity	0.6

Table 6. Fluxes of trace metals in the Spitzbergen Island ecosystems (after Dobrovolsky, 1994).

Trace metal	Mean content in plant species, ppb by dry weight	Trace metal fluxes, g/ha/yr In living plant organisms	 In dead organic matter	 In net annual production	Airborne input*, g/ha/yr
Fe	2,000.0	5,800.0	19,200.0	1,200.0	82.5–110.0
Mn	150.0	435.0	1,440.0	90.0	2.4–3.2
Zn	60.0	174.0	576.0	36.0	93.3–124.4
Cu	6.3	18.3	60.5	3.8	5.1–6.8
Ni	4.3	12.5	41.5	2.6	0.9–1.2
Pb	3.7	10.7	35.5	2.2	2.7–3.6
Co	1.0	2.9	9.6	0.6	0.9–12

* The airborne input was calculated per 300 and 400 mm per year in accordance with annual precipitation rates in the western Spitzbergen coast and trace metal rates shown in Table 4.

the ecosystem's behavior. The excessive deposition input of lead is rather dangerous owing to the unknown physiological and biogeochemical role of this element in plant metabolism. However, the significant amounts of lead can be immobilized in dead organic matter and excluded from biological turnover.

The other output from watershed and slope landscapes positions is related to the surface and subsurface runoff of trace metals. The ecosystems of waterlogged glacial valleys, geochemically subordinate to the above mentioned landscape, can receive with surface runoff an additional amount of various chemical species. This results in 3–4-fold increase of plant productivity in comparison with elevated landscapes and in corresponding increase of all biogeochemical fluxes of elements, which are shown in Table 6. For instance, the accumulation of trace metals in dead peat organic matter of waterlogged valley was assessed as the follows: Fe, $n \times 10^1$ kg/ha, Mn, 1–2 kg/ha, Zn, 0.1–0.3 kg/ha, Cu, Pb, Ni, $n \times 10^{-2}$ kg/ha.

3. BIOGEOCHEMICAL CYCLES AND EXPOSURE ASSESSMENT IN TUNDRA ZONES

The tundra zone and corresponding tundra ecosystems occupy the northernmost strip of the continental area of Eurasia and North America bathed by the seas of the Arctic basin. The climate conditions of the tundra zone provide for a higher productivity of ecosystems and higher activity of biogeochemical cycles of various elements as compared with the Arctic ecosystems. The mosses, lichens, and herbaceous plant species are predominant in the northern part of the Tundra ecosystems and shrubs are prevalent in the southern part.

The edaphic microflora is diversified, and the microbial community is more numerous than that of the arctic soils. The bacterial population varies from 0.5×10^6 to 3.5×10^6 specimens per gram in topsoil horizon.

3.1. Plant Uptake of Pollutants

The ash contents of the total trace elements and nitrogen are similar in Tundra ecosystem biomass. The highest concentrations, >0.1% by dry ash weight, are typical for Ca, K, Mg, P, and Si. We can note the increase of iron, aluminum and silicon contents in the underground parts of any plants.

The uptake of trace metals depends on both from the plant species and metal. Such elements as titanium, zirconium, yttrium, and gallium are poorly absorbed owing to their minor physiological role in plant metabolism. Rockfoils (Genus *Saxifraga*) and mosses (genus *Bryophyta*) are especially sensitive to alternations of trace metal concentrations. The bryophytes are capable of sustaining higher concentrations of some trace metals as compared to vascular plants (Shacklette, 1962). Some species of mosses can accumulate enormous amounts of trace elements and can serve as indicators of copper metal ore deposits with elevated copper contents.

3.2. Tundra Soils and Exposure to Pollutants

The Acidic Brown Tundra soils (Distric Regosol) are formed under the conditions of the free drainage commonly encountered in slopes and the watershed relief positions. The characteristic features of these soils are related to the accumulation of non-decomposed plant residues and the built-up peat layers. Below the peat horizon the soil profile differentiation is indistinct. In the thin indistinct humus horizon underlying the peat layer, the humus content is from 1 to 2.5% with predominance of soluble fulvic acids. This presents an acid reaction of soils, with values of soil pH <5.0. The acid geochemical conditions facilitate the migration of many trace elements, phosphorus, nitrogen and many earth–alkaline metals. The migration of chemical species is mainly in the form of Me–organic or P–organic complexes. This facilitates the exposure of humans and ecosystems to different pollutants.

The deficiency of oxygen is very common in lowland plains with an impeded drainage. This is favorable to the formation of Gley Tundra soils (Gelic Regosol) with a grey gleyic horizon. This horizon includes the gray and rusty spot-like inclusions of precipitated gels of Fe^{3+} oxides. These oxides are the geochemical barriers in the pollutants biogeochemical cycles and they can retard significant amount of various chemical species.

3.3. Exposure to Pollutants and Productivity of Tundra Ecosystems

The biomass of Tundra ecosystems gradually increases from 4–7 ton/ha for moss–lichen tundra to 28–29 ton/ha by dry weight for low-bush tundra. In the northern tundra, the plant biomass and dead organic matter are eventually shared. Southwards this percentage tends to diminish, and low-bush living biomass is smaller than dead plant remains mass. A typical feature of the Tundra ecosystems plant species is the prevalence of underground matter (roots) up to 70–80% of the total biomass.

Table 7. The partition of Tundra ecosystem biomass, ton/ha (after Rodin and Bazilevich, 1976).

Biomass types	Plant living biomass	Dead organic matter	Annual net production	Annual litterfall
Mass	28	83	20.4	20.3

The average mass distribution of Tundra ecosystems is as shown in Table 7.

The biogeochemical turnover of nitrogen is about 50 kg/ha per year. A similar value was shown for the turnover of total mineral elements, 47 kg/ha/yr. The relevant values for various trace and macroelements are shown in Table 8.

Table 8. Annual fluxes of chemical species in the Low-Bush Moss Tundra ecosystem (after Dobrovolsky, 1994).

Chemical species	Chemical species symbol	Plant uptake fluxes, kg/ha/yr
Nitrogen	N	50
Iron	Fe	0.188
Manganese	Mn	0.226
Titanium	Ti	0.031
Zinc	Zn	0.028
Copper	Cu	0.0071
Zirconium	Zr	0.0070
Nickel	Ni	0.00188
Chromium	Cr	0.00165
Vanadium	V	0.00141
Lead	Pb	0.00116
Yttrium	Y	0.00070
Cobalt	Co	0.00047
Molybdenum	Mo	0.00043
Tin	Sn	0.00024
Gallium	Ga	0.00005
Cadmium	Cd	0.00003
Average ash content of plant species, %		2.0
Total uptake of ash elements by vegetation, kg/ha/yr		47

The flux of chemical elements per unit area in tundra ecosystems is not proportional to the plant uptake. Presumably, some elements, like Zn and Cu, are taken up selectively, whereas other trace elements, like Ti, Zr, V, or Y, are absorbed passively, depending on their content in the environmental media.

Finally, this determines the actual and potential exposure of living organisms to pollutants' impact.

CHAPTER 7

BOREAL AND SUB-BOREAL CLIMATIC ZONE

The Boreal and Sub-Boreal Forest ecosystems represent the forests of cold and temperate climate. These ecosystems occupy an extended zone in the northern part of the Northern Hemisphere. The total area is 16.8×10^6 km^2, or 11.2% from the whole World's territory.

The general scheme of biological and biogeochemical cycling in Forest ecosystems is shown in Figure 1.

1. BIOGEOCHEMICAL CYCLING OF ELEMENTS AND POLLUTANTS EXPOSURE IN FOREST ECOSYSTEMS

The plant species biomass of Boreal and Sub-Boreal Forest ecosystems accumulates a significant part of living matter of the whole planet. This value is about 700×10^6 tons of dry weight. The biomass per unit area of different Forest ecosystems varies from 100 to 300 ton/ha and even 400 ton/ha in the Eastern European Oak Forest ecosystems. The annual net primary productivity, NPP, varies from 4.5 to 9.0 ton/ha (Table 1).

The overall biomass accumulated in Forest ecosystems per unit area is 20–50 times higher than the annual productivity. This means that various chemical species are retained during long periods in plant biomass thus being excluded from biological or biogeochemical cycling. The duration of biological cycles may be from 1.5 to >25 years for Broad–Leaved Sub-Boreal Forest and Coniferous North Taiga Forest ecosystems, correspondingly. The slow turnover rates are connected with both a prevalence of aboveground biomass and slow mineralization of plant litterfall on the soil surface.

The microbial activity in forest soils is much more intense in comparison with Tundra ecosystems. Fungi, bacteria and actinomycetes play a significant role in degradation of carbohydrates of forest litterfall (Box 1).

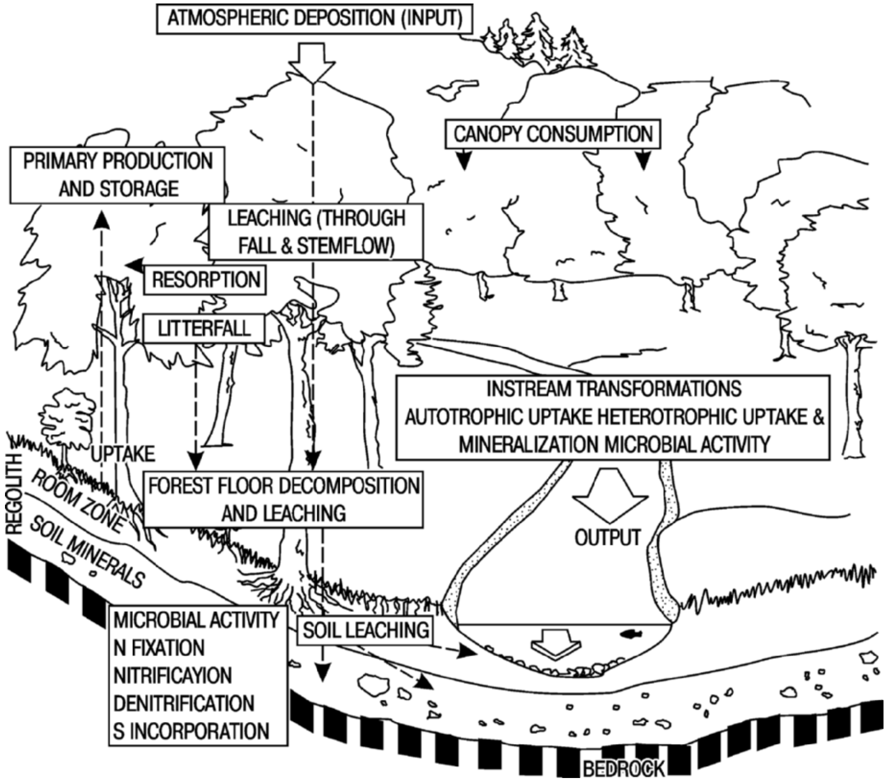


Figure 1. Schematic illustration of the biogeochemical cycling processes in Forest ecosystems (Nihlgard et al., 1994).

Box 1. Microbial regulation in Forest ecosystems (after Nihlgard et al., 1994; Fenchel et al., 1998)

The regulation of biogeochemical cycles by microbial populations is of most direct importance in the cycling of N, S, P, and C. Most of the ecosystem pool of these elements resides as organic forms in forest floor and mineral soil compartments. These organic complexes are subjected to microbial transformations, which regulate nitrate, sulfate and phosphate ions dynamics and availability. In turn, this influences indirectly

Table 1. Net primary productivity of Forest ecosystems, ton/ha.

Ecosystems	Coniferous north taiga forest	Coniferous and mixed south taiga forest	Broad–leaved sub-boreal forest
NPP	4.5	8.0	9.0

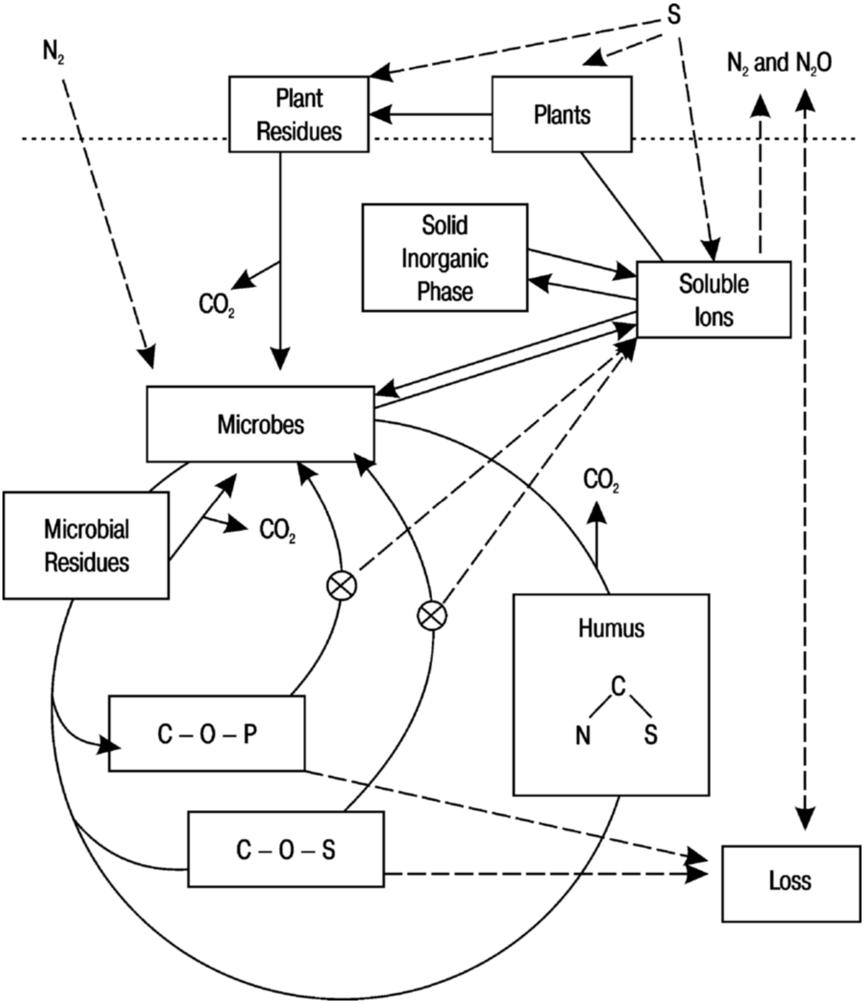


Figure 2. A tentative model illustrating decomposition interactions (Nihlgard et al., 1994).

the migration of other solutes though maintenance of ionic balances of solutions. For quantification of the role of microbes in forest biogeochemical processes, models like that shown in Figure 2 should be applied.

1.1. Nitrogen Cycle and Exposure Pathways

Since nitrogen is a nutrient, which limits the productivity of almost all Boreal and Sub-Boreal Forest ecosystems, its biogeochemical cycling is relatively well understood at present. The major N transformations and fluxes are shown in Figure 3.

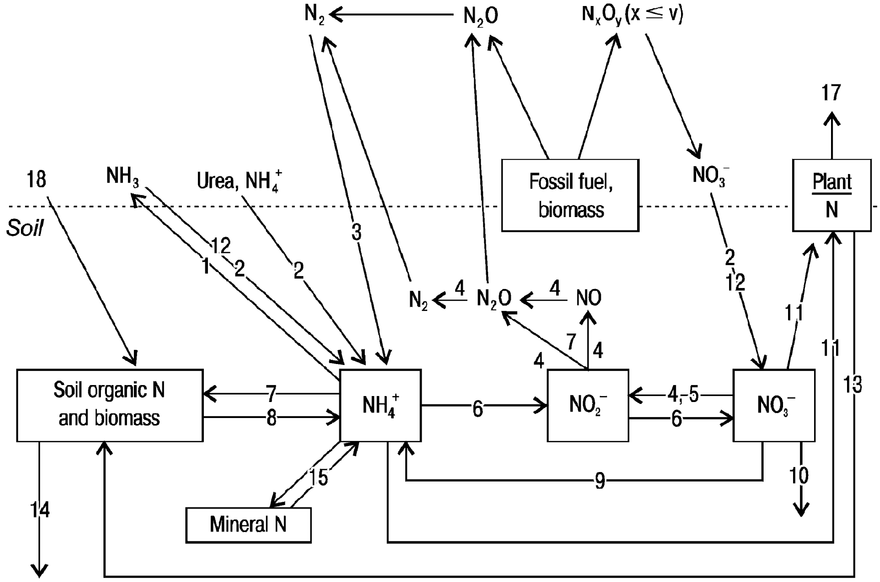


Figure 3. The general nitrogen model for illustrating the biogeochemical cycling in Forest ecosystems. Explanations for the fluxes: 1, ammonia volatilization; 2, forest fertilization; 3, N_2-fixation; 4, denitrification; 5, nitrate respiration; 6, nitrification; 7, immobilization; 8, mineralization; 9, assimilatory and dissimilatory nitrate reduction to ammonium; 10, leaching; 11, plant uptake; 12, deposition N input; 13, residue composition, exudation; 14, soil erosion; 15, ammonium fixation and release by clay minerals; 16, biomass combustion; 17, forest harvesting; 18, litterfall (Bashkin, 2002).

Processes of dinitrogen fixation, mineralization, immobilization, and nitrification have received the most attention, but there is a paucity of information on denitrification in forest ecosystems. The status and fluxes of nitrogen are strongly regulated by rates of N mineralization and immobilization. The rates of mineralization are greatly enhanced after clearcutting. The influence of clear cutting has been demonstrated in the experiments at Habbard Brook Experimental Forest and in Coweeta (see Likens et al., 1977). Over a three-year period after clearcutting a hardwood forest in Habbard Brook, forest floor organic matter decreased by 10.8 ton/ha, soil organic matter declined by 18.9 ton/ha and net N loss from the soil was estimated to be 472 kg/ha with an increased export of inorganic N in the stream waters of 337 kg/ha. Significant alterations of N fluxes have been monitored also at Coweeta. In the first 3 years after clear cut and logging, soil N mineralization increased by 25% and nitrification increased by 200%. However, only a small fraction of this mineralized nitrogen was exported from the ecosystem. The retention was owed partly to rapid revegetation and high rates of nitrogen uptake and partly due to microbial immobilization.

When nitrogen input owed to mineralization and atmospheric deposition exceeds the demand of both the vegetation and the microbes in undisturbed maturated forest ecosystems, the phenomenon of nitrogen saturation takes place (Gunderson and Bashkin, 1994). This phenomenon is accomplished by nitrogen leaching from the forest ecosystems. These nitrogen losses are highly variable, but generally sites in North America and Northern Scandinavia show N loss rates of <1.4 kg/ha/yr, whereas sites in southern Scandinavia and Central Europe exhibit loss rates often >7 kg/ha/yr. Generally, N leaching from undisturbed forest ecosystems starts when the N deposition rates are higher than 10 kg/ha/yr.

Fixation of molecular nitrogen, N_2, to ammonia in forest ecosystems can occur on and/or in a variety of forest substrates including plant canopy and stems, epiphitic plants compartments, wood, litter, soil and roots. A recent review of the magnitude of N inputs to forest ecosystems indicates that non-symbiotic fixation ranges from <1 to 5 kg/ha/yr and symbiotic fixation ranges from about 10 to 160 kg/ha/yr in early successional ecosystems where N_2-fixing species are present.

Denitrification, a dissimilatory pathway of nitrate reduction (see Section 3.3 also) into nitrogen oxides, N_2O, and dinitrogen, N_2, is performed by a wide variety of microorganisms in the forest ecosystems. Measurable rates of N_2O production have been observed in many forest soils. The values from 2.1 to 4.0 kg/ha/yr are typical for forest soils in various places of Boreal and Sub-Boreal Forest ecosystems. All *in situ* studies (field monitoring) of denitrification in forest soils have shown large spatial and temporal variability in response to varying soils characteristics such as acidity, temperature, moisture, oxygen, ambient nitrate and available carbon.

Thus, from the viewpoint of environmental risk assessment (critical loads) the most important exposure pathways are nitrate leaching and denitrification, which are both very sensitive to anthropogenic pollution. These links of biogeochemical nitrogen cycle should be firstly quantitatively parameterized to assessing environmental risk.

1.2. Sulfur Cycle and Exposure Pathways

Both inorganic and organic transformations are important in the sulfur cycle in Forest ecosystems. The major sulfur pools and transformation processes are shown in Figure 4.

Similarly to N, most S pools are found in organic form in forest floor and soil humus. However, unlike nitrogen, there are important abiotic processes, especially sulfate sorption processes, which play a critical role in regulating sulfate dynamics in forest ecosystems. An example of this type of exposure pathway was shown in the Habbard Brook whole-tree harvesting experiment, where the decrease in sulfate output from the watershed was attributed to sulfate adsorption, which was enhanced by soil acidification from nitrification (see above).

Biological exposure pathway of sulfur movement in soils of forest ecosystems is related to microbial transformation of sulfolipids. Back conversion of sulfate-S into organic matter immobilizes the anion and potentially reduces soil cation leaching. Processes of sulfur mineralization and incorporation proceed rapidly in response to several factors, including temperature, moisture, and exogenous sulfate availability in soils and water.

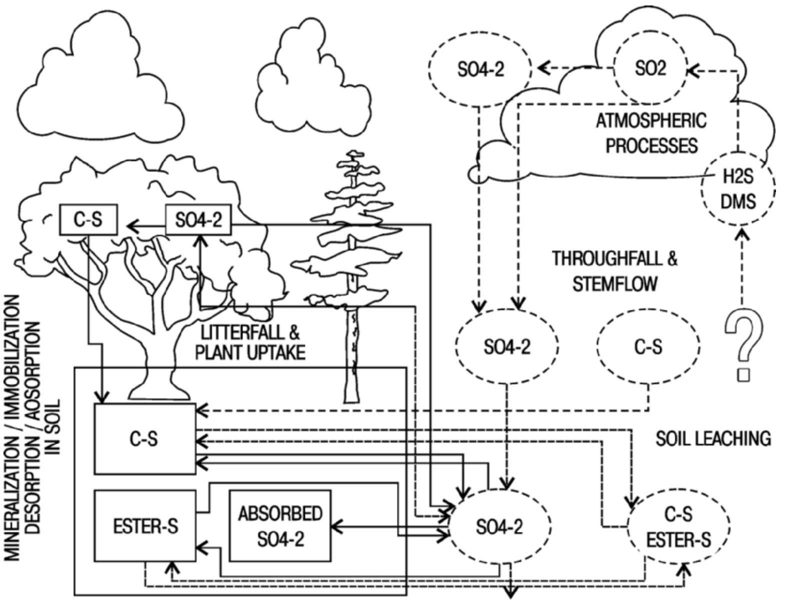


Figure 4. A model illustrating sulfur biogeochemical cycle in forest ecosystems (Bashkin, 2002).

1.3. Phosphorus Cycle and Exposure Pathways

The internal and external regulation of the phosphorus biogeochemical cycle in Forest ecosystems is tightly coupled to soil development and the change of phosphorus pools from the predominance of primary inorganic phosphorus (e.g., apatitte) to that of organic-P, secondary-P, mineral-P and occluded-P as is illustrated in Figure 5.

The organic phosphorus in forest soils is derived mainly by microbial synthesis and the accumulation of plant and animal residues plays a subordinate role. Much of the organic-P occurs in ester linkages (up to 60%) with lesser amounts in other forms. The leaching losses of P are ranged from as little as 7 g/ha/yr at Habbard Brook to up to 500 g/ha/yr for a glacier outwash in New Zealand. Loss rates generally are greatest in young, base-rich soils and lowest in acidic soils ($pH < 5.0$) with high content of sesquioxides, which may fix phosphates. Thus, soils at intermediate stages of development have the highest availability of phosphorus, which is partly regulated by microbial mineralization processes and open for pollutants' exposure.

1.4. Carbon Cycle and Exposure Pathways

The carbon biogeochemical cycle in Forest ecosystems is shown in Figure 6. This cycle is open and exposure to anthropogenic loading will definitely be accompanied by transformation of many cycle links. Global and regional climate change is the only example, the eutrophication of surface waters is the second one, however in the latest case the carbon cycle is coupled with those of nitrogen, phosphorus and

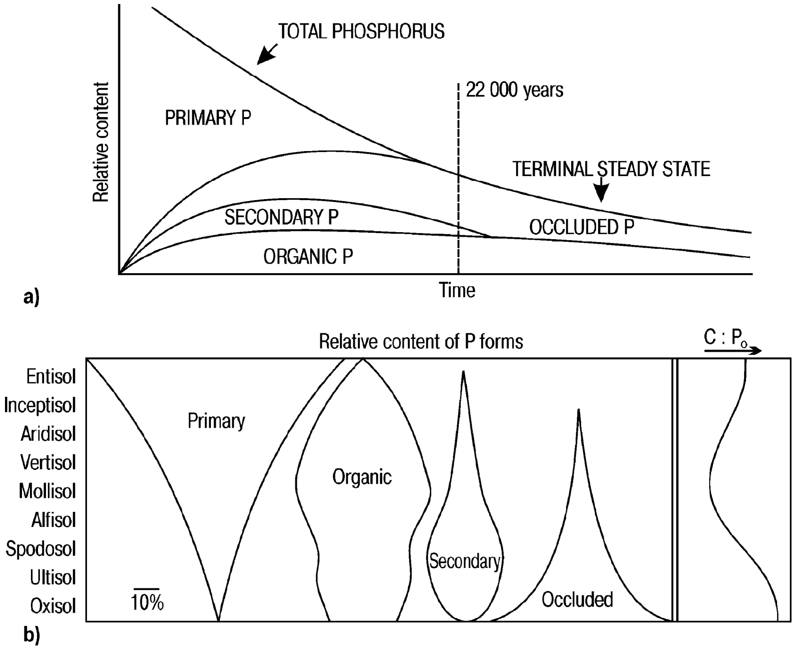


Figure 5. Biogeochemical transformations of phosphorus in forest soils: (a) the long-term relative development of different phosphate fractions in soils of the forest ecosystems; (b) the relative contents of P fractions in different soil types. Also, the idealized carbon to organic-P rates ($C{:}P_o$) are illustrated (Nihlgard et al., 1994).

some microelements like Fe and Mo. Accordingly, exposure to various anthropogenic pollutants is changing the carbon cycle and v/v the knowledge of the most sensitive links of C biogeochemical cycle will allow the regulation of the environmental risk assessment and risk management on a different scale.

Obviously the fates of N, S and P are tightly coupled not only with each other, but also with C dynamics of soils (Bashkin, 2002). For example, it has been suggested that the leaching of dissolved organic species of nitrogen sulfur and phosphorus contributes to the accumulation of these elements in mineral soils. This leaching of organics is an important component of soil formation of Spodosols, which are common especially in Northern Coniferous Forest ecosystems. The ratio between total nitrogen and total carbon, the C:N ratio, is widely applied to predict microbial mineralization–immobilization of nitrogen in soils (Figure 7).

Typically high C:N ratios (>60) for forest plant organic matter have a major impact on the nitrogen cycle. A number of empirical and theoretical analyses have established a strong linkage between nitrogen mineralization, assimilation and organic matter decomposition. In particular, C:N ratios >30 decrease mineralization and increase assimilation instead, with the balance between two processes dependent on the nitrogen content in microbial biomass. The latter parameter sets the minimum

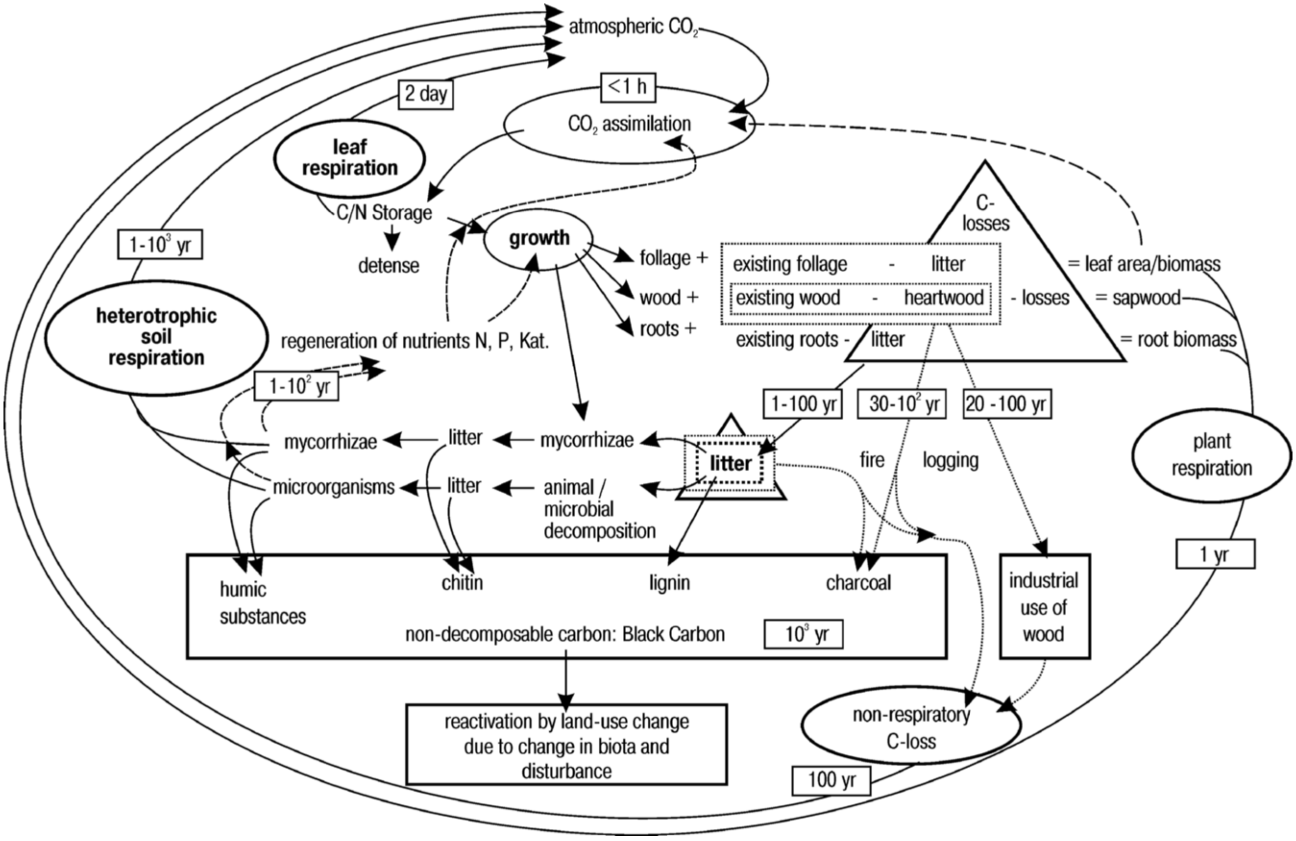


Figure 6. Carbon biogeochemical cycle in the hypothec forest ecosystem (Schulze, 2000).

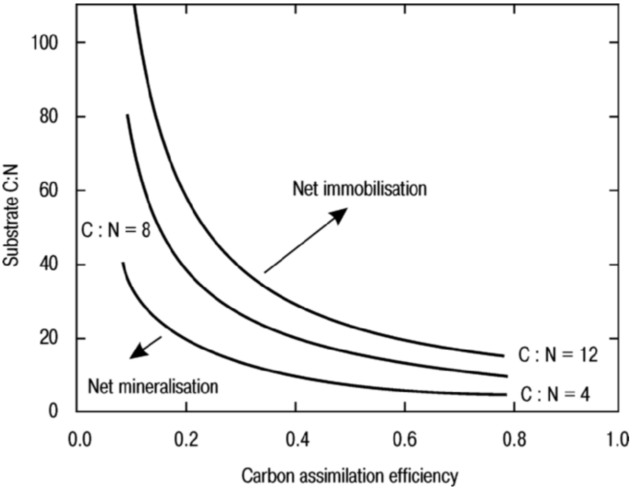


Figure 7. Relationship between net mineralization and immobilization of nitrogen as a function of substrate C:N ratio and microbial assimilation efficiency (F) for three different biomass nitrogen levels equivalent to C:N ratios of 4–8–12 (after Bashkin, 1987; Fenchel et al., 1998).

nitrogen requirement for biosynthesis per unit amount of substrate metabolized. Nonsymbiotic nitrogen fixation can ameliorate nitrogen limitation, and to some extent high C:N ratios may be a determinant of soil microbial diversity.

However, the microbial activity is depressed during long and severe wintertime, and this leads to an accumulation of semi-mineralizable plant residues on the soil surface. With the increasing duration of cold season from south to north, the mass of these half-destroyed remains enlarges from 15 ton/ha of dry organic matter in Broad–Leaved Sub-Boreal Forest ecosystems to 80–85 ton/ha in Northern Taiga Forest ecosystems.

In the Northern Forest ecosystems, the relative content of chemical species in dead organic matter of forest litterfall is higher than that in living biomass. In Mixed and Deciduous Forest ecosystems, this is true for the total mass of chemical species, however some elements are more abundant in living biomass. Thus, the general biogeochemical feature of biological turnover in forest ecosystems is the prolonged retention of many chemical species in dead organic matter and exclusion from cycling (Table 2).

The data of Table 3 provide a general characteristic of trace element fluxes in Boreal and Sub-Boreal Forest ecosystems.

2. GEOGRAPHICAL PECULIARITIES OF BIOGEOCHEMICAL CYCLING AND POLLUTANT EXPOSURE

2.1. North American Forest Ecosystems

In the USA, two focal points for biogeochemical research have been the forest catchment ecosystems at Hubbard Brook Experimental forest in the White Mountains of

Table 2. Averaged fluxes and pools of biological cycling in Forest ecosystems (after Rodin and Bazilevich, 1965; Dobrovolsky, 1994).

	Ecosystems			
Fluxes and pools	Northern Taiga Spruce Forest	Southern Taiga Spruce Forest	Sub-Boreal Oak Forest	Southern Taiga Sphagnum Swamp
Pools, ton/ha				
Total biomass	100	330	400	37
Nitrogen	0.35	0.72	1.15	0.23
Dead organic matter	30	35	15	100
Annual fluxes, ton/ha/yr				
NPP	4.5	8.5	9.0	3.4
Litterfall	3.5	5.5	6.5	2.5
Nitrogen uptake	0.058	0.041	0.095	0.040
Nitrogen return	0.048	0.035	0.057	0.025

New Hampshire and Coweeta Hydrologic Laboratory, located in the southern Appalachians of North Carolina.

The nutrient cycles of the forest catchment ecosystems are to a large extent determined by biota, especially by the primary production of plants and by microbial decomposition. Severe losses from the ecosystem of important nutrients, e.g., Ca, Mg, K and P, are expected to lower the productivity when occurring in the root zone. Most nutrients available for circulation in the temperate forested ecosystems are found in the tree layer or in the accumulated organic mater of soil layer. This is especially true for the most important macronutrients (C, N, P, K, Ca, Mg and S). Nitrogen is almost completely bound to the organic matter and when it is mineralized it is either leached as nitrate or assimilated and immobilized by organisms in the soil. Including the humus horizon, the soil organic matter contains the largest pool of nitrogen in the Boreal Forest ecosystems (Figure 8).

For phosphorus and potassium this pool of organic matter is also of importance, but in the Boreal Forest ecosystems, a relatively higher amount is in the living biomass. The long-term soil development proceeds towards a lower rate of weathering in the root zone and relatively higher amounts in biogeochemical fluxes (Nihlgard et al., 1994).

Thus, one should mention that the quantitative estimates of various links of biogeochemical cycles of elements and their interactions are of crucial importance for environmental risk assessment for the given ecosystems under anthropogenic pressure.

Table 3. Averaged fluxes of trace elements in biological cycling of Boreal and Sub-Boreal Forest ecosystems (after Dobrovolsky, 1994).

	Forest ecosystems			
Ash/chemical species	Northern Taiga Coniferous Forest	Sub-Boreal Coniferous and Small–Leaved Forest	Sub-Boreal Broad–Leaved Forest	Sphagnum Forest Swamp
Average ash content, %	1.7	2.0	3.5	2.5
Total uptake of ash elements, kg/ha/yr	76	170	315	85
Trace element turnover, g/ha/yr				
Fe	304.0	680.0	1,260.0	1,500.0
Mn	364.0	816.0	1,512.0	75.1
Sr	53.0	119.0	221.0	68.0
Ti	49.4	111.0	205.0	401.2
Zn	45.6	102.0	189.0	62.6
Cu	12.2	27.2	50.4	12.2
Zr	11.4	25.5	47.2	14.3
Ni	3.0	6.8	12.6	13.6
Cr	2.6	5.9	11.0	10.9
V	2.3	5.1	9.4	10.2
Pb	1.9	4.2	7.9	12.0
Co	0.7	1.7	3.1	2.3
Mo	0.7	1.5	2.8	1.0
Sn	0.4	0.8	1.6	—
Ga	0.1	0.2	0.3	0.4
Cd	0.05	0.12	0.22	—

2.2. Spruce Forest Ecosystem of Northwestern Eurasia

Table 3 presents the averaged data for the whole forest area of Boreal and Sub-Boreal zone. However, there are definite peculiarities of biological and biogeochemical cycles in the individual ecosystems. We will consider the Spruce Forest ecosystem of the Karelia region, Russia. These ecosystems occur in the wide area of the Karelia, south from 63° N.

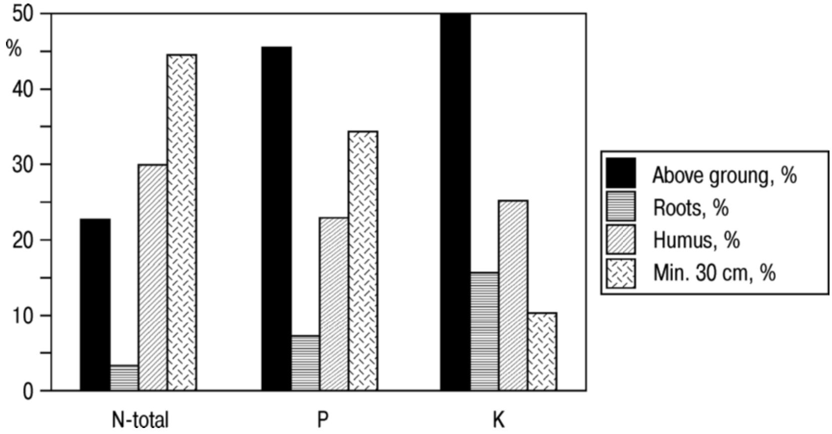


Figure 8. Relative distribution of N, P and K in the Boreal Forest ecosystem. Total amounts for the different fractions are given, expect for in the mineral soils down to 30 cm depth, where exchangeable amounts are given for P and K (Nihlgard et al., 1994).

The dominant species are the spruce (*Picea excelsa*), the birch (*Betula verrucosa, B. pubescens*), the aspen (*Populus tremula*), and the alder (*Alnus incana*). The moss and low bush layer is represented by the blueberry-bush (*Vaccinium myrtiilus*), hypnic mosses, separate species of cowberry (*Vaccinium uliginosum*) and flowering plants. The biomass of these Spruce Forest ecosystems reaches 10 ton/ha at the age of 100–150 years (Table 4).

We can see from Table 4 that most of the Spruce Forest ecosystem biomass is accumulated in trees, with trunk mass predominating. The values of annual Net Primary Production (NPP) and litterfall production are more connected with needles. In living matter, the mass of moss and bush species makes up to 2–3% of the tree biomass, whereas in dead matter (litterfall), it is up to 10%.

The distribution of trace metals in ash of living matter distinguishes from that in dead organic matter. About half of the total ash elements contained in the biomass is confined to the deciduous tree organs, whereas for the shedding, most ash elements are found in the needles. About 80% of ash elements are supplied from conifers to the soil in the shed needles, whereas their supply in the deciduous organs of mass and bush species is a mere 10%. The shedding trace metal losses from the living plant organs are accompanied by their redistribution into outer bark, where they may be retained during a long period. We can consider the retention of trace metals in bark of the conifers as one of the important sink in Spruce Forest ecosystems, which exclude these metals from biogeochemical cycles and regulate the exposure pathways.

The averaged fluxes and sinks of trace metals in biogeochemical turnover in Spruce Forest ecosystems are shown in Table 5.

There are significant differences in plant uptake of trace metals from soils. It is one of the most important pathways characterizing the exposure to various elements

Table 4. Biomass and total ash mass distribution in Spruce Forest ecosystems of the Karelia region, Russia (after Dobrovolsky, 1994).

Biomass components	Ecosystem parameters		
	Biomass	NPP	Litter production
Woody vegetation, ton/ha	40–100	4.0–9.0	2.0–5.5
Of this:			
Needles, %	10–15	36–38	56–60
Twigs, %	12–17	8–9	8–9
Trunks, %	50–60	41–43	22–25
Roots, %	17–19	12–13	9–10
Moss and low-bush vegetation, ton/ha	0.8–3.5	0.2–0.6	0.2–0.6
Total mass of ash elements (100%)			
Components of woody vegetation			
Needles, %	40–50	79–80	76–81
Twigs, %	13–18	4–5	2–3
Trunks, %	19–33	10–11	4
Roots, %	12–14	4–5	2–3
Moss and low-bush vegetation, %	3–8	5–9	7–10

Table 5. Averaged trace element mass budget for Spruce Forest ecosystems, Karelia, Russia (after Dobrovolsky, 1994).

Ecosystem biomass component and ash content, %	Annual NPP, kg/ha		Annual shedding, kg/ha	
	Dry organic matter	Total sum of ash trace metals	Dry organic matter	Total sum of ash trace metals
Conifer needles, 1.7%	1,440–3,420	24.5–58.1	1,120–3,300	19.0–56.1
Conifer bark, 1.3%	200–540	2.6–7.0	100–300	1.3–3.9
Moss and shrub species, 1.7%	200–600	3.4–10.2	200–600	3.4–10.2

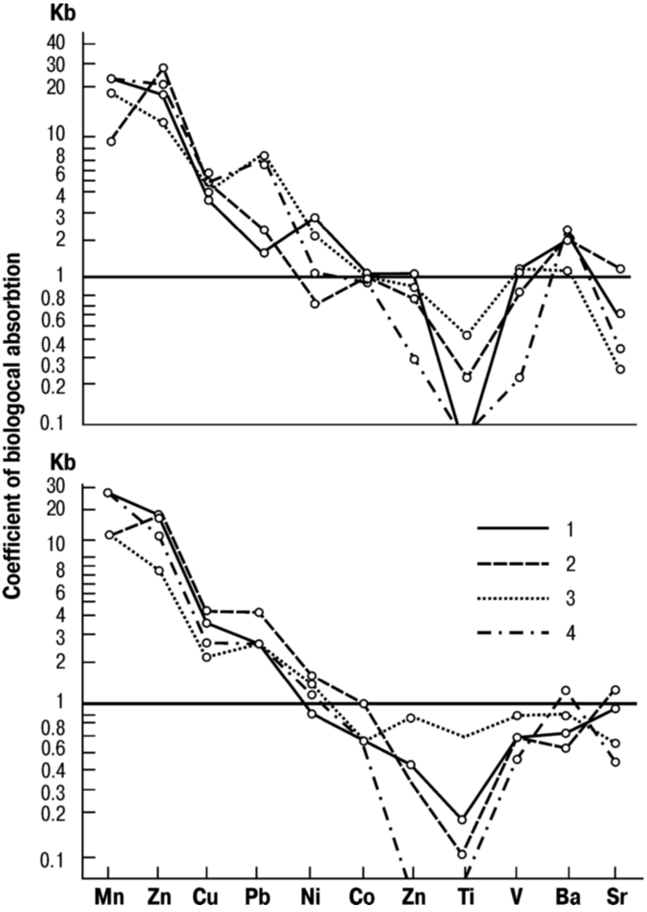


Figure 9. Exposure pathways based on the averaged coefficients of biogeochemical uptake, C_b, of trace metals in Spruce Forest ecosystems of the Karelia: top scheme represents the ecosystem with Podzols on diabase outcrops and bottom scheme represents the ecosystem with Podzols on gneiss outcrops. 1—spruce needles; 2—spruce bark; 3—hypnic mosses; 4—leaves and twigs of blueberry (based on Dobrovolsky, 1994).

accumulated in soil. The coefficient of biogeochemical uptake, C_b, presents the ratio between element content in plant species to its content in soil. Figure 9 shows the averaged values of these coefficients for the most plant species of Spruce Forest ecosystems, Karelia region, Russia.

We can see that the C_b values for lead, zinc, tin, nickel, and copper are an order of magnitude higher than those for zirconium, titanium, and vanadium. We can observe also that the curves follow a similar pattern independently of the composition of the bedrock, diabasis or gneissic, underlying the forest ecosystems. Simultaneously, various plants absorb the same elements at a different rate. For instance, mosses are

Table 6. Averaged major ash element mass budget for Spruce Forest ecosystems, Karelia, Russia (after Dobrovolsky, 1994).

Major ash element	Major ash element content, kg/ha					
	Ecosystem biomass		Annual NNP		Annual shedding	
	Mean	Limits	Mean	Limits	Mean	Limits
Ca	205	150–260	32	20–45	27	15–40
K	110	50–170	15.5	7–24	13	6–20
Si	52	40–65	14.5	10–19	13.5	9–18
Mg	32	25–40	5.5	4–7	4.5	3–6
P	30	15–45	4	2–6	3	1–5
Mn	20	15–25	3.3	2.2–4.5	2.9	1.9–3.9
S	8	6–10	1.6	1.2–2.1	1.5	1.2–1.9
Al	8.5	5–10	1.5	1–2	1.2	0.7–1.8
Fe	0.7	3.5–8.0	0.8	0.5–1.2	0.8	0.4–1.1
Na	1.5	0.5–2.5	0.3	0.1–0.5	0.2	0.1–0.3
Total	429	300–600	79	47–107	67.6	40–90

better accumulators of poorly absorbed metals, like Ti, Zr, V, than tree and small shrubs. The selective accumulation of metals by plants can be used in the exposure pathway characterization during environment risk assessment.

The quantitative parameterization of major ash elements involved in the biogeochemical turnover of Spruce Forest ecosystems is illustrated in Table 6.

One can see that for calcium, potassium, and silicon, biogeochemical turnover is within the limits of 10–30 kg/ha per year. The turnover for magnesium, phosphorus, manganese, sulfur, and aluminum is less than 10 kg/ha per year. These values are about 1 kg/ha per year for iron and sodium. These values can characterize the safety limits of exposure to the given species.

The heavy metal concentrations in spruce and blueberry species as the major components of Spruce Forest ecosystems are summarized in Table 7.

The statistical estimation of heavy metal concentrations in the Spruce Forest ecosystems of the Boreal climatic zone is the subject of wide variation, with coefficient of variation from 36 to 330%. However, we can note the clear trend in biogeochemical peculiarities and relevant exposure to heavy metal uptakes by dominant plant species.

First, the concentration of Sr, Ba, and Ti in spruce bark is relatively higher than in needles, while the latter are enriched by Ni and Zn. Second, the concentration of Zn, Ba, Cu, and Cr is higher in blueberry roots, than in the aerial parts. Third, the effect of zonal and local factors is remarkable. For instance, the Sr content in the needles

Table 7. The statistics of heavy metal contents in the major plant species of Spruce Forest ecosystems of Boreal zone, Karelia, Russia (after Dobrovolsky, 1994).

Heavy metals	Spruce species (*Picea excelsa*)				Blueberry (*Vaccinium myrtillus*)			
	Needles		Barks		Aerial parts		Roots	
	M, ppm	V, %	M, ppm	V, %	M, ppm	V, %	M, ppm	V, %
Zn	1,250	98	1,188	90	751	190	1,515	161
Ba	390	65	456	76	465	71	578	22
Ti	102	100	170	330	113	130	86	110
Cu	86	86	88	60	107	90	124	51
Pb	64	60	62	130	84	77	11	85
Sr	43	60	73	88	35	85	33	84
Zr	38	36	33	61	20	27	28	48
Cr	28	51	26	41	28	37	34	56
Ni	23	100	17	120	19	71	25	53
V	16	42	23	55	19	26	14	41
Co	12	80	13	61	13	70	14	70

Note: M is the arithmetic mean, ppm by dry ash weight, V is variation, %

and in the barks of the spruce is appreciably lower than the average content of this trace metal in the shedding of the World coniferous trees. This should be attributed to the effect of zonal factors influencing the active release of this metal. At the same time, the elevated content of Pb and Zn reflects the specificity of the bedrock since the dispersed sulfide mineralization is a characteristic feature of this Karelia region.

Using the results on biogeochemical uptake and content of trace metals in Spruce Forest ecosystems (Dobrovolsky, 1994), we can calculate the biogeochemical migration rates (Table 8).

We can see that the tree vegetation absorbs annually from soil tens of grams per hectare of Zn and Ba, units of grams of Ni, V, and Co. The absorption of trace metals by low bush species is smaller by an order of magnitude. Simultaneously, a similar amount of metals is released from the living biomass of the Spruce Forest ecosystems.

Of great interest is the calculation of a relative uptake of trace metals by forest species. The C_b values for each metal are similarly independent of the composition of crystalline bedrock and the depth of detrital deposits. For instance, the C_b values for Zn, Mn, Cu, and Pb are in a range from 2 to 30, they are considered as the elements of intense uptake. Poorly absorbed are Ni and Co, with C_b values about 1. The metals, such as Ti, Zr, and V, are very reluctant to be taken up and their C_b values are less than 1.

Table 8. Biogeochemical migration rates of heavy metals in the Spruce Forest ecosystems, Karelia, Russia.

Ecosystem plant components	Rates of biogeochemical migration of heavy metals, g/ha/yr						
	Zn	Ba	Sr	Cu	Pb	Ni	Co
Needles							
New grown	30–70	10–50	1–2	2–5	2–4	0.5–1.0	0.3–1.0
Lost in shedding	25–70	8–20	0.8–2.0	2–5	1–3	0.4–1.0	0.2–0.6
Bark							
New grown	4–8	2–4	0.2–0.4	0.3–0.6	0.2–0.4	0.1–0.2	0.03–0.04
Lost in shedding	2–5	0.7–2	0.1–0.3	0.1–0.4	0.1–0.2	0.1–0.3	0.02–0.04
Shrub vegetation							
New grown	3–8	2–5	0.2–0.5	0.3–10	0.3–0.8	0.08–0.2	0.04–0.1
Lost in shedding	3–8	2–5	0.2–0.5	0.3–10	0.3–0.8	0.08–0.2	0.04–0.1
Total plant uptake	37–86	14–59	1.4–2.9	2.6–6.6	2.5–5.2	0.68–1.4	0.37–1.1
Total shedding	30–83	10.7–27	1.1–2.8	2.4–6.4	1.4–4.0	0.51–1.3	0.26–0.74
Accumulation in tree bark	2–3	1.3–2.0	0.1	0.2	0.1–0.2	0.07–0.1	0.01

There is no doubts that these data are of the significance for pollutants' exposure assessment and environmental risk calculations.

2.3. Swampy Ecosystems of North Eurasia

The remarkable part of the forested area is swampy. In certain regions, like the vast West Siberian plain, swamp and waterlogged ecosystems occupy about 30% of the total area. The biogeochemical cycling in these ecosystems is very complex and specific. The slow rates of biogeochemical turnover, typical for all Boreal Forest ecosystems, are more depressed in Swamp ecosystems. For instance, in the *Sphagnum* Swamp ecosystem, the most widespread type of Swamp ecosystems, the annual NPP is only 10% or less from living plant biomass and less than 1% from the total mass of accumulated dead organic matter of peat. The rate of biogeochemical turnover in such an ecosystem is about 50 years.

There are significant differences between biogeochemical cycling in forest and swampy ecosystems of the Boreal climate zone. The annual growth (NPP) of moor vegetation is about 3.5 ton/ha, which is twice as small as that in a forest ecosystem. In the bog, the degradation of dead organic matter proceeds at a much smaller rate than in the forest. The mass of peat accumulated within a period of 100 years accounts for some 20% of the organic material formed in bog landscape. This is nearly 10 times higher than a relative mass of dead organic matter, preserved in forests.

In spite of small rates of organic matter degradation, the mineralized iron and heavy metals are permanently accumulating in stagnant bog waters. This leads to the larger uptake of these metals by swampy vegetation. In an area of 1 ha the annual uptake of Zn, Ba, Pb, and Ti amounts to tens of grams; of Cu, Zr, Cr, Ni and V to units of grams, Co to tenths of a gram, by moor plant species.

Taking into account the present and future oil and gas explorations extent in these areas the biogeochemical indices can greatly improve the exposure estimates and environmental risk assessment.

2.4. Broad-Leafed Deciduous Forest Ecosystems of Central Europe

Southward from the northern border of Boreal Forest ecosystems, the natural humidity gradually decreases simultaneously with the shortening of the cold winter season, which inhibits biogeochemical processes. Accordingly, the floral composition and geochemical conditions of ecosystems is altered also. The Coniferous Forest ecosystems grade into Mixed Forest ecosystems and then into Deciduous Forest ecosystems. Herbaceous plant species change the small shrubs and mosses. Biogeochemical processes become more active and annual NPP values are increasing as well. The litterfall amount is increasing but that of dead organic mater becomes decreasing. Consequently, changes occur in the chemical composition of plant species and in values of coefficients of biogeochemical uptake, C_b. In turn, it is related to the exposure pathway characterization.

The Broad–Leaved Forest ecosystems are widespread in regions of Sub-Boreal climate zone with a well balanced precipitation:evapotranspiration ratio. The southern periphery of the vast belt of Eurasian boreal and Sub-Boreal Forest ecosystems is represented by Oak Forest ecosystems. These ecosystems exhibit both the largest biomass and annual NPP rates in comparison with other forest ecosystems of this zone. However, the dead mass surface organic matter is 2–3 time less than that of coniferous forests.

The content of nitrogen in fallen leaves as a major shedding component is about twice as much as that in the needles of coniferous trees. The total sum of ash elements in the leaves accounts for 3–5%, average about 4% on dry weight basis. Accordingly, the concentration of calcium increases from 0.5 to 4.0%, potassium from 0.15 to 2.0% and silicon with a wide variation. The row of nutrient uptake is as the following:

$$\mathrm{C > N > K > Si \cong Mg \cong P \cong S > Al \cong Fe \cong Mn.}$$

The amount of nitrogen in the biomass of the Oak Forest ecosystem reaches 900–1,200 kg/ha and the sum of ash elements is about 2,000–3,000 kg/ha, e.g., greatly in excess of nitrogen. The corresponding values for accumulation of nitrogen in annual growth are 80–100 and for ash elements, 200–250 kg/ha. An essential point is that the green leaves store 70–80% of the mass of uptaken elements, and the fallen leaves, 80–90% of the mass of elements eliminated from the biological cycle. Nitrogen as returned in the shedding products, amounts to 40–70 kg/ha, and the ash elements, to 180–200 kg/ha (see Box 2).

Box 2. Biogeochemical fluxes of elements in Oak Forest ecosystem (after Jakucs, 1985)

The distribution and mass budget of chemical species in the Oak Forest ecosystem have been studied in Hungary. The principal timber species is *Quercurs petraea*, accounting for 78% of the wood mass; *Quercus cerris* accounts for 22%. The shrubs are chiefly represented by *Acer campestre* and *Cornus max*, and the grass by the genera *Carex*, *Dactylis*, and *Poa*.

The mass of trees is 241.03; of shrubs, 6.54; of herbaceous grasses, 0.62, and the mosses, 0.0016 ton/ha. The distribution of chemical species in biomass and annual NPP is depicted in Figure 10 and summarized in Table 9.

Amongst the ash elements the most abundant in biomass is calcium, which is accumulated in leaves, in trunk wood, and in twigs. Potassium is dominant in annual NPP. The masses of trace metals in biogeochemical cycling of this Oak Forest ecosystem are roughly in correspondence to their respective average values for the

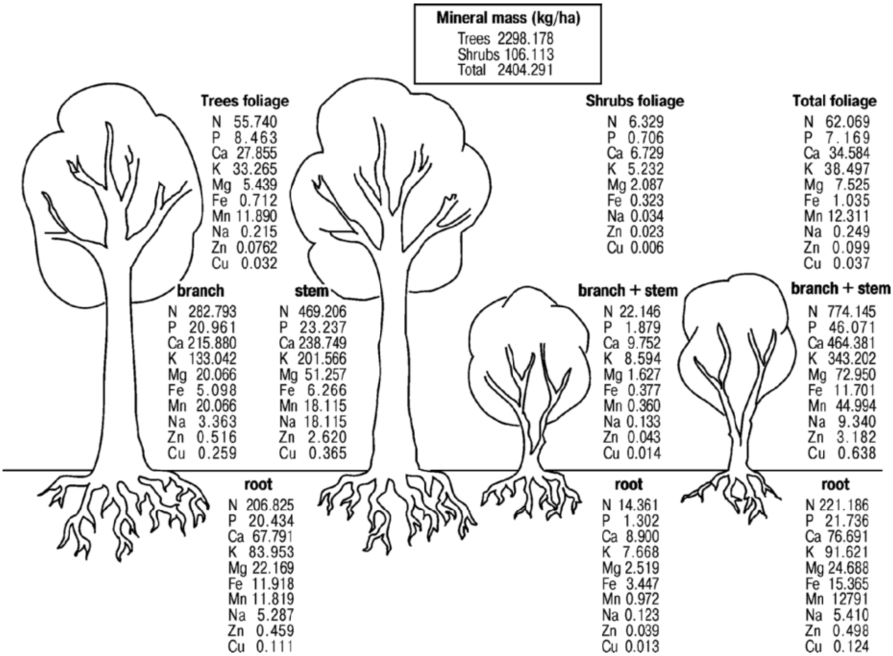


Figure 10. Mass distribution of chemical species in the Oak Forest ecosystem, Central Europe (Jakucs, 1985).

Table 9. The biogeochemical fluxes and pools in the Oak Forest ecosystem of Central Europe.

	Annual plant uptake, kg/ha			Pool in ecosystem, kg/ha		
Element	Trees	Shrubs	Total	Leaves	Stems, twigs	Roots
N	103.39	14.49	117.88	62.07	774.15	221.19
P	11.91	1.58	13.47	7.17	46.07	21.74
Ca	60.87	13.49	74.36	34.58	464.38	76.69
K	79.80	12.28	92.08	38.50	343.20	91.62
Mg	11.89	3.90	15.79	7.53	72.95	24.69
Fe	1.54	1.31	2.85	1.04	11.70	15.37
Mn	19.12	0.86	19.98	12.31	44.99	12.79
Na	1.01	0.14	1.15	0.25	9.34	5.41
Zn	0.28	0.04	0.32	0.10	3.18	0.50
Cu	0.06	0.01	0.07	0.04	0.64	0.12

other Oak Forest ecosystems of the Sub-Boreal climate. An exception to the rule is manganese, with its inordinately large fluxes in pool and annual NPP. Possibly, this phenomenon should be related with local landscape-geochemical peculiarities.

In may be of interest to compare the fluxes of elements in biogeochemical cycles of Oak Forest ecosystem with exposure to airborne deposition input. The latter were (in kg/ha/yr) for N, 17.7; for Ca, 14.7; for Mg, 1.8; for K, 4.2; for Na, 1.4; for P, 1.1; for Fe, 0.07; and for Zn, 0.14. The deposition input of these elements fall into a range of 20% (calcium) to 4.5% (potassium) relative to the respective biogeochemical fluxes (see Table 9). The airborne Fe input accounts for a mere 2.5%. Simultaneously, for some heavy metals, like zinc, the deposition input is commensurate with the fluxes of biogeochemical cycle.

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3. BIOGEOCHEMICAL FLUXES AND EXPOSURE PATHWAYS IN SOIL–WATER SYSTEM OF BOREAL AND SUB-BOREAL ZONES

3.1. Soil Compartment Features

The main soils of Forest Ecosystems are Podzols and Podzoluvisols. There are plenty of various soil subtypes, groups and families among these two main soil types. However, all forest soils have a number of common features originating in the similarity of processes occurring therein. The retarded biological cycle provides the organic materials for the build up of the covering layer on the soil surface. This layer consists

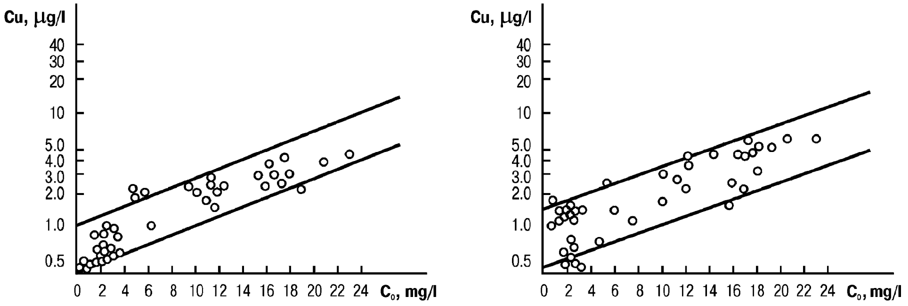


Figure 11. Relationships between organic matter concentration in permafrost soils of East Siberia Taiga Forest ecosystems and concentration of copper (left) and zinc (right) (Nikitina, 1973).

of partly decomposed plant residues and is called forest litter (A_0 horizon). The slow, but permanent, microbial decomposition of these materials leads to the formation of fulvic acids. The predominance of these mobile organic acids in humus structure and the predominance of precipitation over evapotranspiration are favorable to the formation of permeable, readily leached soils.

The second characteristic feature of Forest Ecosystem soils is the accumulation of macronutrients in the litter with sharp decreasing to the download horizon. However, the trace elements show the opposite trend and the concentration of micronutrients is gradually increasing up to the soil-forming rocks.

Two groups of chemical elements can be considered related to their distribution in soil profiles. The first group includes the essential nutrients actively absorbed by vegetation and relatively tightly bound in soil organic matter (Figure 11).

These elements are the main macronutrients, like nitrogen, phosphorus, potassium, and main micronutrients, like copper, zinc, and molybdenum. Their concentration in A_0 horizon is remarkably higher than in soil-forming rocks. For the second group representatives, the concentration in the A_0 horizon, although elevated in comparison with elluvial horizon, fails nevertheless to reach the rocks. The typical elements of the second groups are titanium, zirconium, vanadium, and chromium. The averaged distribution curves are shown in Figure 12.

Various forms of macro- and microelements differ in their ability to migrate and redistribute among the soil profile. The elements contained in clastic minerals are practically immobile. The elements, bound to finely dispersed clay minerals, are either co-transported with clay particles, or are involved in sorption–desorption processes. Part of the elements are found in concretions and also in very thin coating films of hydrated iron oxides; some elements make a part of specially edaphic organic compounds.

The determination of distribution pattern of various forms of both macroelements and heavy metals in soil profile is a very complicated task. We have to know the

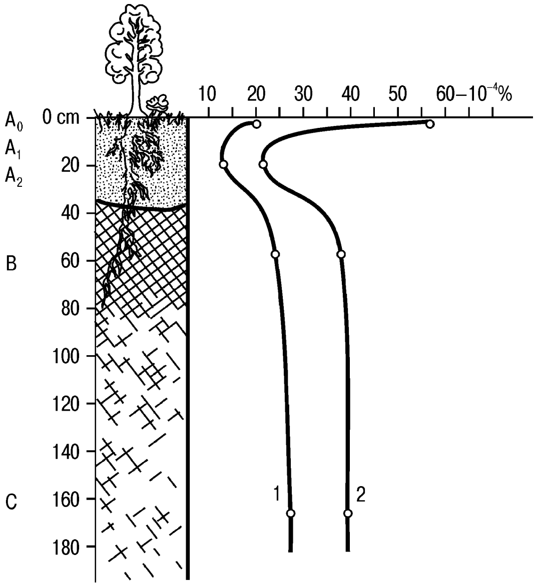


Figure 12. The profile distribution of vanadium (1) and copper (2) in typical Podzol of Boreal Forest ecosystems (ppm, 1 N HCl extraction) (Dobrovolsky, 1994).

distribution of organic matter, mineral particle, and microbes, the existence of different barriers, redox conditions, etc. (Box 3).

Box 3. Distribution of various forms of trace metals in podzols of boreal forest ecosystems (after Dobrovolsky, 1994)

In the Mixed Forest ecosystems a soil fraction less than 1 μm contains most of the elements previously confined in the forest litter and gradually involved in the biogeochemical cycle. In this fraction Cu and Mo forms account for 60–70% of the total soil content. The metals, poorly absorbable by plants, for example, Cr and V, occur in finely dispersed soil fraction in smaller amounts, about 20–30%.

Table 10 illustrates the variations of major forms of Cu and Co in typical Forest ecosystem Podzols of Moscow region, Russia.

We can see that the soluble and exchange forms of these metals are present in small amounts accounting merely for a few percent of the total metal content in soil. The content of organometal species is relatively high in the upper profile rich in humic species, whereas it drops sharply in the mineral horizons. Copper is extensively involved in the biogeochemical cycle in the Forest ecosystems and this is less profound for cobalt. It is noteworthy that a large part of metals (in particular, of copper) become bound to iron hydroxides. This is typical for various trace elements, including arsenic, zinc and other elements with variable valence.

Table 10. Distribution of copper and cobalt in Podzols of East European Boreal Forest ecosystems.

Soil horizon	Total metal content, ppm	Water-soluble and exchangeable	Metals bound with: Organic matter	Metals bound with: Hydrated iron oxides	Metals bound with: Mineral soil matter
		% of the total content of metal in soil			
Copper					
A_1	7.4	3.1	32.4	51.3	13.2
A_1/A_2	7.4	3.6	24.3	45.9	26.2
A_2	6.0	3.2	26.7	55.0	15.1
A_2/B	16.8	2.7	3.6	10.5	53.2
B_1	20.6	3.8	4.4	43.2	48.6
B_2	19.4	3.9	4.6	54.1	37.4
BC	19.8	3.6	4.5	47.0	48.5
Cobalt					
A_1	5.5	4.2	12.7	30.9	52.2
A_2	4.5	3.7	13.3	24.4	58.6
B_1	5.8	3.1	3.4	34.5	59.0
C	5.3	4.5	3.8	34.0	58.3

The excessive ground humidity is favorable to the formation of gley soils in Boreal forest ecosystems. Clay-podzolic soils with a massive forest litter layer provide the conditions for low water saturation. In high water-saturated conditions, a peat horizon is formed in the top layer of soil-forming boggy soils. In the forest litter of Podzols the concentration of fulvic acids is two or three times higher than that of humic acids; in contrast, humic acids are predominant in the peat horizon of Boggy soils. This is reflected in a lower pH of aqueous extraction from the forest litter of Podzols and in more active biogeochemical migration of elements in the corresponding ecosystems.

The concentration of many nutrients and heavy metals in Peat–Boggy soils is often higher than that in Podzols. In boggy soils the relative concentration of elements bound with humic acids is also significantly higher. For instance, in the Spruce Forest ecosystems of Karelia most of the mobile nickel forms are bound to humic acids, and those of copper to the fulvic acids. Consequently copper easily leaches from the soil upper layer with relevant accumulation in the download horizon. The concentrations of the organometal forms of trace elements in the soils of Swamp ecosystems compare with that of Podzols. However, the overall mass of organometal species in boggy soils is appreciably higher.

In the southern direction the Podzols are transferred into Podzoluvisols and Distric Phaerozems. These soils have less acidity and less pronounced migration of various elements. Accordingly, this determines the exposure pathways of pollutants, like heavy metals, in soil compartments of forest ecosystems.

3.2. Biogeochemical Exposure Processes in the Soil–Water System

Almost all biogeochemical exposure processes in Forest ecosystems are connected with aqueous migration in surface and ground water runoff. Low content of dissolved salts and organic species are the most characteristic features of surface runoff waters of Boreal climate forest ecosystems. This feature is particularly distinct in Taiga Forest ecosystems with permafrost soils where the zone of extensive water exchange in the river valleys is confined to supra-permafrost waters and to ice-thaw waters. A review of leaching processes is shown in Box 4.

Box 4. A brief review of soil leaching processes (after Johnson, 1992)

A concept of anion mobility may be considered a useful paradigm for explaining the net retention and loss of cations from soils, and thus exposure pathways. This paradigm relies on the simple fact that total cations must balance total anions in soil solution (or any other solution), and, therefore, total cation leaching can be thought of as a function of total anion leaching. The net production of anions within the soil (e.g., by oxidation or hydrolysis reactions) must result in the net production of cations (normally H^+), whereas the net retention of anions (by either absorption or biological uptake) must result in the net retention of cations.

The major anions in soil solutions are Cl^-, SO_4^{2-}, NO_3^-, HCO_3^-, and organic anions. Chloride may dominate soil solutions only in coastal areas. The four major anions often undergo oxidation–reduction and hydrolysis reactions that cause the net production or consumption of H^+, which in turn strongly affects the net retention or release of base cations from the ecosystem. Carbonic acid, which is formed by the dissolution and hydrolysis of CO_2 in water, is the major natural leaching agent in many temperate ecosystems. Carbonic acid concentrations in soil solution are many times greater than in precipitation or throughfall because of the high levels of CO_2 in the soil atmosphere. On dissociation, carbonic acid forms H^+ and HCO_3^-, H^+ exchanges for a base cation (or causes the dissolution of a mineral), and a bicarbonate salt leaches from the system. Because carbonic acid is a very weak acid, HCO_3^- becomes associated with H^+ to form carbonic acid at low soil pH. Thus, the carbonic acid leaching mechanism is self-limiting, and eventually becomes inoperable during the soil acidification process.

Organic acids are often the major cation leaching agents in extremely acid soils that occupy the boreal regions. These acids are stronger than carbonic acid and can produce low solution pH while providing organic counter-anions for cation leaching. Organic acids are also responsible for the chelation and transport of Fe and Al from surface (E or albic) to subsurface (Bs or spodic) horizons during the podzolization process. In theory, organic acid leaching, like carbonic acid leaching, is self-limiting because organic acids are typically weak acids. However, organic acids can provide very low soil and soil solution pH and still remain active in leaching processes.

Sulfate and nitrate are the anions of strong acids, and therefore leaching by sulfuric and nitric acids is not self-limiting because of solution pH alone. The deposition or other inputs of either S or N in excess of biological demands of these elements will ultimately cause an increase in SO_4^{2-} or NO_3^- availability within soil. In case of SO_4^{2-}, inorganic absorption processes may prevent increased leaching, but this is seldom true in the case of NO_3^-. In that soil SO_4^{2-} absorption is strongly pH dependent (increases with decreasing pH); there can be a negative feedback involved in sulfuric soil leaching that is at least partially self-limiting.

The input of chemical species from atmospheric deposition is the main source of feeding the supra-permafrost ground waters. The deposition contributes the significant amount of elements to natural waters of Boreal ecosystems. The concentration of trace metals in the ground waters of North Siberia Taiga Forest Cryogenic ecosystems is lower than their respective average values for the global riverine waters. In southern Boreal Forest ecosystems, the concentrations of trace metals in ground waters are merely several-fold higher than that in precipitation (Table 11).

The higher concentrations of some heavy metals, like Zn, Cu, Ni, and Pb, in snowmelt waters in comparison with rain waters is possibly related to the elevated content of solid particles in snow. Deposition fluxes are less important in the

Table 11. The concentration of trace metals in atmospheric deposition and ground waters of Siberian Taiga Forest ecosystems, μg/L (after Shvartsev, 1978; Dobrovolsky, 1994).

	Ecosystems				
	Tundra Forest of Middle Siberian High Plain			South Taiga Forest of West Siberia	
Trace metal	Rainwater	Snowmelt water	Ground water	Rainwater	Ground water
Mn	4.0	3.7	12.5	4.2	20.2
Zn	3.0	10.0	8.5	7.2	29.2
Cr	2.2	2.5	1.3	1.1	2.5
Cu	1.0	2.6	3.1	0.2	1.8
Ti	1.0	1.0	1.5	2.4	22.7
V	1.0	0.8	1.0	0.1	0.7
Pb	0.3	1.0	0.4	2.3	0.5
Ni	0.3	0.8	0.8	0.3	1.5

biogeochemical mass budget of elements in Southern ecosystems, than in northern Forest ecosystems.

The content of soluble salts increases in surface and ground water runoff of Forest ecosystems forwarding from north to south with a parallel decrease in soluble organic acids. To a certain extent, this may be related to the changes of soil-forming geological rocks. The biogeochemical processes in Podzols formed on sandy fluvioglacial and ancient alluvial deposits are favorable to a decreased solid salt content in waters and simultaneously to the relatively increased content of fulvic acids. Such a geochemical situation is common for the sandy lowlands of the East European plain, for instance, Meshchera and Belarussian Swamp Forest ecosystems. In contrast, the alteration of sandy deposits to clay rocks formed the clay soils and consequently this is accompanied with increase in both pH and solid salt content. This trend is clearly distinct in Table 12.

We can see the rise of heavy metal groundwater contents in the southward direction with increasing content of total soluble salts. However, this increase is not similar for various metals. For example, Zn is the most abundant metal in the waters of Tundra

Table 12. The average concentrations of trace metals in ground waters of Siberian Boreal and Sub-Boreal Forest ecosystems, μg/L (after Dobrovolsky, 1994).

	Forest ecosystems		
Trace metal	Tundra	Northern Taiga	Mixed
Zn	23.0	31.8	39.5
Sr	21.3	26.3	163.0
Mn	12.3	17.9	55.6
Ba	10.0	9.1	29.4
Li	3.97	6.09	19.0
Cr	2.52	2.16	4.02
Ti	2.34	4.64	21.9
Ni	1.91	1.63	5.29
Pb	1.88	1.16	2.88
Cu	1.70	2.98	5.11
As	0.73	0.99	4.15
Zr	0.68	1.28	2.27
Mo	0.64	0.92	1.28
V	0.50	0.88	1.45
Ga	0.35	0.49	0.63
Sr	0.22	0.50	0.77
Co	0.40	0.24	0.61
U	0.30	0.34	1.01
Ag	0.21	0.37	0.20
Be	0.02	0.04	0.18

and North Coniferous Forest ecosystems, whereas in Mixed Forest ecosystems it recedes to the third place after Sr and Mn.

An important role in the migration of trace metals in Forest ecosystems is connected with organic complexes and colloidal particles. For instance, the role of ionic forms of iron in water biogeochemical migration is of minor importance as compared with migration in metal–organic complexes, accounting for 80% of total content of metal in the soil waters. On average, about 50% of metals are subjected to biogeochemical migration as the metal–organic complexes (see Box 5).

Box 5. The role of metal–organic complexes in biogeochemical migration of trace elements (after Newman and McIntosh, 1991)

Of particular interest to biogeochemical migration of heavy metal is the effect of complexation on metal availability in the presence of natural dissolved organic matter. Humic and fulvic acids (symbolized here as Hum) are very distributed in soil solutions and surface waters, especially in surface waters with visible color. Hum is an important fraction of the dissolved organic matter, even in low color water. Other fractions of natural organic matter, including dissolved nitrogen organic compounds (oligo- and polypeptides) and synthetic organic compounds, such as polyaminocarboxylates (e.g., ethylenetetraacetic [EDTA], nitriloacetic acid [NTA]), may be important complexing agents for heavy metal ions in some waters thus determining their exposure to living organisms.

Metal ions complexed with natural macromolecular organic matter or strong synthetic chelating agents generally are considered not to be directly available to aquatic organisms, whereas inorganic complexes generally are. Aluminum fluoride complexes are important exceptions among inorganic complexes of interest in freshwaters. In addition, organometallic forms of several metals (e.g., methylmercury, triorganotin species), which are lipophilic, are bioaccumulated by aquatic organisms much more so than inorganic forms of the metals, and some organometallic complexes are toxic to aquatic biota.

For a variety of reasons, it is difficult to measure stability constants of metals with Hum, and the use of stability constants measured under a given set of solution conditions (so-called "conditional constants") for a different set of conditions (e.g., at a different pH or different set of metals and Hum concentrations) must be done cautiously. Significant advances were made during the past decade in ways to model metal–Hum binding, and a sufficient variety of conditional binding constants are now available at least to approximate the metal-binding behavior of natural water and soil solutions containing Hum.

The example of calculated heavy metal speciation in Little Rock Lake, Wisconsin, USA is shown below (Table 13).

We can see that the most chelating properties are shown for Cu, in lesser degree for Cd and Pb, and a minimum for Mn and Zn.

Table 13. Calculated heavy metal speciation in Little Rock Lake, Wisconsin, USA.

	% of free ions		
Metal	pH 6.1	pH 4.7	Complexed ions, >1%
Al	<1	18	$ALOH^{2+}$, $Al(OH)_2^+$, $AL(OH)_3^0$, $Al(OH)_4^-$, AlHum, AlF^{2+}, AlF_2^+
Mn	91	95	MnHum
Cd	73	75	CdHum, $CdSO_4^0$
Cu	22	25	CuHum, $Cu(OH)_2^0$
Pb	70	92	PbHum, $PbOH^+$, $PbSO_4^0$
Zn	93	94	ZnHum, $ZnSO_4^0$

During water migration the trace elements (heavy metals) undergo a systematic redistribution with the subsequent elementary landscapes in the catena from the watershed to relief depressions. The lowland swamps are typical subordinate ecosystems in the belt of boreal forests. Migration of metals associates mainly with soluble organic matter. More than 90% of Fe and similar percentage of other metals, like Mn, Cu, Zn, Ni, Cr and V, in lowland swamp waters migrate in the form of soluble metal–organic complexes.

Swamp ecosystems are placed both in watershed and subordinate relief positions. The elevated content of metals is monitored in the latter case (Table 14).

Table 14. The comparative estimation of average content of trace metals in surface waters of Swamp ecosystems, μg/L (after Shvartsev, 1999 and Dobrovolsky, 1994).

	Swamp ecosystem relief position	
Trace metals	Watershed	Subordinate
Mn	41.9	52.5
Ba	11.5	9.23
Zn	5.73	9.86
Cu	0.55	1.20
Ti	2.65	1.10
Pb	0.60	0.89
Ni	0.66	0.72
V	0.10	0.19

The elevated concentrations of trace elements in boggy waters lead to an elevated migration in biogeochemical cycles and finally to the increased accumulation in dead organic matter of peat. The metal content in the low peat lands of the Karelia is higher than that in watershed peat. For instance, for manganese it is higher by 2 times, for cobalt by 3–4 times, for molybdenum and copper by 56 times. In different Forest ecosystems of the World this proportion is similar. However, this is maximally distinguished in the Boreal Forest ecosystems and to a lesser degree in Sub-Boreal ecosystems, where the pH of natural waters tends to increase and the concentration of dissolved organic compounds, to decrease.

These quantitative values of exposure to heavy metals in the relevant pathway are of importance for environment risk assessment procedures in the forest ecosystems areas.

CHAPTER 8

SEMI-ARID AND ARID CLIMATIC ZONES

Biogeochemical cycling of elements and pollutants' exposure in semi-arid and arid climatic zones have very characteristic features since both Steppe and Desert ecosystems are deficient in atmospheric humidity (evapotranspiration exceeds precipitation). The Sub-Boreal, Semi-arid and Arid Steppe and Desert ecosystems occupy a significant part of the global area. This territory includes Sub-Boreal zones (Steppe, Arid Steppe, and Desert Steppe ecosystems) with total area of 9.23×10^6 km^2, as well as subtropical zones (Shrub Steppe and Desert Steppe ecosystems) with total area of 7.04×10^6 km^2. These areas do not include Subtropical and Tropical Sandy Desert ecosystems (5.77×10^6 km^2) and Stony Desert ecosystems (8.96×10^6 km^2). Thus the extra-tropical arid area takes about 20% of the World's terrestrial ecosystems. Most of this area belongs to the inter-continental regions of Eurasia and, partly, of North and South America. The biogeochemistry of semi-arid and arid ecosystems shows distinctive parameters, which allow us to consider the quantitative features of element turnover and dynamics in natural fluxes. In turn, these parameters should be related to the exposure of living organisms to pollutant species.

1. BIOGEOCHEMICAL CYCLING OF ELEMENTS AND POLLUTANTS EXPOSURE IN SEMI-ARID AND ARID CLIMATIC ZONE

1.1. Biogeochemical Cycle and Exposure Pathways in Arid Ecosystems

Grasses, small shrubs and shrubs, with their number of xerophytic and ephemeral forms increasing with aridity, are the chief representatives of semi-arid and arid types of ecosystems. At the north and south peripheries of this zone herbaceous ecosystems are predominant. In regions with a well-balanced atmospheric humidity prior to human activities, of wide occurrence were Meadow Steppe ecosystems intermixed with Broad-Leaved Forests. With the increasing of climate continental properties, the Meadow Steppe ecosystems of Eurasia grade into Forb–Fescue–Stipa and Fescue–Stipa Steppe ecosystems. In turn, the natural vegetation has been destroyed by humans and replaced by pastures and crops. Arid Steppe ecosystems are characterized by the annual precipitation about 300 mm or less; these are Absinthum–Fescue–Stipa Steppe and Fescue–Stipa Steppe ecosystems. With increasing aridity, the small shrubs, mostly those of *Absinthum* species, become relatively abundant. The halophytic species is also of common occurrence in Semi-Arid and Desert ecosystems.

Table 1. The annual biogeochemical fluxes and pools in Steppe and Desert natural ecosystems (after Rodin et al., 1975).

	Pool on biomass, kg/ha		Annual uptake, kg/ha		Annual litter, kg/ha	
Ecosystem	Nitrogen	Ash species	Nitrogen	Ash species	Nitrogen	Ash species
Meadow Steppe	274	909	161	521	161	521
Dry Steppe	103	242	45	116	45	116
Half-Shrub Desert	61	124	18	18	18	41

The biomass of arid ecosystems is significantly less than that of Forest ecosystems and changes from 10 to 25 ton/ha, by dry weight, in Steppe, from 4.0 to 4.5 ton/ha in Desert and from 2 to 3 ton/ha in Extra-Desert Ecosystems of the Central Asia. The overall biomass of Arid Steppe and Desert ecosystems is an order of magnitude less than that of Forest ecosystems (Rodin et al., 1975).

The ash content of Arid Steppe and Desert ecosystem vegetation is about 2 times higher than that of forest species. Accordingly, the biogeochemical fluxes of elements are similar to those in the forest ecosystems, in spite the smaller biomass (see above). The compartments of biogeochemical turnover in Steppe and Desert ecosystems are shown in Table 1.

The characteristic biogeochemical feature inherent in all Steppe and Desert ecosystems is the most intensive cycling of different chemical species in comparison with forest ecosystems. For a Steppe ecosystem the biogeochemical cycle is 2–3 years and this means that the complete renewal of all ecosystems biomass takes place over this period. Remember that in Forest ecosystems the biogeochemical cycling is about 3–>25 years and even about 50 years in Forest Swamp ecosystems. The turnover is the highest in Ephemeral Desert and gradually decreases to the north.

The annual biogeochemical turnover of trace ash elements is calculated in Table 2.

Table 1 shows the average values for Arid ecosystems. However, the local geochemical conditions can alter this tendency significantly. A relevant example can be shown for the Colorado Plateau, USA, where the fluxes of selenium are so high that the forage grasses are toxic for the cattle. In the areas of volcanic eruptions, the arid conditions are favorable to an extensive accumulation of fluorine. In these cases, the annual fluxes of elements and relevant exposure rates in living biota are much higher than the figures shown in Table 2.

1.2. Role of Aqueous and Aerial Migration in Pollutants Exposure

It is well known that the total content of water-soluble solids in natural waters (TSS) is increasing with an increasing aridity. The concentration of some trace elements (heavy metals) correlates significantly with the total content of soluble solids. Comparison

Table 2. Annual turnover of ash trace metals in Arid ecosystems, kg/ha (after Dobrovolsky, 1994).

	Ecosystems	
Ash trace metals	Fescue–Stipa and Absinthum–Fescue–Stipa Steppe	Absinthum-Saxaul Desert
Average ash content, %	3.5–4.0	4.0
Total uptake of ash elements, kg/ha/yr	100–300	40
Trace element turnover, g/ha/yr		
Fe	400–1,200	160
Mn	410–1,230	164
Sr	65–195	28
Ti	60–180	26
Ba	50–150	18
Zn	5–0.150	24
Cu	16–48	6.4
Zr	15–45	6.0
Ni	4–12	1.6
Cr	3.5–10.5	1.4
V	3–9	1.2
Pb	2.5–7.5	1.0
Co	1–3	0.4
Mo	1–3	0.4
Sr	0.5–1.5	0.2
Ga	0.1–0.3	0.04
Cd	0.07–2.1	0.03

of the trace element contents in surface waters in the area of the East European Plain has shown the certain relationships between surface water chemistry and ecosystem types. These data are summarized in Table 3.

We can see that for zinc the average content in surface waters of various ecosystems is increasing in as follows: Forest < Forest Steppe < Steppe. Similar peculiarities are shown for strontium. However, for some metals this tendency is not confirmed or even we can see the opposite direction, for instance for manganese, whose content is higher in waters of Forest ecosystems.

Table 3. Comparative assessment of heavy metal contents in surface waters of various ecosystems from the East European Plain and average values for the similar global corresponding ecosystems, μg/L.

	Ecosystems					
	Forest		Forest Steppe		Steppe	
Heavy metals	East European plain	Global average	East European plain	Global average	East European plain	Global average
Mn	158.0	16.0	94.0	9.4	126.0	13.0
Ti	40.0	13.3	94.0	31.3	106.0	35.3
Sr	36.0	0.5	68.0	0.9	128.0	1.6
Zn	11.0	0.6	28.0	1.4	36.0	1.8
Cr	5.4	5.4	8.0	8.0	9.0	9.0
Pb	4.8	4.8	3.0	3.0	3.0	3.0
Sn	3.5	7.0	4.0	8.0	1.5	3.0
Zr	4.2	1.5	9.0	3.5	2.0	0.8
V	2.7	3.0	6.0	6.7	4.0	4.4
Cu	2.4	0.3	12.0	1.7	10.0	1.4

For understanding these tendencies, we will consider the values of the biogeochemical coefficient of aqueous migration. This coefficient C_w is the ratio between the content of an element in the sum of water-soluble salts and in geological rocks. The values of C_w for certain chemical species are smaller in Arid ecosystems than those in Forest ecosystems. We can suggest two explanations. First, soils of Forest ecosystems are enriched in water-soluble metal–organic complexes (see Chapter 7). Second, most chemical species are trapped in the transpiration barrier of upper soil layers of Arid ecosystems.

The smaller C_w values are also connected with water deficiency in Steppe and Desert ecosystems. However, the concentration of various chemical species in rainwater of background regions is higher than that in the Forest ecosystem belt. The major reason is wind deflation of the soil's surface owing to lack of tree species and only a lean protective layer of grasses and half-shrubs. A large mass of soil particles becomes entrained into the air migration (Bashkin, 2003a). The most characteristic example is connected with the "Yellow sand" phenomenon (see Box 1).

Box 1. "Yellow sand" formation and transport in Asia (after Jie Xuan, 1999, see Bashkin, 2002)

The vast area of Arid and Semi-Arid ecosystems of Central and East Asia is subject to wind erosion. The major natural sources of dust emission are Gobi desert (Xinjiang

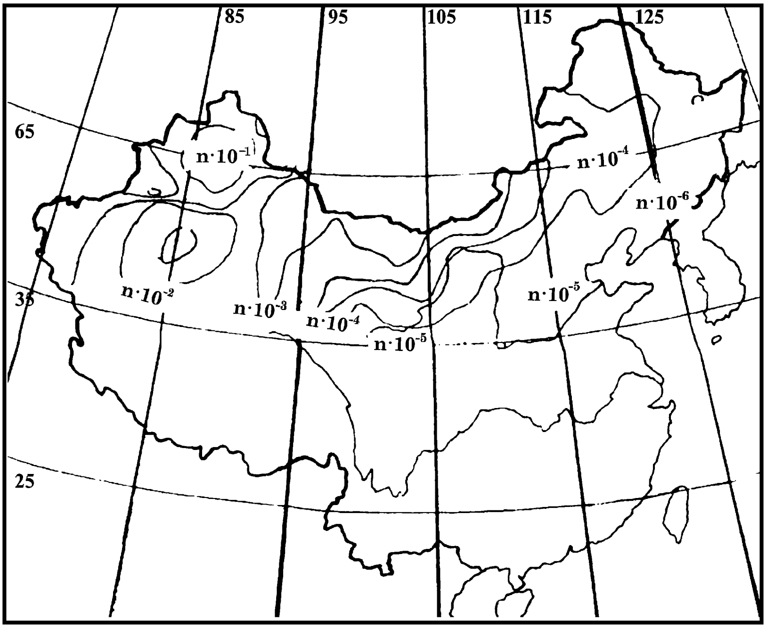


Figure 1. Annual dust emission rates in China (ton/ha/yr).

Province, Northwestern China), Karakum and Kyzylkum deserts (Central Asian areas of Kazakhstan, Uzbekistan and Turkmenistan). The Gobi desert is the second largest desert in the World. The climate is extremely dry and windy. The strongest winds occur during the winter and spring period. These factors influence the deflation of soil surface layers, which are not protected by sparse vegetation, especially during the springtime, after the thawing frozen upper soil horizon.

The annual dust emission rates for the whole China area are shown in Figure 1.

We can see that due to joint effects of aridity and soil texture, the dust emission rates increase from east to west by as much as 5 orders. The maximum emission rate is 1.5 ton/ha/yr. The total dust emission amount of the Gobi desert is estimated as 25 $\times$ 10^6 tons per year and that in spring is 15 $\times$ 10^6 tons per year. The seasonal dust emission amounts in summer, autumn and winter are 1.4 $\times$ 10^6, 5.7 $\times$ 10^6 and 2.9 $\times$ 10^6 tons, correspondingly.

During aerial transportation by wind the dust particles are enriched in heavy metal and other pollutant species, especially during transport over east and southeast industrial areas of China. Further dry and wet deposition leads to human and ecosystem exposure to this pollution and a related increase of environmental risk.

The low rates of aqueous migration of many chemical species in Arid ecosystems and the accumulation of their water-soluble and dispersed forms in the uppermost soil layers play an important role in the geochemistry of aerosol formation and rainwater

Table 4. Rainwater total salt content and salt deposition/exposure rates over various natural ecosystems in Eurasia.

Ecosystems	Total rainwater salt content, mg/L	Total salt deposition rate, kg/ha/yr
Forest	17–20	70–100
Steppe	45–50	170–180
Desert	>150	210–240

chemistry. In turn, biogeochemical processes in soil–plant–air system determine the water chemistry and exposure pathways (Table 4).

Despite the smaller rainfall over the arid areas in comparison to the forest belt, the Arid ecosystems receive more salts from the atmosphere than the areas of excess humidity. Accordingly, this enhances the probability of many lung diseases among the local population.

1.3. Role of Soil Biogeochemistry in the Exposure Pathways in Arid Ecosystems

High biotic activity is characteristic for soils of Meadow Steppe ecosystems with relatively high precipitation. An enormous number of invertebrates promptly disintegrate and digest the plant residues and mix them with the mineral soil matter. The presence of the predominant part of plant biomass as the underground material facilitates greatly this process.

The microbial population in soils of Steppe ecosystems is different from that in forest soils. Fungi, which play a decisive role in destruction of plant remains in Forest ecosystems, are changed by bacteria. The microbial and biochemical transformation of organic matter in the steppe soils leads to the predominant formation of low soluble and low mobile humic acids. The accumulation of humic acids in the upper soil layer is increasing also due to formation of mineral–organic complexes. Furthermore, the migration of many chemical species is also decreasing due to impeded water regime and soil saturation with Ca ions. This provides for a tight coagulation of films of humic acids on the surface areas of mineral particles.

These properties of soils in Steppe ecosystems are favorable to the formation of uppermost humus barrier, where the accumulation of almost all the chemical species occur. The concentration of chemical elements is slightly decreasing downward in soil profile, in parallel with decreasing soil humus content (Figure 2).

The significant part of heavy metals in the soils of Steppe ecosystems are bound with highly dispersed mineral–organic particles, to a lesser degree, with only organic matter. We can see that the water-soluble and exchangeable forms are less than 1% of the total content. Specific forms of heavy metals are bound with carbonate and gypsum in B and C horizons (Table 5).

These barriers are of great importance in exposure pathways for all considered ecosystems placed in semi-arid and arid climate zones.

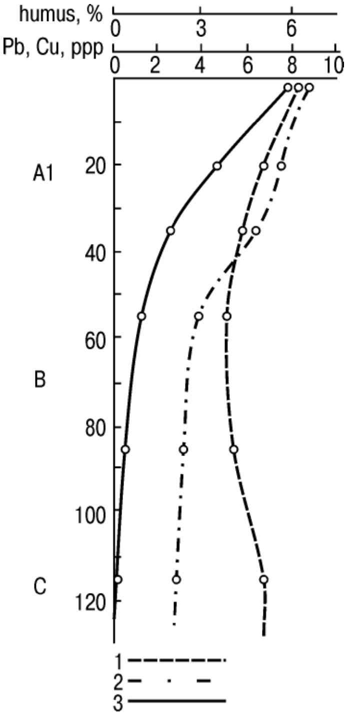


Figure 2. Dowload distribution of mobile forms (1N HCl) of zinc (1), copper (2) and humus (3) in Chernozem profile (Dobrovolsky, 1994).

1.4. Role of Humidity in Soil Exposure Pathway Formation in Steppe and Desert Ecosystems

The water deficiency in Arid ecosystems is the main restricting factor for biogeochemical exposure processes. We know that many links of the biogeochemical food web are connected in Steppe soils with invertebrates. Their population varies very much in Steppe ecosystems depending on the moisture conditions (Table 6). For instance, the wet biomass of soil invertebrates in the Meadow Steppe and Forest Steppe ecosystems exceeds that for the Extra-Dry Rocky Desert ecosystems by 150–300 times.

Table 5. Distribution of Co in Calcaric Chernozem and Chestnut soil of Meadow Steppe ecosystem in the south part of East European Plain.

			Fraction of total Co content bound with, %					
	Total content, ppm		Humus		Clay matter		Carbonate	
Soil horizon	Chernozem	Chestnut soil	Chernozem	Chestnut soil	Chernozem	Chestnut soil	Chernozem	Chestnut soil
A	9.2	11.3	30.4	25.7	43.5	49.5	—	—
B	9.4	10.4	22.2	14.4	48.0	43.3	—	11.5
C	8.5	9.4	4.7	4.7	61.2	60.7	10.9	6.4

Table 6. The influence of water deficiency on invertebrate biomass and humus content in Steppe ecosystems.

Ecosystems	Invertebrate biomass, kg/ha	Humus content, %
Forest Steppe	700	4–6
Meadow Steppe	750	6–8
Semi-Desert	6	2–4
Extra-Dry Rocky Desert	2–4	<1

The humus content in Steppe ecosystem soils reflects the total biomass production and humidity.

The content of heavy metals in Steppe soils is tightly connected with their contents in geological rocks. In formation of soil exposure pathways in Desert ecosystems, water-soluble forms of these metals play the most important role. We can see an analogy between the increasing content of elements in soil dead organic matter as a function of decreasing water excess in Forest ecosystems and the increasing content of water-soluble species of chemical elements in the soils of Dry Steppe and Desert ecosystems as a function of enhanced aridity. The accumulation of water-soluble species occurs in the upper horizon for almost all elements, with exception of strontium. The main factor responsible for the accumulation of water-soluble forms is connected with evapotranspiration.

The existence of an evapotranspiration barrier in the upper soil horizon of Dry and Extra-Dry Desert ecosystems favors the accumulation of alkalinity and alkaline reaction of soil solution. In turn this accelerates the mineralization of organic matter and mobilization of finely dispersed mineral and organic suspensions. This fact provides a plausible explanation of the occurrence of some heavy metals, like Zr, Ti, Ga, Yt and their congeneric elements in the aqueous extracts from soil samples of Dry Desert ecosystems.

The extraction by 1 N NCl yields 5–10% of total heavy metal content. In case of Fe and Mn, these values are even higher. The maximum contents of mobile fractions of trace elements are monitored in the upper horizon. Thus, the role of evapotranspiration barrier in biogeochemical migration of elements in Dry Desert ecosystems pays a very important role in pollutants' exposure.

2. GEOGRAPHICAL PECULIARITIES OF BIOGEOCHEMICAL CYCLING AND POLLUTANT EXPOSURE

2.1. Dry Steppe Ecosystems of South Ural, Eurasia

The various steppe plant species indicate the individual biogeochemical peculiarities related to pollutants exposure. For example, we can discuss the results from the South

Table 7. The content of heavy metals in the aerial parts of plant species of South Ural Steppe ecosystems, ppm, by dry weight (after Skarlygina-Ufimtseva et al., 1976; Dobrovolsky, 1994).

	Plant species				
Trace metals	*Stipa rubens*	*Festuca sulcata*	*Poa*	*Artemisia marshaliana*	*Veronica incana*
Mn	1,650.0	450.0	225.0	975.0	650.0
Zn	750.0	278.0	150.0	373.0	550.0
Ti	250.0	934.0	265.0	242.0	900.0
Ba	215.0	210.0	65.0	47.0	35.8
Sr	200.0	131.4	142.1	406.7	253.8
Pb	110.0	94.3	41.8	35.0	112.0
Cu	35.0	26.4	27.9	174.8	39.8
V	20.0	20.9	15.5	19.6	5.8
Ni	8.0	14.0	13.5	9.6	16.7
Ag	0.6	0.3	0.4	0.4	0.2

Ural region, Russia. Table 7 shows the concentrations of heavy metals in typical plant species of Steppe ecosystems.

The samples were taken from a site covered with thin rubble stone of Pleistocene deposits. The annual precipitation was 380 mm, and the annual evapotranspiration was twice as much. Despite identical growth conditions the accumulation of heavy metals depends on plant species. In feathergrass (*Stipa rubens*), the highest concentrations of Mn and Pb were monitored; in the sheep's fescue (*Festuca sulcata*) of Ti and Zn, in wormwood (*Artemisia marshaliana*), of Cu; in veronica (*Veronica incana*) of Ni. Of course, these data might be changed under different geochemical or climate conditions. However, these biogeochemical peculiarities of pollutants' exposure should be taken into account during risk consideration.

2.2. Meadow Steppe Ecosystems of the East European Plain

For these ecosystems we consider the biogeochemical peculiarities of exposure to heavy metals in the biomass forming whole plant groups, rather than genera. Such groups are grasses, legumes, and forage grasses. These groups differ in accumulation of heavy metals. For instance, the accumulation of Ti, Cu, V, and Ni is characteristic for grasses, Pb and Ba, for forage grasses, and Sr, for legumes (Table 8).

The content of many elements in the roots and in the aerial parts of herbaceous plant species is different. In the root mass of grasses the content of heavy metals

Table 8. Biogeochemical exposure to heavy metals in the main botanical groups of Meadow Steppe ecosystems of East European Plain, accumulation, mg/kg by dry weight (after Dobrovolsky, 1994).

Trace metals	Legumes	Grasses	Forage crops
Sr	1,616.7	458.8	971.4
Ba	341.7	255.0	729.9
Mn	550.0	1,092.4	1,093.5
Ti	203.6	627.8	490.6
Ni	20.5	35.0	26.1
Pb	14.9	19.2	20.9
Zr	10.0	13.6	20.0
V	9.1	50.6	31.4

is higher than that in aerial organs. This is tightly correlated to the coefficients of biogeochemical uptake, C_b, of these metals (Figure 3).

However, in the halo of dispersion of ore deposits many metals (Cu, Mo, Ag, Pg) frequently occur at higher concentrations in the aerial parts (Kovalevsky, 1984). This enlarges greatly the risk of pollutants' accumulation in the biogeochemical food webs (Bashkin, 2002).

With aridity increasing, various plant species of forage crops become gradually less numerous to finally disappear. In Dry Steppe ecosystems xerophylic half-shrubs and salt-tolerant plants replace the grasses. However, the ash content is higher in these species. This is attributed not only to a higher concentration of major ash elements in the plant tissue, but also to the exposure to finely dispersed dust adhered to the plants' exterior (Table 9).

Table 9. The content of ash elements in aerial and root parts of plant species from various Arid ecosystems, %.

Ecosystems	Aerial parts	Root parts
Meadow Steppe	3.0	4.5
Dry Steppe	5.5	6.0
Semi-Dry Desert	7.0	10.1
Dry Desert	12.1	16.5

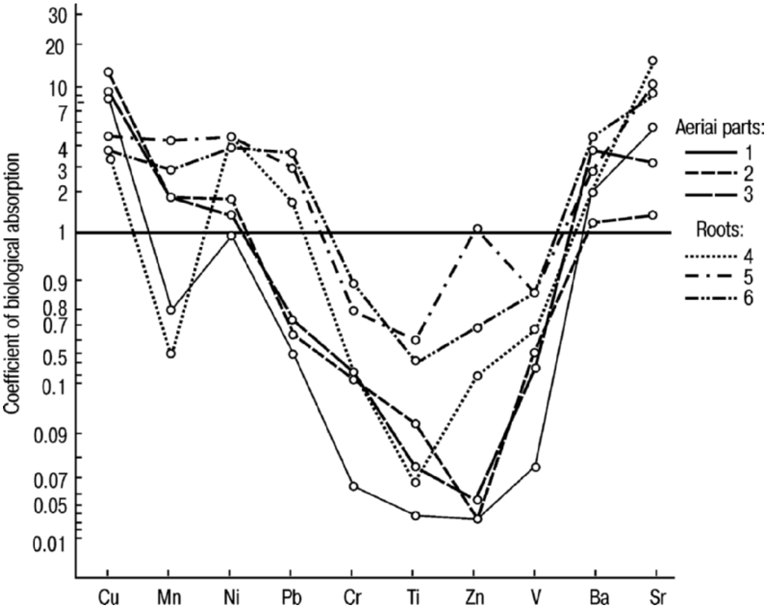


Figure 3. Coefficients of biogeochemical uptake of heavy metals by typical plant species of Meadow Steppe Ecosystems of East European Plain. Aerial parts: 1—legumes; 2—grasses; 3—forage crops; roots: 4—legumes, 5—grasses, 6—forage crops (Dobrovolsky, 1994).

2.3. Dry Desert Ecosystems of Central Eurasia

In Desert ecosystems similar to Steppe ecosystems the plants distinctly exhibit their biogeochemical specificity. We can consider the distribution of heavy metals in Dry Desert ecosystems of the Ustyurt Plateau, Kazakhstan, with predominance of wormwood (*Artemisia terrae albae*) and saxaul (*Anabasis salsa*). In rubble stone territories, of common occurrence is the dense shrubbery of *Sasola anbuscula*. Most elements found in the wormwood occur in their highest concentrations. In the roots of the wormwood and saxaul, higher contents of Mn, Cu, Mo, and Sr have been monitored, whereas the aerial parts contain more Ti, V, and Zr. We can see that the root elements are most biologically active and those in aerial parts, more inert. Possibly their presence was related to the dust exposure and deposition on the plant exterior (see above).

Despite the quantitative variability of salts and silicate dust particles in the plants of Arid ecosystems, we can easily discern a trend towards the selective uptake of trace elements. The calculation of coefficient of biogeochemical uptake (C_b) shows the rates of exposure to heavy metals in biogeochemical food webs. One can see that the elements contained in the plant species of both Steppe and Desert ecosystems are in equal measure susceptible to the influence of environmental factors. The most extensively absorbed are Sr, Cu, Mo, and Zn. Their values of C_b are more than unit. The group of other elements, like Ti, Zr, and V, are poorly taken up, with their values of C_b often dropping below 0.1 (see Figures 4 and 5).

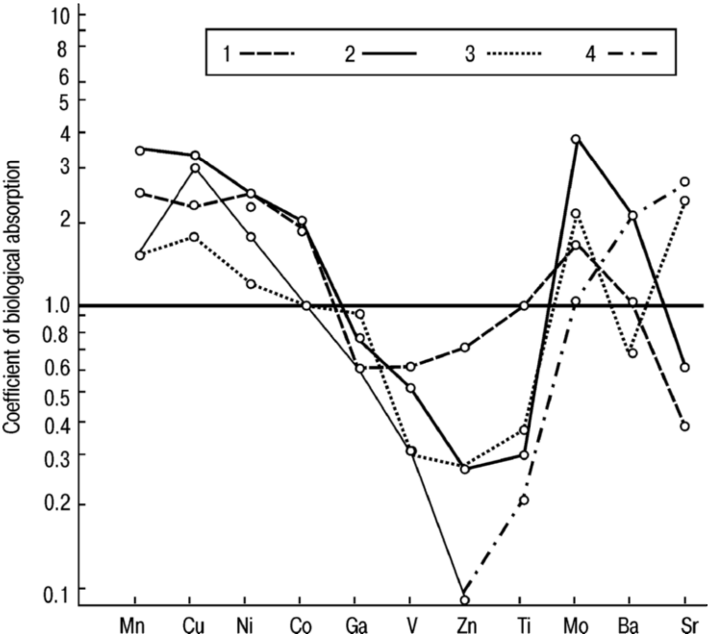


Figure 4. Coefficients of biogeochemical uptake of trace metals by plant species of the Ustyurt Plateau Dry Desert ecosystems. 1—wormwood (Artemisia terrae albae), aerial parts; 2—roots; 3—saxaul (Anabasis salsa), aerial parts; and 4—roots (Dobrovolsky, 1994).

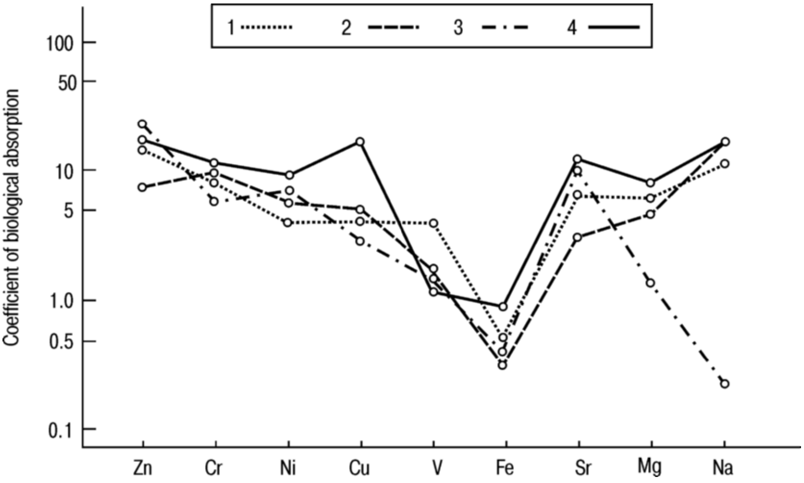


Figure 5. Coefficients of biogeochemical uptake of trace metals by cenospecific plant species of Gobi Extra-Dry Desert ecosystems, Central Asia. 1—Haloxylon ammodendron; 2—Iljina regeli; 3—Ephedra Przewalskii; 4—Anabasis brevifolia (Dobrovolsky, 1994).

The general trend towards increase of ash elements in the plants of steppe ecosystems from Dry to Extra-Dry Desert ecosystems does not seem to affect the C_b values appreciably (see Box 2).

Box 2. Biogeochemical processes and exposure to heavy metals in Central Asian Extra-Arid Desert ecosystems (after Dobrovolsky, 1994)

The biogeochemical processes that occur under the least favorable conditions for life of Extra-Arid Desert ecosystems are of considerable interest. Such extreme environments extend over a vast territory in the middle of the Eurasian continent. The Gobi is one of the most severe deserts in the World. The rainfall in the western part of the Gobi desert is commonly from 20 to 50 mm, whereas the evapotranspiration is about 1,250 mm per annum. The surface of gentle piedmont slopes and intermountain valleys has the aspect of a compact rocky crust, the so-called desert armor. This armor, composed of the pebbles of metamorphic and volcanic rocks with the lustrous black glaze of “desert varnish”, defies even the timid suggestion of an eventual existence of life in this forlorn expanse. Periodically, at an interval of about 10 years, the atmosphere over the Gobi desert becomes invaded with moist air mass, which discharges profuse rains. The runoff streams erode numerous shallow depressions dissecting the

Table 10. Annual biogeochemical exposure fluxes in Gobi Extra-Desert ecosystems, g/ha.

	Ecosystems			
Elements	*Iljina regelii* (desert plains)	*Naloxylon ammodendron* (desert depressions)	*Haloxylon ammodenron* and *Ephedra przewalskii* (desert depressions)	*Anabasis brevifloria and Graminaceae* (Dry Desert ecosystem)
Na	39.6	281.5	912.0	2,718.0
Mg	7.7	86.5	360.0	603.0
Fe	1.1	22.0	71.3	264.4
Sr	0.08	1.07	3.47	17.39
Mn	0.07	2.05	6.65	12.28
Zn	0.04	0.91	2.94	6.58
Cu	0.01	0.16	0.50	2.98
Ni	0.02	0.14	0.44	1.70
V	0.02	0.35	1.14	0.97
Cr	0.03	0.36	1.16	2.54

surface of the rocky hammada into separate extended stretches. Extra-Dry Shrub and Under-Shrub ecosystems are in a large part of the Gobi desert.

The predominant plant species are haloxylon (*Haloxylon ammodenndron*), aphedra (*Ephedra Przewaskii*), and other shrub species, like *Zygophyllum xanthoxylon* and *Reamuria soongoriea*. The under-shrub species include *Anabasis brevifolia* and *Sympegma regelii*. At the periphery of the Extra-Dry Shrub and Under-Shrub ecosystems, grasses (*Stipa glareosa*) and onions (*Allium mongolicum*) are encountered. In the southernmost regions the extra-arid landscapes of rocky hammana are either entirely devoid of vegetation, or provide a scant residence of rare specimens of *Ilinia regelii*, on average 1.3 specimens per 100 m^2. The annual production of the above-ground biomass in Iljina ecosystem is 2.2 kg/ha by dry matter and in Haloxylon-Iljina ecosystem is 2.5 kg/ha. The net annual production of Xerophytic Shrub ecosystems is about 8 kg/ha. The content of chemical species is about 100–1000 ppm for Ca, Mg, Na and Fe; $n \times 10$ ppm for Mn, Zn, Sr, Cr; 1–10 ppm for Cu, Ni and V, and <1 ppm for Pb and Co.

The annual biogeochemical fluxes of various elements are shown in Table 10.

In plain autonomous ecosystems the fluxes of sodium are less 40 g/ha/yr and those of Mg are less than 10 g/ha/yr. For iron these values are close to 1 g/ha/yr, and for all heavy metals, are between 0.01 and 0.04 g/ha/yr. In the geochemically subordinate landscapes (*Naloxylon ammodendron* and *Ephedra przewalskii* ecosystems) which receive additional moisture and chemical elements, the biogeochemical exposure fluxes are 360–912 g/ha/yr for Mg and Na, and from 0.44 to 6.65 g/ha/yr for heavy metals. In the periphery of the Gobi desert, *Anabasis brevifloria* and *Graminaceae* Dry Desert ecosystems show the overall increase of biogeochemical fluxes. The turnover for some elements (Mg, V, Cr) rises but slightly in comparison to their turnover in Extra-Dry ecosystems, whereas the turnover for other elements (Sr, Zn, Cu) increases several times.

CHAPTER 9

SUBTROPIC AND TROPIC CLIMATIC ZONE

Biogeochemical cycling of elements and pollutants' exposure pathways in the tropical ecosystems, which occur between 30°N and 30°S, are both intensive and at high probability of risk for human and ecosystem health. The tropical belt receives about 60% of solar radiation inputting on the Earth's surface. The total area of tropical ecosystems is about 40×10^6 km^2, with exception of the High Mountain and Extra-Dry Sandy Deserts with strongly depressed life processes.

The rates of biogeochemical processes in tropical ecosystems, especially in Tropical Rain Forest ecosystems, are the highest in comparison to other considered ecosystems. This is connected not only with the modern biospheric processes, but, to a great degree, with the history of geological and biological development in these areas. Accordingly, the anthropogenic pollution loading is maximally expressed under tropical climate conditions.

1. BIOGEOCHEMICAL CYCLING OF ELEMENTS AND POLLUTANTS EXPOSURE IN SUBTROPIC AND TROPIC CLIMATIC ZONE

1.1. Biogeochemical Cycles and Exposure Pathways of Chemical Species in Tropical Ecosystems

The different ratios between precipitation and evapotranspiration, duration of dry and wet seasons, relief positions and human activities create a great variability of Tropical ecosystems, varying from African, Australian and American Extra-Dry Deserts to Tropical Rain Forest ecosystems. Due to a prolonged dry season Drought-Deciduous High Grass Tropical Degraded Forest ecosystems are typical in the areas where the annual evaporation exceeds the precipitation. Woody Savanna ecosystems exhibit the clusters of thinly growing trees alternating with the open space of herbaceous vegetation. With increasing aridity, Dry Woody Shrub and Semi-Desert Shrub ecosystems become prevalent, where the trees are replaced by thornbrush and tall grasses grade down to low-growing species with shallow soil coverage.

The proportion of areas with different precipitation rates varies from continent to continent. For instance, different arid ecosystems, from Dry Savanna to Extra-Dry Desert, are predominant in India and Australia. To a lesser degree these ecosystems occur in Central and South America. In an equatorial belt of Africa, the distribution of areas with different precipitation is shown in Table 1.

Table 1. Proportion of African equatorial areas with different precipitation rates.

Annual precipitation, mm	Percent of equatorial belt
>1,800	22
1,000–1,800	48
600–1,000	12
200–600	16
<200	2

We can see that the Tropical Rain Green Forest ecosystems occupy about 1/5 of the African equatorial belt, whereas about 1/2 of this area is Woody and Tall Grass Savanna ecosystems. The rest of the area are occupied by various Dry Steppe and Dry and even Extra-Dry Desert ecosystems, like the Sahara, with annual rainfall less than 200 mm. As it has been mentioned above, the amount of precipitation is of high significance for exposure pathways of pollutants.

1.2. Biogeochemical and Exposure Peculiarities of Tropical Soils

A high rate of edaphic biological processes is the characteristic property of any tropical ecosystem. In the maximum degree this is related to the Tropical Rain Forest ecosystems. For instance, in the African Rain Forest ecosystems the soil surface receives annually from 1200 to 1500 ton/ha of various plant residues. Edaphic invertebrates and microbes transform this large mass very rapidly. A continuous forest litter is practically nonexistent in the Tropical Rain Forest ecosystems and a thin layer of dead leaves alternates with patches of bare ground. All elements that mineralized from litterfall, are taken up by the complex root system of a multi-storied forest to re-input to the biogeochemical cycling. To a great extent this also corresponds to pollutants' exposure.

Most soil-forming rocks of various tropical ecosystems are the products of ancient weathering. These rocks contain a very limited number of nutrients available for plant uptake. Mineralized dead plant organic matter is the main source of essential macro- and microelements. The microbial transformation of tropical plant species residues leads to the dominant formation of soluble fulvic acids. The content of humic acid is 5–7 times less than the former. The typical pH values for soil developed on the leached products of quartz-containing crystalline rock weathering, is about 5. The upper layer of these soils is intensively leached. A different situation is observed when the Tropical Rain Forest ecosystems as confined to a volcanic region and soil formation is in the young products of volcanic rocks weathering, which are enriched in calcium, magnesium, potassium and other alkalis. In this case, most humic acids become neutralized and they condense into larger, less soluble chemical species. This results in a humus accumulation, up to 6–8% that very often serves as a biogeochemical

Table 2. Chemical composition of soils in Australian Tropical Rain Forest ecosystems (after Congdon and Lamb, 1990, see Bashkin, 2002).

Parameters	Parent materials of soils		
	Basalt Pin Gin low hill	Granite Tyson alluvial	Metamorphic Calmara hill
PH	5.7	4.5	4.9
Organic carbon, %	6.4	2.8	1.7
Organic nitrogen, %	0.42	0.18	0.11
Extractable phosphorus, ppm	10	14	7
Total exchange capacity, meq/100 g, inc.	6.6	3.2	2.5
Ca^{2+}	3.1	0.56	0.20
Mg^{2+}	2.2	0.49	0.34
K^{+}	0.52	0.13	0.06

barrier in the exposure pathways. The pH of soil solution is about 6. However, fulvic acids are prevalent over humic acids in any soils of Tropical Rain Forest ecosystems. Accordingly, soils derived on the younger rocks are more acid and depleted in both nutrients and exchange cations that are involved in biogeochemical cycling (Table 2).

The Seasonal Tropical Forest and Woody Savanna ecosystems are common in tropical regions with a short dry period. The characteristic features of soils from these ecosystems are the neutral reaction of soil solution and periodic leaching during wet season. The herbaceous species favor the formation of both sward and humus horizons.

Different conditions are typical for Dry Tropical Wood, Dry Savanna and Dry Woody Shrub ecosystems in areas with precipitation rates of 400–600 mm and a prolonged dry season. The microbial activity is suppressed during a dry season. The soils of these ecosystems have no even periodic leaching, the formation by transpiration of a biogeochemical barrier in the upper soil layer favors the alkaline reaction and accumulation of soluble salts. This decreases also the intensity of exposure to different pollutants for living organisms.

The accumulation of heavy metals in tropical soils depends on the geological rocks. These soils have been developed mostly on re-deposited products of weathering that suffered a small displacement. Furthermore, most tropical areas occupy fragments of the ancient super-continent Gondwana, whose surface during the last 0.5 billion years has not been covered by oceanic waters. The resultant effect of these soil-forming conditions was connected with the pronounced influence of geochemical composition of geological rocks on the biogeochemical cycling in all Tropical ecosystems, and finely on the biogeochemical exposure pathways in the whole tropical area.

Table 3. Content of heavy metals in soils of two Dry Savanna ecosystems from East Africa, ppm (after Dobrovolsky, 1994).

	Soil-forming geological rocks			
	Precambian crystalline rocks (Uzanda)		Cenozoic volcanic rocks (Tanzania)	
Heavy metals	Clark content	Content in humus horizon	Clark content	Content in humus horizon
Ti	1.8	5,820	4.5	14,900
Mn	2.2	1,520	3.1	2,140
V	2.0	153	3.6	271
Cr	6.9	234	4.7	160
Ni	2.9	75	3.6	93
Co	6.6	48	9.6	70
Cu	4.7	105	3.3	72
Pb	3.2	52	2.2	35
Zn	2.5	125	3.7	190
Mo	3.8	5	6.2	8
Be	2.4	6	6.4	16
Sc	2.2	24	1.5	16
Y	1.6	58	1.8	64
La	1.8	85	2.1	95
Nb	2.9	59	11.5	224
Zr	1.3	215	3.9	670
Ga	0.8	16	1.1	20
Cr	0.6	129	2.2	510
Ba	0.4	274	0.9	590

The example of these relationships with the ancient geological rocks is shown in Table 3.

Both of the soils are enriched in various elements, like zirconium, titanium, beryllium, niobium, and strontium, due to their enlarged content in the alkali basalts and phonolites of the East-African Rift. We can see that soils of Tanzanian Dry Savanna ecosystems contain niobium 11 times, beryllium and molybdenum 6 times, and titanium and zirconium 4 times as high as compared to the respective crust concentrations (clarks) of these metals. In the Ugandan soils, the chromium content is 7 times higher

Table 4. Biogeochemical mass balance for the Tropical Flooded Savanna ecosystems, kg/ha/yr (after Vegas-Vilarrubia et al., 1994).

	Mass balance items		
Element	Input	Output	Net
Na	13.92	18.29	−4.37
K	2.62	12.89	−10.67
Ca	7.96	11.26	−3.30
Mg	0.68	7.34	−6.66
P	0.19	0.10	+0.09
Zn	0.60	0.21	+0.29
Cu	0.24	0.06	+0.18

than clark value and that of copper, 5 times. Such a large difference in soil enrichment of heavy metals is related to their different input into biogeochemical cycles of corresponding ecosystems and relevant pathways of exposure to human beings and ecosystems.

1.3. Biogeochemical Exposure Pathways in Soil–Water Systems

Soil links of biogeochemical processes are ultimately connecting with the aqueous links of various biogeochemical cycles. The results of small catchment monitoring are very helpful for understanding the relationships between terrestrial and aqueous links of biogeochemical cycles of various chemical species and their exposure to living biota. Such a monitoring experiment has been carried out in Venezuelan Flooded Savanna ecosystems. The site is located between the rivers Arauca and Apure (7°8′N and 68°45′W), and it presents a flooded area, where savanna ecosystems are developed under alluvial sedimentation processes. Soils in the study area are naturally fertile. Dominant species are *Leersia hexandra* and *Himenachne amplexicaulis*, species with relatively high aboveground net primary production, 5.5–9.1 ton/ha per year. The duration of the wet season is 6 months.

The biogeochemical mass budget of various macro- and microelements for this catchment is shown in Table 4.

The input of elements was accounted only as a result of atmospheric deposition. Assuming that most soils are poorly drained after reaching field water holding capacity (FWHC), the percolation of water through a soil profile is minimal. Consequently, losses of elements from the watershed by deep seepage are negligible. Nutrient budgets are therefore calculated as the difference between input with deposition and output in surface runoff. We can see that negative values of budget are calculated for sodium, potassium, calcium and magnesium, whereas these values were positive for phosphorus, zinc, and copper.

The possible explanation of these results is related to the construction of dikes in this area a few years prior to the experiment. This changed the biogeochemical cycles of many nutrients in natural ecosystems too. Furthermore, the input of nutrients with flooded waters was not taken into account.

As a result of microbial formation of metal-organic complexes with fulvic acids in soils of Tropical Rain Forest ecosystems, the surface and sub-surface runoff waters are enriched in some heavy metals like manganese and copper. A similar tendency has been shown for boron, strontium and fluorine.

Colloidal suspension is the dominant form of riverine migration in tropical ecosystems. These suspensions are mainly composted of products originated from soil biogeochemical metabolism. However, most of these products never reach the river channels and deposit in the subordinated landscapes of relief depressions. During a wet season, tropical grey and black compacted soils with seasonal waterlogged horizon are formed in these landscapes. Seasonal bog ecosystems provide conditions for the accumulation of many chemical compounds, which have leached from the surrounding elevated ecosystems. For this reason biogeochemical provinces with excessive content of heavy elements in food webs and characteristic features of exposure on biota occur in these savanna regions.

2. GEOGRAPHICAL PECULIARITIES OF BIOGEOCHEMICAL CYCLING AND POLLUTANT EXPOSURE

2.1. Biogeochemical Cycling and Pollutant Exposure in Tropical Rain Forest Ecosystems

All types of Tropical Rain Forest ecosystems occupy 20.45×10^6 km^2, or 13.3% of the total global land area. These ecosystems constitute the most powerful plant formation. The abundance of solar energy and water provides for the largest biomass growth, up to 1,700 ton/ha. The only restriction factor is the availability of sunlight for every plant species. To maximize the use of solar energy, several stories of trees has developed in Tropical Rain Forest ecosystems, from the upper story of 30–40 m height down to 2–5 m trees of height well adapted to stray light. A large part of died-off and fallen leaves from taller trees is entrapped for assimilation by numerous epiphytes. This results in fast re-circulation of chemical elements. The average annual Net Primary Production of these ecosystems is 25 ton/ha.

The main specificity of biogeochemical cycling and exposure pathways in Tropical Rain Forest ecosystems is related to its almost closed character. This means that almost the total number of nutrients and/or pollutants is re-circulating in biogeochemical cycles (Figure 1).

This type of closed biogeochemical cycling is very sensitive to uncontrolled intervention into ecosystems. For instance, clearcutting leads to the entire destruction of the whole ecosystem with its multi-annual history. In other words, the deforestation will leave behind a barren soil with completely destroyed biogeochemical turnover and enforce significantly the exposure to different pollutants.

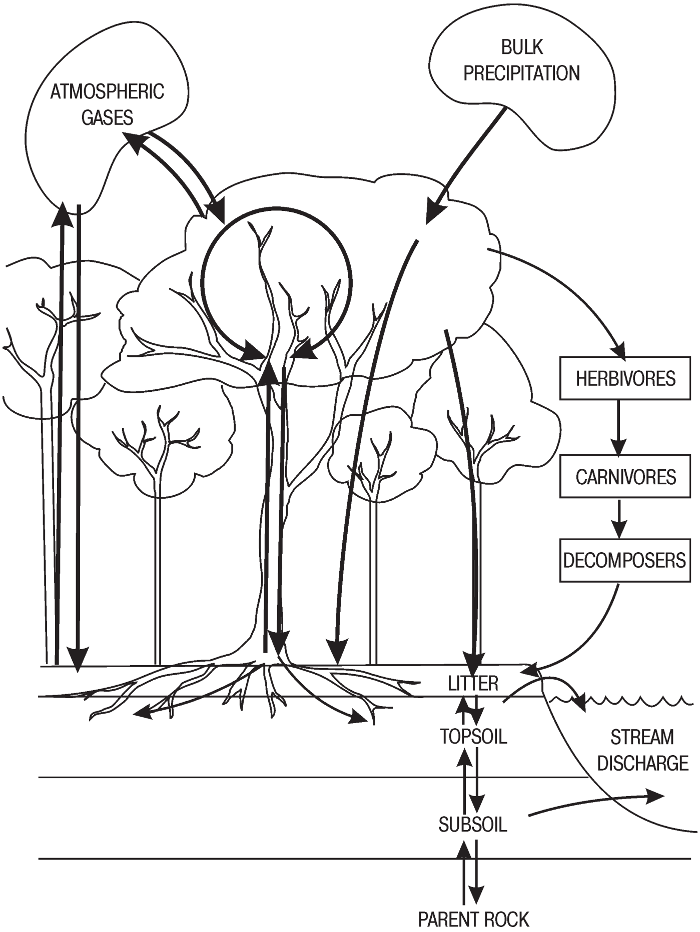


Figure 1. Biogeochemical cycle and exposure pathways in Tropical rain Forest ecosystems.

For instance, clearing tropical forests in the Amazon basin for pasture alters rates of soil nitrogen cycling (Table 5).

The pattern of NH_4^+ and NO_3^- concentrations, and net mineralization and net nitrification rates in soils before and after clearing and burning tropical forest indicate:

(1) forest inorganic N pools are either dominated by NO_3^- or contain NH_4^+ and NO_3^- in roughly equal proportions;

(2) net mineralization and net nitrification rates tend to decline after forest clearing and burning;

Table 5. Inorganic N concentrations, mineralization and nitrification rates, and turnover rates of NH_4^+ and NO_3^- in a chronosequence before and after forest clearing at Nova Vida, Brazil (after Neill et al., 1999).

Forest cutting	NH_4^+, ppm	NO_3^-, ppm	Net mineralization, ppm/day	Net nitrification, ppm/day	Turnover, day NH_4^+	Turnover, day NO_3^-
Before cutting	8.8	13.7	2.72	2.60	1.8	4.9
1.5 months after	6.8	12.6	3.65	2.05	1.5	5.0
6 months after	2.1	10.0	10.0	2.38	1.1	5.5
8 month after	1.5	11.5	11.5	2.30	0.8	4.9

(3) Slash burning in Amazonian Tropical Rain Forest ecosystems is accompanied by a relatively thorough consumption of leaves and other sources of high quality organic material and a large input to soils of low quality, high C-to-N coarse woody debris. This input was probably responsible for the N immobilization recorded by the net mineralization measurements 1.5 months after the burn. No increases have been observed in net mineralization and nitrification rates after the burn, perhaps because microbial communities were diminished by burning and took time to become reestablished. This absence of any increase in mineralization and nitrification rates suggest that the high ammonium and nitrate concentrations, shown in Table 5, were associated with the elimination of plant uptake, rather than accelerated N cycling.

From these results we can conclude that nitrogen is relatively available in soils of Tropical Rain Forest ecosystems and that forest soils mineralize and nitrify large amounts of nitrogen. P. Vitousek and R. Sanford have shown similar results earlier in 1986 studying nitrogen cycling in moist tropical forest. Since nitrogen depending on concentration may be both a pollutant and a nutrient, these data are of importance for nitrogen biogeochemical exposure and relevant risk assessment.

The total biomass and its annual distribution for these ecosystems are shown in Table 6.

Table 6. Plant biomass parameters in Tropical Rain Forest ecosystems, ton/ha.

Biomass parameters	Total biomass	Annual NPP	Annual litterfall
Total mass	520	32.5	25.0
Nitrogen	2.94	0.43	0.26
Ash elements	8.14	1.60	1.28

Table 7. Concentration of chemical species in tropical tree compartments (after Dobrovolsky, 1994).

Sample	Elements, % by the dry weight									Pure ash	Mineral dust admixture
	N	Si	Al	Fe	S	Na	Ca	Mg	P		
Trunk	0.5	0.05	0.01	0.02	0.03	0.01	0.29	0.02	0.02	0.79	0.40
Twig	0.6	0.07	0.03	0.04	0.04	0.03	0.31	0.04	0.03	0.85	0.45
Leaves	2.0	1.06	1.87	1.48	0.04	0.22	0.45	0.27	0.06	9.87	11.3

As a rule the concentration of chemical species in the trunk and twig wood of tropical trees is a few times lower than that in the leaves (Table 7).

The average sum of total ash elements in the biomass of Tropical Rain Forest ecosystems is about 8,000 kg/ha. The annual ash element turnover and heavy metal exposure rates are shown in Table 8.

Geochemical conditions of tropical soils favor the biogeochemical migration of iron and manganese. The turnover of other metals is from 1.1 g/ha/yr for Cd to 1,050.0 g/ha/yr for Sr with the relevant rates of exposure to living organisms.

2.2. Biogeochemical Cycling and Pollutant Exposure in Seasonal Deciduous Tropical Forest and Woody Savanna Ecosystems

The Seasonal Deciduous Tropical Forest and various Savanna ecosystems occupy 14.3×10^6 km^2. The biogeochemical cycling in Seasonal Deciduous Tropical Forest and various Savanna ecosystems is similar to that in the Boreal and Sub-Boreal Deciduous Forest ecosystems. The clear distinction is related to the reasons of periodical inhibition of biogeochemical activity. In the temporal climate it is connected with the winter temperature drop and in tropical areas it relates to the dry season with significant moisture deficit. This refers accordingly to the exposure pathways.

Table 9 compares the contents of heavy metals in the ash of various grass and tree species from the Savanna ecosystems of East Africa. We can see that nickel, barium, and strontium accumulate in the tree organs (twigs), whereas the accumulation of other metals is pronounced in grasses.

The aerial parts of grasses in Savanna ecosystems exhibit a high ash content from 6 to 10%. This is partly due to the presence of minute particles of mineral dust, which are discernible under a microscope or, occasionally, even with the naked eye. The exposure to mineral dust accounts for 2–3% of the weight of dry mass of grass aerial parts. We can consider that this dust is responsible for the elevated concentrations of some minerals, like Ga, which has a low C_b value. This element contains in windblown finely dispersed clay particles. Nevertheless, even with allowance made for the silicate dust content, the total sum of ash elements in grasses of savanna ecosystems is twice as much as that of the grasses from Alpine Meadow ecosystems.

Table 8. Biogeochemical turnover and heavy metal exposure rates in Tropical Rain Forest ecosystems (after Dobrovolsky, 1994).

Heavy metals	Chemical symbol	Annual flux, kg/ha/yr
Average ash content, %		4.6
Overall turnover of ash elements		1,500
Iron	Fe	6.0
Manganese	Mn	6.15
Strontium	Sr	1.05
Titanium	Ti	0.97
Zinc	Zn	0.90
Barium	Ba	0.67
Copper	Cu	0.24
Zirconium	Zr	0.22
Nickel	Ni	0.06
Chromium	Cr	0.052
Vanadium	V	0.045
Lead	Pb	0.037
Cobalt	Co	0.015
Molybdenum	Mn	0.015
Thin	Sn	0.0075
Gallium	Ga	0.0015
Cadmium	Cd	0.0011

Strontium, barium, manganese, copper, molybdenum, and nickel are elements of strong accumulation in plant species of African Savanna ecosystems, in spite of different content in soils and soil-forming rocks. The C_b values are >1. The other elements, like beryllium, zirconium, titanium and vanadium, are less taken up by plants and their C_b values are less than 0.5. These refer to various exposure pathways to both microbes and plants as links in biogeochemical food webs.

2.3. Biogeochemical Cycling and Pollutant Exposure in Dry Desert Tropical Ecosystems

Dry desert tropical ecosystems occupy 4.5×10^6 km^2, or 3.0% of total land area of the Earth. These ecosystems have dry periods during 7–10 months a year. Not only trees, but also numerous grasses cannot grow in such severe conditions. The vegetation

Table 9. Biogeochemical fluxes and exposure to heavy metals in various plant species of Savanna ecosystems of East Africa (after Dobrovolsky, 1994).

Heavy metals	Content, ppm		Coefficient of biogeochemical uptake, C_b		Averaged annual flux, kg/ha
	Grasses	Trees	Grasses	Trees	
Ti	1,140	230	0.1	0.03	0.35
Mn	1,880	943	1.9	0.9	2.05
V	59	45	0.3	0.2	0.015
Cr	28	12	0.2	0.08	0.017
Ni	39	144	0.6	2.0	0.02
Co	20	12	0.6	0.4	0.005
Cu	85	39	1.5	0.7	0.08
Pb	34	21	1.5	0.9	0.012
Zn	118	79	1.2	0.8	0.30
Mo	57	6	7.1	0.8	0.005
Zr	165	92	0.5	0.3	0.075
Ga	36	4	1.6	0.2	0.008
Sr	450	3,340	3.5	25.7	0.35
Ba	440	630	3.0	4.3	0.22

is generally represented by thorny drought-deciduous shrubs. These shrubs, being leafless for a larger part of the year, reduce accordingly the transpiration. The example of these ecosystems is Tar desert, west India. It is a lowland alluvial plain formed by the Indus. The rainfall for this area is 200–600 mm/yr. The scattered tree species (*Acacia, Propopis spicigera, Salvadora persica*), shrubs, and grasses (*Gramineae*) represent the vegetation of this dry desert ecosystem. The sandy deposits are devoid of trees, which confers the image of desert activity. The desertification of the territory is a result of human activity connected with overgrazing during a long-term period. It is known that in 326 B.C., when the troops of Alexander the Great came to the Indus, sal forests (*Schorea rubista Gaerth.f.*) were widespread in the valley. At present these forest ecosystems do not exist.

Table 10 characterizes the plant biomass of the Tar Dry Desert ecosystems.

We can see that trees are major contributors to the plant biomass of this ecosystem. They account for 60% of the root and 98% of the aboveground biomass. The monitoring results showed also that the grasses provide a larger part of the annual

Table 10. Biomass and net primary productivity of the Tar Dry Desert ecosystem, India.

Biomass components	Biomass		NPP	
	ton/ha	%	ton/ha	%
Green parts of plants	2.90	11	2.90	42
Perennial aerial parts of plants	10.60	47	0.40	2
Roots	11.30	42	3.53	56
Total biomass	26.80	100	6.80	100

Table 11. Biogeochemical fluxes and exposure to chemical elements in Tar Dry Desert ecosystem (after Rodin et al., 1975).

Element	Pool in biomass, kg/ha	Content of chemical species in main parts of annual NPP					
		Green parts		Roots		Overall production	
		kg/ha	%	kg/ha	%	kg/ha	%
N	179.34	42.86	59	26.14	36	72.08	100
Ca	256.25	34.22	57	19.28	32	59.78	100
K	111.21	31.57	61	18.68	36	52.04	100
Si	53.81	22.14	52	20.21	8	42.48	100
Mg	48.69	6.80	51	5.40	41	13.30	100
P	12.19	3.57	56	2.68	42	6.42	100
S	17.60	8.86	72	3.18	26	12.39	100
Al	19.37	2.46	52	1.80	38	4.69	100
Fe	11.37	1.64	53	1.21	39	3.11	100
Mn	2.84	1.01	48	1.07	51	2.09	100
Na	9.52	2.79	58	1.95	40	4.82	100
Cl	14.96	5.16	54	4.27	45	9.51	100
Total ash elements	571.81	120.22	57	59.79	38	210.63	100
Total	751.15	163.08	58	85.93	30	282.71	100

net primary production. Grasses are responsible for 76% of green organs and 83% of root biomass of NPP.

The biogeochemical fluxes and exposure to various chemical species are shown in Table 11.

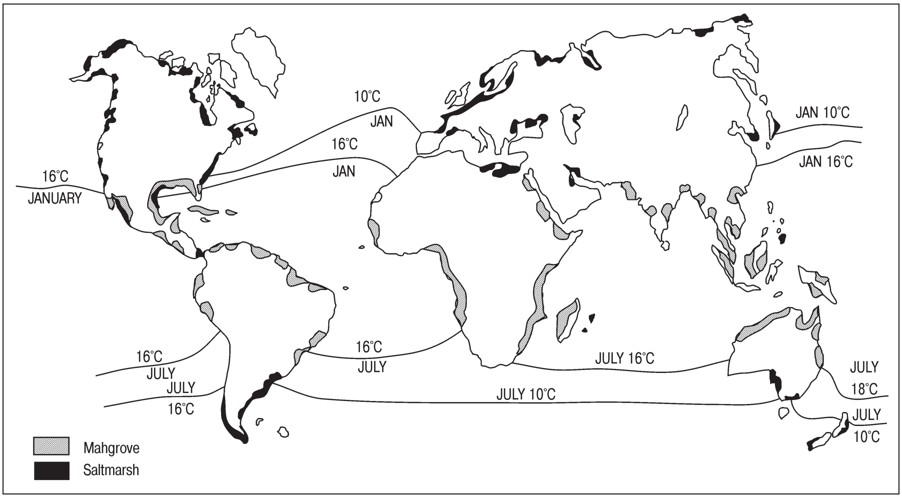


Figure 2. Map showing global pattern of mangroves and saltmarshes in relation to average temperature.

We can see that the green parts of this Tar Dry Desert ecosystem accumulate more than half of both total studied nutrients and ash elements. These values for the root biomass are 30 and 38% from the total and ash elements in NPP. No more than 5% is supplied to the trunk and twigs. In the green tree organs, nitrogen, calcium, potassium, silicon and sulfur are the most extensively accumulated. In the roots, the highest relative accumulation is that of manganese and silicon, which are distributed roughly in equal parts in the annual growth of green organs and roots. Accordingly exposure to both nutrients and pollutants is proportional to the NPP partitioning in aerial and underground parts of plants.

2.4. Biogeochemical Cycling and Pollutant Exposure in Mangrove Ecosystems

The Mangrove Forest ecosystems are typical for the tropical coastline. These ecosystems occupy the narrow coastal strips periodically flooded during the diurnal or the big syzygial tides. We can say that Mangrove ecosystems are transitional from terrestrial to subaquatic marine ecosystems. Depending on the temperature as a limiting factor, these ecosystems spread from 32°N up to 44°S. This is shown in Figure 2.

The biodiversity of Mangrove ecosystems is the most profound in the islands and coastline of the Indo–West–Pacific region, where the occurrence of 44 varieties has been reported. On the Atlantic Ocean coast Mangrove ecosystems are especially widespread in the Caribbean region. The chemical composition of plant species and soils of Mangrove ecosystems have been recently discussed (Dobrovolsky, 1994).

Mangrove Forest ecosystems occur on the surface of compact cavernous reef limestone or on carbonate sands, aleuritic and clayey silts in lagoons and shallow

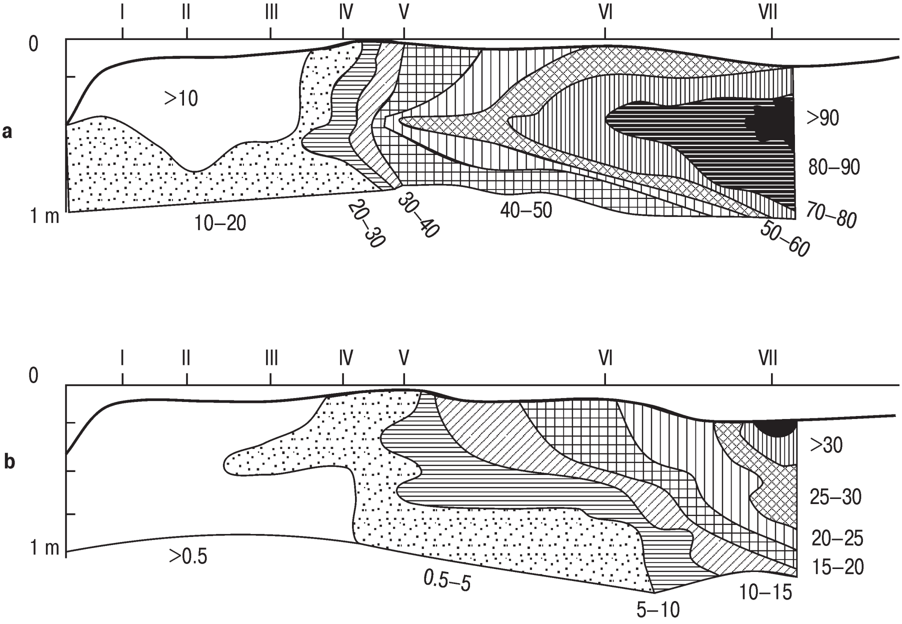


Figure 3. Hydrogenic accumulation of aluminum and silicon oxides in soil solutions of the Mangrove ecosystems of West Africa: a—content of aluminum oxides, mg/L, b—content of aluminum oxides, mg/L (Kovda, 1984).

bays. In some places small spots of Mangrove ecosystems are placed on coastal quartz sands derived from weathering materials of crystalline rocks. The botanic genus of *Rhizophora* (Red Mangroves), *Avicelinnia* (Black Mangroves) and *Laguncularia* (White Mangroves) are predominant in the floral composition of the Mangrove Forest ecosystems. The shrubs of genus *Pemphis* are common residents in the Mangrove ecosystems in the atolls of the Indian Ocean with compact reef limestone ledges at the coastal strip.

The biogeochemical fluxes and exposure pathways of various macro- and microelements are different from those shown for Tropical Rain Forest ecosystems. The chemical composition of leaves of tree species in Mangrove Forest ecosystems is connected with higher content of Mg, Cl and $S{-}SO_4^{2-}$ and lesser content of K and Si as compared to the leaves of trees from Tropical Rain Forest ecosystems. The content of Al is 3–4 times higher than that of Si and this can be related to the values of hydrogenic accumulation of these elements in soils (Figure 3).

The total ash content accounts for 11–23% of the dry weight of plant biomass. We can remember for comparison, that these values for the terrestrial forest ecosystems on similar limestone soils are 5–6% only. These differences can be attributed to the adaptation of Mangrove ecosystems to saline marine waters and relevant exposure to the chemical species.

Table 12. Content of heavy metals in the plant biomass of the Mangrove ecosystems of the Indian Ocean islands, ppm on dry ash weight (after Dobrovolsky, 1994).

Ecosystems	Island	Plant species	Plant organs	Heavy metals				
				Mn	Zn	Cu	Pb	Ni
Mangrove forest of coral islands	North Poivre	*Rhizophora*	Leaves, twigs	36.8	28.4	18.4	0.1	5.0
	South Poivre	*mucronata*	Leaves, twigs	25.0	50.0	35.0	8.8	8.1
	North Farquhar		Leaves	13.8	42.0	15.8	6.9	6.0
	South Farquhar		Twigs	32.0	60.0	36.0	6.4	2.5
Mangrove forest of silicate islands	Silhouette	*Rhizophora mucronata*	Leaves, twigs	71.4	45.3	10.7	0.7	3.8
	Silhouette	*Bruguiera gymnorizha*	Leaves, twigs	306.2	70.0	20.6	0.9	0.9

The common biogeochemical feature of the Mangrove ecosystems is connected with small fluxes of trace metals (Table 12).

Mangrove ecosystems are an example of one of the most productive ecosystems of the World. The biomass pool is in excess of 100 ton/ha of dry matter and annual NPP varies from 10 to 30 ton/ha, including leaf litter production of 8–15 ton/ha. Using average data on annual net primary production and content of various elements, we

Table 13. Average biogeochemical exposure rates of heavy metals species in Mangrove ecosystems.

Elements	Average ash content, ppm	Exposure rates, g/ha/yr
Sr	1,920.0	3,670
Fe	113.0	215
Zn	45.0	85
Mn	27.0	51
Cu	26.0	49
Pb	7.4	14
Ni	5.4	10
Total sum of ash elements	—	4,094

can estimate the values of biogeochemical cycles and exposure to biota of heavy metals (Table 13).

The comparison of biogeochemical fluxes and relevant exposure rates of heavy metals in the Mangrove and Tropical Rain Forest ecosystems shows that the total mass of ash elements per unit area is similar. However, the proportion of various elements is markedly different. The Mangrove plant uptake of Fe and Mn is less and that of Sr is higher than the uptake of these elements in Tropical Rain Forest ecosystems.

In Mangrove ecosystems the nutrients accumulate in leaves and accordingly fall with shed or died-off-leaves to the soil surface. The further biogeochemical transformation of these chemical species depends on the surface properties of soils and underlying layers of rocks. When Mangrove ecosystems develop on compact reef limestone the litterfall layer is not produced. In that case, if the underlying layer is carbonate or carbonate-argillaceous silt, soils with weakly developed humus horizon are formed. Sulfate-reducing bacteria play an important role in the microbial processes occurring in soils of the Mangrove ecosystems. Under the conditions of a shallow seawater level (10–15 cm) and minimal tidal interference, a lean peat horizon is formed at the soil surface. The typical example is the Mangrove ecosystems in the lowland littoral plain in the Batabano bay in southwestern Cuba (Dobrovolsky, 1994).

The composition of organic matter in soils of the Mangrove ecosystems is related to the prevalence of the small-size vegetation detritus resistant to decomposition. The humus content is usually about 1% or so, with increase up to 5% in the peat horizon. Independent of the overall content of organic matter in the upper horizon, the easily soluble fulvate compounds are predominant over humates. In soils of Mangrove ecosystems on limestone, the fulvic acids formed undergo a rapid neutralization by carbonates. This may be inferred from the rise of pH values (from 7.2–7.7 to 8 or higher) of aqueous extract of the humus horizon at a depth of 10–20 cm. Dispersed organic detritus can absorb many heavy metals and during detritus decomposition these metals become bound to water-soluble fulvic acids. This facilitates the leaching to 15–20 cm depth in soil profile. Further migration and exposure pathways is impeded due to the neutralization of fulvic acids yielding water-insoluble calcium fulvates.

The characteristic property of soils from Mangrove ecosystems is related to the accumulation of mobile water-soluble forms of iron, aluminum and silicon. The downward increase in soil profile was shown for iron and aluminum and an opposite trend for silicon (Table 14).

The Mangrove ecosystems perform a role of biogeochemical barrier, which decreases significantly the runoff of chemical species from the coast to the ocean waters. This is correlated with the major biogeochemical parameters of these ecosystems such as high productivity and high values of annual biogeochemical fluxes and relevant exposure rates.

Being on the coastal line, the Mangrove ecosystems are subjected to the influence of tidal activity, which triggers periodic changes in biogeochemical fluxes of various elements (see Box 1). The possible climate changes and relevant sea levels rise may affect greatly the distribution of Mangrove ecosystems.

Table 14. The content of water-soluble species of iron, aluminum and silicon in soils of West African Mangrove ecosystems, ppm (after Kovda, 1973).

Soil layer, cm	Fe	Al	Si
0–13	756.0	83.2	54.9
14–31	889.0	112.5	27.5
>32	132.3	117.4	9.2

Box 1. Potential change of sulfur biogeochemical cycle in Thai Mangrove ecosystems due to sea level rise resulting from climate change scenarios (after Bashkin, 2003a; Rummasak et al., 2002)

Increasing concentration of GHG in the atmosphere will lead to climate change and the most probable scenarios are related to sea level rise. According to these scenarios the mangrove ecosystems of the South East Asia and Thailand coast, in particular, will change many features, especially those connected with the biogeochemical cycle of sulfur.

Mangrove ecosystems are very complex and highly productive, however the quantitative parameterization of various links of their biogeochemical structure is uncertain on both local and regional scales. Several biogeochemical processes in mangroves will be affected by sea level change. Furthermore, at present owing to lack of information, the impact upon biogeochemical reaction of mangrove ecosystems as a result of relative sea level rise is difficult to predict, and the requirement to study such a process quantitatively is of great scientific and political interest. Hence it is important to understand the potential impact of changing climate on mangroves biogeochemical cycling of the most important elements like sulfur, in order to conserve and manage these valuable resources for sustainable management in the future.

For quantitative parameterization of various links of the sulfur biogeochemical cycle, the natural mangrove forest was selected at the mouth of Klong Ngao River in the area of Ranong Biosphere Reserve on the Andaman Sea coast of Thailand. Water and salt (sulfur) biogeochemical fluxes are monitored in the Klong Ngao estuary assuming a two-dimensional flow pattern. These monitoring data are applied to carry out the budget of conservative and non-conservative material. The prognostic model predicting the potential change of biogeochemical cycle of sulfur in this mangrove ecosystem due to sea level rise resulting from climate change scenarios will be developed based on the results of the studied budget. The estimation of fluxes in dry and wet season can present the input data for such a model.

Two box models are used for the parameterization of water as conservative material and salts, including sulfur, as non-conservative material. For example, the first estimates were made up for the wet season. For the coastal water body budget, the following fluxes were monitored and calculated: precipitation, evapotranspiration, runoff, groundwater, and residual flow. These budget estimates give the fresh water residence time as 6.2 days with residual flow equal to -822.34×10^3 m^3 d^{-1}. For Klong Ngao salt budget during wet season, similar fluxes were measured. Salt input into the system through mixing salt flux was equal to $+14, 843 \times 10^3$ kg d^{-1} with similar residual salt flux and the average salinity at high water spring as 18.81 ppt and at low water spring as 12.79 ppt. During the dry season fresh water flow and residence time were decreased, whereas salt input was increased.

The relevant changes in exposure rates are also of importance for predicting the behavior of Mangrove ecosystems and environmental risk assessment for their fate.

PART III

EXPOSURE ASSESSMENT IN TECHNOGENIC BIOGEOCHEMICAL PROVINCES

During the last century, enforced anthropogenic activity led to increasing pollutant loading in all biosphere compartments and relevant terrestrial and aquatic ecosystems. The biogeochemical structure of the biosphere was altered to a significant extent. We can consider the biogeochemical structure as the most flexible indicator of pollution loading. This flexibility, nevertheless, assumes the existence of specific homeostatic intervals, during which the input of polluting elements will be within the limits of natural deviations of various links of biogeochemical food webs. However, considering the modern state-of-the-art of biogeochemical cycling, we can conclude that in most natural biogeochemical sub-regions and provinces, pollutant loading has led to the formation of technobiogeochemical and agrogeochemical structural units.

In modern literature we can find different definitions of environmental pollution, most of which speculate on the increasing rates of pollutant inputs and accumulation in the various media, like soil, waters, air, fodder and foodstuffs. However, varying geochemical background makes the quantitative approach to pollution problems quite controversial. We should take into account the biogeochemical cycling in various terrestrial and aquatic ecosystems with parameterization of biogeochemical pools and fluxes on local, regional and global scales. Thus, from the biogeochemical point of view, *environmental pollution is the reversible and/or irreversible alteration of biogeochemical structure of ecosystems*. This alteration leads to many ecological problems, the major one being the risk to human and ecosystem health.

CHAPTER 10

OIL AND GAS BIOGEOCHEMICAL PROVINCES

Oil and oil treatment products are the predominant environmental pollutants. The oil treatment industry is considered among the first three most severe polluters from 130 industrial branches in the whole World. Oil exploration processes form the vast areas of ecosystem pollution and degradation in practically all places, especially those on the sea shores of the Arctic ocean.

1. BIOGEOCHEMICAL STEPS OF HYDROCARBON FORMATION

During geological Earth's history, kerogen was often depicted as a complex high-molecular weight material formed from random condensation of monomers. These monomers are thought to have been generated by the initial breakdown of polymeric biological precursor molecules during sediment burial. Other biopolymers, which have been altered in various biogeochemical processes, may participate in kerogen formation as well. These biopolymers have undergone various degrees of alteration prior to and after burial. Since kerogen was formed from the altered residues of different marine and terrestrial organisms, it contains information about geological, geochemical, and biogeochemical history of sediments and their transformation to biogenic deposition.

The evolution of sedimentary organic matter (OM) under the influence of increasing burial depth and related temperature rise is termed maturation and this process is commonly subdivided into three stages, i.e., diagenegisis, catagenesis, and metagenesis (Figure 1).

We can determine these stages as follows. Diagenesis is microbial and chemical transformations of sedimentary organic matter at low temperature and it started in recently deposited sediments. Catagenesis has involved the formation of oil and gas from thermal breakdown of kerogen under increasing temperature during burial of sediments. The subsequent and last stage of the evolution of OM in sedimentary basins at high temperature is termed metagenesis.

Transformation of the initially deposited remains of living organisms started in the water columns and in the upper layers of bottom sediments of ancient seas. Random polymerization and condensation reactions of degraded biopolymers are believed to have formed the initial geopolymers, which contain humin, fulvic and humic acids. Until now these compounds (very typical for soil humus as well) are

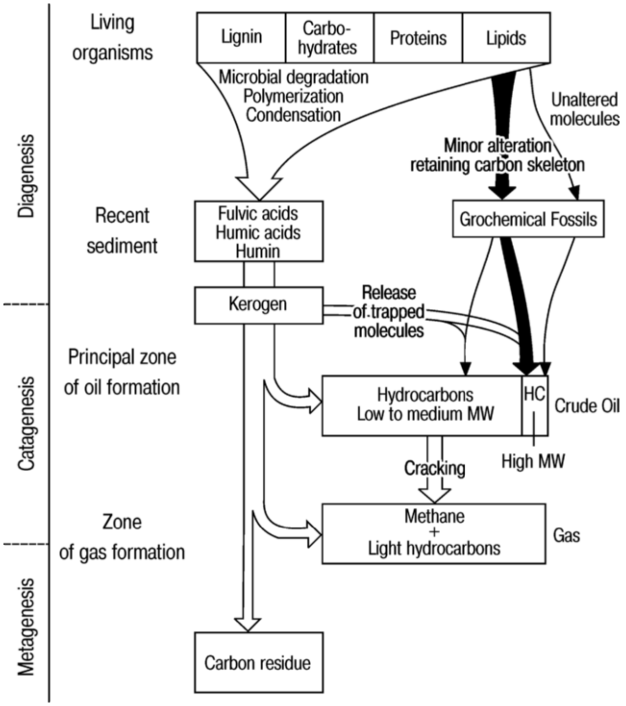


Figure 1. Stages of kerogen transformation and hydrocarbon formation pathways in geological situations. Direct inheritange of low molecule weight compounds is indicated by block arrows (from Engel and Macko, 1993).

not well determined on the molecular level, but they are differentiated on the basis of their solubility in acids and bases.

During oil and gas formation thermal breakdown of kerogen has been occurring in the catagenic stage (Figure 1). Under the influence of elevated temperatures, usually $>50\,^{\circ}$C, and geological time, liquid and gaseous hydrocarbons have been released from kerogen mass. Chemically, it is connected with cleavage of C–C bonds. Other organic compounds containing heteroatoms such as O, S, and N have been originated as well. Oil not expelled from source rocks will be cracked to gas if subsidence continues and higher temperatures reached.

During the ultimate stage, mutagenesis, only dry gas methane was stable. It was originated from previously formed liquid hydrocarbons (Figure 1) mainly due to high temperature decomposition of kerogen.

Petroleum geologists commonly call the catagenesis range, in which oil is effectively produced from kerogen as “oil windows”. One can see this in Figure 2 in a bell-form generation curve.

Formation of oil from kerogen is a disproportionation reaction related to a hydrogen-rich mobile phase and a hydrogen-depleted carbon residue. After crystalline

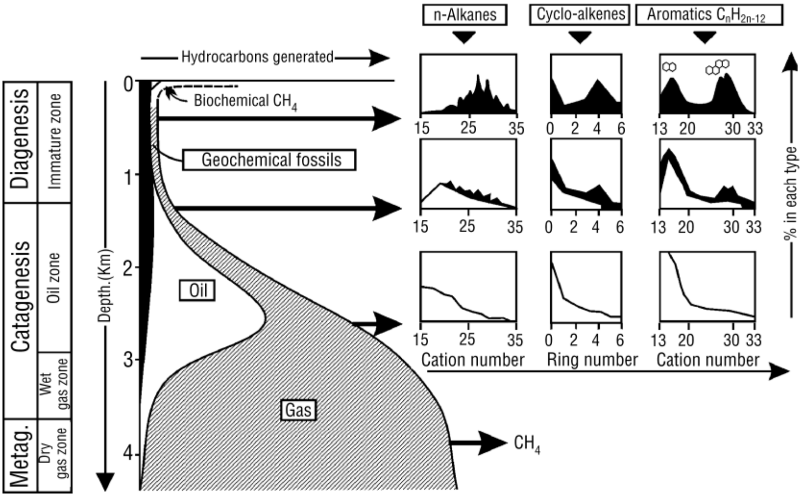


Figure 2. General scheme of hydrocarbon formation as a function of burial of the source rock. The evolution of the hydrocarbon composition for three compound classes is shown schematically in the insets. Depths are only indicative and may vary according to the actual geological situation (from Engel and Macko, 1993).

reordering the last H-depleted phase may ultimately form graphite, at the late metagenesis stage. This elemental evolution of kerogen is commonly illustrated in a diagram of H/C versus O/C atomic ratio or van Krevelen diagram (Figure 3).

In this figure different kerogen types are distinguished due to the different hydrogen and oxygen contents in the precursor materials (types I–II–III). The main evolution pathways, shown in Figure 3, involve the initial decreasing O/C atomic ratio due to the loss of small oxygen-bearing molecules (CO_2, H_2O) during diagenesis. Furthermore, in the stage of early catagenesis the release of bitumen species enriched in heteroatomic compounds has occurred. The significant decrease of the H/C atomic ratio has been lasted during catagenesis and mutagenesis until the kerogen could be transformed into an inert carbon residue.

2. GEOLOGICAL AND BIOLOGICAL FACTORS OF OIL COMPOSITION FORMATION

The depositional environment of the oil source rocks, its thermal evolution, and secondary alteration processes are the most important factors, which determined the composition of crude oil.

Their bulk properties as well as their chemical composition can characterize crude oils. Distillation of crude oil provides fraction profiles over a certain boiling range. The crude oil as well as the distillation fractions can be described in terms of density, viscosity, refractive index, sulfur content, and other bulk parameters.

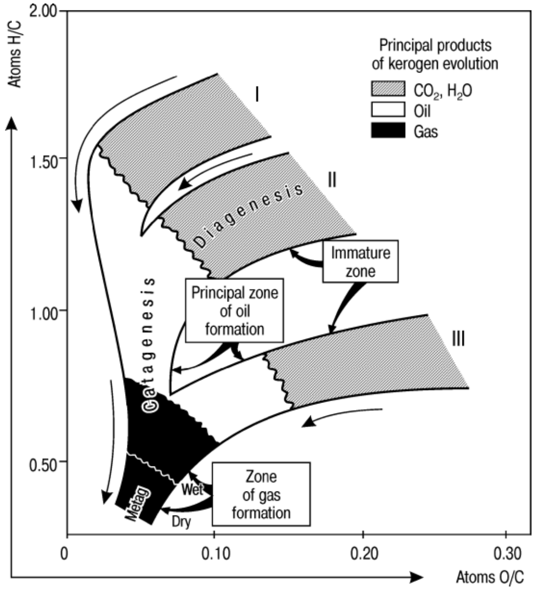


Figure 3. General scheme of kerogen evolution in a van Krevelen diagram (from Engel and Macko, 1993).

Chemically, crude oil can be divided into fractions of different polarities using column or thin-layer liquid chromatography.

The ternary diagram in Figure 4 shows the composition of crude oil samples based on the content of normal plus isoalkenes (paraffiins), cycloalkenes (naphtenes), and aromatic hydrocarbons plus polar, heteroatomic compounds (NSO).

This compound class subdivision provides an optimal spread of the data over the diagram, thus allowing a classification of oil into six groups.

Any composition of crude oil depends on the combination of various factors. Among the environmental factors, those that influence the nature of the organic matter in the source rock and its mineral composition are of primary significance.

Although all hydrocarbon source rocks are deposited under aquatic conditions, they may contain various amounts of land-derived organic matter. The biogeochemical terrestrial cycles can determine the contribution of organic matter, particularly in intercontinental basins and in the deltas of large rivers, which may extend far into the open sea. Terrestrial organic matter is usually enriched by such fractions as cellulose and lignin, which are not considered as oil precursors due to their oxidation state. On the contrary, the subordinate lipid fraction together with the biomass of microorganisms incorporated into source rocks yielded crude oils. These oils are rich in aliphatic units originating from waxes, fats, aliphatic biopolymers, etc., which present straight chain and branched alkanes (paraffines). Polycyclic naphthenes, particularly steranes, are present in trace quantities.

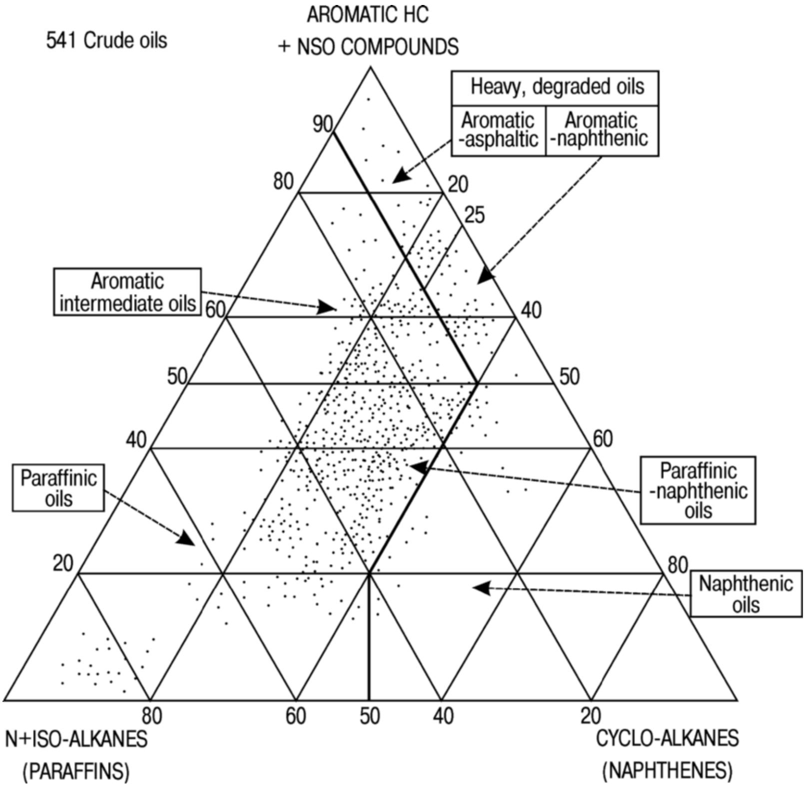


Figure 4. Ternary diagram showing the composition of six classes of crude oils based on the analysis of 541 oils (from Engel and Macko, 1993).

Marine organic matter is usually considered as type II kerogen (see Figure 1). This organic matter produces oils of paraffinic–naphthenic or aromatic–intermediate type (Figure 4). The amount of saturated hydrocarbons is moderate, but isoprenoid alkanes and polycyclic alkanes (like steranos from algal steroids), are relatively more abundant than in oils from terrigenous organic matter. Marine kerogen, particularly when it is very rich in sulfur, is particularly suited to release resin and asphaltenes-rich heavy crude oils at a very early stage of catagenesis.

The sulfur content of crude oil shows a close connection to the type of mineralogical composition of the source rocks. Typically oil is enriched by sulfur when source rocks include the sediments consisting of calcareous (e.g., from dinoflagellates or foraminifera) or siliceous shell fragments (e.g., from diatoms or radiolaria) of decayed planktonic organisms and at the same time containing abundant organic matter. This is related to anoxic conditions, which are required to preserve the organic matter. Under these conditions sulfate-reducing bacteria formed hydrogen sulfide or other reactive inorganic sulfur species. These compounds, reacting with organic matter and

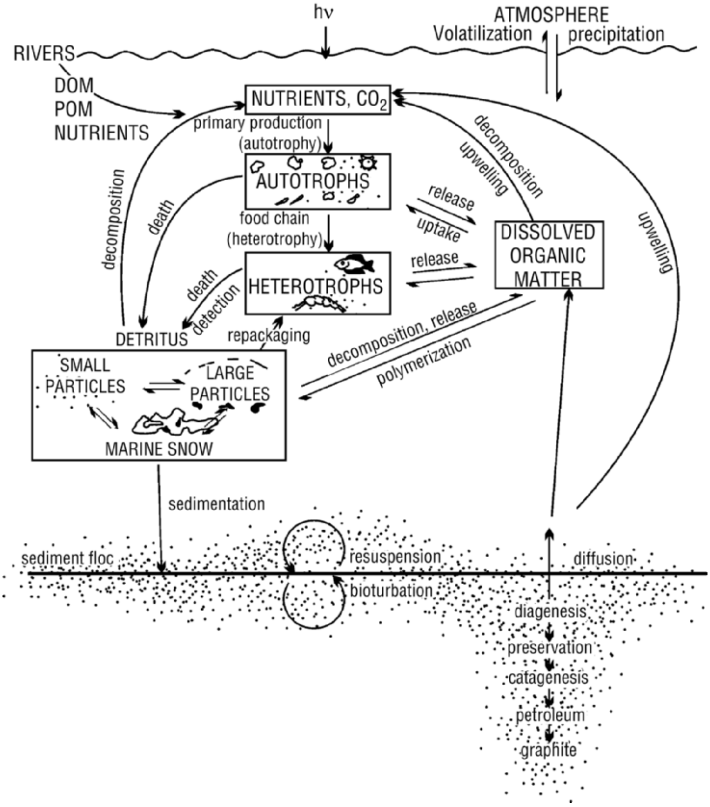


Figure 5. Schematic presentation of organic matter cycle in the ocean. DOM—dissolved organic matter; POM—particulate organic matter (from Engel and Macko, 1993).

sulfur, have been incorporated into the kerogen and furthermore into oil. Examples of such oils can be presented from onshore and offshore of southern California, northern Caspian onshore and offshore deposits and many carbonate source rocks of the Middle Eastern crude oils.

However, this sulfur would have been removed from oil when clastic rocks contained a high amount of detrital clay minerals abundant in iron. Under these conditions most H_2S generated by the sulfate-reducing bacteria would have reacted with iron resulting in iron sulfide depositions. Because terrigenous organic matter is commonly deposited together with detrital mineral matter (e.g., in deltas of large rivers), waxy crude oils derived from type III kerogen usually are depleted in sulfur.

A variety of physical, chemical and biogeochemical processes had worked in concert to alter the organic and inorganic composition of particulate and dissolved organic matter as it was transported through the water column (Figure 5).

Several factors may be named as of special importance: (1) the amount and composition of organic matter transformed from land surface or biosynthesized in surface

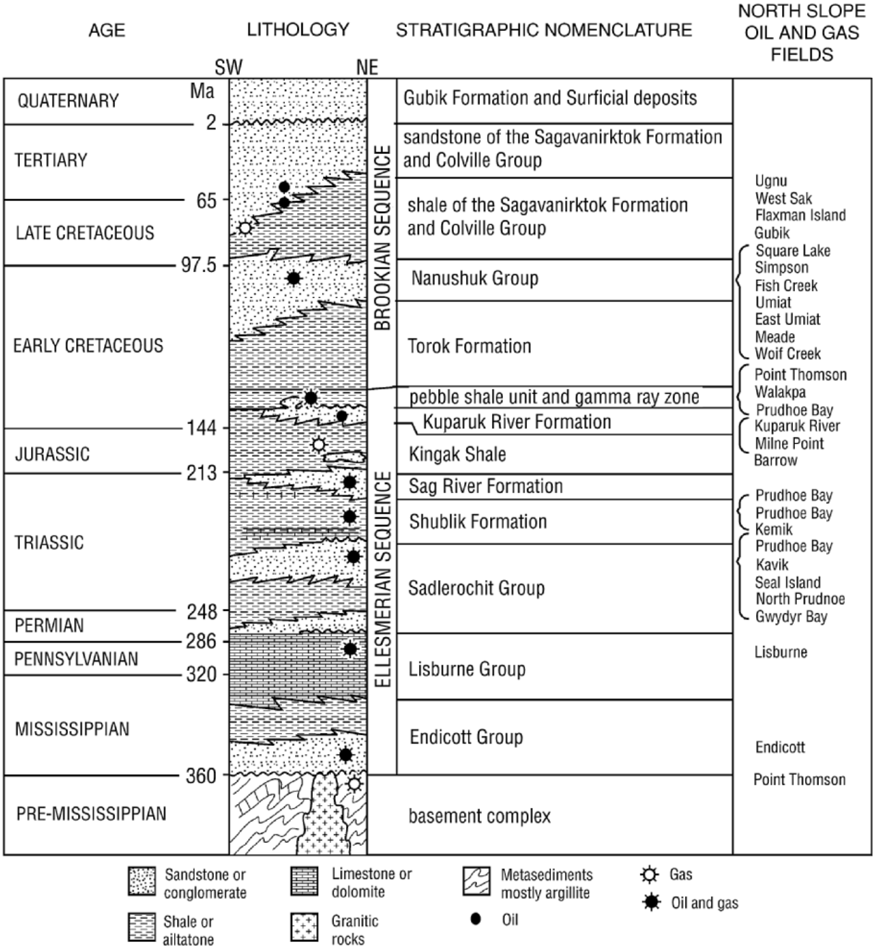


Figure 6. Stratigraphic section above economic basement for the central portion of the North Slope of Alaska. The Brookian and Ellesmerian sequences are separated at the major Lower Cretaceous unconformity. Both commercial and noncommercial oil gas fields are shown at right (from Engel and Macko, 1993).

waters; (2) the transport mechanism involved; (3) the biological community structure mediating the transformation mechanisms; and (4) physical characteristics of water, such as the water column depth, redox state, temperature, etc.

Finally, Figure 6 gives an idea of the ages of the oil sources' rocks.

An example is presented from the North Slope of Alaska, where the largest producing oil field was discovered in 1968. The petroliferous sedimentary rocks of the North Slope consist of Mississippian through Tertiary sandstone, conglomerates, shales, and carbonates. Two major rock sequences comprise the sedimentary succession. The older Ellesmerian sequence, deposited through the Early Cretaceous, is derived from a postulated northern landmass, whereas the younger Brookian sequence consisted of sediments shed from the southerly Brooks Range since the Early Cretaceous. So, the age of various oil deposits is from about 65 to 360 millions years.

3. PECULIARITIES OF ECOLOGICAL RISK ASSESSMENT IN OIL TECHNOBIOGEOCHEMICAL PROVINCES

Oil exploration and transport are accompanied by degradation of natural ecosystems due to huge amounts of various pollutants, from salt solutions up to crude oil leakages. Furthermore, as usual the oil fields are being explored very intensively, for instance, the predominant region of oil exploration in the north of west Siberia includes about 100,000 boring wells.

Practically all substances formed during oil exploration become inputs into geochemical and biogeochemical migration. They enable reactions among soil and water organic and mineral species, inhibit microorganisms and plant development, and finally create the technogenic anomalies of very toxic initial (crude oil) and transformed (separator oil, saltless oil) compounds. These anomalies have different sizes and configurations, and they may be transported either downward in soil-ground profiles or laterally to relief depressions. Sometimes these anomalies are stable on temporal and spatial scales for a long period.

3.1. Vertical Oil Migration

Any soil structure includes different size and shape holes and capillary interstices, which are usually very quickly overfilled by waste oil products in the place of leakage, and after that oil migrates download in soil profiles. The velocity of migration depends greatly on soil characteristics (content of organic matter, granulometric composition, permafrost, etc.), and the granulometric composition is the most important feature (Figure 7).

One can conclude that the oil is mainly accumulated in the organic layers with larger sorption ability and lesser oil leakage. If the oil products migrate to mineral soil layers, much content is shown in sandy and sandy loamy soil of light granulometric composition owing to their higher porosity. They are able to accumulate up to tens of grams per kilogram of soil matter. In spite of high sorption capacity, the heavy grounds do not show oil accumulation due to low porosity and low free inner volume of soil compartments.

High mobility of oil and oil products leads to permanent redistribution of pollutants between different blocks of soils and grounds, and it continues until all of the oil leans away. This is accompanied by a variable distribution of oil in the soil, sometimes differing among contrasting blocks by 2–4 orders of magnitude (Table 1).

The vertical distribution of oil products in a soil profile depends on the fluxes and ground level of soil-ground waters, which both temporally and spatially are very dynamic. In spite of being restricted due to low water solubility, migration of oil products with natural waters in the areas of oil pollution may significantly increase the distance of lateral pollutant transport with surface and sub-surface waters.

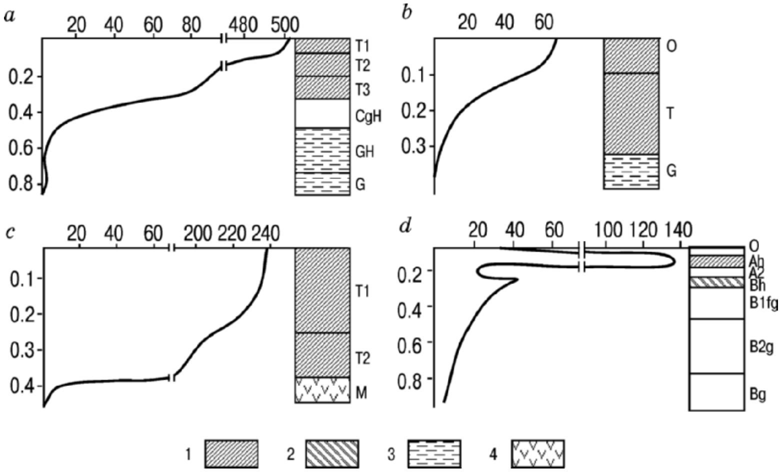


Figure 7. Vertical oil product distribution in different soils (Solntseva and Sadov, 2004): 1—peat layers, 2—clay layers, 3—loam layers, 4—permafrost.

3.2. Lateral Oil Migration

Lateral migration of oil pollutants depends on the relief of the site where oil leakage took place. The distance of oil migration is determined by a combination of soil and ground characteristics, or in other words, by soil structure in the path of oil migration.

Table 1. Content of oil products in the polluted soils of the oil exploration sites (Solntseva and Sadov, 2004).

Type of pollutant	Soil	Soil layer	Depth, cm	Oil products, g/kg
Separator oil	Tundra Peaty gley	T1	0–5	462.0
		T3	12–35	3.75
		Bg	35–53	0.46
		GH	53–85	0.67
Row condensate	Bog peaty	T1	5–10	21.50
		T2	10–20	81.70
		T3	20–35	1.30
Boring well solutions	Podzols	A0	0–9	11.65
		A0A1	9–13	1.87
		Bh	26–42	0.35
		BFe	68–80	0.10
		CG	80–90	0.51

Different soil sorption capacity to oil products leads to accelerating or slowing down the migration processes. Under similar soil characteristics, the distribution of oil pollutants depends on distance from pollution sources and decreases with an increasing distance. However, this situation is rather ideal and in the real conditions of oil exploration fields, especially in the northern areas, the soil structure is very complex. Accordingly, lateral migration of oil pollutants is very irregular and often the content of oil in soils nearby the pollution source is lower than that in a download position of relief. In a large extent it is characteristic for soil-geochemical catena when the upper landscapes have lower sorption capacity in comparison to down slope landscapes with high content of organic matter and relevant higher sorption ability. The latter is typical for tundra and forest tundra landscapes due to very complex soil cover. Furthermore, this is also accompanied by so-called chromatographic distribution of oil pollutants when the heavier fractions accumulate in the center of the pollution site and lighter fractions can migrate both vertically and laterally. Such a migration is followed by a primary redistribution of oil pollution and finally leads to the formation of different zones with varying ecological risk to human and ecosystem health.

3.3. Spatial and Temporal Evolution of Oil Pollution Areas

The shape, size, geochemical and biogeochemical structure of an oil pollution site is changes both temporally and spatially. The principal mechanisms of oil pollutant secondary redistribution are related to physico-chemical and microbiological destruction of oil species, their leakage from soil due to solution in water (soluble fractions) and downward motion under gravitation and inputting water pressure. During snow melting periods and after rains the oil products may migrate in soil cracks and splits, even those that have held for a long time. The secondary leakage of oil from light (sandy and sandy loamy) soils is more pronounced than from heavier (clay and silt) ones.

The secondary oil pollution redistribution is a very complex and long-term process. As usual it occurs during a few years after an accident and is accompanied by the gradual enlarging of the area of pollution both in vertical and lateral directions. Accordingly, the background soils are becoming polluted, however the level of pollution can be quite different depending upon the above mentioned features of soils and grounds (Figure 8).

Moreover, oil transformation products such as 3,4-benz(a)pyrene, can migrate even more rapid than the oil itself (Table 2).

These processes can form the “reverse” pattern of oil pollutant distribution when the content of pollutants is higher at the remote areas than at the closest parts of the pollution source.

Vast areas of underground pollution are formed after the infiltration of oil and oil products to soil and soil-ground waters. Furthermore, the formation of pollutant spots isolated from the total mass is also possible (Figure 9).

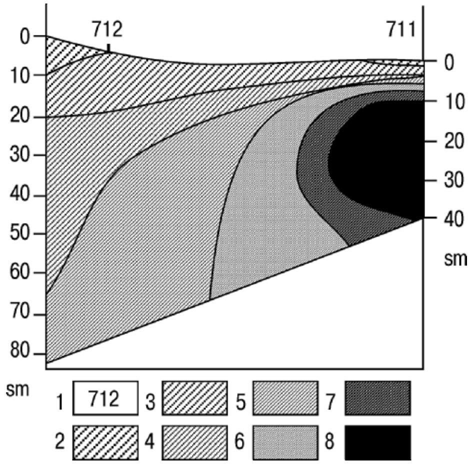


Figure 8. Download distribution of oil residues in soddy gley soil profile, 1 year after a separator oil pollution accident (Solntseva and Sadov, 2004) 1—profile numbers; 2–8 oil content, g/kg of soil: 2, <5; 3, 5–30; 4, 30–40; 5, 40–50; 6, 50–100; 7, 100–150; 8, >150.

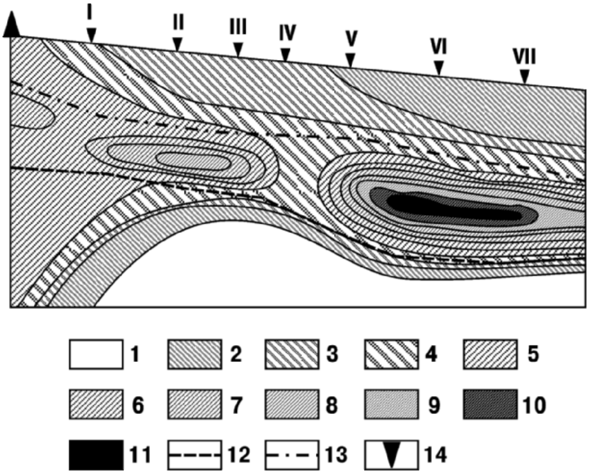


Figure 9. Shifting of oil concentration maximum outside of the primary area of pollutant distribution, 5 years after pollution accident (Solntseva and Sadov, 2004) 1–11, oil products, g/kg of soil: 1, <5; 2, 5–10; 3, 10–15; 4, 15–25; 5, 25–50; 6, 50–75; 7, 75–100; 8, 100–200; 9, 200–300; 10, 300–400; 11, 400–500; 12, the boundary of polluted soil-ground waters; 13, the boundary of capillary line; 14, monitoring points.

Table 2. Distribution of oil and 3,4-benz(a)pyrene at the different distance from pollution source in 1 year after accident in north taiga area, West Siberia, Russia (Solntseva, 1998).

Distance from pollution sources (m)	20	150	180	370
Oil content, g/kg of soil	424	504	287	36
3,4-Benz(a)pyrene content, ng/ kg of soil	72	242	290	16

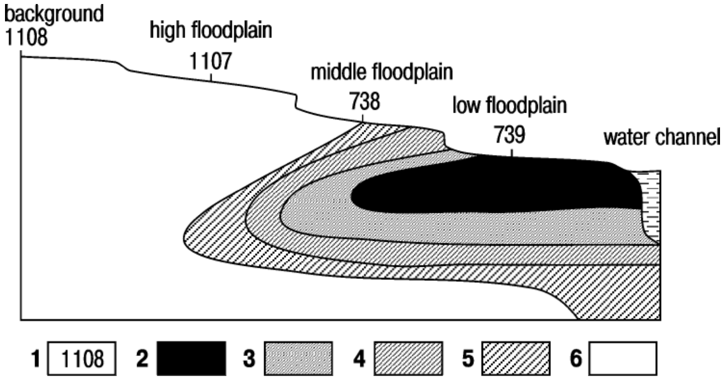


Figure 10. Schematic pattern of oil pollution transport onto river valleys (Solntseva, 1998).1, monitoring points; 2–6 oil content, g/kg of soil: 2, >15; 3, 15–10; 4, 10–5; 5, 5–1; 6, <1.

Multiple overlaying pollution sources and redistribution pattern at the areas of oil exploration fields is accompanied by the shifting of pollutant spoils for a long distance, in many cases up to river channels and river water pollution. The ground water pollution is a matter of fact (Figure 10).

The depth of oil pollutant infiltration is not restricted by the first water layer, and often this reaches the ground water. Under continuous perennial pollution, oil products can infiltrate into the deeper ground water layers where these pollutants are conserved and can drift to discharge areas after a long period. Hypothetically this discharge from one pollution source is possible at different watersheds (Figure 11).

These data show that the areas of underground oil pollution sometimes can exceed the areas of surface pollution, and underground processes of self-purification go slowly due to restricted chemical and microbiological destruction of oil components.

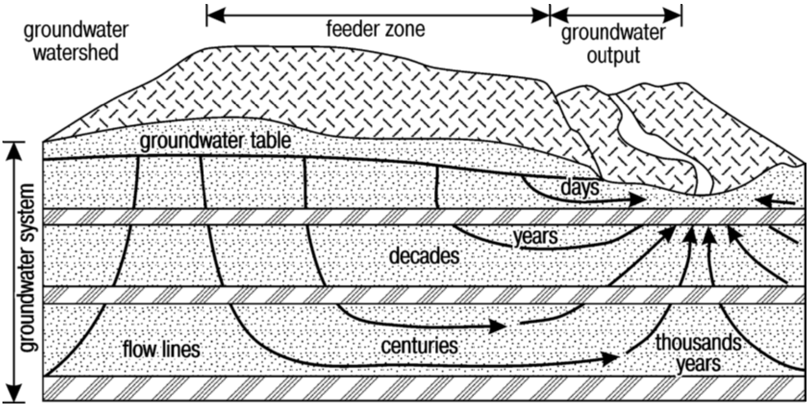


Figure 11. Principal scheme of temporal and spatial pattern for oil pollution transport.

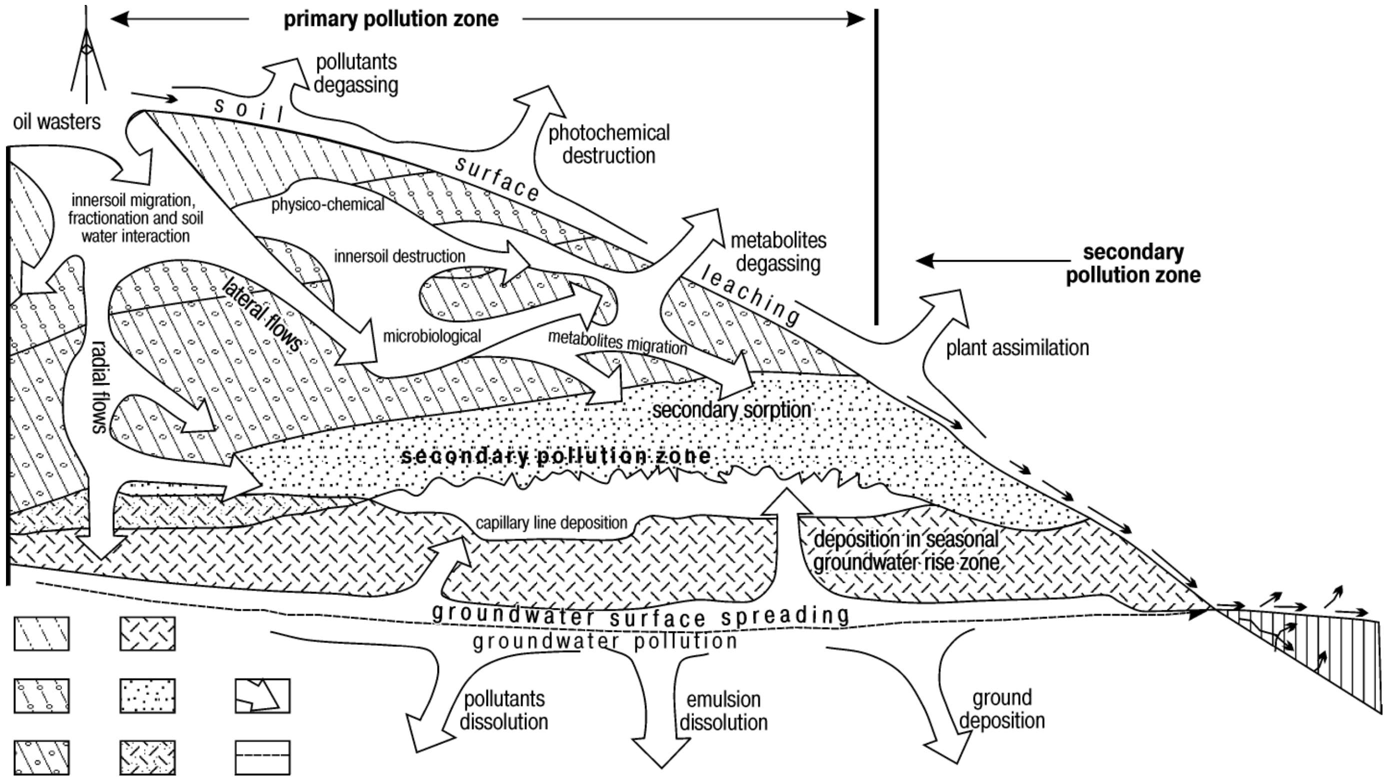


Figure 12. *Generalized model of geochemical and biogeochemical migration of oil pollutants in the environment (after Solntseva, 1998) 1–7, pollution zones: 1, predominant deposition of heavy oil fractions including asphalt resins; 2, predominant deposition of light oil fractions; 3, predominant accumulation of mineralized waters and light oil fractions; 4, polluted capillary line waters; 5, secondary inner soil pollution; 6, seasonal uprising of polluted soil-ground waters; 7, secondary pollution fluxes; 8, permanent level of soil-ground waters.*

3.4. Biogeochemical Feature of Environmental Risk Assessment

Of the number of oil pollution sources, the most dangerous ones are the permanent sources like oil storage pits where various toxic substances have been accumulating for a long time. During this time the infiltration of oil products into soil and soil-ground water forms vast secondary pollutant halos forwarded to the natural water fluxes. In some areas, for example, in north and middle taiga regions in the West Siberia, Russia, the longitude of these halos can exceed 0.5–1.0 km.

Thus the evolution of oil pollutant halos shows the differentiated pattern of oil migration and accumulation both at surface and sub-surface areas. The water migration enlarges significantly these areas. A generalized model of geochemical and biogeochemical migration of oil pollutants in the environment is shown in Figure 12.

Biogeochemical processes that are related to environmental risk assessment include the following: (a) active vertical and lateral migration of pollutants in soils; (b) degassing and photochemical destruction of oil products on the soil surface and inner soil fractionating of complex mixtures during their inputting; (c) involvement of oil metabolites in migration; (d) secondary enlargement of pollution areas due to migration of oil products with soil-ground waters accomplished by pollutants sorption, deposition in the capillary line zone and in the seasonal water uprising zone. As a result of these complicated processes the transformed biogeochemical and geochemical halo is formed with changing temporary and spatial boundaries. The mobility of these pollution halos is the characteristic feature of their existence that determines the quantitative assessment of ecological risk.

To emphasize our perspective, one should cite a known synonym of ecological risk, a chemical time bomb (CTB). In effect it says that the risk is uncertain as of now, but is both possible and highly probable.

CHAPTER 11

METALLOGENIC BIOGEOCHEMICAL PROVINCES

Ore deposits form natural biogeochemical provinces, which geographical placing is shown in Chapter 2. During exploration for ore, large quantities of metals are released into the environment. The technogenic transformation of areas neighboring the metal ores is influenced not only by technologies of exploration, transportation, and treatment, but also by geological, geochemical, biogeochemical and landscape factors. Ranking these factors, we should mention first of all the chemical and mineralogical composition of ores and their areas. The metal enrichment of local ore areas relating to the geochemical background is also of importance. Other factors like hydrogeological conditions, natural aquatic and aerial migration, anthropogenic transport of ore materials and their treatment products also determine the pollutant concentration in metalogenic biogeochemical provinces.

Landscape pollution related to anthropogenic activities in the exploited ore fields is accompanied by dust emissions from open pits, deflation and washing out of tails. The pollution is also enhanced by tailing runoff, emissions of ore materials during transportation, as well owing to solid waste and wastewater of agglomeration plants and mining and smelting factories.

Practically all the metals are toxic for human health, and the most pronounced toxicities are known for heavy metals.

According to chemical classification, heavy metals are elements with atomic mass exceeding 55 carbon units, i.e., starting from iron in Mendeleev's periodic table. Many heavy metals play an important role in biochemical and physiological processes of living organisms, from microbes up to human beings. They are actively taken up into biogeochemical food webs, accumulating on various biogeochemical and geochemical barriers in soil, plant and bottom sediments. Migration of heavy metals is enforced by different anthropogenic factors related to exploration and treating of non-ferrous metals, oil combustion where heavy metals are as the impurities, and acid deposition.

The term "heavy metals" includes various elements. Some of them, being nutrients, have essential biochemical functions (Fe, Cu, Zn, Mo, Mn, et al.), whereas these functions are unknown for others (Cd, As, Pb, Hg), and these elements are considered as toxics. One should mention that even the micronutrients consumed by living organisms are required only at microrates and in the greater doses they are also toxic.

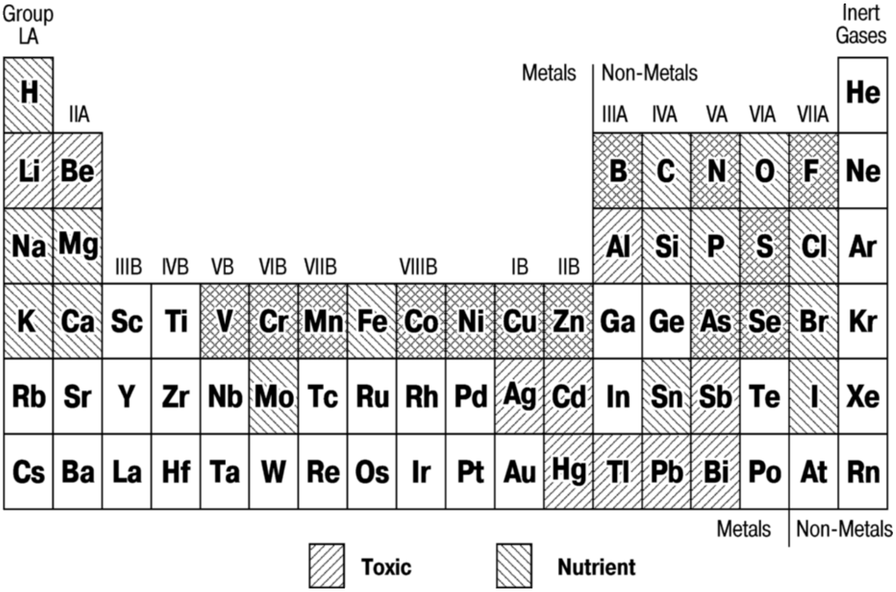


Figure 1. The periodic table showing the essential elements for plant or animal life with an indication of their toxicity.

During the 1970s–1980s, a famous catastrophe of human poisoning by mercury and cadmium struck Japan, and this attracted anthropogenic attention to ecological and ecotoxicological problems related to heavy metals. These were uncovered to be influenced by two characteristic peculiarities of the behavior of heavy metals in the environment:

(a) heavy metals are not transformed by natural processes into simple non-poisoning compounds like persistent organics;

(b) heavy metals are easily adsorbed, concentrated and conserved during long periods in soil mineral–organic matter and bottom sediments of aquatic ecosystems.

These two factors are responsible for long-term environmental functions of heavy metals and pronounced ecological risk.

1. ENVIRONMENTAL RANKING OF METAL TOXICITY

1.1. Heavy Metal Migration in Biogeochemical Food Webs

Like other chemical elements, heavy metals are natural species (Figure 1).

Due to the complex influence of various geological and biological processes during Earth's long history, many heavy metals are irregularly distributed in the biosphere.

In some regions this led to natural enrichment of ecosystems by different elements, in others, to natural depletion. It is known that complex biological, geological and chemical influence is jointly determined as the biogeochemical one, and in the beginning of the 20th century, studying the behavior of heavy metal in the biosphere led to the new discipline, biogeochemistry. In 1929, Vladimir Vernadsky founded the Biogeochemical laboratory in the USSR Academy of Sciences (at present Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences). V. Vernadsky and his colleagues A. Vinogradov and V. Kovalsky have carried out biogeochemical mapping of huge area of northern Eurasia in the former USSR. Biogeochemical regions and provinces differing in heavy metals content were delineated. It was found that in many biogeochemical provinces the enrichment of biogeochemical food webs by some heavy metals is accompanied by depletion of other metals, which creates extremely complex biogeochemical structure of terrestrial and fresh water ecosystems in these provinces. Moreover it is shown that the depleted content of many heavy metals is equally dangerous as the excessive contents.

This complex biogeochemical structure with non-optimal content of heavy metals and some micronutrients induces the development of various endemic diseases of humans and animals (Bashkin, 2002). The biogeochemical structure of the modern biosphere is discussed in more detail in Chapter 2.

Metals from the 6th period in Mendeleev's table are potentially the most toxic (Os, Ir, Pt, Au, Hg, Tl, Pb), however small water solubility of their prevalent salts decreases sharply this toxic influence (Table 1).

In the environment, metals are common as a chemical species, and as usual the metal–organic species are more toxic. For example, the inorganic lead and mercury species are less toxic for living organisms than the organic ones (methyl mercury, tetraethyl lead). However inorganic arsenic compounds are more toxic than organic

Table 1. Classification of chemical elements according to their water solubility, natural abundance and toxicity.

Widely distributed and low toxic metals			Toxic but low soluble and rarely distributed metals		Very toxic and widely distributed metals[a]		
Na	C	F	Ti	Ga	Be	As	Au
K	P	Li	Hf	La	Se	Co	Hg
Mg	Fe	Rb	Zr	Os	Te	Ni	Tl
Ca	S	Sr	W	Rh	Pd	Cu	Pb
H	Cl	Al	Nb	Ir	Ag	Zn	Sb
O	Br	Si	Ta	Ru	Cd	Sn	Bi
N			Re	Ba	Cr		Pt

[a] The most dangerous species especially upon their accumulation in wastes

Table 2. Technophility index of heavy metals.

Metal	Mn =	Fe <	Ni <	Cr <	Zn <	Cu =	Ag <	Hg =	Pb <	Au <	Cd
Technophility index	1	1	2	4	10	20	20	30	30	60	140

species, and fishes can accumulate arsenic as arsenolipides that are practically non-toxic. The most organic and inorganic compounds of tin are non-toxic; the known exception is tri-*n*-butyl species like tri-butyltin that is used as a biocide for preventing the growth of mollusks on the submerged parts of marine ships.

1.2. Sources of Heavy Metals and Their Distribution in the Environment

Global distribution of heavy metals in the biosphere is related to their technophility that is determined as the ratio of global annual exploration to their average concentrations in the Earth's core (Table 2).

The value of technophility indices testifies to a higher actual and potential danger of such metals as Pb, Hg, and Cd in comparison with, let's say, Mn or Fe. These are also supported by registered changes in the global emissions of heavy metals into the atmosphere and oceans (Table 3).

The number of anthropogenic sources includes the followings:

- industrial ore treatment;
- usage of metals and metal-containing materials;
- runoff of heavy metals from wastes;
- human and animal excretes.

Table 4 shows a typical list of heavy metals and relevant industries. One should note that in some technological processes a wide spectrum of metals is used (for example, production of pesticides, electronics, non-ferrous smelting, electrochemistry),

Table 3. Global heavy metals emissions into atmosphere and oceans (10^3 tons per year).

	Emissions to atmosphere			Emissions into oceans	
Element	Natural	anthropogenic	F*	Natural weathering	Municipal wastes
Cd	0.29	5.5	19	36	3
Pb	4	400	100	110	15
Cu	19	260	13	250	42
Zn	36	840	23	720	100

F*—mobilization factor as a ratio of anthropogenic emission into the atmosphere to the natural one

Table 4. Typical use of heavy metals in different technological processes.

Technological processes	As	Cd	Cr	Cu	Pb	Hg	Se	Zn	Ni
Exploration and treatment of non-ferrous metals	×	×	×	×	×	×	×	×	×
Electrochemistry		×	×	×	×	×	×		×
Production of pesticides	×				×	×		×	
Electronics				×	×	×	×		
Dry cleaning	×		×	×		×		×	
Metal surface treatment			×	×				×	
Chemical industry			×	×		×			×
Production of explosive substances	×					×	×		
Rubber and plastics production				×		×		×	
Batteries and accumulators production		×				×		×	×
Pharmaceutical production	×				×	×			
Textile production		×	×					×	
Oil and coal combustion and treatment	×	×	×	×	×	×	×	×	×
Pulp and cardboard production						×			
Leather processing			×						

whereas in others, only one element is used (for example, Cr using in leather-processing or Hg in the pulp industry).

Emissions of actually and potentially dangerous toxic elements may influence the human and ecosystem health on local, regional and global scales. Accumulation of toxic metals may be in soils, waters, bottom sediments and biota. For example, the accumulation of heavy metals in the upper layers of bottom sediments and glaciers occurring during the 20th century is shown in many recent studies.

The global cycle of lead was anthropogenically changed to the maximal extent owing to the use of TEL as a petrol additive (Table 5). The regional aluminum cycle was changed due to acid depositions (Bashkin and Park, 1998; Bashkin, 2003). Differing from lead and aluminum, chromium influence is local, nearby electrochemical and leather-processing plants; Cr-VI form is the most toxic and it is primary regulated. As it has been mentioned, formation of organic compounds accelerates the mobility of heavy metals, and accordingly their toxicity is also enhanced. Migration of many heavy metals increases upon soil and water acidification.

Table 5. Anthropogenic changes in cycles of heavy metals.

Metals	Scale of changes			Diagnostic media	Mechanism of release	Ways to living organisms
	Global	Regional	Local			
Pb	+	+	+	Glaciers, bottom sediments	Volatilization	Air, food
Al	–	+	–	Soils, waters	Dissolution	Water, food
Cr	–	–	+	Soils, waters	Dissolution	Water
Hg	(–)	+	+	Fishes, bottom sediments	Alkilation	Food, air
Cd	(–)	+	+	Soils, waters, bottom sediments	Dissolution, volatilization	Food

One can see that most environmental impacts in global, regional and local scale are related to mercury, lead, and cadmium. These metals are considered in more detail further.

2. USAGE OF METALS

2.1. Anthropogenic Mercury Loading

Mercury is a relatively rare chemical element. In the lithosphere it occurs mainly as sulfides, HgS. Mercury sulfide comes in two forms: cinnibar, which is black, and vermillion. In some places mercury exists in a small proportion as free chemical species.

Mercury refining involves heating the metal sulfide in air in accordance with the following reaction:

$$HgS + O_2 \rightarrow Hg + SO_2.$$

Gaseous mercury is condensed in a water-cooled condenser and redistilled for sale.

At present industrial mercury uses are connected with electric batteries, electric tungsten bulb, pulp bleaching and agrochemical production.

Mercury batteries are used widely in everyday life, in applications such as cameras and hearing aids. About 30% of U.S. production of mercury is used in this way, the reason being the constancy of the voltage in the mercury battery, almost to the point of complete discharge.

The electrical uses of mercury include its application as a seal to exclude air when tungsten light bulb filaments are manufactured. Fluorescent light tubes and mercury arc lamps that are used for street lighting and as germicidal lamps also contain mercury.

Mercury is consumed in the manufacture of organomercurials, which are used in agriculture as fungicides, e.g., for seed dressing.

2.2. Anthropogenic Lead Loading

Lead occurs in nature as the sulfide, galena, PbS. Lead is more electropositive than mercury, and roasting the sulfide in air forms lead oxide.

$$2\mathrm{PbS} + 3\mathrm{O}_2 \rightarrow 2\mathrm{PbO} + 2\mathrm{SO}_2.$$

The oxide is then reduced to metal with coke. The impure metal is refined by electrolysis.

Major anthropogenic sources of lead include the use of Pb as a petrol additive, Pb mining and smelting, printing, Pg paint flakes, sewage sludge and the use of pesticides containing Pb compounds, like lead arsenate.

A well-known use of lead is also in the familiar lead–acid storage battery. This device is an example of a storage cell, meaning that the battery can be discharged and recharged over a large number of cycles. The lead–acid battery is familiar as a battery in your car.

An important disadvantage of the lead–acid battery is its heavy mass, on account the high Pb density. The second disadvantage is that used car batteries distribute a lot of lead into the environment; despite recycling, they are the major source of lead in municipal waste. Recently, the recycling of lead–acid batteries has created problems in the local environment around recycling plants. Most of these plants are located in developing countries of Asia and Latin America and they process batteries imported from industrialized nations. Levels of Pb as high as 60,000–70,000 ppm have been measured in soils in the vicinity of Pb-battery recycling plants in the Philippines, Thailand and Indonesia. The relevant health effects have been observed. This appears to be one example where trying to conserve resources and minimize pollution has gone seriously wrong. In California, soil contaminating 1000 ppm of Pb is considered to be hazardous waste and its disposal is strictly regulated.

Human activity has changed the intensity of natural biogeochemical fluxes of lead during industrial development. However, the history of lead use is the longest of any metals. The period of relatively intensive production and application of lead is about 5000 years. Lead has been used as a metal at least since the times of the Egyptians and Babylonians. The Romans employed lead extensively for conveying water, and the elaborate water distribution systems allowed by bending of the soft metal lead. Through the Middle Ages and beyond, the malleability of lead encouraged its use as a roofing material for the most important constructions, like the great cathedrals in Europe. The modern production of lead is $n \times 10^6$ tons annually (Figure 2).

How Risky are the Pb Background Levels?

The long-term uses of lead explain why this element should be so widely dispersed in the environment. In this regards one should answer the question as to what is the natural background level of lead. At present this is a question of controversy. Lead

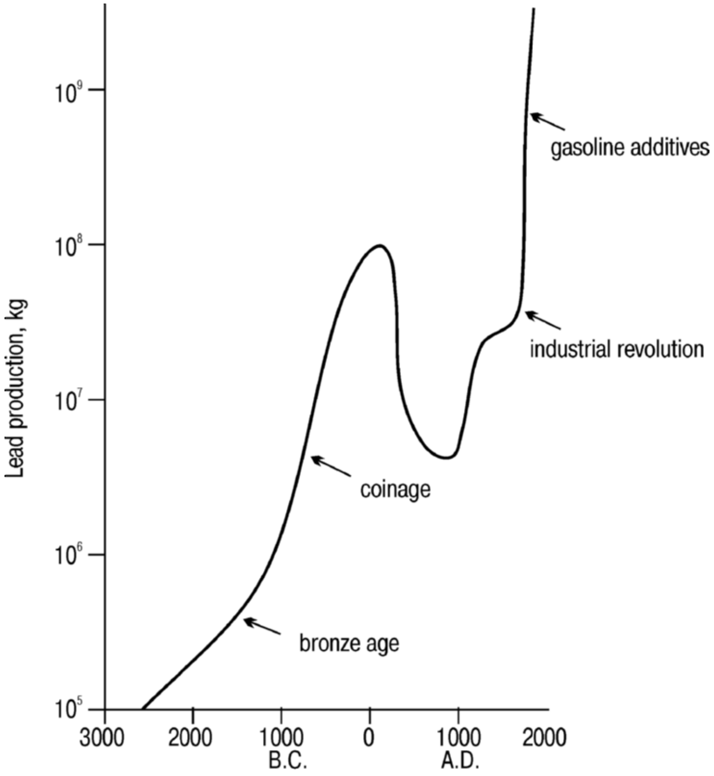


Figure 2. Historical production and consumption of lead (Bunce, 1994).

levels in modern people are frequently 10% of the toxic level. Some analyses of ancient bones and ancient ice cores seem to suggest that this relatively high level is not new and has previously existed in the environment. Accordingly, the assumption was made that life evolved in the presence of this toxic element.

However, recent researches have challenged this viewpoint, claiming that these lead analyses in ancient samples are the results of inadvertent contamination of the samples during their collection and analysis. Dr. C. C. Patterson of the California Institute of Technology argues, for example, that ice cores are contaminated by lead from drilling equipment. His data of chemically careful Pb analysis on Greenland ice cores show the increasing trend of lead pollution (Figure 3).

Similar data reported on the content of lead in meticulously preserved old skeletons contain 0.01–0.001 times as much lead as contemporary skeletons.

A different perspective is provided in the analysis of pre-industrial and contemporary Alaskan Sea otter skeletons. The total concentrations of lead in the two groups of skeletons were similar, but their isotopic compositions were different. The pre-industrial skeletons contained lead with an isotopic ratio corresponding to natural

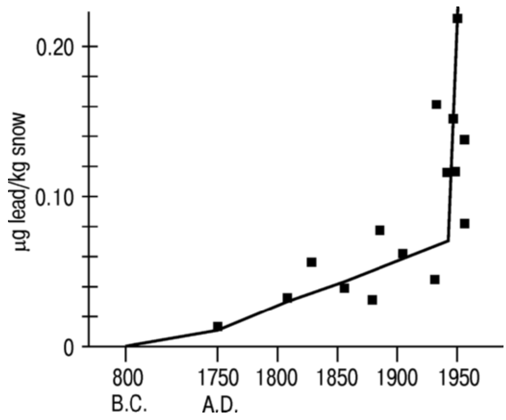


Figure 3. Increase of lead in Greenland snow, 800BC to present (Bunce, 1994).

deposits in the region, while the ratio in the contemporary ones was characteristic of industrial lead from elsewhere (Smith et al., 1990).

2.3. Anthropogenic Cadmium Loading

Cadmium occurs naturally as sulfide co-deposited with zinc, copper, and lead sulfides. It is produced as a by-product in above-mentioned metal processing. Similar to lead and mercury, this heavy metal has no known biological functions in living organisms, and accordingly its accumulation in food and water leads to undesirable consequences to biota. Cadmium toxicology is related to dangerous influence to CNS and excretion systems, firstly, on kidney.

Cadmium content in soils rarely exceeds 0.01–0.05 ppm, however during recent years there has been an increasing tendency to its content in agricultural soils due to high application of phosphorus fertilizers, including cadmium as a mixture since this element like other heavy metals is incorporated into various phosphorus-containing ores. Moreover acid deposition increases cadmium mobility and its transport in biogeochemical food webs. Cadmium is easily taken by agricultural crops, especially by potato and wheat, and accumulated in human and animal food. Its input to soil and crops is enhanced by use of municipal wastewater effluents as fertilizers especially on acid soils or upon acid depositions.

There are also natural geochemical anomalies where soils are enriched by cadmium, for example, in the central parts of Sweden. Here the cultivation of crops accumulating cadmium (grains, potato, some grasses) is not recommended. In the coastal marine areas the cadmium mobility in soils is stimulated by its complexation with chlorine.

Food is the main source of cadmium input to human organisms, however the smokers take in a much larger amount of this element with tobacco smoke. The average period of cadmium storage in the human body is 18 years.

The World Health Organization recommends setting the upper limit of cadmium uptake as 1 μg/day, however in some regions this value is exceeded due to both natural background and environmental pollution.

In aquatic ecosystems, cadmium content depends on the underlying geological deposits and soils in the watersheds. The safety value is 10 ng/L. Cadmium is very toxic to fishes and water invertebrates at rates of a few mg per kg of body weight. Cadmium content in the river water in many industrial regions (Rhine, Mississippi, Volga, Danube, et al.) was highly elevated a few decades ago, but due to serious environmental protection efforts in Western Europe and USA in the 1980s–1990s, the current cadmium content in water is significantly decreased.

Cadmium production is related to its use in electrochemical plants for metal galvanization (about 50%), for nickel–cadmium batteries and special alloys.

Similar to other batteries and accumulators, the burying of cadmium batteries is a very great problem in every country, and Cd seepage from landfills and waste sites (in addition to fertilizers) is responsible for soil and water pollution and environmental risks to human and ecosystem health. The same is true for lead and mercury.

3. TECHNOBIOGEOCHEMICAL STRUCTURE OF METAL EXPLORATION AREAS

3.1. Iron Ore Regions

In many countries of the World, iron deposits are widespread however the industrial iron explorations are concentrated in a few sites. For example, in Russia this is the iron deposit fields in the Kursk region and Ural mountain area, in Germany, the Ruhr area. During exploration the technogenic mechanical transformation of the environment occurs and it is related to the extraction and transportation of huge amounts of rock materials. Accordingly composition of pollutants depends on the genetic ore types. When the metal sulfides dominate, the sulfur iron biogeochemical provinces are formed. Furthermore, iron and sulfur seep from the rock and tails and migrate with acid waters for a long distance. Moreover, the area of air transport is also large, for instance, from the Kursk iron pits the iron containing dust is transported for 10–15 km.

As a rule, the iron ores are treated either nearby the exploration (in the south Ural, Russia) or by short distance shipping operations (in Kursk-Lipetsk area, Russia). Environmental pollution is mainly related to the iron melting plants where different pollutants are accumulated. For instance, in the South Ural area, iron treatment is concentrated in the city of Magnitogorsk, and during 70 years period of this activity a circular 2–5 km zone with high content of lead, zinc, copper and other heavy metals was formed. The concentrations of pollutants in this area exceed the background levels by 30–60 times. In addition to heavy metals, the PAH pollution is also pronounced due to organic fuel combustion and coke-chemical production. The example of PAH's pollutant is 3,4-benz(a)pyrene, and its content exceeds the background level by 2 times. The hydrocarbon pollution is widespread up to 30 km from Magnitogorsk. However, low accumulation of heavy metals in plants is monitored owing to local peculiarities of soil composition (high carbonate content), emission products composition (water insoluble forms of metals) and prevalent emission of iron dust (Perelman, Kasimov, 1999).

3.2. Non-Iron Ore Areas

These regions are in the mountainous areas. In the USA, these are the Rocky Mountains, in Europe, the Alps, in Northern Eurasia, the Ural, Altai, etc., mountains. For instance, in the Ural and Altai mountains, Russia, there are areas where the content of copper, lead, zinc, mercury and many other metals in the biogeochemical food webs exceeds the background levels by 3–5 times. These areas are called "natural biogeochemical regions" (see Chapter 2). Natural biogeochemical provinces were formed in the ore areas where the content of different metals in various components of biosphere (grounds, soils, waters, plants) exceeds the background values by 1–2 orders of magnitude, and these provinces occur on areas of $n \times 10^1$–10^2 km^2. In some biogeochemical provinces the concentration of non-ferrous metals (tin, cadmium, and molybdenum) exceeds the local background by 3–4 orders of magnitude, and that is accompanied by the natural enrichment of the biogeochemical food webs. During the industrial exploration of metal ores the environmental pollution takes place and this enhances the ecological risk of endemic diseases of human and animals.

The metals sulfides are the most dangerous since after aerobic weathering they are transformed into water-soluble sulfates of different metals. Accordingly, in the areas of non-ferrous and rare metal ore exploration and treatments, the acid sulfate landscapes are formed with high content of toxic metals. The biogeochemical technogenic provinces are known, for instance, copper–nickel provinces in the Kola Peninsula, Fennoscandia; molybdenum provinces in the Caucasian region, copper and chromium–nickel ones in the South Ural, poly-metal ones, in the Pacific coast of eastern Eurasia (Russia, China, and Korea), etc.

In many mountain-industrial areas there are 3–4 landscape-functional zones with different extents of the anthropogenic transformation of natural environments. As a rule, *the first zone* is the spatial complex joining mines, pits and tails site area with almost whole degradation of soil and vegetation cover and high metal concentrations in dust, technogenic depositions, waters and plants.

The second zone is the area of direct impacts of mines and metal treatment facilities with a complete or very significant transformation of the initial natural structure due to soil degradation and sealing under excavation sites and constructions and pollution by toxic emissions, waste and runoffs. During metals smelting and agglomeration their contents in the environment increase. The metal and dust content in the air of this 2–3 km zone exceeds the maximal permissible levels (MPL) by 1–2 orders of magnitude and even more. We should mention that the metal concentrations decrease as follows: emissions—atmospheric depositions (snow and rain)—soils. The area and configuration of these technogenic anomalies depend on the ways in which the pollutants enter the atmosphere (explosion character in the pit or stack hight), meteorological conditions (wind direction and velocity, inversion frequency, etc.), and relief (plains, mountains). Generally the content of pollutants in the environmental media decreases from point pollution sources (mines, pits and treatment . . . plants) exponentially, i.e., the air pollution rates inversely proportional to the quadratic value of distance from pollution source. Soil and vegetation pollution is similar, however there are some exceptions like the area of Sudbury nickel smelter, Ontario, Canada where the construction of the 400 m high "superstack" has promoted emission dilution and recolonization of vegetation in the Sudbury region.

The third zone of strong pollution of air, soils, snow and plants in the plains occurs in the 3–5 km area surrounding the pollution source. The pollutant concentrations are lower as a rule by 1–2 orders of magnitude than in the first and second zones. In the mountains the most important is the slope exposition and downward direction of river valleys where the pollution is monitored in water and bottom sediments at distances of 10–15 km (Perelman, Kasimov, 1999).

The forth zone of the moderate spatial pollution has unstable form and occurs in an area surrounding the pollution source from 3–5 up to 10–20 km. The background landscapes are spread usually further 15–20 km from the sources of mine emissions and runoffs (Perelman, Kasimov, 1999).

In accordance with this zoning the environmental risk assessment procedure should be developed, especially those related to exposure pathway and risk characterization steps.

3.3. Uranium Ores

The characteristic feature of the uranium exploration industry is the radioactivity of all wastes. The quality of these wastes, such as radon, radioactive aerosols, and dust emitted to the atmosphere, depends on mine production and the radioactive budget in the mines. For example, middle range mine exploring the ores with $n \times 10^{-1}$–10^{-2}% of U content emits to the atmosphere up to 8×10^{10} Bq/day of radon.

The amount of solid waste depends on the method of uranium ore exploration. By deep mining, each ton of ore is supplemented by 0.2–0.3 tons of waste ores, and by open pit mining, per 1 ton of ore up to 8–10 tons of excavation materials are produced. Moreover, uranium ores contain from 5% up to 25–30% of waste ores, which are deposited as mine tails.

The liquid mine wastes are mainly represented by underground drainage waters (up to 2000 m^3/day and even more), as well as low radioactive waste water from uranium treatment plants (from 100 up to 300 m^3/day). The uranium isotopes, radium-226, thorium-230, polonium-210, lead-210 are the most dangerous. Their total activity in waste waters reaches often 10–50 Bq/L at the MPC values for natural waters of 0.111 Bq/L.

The uranium mine tails contain the equal masses of water and solids. Furthermore the treatment of each ton of uranium ore is accompanied by receiving about 3 tons of rafinate, and finally the treatment of 1 ton of uranium ore gives about 4 tons of liquid wastes of different chemical composition, which in turn depends on the treatment technology.

The relative area of mine solid waste tails (per 100,000 M^3 of rock mass) is 0.7–0.8 of the total area. On average, the disturbed areas of uranium ore exploration site are partitioned as follows: 32.3% of disturbed land is occupied by dumps, 27.2%, by pits, 20.3%, by industrial areas, 13.3%, by tails, and about 10%, by other types of land disturbance.

The further transformation of uranium exploration areas depends on the landscape biogeochemical conditions. Let us consider two examples of different conditions, dry steppe and permafrost taiga regions (Perelman, Kasimov, 1999).

Biogeochemistry of Dry Steppe Landscapes in Uranium Mine Areas

Dry climate conditions depress the uranium species from soils and grounds, however owing to strong and frequent winds, the aerial migration of uranium containing dust from dumps and tails take place. This favors the pollution of nearby settlements. The transpiration accumulation of uranium salts is monitored in depressions and relevant salted soils, and this process is connected with mine waste water runoff. This gives an origin of uranium containing soils—solonchaks where the content of a given element exceeds the background level by a few orders of magnitude. Furthermore, uranium absorbed by plants and finally by animals and humans as the top consumers in the biogeochemical food webs. The risk of uranium induced endemic diseases increases in such areas. Under deep mining method of ore exploration connected with water dissolution of uranium deposits, simultaneously some other toxic elements like selenium and other uranium chemical co-species are mobilized, and it leads to poisoned water. The further accumulation of uranium is connected not only to natural biogeochemical barriers like carbonate and organic layers in soils but also to the new formed technogenic barriers such as waste ore dumps and tails.

Biogeochemistry of Permafrost Taiga Landscape in Uranium Mine Areas

In this area the role of wind is related mainly to transport of polluted snow and to a lesser extent, to dump deflation. The perennial permafrost determines the migration of uranium and other radionuclides. Its influence depends on the type of spatial distribution: in the northern areas it is a continuous layer whereas in the south, very local ones. For instance, in the mountains of south Siberia, the permafrost islands are common in the north exposition of range slopes. In the upper layers of taiga permafrost soils the leakage of uranium species is common, however the opposite process—cryoturbation—prevents the deeper percolation of these species. The development of a solifluction process favors a long distance migration of uranium species together with soil small particles even on the flat slopes. The local pedogenic processes accelerate also the uranium migration as complexes with organic matter. Such a migration is also monitored in bottom sediments and river water. In some cases, the separate migration and accumulation of uranium and radium species takes place: uranium species are concentrated on the reduction barriers in the peat whereas the radium species, on the clay barriers formed due to mechanical weathering of geological rocks.

The moist climate determines both very low background concentrations in the natural waters ($n \times 10^{-4}$ ppm) and relatively low content in the technogenic runoff due to dilution. The accumulation of uranium in plants occurs due to the biogeochemical barrier, however the details of biogeochemical migration and accumulation depend on the area since the permafrost is widespread in the huge taiga zone with different soil and relief conditions. Accordingly, the ecological risk assessment and management will be also different.

3.4. Agricultural Fertilizer Ores

Apatite exploration takes place in various regions of the World, and the most known are Kola Peninsula (Russia) and northwest Africa (Morocco). In both places, the apatite ores contain not only phosphorus as a main element but also many heavy metals, which are toxic for humans and animals. The given elements are F, As, Y, some rare earth species, Sr, Pb, Cd, Sn. The underground waters in these regions are enriched by F, Li, Nb, some rare earth species with alkaline reaction that facilitates the migration of many ore elements. Some phosphorus containing ores are radioactive owing to the mixtures of uranium and thorium.

The toxic impurities of phosphorus ores are conserved in phosphorus fertilizers produced from these ores, and finally they are accumulated in the agroecosystems (see Chapter 13). These pollutants can enter into biogeochemical food webs and increase the ecological risk especially under acid soils distributed in many regions of the World (Europe, Asia and North and South America).

CHAPTER 12

URBAN BIOGEOCHEMICAL PROVINCES

Urban biogeochemical provinces are formed by extensive urbanization, which is a process that leads to permanent increase of urban areas and population, transformation of rural population living style to the urban one, enhancement of cities' role in social and economic development, as well as formation of urban animal and plant population with very specific features. This urbanization process includes also development of urban landscapes as a specific sphere of land use organization in the urban agglomeration areas (Kurbatova et al., 2004). An integral part of urban development is increasing environmental pollution and relevant ecological risks for human and ecosystem health due to disturbance of biogeochemical food webs (Bashkin, 2002).

1. CRITERIA OF URBAN AREAS CLASSIFICATION

One of the most usable approaches to distinguishing urban areas from other populated ones is the formal approach of population number. This approach is in wide usage in many countries, for example, in Denmark, where the area with a compact population of more than 250 people is considered as a town. However the functional approach, taking into account the labor types of the local population is also applied. For instance, in Russia the urban status requires that 75% of the local population should be employed in non-agricultural labor activity and the number of people should not be less than 12 thousand.

Nevertheless, a common approach is absent in spite of UN recommendations to consider as a city any area with compact population more than 20 thousand. Sometimes city status has historical roots and this is often found in Europe. For example, Vereya city was a large and important place during the historical development of Russia, however at present its role has been lost and its population has decreased up to a few thousand but still maintains city status.

2. ECOLOGICAL PROBLEMS OF URBANIZATION

Urbanization is the most important global process. At present the World's urban population is about 3 billion or very close to 50% of all global inhabitants. During

Table 1. Urban population growth (Golubev, 1999).

	Population, million			Urban population rate, %		
Continent	1975	1995	2025	1975	1995	2025
Africa	104	250	804	25	34	54
Europe	454	535	598	67	74	83
North and Central America	235	332	508	57	68	79
South America	138	249	406	64	78	88
Asia	592	1,198	2,718	25	35	55
Oceania	15	20	31	72	70	75
Global	1,538	2,584	5,065	38	45	61

the 1990s the urban population growth was 2.5% whereas the rural one, is 0.8%. In developing countries the daily increment of urban population is about 150 thousand.

The main reasons for urban population growth are related: (a) local migrations from rural areas as well as from other countries, and (b) urban population growth due to higher birth rates in comparison to mortality (Golubev, 1999).

Both retrospective and prospective planning are also impressive (Table 1).

The ecological problems of urbanization are different in developing and developed countries. The extremely high urban growth in the poorest countries is accompanied by intensive anthropogenic loading of the environment. All life supporting municipal systems become overloaded and their enhancement rates are much less than the rate of urban population increase. These systems include water supply, drainage and canalization, waste collection and treatment as well as education, health and social service. As a result the urban environments have become dangerous for local population life. Based on UN statistics, more than 300 million city-dwellers have no suitable drinking water supply, and more than 500 billion have no access to even primitive toilets. In developing countries from 30 to 70% of municipal waste are not treated. This waste is currently accumulated especially in the poorest population urban areas. These areas are very far from traditional urban territories but the most part of the new urban population in developing countries is living in the given conditions, which can be very relatively termed as the urban ones (ESCAP, 2000; Bashkin, 2003).

In the developed countries some the most important urban ecological problems have been solved due to massive financial investments. It is known that the successful ecological solutions require 3–5% from total municipal budget. During last decades the air and water quality was improved in many developed cities. For instance, in 1960s the police officers in Tokyo had to use the oxygen masks and at present the improvement is very distinguishing. The similar improvement is shown in other urban agglomerations of the World however the ecological risk from air pollution is still the most significant in the global scale.

3. URBAN BIOGEOCHEMISTRY

At present most cities are powerful sources of technogenic materials, which influence environmental pollution not only in the urban areas but also in the suburbs and surrounding regions. Many urban areas represent technogenic and biogeochemical provinces (anomalies) with high ranks of soil, air, plant, and water pollution. Urban industrial agglomerations are centers both of huge populations and tremendous masses of pollutants entering urban areas with industrial, transport and municipal wastes and wastewaters. These pollutants form biogeochemical anomalies, which enhance the regional migration fluxes and increase the area of pollution around the agglomerations.

As a rule the anthropogenic loading in large cities is owing to the extremely high concentration of industrial production, rapid growth of transport vehicle numbers, lack of resource saving and inadequate waste technologies as well as many other economic and social forces combine to negatively influence the urban environment and human health.

These peculiarities of urban area development led to the technogenic biogeochemical provinces, i.e., the areas with local increase of pollutants in different components of urban ecosystems such as soils, grounds, surface and ground waters, plants, atmosphere. These pollutants create ecological risk to human and ecosystem health by their accumulation in the biogeochemical food webs (food stuffs and water).

As a whole, biogeochemical conditions in urban territories depend on the ratio between natural and technogenic factors of urban development. Accordingly, the analyses of biogeochemical cycling of pollutants in urban ecosystems should be based on geochemical background including the characteristic of pollution species migration and self-purification.

There are two different types of biogeochemical cycling transformation in the urban areas. The first type is connected with an accumulation of pollutants in these biogeochemical cycles, for instance, accumulation of heavy metals in various links of biogeochemical food webs, due to both natural and anthropogenic conditions. These conditions may be related to: (a) placing of cities in depressions like Novgorod city in the bank of the Ilmen lake in Russia; (b) heavy granulometric composition of soils and grounds that immobilize the metals dissolved in the infiltrating waters; (c) local geochemical background with high content of heavy metals; (d) formation of anthropogenic and natural barriers like the carbonate barrier in steppe soils. The second type is connected with the anthropogenic increase of pollutants migration, like acid deposition enhancing migration due to environmental acidification.

4. MODERN APPROACHES TO EXPOSURE ASSESSMENT IN URBAN AREAS

The concept of urban air pollution has changed significantly during the past several decades. Thirty or fifty years ago, air pollution was only associated with smoke, soot, and odor. At present, we should suggest the following definition that encompasses the concentration of many chemical species in urban air. *Air pollution is the presence of any substance in the atmosphere at a concentration high enough to produce an objectionable effect on humans, animals, vegetation, or materials, or to alter the natural biogeochemical cycling of various elements and their mass balance*. These substances can be solids, liquids, or gases, and can be produced by anthropogenic activities or natural sources. In this chapter, however, only non-biological materials will be considered. Airborne pathogens and pollens, molds, and spores will not be discussed. Airborne radioactive contaminants will not be discussed either. The natural urban air pollution due to forest fires and corresponding haze problem have been considered earlier (Bashkin, 2003).

Air pollution in cities can be considered to have three components: sources, transport and transformations in the troposphere, and receptors. The sources are processes, devices, or activities that emits airborne substances. When the substances are released, they are transported through the atmosphere, and are transformed into different substances. Air pollutants that are emitted directly to the atmosphere are called *primary pollutants*. Pollutants that are formed in the atmosphere as a result of transformations are called *secondary pollutants*. The reactants that undergo the transformation are referred to as *precursors*. An example of a secondary pollutant is troposphere ozone, O_3, and its precursors are nitrogen oxides ($NO_x = NO + NO_2$) and non-methane hydrocarbons, NMHC. The receptors are the person, animal, plant, material, or urban ecosystems affected by the emissions (Wolff, 1999).

5. CASE STUDIES OF URBAN AIR POLLUTION IN ASIA

5.1. Outdoor Pollution

The rapid growth of cities, has, together with associated industry and transport systems, resulted in an equally rapid increase in urban air pollution in the Asian region. Air pollution is principally generated by fossil fuel combustion in the energy, industrial and transportation systems. Use of poor quality fuel (e.g., coal with high sulfur content and leaded gasoline), inefficient methods of energy production and use, poor condition of automobiles and roads, traffic congestion and inappropriate mining methods in developing countries are major causes of increasing airborne emissions of sulfur dioxide (SO_2), nitrogen oxides (NO_x), suspended particulate matter (SPM), lead (Pb), carbon monoxide (CO) and ozone O_3). Predominant outdoor pollutants are shown in Table 2.

Air quality is worsening in virtually all Asian cities, except perhaps in Singapore, South Korea and Japan. Air pollutants, mainly in the form of suspended particulate and sulfur dioxide is most common in the cities of the developing countries. Among mega-cities in the region and in the world for that matter, Beijing and Bangkok are the two most polluted cities. In general, cities in high-income countries like Tokyo, Osaka, and Seoul, have relatively lower levels of SPM and SO_2 in the air than cities in the developing countries, for instance, Shenyang, New Delhi, Tehran and Jakarta, where WHO Guidelines for these species are invariably exceeded. Air pollution by nitrogen oxides is one of the major problems in the cities of developed countries like Japan (see Bashkin, 2003). In China, the annual average concentration of SO_2 is

Table 2. Predominant outdoor pollutants and their sources.

Pollutants	Sources
Sulfur oxides	Coal and oil combustion, smelters
Ozone	Photochemical reactions
Lead, manganese	Automobiles, smelters
Calcium, chlorine, silicon, cadmium	Soil particulate and industrial emissions
Organic substances	Petrochemical solvents, unburned fuel

66 $\mu g/m^3$, nitrogen oxide, 45 $\mu g/m^3$, and total SPM, 291 $\mu g/m^3$. In New Delhi, air pollution is so heavy, that one day of breathing is comparable to smoking 10 to 20 cigarettes a day (ESCAP, 2000). You can see these data in comparison with WHO Guidelines in Figures 1–3.

The deterioration of air quality in urban areas is mainly the results of increases in industrial and manufacturing activities and in the number of motor vehicles. Motor vehicles normally concentrate in the urban areas and contribute significantly to the production of various types of air pollutants, including carbon monoxide, hydrocarbons, nitrogen oxides and particulates. For example, it is estimated that around 56 tons of CO, 18 tons of hydrocarbons, 7 tons of NO_x, and less than one ton each of SO_2 and particulate matter are discharged daily through the tile pipes of vehicles in Kathmandu alone. In Shanghai, the contribution of CO, hydrocarbon, and NO_x emission by automobiles to the air was over 75, 93 and 44%, respectively. These figures are estimated to increase further to 94% for NO_x, 98% for hydrocarbons, and 75%

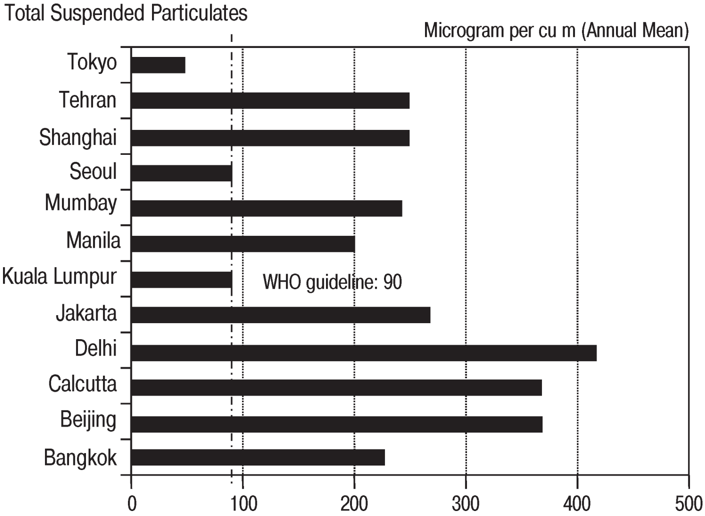


Figure 1. Ambient levels of TSP in Asian cities (ESCAP, 2000).

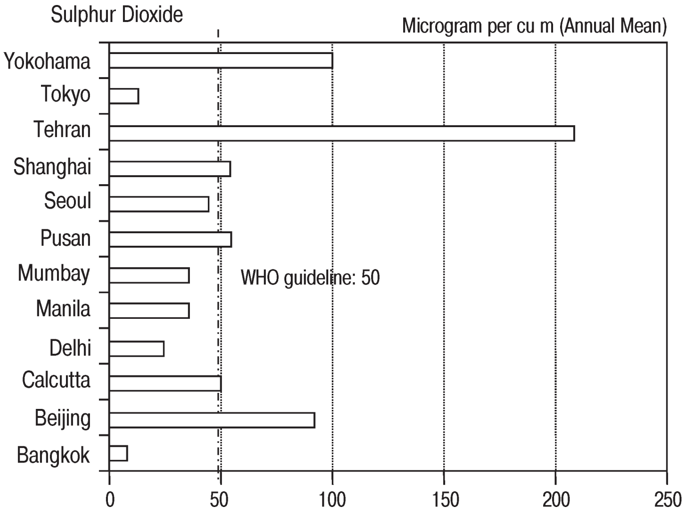


Figure 2. Ambient levels of SO_2 in Asian cities (ESCAP, 2000).

for NO_x by 2010. In Delhi, vehicles already account for 70% of the total emissions of nitrogen oxides, not to mention the amount of lead pollution from using leaded gas.

In the wake of growing numbers of motor vehicles, the problem is likely to become more acute in the future. Many Asian cities within the more prosperous economics had already tripled or quadrupled in the number of passenger cars over the last 10–15 years. In Bangkok, for example, the number of road vehicles grew more than sevenfold between 1970 and 1990 and more than 300,000 new vehicles are added to the streets of this city every year. In China, it is projected that by 2015, there will be

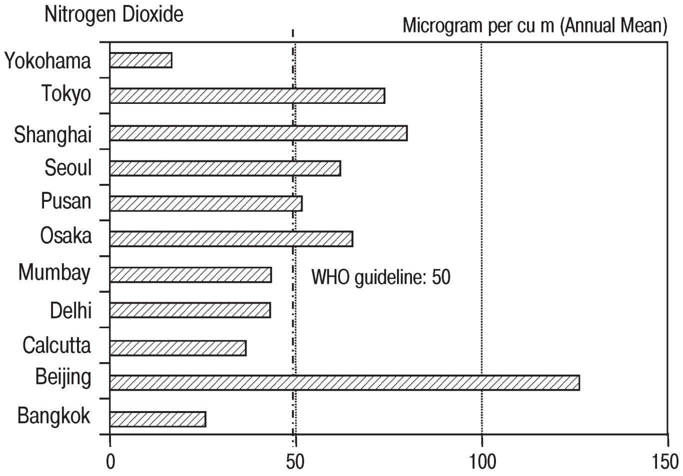


Figure 3. Ambient levels of NO_x in Asian cities (ESCAP, 2000).

30 million trucks and 100 million cars, and that the scope for future growth will still be huge. The forces driving this level of growth in vehicle numbers in the region range from demographic factors (urbanization, increasing population, and smaller households), to economic factors (higher incomes and declining car prices), to social factors (increased leisure time and the status associated with vehicle ownership), to political factors (powerful lobbies and governments that view the automobile industry as an important generator of economic growth).

Most of the growth in motor vehicle fleets in the developing countries is concentrated in large urban areas. Primary cities draw the largest concentration of vehicles. For instance, in Iran, South Korea and Thailand, about half of these countries automobiles' are in the capital cities. In Shanghai, the number of automobiles doubled between 1985 and 1990, and at present, is more than half a million. However, the growth in the vehicle fleet results primarily from increases in the number of motorized two-wheel and three-wheel vehicles, which are more affordable than cars for large segments of the population and often serve as a stepping-stone to car ownership. In Thailand, Malaysia and Indonesia, for instance, two- and three-wheelers make up over half of motor vehicles. The number of two- and three-wheel vehicles is expected to grow most rapidly in China, India and in other densely populated low-income countries. In China, it is projected that there will be 70 million motorcycles by 2015. Production of motorcycles and cars in India is also increasingly 20% annually, outstripping that for buses, which grow at three percent per year. In Nepal, the registered motor vehicles as of 1998 totals to over 200,000, with more than half comprised of two wheelers. Over half of these are concentrated in Katmandu.

Owning to the tremendous rise in the number of vehicles in several countries of the region, the increase in per capita energy consumption has also been quite dramatic. It is projected that energy use in the region will double between 1990 and 2010. In kilograms oil equivalent, it has increased from 91 to 219 in Indonesia, 80 to 343 in Thailand, 312 to 826 in Malaysia, and 670 to 2,165 in Singapore. In urban areas, high-energy use contributes to local air pollution. Cars consume about five times more energy, and produce six times more pollutants than buses. Another environmental impact of this development besides the related air pollution is the depletion of non-renewable natural resources. Like the air pollution problem, the depletion of non-renewable sources of energy also has global implications.

The mounting cost of pollution in the cities of the developing Asian countries is a waste of human and physical resources. In Bangkok, Jakarta and Kuala Lampur, the annual cost from dust and lead pollution is estimated at US$ 5 billion, or about 10% of combined city income (Bashkin, 2003). Air pollution also pushes up the incidence and severity of respiratory-related diseases. Mortality due to cardiovascular disease, particularly of the aged (over 65 years) population, increases with air pollution because labored breathing strains the heart. Studies in China revealed that air pollution, along with smoking, also greatly increases the risk of lung cancer.

The more developed nations in the region have exhibited improvement in air quality in recent years due to a number of measures taken to mitigate air pollution problems. For instance, in South Korea, levels of sulfur dioxide and total suspended particulates have been declining in Seoul and Pusan since 1990. However, slight increases in concentration of other pollutants such as nitrogen oxides, ozone and carbon dioxide in major cities of South Korea has been recorded. In Hong Kong, SO_2, NO_2 and TSP levels averaged 80 $\mu g/m^3$ in 1998. Air quality in Singapore has also significantly improved with the adoption of various strategies to prevent air pollution at its source. Several countries of the region are now promoting the use of unleaded gas. China is planning to convert fully to unleaded gas in 2010 (ESCAP, 2000).

Physical Description of Photosmog

Physical characteristics of photosmog include a yellow-brown haze, which reduces visibility, and the presence of substances which irritate the respiratory tract and cause eye-watering. The yellowish color is owed to NO_2, whilst the irritant substances include ozone, aliphatic aldehydes, and organic nitrates. The four conditions necessary before photosmog can develop are:

- sunlight;
- hydrocarbons;
- nitrogen oxides;
- temperatures above 18 °C.

Sunlight is needed for the formation of OH radicals and initiation of the photochemical reactions of nitrogen oxides in the troposphere. Nitrogen dioxide, NO_2, is important as the only tropospheric gas with appreciable absorption in the visible region of the spectrum. The chemical reactions of photosmog involve the attack of a hydroxyl radical on organic substances. The temperature being above 18 °C gives an idea of the temperature-dependent reactions that increase production of obnoxious by-products to build up to the levels associated with urban air pollution.

The reader can easily estimate whether or not the local conditions in his/her region are suitable for photochemical smog formation.

Photochemical smog was recognized as an urban air pollution problem in Los Angeles, California, USA, in 1949. From that time this phenomenon has been documented in many other sunny locations in the United States and elsewhere in the world like Sao Paulo, Brazil; Mexico City, Mexico; Metro Manila, Philippines; Bangkok, Thailand; New Delhi, India; Shanghai, China and in many other Asian cities with urban pollution from automobile transport. As long ago as the 1950s the automobile was identified as the leading contributor to photochemical smog. Los Angeles was the first major American city to build an extensive freeway system and to rely principally on private automobiles rather than public facilities for transportation. At present this is common in many Asian cities (Bashkin, 2003).

The evidence against the automobile is illustrated in Figure 4, which can be interpreted as follows. Early in the morning pollution levels are low. Nitrogen oxide

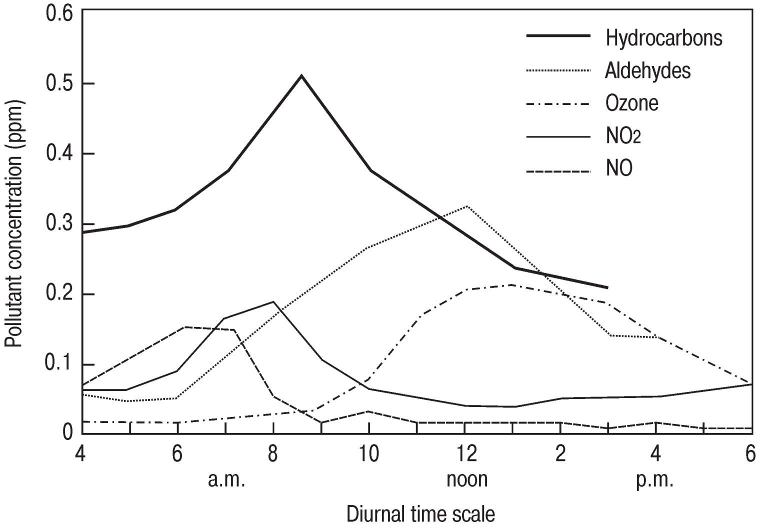


Figure 4. Sketch of the diurnal variation in the concentrations of nitrogen oxides, hydrocarbons, ozone and aldehydes under conditions of photosmog (Manahan, 1994).

and unburned hydrocarbon concentrations rise as people drive to work. As the sun rises higher in the sky, NO is converted to NO_2, and subsequently levels of ozone and aldehydes increase. The latter maximize towards midday, when the solar intensity is highest. Notice that the concentration of NO_x falls after about 10 a.m. and does not rise again during the evening rush hours. There is no second peak at the evening rush hour, because by then the free radical chain reactions are already fully under way.

Automobile emissions cause elevated concentrations of NO, which is oxidized to NO_2. Nitrogen dioxide is photolyzed in sunlight, and this reaction proceeds faster the higher the photon intensity. Tropospheric ground level (as opposed to stratospheric ozone) ozone is formed, and its photolysis leads to the formation of OH. Automobile emissions also provide the organic substances (substrates) for reaction with OH; intermediates and by-products—such as aldehydes and organic nitrates—of the oxidation of these substrates to CO_2 and H_2O are the irritating compounds of the smog. Many of these reactions are temperature-dependent, and so photochemical smog becomes increasingly noticeable the hotter the weather.

All four conditions for photochemical smog must be met simultaneously; consequently, the location and the seasons where this phenomenon is likely to be observed may be predicted. Since automobiles provide the NO_x and HC, photosmog is a big city phenomenon. Sunlight and high temperatures are needed. Other factors contributing to photosmog include orografic features, which may hinder the dispersal of the pollutant plume; this is a factor in the Los Angeles district, where mountains to the east tend to trap the air close to the city. Temperature inversions and lack of wind both serve to localize the pollutant plume and hinder its dispersal. Thus this type of urban air pollution is called photochemical smog of Los Angeles type. This air pollution phenomenon is very frequent in many Asian cities, especially those in subtropical and tropical zone.

5.2. Indoor Air Quality

Indoor air pollution in urban centers occurs both at the home and in the workplace. It can often pose a greater threat to human health than outdoor air pollution, both in developed and developing countries of the Asian region. In particular, women and young children from low-income households are often at significant risk from exposure to high concentrations of pollutants from cooking in poorly ventilated houses.

In Ahmedabad, India, mean values of SPM during cooking were as high as 25,000 $\mu g\ m^{-3}$ in coal-burning households, and 15,000–20,000 $\mu g\ m^{-3}$ where wood and dung were used. This is 130 times higher than the threshold set by US safety standards, not to be exceeded more than once a year. In addition, mean levels for the carcinogen, benz(a)pyrene, BaP, were as high as 9,000 ng m^{-3} during cooking: some 45 times higher than US standards for occupational (8 h) exposure (ESCAP, 1995).

Another example is the high concentrations of SPM, SO_2, CO and BaP, which have been recorded in coal-burning households in many Chinese cities. In Shenyang, lung cancer risk is thought to be 50–70% higher among those who spend most of their lives indoors.

A study on indoor air pollution abatement through household fuel switching in three cities—Pune, India, Beijing, China, and Bangkok, Thailand—revealed that moving up the "energy ladder", from biomass to kerosene, leads to substantial reductions in health damaging emissions (Tables 3 and 4). Similar effects were noticed shifting from kerosene to LPG, and from coal (vented) to gas (Smith et al., 1994).

Table 3. Estimated daily exposures from cooking fuel among energy ladder in Pune, India (Smith et al., 1994).

	Estimated daily exposure, mg h/m^3	
Fuel	PM_{10}	NO_2
Biomass	17–26	0.22–0.66
Kerosene	2.4–3.6	0.08–0.11
LPG	0.4	0.05
Indian standards	0.98	0.28
WHO recommendation	0.56	0.70

Table 4. Estimated daily exposure from household fuel use along the energy ladder in Beijing (Smith et al., 1994).

Fuel	Estimated daily exposure, mg h/m^3		
	PM_{10}	NO_2	CO
Coal (vented)	2.3–3.5	0.31–0.51	310–430
Gas	1.4	0.15	60
Chinese standards	0.7	0.7	56
WHO recommendation	0.56	0.70	140

5.3. Urban Air Pollution and Health Effects

The high exposure to both indoor and outdoor ambient air pollution has been associated with a number of illnesses, including:

- acute respiratory infections (particularly in children);
- chronic lung disease, such as asthma, tuberculosis, and associated heart diseases;
- pregnancy stillbirths; and
- cancer.

Since urban air is generally more polluted, the incidence of related diseases is more common in cities. For example, lung cancer mortality is higher in Chinese cities than in the nation as a whole; and 60% of Calcutta residents, India, suffer from respiratory diseases, compared to the national average of 3%. Furthermore, it has been estimated in Bangkok that SPM could cause up to 1,400 deaths in the city per year, and that lead pollution could cause 200,000–500,000 causes of hypertension, 300–900 cases of heart attack and stroke, and 200–400 deaths per year (ESCAP, 1995). In spite of significant reduction of lead concentration in the Bangkok urban air due to lead–gasoline phasing out during the second part of the 1990s, some studies indicate that the long-time effects of lead poisoning on children in Bangkok could cause an average loss of 3.5 IQ points per child before the age of seven, i.e., an estimated total loss of 400,000–700,000 IQ points per year.

Acute Respiratory Infections

Acute Respiratory Infection (ARI), as pneumonia, is one of the biggest causes of death for young children in the Asian region. ARI is also responsible for more episodes of illness than any other disease, with the exception of diarrhoea, and it is well known that ARI is aggravated by exposure to pollutants and indoor environmental tobacco smoke (ETS).

Table 5. Tuberculosis notification in selected countries of Asia, notification rate per 100,000 population (ESCAP, 1995).

	All forms		Smear positive, of total reported	
Country	Number	Rate	Percent	Rate
Bangladesh	56,052	47.2	35	16.5
Bhutan	996	169.6	30	50.9
India	1,555,353	182.5	22	40.6
Indonesia	469,832	245.4	16	39.6
Maldives	380	172.4	31	53.4
Mongolia	1,611	71.6	7	5.0
Myanmar	16,440	38.3	72	27.9
Nepal	8,993	45.8	47	21.5
Sri Lanka	6,174	35.4	54	19.1
Thailand	50,185	88.7	76	66.5

According to WHO estimates, Bangladesh, India, Indonesia and Nepal together account for about 40% of global mortality in young children caused by pneumonia, with infant mortality rates above 40.0 per 1,000 live births. The case-fatality rates due to pneumonia among hospitalized children are between 4.2 and 18.3%. Furthermore, a study in Nepal (Pandey et al., 1989) involving a weekly examination of 240 children under 2 years of age over a six-month period, for ARI incidence and severity, demonstrated a strong relationship between the number of hours per day the children spent indoor by fire, and the incidence of moderate and severe ARI cases.

Chronic Obstructive Lung Disease (COLD) and Cor pulmonale

COLD is known to be an outcome of chronic air pollution exposure. Although tobacco smoke is known to be the major risk factor, studies in India and Nepal have found that non-smoking women who regularly cook on biomass stoves exhibit a higher prevalence of COLD than would be expected, or which appears in women who use them less frequently. Indeed, due to indoor exposure, nearly 15% of non-smoking women in Nepal (20 years and older) had chronic bronchitis; a very high rate for nonsmokers (ESCAP, 1995).

In China, COLD was associated with long term exposure to indoor coal smoke (Chen et al., 1998), and in India, Cor pulmonale (heart disease secondary to chronic lung disease) has been found to be more prevalent, and on average to develop earlier, in non-smoking women who cook with biomass fuels than those do not.

Tuberculosis

Tuberculosis, which continues to be a serious public health problem in the region, is also aggravated by air pollution. In 1991, more than 2,000 000 cases were reported in India and Indonesia alone (Table 5), and just 10 countries in the Asian region accounted for over one million deaths.

Around 40% of the population in South and South-East Asia were infected with HIV and M. Tuberculosis, which is extremely high in the region, the number of cases of active tuberculosis may rise by a factor of seven during the coming decade. Furthermore, the age group, which is economically most productive (15–59 years) is particularly vulnerable to the disease. As shown in Table 5, notification rates per 100,000 population were particularly high for all forms of the disease in Indonesia, India, Maldives, and for smear-positive cases were above 50 per 100,000 in Thailand, Maldives and Bhutan. Also of note is the extremely low smear-positive rate in Mongolia (5 per 100,000) where the level of urban air pollution is minimal among Asian countries.

Pregnancy Stillbirths

A study in India found that pregnant women who cook over open biomass stoves have almost 50% greater chance of stillbirth, although there was no measured increase in neonatal death rates (Mavalankar et al., 1991). The main threat to pregnancy appears to come from carbon monoxide, which enters the blood in substantial amounts during cooking.

Table 6. Probability of dying from cancer and cardiovascular diseases between ages 15 and 60 years for males and females in China and India, in percent (Murray and Lopez, 1994).

	China		India	
Disease	Male	Female	Male	Female
Stomach cancer	1.06	0.58	0.37	0.21
Colorectal cancer	0.25	0.23	0.12	0.1
Liver cancer	1.81	0.59	0.14	0.1
Lung cancer	0.65	0.34	0.38	0.1
Diabetes mellitus	0.14	0.17	0.49	0.65
Rheumatic heart disease	0.39	0.64	0.35	0.86
Ischaemic heart disease	0.87	0.45	2.61	1.09
Cerebrovascular disease	2.06	1.75	1.08	1.32
Inflammatory cardiac disease	0.20	0.17	2.31	1.48

Table 7. Ambient air quality standards in some Asian countries, all concentrations in μg m^{-3}, except CO in mg m^{-3} (Radojevic and Bashkin, 1999).

Pollutant	Averaging time	Malaysia	Thailand	Indonesia	Philippines	Singapore	Japan
SO_2	10 min	500	–	–	–	–	–
	1 h	350	–	900	850	–	285
	24 h	105	300	300	370	365	114
	Annual	–	100	60	–	80	–
NO_2	30 min	–	–	–	300	–	
	1 h	320	320	–	–	–	205
	24 h						102
	Annual	–	–	100	–	100	–
CO	1 h	35	50	30	35	40	25
	8 h	10	20	10	10	10	–
	24 h	–	–	–	–	–	12
O_3	30 min	–	–	–	200	–	–
	1 h	200	200	160	–	235	128
	8 h	120	–	–	–	–	–
SPM	24 h	260	330	230	180	260	200
	Annual	90	100	90	–	75	100
Lead	24 h	–	10	2	–	–	–
	3 months	1.5	–	–	20	1.5	–

Cancer

Air pollution has also resulted in an increased incidence of lung and other cancers in the Asian region. One study in Japan (Subue, 1990), found that women who reported cooking with straw or wood fuel when they were 30 years of age, subsequently had an 80% increased chance of developing lung cancer in later life. We know that cancer, like chronic lung disease, takes many years to develop after exposure. Furthermore, there is mounting evidence that lung cancer can also be associated with exposure to coal smoke. The corresponding statistical assessments have been shown in China (Chen et al., 1998).

Current knowledge suggests that social habits and diet are as much a cause of cancer and cardiovascular diseases, as are exposure to environmental hazards such as carcinogens and viruses. Apart from the obvious activities of smoking and hard drinking, other examples of ways in which diet can increase the risk of cancer include preserving food through salting, smoking and pickling, which have been shown to increase the risk of oral and stomach cancer.

Indoor and outdoor exposure to many chemical substances (formaldehyde, asbestos, PVC, many metals, like Cr, As, Be, Ti, V, pesticides and nitrosoamines) can also spur the development of cancer. Here we can only state that the International Agency for Research of cancer has identified 60 environmental agents that can aggravate cancer for humans during exposure to polluted urban air (Misch, 1994).

The probabilities of cancer development in urban environments of two of the most polluted Asian countries are shown in Table 6.

The development of all above-mentioned diseases is related to exceeding the air quality standards in many cities of the Asian regions. These standards for the most frequent pollutants are shown in Table 7. The readers can compare the air quality monitoring results in his/her cities with environmental standards.

CHAPTER 13

AGROGENIC BIOGEOCHEMICAL PROVINCES

On a global scale, arable lands occupy 12% of the terrestrial ecosystems, and pastures occupy 25%. On the whole, the agrolandscapes occupy ∼40% of the Earth's land. At present the most used areas are in the moderate climate zone (25%) and subtropical and tropical ones (18%). To the maximal extent, natural landscapes and their relevant biogeochemical cycles are transformed into agrogeochemical provinces with a predominance of agrogeochemical cycles of many elements in Europe (>30%) and Asia (>20%).

In the agrogeochemical provinces in order to achieve maximal crop yields, as a rule high rates of fertilizers are used and this leads to environmental pollution of all components of agroecosystems, such as soils, waters, local atmosphere and vegetation (crop production). In many parts of Europe, including the chernozemic belt of Russia, arable lands make up 85–90% of the area, all of which are subject to soil and water pollution by fertilizer and pesticide residues. These processes are widespread both in developed and developing countries. Thus methods to achieve ecologically sound crop yields (green farming) are the most important contributions to biogeochemical optimization of agrolandscapes and a decrease in ecological risk.

1. IMPACT OF AGROCHEMICALS ON THE NATURAL BIOGEOCHEMICAL CYCLING

1.1. Mineral Fertilizers

In the context of biogeochemical cycles, the soil is an open system which receives inputs and outputs of many macroelements, such as C, N, Ca, Mg, Si, P, and K. The primary productivity of terrestrial ecosystems basically depends on soil fertility. The fluxes of chemical species from rainfalls pass through soil profiles to river channels and accordingly soil is a regulator of geochemical and biogeochemical migration. Thus, soil occupies a key position and it plays an extremely complex role in any biogeochemical cycle, especially in agrolandscapes.

For refilling nutrient contents in the soils of agroecosystems which are uptaken by crops, fighting with weeds and crop illnesses, pests, insects, dangerous microbes, the agrochemicals (mineral and organic fertilizers, pesticides, insecticides, fungicides, and other chemical species) are applied. It is known however that together with useful effects the application of agrochemicals is accomplished by unwilling transformation of cycling of many elements both of natural and anthropogenic (agrochemicals) origin.

This transformation and alteration of the biogeochemical cycling leads to excessive accumulation of various chemical species in soil, water, plants and biogeochemical food webs. Among these chemical species are various species of nitrogen and phosphorus, heavy metals and pesticides, all of which, depending on the environmental concentrations, can be both useful and dangerous. The levels of pollution and species composition vary greatly in various places. On the whole mineral fertilizers and other agrochemicals are the most powerful factors of agrolandscape pollution, and finally they can be included into biogeochemical food webs of living organisms and humans as the top consumers. This requires studying the transformation of biological transformation and geochemical structure of agrolandscapes, especially the peculiarities of vertical and lateral migration of pollutants.

The complex and regional character of applied agrochemicals at all the components of agrolandscapes requires of assessing the pollutants migration and transformation not only at the local scale (field level), which is partly the task of agrochemistry, but in the larger territorial systems, such as soil-geochemical catenas, landscapes and river basins. The risk of human and animal diseases induced by accumulation of agrochemicals in the wood webs should be also studied. Accordingly, the biogeochemical approaches should be taken into account to study the impact of agrochemicals on the natural biogeochemical cycles (Bashkin, 1987).

According to modern standards mineral fertilizers are partitioned into two groups: standardized and non-standardized. The standardized fertilizers include nitrogen, phosphorus, potassium, complex, and micro-fertilizers that contain the nutrients at the standard basis. The non-standardized fertilizers are municipal wastewater effluents, municipal solid wastes, polluted river waters used for irrigation, etc., which are not characterized by standard content of nutrients. However one should add that in all fertilizers including standardized type there are the admixtures, which pollute the agrolandscape. The known examples are phosphorus fertilizers and any municipal waste and wastewater with a pool of heavy metals and various organic pollutants.

1.2. Disturbance of Nitrogen Biogeochemical Cycle in Agrolandscapes

About 15–20% of nitrogen uptaken by crops in the agrolandscapes are from mineral fertilizers (Boyer and Howarth, 2002). In China, Japan, South Korea and many European countries this part is up to 25–35% (Bashkin, 2003). In agrolandscape removed from the sources of industrial pollution, these fertilizers are the main environmental pollutants increasing the risk of nitrogen species to humans and animals. In small river basins of central and western Europe as well as in the center of the former USSR in the 1980s, the fertilizer nitrogen amounted to 70–80% of the total input of this element to agrolandscapes.

The major input of nitrogen to the terrestrial and aquatic (fresh and marine water) ecosystems in the Asian region is application of nitrogen fertilizers. In the late 1990s, the total use of mineral fertilizers in the Asian region was about 60 million tons, as a sum of nitrogen, phosphorus and potassium fertilizers, and nitrogen fertilizers accounted for the 65–70%. The demand for food and other agricultural products is expected to rise by 30–100% between now and 2020 in parallel with a growing population. Yet, the net cropped area may be decreased in many countries over the same period, partly owing to a competing demand for arable land from on-going urban growth. To some experts, this implies a greater reliance on technology and chemical inputs, first of all, nitrogen fertilizers, to realize higher target yields, merely to maintain the current per capita food availability. Thus, nitrogen is an essential nutrient for the Asian agriculture, however, extensive application of nitrogen is accompanied by losses of this element due to denitrification as nitrous oxide, leaching as nitrate and ammonium to surface and ground water and accumulation in foodstuffs. These processes are of great environmental concern, as we have discussed earlier.

In various regions of the World with intensive agriculture the nitrogen balance becomes positive with an open nitrogen biogeochemical cycle. This is due to increasing input of technogenic nitrogen into the agrolandscape and the exceeding input over output balance items, often by 20–30%. The accumulation of nitrogen is monitored in different links of the biogeochemical cycle, such as soils, surface and ground waters, and agricultural production. In many agrolandscapes the maximal permissible concentration of nitrogen species in drinking water and foodstuffs is exceeded and leads to increasing ecological risk for human beings. The agrolandscape pollution is also due to application of phosphorus fertilizers. Among the standardized fertilizers they contain the widest spectrum of heavy metals. So superphosphate fertilizer in addition to phosphorus as a nutrient includes as a rule up to 1.5% of F, 0.005% of Cd, 0.005–0.03% of As, 0.001–0.005% of Sr, Cu, Pb, Th, V, and other rare earth elements (Kudeyarova and Bashkin, 1984). In spite of the use of fertilizers with less than 5% of natural soil content, this fertilizer phosphorus is much more available for plants. Accordingly in agrolandscape the main part of plant demand in this nutrient is from mineral fertilizers. This provides the required crop yield growth but simultaneously leads to environmental pollution due to admixtures of heavy metals in fertilizer composition, since many rare elements are uptaken by crops in micro-quantities and the excessive amounts are accumulating in various components of agrolandscapes involved in the biogeochemical wood webs.

The excessive amounts of nitrogen and phosphorus as well as heavy metals migrate with water fluxes and enter into surface waters. This is accompanied by eutrophication of surface water bodies.

As a consequence of intensive application of mineral fertilizers, nitrogen and phosphorus biogeochemical provinces have been formed in many regions, for instance, in Central and South East Asia, East Europe, etc.

1.3. Disturbance of Phosphorus Biogeochemical Cycle in Agrolandscapes

Conceptual ideas behind simulation of P cycling are related to construction of models for freshwater terrestrial ecosystems and a generalized oceanic system and understanding the restrictions of its application.

In a general way, the overall movement of phosphorus on the continents can be considered as the constant water erosion of rock and transport of P in both particulate and dissolved forms with surface runoff to river channels and further to the oceans. The intermediate transformations are connected with uptake of P as a nutrient by

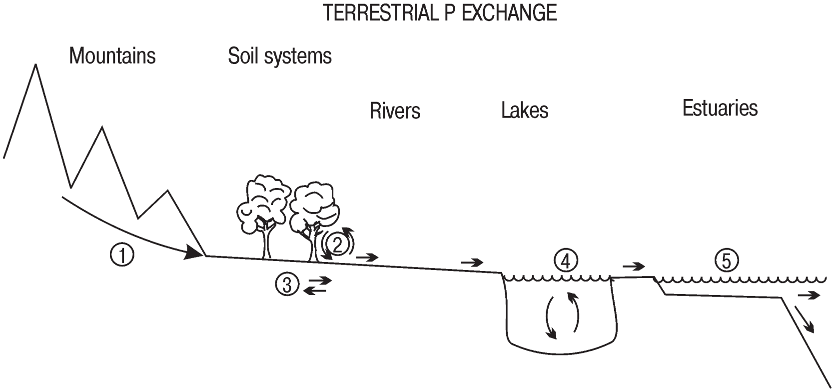


Figure 1. Schematic representation of the transport of P through the terrestrial system. The dominant processes considered in this description are: (1) mechanical and chemical weathering of rocks, (2) incorporation of P into terrestrial biomass and its return to the soil system through decomposition, (3) exchange reactions between groundwater and soil particles, (4) cycling in freshwater lakes, and (5) transport through the estuaries to the oceans of both particulate and dissolved P (Jahnke, 1992).

biota and interactions between river waters and bottom sediments. The majority (up to 90%) of eroded P remains trapped in the mineral lattices of the particulate matter and will reach the estuaries and ocean without entering the biological cycle. The smallest soluble part of eroded phosphorus is readily available to enter the biological cycle (Figure 1).

Dissolved P in ground and subsurface waters may be taken by plants and microbes. When organisms die, the organic P species decompose and return to the mineral turnover. Inorganic chemical reactions in the soil–water system also greatly determine the geochemical mobility of phosphorus. These reactions include the dissolution or precipitation of P-containing minerals or the adsorption and desorption onto and from mineral surfaces. The inorganic mobility of P is pH dependent. In alkaline soils apatite is less dissolved than in acid soils and the aluminum phosphates are the main forms in the latter environment. Formation of complexes between phosphate and iron and aluminum oxyhydroxides and clays during adsorption reactions may limit the solubility and migration of this species. Thus, these links of P biogeochemical cycle influence its behavior on the way towards the ocean.

Lakes also constitute an important component of the terrestrial phosphorus system. The degree of trophic stage of water body and its productivity in many cases directly depend on the P content in the water. In the water column, in summer, warming of the surface layers produces strong stratification, which restricts exchange between the lighter, warm surface water and the colder, denser deep water. During photosynthesis, the dissolved P in the photic zone is incorporated into plants and is eventually transported below the thermocline on sinking particles. The upward motion of this

P is very slowly due to water column stratification. The P depletion of water pool leads to low P content and finally limits the biological productivity of the aquatic ecosystem.

Export of Phosphorus from Agricultural Systems in the USA

Several surveys of U.S. watersheds have clearly shown that phosphorus loss in runoff increases as the portion of the watershed under forest decreases and agriculture increases. In general, forested watersheds conserve phosphorus, with phosphorus input in dust and in rainfall usually exceeding outputs in stream flow. Surface runoff from forests, grasslands, and other noncultivated soils carries little sediment, so phosphorus fluxes are low and the export that occurs is generally dominated by dissolved phosphorus. This loss of phosphorus from forested land tends to be similar to that found in subsurface or dissolved base flow from agricultural land. The cultivation of land in agriculture greatly increases erosion and with it the export of particle-bound phosphorus. Typically, particulate fluxes constitute 60–90% of phosphorus exported from most cultivated land. In the eastern United States, conversion of land from forests to agriculture between 1700 and 1900 resulted in a 10-fold increase in soil erosion and a presumed similar increase in phosphorus export to coastal waters, even without any addition of phosphorus fertilizer (Howarth et al., 1995). The soil-bound phosphorus includes both inorganic phosphorus associated with soil particles and phosphorus bound in organic material eroded during flow events. Some of the sediment-bound phosphorus is not readily available, but much of it can be a long-term source of phosphorus for aquatic biota.

Increases in phosphorus export from agricultural landscapes have been measured after the application of phosphorus. Phosphorus losses are influenced by the rate, time, and method of phosphorus application, form of fertilizer or manure applied, amount and time of rainfall after application, and land cover. These losses are often small from the standpoint of farmers (generally less than 200 kg P km^{-2}) and represent a minor proportion of fertilizer or manure phosphorus applied (generally less than 5%). Thus, these losses are not of economic importance to farmers in terms of irreplaceable fertility. However, they can contribute to eutrophication of downstream aquatic ecosystems.

While phosphorus export from agricultural systems is usually dominated by surface runoff, important exceptions occur in sandy, acid organic, or peaty soils that have low phosphorus adsorption capacities and in soils where the preferential flow of water can occur rapidly through macropores (Sharpley et al., 1998; Sims et al., 1998). Soils that allow substantial subsurface exports of dissolved phosphorus are common on parts of the Atlantic coastal plain and Florida, and are thus important to consider in the management of coastal eutrophication in these regions.

Although there exists a good understanding of the chemistry of phosphorus in soil–water systems, the hydrologic pathways linking spatially variable phosphorus sources, sinks, temporary storages, and transport processes in landscapes are less well understood. This information is critical to the development of effective management programs that address the reduction of phosphorus export from agricultural watersheds.

Runoff production in many watersheds in humid climates is controlled by the variable source area concept of watershed hydrology. Here, surface runoff is usually generated only from limited source areas in a watershed. These source areas vary over time, expanding and contracting rapidly during a storm as a function of precipitation, temperature, soils, topography, ground water, and moisture status over the watershed. Surface runoff from these areas is limited by soil–water storage rather than infiltration capacity. This situation usually results from high water tables or soil moisture contents in near-stream areas.

The boundaries of surface runoff-producing areas will be dynamic both in and between rainfalls. During a rainfall, area boundaries will migrate upslope as rainwater input increases. In dry summer months, the runoff-producing area will be closer to the stream than during wetter winter months, when the boundaries expand away from the stream channel.

Soil structure, geologic strata, and topography influence the location and movement of variable source areas of surface runoff in a watershed. Fragipans or other layers, such as clay pans of distinct permeability changes, can determine when and where perched water tables occur. Shale or sandstone strata also influence soil moisture content and location of saturated zones. For example, water will perch on less permeable layers in the subsurface profile and become evident as surface flow or springs at specific locations in a watershed. Converging topography in vertical or horizontal planes, slope breaks, and hill slope depressions or spurs, also influence variable source area hydrology in watersheds. Net precipitation (precipitation minus evapotranspiration) governs watershed discharge and thus total phosphorus loads to surface waters. This should be taken into account when comparing the load estimates from different regions. It is also one reason why there seems to be more concern with phosphorus in humid regions than in more arid regions.

In watersheds where surface runoff is limited by infiltration rate rather than soil–water storage capacity, areas of the watershed can alternate between sources and sinks of surface flow. This again will be a function of soil properties, rainfall intensity and duration, and antecedent moisture condition. As surface runoff is the main mechanism by which phosphorus is exported from most watersheds, it is clear that, if surface runoff does not occur, phosphorus export can be small. Thus, consideration of hydrologic pathways and variable source areas is critical to a more detailed understanding of phosphorus export from agricultural watersheds.

Human activity has an enormous influence on the global cycling of nutrients, especially on the movement of nutrients to estuaries and other coastal waters. For phosphorus, global fluxes are dominated by the essentially one way flow of phosphorus carried in eroded materials and wastewater from the land to the oceans, where it is ultimately buried in ocean sediments. The size of this flux is currently estimated at 22×10^6 tons per year. Prior to increased human agricultural and industrial activity, the flow is estimated to have been around 8 × 10^6 ton per year (Howarth et al., 1995). Thus, current human activities cause an extra 14 × 10^6 tons of phosphorus annually to flow into the ocean sediment sink each year, or approximately the same as the amount of phosphorus fertilizer (16 × 10^6 tons per year) applied to agricultural land each year.

The global biogeochemical cycle of P is almost open. This differentiates phosphorus from carbon and nitrogen, whose natural biogeochemical cycles are, on the contrary, almost closed.

2. IMPACT OF PESTICIDES IN AGROLANDSCAPES

The toxic persistent organic pollutants (POP) are of great environmental concern. The well-known insecticide DDT is only one of the dangerous substances that belong to POPs. POPs are long-lived organic compounds that become more concentrated as they move up the food chain, i.e., they have high values of bioconcentration. Moreover, these compounds can travel with air mass thousands of kilometers from their points of release. Although POPs cover a broad range of chemical classes, the concern and much of research activity in the World focus on about a dozen chemicals, like various pesticides, polychlorinated biphenyls, dioxins, furans, chlorophenols, etc. Most of these chemicals have now been phased out in developed countries but they are still in production and use in most Asian and other countries. The impact of pesticides on the agrolandscapes and relevant environmental risk we will consider on the Asian example.

2.1. Pesticides in the Asian Countries

The term *pesticide* is used to indicate any substance, preparation, or organism used for destroying pests. This broad definition covers substances used for many purposes, including insecticides, herbicides, fungicides, nematocides, acaricides, lumbricides, growth regulators, and insect repellents. The latter two groups are usually included as pesticides, even though they do not kill the target organisms. An enormous spectrum of chemical types of pesticides is covered by the definition of pesticides. According to their chemical nature, a first rough classification distinguishes between organic and inorganic pesticides. Actually, organic chemical pesticides receive virtually all of the regulatory attention and public concern, and these are the subject of this section. The most important classes of pesticides are organochlorines, organophosphates, carbamates, triazines, phenoxyacids, phenylureas and sulfonylureas, acetoanilides, benzimidazoles, and pyrethroides. In some cases, compounds with different chemical natures that are used similarly are classified as a single group; for example, the fumugants, which include compounds that have an elevated vapor pressure and act as vapors.

In comparison with developed countries, some Asian countries have emerged as large users of pesticides, less so in the case of fungicides and herbicides. Total sale of pesticides in the Asian region has grown from ≈US$ 5.0 billion in 1983 to almost

Table 1. Selected indicators of pesticide consumption in the Asian region (ESCAP, 2000).*

Item	1983	1988	1993	1998	2003
Consumption, tons	885	806	784	819	870
Cost, US$/kg	6.29	7.48	8.69	10.22	11.94
Consumption, US$ millions	5,571	6,025	6,814	8,370	10,390
Herbicides	1,750	1,970	2,180	2,600	3,150
Insecticides	2,318	2,470	2,790	3,400	4,200
Fungicides	990	1,100	1,260	1,580	2,000
Other	513	485	584	790	1,040

* Including the Oceania region

US$ 8.0 billion in 1998 and the amount is projected to reach US$ 10.3 billion in 2003 (ESCAP, 2000). The decrease in pesticide application at the end of the 1980s has been reversed to constant growth in 1990s (Table 1).

At present, Asia accounts for 10% of global sales of pesticides (Bashkin, 2003; World Resources Institute, 1998). It is estimated that agriculture accounts for 85% of total pesticide use. Unlike the developed countries, pesticides in developing countries are mostly insecticides with a higher level of acute and chronic toxicity. As in the case of fertilizers, pesticide sale and application have been accelerated with the spread of the so-called green revolution. Use of these chemicals started in a big way with the introduction of new high yielding varieties of wheat, rice and other crops mostly in the 1970s–1980s.

Pesticide use has been associated with pesticide resistance, health damage, loss of biodiversity and environmental problems. With increasing use of larger amounts and stronger pesticides, an ever-increasing number of species of insects (over 900 now against 182 in 1965), pathogens and weeds are becoming resistant to these chemicals.

2.2. Major Environmental Exposure Pathways

The major environmental pathways of pesticides into streams and into the food chains are presented in Figure 2.

Transport in Soil and Groundwater

The soil pays a major role for both transport and biodegradation of a pesticide. The upper soil layer above the plough horizon is the most active zone for microorganisms. From experimental results obtained by artificial soil columns it is unlikely for many pesticides that significant amounts can pass this zone. The most part is absorbed in the solid organo-mineral mass of soils. A possible exception is the irrigated sandy soils with heavy water drainage (Galiulin et al., 2001). However, the pollution of

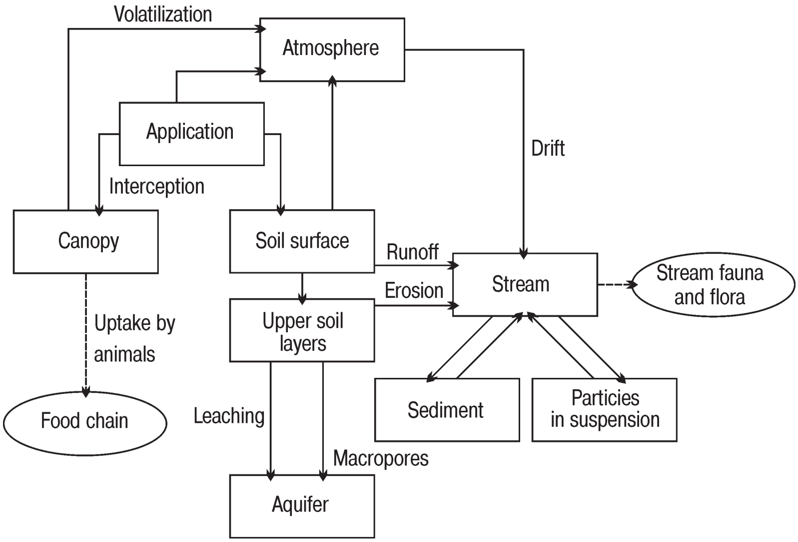


Figure 2. Major environmental pathways for the distribution of pesticides in the biosphere.

groundwater is well documented in many Asian countries. One possible reason is that the random structure of real soils with cracks and micropores facilitates fast transition to deeper layers (Figure 3)

During dry season, the formation of soil cracks, macro- and micropores is common in the Asian countries with monsoon climate. This process is especially important in

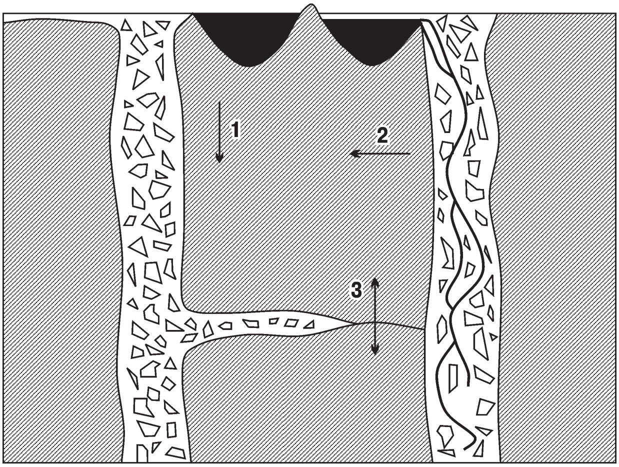


Figure 3. Water fluxes in soil with micropores. The following processes are relevant: (1) infiltration into soil matrix, (2) lateral infiltration from macropores, and (3) exchange between aggregates (Richter, 1999).

irrigation fields where water fluxes will stimulate the pesticide migration downward in soil profile.

Drift, Volatilization and Runoff

Drift and volatilization are important factors for large-scale transport from the treated plots. Whereas the range of drift of pesticide in droplets is limited to adjacent ecosystems, volatilization (i.e., vaporization) may lead to a large-scale aerial transport. The physics of spray drift involves Stoke's law for the derivation of sedimentation velocities of droplets.

In recent studies, pesticides such as atrazine have been found in precipitation. Therefore volatilization and subsequent transport in the gaseous phase is an important environmental pathway. Vaporization rates of pesticides deposited on surface of soil and plant leaves depend on the physical–chemical properties of the substance. A useful physicochemical criterion is Henry's constant, K_{H}, which is defined as the equilibrium air-to-water partial pressure ratio of the substance (see Chapter 7).

As an example, we can compare the solubility of lindane and 2,4-D pesticides with respect to their major loss pathways. The K_{H} values of these pesticides are 1.33×10^{-4} and 5.5×10^{-9} mol L^{-1}, respectively. In addition, the retardation coefficient or degree of sorption of lindane is much higher than that of 2,4-D. Therefore, 2,4-D is more likely to be leached, whereas lindane is more likely to remain near the soil surface from which it can vaporize. Volatilization is thus the major pathway of lindane, and degradation and leaching are the major loss pathways of 2,4-D in the Asian environments.

The volatilization rate at the surface is further influenced by temperature and by the thickness of the stagnant air layer over the surface. Furthermore, random micrometeorological conditions of the crop stand are also very important (turbulence, thickness of boundary layer, humidity, and wind velocity). Special models are available to calculate the volatilization and vaporization rates of pesticides (Richter, 1999).

In the Asian region with prevalent monsoon climate and heavy rain events during rain seasons, surface runoff plays the most important role in the environmental pathways of many pesticides. The major factors influencing the amount of pesticides carried away by runoff are as follows (Richter, 1999):

- the time course of the rainfall event characterized by the total precipitation and peak values;
- the timing of spraying with respect to an event;
- the degree of water saturation of the soil prior to the event;
- soil structure and texture;
- surface crusting and compaction;

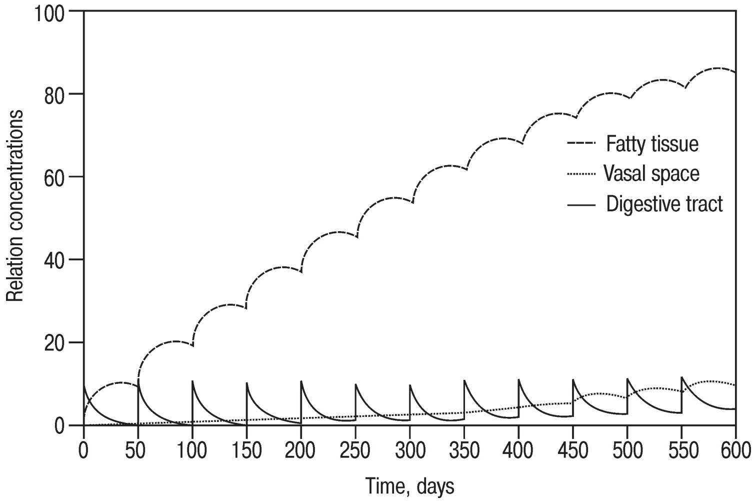


Figure 4. Simulation of the accumulation of an organochlorine in fatty tissue under a long-term intake scheme (Richter, 1999).

- hill slope;
- vegetation cover;
- management practices, for example, vegetative buffer strips near river with high resistance to flow or contour ploughing.

Some models like CREAMS (Chemicals, Runoff and Erosion from Agricultural Management systems) are available for simulation of pesticide surface runoff (Knisel, 1980).

Transport in the Food Chain

Due to organochlorines dissolving in fats and oil, bioaccumulation in the food chain may occur. Figure 4 shows the simulation of the accumulation of a substance in fatty tissues under a regular intake.

We can see that increasing accumulation of organochlorine compound is occurring in fatty tissues whereas in vasal space and digestive tract this accumulation is much less expressed. However, when the intake is decreasing, then the concentration of any organochlorine compound in fatty tissues will be reduced with a compensative increase in vasal space and digestive tract (Figure 5).

This leads to a release of the pesticide from fatty tissue into other compartments of the body. Since milk contains fat, mother's milk also constitutes a storage for the pesticide (see below the example of DDT and TCDD).

Let's consider now the food chain. Chemicals that accumulate in one organism at one trophic level in the food chain (a prey) due to tissue binding are further

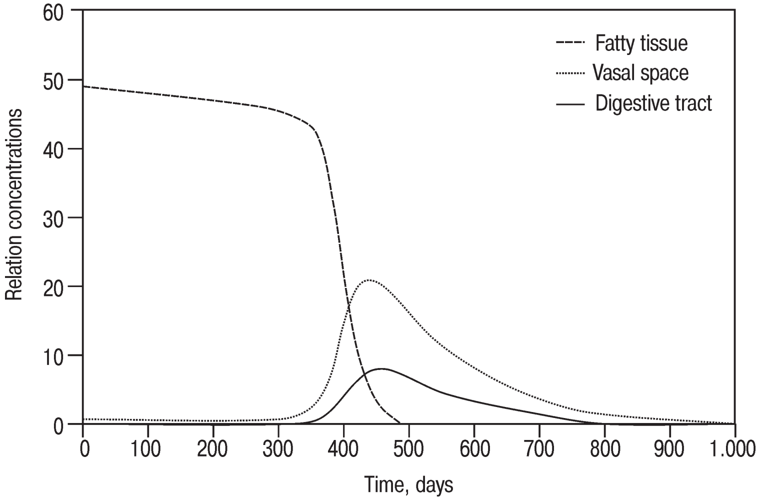


Figure 5. Simulated effect of reduction of fatty tissue concentration of organochlorine with relevant increase in other tissues (Richter, 1999).

concentrated at the subsequent trophic level. The highest tissue will occur at the top of the trophic pyramid. This holds especially true for human beings who are indeed at the top of different food chains.

The mechanism of bioaccumulation can be best understood by a simple ecosystem model (Spain, 1982). Figure 6 shows the time course of concentration of a non-metabolized pesticide at each trophic level following the constant influx of a pesticide into the environmental compartments.

The influx is stopped at time $t = 500$ weeks. One can see from this simulation that the pesticide is concentrated from level to level and that high levels are maintained even after release of the pesticide is stopped.

This model is the most fitting for the non-metabolized or very slow metabolized organochlorines like dioxin or DDT. We can see that this is an additional step in understanding the dioxin bioaccumulation in ecosystems.

2.3. DDT Example of Environmental Exposure Pathway

Ecotoxicology of DDT and Its Metabolites

Early investigations of DDT toxicology were aware of its negative properties, such as aching joints, tremors, and depression symptoms among highly exposed soldiers. These slowly disappearing symptoms indicate that DDT affects the nervous system. Toxicologically, this is related to the accumulation of lipid-soluble DDT in the insulating myelin sheaths around the nerves. Laboratory rats suffered fatty degeneration of the liver and kidneys after prolonged high exposure to DDT. The lipid solubility of DDT caused it to appear in milk, and in as earlier as 1947, DDT was phased out for pastures and vegetable crops for human consumption in the USA. By 1946 it

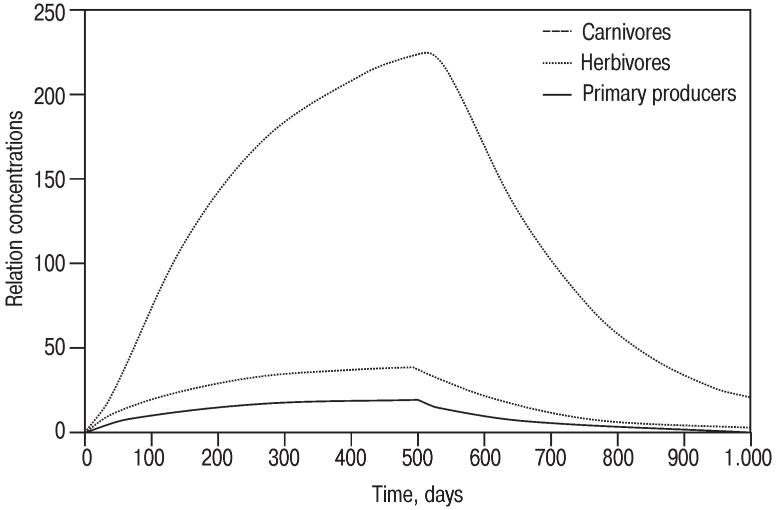


Figure 6. Simulated bioaccumulation of fat-soluble pesticide in the food chain (Richter, 1999).

was known that excessive use of DDT could cause the death of fish, birds, and other wildlife and that residues of DDT were detected in the adipose tissue of a wide range of wildlife, especially carnivores. This is an earlier example of DDT biomagnification. Carnivorous birds appeared to fare particularly badly; reduced hatchability of eggs and physical deformities in the chicks were linked statistically to high DDT levels in the parents.

Humans are also at the top of food webs, and by the late 1960s citizens of several countries were horrified to learn that the levels of DDT in mothers' milk ranged up to 130 ppb, which would have been classified as unfit for human consumption.

Until recently, DDT isomers were thought to be of no significance; however, current evidence suggests that *o,p*-DDT can act in the environment as an estrogen mimic, meaning that it can interfere with the normal signal processing of the female sex hormone estradiol (Bunce, 1994). In humans, concern about exposure to environmental estrogens, including *o,p*-DDT, exists over their role in the development of estrogen-dependent breast, uterine and ovarian cancers in females, and demasculinization effects in males.

Societal Risk Concern on DDT Application

Rachel Carson's book "Silent Spring" that was published in 1962, was the first popular work to bring the uncontrolled environmental contamination by pesticides to public attention. Well-publicized and well-organized campaigns were mounted in several countries to prohibit the use of DDT and other persistent chlorinated insecticides such as Aldrin and heptachlor. Governments in many developed countries like USA, UK, Italy, USSR, Sweden, Norway, Denmark and Finland, proclaimed bans on DDT or severely restricted its use around 1960–1970.

Despite problems with its use, DDT has saved countless lives in regions where malaria is endemic. Tropical Asian countries, which have discontinued its use, have seen malaria incidence increase; India and some other countries still cling to use of DDT because it is cheap and effective. Tissue levels in wildlife of the regions where DDT was banned began to decline about 10 years after DDT was banned; however, DDT and its metabolites may routinely be detected in soil and bottom sediments even today (Galiulin and Bashkin, 1996). Over a long time, DDT is subject to atmospheric migration, for example from India to the Asian polar zone, to contribute to the contamination of local ecosystems as well.

PART IV

ENVIRONMENTAL RISK ASSESSMENT IN A REGIONAL SCALE

Many quantitative aspects of exposure pathways and their relevant application during environmental risk assessment depend on regional biogeochemical peculiarities and should be undoubtedly considered on the regional scale. Accordingly this part includes some characteristic examples and case studies from local up to regional and continental dimensions. We discuss the importance of the trans-boundary of pollutant exposure as well as the application of critical load methodology for risk estimates.

CHAPTER 14

CALIFORNIA CASE STUDIES

California is the most populated and the most extensively anthropogenically modified area of the USA. Moreover, this is a very complicated natural biogeochemical structure with numerous biogeochemical provinces charactered by different organization of food webs. A typical example is the selenium biogeochemical province in the Joaquin River valley where the exposure pathways have changed dramatically during the last century.

1. SELENIUM EFFECTS RESEARCH

1.1. San Joaquin River Valley, California

The characteristic example of Se-enriched regions is the San Joaquin Valley in California, USA (Figure 1).

The irrigation systems were constructed in this valley in 1930–1960s. It was found afterward that irrigation drainage water from parts of the San Joaquin Valley contains levels of selenium and other trace elements that have been implicated in bird deformations in the Kesterson Reservoir. Depending on location and season, the drainage water contains 100–1400 μg/L Se, predominantly as selenate (SeO_4^{-2}, Se-IV), the most soluble form, whereas the California State Water Resources Control Board has recommended an interim maximum mean monthly selenium concentration of 2–5 μg/L in receiving waters and wetlands.

Selenium concentrations in drainage and groundwater underlying agricultural areas of the western San Joaquin Valley result from the complex interactions amongst irrigated agricultural practices and physical and chemical processes. Although irrigated agriculture in the western valley began in the late 1800s, most of the area remained unirrigated until the 1930s and 1940s. The total area of land irrigated by pumped groundwater increased more than threefold in 1924 and continued to increase through to 1955. Surface water imported from northern California replaced groundwater for irrigation from the early 1950s and in the late 1960s and further increased the amount of irrigated acreage.

Irrigation using surface and ground water in this region has substantially altered the physical and chemical nature of the groundwater flow system and finally the total biogeochemical food web.

The deposits of the San Joaquin Valley are derived from the Sierra Nevada on the East and the Coast Range on the West. The Sierra Nevada, a fault block that dips

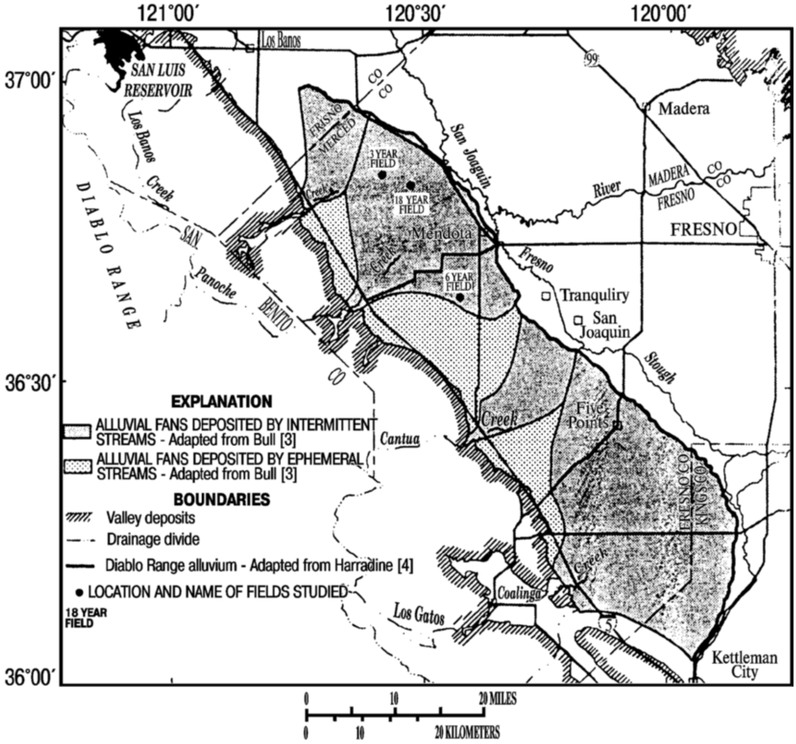


Figure 1. Location and geographic features of the western San Joaquin Valley (Deverel et al., 1994).

southwestward, is composed of igneous and metamorphic rock of mostly pre-Tertiary age. The Diablo Range of the California Coast Range, which borders the study area to the west, consists of an exposed program assemblage of Cretaceous and Upper Jurassic age and overlain by and juxtaposed with marine deposits of Cretaceous age and marine and continental deposits of Tertiary age. The alluvial fan deposits of the western valley are derived from the Diablo Range. The fans deposited by ephemeral streams are smaller than and enriched by the four major alluvial fans deposited by intermittent streams (Little Panoche, Panoche, Cantua, and Los Gatos Creeks) as shown in Figure 1 (Deverel et al., 1994).

Under natural conditions, groundwater discharge was primarily due to an infiltration of water from intermittent streams in the upper parts of the alluvial fans. This was changed during irrigation period. Pumping of groundwater increased the depth of the water table, and irrigation with pumped groundwater caused downward displacement of soil salts. Replacement of groundwater with surface water imported from northern California in the 1960s caused hydraulic pressures to increase and the water table to rise, creating a need for drainage in low-lying areas of the valley. Soil salts, including selenium species, were further displaced in the valley where irrigation water generally had not been applied previously. Application of irrigation water caused leaching of soil selenium salts and increase selenium concentrations in the groundwater. Subsequent evaporation of shallow groundwater increased selenium concentrations in the valley through and lower alluvial fans. Drainage systems were installed to prevent evaporation and to leach accumulated salts (Figure 2).

Concentrations of selenium in shallow groundwater generally were less than 20 μg/L in the middle alluvial fan deposits (Figure 3).

In the lower fan areas Se concentrations were monitored up to 400 μg/L. Similar historical distribution of soil Se content and shallow groundwater content indicate that dissolved selenium species were leached from saline soils by irrigation water. The drainage discharge of shallow groundwater and subsurface irrigation water was accompanied by increasing accumulation of Se in Kesterson Reservoir.

Aquatic birds nesting at Kesterson Reservoir in 1983 were found to have high rates of embryo deformities and mortality. Beginning in 1984, adult birds were also found dead in unusually high numbers. Through a series of field and laboratory studies, these effects were attributed to the exceptionally high concentrations of selenium in the biogeochemical food web of the birds.

1.2. Selenium in Fodder Crops of the USA

The spatial distribution of selenium content in fodder crops of the USA area is shown in Figure 4.

Plants exhibit genetic differences in Se uptake when grown on seleniferous soil. Some plants accumulate surprisingly low levels of Se. For example, white clover (*Trifolium repens*), buffalograss (*Buchloe dactiloides*) and grama (*Bouteloua* spp.) are poor accumulators of selenium. On the other hand, Se-rich plants like *Brassica* spp. (mustard, cabbage, broccoli, and sunflower) and other crucifers are good concentrators of this element.

2. POLLUTANTS EXPOSURE PATHWAYS

2.1. Chemical Exposure

A major research area for the assessment of chemical exposure pathways is the development of approaches for the specification, collection and analysis of environmental exposure and job task data for the purpose of hazard surveillance/epidemiology and for informing risk assessment where there is exposure to multiple chemical agents. A major area of research is the development of an integrated theory, approach and methodology to exposure assessment and hazard surveillance which emphasizes characterization of exposure to multiple chemical and physical agents. As an example, the following ongoing research projects are elements of the overall approach to the development of methods for studying multiple chemical exposure (Box 1).

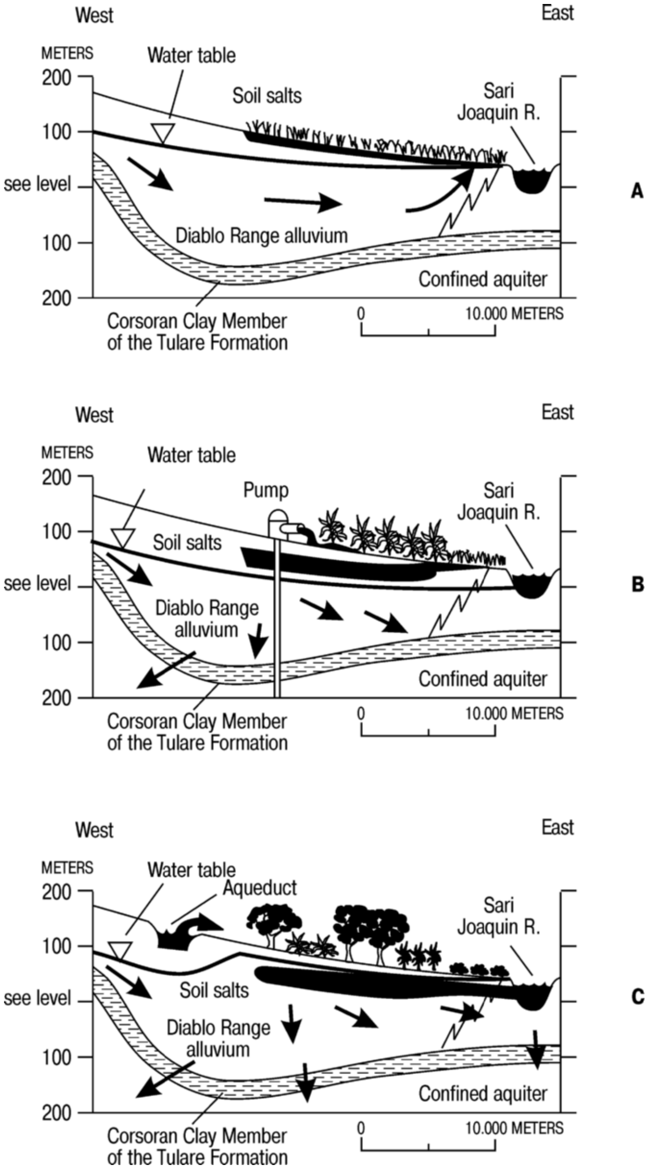


Figure 2. Geohydrologic sections through Panoche Creek alluvial fan illustrating the evolution of groundwater flow system and the concentration of selenium in these waters in the western San Joaquin Valley. Arrows indicate direction of flow. (A) Shallow distribution of soil selenium salts and primary horizontal direction of groundwater flow between recharge areas in the upper part of the fan and discharge areas along the San Joaguin River during pre-irrigation time. (B) Changes in groundwater flow direction and distribution of soil salts from the 1930s through the 1960s. (C) Discontinuation of pumping in the late 1960s caused a rise in the water table. Irrigation of low-lying areas and continued irrigation of middle and upper fan areas caused further downward displacement of soil selenium-containing salts and increasing their content in ground and drainage waters (Deverel et al., 1994).

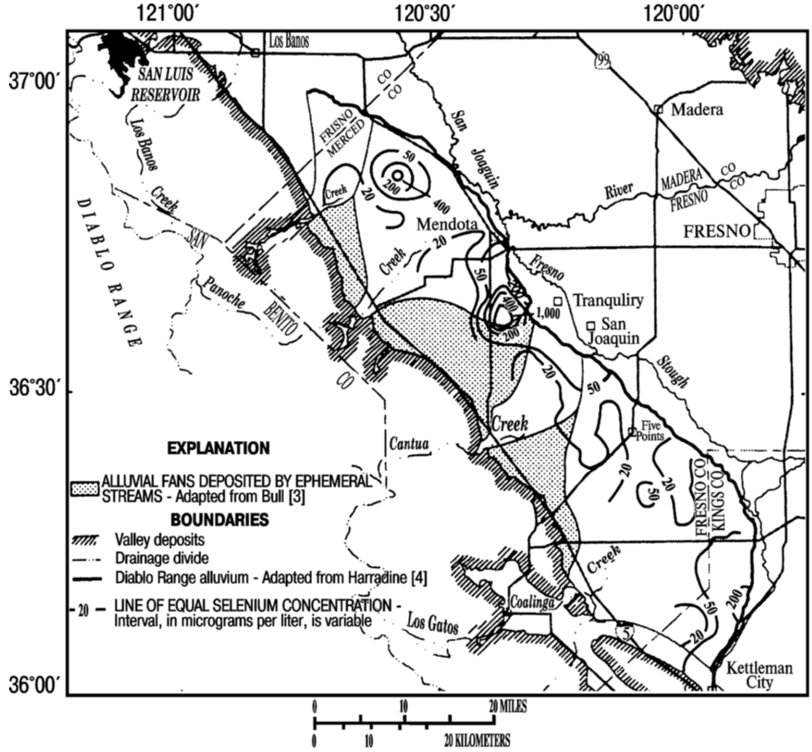


Figure 3. Concentrations of selenium in shallow groundwater in the middle alluvial fan deposits (Deverel et al., 1994).

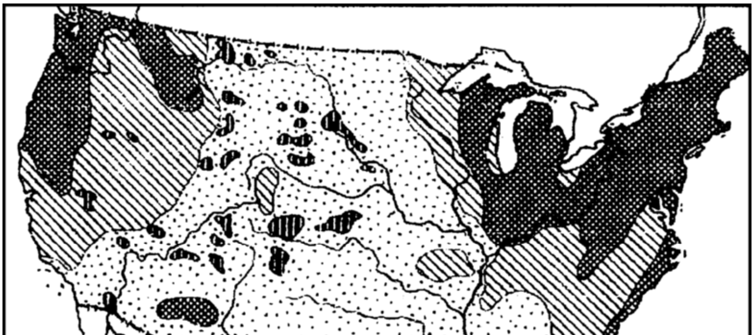


Figure 4. Content of Se in fodder crops in USA, ppm: 1—low, <0.05; 2—intermediate; 3—sufficient, >0.1 ppm, and 4—high, up to 5,000 and more (Besson and Martone, 1976).

Box 1. Multiple chemical agent exposure assessment (EARC, 2005)

A major research area for the EARC was the development of approaches for the specification, collection and analysis of environmental exposure and job task data for the purpose of hazard surveillance/epidemiology and for informing risk assessment where there is exposure to multiple chemical agents. A major area of research is the development of an integrated theory, approach and methodology to exposure assessment and hazard surveillance which emphasizes characterization of exposure to multiple chemical and physical agents. The following ongoing research projects are elements of the overall approach to the development of methods for studying multiple chemical exposure:

- The application of toxicokinetic modeling to the assessment of interactive effects between hexane, ketones and aromatic compounds. Investigation of dermal absorption of polycyclic aromatic compounds (PAHs). Research indicates dermal absorption of PAHs in a number of industries including aluminum smelting, coke ovens, creosote production and others is significantly more important than previously recognized.
- Modeling pollutant concentration between source and worker; prediction of small-scale dispersion of contaminants using data collected with a high-resolution three-axis sonic anemometer. The ultimate goal is to convert information collected by the anemometer into eddy diffusion coefficients, which can be used to estimate contaminant concentrations at any point within indoor environments.
- Short-term non-invasive biomarkers for processes producing long-term lung damage-evaluation of the feasibility of candidate measurement systems. Toxicokinetic models have been developed to determine whether breath analysis of pentane and ethane can be used to estimate chronic lung damage from toxicants.
- Optimization of the sampling of chemicals and mixtures deposited on surfaces that could be sources of human exposures. Specific collection methods have been assessed and laboratory based research work is underway to define optimization procedures for sampling.
- Adverse effects associated with multiple chemical exposures associated with rocket testing at a commercial defense test facility. This study evaluated the excess mortality of workers employed at a rocket test site over a period beginning in the 1950s. Excess lung cancer was identified in this cohort of workers and their health outcomes were possibly associated with exposure to hydrazines, nitrosamines, asbestos, trichloroethylene, and other chemicals.

2.2. Characterization of the Composition of Personal, Indoor, and Outdoor Particulate Exposure

This is a temporal study of personal exposures to particulate matter in a panel of patients with chronic obstructive pulmonary disease. Fifteen subjects will be monitored over 15 days (in each of two seasons) for personal, indoor and outdoor concentrations of particulate matter. This study explores whether a high-risk group modifies its exposure to air pollution through its activities and/or avoidance behaviors. The study will also determine the feasibility of direct exposure measurement in a panel study of acute health responses to environmental exposures (Box 2).

Box 2. Controlled laboratory evaluation of acute cardiopulmonary responses to concentrated particulates (EARC, 2005)

To assess the respiratory effects of concentrated ambient particles in volunteer human subjects, a two-stage fine particle concentrator was fabricated and installed in a movable exposure laboratory at Rancho Los Amigos Medical Center (http://www.rancho.org). Subjects' biomedical responses (respiratory irritation, airways inflammation, and alterations in cardiovascular function) to these exposures are being compared to responses under clean-air control conditions to assess the following hypotheses: (1) acute exposure to concentrated ambient fine particles in the South Coast Basin causes acute cardiopulmonary dysfunction; (2) the nature and magnitude of dysfunction differ according to the age and/or health status of the person exposed; (3) the nature and/or magnitude of dysfunction differs according to the characteristics of the particles inhaled.

2.3. Beryllium Exposure

A new area of research concerns exposure assessment for beryllium in the production of nuclear weapons at nuclear defense industries. A safe level of exposure to beryllium is still unknown. Potential explanations include: (1) the current exposure standard may not be protective enough to prevent sensitization, or (2) past exposure surveillance may have underestimated the actual exposure level because of a lack of understanding of the complexity of beryllium exposures. Task-based exposure assessment provides information not directly available through conventional sampling. It directly links exposure to specific activity associated with contaminant generation and provides in-depth evaluation of the worker's role in a specific task. In-depth task analysis is being used to examine physical, postural, and cognitive demands of various tasks.

Program faculty members are developing an automated cascade impactor for collection of task-based size distribution data of beryllium-containing aerosols. Based on the size distribution, the fraction of beryllium-containing aerosol penetrating a respirator and the inhalation and deposition in different regions of the lungs can be estimated.

3. OCCUPATIONAL EXPOSURE

3.1. Occupational Exposure to Multiple Pesticides

Agricultural production has increased substantially due to the commercialization and intensification of agriculture in developing countries such as Mexico. Identification of pesticide use and exposure sources, direct measures of pesticide exposure, quantification of internal dose, and variation over time present the most difficult challenges in performing pesticide exposure assessment. These factors are complicated in developing countries where pesticide sales and use reports, illness reports, and regulatory oversight of applications are limited.

The primary objective of this research is to quantitatively assess organophosphate (OP) pesticide exposure in agricultural workers and their families. We are studying children of agricultural workers living in close proximity to fields where their fathers work, pesticide applicators, and individuals in harvesting activities. Preliminary work in this region identified the major pesticides used in the home, use and application patterns in the field, hygiene practices during application, and storage practices. Micro-environmental, occupational, and biological monitoring of agricultural workers and their families is being conducted three times during the agricultural season.

3.2. Occupational Exposure to Arsenic

Center investigators are collaborating with scientists at NIEHS on investigation of the mechanism of arsenic carcinogenicity. The hypothesis is that there is increased susceptibility to arsenic tumorigenesis from genetic limitations in methylation capacity or as a result of nutritional deficiencies. A murine model for the induction of cancer in methyl-deficient C57Bl/6 mice is being developed. A subchronic study (funded by an SCEHSC pilot project grant) included mice fed methyl sufficient diets, methyl-deficient diets, and four concentrations of arsenic in methyl-deficient animals. NIEHS pathologists have completed the histopathology on the animals from the subchronic study and there is evidence of hyperplasia of the bladder in the methyl-deficient, arsenic exposed mice.

This research is an outgrowth of an earlier project which sought to characterize the mechanism of arsenic metabolism in a population currently drinking arsenic-contaminated water in Taiwan. There were three parts to the study, a cohort study, a case control study for skin cancer, and a study of intra-individual variability associated with chronic arsenic exposure. The latter three research projects are complete and being submitted for publication. The results of this research are highly relevant since they indicate that alterations in methylation capacity may affect arsenic carcinogenesis.

3.3. Air Pollutants

Relationship Between Personal, Outdoor and Indoor Air Concentrations (RIOPA)

The overall goal of the national multicenter (Elizabeth, NJ, Houston, TX, and Los Angeles County, CA) RIOPA study is to establish a scientific foundation for effective, timely, public health intervention strategies. Outdoor, indoor, and personal exposures of adults and children to PM are measured and evaluated by mass, elemental, chemical, and source apportionment analyses in the other research programs. Non-smoking asthmatic and non-asthmatic adults and their children are included. Monitoring occurs continuously ("real time") for 48 h during each of two seasons. Harvard impactor samplers (PM2.5 and elemental analysis for metals) and MSP sampling heads (PM2.5 and organic vapors) are used to characterize the interdependency of absolute levels and variations in outdoor and indoor microenvironment PM concentrations. Monitoring also includes carbonyl and volatile organic compounds with active and passive samplers. Time-activity patterns are assessed from subjects' diaries; standard instructions and examples of entries are developed. PM2.5 and air toxics data are compared with historical data from EPA/ARB outdoor PM and air toxins monitoring networks, respectively, for later use in the Regional Human Exposure (REHEX).

Chronic Effects of Ambient Air Pollutants

This 10-year longitudinal study is focused on the potential associations between ambient air pollution and respiratory health in children. The objectives are to document the respiratory growth of study participants, to assess whether ambient pollutants play a role in respiratory health, and to identify which pollutants are responsible for any observed effects. Ambient air quality is being monitored in each of twelve communities by centrally located regional stations, CA, which also collect standard meteorological data. Gaseous pollutants are monitored continuously, while ambient particle concentration and size are determined by a number of approaches. Additional exposure assessment occurs because of the establishment of the Particle Center, including more extensive particle size number, surface area, and volume distribution measurements.

Regional Human Exposure Modeling of Benzene in the California South Coast Air Basin

This project involved human exposure modeling to assess the change in benzene exposure between 1989 and 1997 in the California South Coast Air Basin using the REHEX model. The model, developed by Lurmann and Winer in 1989, is a stochastic model that utilizes available data on air quality (both indoor and outdoor), personal mobility, time activity and demographics. The model was the basis for the first comprehensive assessment of the health and economic benefits of meeting state and federal air quality standards for ozone and PM-10 in the South Coast Air Basin. Recent efforts include extending REHEX to the assessment of exposure of the Southern California population to environmental benzene, evaluation of indoor and in-vehicle microenvironments, benzene exposure due to passive smoking, gasoline stations, and underground parking garages.

Ambient Endotoxin Measurements in Southern California

Particulate matter (PM) is associated with adverse human respiratory health effects. Although much research has focused on the fine particle component (PM2.5), recent results from the USC Children's Health Study suggest that the coarse fraction may also affect respiratory health in children. Specific components of the coarse fraction responsible for these effects have not been identified, but ambient endotoxin is a strong candidate, based on toxicologic and epidemiologic studies. This study is collecting ambient endotoxin samples in each of the twelve Children's Health Study communities to assess seasonal and inter-community variability. Analysis of the collected samples is performed at the University of Iowa. The exposure information is then used to determine its relationship to respiratory effects in children.

Allergen Content of Paved Road Dust

The long-term study of the nature of man-caused emissions of allergens to the atmosphere and their resulting atmospheric concentration was studied using immunoassay techniques for the detection of latex allergens in environmental samples and applied those methods to the study of latex proteins that are extractable from authentic tire dust samples and from airborne particle samples. The study of the allergen content of paved road dust emissions that occur as vehicle traffic moves over the streets was undertaken. The investigators found more than 20 allergens associated with molds and pollen fragments in paved road dust samples collected in Southern California, and up to approximately 12% of the allergen concentrations in the atmosphere of some communities are contributed by paved road dust emissions. This may help to explain persistent reports of increased asthma incidence among persons living close to heavily-traveled streets. A companion study of allergen concentrations in woodsmokes is also underway (EARC, 2005).

4. CANCER RESEARCHES

4.1. Childhood Cancer Research Program

The primary goal of the Childhood Cancer Research Program is to identify environmental factors responsible for childhood cancer. Specific aims are to understand the interactions between environmental causes of childhood cancer and host factors that influence reaction to environmental exposure.

The etiology of childhood cancer has been a long-standing interest of faculty in the USC Department of Preventive Medicine. Epidemiological study of these cancers has been hampered by their rarity, but a number of factors have assisted researchers in development of the Childhood Cancer Research Program. The first is the population base of the Los Angeles County Cancer Surveillance Program, a tumor registry which has provided an adequate number of cases for several case-control studies of the two commonest malignancies, acute leukemia and brain tumors. The second are the necessities to expand the population base for research on the causes of childhood brain tumors. While researchers are far from understanding the basis of most childhood cancers, the picture that has emerged from recent research, and others, is as follows. There are clearly heritable genetic factors responsible for some cancers (notably, retinoblastoma), but family studies in general suggest that the contribution of such factors is small. On the other hand, there is substantial evidence implicating a number of environmental factors in childhood cancer, including both direct exposures to the child and indirect parental exposures.

Controversy has arisen recently regarding the apparent increase in incidence of childhood cancer in the U.S. Some investigators, particularly at the EPA, have raised concerns that this increase may reflect new or increasing environmental exposures. The alternative view is that there has been little secular change in incidence, and that apparent increases in, for example, brain tumors, reflect changes in medical practice and diagnostic methods rather than a true increase in incidence. Part of the difficulty in understanding childhood cancer trends lies in the relative rarity of most cancer types and the lack of a national system of cancer registration that would provide the ability to track incidence on a nationwide scale.

For the most part, environmental associations that have been reported for childhood cancers have been of moderate magnitude (and thus readily interpretable as due to unrecognized confounding) and relatively inconsistent across studies. The challenge for the future is to confirm the genuine associations through larger, more focused studies, and to reduce potential bias and increase the accuracy and specificity of the exposure assessments through direct measurement where possible.

4.2. Adult Cancer Research Program

The specific aims of the Adult Cancer Research Program are:

- To identify new or provide more detailed evaluation of known environmental causes of adult cancer.
- To identify or develop improved methods of exposure assessment for environmental carcinogens.
- To develop methods to identify individual or population susceptibility to environmental carcinogens, focusing on regulatory mechanisms for metabolism of carcinogens or repair mechanisms for carcinogen induced DNA damage between individuals or populations.
- To identify environmental exposures which alter penetrance of "cancer susceptibility" genes and to quantify these gene–environment interactions.
- To provide an infrastructure to promote communication between laboratory scientists and epidemiologists for the purpose of developing interdisciplinary research on gene–environment interactions in cancer etiology.

Research on the environmental etiology of cancer by epidemiologic means at USC began in 1970 as part of an NCI program in viral oncology. Early in the development of the program the Cancer Surveillance Program, the population-based cancer registry of Los Angeles County was begun, and the senior members of the program were recruited. As the program expanded the environmental exposures of interest were broadened from infectious agents, air pollutants, and endogenous hormones to include occupational exposures, iatrogenic exposures, and aspects of lifestyle, including diet. Other resources were established, including cohorts locally and in East Asia, and registries of affected and healthy twins.

The adult cancer research program has an extensive history in studying the environmental causes of adult cancer and, with the advent of new laboratory technology to explore genetic causes of cancer in large-scale studies, has moved rapidly toward the exploration of genetic modification of environmental risk factors. The program's strengths have been built in part around the development of large multipurpose databases. Among those most extensively utilized currently are:

- The Cancer Surveillance Program, the population-based SEER cancer registry of Los Angeles County which we developed and operate.
- The California Teachers study, a prospective study of 133,000 female California teachers.
- The Hawaii–Los Angeles Multiethnic Cohort study, a prospective study of 212,000 men and women from four racial-ethnic groups in Hawaii and Los Angeles.
- The International and California Twin Registries, the former including 12,000 pairs of twins at least one of whom has cancer and the latter including over 40,000 healthy twins being followed for cancer development.
- The Shanghai Cohort study, a prospective biomarker-based study of 18,000 middle-aged men in Shanghai.
- The Family Colon Cancer Registry, a multi-institutional study headquartered here of 4,000 multiplex colon cancer families.
- The Singapore Cohort study, a prospective study of 60,000 male and female Chinese adults in Singapore.

5. RESPIRATORY EFFECTS RESEARCH

The primary purpose for the respiratory effects research is to conduct research on the acute and chronic effects of environmental factors on human lungs, in particular, both outdoor and indoor air pollution and its many components, occupational exposures, passive smoking, heating and cooking gases, formaldehyde and bioaerosols. Investigators are equally interested in determining the extent to which host factors modify response. These factors might be specific such as genotype or general such as nutritional status, socioeconomic status, race, or gender. The program is set up to study these problems either on a large scale in populations or on a smaller scale in exposure chambers set up to deliver a specific exposure or mixture of exposures. The program offers a wide range of approaches to determining the acute and chronic respiratory effects of inhaled pollutants on a clinical or epidemiologic scale. To the extent possible, these studies evaluate the effects of individual pollutants. Successful completion of the studies relies on interaction with several other Programs—most importantly the Exposure Assessment Research Program, the Statistical Methods Research Program, and the Biostatistics Service Program Facility.

Respiratory disease (including asthma) continues to be a major public health problem. Chronic obstructive lung disease, chronic bronchitis and asthma continue to produce considerable morbidity and mortality in both adults and children. Environmental factors have long been recognized as important in the causation of these diseases. The identification of these factors has had and continues to have important public health (preventive) implications. For example, there has been recent recognition that particulate air pollution may be accounting for excess morbidity and mortality, a problem with enormous regulatory significance, however, little is known about the nature of the particles we breathe. We are only beginning to understand the true relationships of indoor and outdoor pollution with the various forms of respiratory disease. This research program is set up to study these kinds of problems either on a large scale in populations or on a smaller scale in an exposure chamber set up to deliver a specific exposure or mixture of exposures. The activities include chamber facilities in which acute exposures to individual pollutants are delivered to sedentary and to exercising individuals who may be healthy or unhealthy (asthma panels for example). The program offers a wide range of approaches to determining the acute and chronic respiratory effects of pollutants on a clinical or epidemiologic scale.

Asthma rates in children in Southern California are high and oxidant pollution levels are likewise high. It is important to determine the relationship between the two. It is also important to determine whether there are chronic pulmonary effects produced by either these oxidants and/or particulate pollution. Since children spend more time outdoors than adults and since they exercise more while outdoors, the added assault from increased ventilation may be of importance. The studies feature a comprehensive exposure assessment that has led to a better understanding of the relationship between exposure and effects. It is also important to identify sub-populations of children and adults who are more susceptible to air pollution-related respiratory effects if they exist. Altered susceptibility could be based on genetic or non-genetic mechanisms (nutritional status for example). Both the epidemiologic and chamber studies provide opportunities to examine issues of hypersusceptibility and to determine the reasons for it if it exists.

CHAPTER 15

EURASIAN CASE STUDIES

Eurasia is the biggest continent of the World. Because of the huge size of Eurasia, all types of ecosystems and climatic belts are represented, from arctic deserts up to tropical rain forests. Accordingly, some characteristic examples will be given here with special attention to biogeochemical provinces where biogeochemical exposure pathways induce the relevant diseases.

1. ENVIRONMENTAL RISK ASSESSMENT OF Se INDUCED DISEASES

1.1. Northern Eurasia

In the Asian part of Russia the biogeochemical sub-region with excessive content of Se in different biogeochemical food webs was monitored. The excessive Se content is connected with high concentration of this metal in local sedimentary rocks of the Tuva administrative region (South of Central Siberia). This sub-region is placed in the Ulug-Hemsk and Turan-Uluks depressions and two corresponding biogeochemical provinces were described (Figure 1).

The first province is shown in Figure 2 and it has been studied extensively (Ermakov, 1993).

This province occupies the central part of the Baryk valley. The geological composition includes Carbon sediments over the Devonian rocks. Selenium was accumulated in the Middle Devonian pink-gray sandstone up to 20 ppm. This has led to the formation of soils enriched by Se up to 6.0 ppm with corresponding enrichment of plant species of *Cruciferae*, *Leguminae* and various multiflorous botanic families. These species are *Alyssum lenese Adams*, Se accumulation up to 13.1 ppm by dry weight, *Artemisia glauca Pall*, Se accumulation up to 6.0 ppm by dry weight, etc. Biogeochemical researches have shown that only microbial communities have adapted to this Se enrichment. The plant species indicate the chlorosis and necrosis of leaves. Various physiological abnormalities have been monitored in sheep, like hoof deformation, baldness, hypochromic anemia and increasing activity of phosphatase in different organs. The content of Se in various organs and tissues of sheep is 2.5 times higher in the Ulug-Hemsk biogeochemical province in comparison with other studied sites of the Tuva administrative region.

The average concentration of selenium in various biogeochemical food webs is shown in Table 1.

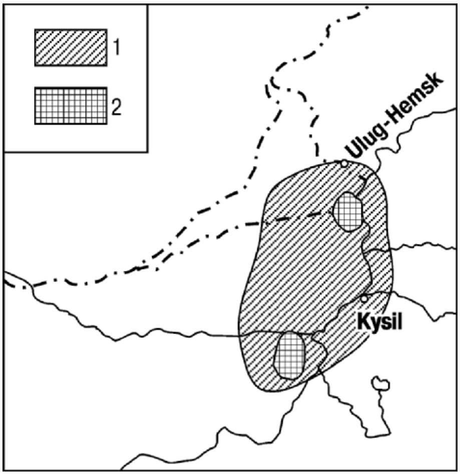


Figure 1. Biogeochemical sub-region and provinces enriched by selenium. 1—sub-region with Se content in soil from 0.2 to 0.5 ppm and in plant species from 0.08 to 0.5 ppm; 2—Ulug-Hemsk and Turan-Uluks biogeochemical provinces with Se content in soil as much as 0.3–6.0 ppm and in plant species from 0.1 to 13.1 ppm by dry weight (Ermakov, 1993).

Similar regions were monitored in other sites of Russia, especially in the South Ural mountains, where the elevated contents of selenium in soils and natural waters coincide with increasing rates of corresponding animal diseases. The analogous biogeochemical provinces have been also monitored in Uzbekistan.

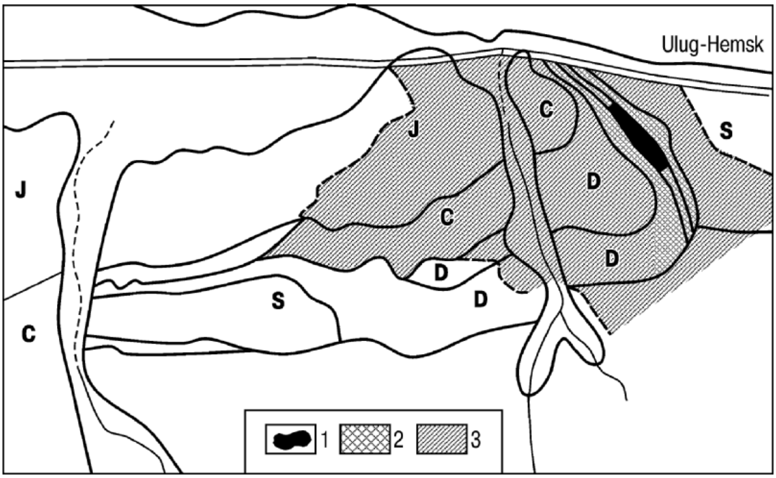


Figure 2. The map of Ulug-Hemsk biogeochemical province with high-Se concentrations in biogeochemical food web. Se concentration, ppm: 1—in soil 2–4, in plant 0.7–13.1; 2—in soil 0.7–1.0, in plant 0.4–6.0; 3—in soil 0.4–0.7, in plant 0.1–2.4 (Ermakov, 1993).

Table 1. Se concentrations in biogeochemical food webs of the Tuva biogeochemical sub-region and selenium biogeochemical province (after Ermakov, 1993).

Links of biogeochemical food web	Se content in enriched biogeochemical areas, ppm	
	Tuva sub-region	Ulug-Hemsk province
Geological rock	2.64 ± 0.43	0.29 ± 0.02
Soils	0.82 ± 0.09	0.18 ± 0.02
Natural waters, ppb	3.45 ± 0.85	0.47 ± 0.26
Plants	2.18 ± 0.52	0.38 ± 0.02

There are physiological standards for diagnosis of both Se deficit and excess. The standard content of Se in blood samples is 4–10 ppb, and in kidney, 10–20 ppb. Under Se deficit this content decreases till 1–3 ppb, and under excessive intake, it increases up to 40–100 ppb (Ermakov, 1993).

The comparison of different selenium biogeochemical regions is shown in Table 2.

We can see that Se deficit is often monitored in the biogeochemical food webs in the Chita region, Russia, and Latvia and the Se enrichment in the Fergana valley of Uzbekistan. The Se deficit is also connected with the lower values of C_b in the first two regions in comparison with the latter, where selenium is more mobile due to

Table 2. The average relative selenium contents in biogeochemical food webs of different biogeochemical sub-regions in Eurasia (percent of the physiological standard values).

Biogeochemical food webs						
Rocks	Soils	Fodder crops	Winter wheat	Sheep wool	Sheep blood	Activity of sheep glutathion peroxidase ferment
Chita administration region, Russia, C_b—0.08						
50	60	15	20	30	25	25
North-Latvian moraine plain, Latvia, C_b—0.2–0.08						
300	70–200	50	60	30	40	40
Fergana valley, Uzbekistan, C_b—1.50						
200	100	450	160	130	180	130

Note: C_b, coefficient of biogeochemical plant uptake, is the ratio between Se content in plant and soils.

the alkaline reaction of soils. The lower biogeochemical mobility of selenium in the south Siberia (Chita region) is related to the low level of this trace metal in rocks and in Latvia it is connected with low mobility of Se in predominant local acid sand and peat soils.

1.2. Selenium in China's Ecosystems

At the end of the 1960s the biogeochemical studies of selenium were initiated in China to determine the causes of two endemic human diseases, Keshan disease and Kachin-Beck disease. The former is an endemic cardiomyopathy, and the latter is an endemic osteoarthrosis (Tan et al., 1994).

The distribution of both endemic diseases has been found to relate to selenium content in the soils. The two diseases are distributed mainly in a distinct wide belt, usually referred to as the disease belt, running from the northeast to southeast of China and located in the middle transition belt from the southern coast to the northwest inland region (Figures 3 and 4).

The belt is mainly represented by Temperate Forest ecosystems on forest–steppe soils (Brown Earth). The analyses of selenium content in various links of the biogeochemical food web (rock, water, soils, grains, hair, etc.) has shown that these

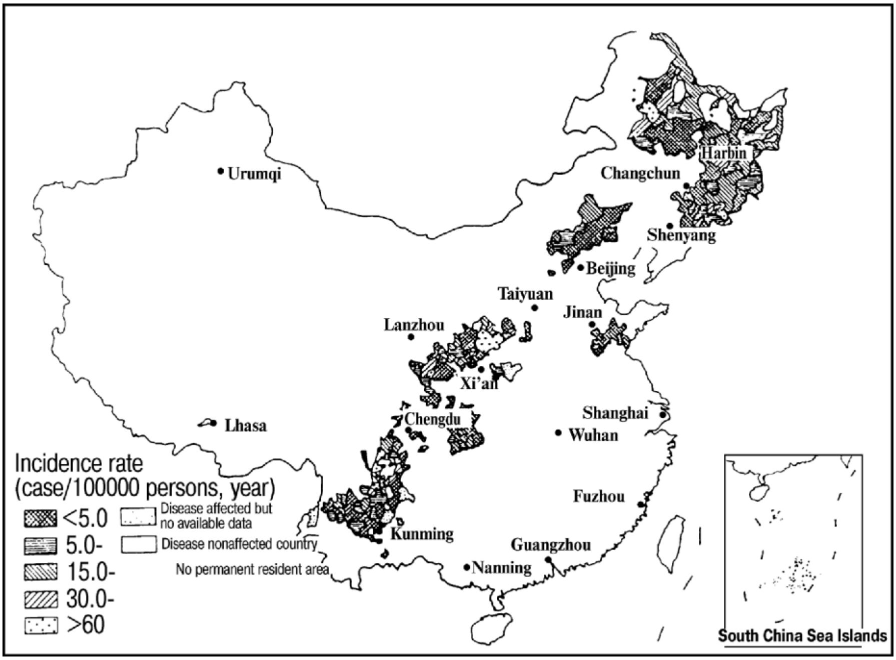


Figure 3. Distribution map of annual average incidences of Keshan disease (acute and subacute) in China (Tan et al., 1994).

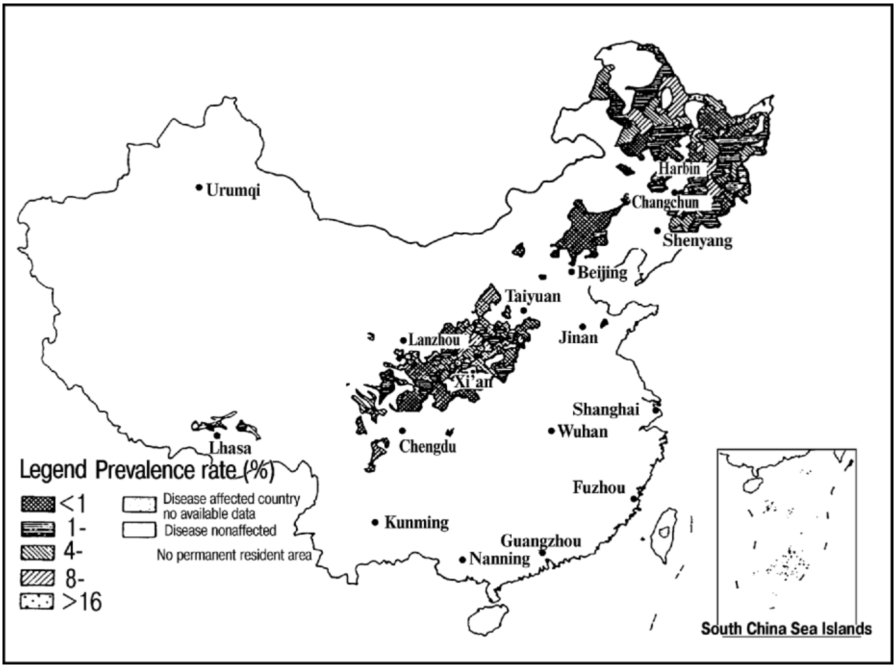
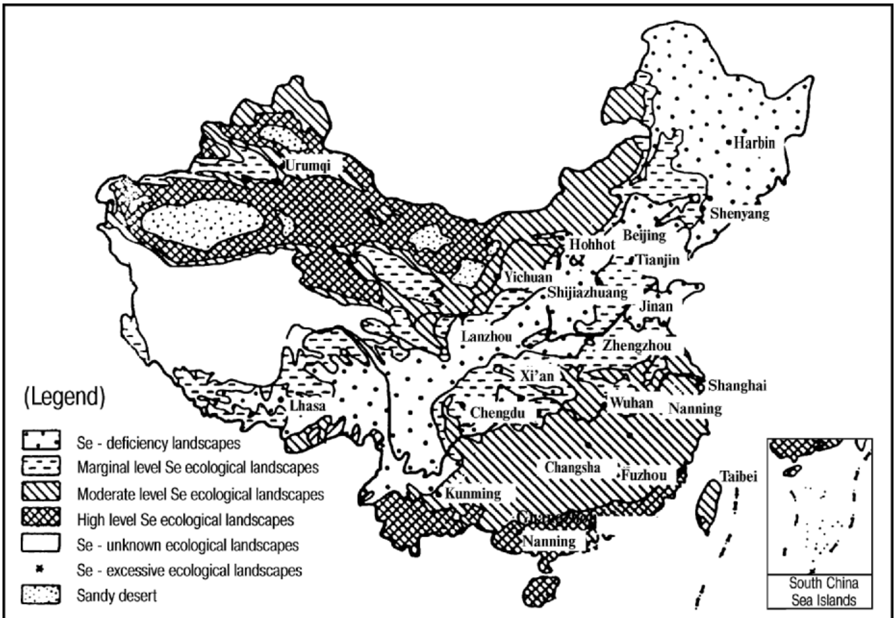


Figure 4. Distribution map of annual average incidences of Kachin–Beck in China (Tan et al., 1994).

two diseases are always located in low-selenium biogeochemical sub-regions of the biosphere.

The following biogeochemical mapping of Se content in China's ecosystems has been suggested.

1. The low-Se ecosystems occur mainly in and near the temperate forest and forest steppe landscapes as an axis in China, and the relatively high-Se content in the ecosystems usually appear in the typical humid tropical and subtropical landscapes and typical temperate desert and steppe landscapes.
2. In juvenile soil landscapes, Se from parent materials is a very important factor controlling the biogeochemical food web in the whole ecosystem.
3. In some mountain districts or elevated areas, the distribution of the low-Se ecosystems is also associated with vertical distribution of such mountain landscapes, as mountain forest, forest steppe, and meadow steppes.
4. Relatively high-Se contents are in the ecosystems of large accumulation plains, such as the Songliao, Weine, and Hua Bei plains, compared with the above-located landscapes of similar area.



Threshold values for Se Dividing Ecological Landscape (ppm)

So content grading	Total in topsoil	**Water-soluble** In topsoil	Food grains	Hair	Effect
Deficient	<0.125	<0.003	<0.025	<0.200	Se responsive diseases
Marginal	0.125-0.175	0.003-0.006	0.025-0.04	0.200-0.25	Potential Se deficiency
Moderate	0.175-0.40	0.006-0.008	0.040-0.070	0.25-0.500	
High	0.40	0.008	0.070	0.500	
Excessive	≥3.0	≥0.02	≥1.0	≥3.0	Se poisoning

Figure 5. Selenium biogeochemical map of China (Tan et al., 1994).

These four principles of mapping are shown in Figure 5 and represent the low-Se belt running from northwest to southeast, whereas two relatively high-Se belts flanks it on both sides, to the southeast and northeast.

2. ENVIRONMENTAL RISK ASSESSMENT OF Co–Zn–Ni INDUCED DISEASES

2.1. Biogeochemical Cycles of Heavy Metals in the South Ural Region, Russia

This territory occupies the watershed between rivers Ural and Sakmara, with total area of 14,890 km^2. The region is a weakly hilly plain, 200–500 m above sea level. The soil-forming geological rocks are metamorphic, basic and ancient volcanic deposits. The main soils are Chernozems and Kastanozems. In this area, there are two large copper ore deposits with admixtures of other non-ferrous metals, like Zn, Co, Ni, etc. During 1970–1980, the various links of biogeochemical food webs have been monitored to carry out biogeochemical mapping of this region. The results are shown in Tables 3–5.

Table 3. Biogeochemical cycles of copper, zinc, cobalt and nickel in South Ural sub-region (after Kovalsky, 1981).

Links of biogeochemical food webs	Units	Chemical element	Sub-region	Biogeochemical provinces		Control region
				Baimak	Uldybaev–Chalil	
Rocks	ppm	Cu	20–2,000	100.0	33.1	35
		Zn	70–4,300	130.0	75.2	70.0
		Co	10–180	45.2	80.2	10.4
		Ni	55–1,800	160.0	1,250.0	55.4
Soils	ppm	Cu	76.3	98.0	37.1	3.7
		Zn	155.2	201.1	94.3	40.2
		Co	30.6	27.5	51.4	18.3
		Ni	235.3	185.4	663.0	57.3
Waters	ppb	Cu	7.1	14.0	5.6	4.7
		Zn	22.3	31.7	20.3	10.0
		Co	1.8	1.9	1.8	1.1
		Ni	17.4	20.9	16.7	5.1
Air	ppb	Cu	0.72	—	—	0.17
		Zn	2.80	—	—	10.92
Accumulation by microbial biomass	kg/ha in 20 cm layer	Cu	—	0.161	0.067	0.031
		Zn	—	0.120	0.059	0.034
		Co	—	0.021	0.061	—
		Ni	—	0.097	0.109	—
Terrestrial plants	ppm	Cu	25.3	30.0	19.0	5.3
		Zn	46.5	60.1	32.9	21.1
		Co	1.02	0.65	1.38	0.68
		Ni	14.4	6.5	21.3	6.2
Bottom sediment	ppm	Cu	45.4	98.1	34.5	15.0
		Zn	248.0	185.2	295.1	37.9
		Co	10.3	6.9	11.6	8.1
		Ni	124.0	60.3	124.4	31.1

(*Conti.*)

Table 3. (Continued)

Links of biogeochemical food webs	Units	Chemical element	Sub-region	Biogeochemical provinces		Control region
				Baimak	Uldybaev–Chalil	
Aquatic plants	ppm	Cu	18.3	17.3	21.1	15.9
		Zn	70.2	126.9	73.3	24.5
		Co	8.5	6.0	10.5	0.3
		Ni	19.2	16.1	26.4	2.9
Plankton	ppm	Cu	—	—	9.5	—
		Zn	—	—	78.5	—
		Co	—	—	5.0	—
		Ni	—	—	23.0	—
Fish	ppm	Cu	4.1	3.5	5.0	—
		Zn	71.3	69.5	73.1	—
		Co	0.56	0.3	73.1	—
		Ni	1.9	1.5	2.2	—
Bentos	ppm	Cu	23.6	29.6	19.6	—
		Zn	70.0	101.0	50.4	—
		Co	3.2	2.5	3.6	—
		Ni	5.9	3.6	7.1	—

Table 4. Content of metals in forage crops from Udlybaev–Chalil Ni–Cu–Co biogeochemical provinces of South Ural sub-region of biosphere, ppm by dry weight.

Plant species	Cu	Zn	Co	Ni
Mix-grasses	25.1	62.2	2.8	25.0
Legumes	8.2	27.3	1.2	15.2
Herbaceous	22.3	38.4	0.8	18.2
Silage	15.2	62.3	0.9	8.0
Dry mixture	8.3	117.0	0.7	6.5

Table 5. Content of copper in foodstuffs from Baimak Cu–Zn biogeochemical provinces of South Ural sub-region of biosphere, ppm by dry weight.

Foodstuffs	Bairak biogeochemical province	Control region
Wheat	20.16 ± 0.91	3.73 ± 0.36
Potato	7.15 ± 1.26	2.05 ± 0.85
Meat	3.45 ± 0.38	0.43 ± 0.04
Milk	1.33 ± 0.39	0.30 ± 0.01

2.2. Endemic Diseases Biogeochemical Exposure Pathways

The results of biogeochemical monitoring are correlated with endemic diseases and morphological alterations in both biogeochemical provinces. In the Baimak Cu–Zn biogeochemical province, the chlorosis, necrosis, alterations of organs, reduction of flowers, sterility and infertility are shown for *Salvia stepposa, Verbascum phoniceum, Astragalus macropus, Galium verum* and *Phomis tuberosa*. In the Uldybaev–Chalil Ni–Cu–Co biogeochemical province, the chlorosis, necrosis, growth depression, alterations of organs, reduction of flowers, sterility and infertility are shown for *Salvia stepposa, Verbascum phoniceum, Astragalus macropus, Galium verum* and *Phomis tuberosa*, *Salvia stepposa, Verbascum phoniceum, Perethrum multifoliatum, Potentilla humiphusa,* and *Phomis tuberosa*. The biological reactions of animals are related to endemic copper toxicology in the Baimak biogeochemical province and the eye diseases, like disturbance of cornea, and atypical skin diseases in the Uldybaev–Chalil Ni–Cu–Co biogeochemical province. The endemic copper anemia is monitored in humans only in Cu–Zn enrichment in Baimak biogeochemical province.

These results are shown in Figure 6.

Thus, the monitoring of biogeochemical food webs of copper, zinc, cobalt and nickel in biogeochemical provinces, enriched by these elements, showed that, in comparison with the control Steppe Chernozem biogeochemical sub-region of biosphere, the South Ural sub-region of biosphere and corresponding biogeochemical provinces are the areas with straightly altered biochemical and physiological activities of plants, domestic animals and humans. These have led to endemic diseases, morphological alterations and adaptations.

3. ENVIRONMENTAL RISK ASSESSMENT OF AIR POLLUTION INDUCED DISEASES

3.1. Estimating and Valuing the Health Impacts of Urban Air Pollution

Air pollution has been associated with a variety of adverse health effects (Table 6). These include impairments in lung function, increased incidence of chronic bronchitis,

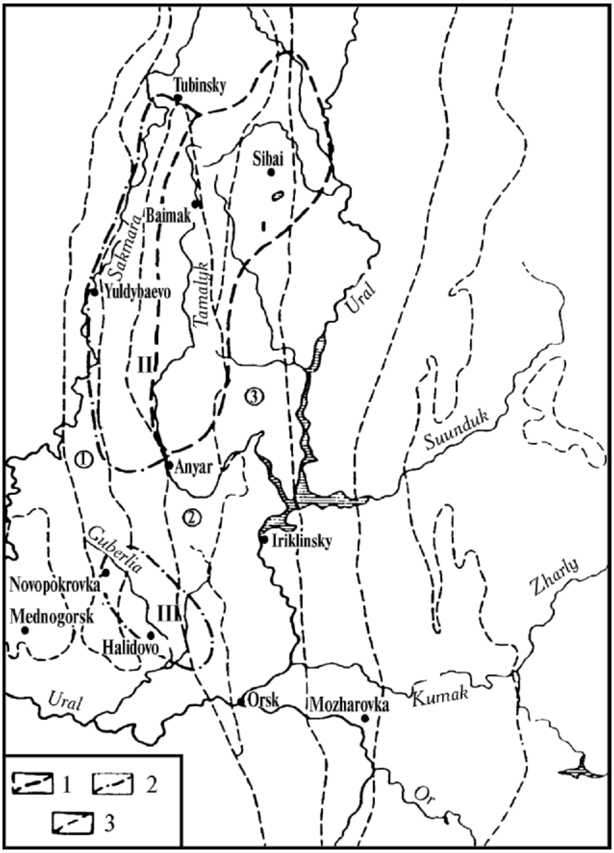


Figure 6. Biogeochemical exposure mapping of South Ural sub-region of biosphere, Russia. 1—the Baimak Cu–Zn biogeochemical province (I); 2—the Uldybaev Ni–Cu–Co biogeochemical province (II), the Chalil Ni–Cu–Co biogeochemical province (III).

exacerbation of chronic respiratory disease (that is, asthma) or coronary disease (such as angina), and premature mortality from respiratory and cardiovascular disease. Less serious effects include increased incidence of acute respiratory illness (colds and sinus problems) and sub-clinical effects (itchy, watery eyes).

The most important health effects, in terms of economic damages that can be assigned monetary values, are premature mortality and increased incidence of chronic heart and lung disease. The air pollutants that have shown the strongest association with premature mortality and heart and lung disease are PM and airborne lead. PM has also been associated with hospital admissions, respiratory infections, and asthma attacks. Ozone has also been associated with mortality, hospital admissions, asthma attacks and respiratory restricted activity days (RADs), days on which a person cuts back on his or her normal activities, but does not necessarily miss work or stay in bed. SO_2 and NO_x do not have such significant direct effects, though they do have

Table 6. Human health effects of the common air pollutants.

Lead	Mortality Morbidity:	Health effecs for individuals in age ranges other than those studied
	Hypertension	Neurobehavioral function
	Nonfatal coronary heart disease	Other cardiovascular diseases
	Nonfatal strokes	Reproductive effects
	Intelligence quotient (IQ) loss effect on lifetime earnings	Fetal effects from maternal exposure
	IQ loss effects on special education needs	Delinquent and antisocial behavior in children

Source: U.S. EPA (1997)

important health consequences because of secondary particulate formation: sulfates and nitrates react with ammonia and other substances in the atmosphere to form particulate matter, such as ammonium sulfate and ammonium nitrate.

3.2. Human Health Risk Estimates

Let us consider the methods used to estimate the health impacts of particulate air pollution, followed by those used to perform economic valuation of changes in illness and premature mortality, and discusses the appropriateness of transferring health benefit estimates from studies in other regions to developing countries.

Estimating the health impacts of air pollution reductions entails three steps. First, the demographic groups susceptible to air pollution and associated health outcomes are identified based almost exclusively on epidemiological studies. These studies determine relationships—referred to as concentration-response (CR) functions—between air pollution and health effects in human populations. CR functions empirically explain variations in the number of cases of illness or death observed in a population based on changes in the ambient concentrations of the air pollutants and other known explanatory factors. These other factors, called *complicating factors* (those that also affect health outcomes, making it difficult to attribute cause), include demographics (such as age, gender, marital status, diet, body mass, smoking, health habits, occupational exposure, education, and income), other pollutants, and time-varying factors (temperature, seasonality, day of week). CR functions may apply to the whole population or to specific demographic groups only. Virtually all CR functions assume that each unit decrease in the ambient concentration of a pollutant results in a fixed percentage change in the cases of illness or deaths avoided, independent of the initial pollution level. This assumption may not be valid when ambient concentration levels are several-fold higher than in cities where studies have been conducted, as is the case when applying CR functions estimated in industrial countries for fine particles to cities in developing countries.

Ideally, cities considering significant policy changes to address air pollution problems should conduct an epidemiological study locally. In practice, the complexity and costs of undertaking these studies have limited the number of such studies. Instead, cities typically transfer information on health impacts of pollutants on the susceptible demographic groups from existing studies conducted elsewhere. An example is given for a CR function transferred in a health impact estimation study of Mexico City (World Bank, 2002). Similar functions are available for other health impacts from PM10 as well as other pollutants such as ozone. The appropriateness of transferring these functions depends on whether the complicating factors for the city are similar to those for the cities included in the transferred epidemiological studies.

3.3. Case Epidemiological Studies

Epidemiological studies can be grouped according to how exposure is measured (acute exposure studies and chronic exposure studies) and how health effects are measured (individual-based panel or cohort studies and population-based or ecological studies). Most studies in the scientific literature have examined acute, not chronic, health consequences.

Human Health Impacts of Acute Exposure to Particulate Air Pollution

Acute exposure studies examine the associations between short-term (daily or multiday average) variations in PM concentrations and short-term counts of total deaths, cause of specific deaths, or incidence of specific illness in an area (typically a city). The popularity of these studies stems from their minimal data requirement compared with other study designs. Problems associated with complicating are reduced in these studies because population characteristics (such as smoking and occupational exposures) do not change much over the study period for the population being studied. In addition to air pollution, temporal and meteorological conditions and the age of the individual are the main factors that are included in these studies. While these studies provide health impact estimates for the city being studied, the CR functions obtained are not readily transferable to cities with different population characteristics.

However, the consistent findings across a wide array of cities, including those in developing countries with diverse population and possibly PM characteristics, strongly indicate that the health gains indeed result from PM pollution reductions. Meta-analysis—which pools results from several studies—of acute exposure studies provides health impact estimates that are more transferable than results from individual studies. These results indicate that every 10 mg/m^3 increase in the daily or multiday average concentration of PM10 increases (1) non-trauma deaths by 0.8%; (2) hospital admissions for respiratory and cardiovascular diseases by 1.4 and 0.6%, respectively; (3) emergency room visits by 3.1%; (4) restricted activity days by 7.7%; and (5) cough with phlegm in children by 3.3–4.5 (ESCAP, 2000). The studies also indicate higher risk for the elderly with chronic heart and lung disease and for infants.

Human Health Impacts of Chronic Exposure to Particulate Air Pollution

Chronic exposure studies examine the impact of long-term exposure to PM air pollution as well as the cumulative effects of short-term elevated PM levels. These studies

Table 7. Percent contributions of different sources to ambient PM2.5.

City and season	Diesel	Gasoline	Road dust	Coal	Biomass	Secondary sulfates	Secondary nitrates	Secondary ammonium	Total
Chandigarh summer	7%	17%	32%	0%	9%	16%	2%	6%	90%
Delhi spring	18%	4%	16%	2%	22%	8%	2%	6%	77%
Delhi summer	23%	2%	41%	1%	10%	10%	3%	3%	91%
Delhi autumn	15%	3%	18%	2%	21%	6%	7%	2%	75%
Delhi winter	ie%	7%	4%	9%	29%	8%	7%	5%	85%
Kolkata spring	24%	11%	28%	4%	19%	15%	2%	3%	107%
Kolkata summer	61%	8%	21%	1%	24%	10%	3%	1%	130%
Kolkata autumn	43%	21%	7%	5%	32%	8%	1%	2%	120%
Kolkata winter	15%	9%	5%	13%	17%	4%	3%	3%	70%
Mumbai spring	25%	3%	38%	0%	13%	15%	2%	2%	98%
Mumbai autumn	20%	2%	23%	1%	21%	12%	3%	3%	84%
Mumbai winter	21%	5%	16%	4%	13%	12%	3%	4%	78%

Note: Insufficient sample was collected in summer in Mumbai to carry out hydrocarbon speciation.

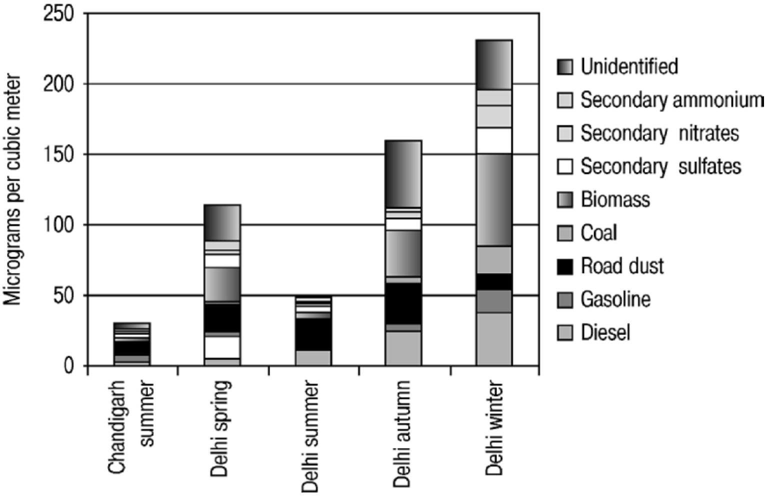


Figure 7. Estimates of PM2.5 sources in Chandigarh and Delhi (India).

compare differences in health outcomes across several locations at a selected period in time. Some portion of the long-term impacts indicated by these studies corresponds to the impact of acute effects revealed in acute exposure studies. The remainder is caused by latent or chronic effects of cumulative exposure.

Ecological studies, which use population-wide measures of health outcomes, have consistently found increased mortality rates in cities with higher PM levels. However, the inability to isolate the effects of PM from alternative explanatory factors (that is,

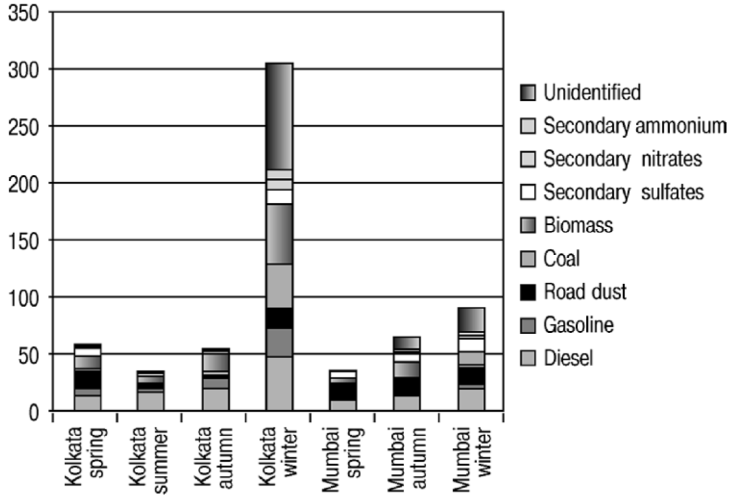


Figure 8. Breakdown of PM2.5 sources in Chandigarh and Delhi (India).

complicating factors such as smoking, dietary habits, age, and income) that might vary among populations in different cities raises doubts about the reliability of these CR functions.

Cohort design studies overcome these questions by following a sample of individuals, thereby making it easier to isolate the effects of complicating factors. These studies provide the most compelling evidence about mortality effects from chronic exposure to PM. The largest study to date (Pope et al., 2002) indicates that a change in long-term exposure to PM2.5 of 10 mg/m^3 leads to a 4, 6, and 8% increase in the risk of all-cause mortality, cardiopulmonary mortality, and lung cancer mortality, respectively. The study did not find consistent relationships between long-term exposure to particles larger than 2.5 mm and premature death.

Source Contributions

Based on the results of chemical analysis and comparing them with chemical profiles of some of the important sources, estimates of contributions of different sources were made. The markers used in this study include hopanes and steranes, found in lubricating oil in gasoline and diesel vehicles and stationary diesel. The chemical mass balance model used in this study quantifies sources according to primary organic carbon from primary emissions (as opposed to secondary organic carbon formed in the atmosphere). After extensive analysis, five primary source profiles were retained: gasoline, diesel, road dust, coal, and biomass. Of the five, regional source profiles were available only for biomass: coconut leaves, rice straw, cow dung, biomass briquette, and jackfruit branches, all from Bangladesh. Source profiles for gasoline, diesel, and road dust obtained in the United States, and that for coal in Beijing were used for the remaining four sources. The absence of local source profiles is an important source of modeling uncertainties. The profiles for gasoline, diesel, and coal can indicate the fuel used but not how or in which sector the fuel is combusted. For example, while virtually all gasoline can be safely attributed to mobile sources, it is not possible to distinguish between diesel burned in vehicles and diesel burned in stationary sources (such as small diesel power generators frequently used by shops in India). That said, external combustion engines emit much less particulate matter per unit of fuel burned than internal combustion engines. It should be mentioned that diesel in this study includes kerosene used in conjunction with lubricating oil (such as kerosene burned in engines, including vehicle engines) but not kerosene used in cooking because cook stoves do not use lubricant. Similarly, biomass burned by households is indistinguishable from biomass burned in bakeries and cottage industries. Nor is it possible to trace secondary sulfates, nitrates, and ammonium (obtained by subtracting calculated primary sulfates, nitrates, and ammonium from the total amounts measured in ambient samples) to different sources. Of the 13 seasons examined (four seasons in three cities and one in Chandigarh), one season (summer in Mumbai) gave organic carbon that was below the detection limit for hydrocarbon speciation by GC–MS. The results from the remaining 12 seasons are shown by city and season in Table 7. The corresponding figures in μg/m^3 are given in Figure 7.

Similar values are shown for Colcata and Mumbai (India) in Figure 8.

CHAPTER 16

CASPIAN SEA ENVIRONMENTS

The landlocked Caspian Sea is the largest inland body of water on Earth. Surrounded by Azerbaijan, Iran, Kazakhstan, Russia, and Turkmenistan, the Caspian Sea is home to myriad ecosystems. At the meeting point of the Middle East, Europe, and Asia, the Caspian region includes steppe land in the north, cold, continental deserts and semi-deserts in the northeast and east, and warmer mountain and highland systems in the south and southwest. The coastal wetlands of the Caspian basin include many shallow, saline pools, which attract a variety of bird life and biodiversity; over 400 species are unique to the Caspian. In addition, the sea's native sturgeon is famous the world around for the roe it produces: sturgeon from the Caspian Sea accounts for approximately 90% of the world's caviar industry.

1. MODERN STATE OF THE ENVIRONMENT

1.1. Geoecological Situation

Although oil has been produced in what is present-day Azerbaijan for more than 100 years, the dissolution of the Soviet Union in 1991 led to heightened interest in the region, especially among Western energy companies that previously were shut out of the area. The Caspian Sea's energy potential already was well known, and the confirmation of that potential with the discovery of significant hydrocarbon deposits in the mid-1990s brought an influx of foreign investment in energy development in the region, particularly in Azerbaijan and Kazakhstan. The spotlight on the Caspian region's oil and gas reserves also highlighted the appalling state of the environment in and around the sea. Years of neglect have left the sea and the surrounding region in a precarious position environmentally. Petrochemical and refining complexes on the Absheron peninsula in Azerbaijan are major sources of land-based pollution, and discharges and spills from oil and gas drilling—both onshore and in the sea itself—have had serious impacts on the environment. Untreated waste from the Volga River—into which half the population of Russia and most of its heavy industry drains its sewage—empties directly into the Caspian Sea, while pesticides and chemicals from agricultural run-off are threats to the sea's flora and fauna. Thousands of seals that live in the Caspian Sea have died since 2000, and one of the possibilities to explain this phenomenon is pollution that weakened their immune systems, and overfishing, especially of the prized sturgeon, has caused a dramatic decline in fish stocks.

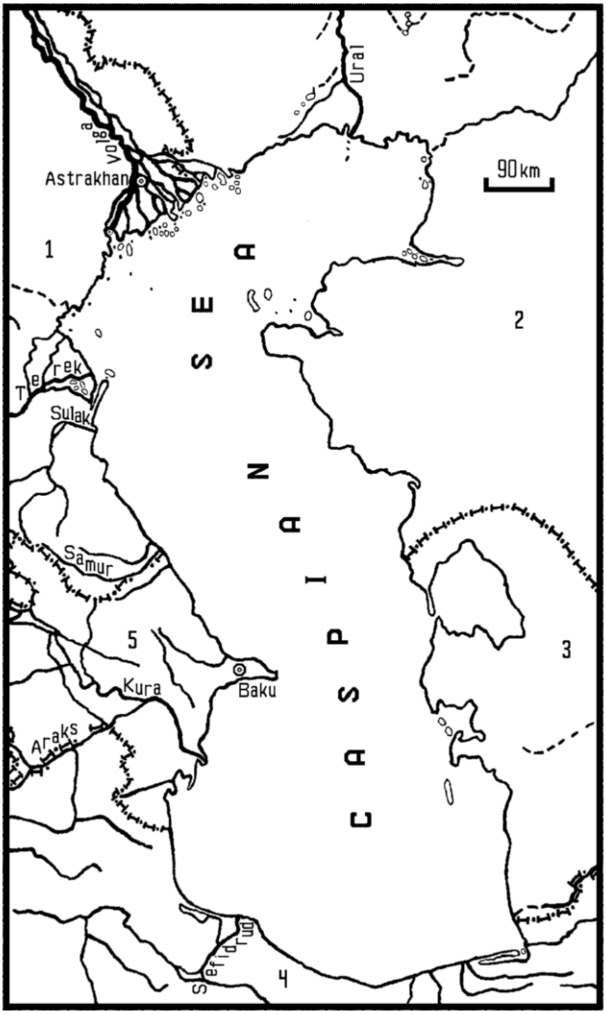


Figure 1. The Caspian Sea and rivers of its basin. The Caspian Sea's states: 1—Russia, 2—Kazakhstan, 3—Turkmenistan, 4—Iran, 5—Azerbaijan.

The Caspian Sea receives waters from a number of rivers such as Ural, Volga, Terek, Sulak, Samur, Kura, Sefidrud, etc. with an annual discharge 240–330 km^3/yr, with more than 80% from the Volga, Figure 1 (Geographical encyclopedic dictionary, 1989). According to Bukharitsin and Luneva (1994) and Shaporenko (1997), a whole set of pollutants (oil-products, synthetic surfactants, pesticides, etc.) can enter the Sea by river discharge. Prospecting and extraction of hydrocarbon materials in the surrounding Caspian coastal regions are accompanied by further water contamination and deterioration of an already strained geoecological situation. The contamination

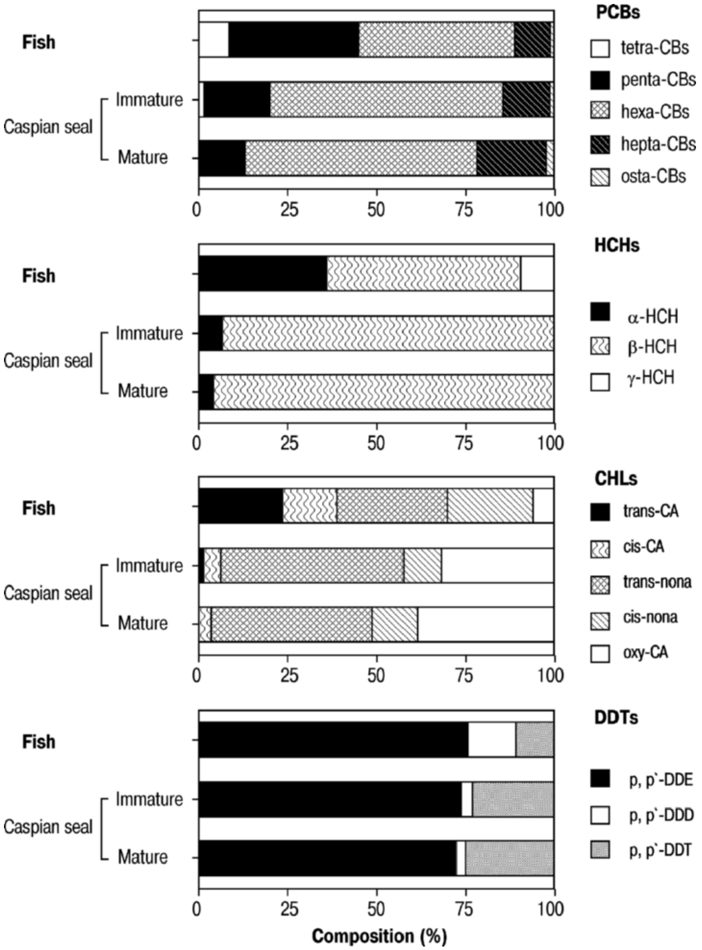


Figure 2. Composition of PCB congeners, HCH isomers, CHL compounds, and DDT compounds in immature and mature Caspian seals and their diet fish (Hall et al., 2002).

of river waters entering into the Caspian Sea by persistent organochlorinated compounds (DDT and HCH insecticides, substances for industrial use—polychlorinated biphenyls, PCBs) with acute and chronic toxic effects on organisms are of special interest (Braginskii, 1972; Polychlorinated, 1980; Vrochinskii, 1981; Shcherbakov, 1981; Vlasenko et al., 1996; Maksimova, 1996; Oradovskii et al., 1997; Korotova et al., 1998; Elpiner 1999; Goryunova et al., 2000; Galiulin et al., 2002). These contaminants are shown in Figure 2.

In addition to the existing problems, several other issues could compound the Caspian region's environmental difficulties. Oil and gas production in the sea inevitably will result in the construction of pipelines and infrastructure to export these resources to consumers, raising the possibility of loss of habitats for marine life as well as the specter of accidental spills. The mysterious rise of the Caspian Sea could flood oil wells, rigs, and earth-walled reservoirs on the coastline, spilling into water tables and contaminating drinking water supplies. This is already the fact in the coastal area nearby the Atyrau, Kazakhstan. A lack of regional cooperation, highlighted by the still unresolved legal status of the Caspian Sea, as well as weak environmental laws and regulations and the inability to enforce them, already is affecting efforts to protect the Caspian's environment. This enhances also the environmental risk to human and ecosystems health.

The economic decline that accompanied the breakup of the Soviet Union reduced industrial production in the region (and thus the flow of contaminants into the Caspian) in the early and mid-1990s. However, as economic growth in the region has rebounded, so have pollution levels. Polluted beaches and coastlines means that swimming in most areas of the sea is hazardous, and toxic waste threatens to contaminate drinking water supplies for people living in the region. The impact of the environmental degradation on human health has been measurable, with higher rates of cancer recorded in the area, and the precipitous decline in the Caspian's (official) sturgeon catch is threatening the survival of the region's caviar industry.

Thus, there is an urgent need to protect the Caspian environment in order to maintain it for future generations. Continued economic development, improved regional cooperation, and the implementation of modern technology will be required in order to improve the state of the environment in and around the Caspian Sea in coming years and decrease accordingly the environmental risk values.

1.2. Oil- and Gas-Related Pollution

The collapse of the Soviet Union in 1991 exposed to the world the regime's poor environmental record in the Caspian. Rusty derricks, poisoned soil and water, pools of oil scum, and uncontrolled well fires were byproducts of the Soviets' oil exploitation in the Caspian region. Despite the influx of billions of dollars in foreign investment, many Soviet era wells remain in place. The long history of contamination, combined with short-term economic pressures to exploit the sea's potential, will mean that threats to the Caspian environment from oil and gas production will continue to loom large. Oil and gas extraction, along with transportation and industrial production, has been the source of severe air, water, and soil pollution in the Caspian region. Systematic water sampling in different parts of the Caspian basin shows contamination from phenols, oil-products, and other sources. Mineral deposit exploration, particularly oil extraction and pipeline construction, have contributed to the pollution of about 30,000 hectares of land. Pollution from oil fields and refineries continues at a high rate due to the use of outdated technology, malfunctioning equipment, and/or simple human disregard. However, even normal processes for oil and gas extraction have environmental side effects. Loud sounds used in seismic surveys in oil and gas exploration can have a range of negative effects on living creatures, particularly fish. The drilling of offshore exploratory wells involves the introduction of various materials into the marine environment, including such non-toxic materials as water-based drilling mud and rock cuttings but also potentially toxic drilling fluids. Discharges from drilling rigs—accidental or otherwise—can include sewage and wastewater from crew facilities as well as deck wash, which can include lubricants such as greases, hydraulic fluids, cement slurry, drill testing fluids, and incidental fuels.

In addition, there is always the chance of an accidental spill from an oil derrick, where a blowout results in an uncontrolled release of hydrocarbons for hours, weeks or even months until the well can be controlled. Although blowouts are rare in offshore exploration, the likelihood is slightly higher than for production wells. Approximately 1% of exploratory wells worldwide have had blowouts and the resulting releases are normally relatively small. Heavy crude oils tend to stay in the marine environment longer than lighter API gravity oils. Furthermore, the purposeful flaring of associated gas from oil wells releases carbon emissions into the atmosphere.

The effects of oil and gas exploration and production in the Caspian region have been felt most strongly in Azerbaijan, where a century's worth of oil production has resulted in acute soil degradation and contamination problems, particularly on the Absheron peninsula. Scant environmental consideration was given to industrial and energy development in Azerbaijan, with disastrous consequences: oil production has left behind vast areas of wasteland, with standing oil ponds and severely contaminated soil, a shore along Baku Bay that is black with oil residue, and high levels of pollution in the Caspian Sea.

While Azerbaijan has been hardest hit by pollution from oil exploitation, other littoral and neighboring states also have been adversely affected. In Kazakhstan, environmental tests have noted that cases of blood disease, tuberculosis, and other diseases as well as the relevant enviroenmental risks are four times more common in the Caspian area than the rest of the country's average. Although the tests showed that the environmental contamination in the northeast Caspian is less than what has been recorded previously, water which has been contaminated by oil-products in Kazakhstan is still used for drinking water. This contamination is cited as a main reason for intestinal infections in Kazakhstan's coastal areas.

1.3. Oil and Gas Transport Issues

In addition to the health and environmental threats due to oil and gas production in the Caspian, the sea's geographic location is another factor complicating efforts to protect the regional environment. Since the sea is landlocked and the littoral states are not major energy consumers (with the exception of Russia, which is a major consumer but also a net energy exporter), in order for the oil and gas produced in the Caspian region to reach intended customers it must be transported via pipeline. A number of Caspian region oil pipelines have been built or are under construction, and several regional gas pipelines have been proposed as well (Box 1).

Environmental issues have played an important part in the selection of export routes for Caspian oil and gas. As proposed east-west routes have predominated, the environmental health of the Black Sea in general and the Bosporus Straits in particular

Box 1. Natural gas export routes and options in the Caspian Sea region (Caspian Environmental Program, 2001)

Name/ location	Route	Natural gas capacity	Length	Cost estimate	Status
Baku–Erzurum	Baku (Azerbaijan) via Tbilisi (Georgia) to Erzurum (Turkey), linking with Turkish natural gas pipeline system	Planned 254 Bcf capacity	540 miles	$ 1 billion (includes up to $ 500 million to construct new Azeri section)	November 2000 inspection of existing Gazi pipeline deemed that extensive repairs were necessary; new pipeline will be necessary
"Centgas" (Central Asia Gas)	Daulatabad (Turkmenistan) via Herat (Afghanistan) to Multan (Pakistan). Could extend to India	700 Bcf/yr	870 miles to Multan (additional 400 miles to India)	$ 2 billion to Pakistan (additional $ 500 million to India)	Memorandum of Understanding signed by Turkmenistan, Pakistan, Afghanistan, and Uzbekistan. Project stalled
Central Asia Center Pipeline	Turkmenistan and Uzbekistan via Kazakhstan to Saratov (Russia), linking to Russian natural gas pipeline system	3.5 Tcf/yr	Existing route	N/A	Operational. Turkmenistan is using this pipeline to export a total of 8.83 Tcf to Ukraine (via Russia) from 2002 to 2006, as well as smaller amounts to Russia
China Gas Pipeline	Turkmenistan to Xinjiang (China). Could extend to Japan	1 Tcf/yr	4,161 miles; more if to Japan	$ 10 billion to China; more if to Japan	Preliminary feasibility study done by Exxon-Mobil, Mitsubishi, and CNPC
Trans-Caspian Gas Pipeline (TCGP)	Turkmenbashy (Turkmenistan) via Baku and Tbilisi to Erzurum, linking with Turkish natural gas pipeline system	565 Bcf in first stage, eventually rising to 1.1 Tcf/yr	1,020 miles	$ 2 billion to $ 3 billion	Project stalled; negotiations between Turkmenistan and Azerbaijan over pipeline volumes restarted in October 2001
Korpezhe–Kurt–Kui	Korpezhe (Turkmenistan) to Kurt-Kui (Iran)	283–350 Bcf/yr; expansion proposed to 459 Bcf/yr by 2005	124 miles	$ 190 million; 2005 expansion: $ 300 million to $ 400 million	Operational since December 1997

has become an important factor influencing the selection of final routes, especially for oil. With the launch of the Caspian Pipeline Consortium's Tengiz-Novorossiisk pipeline in 2001, tanker traffic leaving the Black Sea port of Novorossiisk and exiting the Bosporus en route to the Mediterranean Sea has increased.

The Bosporus is already a major chokepoint for oil tanker shipments, and traffic is projected to increase substantially as the CPC pipeline reaches its eventual 1.34-million-barrel-per-day-capacity. Thus, Turkey has argued against export routes that utilize the Black Sea, noting that the projected increase in large oil tankers will pose serious navigational, safety, and environmental threats to the Bosporus. Several "Bosporus bypass" pipelines have been proposed to avert the threat of an oil spill or gas explosion on a tanker navigating the Bosporus through the heart of Istanbul.

Construction of new pipelines, such as the Baku–Tbilisi–Ceyhan (BTC) oil export pipeline (under construction) and the planned Baku–Tbilisi–Erzurum gas pipeline, will necessitate the construction of new roads and infrastructure, which could lead to habitat loss. The Georgian government has expressed worries that the BTC's planned route traverses the country's Borjomi Valley, home of Georgia's famed mineral water. However, BP, which is the operator of the consortium constructing the BTC pipeline, has conducted a thorough environmental impact assessment for the underground pipeline, and built-in precautions, such as automatic shut-off valves in the event of a leak, are geared to mitigate any negative environmental effects. The results of the environmental impact assessment seem to have alleviated the Georgian government's concerns, although there remains opposition to the pipeline among Georgian environmentalists.

Several proposed export routes for Caspian oil and gas entail the construction of trans-Caspian pipelines or tanker deliveries from oil terminals to export pipelines. A trans-Caspian gas pipeline from Turkmenistan to Azerbaijan has been proposed, as has a possible pipeline link across the Caspian to transport oil from the Kazakh port of Aqtau to Baku. Tanker traffic, mostly from Aqtau and the Turkmen port of Turkmenbashy to Baku and the Russian port of Makhachkala, could impact fish migration routes. The northern Caspian Sea, which is characterized by relatively shallow waters and the lack of currents, is home to more than 80% of the sea's netted fish, making it more difficult to regenerate its natural resources in the event of an environmental problem. The laying of pipelines on the Caspian seabed could have a negative effect on marine life as well, and both Russia and Iran have opposed trans-Caspian pipelines on environmental grounds.

Transporting oil and gas via pipeline has inherent risks, with the possibility of leakage and spills, but in the Caspian region these risks are heightened due to the possibility of sabotage. A number of conflicts in the Caspian region remain unresolved, and the difficulty in securing pipelines over long distances, as well as the economic dependence on states such as Azerbaijan on export revenues, could make Caspian oil and gas pipelines prime targets for sabotage. Separatist groups targeting an oil or gas pipeline could cause an environmental catastrophe in the event that an explosion on the pipeline results in a major leak. Illegal tapping, rather than sabotage, of both the Baku-Novorossiisk pipeline in Chechnya and the Baku-Supsa pipeline in Georgia already has caused major leakage problems.

1.4. Agricultural, Industrial, and Municipal Waste Discharges

Although environmental damage from oil and gas production in the Caspian Sea and surrounding areas is considerable, oil-related pollution is less serious than it sometimes seems because most hydrocarbons deteriorate in seawater. Far more serious, however, are the agricultural, industrial, and municipal wastes—mostly untreated—that pour into the sea. Although the decline in the region's industrial and agricultural output during the 1990s reduced air pollution and industrial and agricultural discharges into the Caspian, Azerbaijan's Ecology Minister, Gusein Bagirov, has estimated that pollution from rivers that feed into the sea still accounts for 85–90% of the pollution.

Approximately 130 large and small rivers flow into the Caspian Sea, nearly all of which flow into the north or west coast. The Volga River, the sea's largest single source, splits into a thousand smaller streams as it flows through a largely uninhabited delta feeding into the Caspian Sea. This marsh serves as a filter, cleansing the river of some of the upstream pollution, which comes mainly from Russian factories in the Ural Mountains, but sufficient amounts still reach the Caspian to cause major imbalances, especially in the shallow north basin which has limited absorption capacity. The Caspian still has miles of undeveloped coastline, especially along the eastern shore in Kazakhstan and Turkmenistan where there are no permanent inflows. Yet the south end of the sea is deep, dark gray and polluted by discharges from sewer pipes and factory drains from the five littoral states. Air pollution from Tehran, due largely to the abundance of old cars that lack catalytic converters, falls out in the Caspian when the wind blows the smog north from Iran, contributing to the sea's environmental problem. However, waste discharges account for the lion's share of pollution in the Caspian. The World Bank has estimated that perhaps one million cubic meters of untreated industrial wastewater is discharged into the Caspian annually.

A major culprit is the Azeri coastal city of Sumgayit. During the Soviet era, the city was planned as a model center for petrochemical industries, but in an effort to keep up with the continually increasing production quotas, the environment was subjugated to industrial goals. Hundreds of thousands of tons of toxic wastes each year were released into the atmosphere or dumped into a creek that fed into the Caspian. The result was predictable: pollution overwhelmed the sea around Sumgayit and Baku, creating a virtual dead zone, and the area witnessed a dramatic rise in stillbirths and miscarriages. The legacy lives on, as untreated sewage is still dumped into the Caspian, and mercury-contaminated sludge wastes (from the use of mercury in chlor-alkali production) are accumulating. Since the wastes often are stored inadequately, ground water contamination and leakage into the Caspian Sea is likely. Discharges of processed water already have contaminated sea bottom sediments in the Caspian severely.

1.5. Overfishing and Poaching

Recently, an increased interest has been observed in geoecological situation assessment in the Caspian Sea, known as the World greatest intracontinental undischarged salt reservoir with more than 80% of World fishing of sturgeons (*Huso huso*, *Acipenser nudiventris*, *A. guldenstadti*, *A. stellatus*), and also bream (*Abramis brama*), wild carp or sazan (*Cyprinus carpio*), zanders or pike-perch (*Stizostedion lucioperca*, *S. marinus*), herring (*Alosa brashnikovi*, *A. saposhnikovi*, *A. sphaerocephala*, *A. curensis,* etc.), sprat (*Clupeonella delicatula caspia*, *C. engrauliformis*, *C. macrophthalma*) and Caspian seal (*Phoca caspica*) (Geographical encyclopedic dictionary, 1989).

The Caspian Sea is the source of about 90% of the world's caviar. However, the lack of an international agreement safeguarding the Sea's environment has led to overfishing and poaching of sturgeon, the fish whose roe is used to make the delicacy, resulting in dwindling fish stocks. Environmentalists have warned that poaching of beluga, the largest and rarest of the sturgeon, is threatening to push the species into extinction. Iranian officials have reported a steady drop in caviar production, one of their major non-oil exports, blaming poaching and oil prospecting.

Legal trade in the black fish eggs from the Caspian is estimated to be worth $100 million per year, but the illegal catch in the four former Soviet republics is believed to be 10–12 times higher. In the spring of 2001, the United Nations' Convention on International Trade in Endangered Species (CITES) banned exports of caviar from Azerbaijan, Kazakhstan, Russia, and Turkmenistan. The ban led to a higher price for beluga caviar, which in turn gave further incentive to poachers. Despite opposition from environmentalists, in March 2002 CITES lifted the export ban on the former Soviet republics, citing improved management of their sturgeon stocks.

1.6. Fluctuating Sea Level

In addition to the man-made environmental problems that have affected the Caspian adversely, the sea has exhibited a curious natural variation in its water level that has created additional problems and has wrought havoc on coastal infrastructure. Since 1978, the sea level has risen almost 7.5 feet. Flooding in coastal zones has inundated residential areas, transport, telecommunications and energy infrastructure, chemical and petrochemical industries, croplands and hatcheries, forcing thousands of residents to be evacuated from flooded homes. In Turkmenistan, the town of Dervish, which is detached from the western part of the mainland, is turning into an island due to the rise in sea level, and Cheleken and Karakul are sinking into the water as well.

Given the problems involved in drilling, large amounts of oil keep spilling over onto the surface in the Caspian, polluting the water. Earth walls are being built to enclose the polluted zones, so polluted water will not mix with clean water, but the rising sea level is resulting in the mixing of polluted and clean waters. Gradual flooding has precipitated abrasive erosion of sea shelves, endangering oil infrastructure, and the rising seawater threatens to flood oil wells along the coast and cause spills directly into the sea. At the onshore Tengiz oil field in Kazakhstan, more than 100 wells have been flooded, and about 1,200 wells and refinery installations on the shallow northeast coastline are at risk.

In addition to the danger posed to oil fields in Kazakhstan and Azerbaijan, the sea-level rise results in changes in water regime, hydrochemical regime of river mouths, dynamics and chemical composition of groundwater, structure and productivity of biological communities in the littoral and in river mouths, sediment deposition patterns, pollution by heavy metals, petroleum products, synthetic substances, radioactive isotopes, and other substances. A 6-mile sewage pipeline in the Azeri coastal district of Azizbayov has been partially submerged by the rising water level, causing the pump station there to malfunction and allowing sewage from the area to be discharged directly into the sea. Up to 100,000 people in coastal cities and towns in Azerbaijan alone have been affected by the spread of toxic wastes, contamination of water supplies, and the loss of infrastructure due to the rising sea level.

The sea's rise has confounded scientists and engineers who have monitored the sea level. From 1933 to 1941, experts recorded that the Caspian's water level consistently *decreased*, by a total of 5.5 feet. The pattern of Baku–Tbilisi–Erzurum increase since 1978 has played havoc with engineers who have attempted to deal with the natural water variation. For example, at the beginning of the 20th century, the strait between the Garabogazkol Gulf in Turkmenistan and the Caspian allowed for significant water flow to the smaller basin. As the sea level fell in the mid-20th century, the flow consistently decreased. In March 1980, Soviet engineers constructed a solid dam across the Strait to stem any further drop in sea level.

However, the average sea level had already begun to increase in 1978, and by September 1984 planners were forced to open a spillway in the dam to permit some discharge of water in the Gulf. The dam also created other environmental problems: in addition to barring sturgeon from their spawning grounds, the dam dried up what had been a stable salt lagoon. The result was salt-laden dust storms that turned surrounding towns and villages into ghost towns. Desertification and other environmental damage accelerated until the dam was finally demolished in June 1992. This example highlights the difficulty in anticipating natural variations in the hydrologic cycle and creating engineering works to counter this natural variability effectively.

1.7. Environmental Legislation and Regulation in Respect to ERA

An additional issue compounding the region's environmental problems and adding to the difficulty in finding solutions is the weak state of existing environmental legislation and regulation in the littoral states. Environmental law was virtually nonexistent during the Soviet era, and post-Soviet environmental legislation and environmentalism is still in its infancy in Azerbaijan, Kazakhstan, Russia, and Turkmenistan.

Although environmental legislation has been passed in the four Soviet states, as in Iran, the application and enforcement of these new laws is often suspect. Poverty in the Caspian region means that corruption is rampant, and since oil and gas production are the driving forces behind the growth of the region's economies, the enforcement of environmental laws sometimes has been subjugated to economic development goals. In the early and mid-1990s, strong environmental laws were viewed by governments in the region as a threat to the continued influx of foreign investment that was pouring into the region, in particular into Azerbaijan and Kazakhstan. As a result, governments were reluctant to issue regulations endorsing more rigorous environmental standards.

For their part, energy companies involved in exploration and drilling in the Caspian shelf have complained of overlapping environmental authorities, conflicting regulation between local and national authorities, and the lack of specific environmental regulations that are required in environmental laws. In Azerbaijan, for example, the country's Energy Law appears to be in direct contradiction to its Subsoil Law. Several layers of bureaucracy, as well as constant changes to legislation and regulations, complicate business operations and the ability to comply with environmental standards, according to Western investors in the Caspian region.

However, as economic growth continues and environmental awareness in the Caspian improves, the region's governments increasingly are taking a stronger stand on environmental issues. Both Azerbaijan and Kazakhstan have passed legislation requiring energy companies to utilize associated gas that is produced during oil extraction where previously the gas typically was flared. Environmental impact assessments (EIAs) have become mandatory for regional oil and gas export pipelines, and new development projects are required to carry environmental insurance as well as to conduct EIAs. Whereas previously the governments were not always very diligent in enforcing environmental regulations, several high-profile incidents have demonstrated that the Caspian region governments are becoming stricter in enforcing environmental standards.

In August 2001, Tengizchevroil, the ChevronTexaco-led international consortium developing the giant Tengiz oil field in western Kazakhstan, was fined around $75 million for ecological damage. In addition, Kazakhstan forced Agip KCO, the consortium developing the offshore Kashagan field in shallow water, to halt operations temporarily and pay a hefty fine after several oil spills from exploratory wells operated by the consortium. The Kazakh government, in particular, has become more aggressive in its environmental stewardship: in the past, the country only fined polluters, but now it is prepared to make sure that criminal charges are brought against the management of the enterprises which break the country's environmental protection legislation.

1.8. The Caspian Environmental Outlook

The current oil bonanza has focused more attention on the plight of the Caspian environment, highlighting the need to take action. However, environmental remediation of existing hotspots has not been a priority for the region's governments, and their desire to develop the Caspian's oil and gas resources as a driver for economic development means that environmental protection measures are likely to take a back seat in the near-term.

Nevertheless, the involvement of Western energy companies using more modern technology actually should result in an improvement in the way oil and gas is extracted in the Caspian basin. For example, gas flares can be contained with Western technology, and drilling discharges can be mitigated by following proper techniques. In addition, pressure from shareholders will make publicly-traded energy companies carry out their operations in the Caspian region in an environmentally-responsible fashion.

While the countries of the region have begun to take added measures to prevent pollution, including conducting oil spill response exercises and increasing state funds for enforcement of environmental regulations, the lack of regional cooperation among the Caspian littoral states continues to undermine individual state efforts to protect the sea and the surrounding region. The absence of a multilateral agreement on the legal status of the Caspian Sea has hampered efforts to craft and to implement an overall regional strategy to safeguard the sea's flora and fauna, as well as human health. The overfishing that threatens the Caspian's sturgeon population is a direct result of the inability to reach a new agreement to divide the sea.

Although a final multilateral solution still eludes the Caspian littoral states, an encouraging sign has been a move towards greater cooperation. Several initiatives have boosted regional cooperation in protecting the environment, including the establishment of the Caspian Environment Programme (CEP) in conjunction with the World Bank's Global Environmental Facility. The aim of the CEP is defined as "environmentally sustainable development and management of the Caspian environment, including living resources and water quality, so as to obtain the utmost long-term benefits for the human populations of the region, while protecting human health, ecological integrity, and the region's sustainability for future generations."

Implementation of these goals will be extremely difficult, especially in light of the region's economic situation, but it is hoped that bilateral agreements between several of the Caspian states will help lead to an overall multilateral agreement. Azerbaijan, Kazakhstan, and Russia have signed bilateral agreements with each other to divide the Caspian seabed into national sectors, a move that could facilitate bilateral environmental agreements. As oil and gas extraction in the region continues at a brisk pace, the challenge of protecting the Caspian's environment will become more difficult. Without increased cooperation by the littoral states, the state of the environment in the Caspian Sea and surrounding areas will remain threatened.

2. BIOGEOCHEMICAL PECULIARITIES

2.1. Biogeochemical Food Webs

The Caspian Sea is the largest inland water body on earth (386,400 km^2, maximum depth 1025 m). With its long history of oil and industrial development, the Caspian is often regarded as severely polluted and ecologically degraded. The North Basin of the Caspian Sea is a large (25% of the Caspian Sea surface area), shallow (median depth 4 m), well-mixed, slightly brackish estuary fed by the Volga and Ural Rivers. We have synthesized historical Soviet data, post-Soviet data and data from a recent sampling cruise in September 2003 to investigate the current ecological status of the North Basin of the Caspian Sea. The Volga River supplies approximately 80% of the water input to the entire Caspian Sea and is the major source of nutrients and pollutants to the North Basin. The North Basin of the Caspian Sea is less polluted with heavy metals, pesticides and probably hydrocarbons than commonly assumed and less polluted now than during the Soviet era. Pollutant levels in organisms such as fish and seals are generally lower or comparable to those of other large seas and lakes, such as the Mediterranean, Black, and Baltic Seas. Autochthonous primary production supplies the majority of the organic carbon inputs with more than 50% provided by phytoplankton (14–22 TG C/yr) and about 4–9 TG C/yr added by the Volga River (see also Leonov and Stygar, 2001). Primary production in the North Basin is usually phosphorus-limited and significant oxygen depletion seldom develops. Commercial fish stocks in the North Caspian have declined significantly in recent years due to overfishing. The Caspian Sea supplies about 90% of the world's caviar but less than 1% of the remaining Beluga sturgeon (Huso huso) are mature breeders. Accurate, independent information on the size and age class distribution of valuable sturgeon species and the Caspian Seal are not available (Tartowski et al., 2004).

Organochlorine contaminants (pesticides and individual polychlorinated biphenyl congeners, PCBs) were measured in Caspian (Phoca caspica) seal blubber and compared with concentrations in Harbour (Phoca vitulina) seal blubber. Concentrations of total dichlorodiphenyltrichloroethane (DDT) and its metabolites were significantly higher in Caspian seal than Harbour seal samples, whereas PCB congeners were significantly higher in Harbour than Caspian seals. Our finding suggests that Caspian seals are exposed to high levels of DDT pesticides. In contrast, PCBs are circulating in this population at much lower levels than in marine mammals from the North Sea (Hall et al., 2002).

2.2. Heavy Metals

Concentrations of V, Mn, Fe, Cr, Co, Cu, Zn, As, Se, Mo, Ag, Cd, Tl, Hg, Pb, and organic mercury (Org-Hg) were determined in liver, kidney, and muscle of healthy Caspian seals (Phoca caspica) collected in 1998. These concentrations were compared with those of seals infected with canine distemper virus (CDV) found stranded along the coastal areas in 2000 (Table 1). Concentrations of toxic elements (As, Ag, Cd, Tl, Hg, Pb, and Org-Hg) in Caspian seals stranded in 2000 were comparable or lower than those of samples collected in 1998 and in other pinnipeds. Thus it may be inferred that these elements were not the causative agents in the deaths of the seals. In contrast, concentrations of Zn and Fe were much higher in diseased Caspian seals than those in other pinnipeds. Zinc concentrations in all tissues of Caspian seals also increased during 1993–2000. Furthermore, negative correlations were found between blubber thickness and hepatic and renal Zn concentrations. These results imply the disturbance

Table 1. Heavy metal concentrations (mean ± SD and range ppb) in the muscle of Caspian seals.

	Fe	Mn	Zn	Cu	Pb	Ni	Cd	Co	Hg
All 0–41.5 yean	200 ± 64 52–330 (42)	0.18 ± 0.06 0.08–0.37 (42)	30 ± 9 16–51 (42)	1.1 ± 0.2 0.7–1.7 (42)	0.027 ± 0.028 <0.01–0.14 (22)	<0.04 (0)	0.011 ± 0.017 <0.001–0.099 (36)	0.010 ± 0.003 <0.005–0.016 (10)	0.55 ± 0.30 0.19–1.8 (42)
All except fetus 0.5–41.5 yean	200 ± 61 99–330 (41)	0.18 ± 0.06 0.08–0.37 (41)	30 ± 9 16–51 (41)	1.1 ± 0.2 0.7–1.6 (41)	0.027 ± 0.028 <0.01–0.14 (22)	<0.04 (0)	0.011 ± 0.017 <0.001–0.099 (36)	0.010 ± 0.003 <0.005–0.016 (10)	0.55 ± 0.31 0.19–1.8 (41)
Fetus	52 (1)	0.15 (1)	23 (1)	1.7 (1)	<0.01 (0)	<0.04 (0)	<0.001 (0)	<0.005 (0)	0.53 (1)
Immature (M+F) 0.5–7.5 yean	200 ± 64 130–330 (21)	0.20 ± 0.06 0.08–0.37 (21)	28 ± 8 18–49 (21)	1.2 ± 0.2 0.8–1.6 (21)	0.024 ± 0.013 <0.01–0.056 (15)	<0.04 (0)	0.004 ± 0.003 <0.001–0.011 (16)	0.010 ± 0.004 <0.005–0.016 (5)	0.48 ± 0.14 0.27–0.71 (21)
Aduh male 8.5–22.5 yean	200 ± 39 160–250 (4)	0.19 ± 0.06 0.13–0.25 (4)	26 ± 6 20–33 (4)	1.1 ± 0.3 0.8–1.3 (4)	0.011 <0.01–0.015 (2)	<0.04 (0)	0.008 ± 0.005 0.003–0.015 (4)	0.012 <0.005–0.016 (2)	0.65 ± 0.34 0.27–0.96 (4)
Aduh female 9.5–41.5 yean	210 ± 61 99–330 (15)	0.15 ± 0.05 0.09–0.25 (15)	33 ± 11 16–51 (15)	1.0 ± 0.1 0.7–1.2 (15)	0.042 ± 0.057 <0.01–0.14 (5)	<0.04 (0)	0.019 ± 0.024 0.005–0.099 (15)	0.008 ± 0.000 <0.005–0.009 (3)	0.58 ± 0.44 0.19–1.8 (15)
Pregnant 9.5–28.5 yean	200 ± 50 150–280 (6)	0.16 ± 0.07 0.09–0.25 (6)	36 ± 12 27–51 (6)	1.0 ± 0.1 0.9–1.2 (6)	0.020 ± 0.013 <0.01–0.033 (3)	<0.04 (0)	0.011 ± 0.005 0.005–0.019 (6)	0.009 <0.005–0.009 (1)	0.47 ± 0.19 0 23–0.75 (6)
Nonpregnant 14.5–41.5 yean	220 ± 70 99–330 (9)	0.14 ± 0.04 0.09–0.22 (9)	31 ± 10 16–45 (9)	1.0 ± 0.1 0.7–1.1 (9)	0.074 <0.01–0.14 (2)	<0.04 (0)	0.025 ± 0.030 0.005–0.099 (9)	0.008 <0.005–0.008 (2)	0.66 ± 0.55 0.19–1.8 (9)

Number of samples with detectable is in parentheses in homeostatic control and nutritional status of essential elements in Caspian seals stranded in 2000.

Heavy metal concentrations were determined in muscle, liver, and kidney of Caspian seals to elucidate the status of toxic metal accumulations and to understand possible pollution by heavy metals in the Caspian Sea. Relatively low concentrations of toxic metals (such as Hg and Cd) were found. However these levels were higher than those of seals in Lake Baikal, which is also a land-locked water. Based on Hg and Cd concentrations in the liver, pinniped species were separated into two groups. One group accumulated higher levels of Hg than Cd, and another accumulated higher Cd levels than Hg. Caspian seals were likely to belong to high-Hg-accumulating group. This might be attributable to their dietary habit of feeding on fish in the Caspian Sea. Hg and Cd concentration ratio is suggested as a useful indicator to understand the feeding habit of marine mammals. Age-related accumulation of toxic metals was found in the liver, kidney, and muscle tissues of Caspian seals. Cd concentrations increased up to 16.5 years and then decreased with age (Table 2).

Hg concentrations increased continuously. This trend might be due to the different rate of Hg and Cd uptake from diet arising from the shift in prey items with age. In the case of essential metals, higher Mn and lower Fe concentrations were found in the liver of Caspian seals as compared to marine pinnipeds. This feature was different from that of Baikal seals, which is a taxonomically close relative with high diving ability. This specific pattern of Fe accumulation is likely to be explained by the habitat of Caspian seals, which evolved in shallower waters in the Caspian Sea. Lower Cu concentrations found in the liver of Caspian seals when compared with other marine pinnipeds was similar to that in Baikal and ringed seals. The low accumulation of Cu might be a characteristic of subgenus *Pusa*.

2.3. Organochlorine Contaminants

The content of organochlorine species in the blubber of male Caspian seals in comparison with those in other seals is shown in Table 3.

Compositions of PCB congeners, HCH isomers, DDT compounds, and CHL compounds in immature and mature Caspian seals and their diet fish are shown in Figure 3. Except for DDTs, relatively persistent congeners or derivatives (such as heptaand octa-CBs, b-HCH, and oxychlordane) dominated in Caspian seals, whereas diet fish retained relatively less persistent compounds (such as penta-CBs, a-HCH, *trans*- and *cis*-chlordane), which constitute a larger proportion in commercial preparations. Percentages of persistent congeners and compounds of PCBs, HCHs, and CHLs were smaller in immature seals than adults (Figure 3). This is due to the greater influence of compositions in diet fish to immature animals, because fish retained considerable amounts of less persistent congeners and compounds and the body burdens of organochlorines in immature Caspian seals are lower than those in mature ones. Interestingly, percentage of p,p-8-DDE was comparable in immature and mature seals and their diet fish (Figure 3). Although the reason for this is yet unclear, this may be suggestive of the decline in recent input of DDT in Caspian Sea.

Table 2. Heavy metal budget in the liver, kidney and muscle of Caspian seal.

	Fe (g)	Mn (mg)	Zn (g)	Cu (mg)	Pb (mg)	Ni (mg)	Cd (mg)	Co (mg)	Hg (mg)
Liver									
Nonpregnant female 0.07–3.3 (11)	0.80 ± 1.0 2.8–9.2 (11)	5.1 ± 2.3 0.030–0.080 (11)	0.045 ± 0.015 4–20 (11)	11 ± 5 NC–120 (9)	31 ± 39 (0)	NC 0.2–6.4 (11)	1.6 ± 1.8 NC–89 (7)	45 ± 27 5–150 (11)	35 ± 46
Pregnant female	0.75 ± 0.9 0.09–22 (5)	4.6 ± 1.7 2.8–7.3 (5)	0.037 ± 0.009 0.028–0.052 (5)	10 ± 4 5–15 (5)	19 ± 16 NC–40 (4)	NC (0)	0.9 ± 0.2 0.6–1.2 (5)	35 ± 13 NC–49 (4)	15 ± 8 2–42 (5)
Kidney									
Nonpregnant female	0.022 ± 0.008 0.009–0.036 (11)	0.13 ± 0.04 0.07–0.19 (11)	0.0040 ± 0.0008 0.0029–0.0055 (11)	0.43 ± 0.11 0.31–0.66 (11)	14 ± 14 NC–46 (8)	13 NC 17 (2)	1.9 ± 1.5 0.5–4.6 (11)	5.5 ± 2.3 NC–8.8 (10)	0.34 ± 0.38 0.08–1.3 (11)
Pregnant female	0.024 ± 0.008 0.015–0.035 (6)	0.12 ± 0.03 0.08–0.16 (≪>)	0.0034 ± 0.0005 0.0027–0.0041 (6)	0.37 ± 0.07 0.25–0.47 (6)	6.2 ± 2.1 NC–10 (5)	5.8 ± 2.1 NC–8.1 (3)	1.7 ± 1.0 0.9–3.5 (≪>)	6.5 ± 1.1 5.2–8.3 $(<^{*})$	0.18 ± 0.10 0.09–0.31 (6)
Muscle									
Nonpregnant female	1.7 ± 0.5 1.0–2.3 (8)	1.3 ± 0.3 0.8–1.7 (8)	0.23 ± 0.08 0.15–0.40 (8)	7.4 ± 1.5 5.9–10 (8)	480 ± 590 NC–1,400 (4)	NC (0)	0.10 ± 0.06 0.03–0.18 (8)	55 ± 5 NC–59 (3)	5.0 ± 5.0 1.4–17 (8)
Pregnant female	1.9 ± 0.4 1.6–2.5 (5)	1.6 ± 0.7 0.8–2.7 (5)	0.33 ± 0.09 0.24–0.47 (5)	9.4 ± 1.6 7.1–11 (5)	180 ± 100 NC–250 (3)	NC (0)	0.09 ± 0.03 0.05–0.14 (5)	67 NC–67 (1)	4.0 ± 1.8 1.7–6.5 (5)

Number of samples in parentheses. NC: not calculated

Table 3. Comparison of organochlorine concentrations (mean and range in parenthesis, μg/g of wet weight) species in the blubber of male Caspian seals with those in other seals collected in 1980s and 1990s from various areas (Hall et al., 2002).

Species	Location	Year	*n*	Age (years)	Fat (%)	PCBs	DDTs	HCHs
Caspian seal	Caspian Sea	1993	10	0.5–4.5	84 (80–90)	5.7 (3.2–9.5)	14 (7.2–22)	1.0 (0.56–1.3)
Caspian seal	Caspian Sea	1993	6	6.5–23	85 (71–91)	9.7 (4.2–15)	19 (8.6–30)	1.3 (0.86–1.9)
Baikal seal	Lake Baikal	1992	16	8.5–36	87 (81–94)	27 (9.4–56)	55 (14–140)	0.077 (0.033–0.13)
Ringed seal	Barrow Strait, Canadian Arctic	1984	19	10	90 (NA)	0.57 (NA)	0.71 (NA)	0.27 (NA)
Ringed seal	Kara Sea, Russian Arctic Arctic	1995	29	1.9–9.5	89 (73–93)	4. 2 (1.9–11)	3.6 (1.1–14)	0.18 (0.066–0.37)
Grey seal	Baltic Sea	1982–88	5	9–20	90 (87–92)	110* (66–180)*	33* (11–54)*	NA
Ringed seal	Baltic Sea	1981–86	5	20–40	89 (87–92)	320* (150–770)*	340 (160–820)*	NA
Harbor seal	Skagerrak	1988	4	5.0–7.0	86 (80–89)	47* (28–82)*	8.4* (7.0–10)*	NA
Harbor seal	Skagerrak	1988	4	10–22	84 (81–87)	84* (47–110)*	7.0* (4.3–11)*	NA
Harbor seal	Wadden Sea	1988	3	5	70 (64–79)	29 (24–35)	2.1** (1.3–2.5)	NA

(*Conti.*)

Table 3. (*Continued*)

Species	Location	Year	*n*	Age (years)	Fat (%)	PCBs	DDTs	HCHs
Monk seal	Mediterranean Sea	1990	1	6+	87	15	17	0.027***
Larga seal	Western coast of North Japan	1994	1	Adult	74	12	19	0.73
Larga seal	Western coast of North Japan	1992–94	3	Immature	76 (71–80)	7.4 (3.2–12)	7.9 (3.4–13)	1.1 (0.58–1.6)
Larga seal	Sea of Okhotsk, Japan	1996	8	Adult	83 (67–89)	3.2 (1.4–6.5)	2.8 (1.5–5.0)	0.33 (0.21–0.66)
Weddel seal	Showa Station, Ant arctic	1981	1	13 or 14	88	0.043	0.19	NA
Ross seal	Queen Maud Land, Ant arctic	1981/82	3	NA	NA	0.039 (0.005–0.095)	0.088 (0.047–0.12)	NA

NA: No data available; *Lipid weight basis; **p-p'-DDE only; ***α- and γ-isomers only

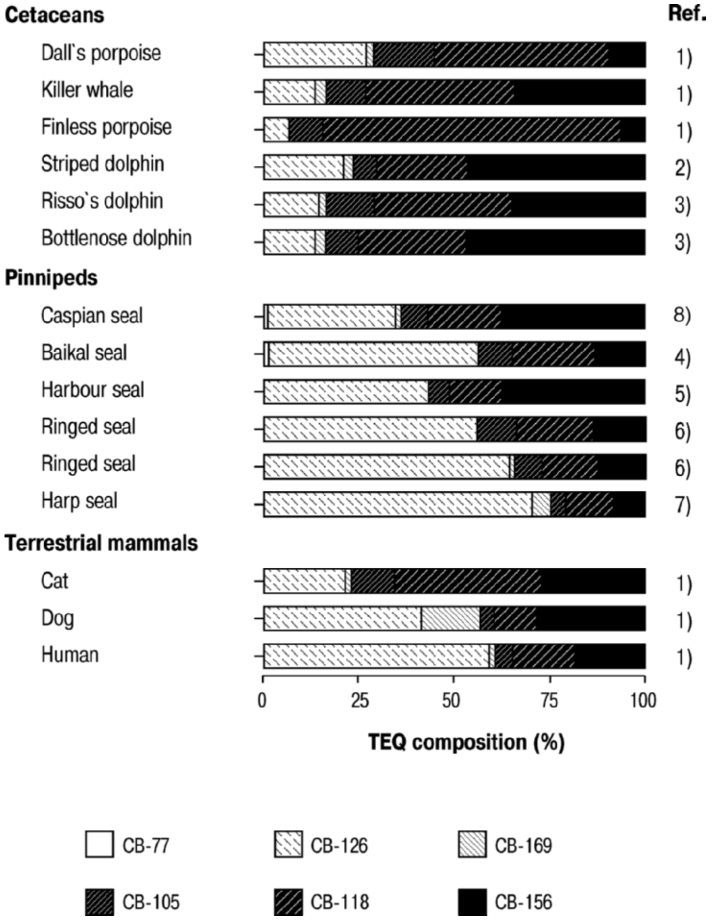


Figure 3. Comparison of TEQ compositions of non- and mono-ortho coplanar PCBs in Caspian seal and those on other higher trophic animals. Data from (1) Kannan et al. (1989); (2) Kannan et al. (1993); (3) Corsolini et al. (1995); (4) Nakata et al. (1997); (5) Storr-Hansen and Spliid (1993); (6) Muir et al. (1995); (7) Oehm et al. (1994); (8) Hall et al. (2002).

2.4. Environmental Risk Assessment of Organochlorine Species

Table 3 shows mean and range of TEQ values for non-, mono-, and di-*ortho* coplanar PCBs in Caspian seals and other seals from various waters. TEQs were estimated using TEF (Hall et al., 1994). Mean and range of STEQs in Caspian seals were 51 pg/g and 18–140 pg/g (wet weight), except for a seal of CS39. STEQs in CS39 were extraordinarily high compared with those in other Caspian seals. Except for this animal, STEQs in Caspian seals were apparently lower than those in Baikal seals from the Lake Baikal and immature harbor seals (*Phoca vitulina*) from the North Sea, where mass mortality has taken place in the past (Figure 4). Furthermore, range

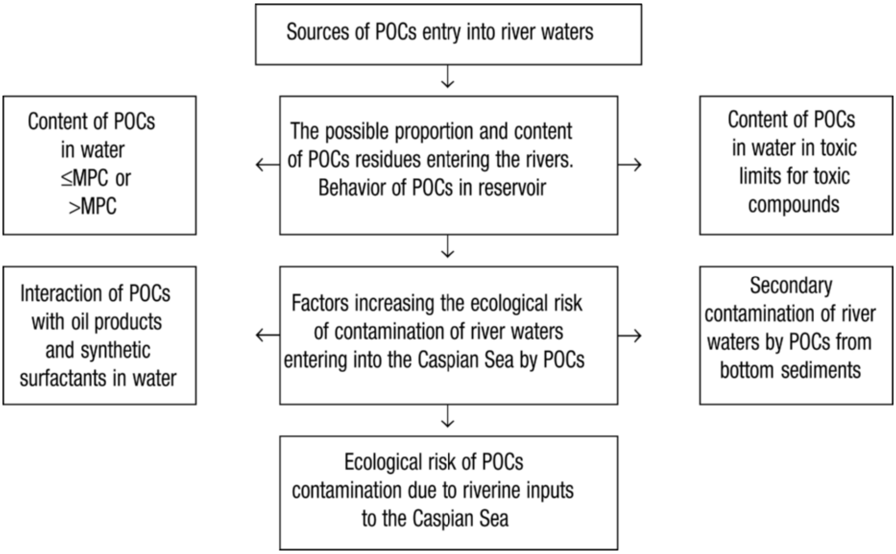


Figure 4. A conceptual model of the ecological risk assessment of persistent organochlorinated compounds (POCs) contamination due to riverine inputs into the Caspian Sea.

and mean of STEQs in Caspian seals were comparable to those noted in seals from the Canadian Arctic and in larga seals from the Sea of Okhotsk (mean TEQs were reported on 42 pg/g on lipid weight) (Nakata et al. 1997). These observations might be attributable to the lesser exposure to PCBs and high degradation capacity for coplanar PCBs in Caspian seals as discussed earlier. Lower TEQs in Caspian seals imply that the effect of coplanar PCBs is not a prominent factor for the abnormal mortality that took place in 1997 in Caspian Sea.

In Caspian seals, TEQs of non- and mono-*ortho* coplanar PCBs occupied 33% and 59% in STEQs, whereas those of di-*ortho* coplanar PCBs were only 7.8% (Table 3). Among non- and mono-*ortho* coplanar PCBs, TEQs of IUPAC 126 and 156 were comparable with the highest contribution in this seal, followed by IUPAC 118, 105, 169 and 77 (Figure 3). Compared to TEQ contribution in other seals, the lowest percentage of non-*ortho* coplanar PCBs, but higher proportion of IUPAC 156 in Caspian seals was observed (Figure 3). This pattern was rather close by similar to those in cetaceans. Such a unique pattern of TEQ composition found in Caspian seals seems to have risen from high activity of CYP1A isozymes, which have a potency to degrade non-*ortho* coplanar PCBs.

3. CONCEPTUAL MODEL FOR THE ENVIRONMENTAL RISK ASSESSMENT OF POLLUTANTS ENTERING THE CASPIAN SEA

The elaborated conceptual model is a schematic image of studied phenomenon in the form of interconnected information blocks: sources of persistent organic compounds, POCs; proportions and content of POCs in river waters compared with maximum permissible concentration (MPC, for DDT, HCH and PCB, are equal to 100, 20 and 1 ppb correspondingly for water and 100, 100 and 100 for bottom sediments); behavior of toxic compounds in the water body; factors promoting an increase of the ecological risk of polluted riverine input into the Caspian Sea (Figure 4).

The interactions of POCs with oil-products and synthetic surfactants in river and marine waters are considered, as well as secondary contamination of waters by POCs from bottom sediments. The "black box" principle was applied to estimating the ecological risk of toxic compounds contamination.

3.1. DDT and HCH Insecticides

The whole production of DDT was approximately 4.5 million tons from 1950 to 1970 and it is used today in some regions (Zakharenko and Mel'nikov, 1996). The environmental behavior of DDT, HCH and other pesticides is characterized by partial removal from the soil with surface runoff and discharge of toxic compounds into the rivers (Galiulin, 1999). Land erosion plays the most important role for soil particles with the adsorbed POCs to enter surface waters (Vrochinskii and Makovskii, 1979). The most intensive removal of pesticide residues occurs in the irrigated agrolandscapes with surface and drainage runoff. Usually the content of pesticides in the drainage discharge is higher than that in the receiving waters.

At present, the main source of surface water pollution by DDT and HCH insecticides may be related to their loss or leaching from the contaminated regional soils where these chemicals were used to protect agricultural crops and perennial plants from various pests and diseases. These insecticides were stored and accumulated in soils due to their high persistence, forming so-called "regional pedogeochemical anomalies (RPA)" characterized by increased toxic compound content as compared with regional background (Galiulin, 1999). According to Bobovnikova et al. (1980), the loss of DDT and HCH residues from the soil surface is relatively small, annually about 0.1–1.0% from the soil pool. This is an evidence of long-term period for insecticide residues entering into surface waters.

The higher content of DDT metabolites (DDE + DDD) compared with DDT itself (i.e., (DDE + DDD)/DDT > 1) in surface waters indicates a high degree of microbial transformation of the initial compound in the soil. The DDE and DDD are formed by DDT dehydrochlorination and dechlorination, respectively. On the whole it means that loss or leaching of toxic compounds take place from RPA formed some decades ago.

It is known that HCH preparation is as the eight isomers mixture (α, β, γ, δ, etc.), and therefore the detection of two and more of its isomers in water testifies on its regional usage (Figure 5).

A detection of β-isomer HCH in water in relatively larger quantities in comparison with other isomers shows a high degree of insecticide transformation in the soil (mainly by microorganisms), and hence loss or leaching of insecticide residues deposited some decades ago. It is known that β-isomer HCH is the most stable compound among others of HCH isomers, i.e., it is not or very weakly exposed to elimination reaction—dehydrochlorination (Cristol, 1947). High persistence of HCH β-isomer is

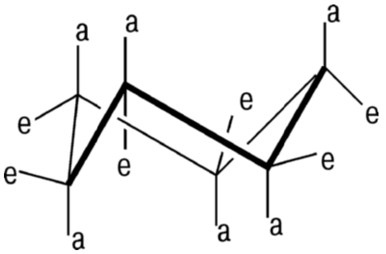


Figure 5. Isomers of HCH. Orientation of chlorine atoms in molecules of different isomers of HCH. α—aaeeee; β—eeeeee; γ—aaaeee; δ—aeeeee; ε—aeeaee; ξ—aaeaee; η—aeaaee; θ—aeaeee (Mel'nikov, 1974).

connected with its chlorine atoms, equatorial conformation, which provides the most energetically favorable configuration of the substance (Chessells et al., 1988).

The detection of DDT in surface waters as (DDE + DDD)/DDT < 1 reflects minor transformation of the initial insecticide in the soil and hence the toxicants loss or leaching from recently formed RPA or so-called local pedogeochemical anomalies, LPA (former action zone of plants for DDT preparations production; places of accidental spillage or output of the preparations; areas of storage or burial—tombs, etc. that are characterized by extremely high contamination level (Lunev, 1997; Silowiecki et al., 1998).

Meanwhile, the detection of α- or γ-isomer HCH in relatively high concentrations when compared with other isomers suggest relatively little transformation of HCH or lindane, which are known to include up to 70% of α-isomer and no less than 99% of γ-isomer, respectively. On the whole this would suggest a loss or leaching from recently formed RPA or LPA.

The monitored proportions of DDT ((DDE + DDD)/DDT > 1 or <1), HCH ($\beta > \alpha$, $\beta > \gamma$, $\beta > \delta$, etc.; $\alpha > \beta$, $\alpha > \gamma$, $\alpha > \delta$, etc.) and lindane ($\gamma > \alpha, \gamma > \beta, \gamma > \delta$, etc.) may be considered for interpreting their behavior, in particular, transformation in bottom sediments as an accumulating compartment of an aquatic ecosystem.

The pesticide residues entering receiving waters are transported as water soluble, adsorbed on suspended particles and colloidal forms. Here, they are subjected to different processes like deposition, volatilization, hydrolysis, microbiological and photochemical transformation (Mel'nikov et al., 1977; Vrochinskii and Makovskii, 1979; Allan, 1994). According to Komarovskii et al. (1981), in running water the deposition of DDT and HCH to bottom sediments is minimal. Another situation is observed at slow current when the vast silting zones begin to form and the movement of water masses along the riverbed is hampered or stopped. Under these conditions the pesticide residues, being absorbed to suspended particles, are removed from the water mass and, due to sedimentation, precipitate and accumulate on the bottom. Shcherbakov (1981) has also concluded that accumulation of residual DDT and HCH in the bottom sediments of reservoirs was strongly affected by the velocity of the water current and the type of sediment. In flowing water bodies, the pesticides are removed almost completely near the river mouth. Therefore, their residual amounts are minor in the places of entry, where the current velocity is higher. This fact allows us to explain the non-uniform distribution of organochlorinated pesticides in bottom sediments of reservoirs. The content of pesticides in the sandy sediments is lower than that in the silted ones, and much lower compared to the clay sediments.

Bottom sediments in water bodies accumulate various toxic compounds due to their high adsorption rate on the particle surface (this varies with particle type) and low temperature of the bottom layer, which reduces the transformation rates. The largest amount of toxic compounds is accumulated in the subsurface silt or clay layers with anaerobic conditions (Rhee et al., 1989). At present a hundred thousands tons of POCs have been "stored" in the bottom sediments, and their continued input into the water column adds to present contamination (Afanasiev et al., 1989).

Persistent organochlorinated pesticides entering with surface discharge into a water body may enter into the biogeochemical food web of aquatic ecosystems: water → bottom sediments → invertebrates → vertebrates (Shcherbakov, 1981; Bashkin, 2003). In contaminated fresh and salt waters, pesticides are prone to bioaccumulation in bottom sediments, water plants, phyto- and zooplankton, and benthic organisms, fish and other aquatic organisms, and eventually may be transferred via the food chain to humans. For example, Komarovskii et al. (1981) showed that distribution of DDT between the elements of biota occurred according to the principle of biological intensification, i.e., one order of magnitude higher concentration in every link of the trophic (food) chain in accordance to biomagnification. The increase of concentration is distinctly observed by the value of accumulation coefficients of insecticide residues in the trophic chains: "zooplankton–planktonivorous fishes–piscivorous fishes–mammals–silt–zoobentos–bentosivorous fishes".

The simplest model used in aquatic ecosystems is based on the simplified food chain:

water → fish or mussel → fish or mussel eating birds/mammals.

Assuming that the mammals or birds feed on fish or mussels, the simplest model to calculate an MPC based on this food web is:

$$\mathrm{MPC}_{\mathrm{water}} = \mathrm{NOEC}_{\mathrm{species\ of\ concern}} / \mathrm{BCF}_{\mathrm{food\ species\ of\ concern}}$$

where: $\mathrm{MPC}_{\mathrm{water}}$ is Maximum Permissible Concentration of a chemical in water, ppb; $\mathrm{NOEC}_{\mathrm{species\ of\ concern}}$ is No Observed Effect Concentration of the food (invertebrate) corrected for the species of concern (mammals or birds, ppb); $\mathrm{BCF}_{\mathrm{food\ species\ of\ concern}}$ is Bioconcentration Factor, representing the ratio between the concentration in the invertebrate, being the food of the species of concern, and the concentration in water.

A simplified scheme of a POC's transformation in a biogeochemical food web in an aquatic ecosystem is shown in Figure 6.

Histological researches showed that persistent organochlorinated pesticides found in fish organs had exerted a polytrophic action, i.e., affected the central nervous system,

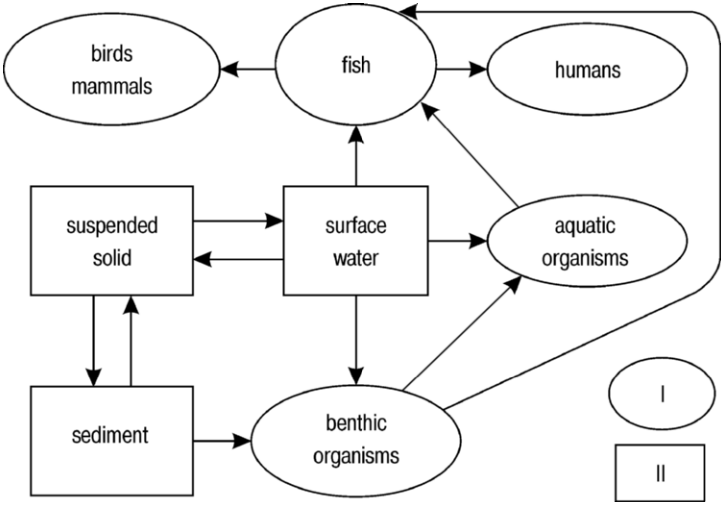


Figure 6. Simplified scheme of a POC's transformation in a biogeochemical food web in an aquatic ecosystem. I—receptor, II—compartment.

liver, gills, kidneys, spleen and digestion tract (Shcherbakov, 1981). Changes of fish organs manifested from minor disorder of blood circulation and dystrophic changes up to formation of necrosis and necrotic centers. Accumulated in gonads the pesticides affect not only the individual, but also their offspring. This may facilitate various lethal and chronic effects, such as lethal mutations deformity, stop the processes of individual evolution, provoke mortality at the early stages of the caviar development, and lead to the birth of nonviable youth (Braginskii, 1972).

Meanwhile, in Russia and Kazakhstan the complete absence of DDT and HCH isomers residues is required for water of the fish farming water bodies (Afanasiev et al., 1989; Korotova et al., 1998). An acute toxic effect of DDT and HCH insecticides and other organochlorinated preparations on the most sensitive organisms ranges within concentrations of 0.001–1,000,000 ppb (Braginskii, 1972). Such high sensitivity to these concentrations is determined, on the one hand, by extraordinary toxicity of the substances, and on the other hand, by specific character of their effect on vitally important functions, which is common for insects and many water animals. The toxicity range is wide: they easily affect many representatives of *Arthropoda*, in particular *Crustacea*, which are the major part of sea and fresh water zooplankton. Therefore, the concentration of pesticides found in water deserves comparison with the so-called toxic quantities for organisms or NOEC values.

3.2. *Substances for Industrial Use—PCBs*

PCBs represent chlorine derivatives of biphenyl, containing from 1 to 10 atoms of chlorine in a molecule that is expressed as 10 different homologues (Figure 2). Having no ethane bridge between the aromatic rings, as opposed to DDT, PCBs are more stable in the environment (Surnina and Tarasov, 1992). According to the data of Samson et al. (1990), the T_{50} value of highly chlorinated PCBs can be up to a few decades.

The main source of environmental pollution with PCBs is industrial and waste inputs. PCBs enter into the environment due to the leakage from transformers, condensers, heat exchangers or hydraulic systems, leaching and evaporation from different technical devices, disposal of liquid waste waters, as well as owing to application of PCBs as filler for pesticide preparations (Tyteliyan and Lashneva, 1988). The direct disposal from ships of used hydraulic liquids and greases is of local importance. From 35% (Surnina and Tarasov, 1992) to 80% (Tuteliyan and Lashneva, 1988; Bunce, 1994) of global PCB production was discarded into the environment with other wastes. Meanwhile a great part of these toxic compounds entered into surface and marine waters. In recent decades 1.1–1.2 million tons of these preparations have been globally produced (Surnina and Tarasov, 1992; Amend and Lederman, 1992). The contamination of bottom sediments in the world reservoirs, including a number of Volga river reservoirs, by PCBs is higher than by persistent organochlorinated pesticides (Afanasiev et al., 1991; Khadjibaeva et al., 1996). Both PCBs and organochlorinated pesticides are transported in water-soluble form, adsorbed on the particles and colloidal forms (Allan, 1994). The water organisms enable accumulation of PCBs, and their concentrations in algae, plankton and fish are positively correlated with concentrations in bottom sediments (Tuteliyan and Lashneva, 1988). A single contamination of silts by PCBs may result in constant local uptake by water organisms for a long time (up to several years), once the incident has occurred. The effect of PCBs, for example, on fish has a cumulative character and their toxicity increases with decreasing degree of chlorination of the compound (Polychlorinated, 1980; Bashkin, 2003a). It should be noted that in Russia PCBs are not allowed in water of fish farming water bodies (Ecological Herald of Russia, 2002).

3.3. Other Factors Increasing POCS Environmental Risk

Interaction of POCs with Oil-Products and Synthetic Surfactants

The oil-products (fuel, petrol oils and solvents, illuminating kerosene, etc.) and synthetic surfactants in river waters entering the Caspian Sea may interact with POCs and enhance the toxic effect of these compounds. It is known that synthetic surfactants are used in production of detergents, pesticides and also oil-processing and petrochemical industries. Therefore synthetic surfactants may increase the ecological risk of contamination by POCs. Organochlorinated insecticides, brought into the sea as suspended particles by the rivers, can be dissolved in oil-products of contaminated seawaters. These combined pollutants can suppress photosynthesis of phytoplankton by up to 95%, under concentrations of about 1 μg/l. This leads to a decrease of primary production in vast areas of the sea (Braginskii, 1972). The following mechanism may be suggested. The formation of POCs–oil complexes will be inevitably accompanied by decreasing photosynthetic re-aeration and weakening oxidative function of water plants, one of the main factors of self-purification of reservoir from petrol contamination. On the other hand, the complex of unsaturated compounds and oil-products (like petrol oils) suppresses the activity of organochlorinated insecticides. This is connected with involvement of insecticides into telomerization reaction—the chain reaction of unsaturated compounds—monomers with the substance—the carrier of the reaction chain—telogen (Melnikov, 1974). Moreover some oil-products earlier were used as insecticides, i.e., oil preparations and solvents for various insecticide, fungicide and herbicide concentrated emulsions, etc. Besides the oil-products with high quantity of aromatic hydrocarbons have the effect of long- term herbicides on aquatic plants.

In water, redistribution of pesticides may occur. Being conditioned by the synthetic surfactants they transfer from water mass to the surface, forming a surface film of microscopic thickness, which is characterized by extremely high concentration of pollutants (Il'in, 1985). Under favorable conditions, up to 80% of water borne pollutants transfer into the surface film. For example, HCH is concentrated in an adsorbed layer in the amount of 19.7×10^4 MPC (the translocation rate was 56%). Water-insoluble pesticides entering aquatic systems with fine-texture solid particles and also pesticides with an aromatic ring in the molecule are adsorbed most effectively by the surface layer. The water solubility of DDT as a representative of chlorine derivatives of aromatic hydrocarbons is approximately 1 ppb, and HCH isomers as the representatives of chlorine derivatives of alyciclic hydrocarbons is higher, i.e., 1–10 ppm (Popov, 1956; Mel'nikov, 1974). Accordingly, one may propose that translocation level of DDT in the surface layer will be higher than HCH. As far as PCBs are concerned, the rate of their translocation into surface film will be also increased with decreasing water solubility of separate homologues—from 4.4 to 0.00006 ppm for mono- and decachlorobiphenyls respectively (Surnina and Tarasov, 1992).

Experimental studies of PCBs and DDT transformation in marine waters showed that PCBs inhibited decomposition of DDT at the concentration ratio of DDT to PCBs of 1:100–1:200 that may lead to prolongation of circulation time and toxic effect of this compound at water ecosystem (Tuteliyan and Lashneva, 1988). It is also known that in the past, PCBs were often added to HCH to increase the longevity of the insecticide (Mel'nikov, 1974).

Secondary Contamination of River Waters by POCs from Bottom Sediments

Accumulation of POCs is possible in bottom sediments of rivers, and, especially, artificial water-storage reservoirs of the Caspian Sea basin (Glazovskaya, 1979). The exchange between the water and bottom sediments proceeds practically all the time and may result in secondary contamination of river waters entering into the Caspian Sea as a consequence of POCs desorption from bottom sediments (Vrochinskii and Makovskii, 1979; Surnina and Tarasov, 1992; Popov, 2001). Nevertheless, these sediments may be a source of the given process only under specific conditions, i.e., when the proportion between concentration of a pollutant in water to bottom sediments is less than 1. The most intensive contamination of water mass occurs in the period of floating (expansion) of the bottom sediments by accumulated gases, and also wind or water driven resuspension. Desorption of pesticide residues from bottom sediments into water is possible also under sharp changes of pH or temperature (Sokolov et al., 1977) that is possible when industrial wastewaters with extreme pH values (acid and

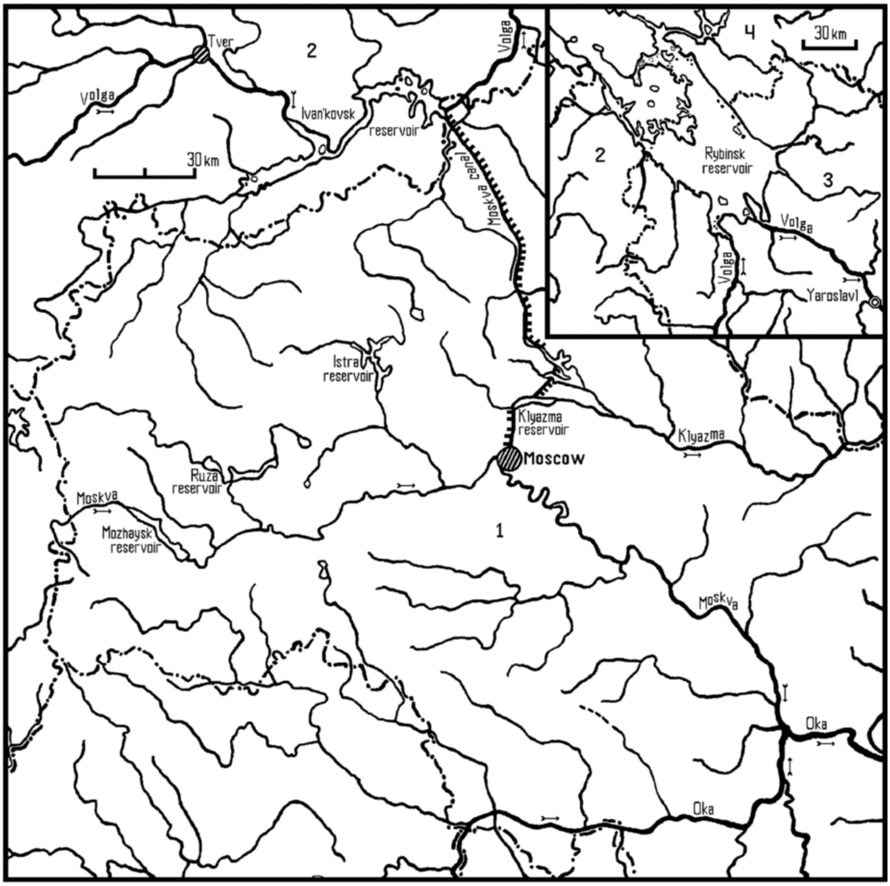


Figure 7. Location of rivers and reservoirs of different regions of Russia: Moscow (1), Kaluga (2), Smolensk (3), Tver (4), Vladimir (5), and Yaroslavl (6) regions.

alkali contamination) or high temperature (heat contamination) enter into the water currents.

3.4. Examples of Conceptual Model Use

The Caspian Sea receives most pollutants from river discharge, mainly due to the Volga River. Recently, the annual quantity of oil hydrocarbons entered into the Caspian Sea with river discharge reaching 55,990 tons, synthetic surfactants, 12,695 tons, and organochlorinated pesticides, 66 tons (Shaporenko, 1997).

Let's consider examples of a conceptual model using recent POCs monitoring data for water and bottom sediments of water bodies (rivers and flowing water-storage reservoirs) in the basins of the Volga, Ural, Terek and Kura rivers.

In the Rybinsk reservoir constructed in the upper Volga (Yaroslavl, Vologda and Tver regions), the ratio of PCBs in water and silts, in some places, was less than 1, which would suggest probable secondary contamination of water (Figure 7, Table 4)

According to Khadjibaeva et al. (1996) and Kozlovkaya and German (1997), monitored composition and ratio of HCH isomers in water samples of Ivan'kovsk (Tver region), Istra, Ruza and Klyazma water reservoirs (Moscow region) suggests the former usage of HCH insecticide in these regions. One can suppose that its residues are lost or leached from the RPA formed a few decades ago because the relative content of β-isomer HCH is higher than α- and γ-isomers. The ratio of HCH isomers in bottom sediments of Istra and Klyazma water reservoirs may reflect a relatively little transformation of insecticide in silts because α- and γ-isomers content was relatively higher than β-isomer quantity. In the bottom sediments of Mozhaysk, Istra, Ruza and Klyazma water reservoirs (Moscow region), the proportion of DDT residues was as $(\mathrm{DDE} + \mathrm{DDD})/\mathrm{DDT} > 1$. Thus there was significant insecticide transformation of DDT in the bottom sediments. The ratio of POCs (DDT, HCH and PCBs) residues in water compared to bottom sediments of Istra, Ruza and Klyazma water reservoirs, in a number of cases, was less than 1. This indicates the possible secondary contamination of water under present conditions (Khadjibaeva et al., 1996).

Our studies (Galiulin and Bashkin, 1996) accomplished in Klyazma and Ivan'kovsk water reservoirs suggested loss or leaching of HCH and lindane in relatively little transformed form from LPA because the α- and γ-isomers content was similar (Table I). The proportion of DDT in bottom sediments of the Klyazma river, tributaries of the Moskva and Oka rivers (Moscow region) was as $(\mathrm{DDE} + \mathrm{DDD})/\mathrm{DDT} < 1$, suggesting relatively little insecticide transformation in silts of bottom sediments.

There was high contamination by persistent organochlorinated pesticides in the rivers of Bashkortostan, Tatarstan and Samara region, middle Volga river basin (Table II) (Ovanesyants et al., 2001, 2003; Kochneva et al., 2002). Meanwhile, the significant increase of DDT content above its product (DDE) suggests the loss and leaching of insecticide residues in relatively little transformed form from LPA. Analogously, the relatively high concentration of α-isomer over γ-isomer may be due to loss or leaching of HCH insecticide also in relatively little transformed form from LPA. The same phenomenon is revealed for other data (Korotova et al., 1998) in respect to the Volga and Ural River basin. The increasing of DDT over DDE suggests loss or leaching of DDT in relatively little transformed form from LPA. However, the increasing of γ-isomer HCH content over α-isomer concentration in surface waters of the Volga, Ural and Terek river basins suggests loss or leaching of lindane and HCH residues in relatively little transformed form from LPA.

Our monitoring (Galiulin, 1995) carried out in the Mugano-Salyansk land region (Azerbaijan) showed that the content of HCH isomers sum (α-, β-, γ- and δ-) and DDT in irrigation water draining into the south part of the Caspian Sea, was higher than in water of the Araks and Kura rivers (Table 5). This is due to more intensive draining of toxic compounds from irrigated areas. The relative part of HCH α-isomer content in both water types was higher than other isomers. This may testify a primary usage of

Table 4. The POCs concentration (ppb) in water* *and bottom sediments*** *of the upper Volga water bodies.*

				HCH				
Water bodies	DDT	DDE	DDD	α	β	γ	PCBs	References
Rybinsk reservoir							0.33*–4840**	Kozlovskaya a. German, 1997
Ivan'kovsk, Istra, Ruza and Klyazma reservoirs				0.002–0.004*	0.003–0.006*	0.002*		Khadjibaeva et al., 1996
Mozhaysk, Istra, Ruza and Klyazma reservoirs	0.2–0.3**	0.1–0.9**	0.2–4.0**	0.02–0.50**	0.02**	0.02–0.10**	2–98**	
Ivan'kovsk and Klyazma reservoirs	0.08–0.176*			0.059–0.066*		0.075–0.077*		Galiulin a. Bashkin, 1996
Moskva river and one of its tributary	0.046–0.76*							
Klyazma river and tributaries of Moskva and Oka rivers	98.3**	3.2–14.4**	18.4**				6.6–7.5**	

Table 5. The DDT and HCH (ppb) in water of different river basins.

Basin	DDT	DDE	HCH	HCH isomers			References
				α	β	γ	
Middle Volga river	3240–10,500	800–880	106–252				Ovanesyants et al., 2001
Middle Volga river			90				Kochneva et al., 2002
Middle Volga river				224		134	Ovanesyants et al., 2003
Volga river	3.36	0.27		3.81	0.06	7.31	
Ural river	0.42	0.05		0.32		0.38	Korotova et al., 1998
Terek river		0.06	0.05		0.52		

HCH insecticide in agricultural areas of the Mugano-Salyansk land region and also loss or leaching of its residues from recently formed RPA (Galiulin and Galiulina, 1996). Meanwhile the proportion of DDT in the bottom sediments of rivers was DDE + DDD/DDT < 1, that may indicate a relatively little transformation of this insecticide in the present environment (Galiulin, 1994).

In the northern part of the Caspian Sea, the POCs were detected in various links of the food webs, especially in the Caspian sturgeon (Table 6). These high concentrations

Table 6. Concentrations and ratio of persistent organochlorinated pesticides in water currents of the Mugano-Salyansk region (Azerbaijan) entering the Caspian Sea (Galiulin 1995).

Organochlorinated pesticides	In water of the Araks and Kura rivers		In irrigation water entering South Caspian	
	ppb	%	ppb	%
α−HCH	0.09–0.18	53.9*	0.08–0.29	48.3*
β−HCH	0.04–0.13	20.4*	0.02–0.15	15.9*
γ−HCH	0.06–0.13	22.6*	0.03–0.15	23.2*
δ−HCH	0.06	3.1*	0.03–0.11	12.6*
Isomers sum of HCH	0.14–0.40	74.8**	0.16–0.61	45.3**
DDT	0.14–0.21	25.2**	0.10–0.66	54.7**

*Relative part of HCH isomers
**Relative part of sum of HCH isomers and DDT

are connected both with direct riverine input of these compounds to the north and south Caspian Sea and current water redistribution in the whole sea area. For example, POCs entering the south Caspian Sea with the Kura River, may be transported to the northern part along the eastern coast. As a consequence of water contamination by oil-products, POCs and other pollutants, the pathology of sturgeon has been detected (Altufiev and Geraskin, 2003). The greatest degree of muscle tissue disturbance was monitored for West coasts of Middle and South Caspian and near mouth spaces of Kura and Terek rivers that are connected with oil and pesticide contamination of these regions. By experiments with sturgeon youth, it the probability of a synergetic affect of toxicants, in particularly, due to "oil-products+organoclorinated pesticides" complex on muscle tissue, has been confirmed.

We should point out that at the scale of the whole Caspian Sea the present monitoring results are limited (Bukharitsin and Luneva, 1994; Kuksa, 1996). However, we can conclude that the highest concentrations of DDT in water in the late 1980s were recorded in coastal waters of the Ural and Volga rivers and in the deeper western part of the North Caspian. Taking into account that the maximal content of synthetic surfactants were also observed in the same sea regions, one can postulate that most DDT enters the sea with river discharge in concentrated form, mainly in surface film composition formed by synthetic surfactants.

Thus the application of the conceptual model to monitoring data shows an existence of the ecological risk of river waters entering in the Caspian Sea. This is connected with (a) loss or leaching of DDT and HCH residues with relatively low transformation from LPA, (b) possible secondary risk of water contamination by POCs desorbed from bottom sediments, and (c) POCs content in aquatic ecosystems at toxic concentrations for the most sensitive organisms.

Thus, at present, the input of unused DDT and HCH insecticides in water and bottom sediments of the rivers and reservoirs of the Caspian Sea basin is mainly connected with loss or leaching from "old" RPA or "young" LPA. As regards PCBs, their input is mainly related to industrial sources. The high toxicity of POCs for organisms and their persistence in the water and sediments are the principal forms of ecological risk for rivers and the Caspian Sea. The behavior of POCs in the northern part of

Table 7. Content of organochlorinated pesticides (ppb) and tissue disturbance ranks (dimensionless values) for Caspian sturgeon in the different regions of the Caspian Sea in the late 1980s–early 1990s (Terziev, 1996).

				Tissue disturbance rank		
Area	DDT	HCH	Oil	1987	1989	1991
North Caspian					2.3	
Middle Caspian	26.1–180.8	0.7–24.4	150–260	2.8–3.6	2.7–3.6	2.7–3.6
South Caspian	259.2	11.9	140	2.1	2.8	2.8

the Caspian Sea is more aggravated due to possible interaction of these compounds with each other, as well as with oil-products and synthetic surfactants. This may increase the duration of their preservation in water medium and also enhance the risk of secondary contamination by toxic compounds from bottom sediments. The relevant example of POPs accumulation in biota due to exposure from water and bottom sediments is shown in Table 7.

Entering into the Caspian Sea, as an undischarged water body, the toxicants will migrate for a long time, owing to prevalence of water circulation, and bioconcentrate in marine food webs, the final link of which is a human.

The most important future research needs are as follows:

(1) Monitoring POCs concentrations in waters and bottom sediments of the Caspian Sea;

(2) Understanding POCs interactions with crude oil, oil-products and synthetic surfactants in fresh and salt waters;

(3) Rates of POCs secondary contamination of fresh and salt waters from bottom sediments;

(4) Pollutants additive and synergetic effects on fresh and marine water organisms.

This would allow a more comprehensive ecological risk assessment, and also predict a perspective of the geoecological situation changes, in particularly, in the Northern Caspian under varying input of different pollutants into the “river–sea” system.

CHAPTER 17

TRANSBOUNDARY N AND S AIR POLLUTION

The acidity of rain is determined by the concentration of hydrogen ions, and this concentration depends on two things: the presence of acid-forming substances such as sulfates and nitrates, and the availability of acid-neutralizing substances such as calcium and magnesium salts. Clean rain has a pH value of about 5.6. By comparison, vinegar has a pH of 3. The calculation and mapping of critical loads (CLs) of acidity, sulfur and nitrogen form a basis for assessing the effects of changes in emission and deposition of S and N compounds. So far, these assessments have focused on the relationships between emission reductions of sulfur and nitrogen and the effects of the resulting deposition levels on terrestrial and aquatic ecosystems. Accordingly, the exceedances' values of critical loads represent the environmental risk assessment to ecosystems and furthermore to human health.

1. ASSESSMENT OF ENVIRONMENTAL RISK TO ACID DEPOSITION IN EUROPE

1.1. Maps of Critical Loads and Their Exceedances

In this section, we present European maps of critical loads and their exceedances. These values have been used for multi-pollutant, multi-effect Protocol of UNECE Long-Range Trans-boundary Air Pollution Convention signed in Gothenburg in December 1999.

Figures 1 and 2 are maps of 5th percentiles of the maximum critical loads of sulfur, CLmasS, the minimum critical load of nitrogen, CLminN, the maximum critical load of acidifying nitrogen, CLmaxN, and the critical load of nutrient nitrogen, ClnutN (see Chapter 3 for details). They show that values of CLmaxS and CLmaxN are lowest in the northwest and highest in the southwest. The low values of CLminN, as compared to ClnutN, in the south (Italy, Hungary, Croatia) indicate low values of nitrogen uptake and immobilization, but relatively high values for N leaching and denitrification.

Figure 3 shows snapshots of the temporal development (1960–2010) of the exceedances of the 5th percentile maximum critical load of sulfur, CLmaxS. The exceedance is calculated due to sulfur deposition alone, implicitly assuming that nitrogen does not contribute to acidification. Although this is probably true at present in many countries as most of the deposited nitrogen is still immobilized in the soil organic matter or taken by vegetation, the long-term sustainable maximum deposition for N

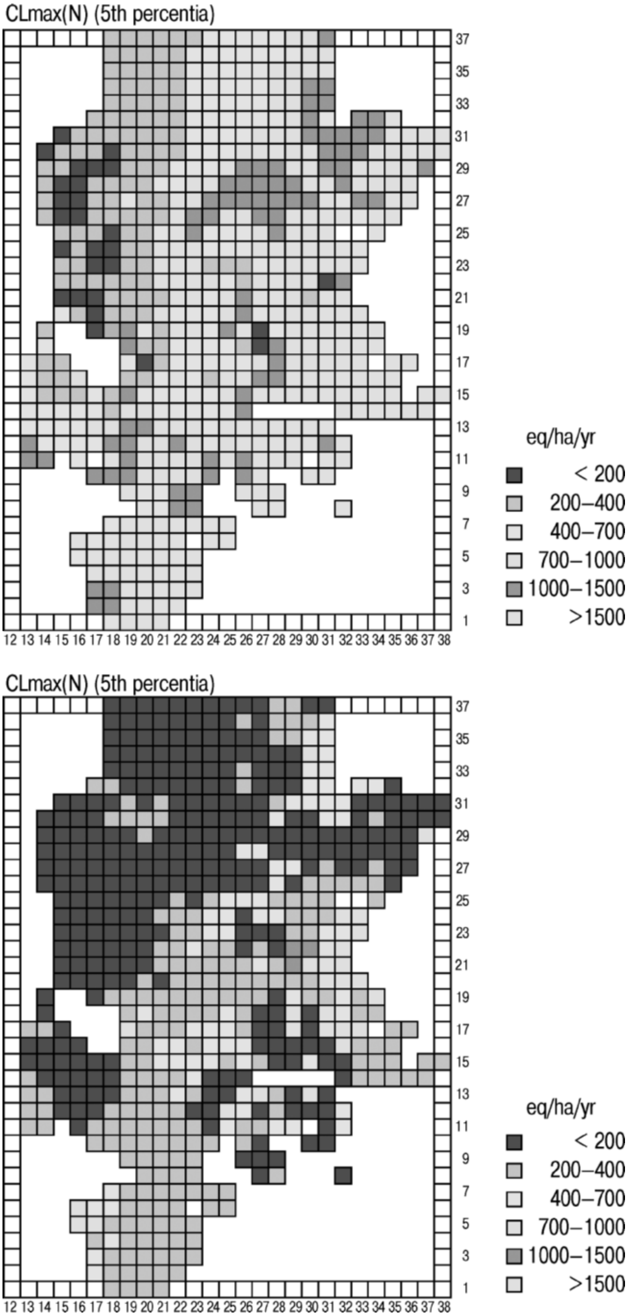


Figure 1. The 5th percentiles of the maximum critical loads of sulfur, CLmaxS, and of the minimum critical load of acidifying nitrogen, CLminN (Posch et al., 1999).

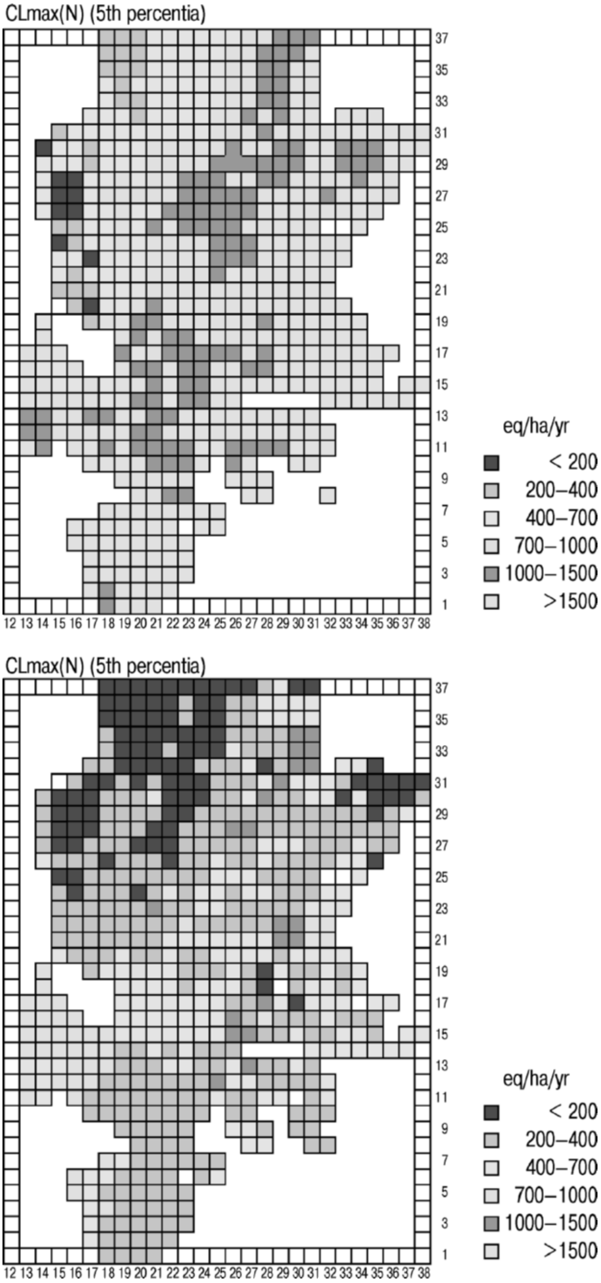


Figure 2. The 5th percentiles of the maximum critical loads of acidifying nitrogen, CLmaxN, and of the minimum critical load of nutrient nitrogen, CLnutN (Posch et al., 1999).

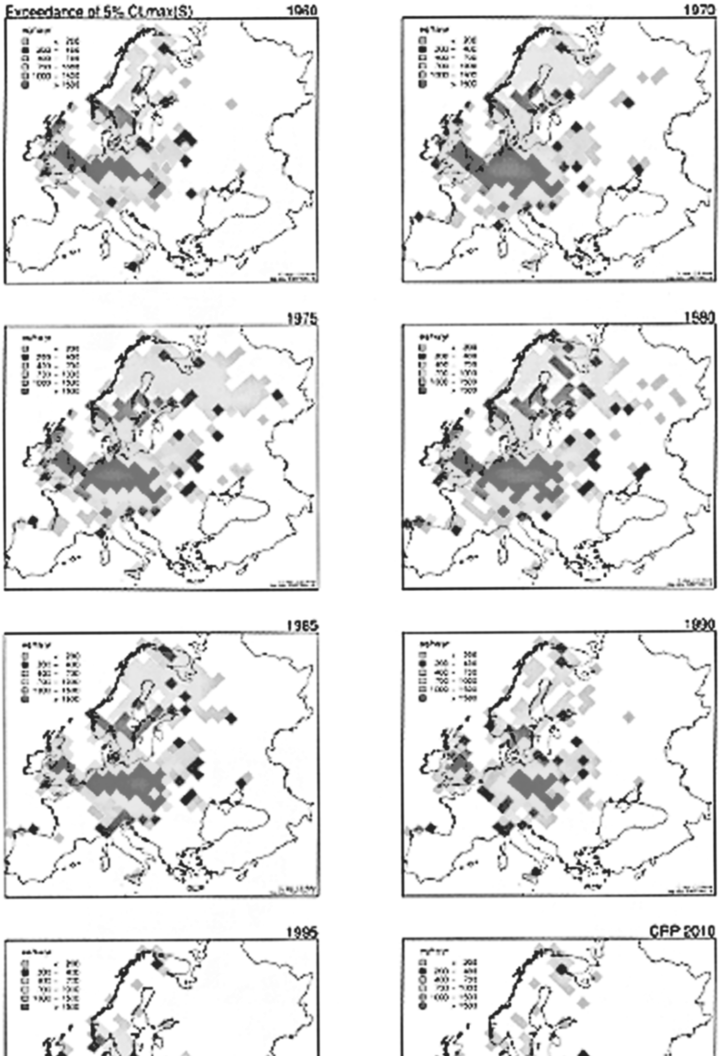


Figure 3. Temporal development (1960–2020) of the exceedance of the 5th percentile maximum critical load of sulfur. While areas indicate non-exceedance or lack of data (e.g., Turkey). Sulfur deposition data were provided by the EMEP/MSC-W (Posch et al.,1999).

not to contribute to acidification is given by CLminN. However, the main purpose of Figure 3 is to illustrate the changes in the acidity critical load exceedances over time. As can be seen from the map, the size of area and magnitude of exceedance peaked around 1980, with a decline afterwards to a situation in 1995, which is better than in 1960.

As mentioned earlier (see Chapter 3), a unique exceedance does not exist when considering both sulfur and nitrogen, but for a given deposition of S and N one can always determine whether there is non-exceedance or not. The two maps on the top of Figure 4 show that the percent of ecosystem area is protected from acidifying deposition of S and N in 1990 and 2010. In 1990 less than 10% of the ecosystem area is protected in large parts of central and western Europe as well as on the Kola peninsula, Russia. Under the scenario of the 1999 multi-pollutant, multi-effect Protocol of UNECE LRTAP Convention (CDR 2010), the situation improves almost everywhere, but is still far from reaching complete protection.

To compare the deposition of S and N with the acidity critical load function, an exceedance quantity has been defined. This average accumulated exceedance (AAE) is the amount of excess acidity averaged over the total ecosystems area in a grid square. The two maps of the bottom of Figure 4 show the AAE for 1990 and 2010 (CRP scenario). In 1990 the highest acidity excess occurs in central Europe, the pattern roughly matching with the ecosystem protection percentages for the same year. Under the CRP scenario in 2010, excess acidity is reduced nearly everywhere, with a peak remaining in the “Black Triangle” of Germany, Poland and the Czech Republic. Thus, the values of critical load exceedances characterize the environmental risk to ecosystems in various parts of Europe owing to acid deposition of sulfur and nitrogen species. This risk is related to acidification and eutrophication processes in both terrestrial and aquatic ecosystems (Bashkin, 2002; Posch et al., 2003).

1.2. Acidification

The analyses of modern efforts of both scientific and business communities allow us to summarize the following positive improvements in the Europe (Gregor and Bashkin, 2004).

During the last decade continued improvement in the chemical status of acid-sensitive lakes and streams led to biological recovery. The decreasing trends of corrosion of materials have been broken in some regions in Europe even though the SO_2 concentrations are still decreasing, possibly due to contributions from HNO_3 and particles. Proton budgets at ICP Integrated Monitoring sites over all of the Europe are a useful tool for integrating the net effects of several complex processes in acidified catchments. A cooperative study with MSC-West has shown that, using the updated critical loads database and applying the improved and unified EMEP model, the remaining area with exceedance of CL (acidity) was 11% in 2000 (Figure 5) and will be 8% in 2010, a figure well above the intended value (2.3%) of the Göthenburg Protocol.

Here we should again point out that Average Accumulated Exceedance (AAE) values are indeed the environment risk assessment values made up on the basis of biogeochemical approaches.

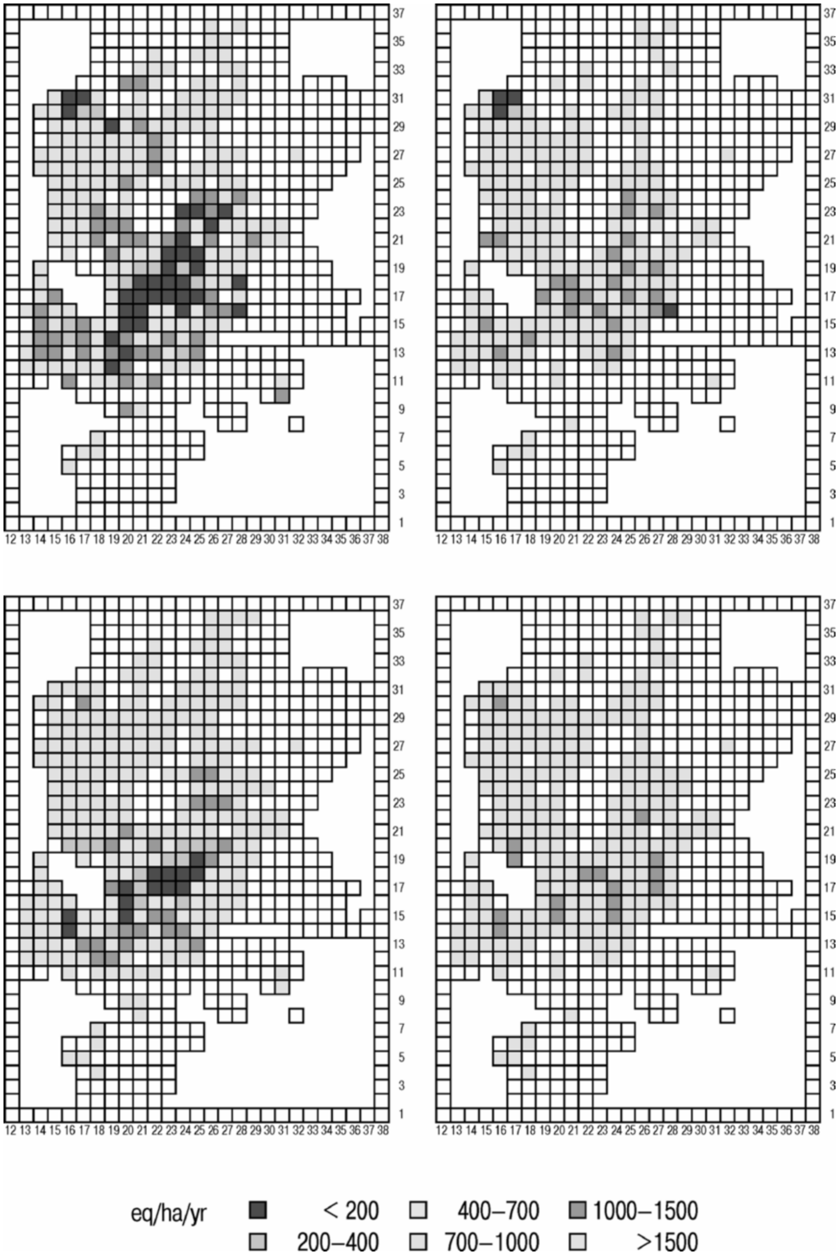


Figure 4. Top: The percentage of ecosystem area protected (i.e., non-exceedance of critical loads) from acidifying deposition of sulfur and nitrogen in 1990 (left) and in the year 2010 according to current emission reduction plans in Europe (right). Bottom: The accumulated average exceedance (AAE) of the acidity critical loads by sulfur and nitrogen deposition in 1990 (left) and 2010 (right). Sulfur deposition data were provided by the EMEP/MSC–W (Posch et al., 1999).

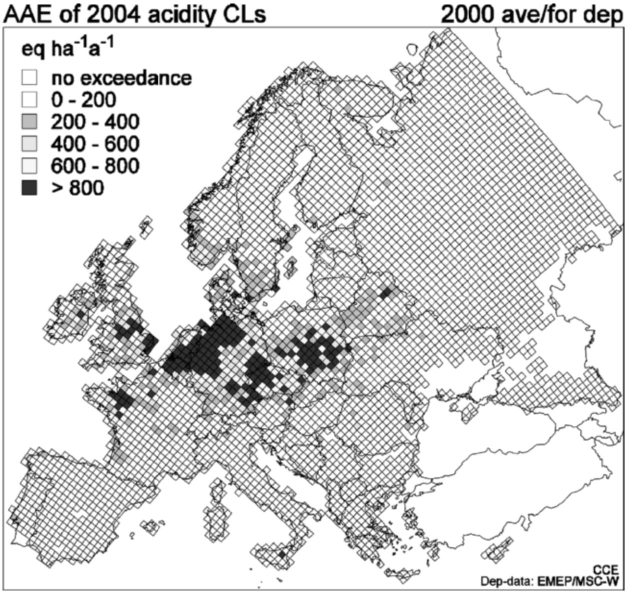


Figure 5. Average Accumulated Exceedance (AAE) of critical loads of acidity (update 2004) for Europe by acid deposition in 2000 (Hettelingh et al., 2004).

1.3. Eutrophication

At present the trends of NO_3 and NH_4 (and SO_4) concentrations in bulk deposition, observed at monitoring sites in forests during 1996–2001 were not significant. Increased height increment and wood volume increment was observed, which revealed generally accelerated tree growth across Europe. However to reduce the uncertainties in environmental risk estimates, further investigation of the relationships between atmospheric deposition, climate change and tree growth are necessary. Here we should mention that C/N ratio in the organic horizon of soil at monitoring sites was shown to be a useful indicator for the risk of nitrogen leaching.

Latest calculations showed that critical loads of nutrient nitrogen will be exceeded in 35% of the ecosystem area in 2010 even after implementation of the Gothenburg Protocol (Table 1).

2. ASSESSMENT OF ENVIRONMENTAL RISK TO ACID DEPOSITION IN NORTH AMERICA

2.1. Acid Rains Over Canada and the USA

Since the late 1970s, precipitation-monitoring programs have been placed in the USA and Canada; eleven Canadian networks (approx. 110 sites) and two large-scale US networks (approx. 220 sites) are currently operational. The various networks have now accumulated information for well over 15 years about ion concentrations in

Table 1. Percentage of the ecosystem area for which nutrient nitrogen critical loads are exceeded in 2000 and 2010, consideration of ecosystem specific deposition has the strongest influence (Hettelingh et al., 2004).

	2000		2010	
Calculation methods	Europe in the whole	EU 25 only	Europe in the whole	EU25 only
Lagrangian model				
1998 critical loads	26.0	60.7	24.6	54.4
2004 critical loads	24.5	56.0	23.1	49.0
Unified model & 2004 critical loads				
Grid average deposition	29.1	64.9	28.5	59.2
Ecosystem-specific deposition	35.1	77.7	34.7	73.0

precipitation and wet deposition. Acid rain was recognized as a problem in North America in the 1950s. Two decades later, scientists noted losses of fish populations in some highly acidified lakes of the East Coast of USA and Canada. The reason was related to acid rain caused by pollutants such as sulfur dioxide and nitrogen oxides, which in the atmosphere are chemically converted to sulfuric and nitric acids. At present, acid rain is the major environmental problem in USA and Canada.

Acidic precipitation has been most recognized as a serous environmental problem in areas of granite rocks, namely Northern and Eastern Canada and the Northeastern United States, where the forests are under assault and the lakes have been becoming progressively acidified during the 1980s. The content of base cations and alkalinity in these soils and surface waters is low. Correspondingly, the buffer capacity of the ecosystems to acidity loading is also low. In these poorly buffered lakes a "normal", natural pH would probably be in the range 6.5–7.0. In the mid-1990s, many lakes in these areas record pH levels of 5.0 and lower.

The averaged values of pH in precipitation are shown in Figure 6.

The separate values for acidity (H^+) input in some Canadian lakes are in Figure 7.

2.2. Acidifying Emissions in Canada and the USA

Sulfur dioxide emissions in both Canada and the USA peaked in the early 1970s and have declined ever since with year-to-year variability. Actions to reduce acid deposition have been focused mainly on SO_2 emissions because they play generally a much higher role in rainfall acidification than nitrogen oxides. However, this is not the case in some areas of North America, like California, where nitrogen emissions are predominant and consequently contribute the major part in acidity as well.

Since approximately half of the acid precipitation in eastern Canada has come from American sources, the Canada–United States Air Quality Agreement was signed

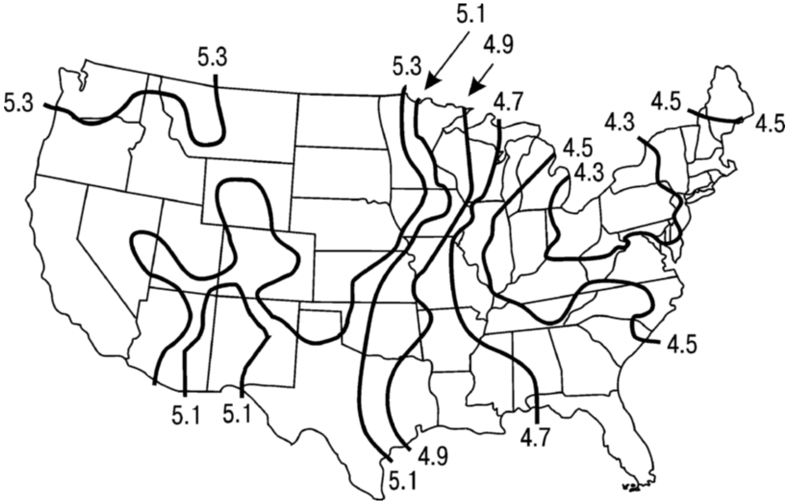


Figure 6. Averaged values of pH in precipitation in North America in early 1990s (Smith, 1999).

in 1991 to reduce sulfur emissions and also set up a framework for dealing with nitrogen oxides and other pollutants that commonly cross the USA–Canada border. As a result, SO_2 emissions in two countries have declined substantially. Under the current programs, total emissions from the two countries are expected to drop from 28.2 million tons (MT) (Canada 4.6 + USA 23.6) to 18.3 MT (Canada 2.9 + USA 15.4) by the year 2010. In Canada alone sulfur dioxide emissions have declined considerably over the 1980–1990s and, by 1995, had been reduced to 2.65 MT, lower than the agreed upon limit of 2.9 MT (Ro et al., 1999).

Since environmental damage due to acid deposition has largely been limited to the eastern parts of Canada (east of the Manitoba–Ontario border) and the USA (east of the Mississippi River), most of the emission reductions have occurred in those areas. Figure 8 illustrates the SO_2 emission totals in eastern Canada, eastern USA and total North America.

In contrast to the situation with sulfur emissions, neither Canada nor USA has made significant progress in reducing NO_x emission, the other major acidifying pollutant. Although technological innovations such as catalytic converters have greatly reduced NO_x emissions from individual sources, the gains have been offset by a continuous increase in the number of emission sources, particularly cars and trucks. In 1995, eastern Canadian NO_x emissions stood at 1 MT, while the eastern US sources were responsible for 11 MT. During recent years, these levels have not been changed appreciably in either country.

2.3. *Wet Deposition of Sulfate in Eastern North America*

In theory, significant reduction in SO_2 emissions should, over a long-term period and large areas, produce detectable reductions in the amount of wet sulfate deposition.

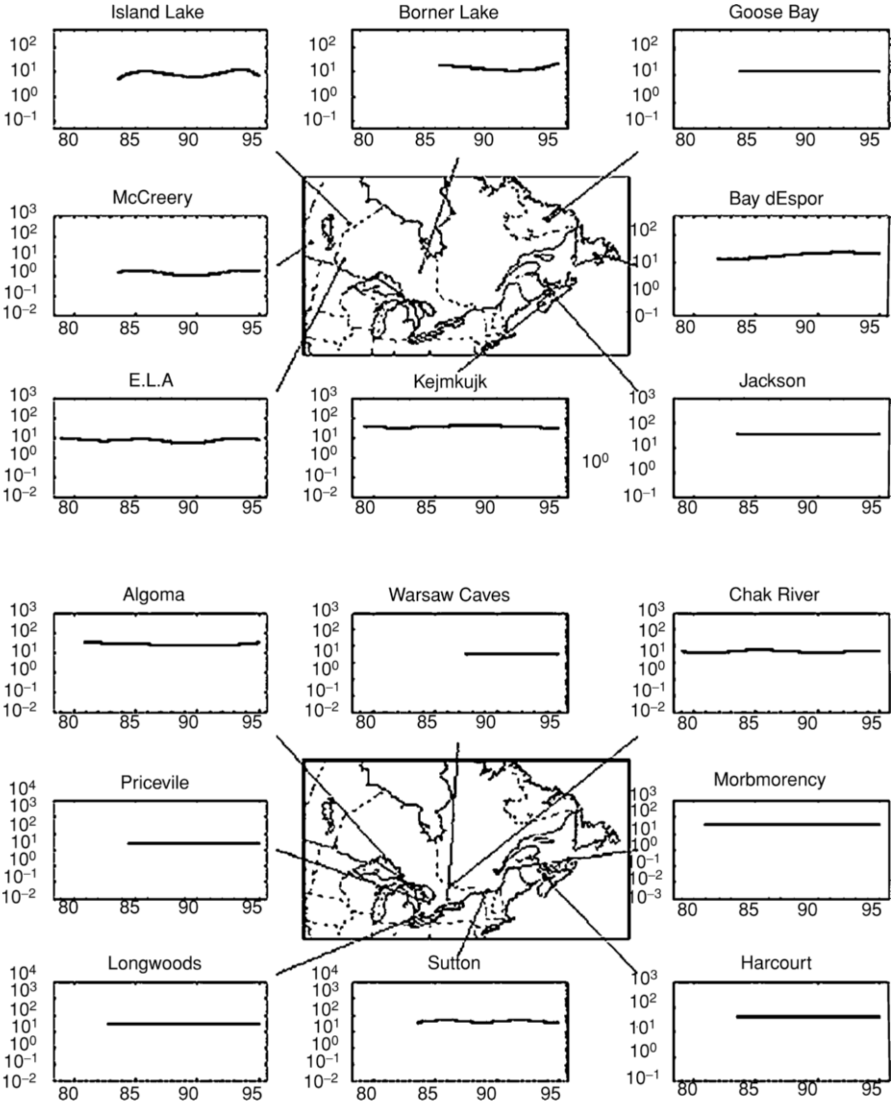


Figure 7. Estimated long-term trends of hydrogen ion (H^+) concentrations per micro liter in precipitation at CAPMoN sites.

Acid rain monitoring data in North America have been gathered by Environment Canada and stored in the National Atmospheric Chemistry (NatChem) Database, details of which can be found at www.airquality.tor.ec.gc.ca/natchem. Analysis of the deposition chemistry data has confirmed that wet sulfate deposition did indeed decline in concert with the decline in SO_2 emissions in both eastern Canada and the

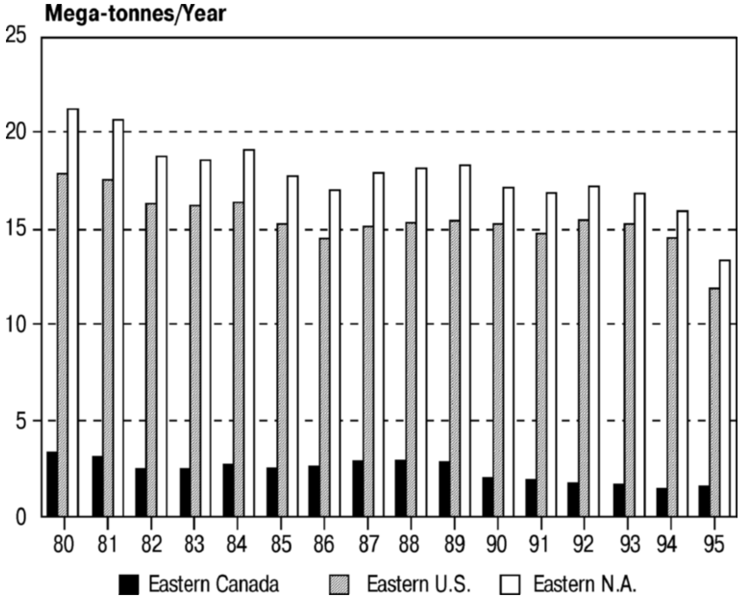


Figure 8. Sulfur dioxide emissions in eastern Canada, eastern USA and total North America (Ro et al., 1997).

eastern USA. Wet deposition declined markedly. In fact, close inspection reveals the total area that received $\geq$20 kg/ha/yr in 1980 had virtually disappeared in 1995, a total area reduction of 87%. However, in accordance with insignificant reduction of NO_x emissions, the wet deposition of nitrate has practically not been changed.

2.4. Ecological Impacts of Acid Deposition in Eastern North America

Surprisingly, and disappointingly, despite cutting SO_2 emissions in half in eastern Canada, rain is still acidic. That is because calcium and magnesium salts have also decreased more or less in tandem with the reduction in sulfur dioxide emissions. As a result, there has been some decrease in acidity, but not as much as expected. (The reasons behind the decrease in concentrations of acid-neutralizing salts are not yet fully understood.). For example, the pH of rain in Ontario's Muskoka-Haliburton area ranges between 3.9 and 4.4–about 40 times more acidic than normal.

Lakes that have been acidified cannot support the same variety of life as healthy lakes. As a lake becomes more acidic, crayfish and clam populations are the first to disappear, then various types of fish. Many types of plankton—minute organisms that form the basis of the lake's food chain—are also affected. As fish stocks dwindle, so do populations of loons and other water birds that feed on them. The lakes, however, do not become totally dead. Some life forms actually benefit from the increased acidity. Lake-bottom plants and mosses, for instance, thrive in acid lakes. So do blackfly larvae.

Not all lakes that are exposed to acid rain become acidified. In areas where there is plenty of limestone rock, lakes are better able to neutralize acid. In areas where rock is mostly granite, the lakes cannot neutralize acid. Unfortunately, much of eastern Canada—where most of the acid rain falls—has a lot of granite rock and therefore a very low capacity for neutralizing acids.

There are many ways the acidification of lakes, rivers and streams harm fish. Mass fish mortalities occur (during the spring snow melt) when highly acidic pollutants—that have built up in the snow over the winter—begin to drain into common waterways. Such happenings have been well documented for salmon and trout in Norway.

More often, fish gradually disappear from these waterways as their environment slowly becomes intolerable. Some kinds of fish such as smallmouth bass, walleye, brook trout and salmon, are more sensitive to acidity than others and tend to disappear first.

Even those species that appear to be surviving may be suffering from acid stress in a number of different ways. One of the first signs of acid stress is the failure of females to spawn. Sometimes, even if the female is successful in spawning, the hatchlings or fry are unable to survive in the highly acidic waters. This explains why some acidic lakes only have older fish in them. A good catch of adult fish in such a lake could mislead an angler into thinking that all is well.

Other effects of acidified lakes on fish include: decreased growth, inability to regulate their own body chemistry, reduced egg deposition, deformities in young fish and increased susceptibility to naturally occurring diseases (Table 2).

It is roughly estimated that there are more than 1,200,000 water bodies in eastern North America that are currently affected by acid deposition. A subset of these lakes has been sampled since early 1980s in order to monitor the changes in lake water chemistry induced by the declining sulfur dioxide emissions and wet sulfate deposition

Table 2. The effects of acidity on the aquatic ecosystem.

Water pH	Effects
6.0	• crustaceans, insects, and some plankton species begin to disappear
5.0	• major changes in the makeup of the plankton community occur • less desirable species of mosses and plankton may begin to invade • the progressive loss of some fish populations is likely, with the more highly valued species being generally the least tolerant of acidity
Less than 5.0	• the water is largely devoid of fish • the bottom is covered with undecayed material • the nearshore areas may be dominated by mosses • terrestrial animals, dependent on aquatic ecosystems, are affected. Waterfowl, for example, depend on aquatic organisms for nourishment and nutrients. As these food sources are reduced or eliminated, the quality of habitat declines and the reproductive success of birds is affected

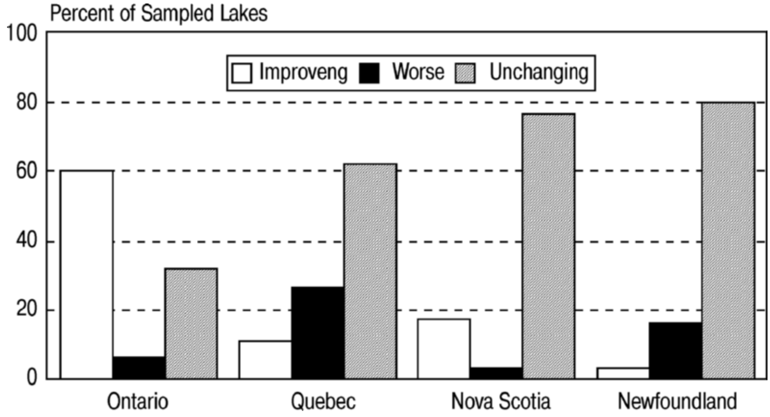


Figure 9. Trends in lake acidity between 1981 and 1994 (Environment Canada, 1997).

loading. Sampling at several hundred of these lakes during 1980–1990s indicated that water-quality improvement has been slow and inconsistent. For instance, of 202 lakes in southeastern Canada that were consistently monitored from 1981 to 1994, 56% showed no improvement in acidity, 11% became more acidic and 33% became less acidic (Figure 9).

Most of the lakes showing improvement were located in the area around Sudbury, Ontario, where smelter emissions declined dramatically, from 2,000,000 tons in 1970 to 265,000 tons by 1994 (Bunce, 1994).

There are several possible explanations for the slow and uneven recovery of these lakes (Ro et al., 1997):

(1) insufficient time for major recovery to become apparent;

(2) lakes continuing to receive sulfate wet deposition well above critical loads, i.e., reductions in deposition have been insufficient;

(3) lakes experiencing declining base concentrations, which, in turn, have reduced their ability to neutralize acids;

(4) acidification due to nitrate deposition in watersheds that are nitrogen saturated.

Forest damage caused by acid deposition has been found in many areas of eastern North America. For example, acid fogs have been found to cause damage in Birch Forest ecosystems in the Bay of Fundy area of New Brunswick and in high elevation areas of eastern Canada, where they prevent the germination of pollen in certain birch species, and reduce the frost hardiness of red spruce trees. Red Oak, Red Pine and Sugar Maple Forest ecosystems in acidic soils in Quebec and Ontario have exhibited damage due to acid deposition. Other areas of Ontario have experienced accelerated nutrient loss and declining acid-neutralizing capacity of soils. Reduced growth rates have been found over the past 30 years in Sugar Maple Forest ecosystems covering large areas of northern Ontario and Quebec.

Long-term measurements at the Hubbard Brook Experimental Forest, NH have shown declines in annual volume-weighted concentrations of sulfate in bulk deposition and streamwater, which are consistent with decreases in emissions of sulfur dioxide in the eastern U.S. There have been no long-term changes in volume-weighted concentrations of ammonium or nitrate in bulk precipitation. Following an early ($\sim$ 10 yr) increase in nitrate, there has been a long-term decline in stream concentrations. In contrast to sulfate, no relationships were evident between emissions of nitrogen oxides and volume-weighted concentrations in bulk precipitation or streamwater. These changes have resulted in limited recovery of streamwater pH. This delay in increases in stream pH is likely due to: (1) depletion of labile pools of soil basic cations, (2) additional (unmeasured) inputs of sulfate and (3) pH buffering by aluminum. Results of long-term stream measurements are compatible to results of model calculation used to evaluate the effects of acidic deposition (Drisscoll et al., 1998).

Biogeochemical mass-balance assessments of calcium status in southeastern USA forests indicate that nutrient losses from tree harvesting and soil leaching often exceed inputs from atmospheric deposition and mineral weathering. Many forest soils of the southeastern USA are particularly sensitive to calcium depletion. These highly weathered soils and the underlying saprolite from which they are derived are largely depleted of weatherable calcium. Furthermore, in many areas, forest soils were badly eroded during periods of cultivation in the late 1800s and early 1900s.

At most sites, calcium uptake into merchantable wood equals or exceeds soil-leaching losses. Long-term studies at several southeastern USA sites have demonstrated declines in exchangeable soil calcium pools over the last several decades, indicating that mineral weathering and atmospheric deposition inputs together are insufficient to replenish losses through vegetation uptake and soil leaching. At the Panola Mountain Research Watershed, located in the Georgia Piedmont, and at most of the intensively studied sites in the southeastern USA, soil calcium reserves have been, or likely will be, reduced to less than twice the requirement for a merchantable forest stand in less than 120 years from the present time. Although atmospheric deposition of sulfuric acid has declined in recent years, acid loading continues at rates substantially above pre-industrial levels. Acidic loading in excess of the ecosystem's capacity to retain sulfate and nitrate, results in leaching loss of base cations. At Panola Mountain, an analysis of sulfate mass balance over the last 12 years suggests that the capacity of the surface soil for sulfate adsorption has diminished. When the capacity of the surface soil to retain sulfate declines, sulfate and associated cation leaching increases. Soil acidification associated with acidic deposition and base cation uptake by trees usually results in increased aluminum and decreased calcium concentrations in soil water and stream water. Declines in atmospheric deposition of calcium over the last two decades have also accelerated calcium depletion because this source of replenishment has decreased.

Assessment of the regional extent of forest ecosystems sensitive to calcium depletion will be possible using a combination of data obtained from watershed studies, monitoring programs, and soil, geologic, and water-quality databases. A comparison between calcium storage and fluxes at intensively studied sites, with these variables estimated for larger geographic areas, strongly suggests the potential for a regional problem in forest nutrition.

The ability of forests to withstand acid rain depends on the capacity of the soil to neutralize the inputting acidity. This is largely determined by local geology, in much the same way that it affects the acidification of lakes. Acidification is mainly a problem in areas where the underlying rocks provide poor buffering capacity. Rocks such as granite offer little buffering protection. Chalk and limestone neutralize added acid, and so soils, lakes and streams in limestone areas are fairly insensitive to acidic precipitation. The following equation depicts this process:

$$2H^+ + CaCO_3 \rightarrow Ca^{2+} + CO_2 + H_2O.$$

The mechanisms underlying this reaction is that H^+ ions react with the HCO_3^- ions which are responsible for the alkalinity of the water, and solid $CaCO_3$ from bottom sediments dissolves to restore equilibrium. As a result, the pH in the aqueous phase is not changed significantly by the addition of the acidic rainwater.

Most of the eastern North America area is underlain by granite geological rocks, whose acid-neutralizing capacity is low and is exhausted rapidly under acidity loading. As a result, areas of forest sensitivity correspond closely to the areas where aquatic ecosystems are also sensitive. In southeastern Canada, these areas are in Central Ontario, southern Quebec and the Atlantic provinces. Estimates have been made that Forest ecosystems in these areas receive about twice the level of acid rain that these ecosystems can tolerate without long-term damage. The damage depends very much on the soil type, geological rocks and type of ecosystems. Documented damage in eastern Canada includes loss of nutrients in forest soils, declining growth rates (NPP), excessive aluminum uptake, cuticle damage, decreased photosynthesis, interference with pollen germination, defoliation, and reduced ability of tress to cope with other stresses such as insects, drought, diseases and increased ultraviolet radiation. These effects are very similar to those shown in other places of the World, like Europe and East Asia.

Prolonged exposure to acid rain causes forest soils to lose valuable nutrients. It also increases the concentration of aluminum in the soil, which interferes with the uptake of nutrients by the trees. Lack of nutrients causes trees to grow more slowly or to stop growing altogether. More visible damage, such as defoliation, may show up later. Trees exposed to acid rain may also have more difficulty withstanding other stresses, such as drought, disease, insect pests and cold weather.

The ability of forests to withstand acidification depends on the ability of the forest soils to neutralize the acids. This is determined by much the same geological conditions that affect the acidification of lakes. Consequently, the threat to forests is largest in those areas where lakes are also seriously threatened—in central Ontario, southern Quebec, and the Atlantic provinces. These areas receive about twice the level of acid rain that forests can tolerate without long-term damage. Forests in upland areas may also experience damage from acid fog that often forms at higher elevations.

Acid rain has caused severe depletion of nutrients in forest soils in parts of Ontario, Quebec and the Atlantic provinces, as well as in the northeastern United States. While this may be reversible, it would take many years—in some areas hundreds of years—for soil nutrients to be replenished to former levels through natural processes such as weathering, even if acid rain were eliminated completely. For now, forests in affected areas—where acid rain exceeds the critical loads—are using the pool of minerals accumulated during pre-industrial times, although some monitoring sites are already deficient and visual damage has appeared. The loss of nutrients in forest soils may threaten the long-term sustainability of forests in areas with sensitive soils.

2.5. The Impact-Oriented Critical Load Approach to SO_2 Emission Reduction Strategy

Critical Load Calculations

In 1985, the federal government of Canada and the seven easternmost provinces signed the Eastern Canadian Acid Rain Program, the purpose of which was to reduce SO_2 emissions in eastern Canada to 50% of the 1980 levels by 1994. Based on the best modeling and experimental studies of the time, it was hoped that these sulfur dioxide emission cutbacks would reduce sulfate wet deposition from the levels as high as 40 kg/ha/yr to less than 20 kg/ha/yr throughout eastern Canada. The specific value of 20 kg/ha/yr was deemed a "target critical load", which was expected to protect moderately sensitive aquatic ecosystems from acidic deposition. Highly sensitive ecosystems were left vulnerable.

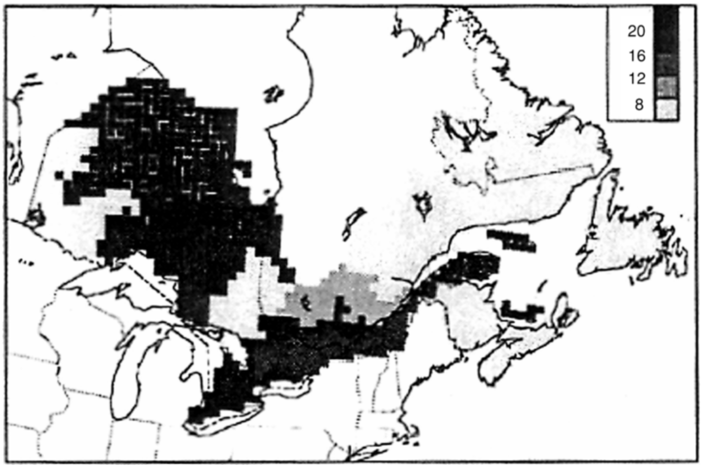


Figure 10. Regional critical loads in eastern Canada (from RMCC, 1990). Different shaded areas show the critical loads of wet sulfate deposition (kg/ha/yr) that can be tolerated by lakes in those areas.

The Eastern Canadian Acid Rain Program was highly successful at reducing SO_2 emissions and sulfate wet deposition in eastern Canada (see Figure 10). Sulfur emissions actually declined more than the desired 50% by 1994, and have continued to decline modestly in the present. These SO_2 emissions in the United States have also reduced dramatically, particularly since the implementation of the Canada–United States Air Quality Accord in 1991. This has been especially important to the aquatic and terrestrial ecosystems in eastern Canada, since US emissions are responsible for a large proportion of the acid deposition received in eastern Canada due to transboundary transport.

Current atmospheric transport and deposition models predict that all of the acid-sensitive areas of eastern Canada will receive less than the target critical load of 20 kg/ha/yr of sulfate wet deposition by 2010, the year that USA emission reductions will be fully enacted. Unfortunately, there is strong evidence that even these levels of sulfate wet deposition will be too high, and large areas of eastern Canada will still be vulnerable to acid rain. To assist policy makers in developing better deposition targets for the future, scientists used the critical load concept. Here, critical load is determined as an estimate of the amount of deposition that a particular region can receive without significant damage to its ecosystems. This definition is similar to that used in Europe (see above). The critical load concept, as applied in Canada, has been a useful tool for identifying ecosystems at risk and for estimating future needs for emission abatement strategy. The concept integrates monitoring information on wet deposition and aquatic chemistry with model predictions on long-range transport of air pollutants, ecosystem response to airborne pollutants, and emission cutback scenarios.

As applied to aquatic ecosystems in eastern Canada, *critical load is defined as the amount of wet sulfate deposition that must not be exceeded in order to protect at least 95% of lakes in a region from acidifying to a pH level of less than 6.0* (Ro et al., 1997).

Recent studies suggest that pH of 6.0 is needed to protect most aquatic organisms (see Table 2).

It is worth noting that, with this definition of critical load:

(a) wet sulfate deposition plays as a surrogate for total (wet and dry) deposition of all acid-forming compounds that contribute to lake acidification;

(b) 5% of lakes in a given region will be left vulnerable to the continued effects of acidity loading.

The critical load concept was applied to eastern Canada for two reasons, mainly:

(1) to identify the areas of Canada that receive sulfate wet deposition in excess of the calculated critical loads, and

(2) to estimate future SO_2 emission reductions necessary to ensure that all areas of eastern Canada will receive wet deposition of sulfate less than the critical loads.

The first step in the application of the concept was to determine the critical load values for the different regions of eastern Canada. This was done using historical measurements of lake acidity in concert with the Integrated Assessment Model (IAM) which links atmospheric transport and deposition models with water chemistry and empirical biological response models. Details of the method are given in Jeffries and Lam (1993).

The critical loads calculated for eastern Canada is shown in Figure 10.

The lightly shaded areas in Figure 10 have the lowest critical loads and are therefore most sensitive to wet sulfate deposition and lake acidification. The dark areas have high critical loads (>20 kg/ha/yr) and are least sensitive. The areas with lowest critical loads occur on the Precambrian Shield region of Ontario and Quebec because of the underlying granitic bedrock and the shallow, poorly buffered soils. The Atlantic coast also has low critical loads because of lower base cation concentrations in the lakes, i.e., lower acid-neutralizing capacity (Jeffries et al., 1986). We can see that large areas of eastern Canada have critical loads considerably less than the old "target critical load" of 20 kg/ha/yr. This demonstrates that, while the "target critical load" was useful at a policy-making tool in the 1980s, it was clearly insufficient to protect many lakes in eastern Canada.

Environmental Risk Estimates

After calculation and mapping of critical loads, the next step is to identify those areas where the critical loads were/are exceeded, i.e., where the wet deposition loading of sulfate exceeds the critical loads. In these areas of exceedance, lakes will continue to have pH values lower than 6.0 until such time that wet sulfate deposition decreases below the critical loads.

The critical load exceedance pattern is shown across eastern Canada for the years 1980 and 1995. The differences in the exceedance patterns of 1980 and 1995 indicate that the area of exceedance, and the amount of exceedance in most areas, declined considerably in 15 years. By way of comparison, the 1995 area of exceedance is 61% lower than that in 1980, a clear illustration that the decline in annual sulfate deposition from 1980 to 1995 resulted in a large reduction to the number of lakes vulnerable to acid rain. In spite of the decline, there still exist in 1995 large areas in eastern Canada where the critical loads are exceeded. In 1995, this area was approximately 510,000 km^2 and encompassed roughly 60,000 lakes.

Year-to-year changes in the area of exceedance are shown in Figure 11.

Three curves are shown, corresponding respectively to the areas where critical load exceedances are >8, 4, and 0 kg/ha/yr. The diagram clearly indicates that the exceedance areas declined markedly from 1980 to 1995, with the areas of very high exceedances (>8 kg/ha/yr) almost disappearing by 1995.

Figure 12 illustrates the year-to-year change in the total amount of wet sulfate deposition (non-sea-salt) that exceeded the critical loads in eastern Canada.

The values in the diagram were calculated as the sum of all the sulfate exceedances across eastern Canada (e.g., exceedance amount equals the sum of all exceedances

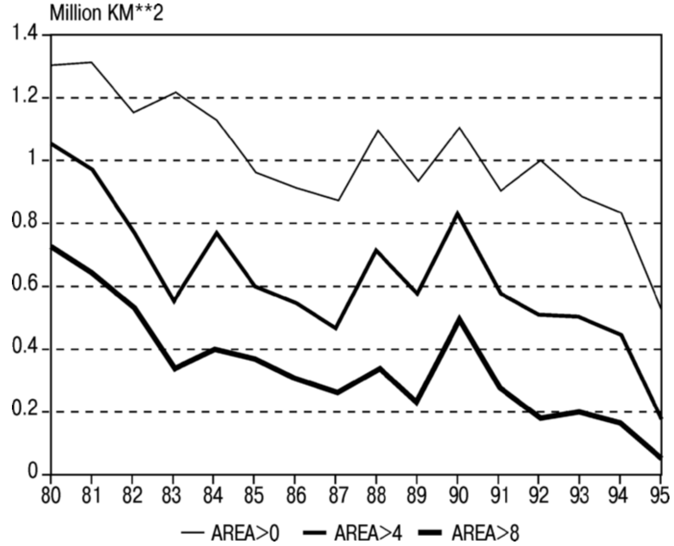


Figure 11. Temporal trends in Exceedance Area associated with critical load exceedance greater than 0, 4 and 8 kg/ha/yr in eastern Canada. The area with >0 exceedance declined by more than 50% by 1995 compared to 1980, and the area with >8 kg/ha/yr exceedances declined by roughly 90%. All three categories reached a minimum exceedance area in 1995 (Ro et al., 1997).

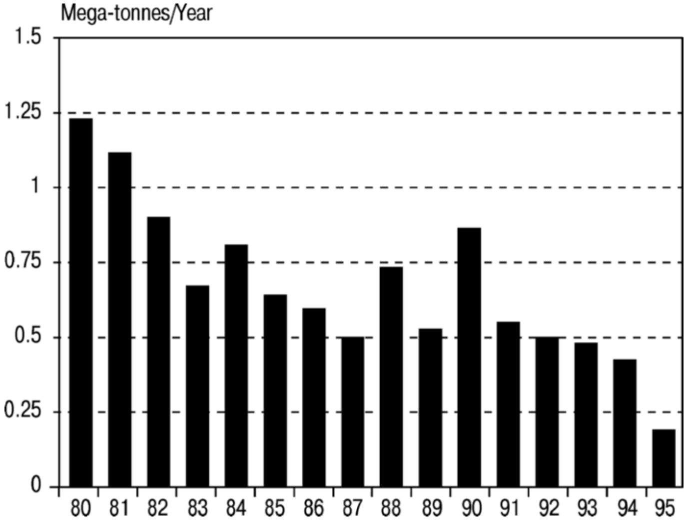


Figure 12. Annual integral Exceedance Amounts of sea-salt corrected wet sulfate in eastern Canada. Note: the markedly higher exceedance amount in 1990 is due to in part to a higher precipitation amount in this year (Ro et al., 1997).

shown in Figures 10.18a and 10.18b for 1980 and 1995, respectively). Figure 12 shows a decline in the exceedance amounts from 1980 to 1995, with the biggest declines occurring in two periods, such as the early 1980s and in 1995. Both of these were periods of rapidly declining SO_2 emissions in the USA. It is clear from Figure 12 that the amount of wet-deposited sulfate in excess of the critical loads in eastern Canada has declined markedly. Nevertheless, greater than 0.18 MT of sulfate in excess of the critical loads was wet-deposited in 1995 and continued to put lakes in eastern Canada at risk of continued acidification.

A similar picture was shown in the USA. Reductions in acid deposition have the potential to improve the condition, for example, of Maryland surface waters, particularly in small streams most susceptible to acidification. To evaluate changes in stream chemistry associated with implementation of the 1990 Clean Air Act Amendments Title IV, Phase I (CAAA), wet deposition patterns determined from a regional wet deposition model were compared to critical load estimates and results from the 1995–1997 Maryland Biological Stream Survey (MBSS). Critical loads were estimated from modeled source/receptor relationships at 73 streams in the state using resident fish species as indicator organisms. The results of this analysis suggest that critical loads continue to be exceeded in some areas of the state despite reductions in sulfate deposition. Above average precipitation amounts in 1996 contributed to sulfate deposition in excess of critical loads in a number of sensitive areas. Fish communities in affected areas exhibited low species richness and abundance; in cases with extremely low pH, fish were absent. Although Phase I results are encouraging, it is unlikely that complete implementation of Title IV will eliminate the acidification problems in some Maryland streams (Miller et al., 1998).

2.6. *Sulfur Dioxide Emission Abatement Scenario in North America Based on Critical Loads and Their Exceedances*

The results indicated that sulfate concentrations in precipitation decreased as much as 25% at some stations in and immediately downwind of the Ohio River Valley, the same area affected most by Phase I of the CAAA, Title IV. Lower sulfate concentrations were also observed as far north and east as Maine. Concurrent reductions in hydrogen ion concentrations were also observed. In contrast, nitrate concentrations were largely unaffected. Based on stoichiometric analyses, approximately 75% of the reduction in hydrogen ion concentrations could be attributed to reductions in sulfate concentrations in precipitation. Changes in wet sulfate, nitrate, and hydrogen ion depositions were very similar to changes in the concentrations of these ions. Significant reductions in annual wet sulfate and hydrogen depositions were observed over the Ohio River Valley and large portions of the Mid-Atlantic region and New England. Based on these results, it appears that Phase I of the CAAA, Title IV has been effective in reducing atmospheric deposition in a large portion of the Eastern USA (Lynch et al., 1998).

Having demonstrated that large areas of critical load exceedance still exist, the final step in the analysis is to predict, using long-range transport models, the amount by which SO_2 emissions should be reduced in both Canada and USA so that no areas in eastern Canada receive deposition in excess of critical loads. This was done using the Canadian long-range transport model known as the Atmospheric Deposition and Oxidants Model (ADOM). Details of the model and the modeling exercise are described in Moran (1997) and are too lengthy to describe in this text. Simply stated, several different emission control scenarios were run through the model, and the predicted sulfate wet deposition results were compared to the critical loads. Two important conclusions were derived from the analysis (Moran, 1997 and Venkatesh et al., 2000):

(1) Hundreds of thousands of square kilometers in eastern Canada, encompassing tens of thousands of lakes, will continue to receive wet sulfate deposition above the critical loads for aquatic ecosystems, even after the existing Canadian and USA SO_2 emission control programs are fully implemented in the year 2010;

(2) Further SO_2 emission reductions, estimated to be of the order of 75% beyond current reduction commitments, are required in both Canada and the United States to protect lakes in eastern Canada from sulfate deposition in excess of the critical loads.

The estimate of 75% further emission reductions contains uncertainties inherent to the entire critical loads/atmospheric modeling exercise. Nevertheless, it clear indicates that large reductions in emissions must be initiated in the future if the remaining acid-sensitive aquatic ecosystems in eastern Canada are to be saved from the effects of acid rain. Recognizing this, the federal and provincial governments of Canada have signed a cooperative agreement on acid rain known as the Canada–Wide Acid Rain Strategy for post-2000. The long-term goal of this agreement is to develop new targets for future sulfur dioxide reductions and to conduct future research into the contribution of nitrogen to the acidity loading.

Finally, this will reduce the environmental risk to ecosystem and human health.

3. ASSESSMENT OF ENVIRONMENTAL RISK TO ACID DEPOSITION IN ASIA

3.1. Characterization of Environmental Conditions in Asia

There is agreement both nationally and internationally that long-range transboundary air pollution may span continents: pollutants are transferred from Europe to North America and Asia as well as in the opposite directions (Sofiev, 1998). Consequently, the calculation and mapping of critical loads as indicators of ecosystem sensitivity to acid deposition in regions outside of Europe and North America are of great scientific and political interest. Some researches have been made to calculate the acidification loading for Asia (Dianwu et al., 1994; Shindo et al., 1995, 1998; World Bank, 1994; Kuylenstierna et al., 1995; Kozlov et al., 1997; Bashkin and Kozlov, 1999, Bashkin and Park, 1998).

It has been argued (Bashkin et al., 1996) that the best approach to the calculation and mapping of critical loads on ecosystems in Asia is to use various combinations of expert approaches and geoinformation systems, including different modern methods of expert modeling and environmental risk assessment. These systems can operate using databases and knowledge bases relative to the areas with great spatial data uncertainty. As a rule, the given systems include an analysis of the cycles of various elements in the key plots, a choice of algorithms describing these cycles, and corresponding interpretation of the data. This approach requires numerous cartographic data, such as vegetation, soil, geochemical and biogeochemical maps, information on pollution and buffering capacity of soil, water and atmosphere. This approach is the most appropriate for Russia as well as for other Asian countries such as China, India, and Thailand where, at present, adequate information on the great spatial variability of natural and anthropogenic factors is either limited or absent.

The applicability of these approaches for the assessment of acidification loading on the terrestrial ecosystems in Asia is made here using the examples of Asian domain (Asian part of Russia, China, Japan, Taiwan, Korea and Thailand). In spite of the great differences in climate, soil and vegetation conditions, these regions can serve as a good test of the proposed methodology.

The interest in acidic deposition has resulted in the development of intensive biogeochemical investigations of a large number of ecosystems in North America, Europe, Asia and South America (Moldan and Cherny 1994; Bashkin and Park 1998). The biogeochemical cycling concept is designed to summarize the cycling process within various components of ecosystems such as soil, surface and ground water, bottom sediments, biota and atmosphere. Ecosystem and soil maps can serve as a basis for biogeochemical mapping (see Chapter 2).

3.2. Monitoring of Acid Rain in Asia

As regards the pollutants monitoring, from the measurements available so far it could be concluded that acid rain is coming to be a major problem in Asia. In many industrially developed and new developed countries such as Japan, China, Taiwan, South Korea, Thailand *etc.*, values of pH <5 are encountered at many sites, and they represent more than 50% of monitored rain events on a regional scale. In some developing countries of South-East Asia (Myanmar, Laos, Cambodia) most rainwater pH measurements tend to be around 5.6, the pH of "natural" rainwater, and the acid rain precipitation is mainly due to localized industrial pollution. There is some evidence that pH values below 5 at unpolluted sites may be due to the contribution of weak organic acids, such as formic and acetic acids (Radojevic, 1998).

The experimental results obtained by Chinese scientists obviously show that the areas suffering from acid rain in China have extended northwards from the south of the Yangtze River in 1986 to the whole East China at present. The statistical results from the Acid Rain Survey in 82 cities from 1991 to 1995 indicate that the annual average pH value of the precipitation was lower than pH 5.6 in nearly half of these cities or in 87% of the southern cities, which are located in the south to the Qingling

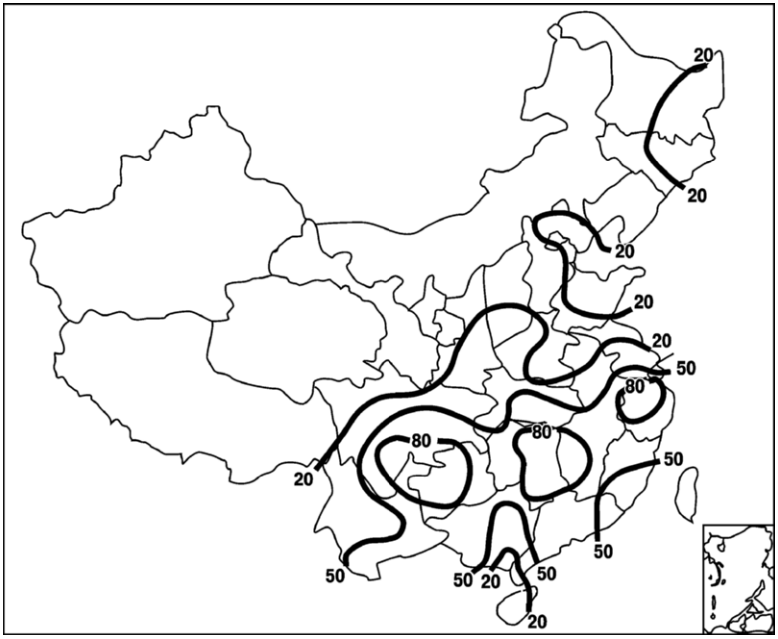


Figure 13. Contours of acid rain frequency corresponding to pH 5.6 in China (Hao et al., 1998).

Mountain and Huaihe River, and the lowest even reached pH 3.52 in Changsha, Hunan province (Figure 13).

In addition, the frequency of acid rain was very high (higher than 60%) in one fourth of these cities (Hao et al., 1998). The chemical composition of acid rain in China is generally different from that in Europe, with a lower pH value and higher sulfate, calcium and ammonium concentrations. Another difference is that the concentration of calcium relative to sulfate is very high in China, while the nitrate concentration relative to other components is low. In some cases, the fluoride concentration in precipitation appears also high in China, owing possibly to the combustion of coal with high fluoride content. Besides, the alkaline fly ash and soil dust build up the capacity for acid-neutralizing during washout.

The influence of acid rain on the environment is related to the various properties of different ecosystems and varies depending upon physical-chemical characteristics of soil, vegetation type, stemflow and throughfall interactions of rainwater with canopy of different botanic species. For instance, it is well known in Japan that soils close to the stems of Japanese cedar (Cryptomeria japonica) trees are strongly acidic. This is partly due to the leaching of hydrogen ions from the stems. Soil solutions close to a stem (10 cm) are markedly acidic (pH $\sim$ 4.5) and contain 47 μM of total Al in average. Furthermore, more than 55% of the Al are in the form of Al^{3+}. Figure 14 shows that the BC–Al ratios in winter decline to as low as 2, a value close to 1, which is known to be used as critical value for starting soil acidification and appearance of harmful free aluminum ions (Kato et al., 1998).

Approximately 70% of the precipitation monitored in Taiwan is considered acid rain (exhibiting a pH lower than 5.6). Acid deposition shows large spatial variation with northern Taiwan exhibiting the highest acid deposition and southeastern Taiwan showing the lowest deposition. The spatial pattern of acid deposition is correlated with the degree of urbanization and industrialization. Continuous exposure to high levels of acid deposition could lead the forest to nutrient imbalance and thereby undermine forest health (Lin, 1998). It is also known that the geochemical and biogeochemical mobility and migration of the majority of heavy metals are increasing with the decreasing soil and water pH values that are occurring due to acid deposition. Thus, it has been shown that the biological accumulation of Cd, Cu, and Zn, expect for Pb, in the leaves of vegetables was affected by the acid rain, and the rating of effectiveness on the phytoavailability of heavy metals caused by acid deposition followed the trend: Cd $>$ Zn $>$ Cu $\gg$ Pb (Chen et al., 1998). The harmful single and synergetic effects of acidity, SO_2, NO_x and O_3 are experimentally shown for various Asian species (Kohno et al., 1998).

3.3. Critical Load Values of Acid-Forming Compounds on Ecosystems of North-East Asia

The experimental data obtained in various countries of East Asia allow us to consider the applicability of methodology of critical loads related to an assessment of ecosystem sensitivity to acid rains. The critical load (CL) and Environmental Risk Assessment (ERA) approaches were used for the evaluation of ecosystem sustainability to acid deposition in the East Asia. The calculations of critical loads for the assessment of the sensitivity of the ecosystem to acidic deposition have been made using biogeochemical approaches including the intensity of biogeochemical cycling and periods of active temperature duration. On the basis of these coefficients the soil-biogeochemical regionalization is carried out for the whole area of Asia and the values of critical loads for acid-forming compounds are calculated using modified steady-state mass-balance (SSMB) equations.

In the ecosystems of the Asian part of Russia the values of critical loads for N, CL(N), and S, CL(S), compounds are shown to be less than in Europe due to many peculiarities of climate regime (long winter with accumulation of pollutants in snow cover) and depressed biogeochemical cycling of elements (see section 1). The minimum values of both CL(N) and CL(S) are <50 eq/ha/yr and the maximum ones are >300 eq/ha/yr (Figures 15 and 16).

At current rate of atmospheric deposition 88.0% and 72.7% of ecosystems in North Asia have no or small (<50 eq/ha/yr) exceedances of CL(N) and CL(S), respectively (Table 3).

However, atmospheric deposition in excess of calculated critical loads of N and S are exceeded for 10% and 20%, respectively, of the studied ecosystems in this region.

A comparison of these critical load values with those calculated for corresponding ecosystems in Europe (see above Section 1) reveals lower values in the Asian areas. This can be explained by the more prolonged winter period causing an accumulation

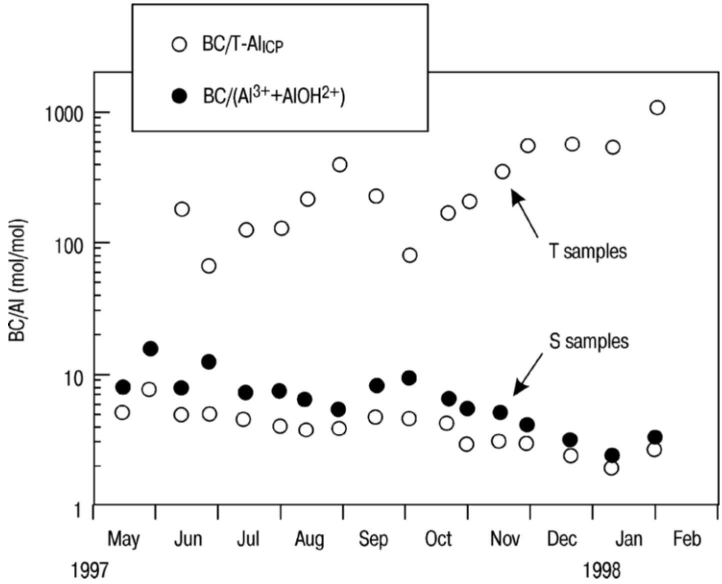


Figure 14. *Seasonal variation of the molar BC/AL ratios in soils of Japanese Cedar ecosystems (Kato et al., 1998).*

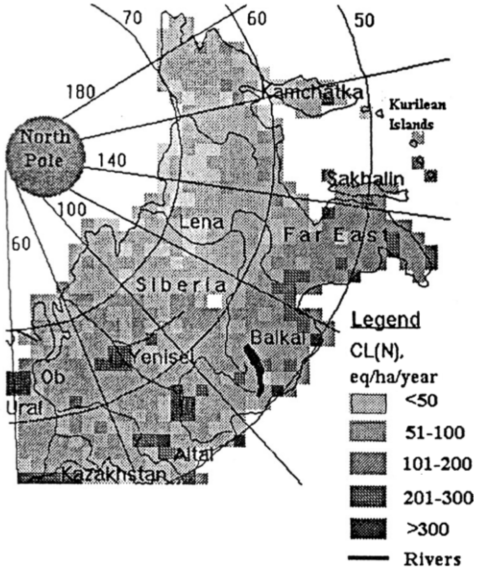


Figure 15. *Critical loads of nitrogen on the ecosystems in the Russian Northern Asia (Bashkin and Kozlov, 1999).*

Table 3. Distribution of critical load values of sulfur, nitrogen and their exceedances for the North Asian ecosystems.

Values range, eg/ha/yr	Percentage of area under different values of critical: For nitrogen	Percentage of area under different values of critical: For sulfur	Percentage of area under different critical load values load exceedances: For nitrogen	Percentage of area under different critical load values load exceedances: For sulfur
<50	8.3	40.5	88.0	72.7
50–100	40.8	32.4	6.9	14.3
101–200	41.3	18.2	3.9	8.3
201–300	8.0	1.5	1.1	2.6
>300	1.6	7.4	0.1	2.1

of pollutants in the snow layer and their influence on biogeochemical cycling of nutrients during the short spring and summer period. The values of active temperature coefficient, C_t are within the limits of 0.15–0.57 for the majority of the North Asian ecosystems, whereas in the European part of Russia, for example, the corresponding values are 0.25–0.87. This points out the shorter but very active periods of biogeochemical turnover in almost all of North Asian ecosystems, accelerating the effects of the acidification loading on the ecosystems.

The uncertainty analysis of acidity critical loads has been carried out and different endpoints have been assessed in terrestrial ecosystems of the Asian part of Russia. The strongest influential factor for the values of CL(N) is the parameter "nitrogen uptake by plant biomass, N_u". For the biggest part of Siberia and Far East territory this endpoint parameter has the first rank and only in the case of Humid Cambisols and Cryic Gleysols ecosystems is its rank the second. Among others, nitrogen immobilization, N_i and nitrogen denitrification, N_{de}, endpoint parameters, which are closely inter–correlated, are the weakest ones. The given parameters do not have any practical influence on the values of CL(N), except Dyctric Cambisol ecosystems. The influence of nitrogen leaching, N_l, endpoint values is decreasing in the following row of ecosystem-forming soils: Regosols > Humid Cambisols = Cryic Gleysols = Gelic Podzols > Andosols > Dystric Cambisols > Eutric Cambisols > Luvic Phaeozems = Chernozems > Kashtanozems. These results reflect, to a significant extent, the geographical change of ecosystems from north to south and correspondingly an alteration of relationship of temperature and moisture constituents in hydrothermic coefficient. So, the main impact to the assessment of the influence of inputting parameters (N_u, N_i, N_{de}, N_l) on both uncertainty and sensitivity of outputting values of CL(N) belongs to N_u. It is connected firstly with a deficit of nitrogen as the main nutrient in all North Asian ecosystems as well as an existing spatial and temporal variability of this parameter that relates to a significance and correctness of experimental and computed values of N_u. In accordance with relatively better knowledge of the hydrological picture and relatively homogenous values of critical concentration of nitrogen in surface waters,

Table 4. Percentage of various endpoints contribution to total environmental risk assessment of ecosystem sensitivity to acid deposition in Northern Asia (Bashkin, 1998).

		Endpoints			
Ecosystem-forming soils	Endpoint assessment method	N content in plant issues, N_u	N content in surface waters, N_l	Denitrified N, N_{de}	N enrichment of soil, N_i
Regosols and Lithosols	SRC	50	41	2	7
	RTU	30	27	21	22
Cryic Gleysols and	SRC	37	56	2	5
Humic Cambisols	RTU	22	37	21	20
Gelic Podzols	SRC	47	45	3	5
	RTU	40	39	10	11
Andosols	SRC	40	39	10	11
	RTU	81	17	1	1
Eutric Cambisols	SRC	41	9	25	25
	RTU	63	10	14	13
Distric Cambisols	SRC	96	2	1	1
	RTU	38	32	16	14
Luvic Phaerozems and Chernozems	SRC	96	1	1	2
	RTN	65	6	12	17
Kashtanozems	SRC	95	1	4	5
	RTU	61	5	19	15

Note: SRC—Standard Regression Coefficient; RTU—Root of the Uncertainty

C_{Ncrit}, included in the calculation of critical nitrogen leaching, $N_{l(crit)}$, values, the input of this endpoint parameter into the uncertainty of CL(N) is expressed in a lesser degree. Furthermore, the runoff processes are practically not significant for ecosystems of Luvic Phaeozems, Chernozems and Kashtanozems due to low P:PE ratio. During the calculations of CL(N) for ecosystems of North East Asia, the values of critical immobilization and denitrification from N depositions as the endpoints both in relative and absolute meanings played a subordinate role that obviously reflects their minor contribution into uncertainty and sensitivity analysis of the computed output values of ecosystem sensitivity to acidic deposition.

Thus, the ERA estimates shown in Table 4 characterize the significance of the endpoints, such as nitrogen content in plant issues and surface waters for many ecosystems

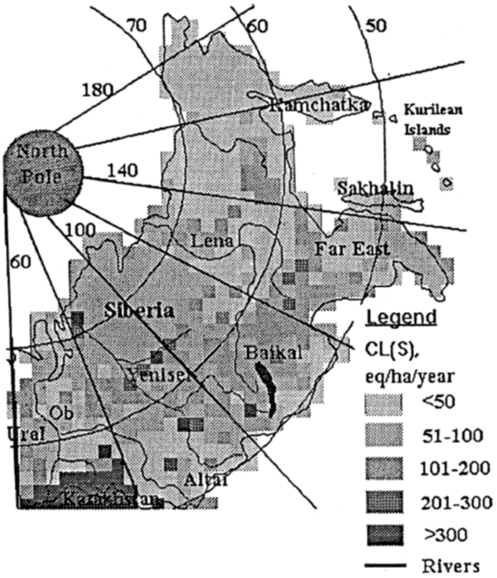


Figure 16. Critical loads of sulfur on the ecosystems in the Russian Northern Asia (Bashkin and Kozlov, 1999).

of North East Asia. These endpoints have to be taken into account during the risk management step of the ERA flowchart for emission abatement strategy development.

3.4. Critical Loads of Sulfur and Acidity on Chinese Ecosystems

Based on the mineralogy controlling weathering and soil development, sensitivity of the ecosystem to acid deposition is assessed with a comprehensive consideration on the effect of temperature, soil texture, land use and precipitation. The results show that the most sensitive area to acid deposition in China is Podzolic soil zone in the Northeast, then followed by Latosol, Dark Brown Forest soil and Black soil zones. The less sensitive area is Ferralsol and Yellow–Brown Earth zone in the Southeast, and the least sensitive areas are mainly referred to as Xerosol zone in the Northwest, Alpine soil zone in the Tibet Plateau, and Dark Loessial soil and Chernozem soil zone in central China. These regional different soil sensitivities to acid deposition can be attributed to the differences in temperature, humidity and soil texture (Hao et al., 1998). It has been shown that the assessment of ecosystem sensitivity to acidic loading depends strongly on the calculation of chemical weathering of soil base cations due to an input of proton with depositions.

The critical loads of acid deposition have been mapped for the Chinese ecosystems, as shown in Figure 17.

It can be seen that most areas sensitive to acid deposition are in Southeast China, and that insensitive areas are in the Northwest. The sensitive areas, including the catchment of the Changjiang (Yangtze) River and the wide areas to the southward, are warm and rain-abundant. The natural vegetation is the Tropic Rain Forest, Seasonal Rain Forest, and Subtropical Evergreen Forest ecosystems. The dominant soils in these areas are acid Ferralsols, with obvious accumulation of iron and aluminum. These soils can tolerate approximately 0.8–1.6 g/m^2/yr of sulfur from acid deposition and belong to the intermediate sensitivity class 3. In Northwest China, the climate is semiarid or arid. The predominant ecosystems are Dry Steppe and agroecosystems, with spots of Deciduous Forest or Mixed Forest ecosystems. The soils represented by Xerosol and Alpine types are carbonate-rich and saline. Consequently, they are resistant to acidification.

The critical load class 1, the most sensitive class of ecosystems, is chiefly referred to Podzol soils of Coniferous Forest ecosystems. This class occupies the small areas in the northeast of China, mostly on the north part of Da-xing-an-ling Mountain, which is covered by coniferous forest, with annual precipitation 400–500 mm and annual mean temperature –4.9–0 °C. Podzol soils were derived from acid granite or quartz rocks and their formation was often influenced by leaching and settling of organic acid complex compounds. Hence, the soils show acid reactions and the base saturation is very low. The soil clay minerals are composed of hydrous mica and small amounts of other unweatherable minerals such as montmorillonite, kaolinite, roseite and chlorite. The low temperature and the coarse texture of soil constitute the importance to the low weathering rate of soil minerals there. Therefore, these areas must be paid great attention, even if acid deposition has not yet appeared.

Class 2 is found in Dark Brown Forest soil and Black soil zones in the Northeast, and Latosol soil zone in the south of the Taiwan province, in the north of Hainan province and near Hekou in the Yunnan province. The Dark Brown soil zone, with annual mean temperature from –1 to –5 °C, is covered by coniferous forest. The coarse soil was derived from granite parent rocks and the chief clay mineral is hydrous mica. As in the Dark Brown soil zone, the temperature in Black soil areas is very low. The Black soil contains clay minerals such as hydrous mica, fulonite, gibbsite and kaolinite. It is obvious that the climate conditions and the mineral composition favor the chemical weathering of soil minerals. Contrarily, Latosol soil zone is under high temperature rain abundant conditions where the annual mean precipitation is 1,900 mm and the annual mean temperature is 12 °C. The texture of Latosol is fine and the fraction of clay in the soil is high, which is advantageous to weathering. However, the clay minerals in this soil are dominated by kaolinite and gibbsite. Anorthite has completely decomposed and K-feldspar is rare. The weathering rate is still low as a result of the lack of weatherable minerals.

Soils of class 3 include Lateritic Red Earth in the areas southward from the Nanling Mountain, Red Earth and Yellow Earth between the Nanling Mountain and the Changjiang (Yangtzee) River, Yellow–Brown Earth in the lower reaches of the Changjiang(Yangtzee) River, Subalpine Meadow soil and Alpine Meadow soil on the Plateau of Tibet.

Class 4 is found in Paddy soil zones sporadically distributed throughout China and in the Purplish soil zone in the Sichuan River Basin.

Class 5 (the least sensitive) soil include Kashtanozem, Brown soil and Sierozem soil zones in the Plateau of Inner Mongolia and the Loess Plateau, Desert soil zones in He-xi-zou-lang and the Talimu River Basin, Subalpine Steppe soil, Alpine Steppe soil and Alpine Desert soil in the Plateau of Tibet. These kinds of soils, belonging to the soil class of Xerosol or Alpine soil, consist of easy weathering minerals such as carbonate. They show alkaline reactions, with weak leaching and sparse vegetation. Those kinds of soils are insensitive to acid deposition.

In summary, the sensitivity of an area to acid deposition and the critical load values are dependent on soil and vegetation types and meteorological conditions. In China, acid deposition often occurs in the Allite areas in the southeast of China, where soils are of intermediate sensitivity except Latosol. The annual mean temperature in these tropic or subtropic areas is 16–25 °C, the accumulated temperature of $\geq$10 °C is 5,000–9,000 °C, and precipitation more than 1500 mm. The characteristics of high temperature, abundant rain, and wet warm conditions in same season, promote reactions of soil minerals and cause the rapid weathering of soil minerals and the rapid circulation of biological materials. As a result, the weathering rates are sufficient enough for high values of corresponding critical loads. On the other hand, the areas of Podzol soil, Dark Brown Forest soil and Black soil are in frigid temperate conditions. The accumulated temperature of $\geq$10 °C is about 2,000, the annual mean temperature is lower than 5 °C, and the precipitation is low. These soils contain large sand and small clay fractions. Thus, the chemical weathering rates are low and critical loads are also low.

It can be concluded that high temperature and high humidity in the same season and high concentrations of clay and loam, are important reasons why soils and water bodies have not been found acidified in heavy acid rain areas such as the Chongqing, Guiyang and provinces of Guangdong and Guangxi. However, it should be noted that the weatherable minerals in soils in south China are scarce, and these soils are potentially at risk of acidification. Acid deposition must be strongly controlled in the Northeast area of China to protect terrestrial and aquatic ecosystems from acidification and decrease of forest production like those in Central and North Europe and North America (see Figure 17).

Comparison of the calculated critical loads with the sulfur deposition in China (Hao et al., 1998) led to the critical load exceedance map of sulfur deposition (Figure 18).

As we can see from this map, sulfur deposition exceeds critical load in a wide land area that amounts to 25% of total Chinese ecosystems, which mainly refers to the southeast of China. Among these areas, the exceedances are especially serious in the lower reaches of Changjiang (Yangtze) River, in the Sichuan River Basin, and in the Delta of Zhujiang River.

3.5. Critical Loads of Sulfur in South Korea

Air pollution is still of crucial importance in South Korea. Emission of sulfur dioxide, nitrogen oxides and ammonia that have been rising in recent decades are responsible for air pollution in many places of the country. The amount of sulfur dioxide emitted

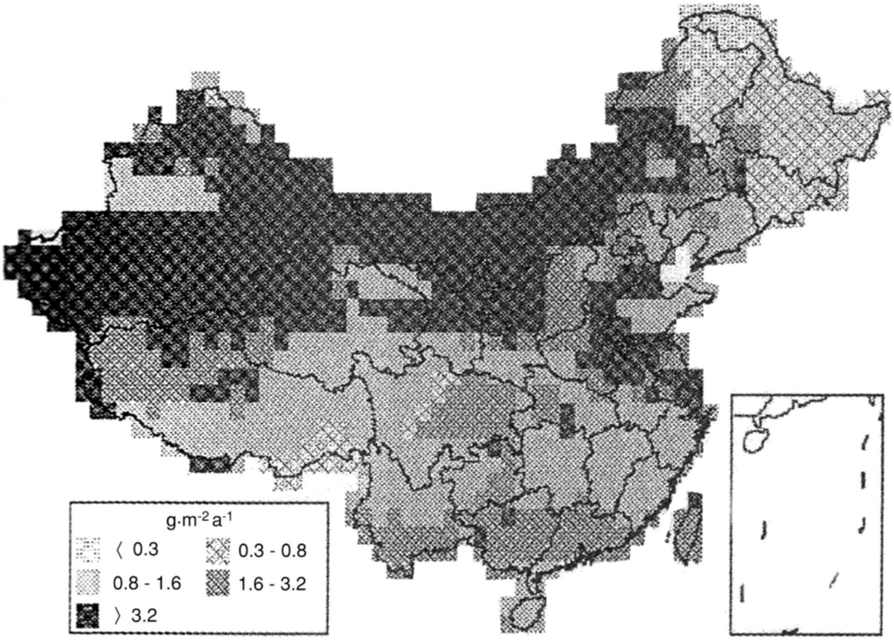


Figure 17. Critical loads of sulfur at terrestrial ecosystems of China (Hao et al., 1998).

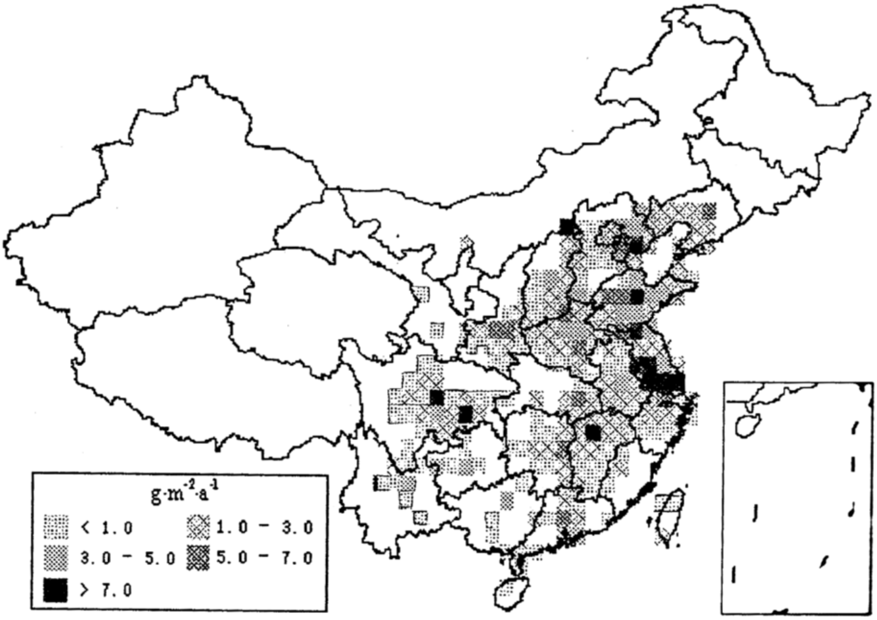


Figure 18. Sulfur critical load exceedance map of China (Hao et al., 1998).

in the area of South Korea was 1,494,000 tons in 1995 and was gradually decreasing to 1,490,000 tons in 1997.

However, it is well known that various pollutants including sulfur compounds can be transported by air from country to country in the whole Asian domain and especially in North East Asia. Thus, model calculations have shown that in 1991–1994 about 35% of oxidized sulfur species deposited in South Korea was transported from other locations, mainly from China (Sofiev, 1999). Accordingly, in spite of a national reduction in SO_2 emission, the sulfur depositions are still very significant.

Preliminary research has shown a high sensitivity of most South Korean ecosystems to input of acid-forming sulfur compounds (World Bank, 1994). This is generally related to acid geological rocks (predominantly, gneisses and granites acting as a soil parent material), acid soils with predominant light texture and low buffering capacity and sensitive Coniferous Forest (mainly pine species) ecosystems.

It has been argued that the best approach to the calculation and mapping of critical loads on ecosystems of East Asia is to use various combinations of expert approaches and geoinformation systems (EM GIS), including different modern techniques of expert modeling. However, this approach is difficult in practice due to a scarcity of data and insufficient understanding of basic controls over major pathways in the biogeochemical structure of many Asian ecosystems and their alteration under the influence of different air pollutants. Under the given conditions the EM GIS can operate using databases and knowledge basis relative to the areas with different spatial data uncertainty. As a rule the given systems include an analysis of the cycles of various elements in the key plots, a choice of algorithms describing these cycles, and corresponding interpretation of the results. This approach requires the cartographic data, such as vegetation, soil and geological maps, information on buffering capacities of soils, precipitation and runoff patterns.

Indeed this approach is shown to be the most appropriate for the Asian part of Russia, China, Thailand, Taiwan, where, at present, adequate information on the great spatial variability of natural and anthropogenic factors is either limited or absent (Bashkin and Park, 1998).

During the last decades significant efforts have been applied for monitoring of main environmental compartments in South Korea. The soil, geological, and vegetation maps were created in different scales, from 1:25,000 to 1,000,000. The monitoring networks of precipitation and their chemical composition were enlarged to cover the whole area of the country. However, till now there are significant gaps in precise understanding of biogeochemical structure of different terrestrial and aquatic ecosystems that governs the sustainability of these ecosystems to acidity loading.

The Comprehensive Acid Deposition Model (CADM) has been created for calculation of dry and wet deposition of sulfur species over South Korea (Park et al., 1997, 1999a). This model presents quantitative assessment of the acidity loading and alterations in deposition rates.

South Korea is in the southern part of mountainous Korean peninsula between 126°E–130°E and 33°N–38°N. Geographically this is the northern temperate zone of the Eastern Hemisphere. The overall area of Republic of Korea (ROK) comprises 99,766 km^2.

In accordance with international approaches the following information has been collected for calculation of sulfur critical loads for all Korean ecosystems:

- general information: soil map, scale 1:1,000,000; land use map, scale 1×1km; geological map, scale 1:1,000,000;
- soil chemical and physical parameters: soil texture; soil layer height; moisture content; soil bulk density; Mg + Ca + K content; log K gibbsite; pH; soil temperature; soil cation exchange capacity;
- vegetation type parameters: annual net productivity growth; net uptake of nutrients (N, Ca, Mg, K, Na, S);
- geochemical analysis: Ca, Mg, K, Na, Al, trace elements; base cation chemical weathering from soils and underlying geological parent material.

The calculation of critical loads of maximum sulfur was carried out on a scale of 11 × 14 km cells. There are 665 cells in the area of South Korea.

The calculations were carried out for the 1994–1997 period that allows us to account for the temporal variations of temperature and precipitation as well as the dynamic pattern of sulfur and base cation depositions.

Using the above-mentioned constituents, the critical loads of sulfur were calculated for the natural terrestrial ecosystems over Korea. Geographical distribution of CLmaxS values is shown in Figure 19.

We can see that about 71% of Korean ecosystems have the rank of 1,000–2,000 eq/ha/yr. Very low values of critical loads (<500 eq/ha/yr) are characteristic for insignificant parts of ecosystems (1.0%), low values (500–1,000 eq/ha/yr) are for 15.5% of ecosystems and on the contrary high values (>2,000 eq/ha/yr) are shown for 12.1% of considered ecosystem types.

These values are significantly different from those that have been earlier calculated by RAIN–ASIA model (World Bank, 1994). These differences might be related to the much more detailed and comprehensive national data sets on geological, soil, climate (precipitation, temperature, evapotranspiration, runoff, etc.) and vegetation mapping, physico-chemical properties of soils and geological rocks. This allows the authors to calculate more precise values of all constituents used for maximum sulfur critical load calculation and mapping.

Accordingly, these CLmaxS values are generally higher than those from RAIN–ASIA model. The latter were in the range of 200–2,000 eq/ha/yr, mainly 200–500 eq/ha/yr, whereas ours are mainly in the limits of 1,000–2,000 eq/ha/yr. This is related to the peculiarities of precipitation and topography patterns in South Korea. These in turn lead to high values of surface runoff of annual mean of 6,200 m^3/ha/yr, and correspondingly to high values of acid-neutralizing capacity leaching. The intensive leaching of sulfur from the soil profiles makes the local ecosystems more sustainable to high values of sulfur deposition.

During the 1994–1997 period the mean sulfur dry and wet deposition totally amounted to about 47 kg/ha/yr or about 3,000 eq/ha/yr (Park et al., 1998, 1999b, 2001). These values were maximum in the south-eastern part of the country, where

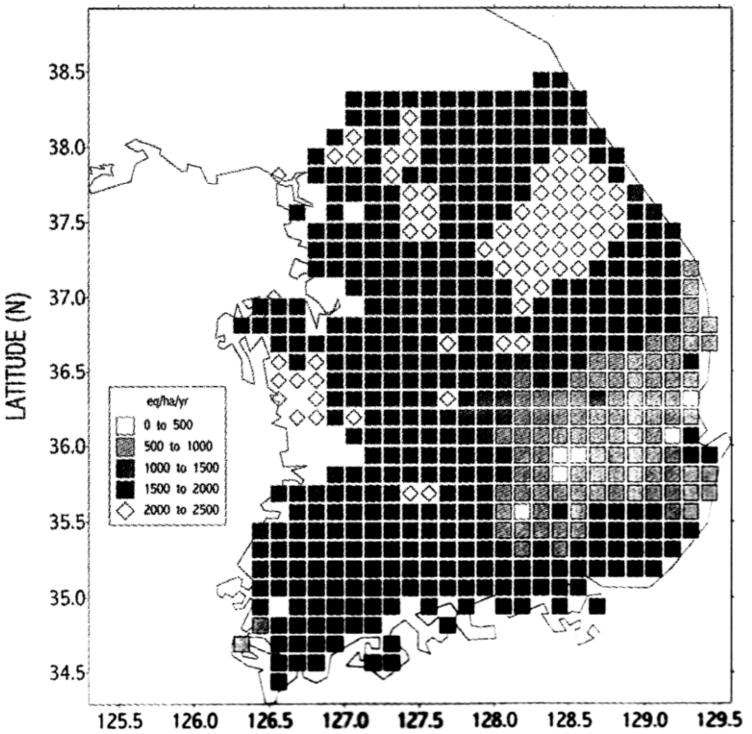


Figure 19. Critical loads of sulfur at terrestrial ecosystems of South Korea (Park and Bashkin, 2001).

the Pusan-Ulsan industrial agglomeration takes place and minimum in the north-eastern part.

Accordingly, a significant part of Korean ecosystems was subjected *n* intensive input of *S* acid-forming compounds. The values of exceedances of sulfur deposition over sulfur critical loads (ExS) are shown in Figure 20.

During 1994–1997 the S_{dep} values were higher than CLmaxS values at about one third of terrestrial Korean ecosystems (38%). Among them, the ExS values were in the range 176–500 eq/ha/yr for 16.1% of total number of ecosystems, in the range of 500–1,000 eq/ha/yr were for 7.9%, in the range of 1,000–2,000 eq/ha/yr were 10.7% and the values even higher than 2,000 eq/ha/yr were found for 3.5% of Korean ecosystems.

The other part of Korean territory (61.8%), where the sulfur depositions were relatively less but critical load values are relatively higher (see Figure 18), was not subjected to excessive input of sulfur-induced acidity. This area can be considered as sustainable to sulfur input.

As we have mentioned above, during the 1990s up to 30–35% of sulfur deposition was due to emission of SO_2 by transboundary sources, occurred mainly in China.

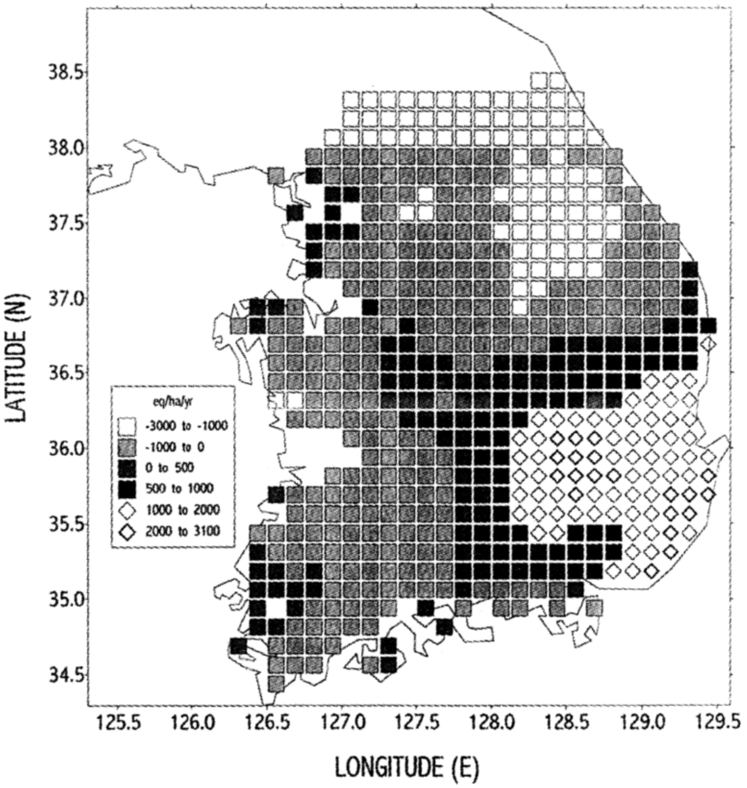


Figure 20. Exceedances of critical loads of sulfur over South Korea (Park and Bashkin, 2001).

Thus, the emission abatement strategy in South Korea has to be developed taking into account both local and transboundary emission reduction in the whole East Asian domain. The values of CL and their mapping can present a good possibility for the creation of ecological optimization models. At present, these CL values and corresponding mappings have been carried out by national research teams in almost all the East Asian countries, such as China, Japan, South Korea, Asian part of Russia and Taiwan (Bashkin and Park, 1998). Accordingly, this national-based mapping can be considered as a scientific basis for decreasing local and regional air pollution in the East Asian domain.

3.6. Acid Deposition Influence on the Biogeochemical Migration of Heavy Metals in Food Webs

An interesting study of acid rain effects on the biogeochemical accumulation of heavy metals (Cd, Cu, Pb, and Zn) in crops has been presented by Chen et al., 1998. The authors have compared the ratios of relative concentration of four heavy metals in the brown rice and leaves of vegetables sampled from acid rain affected areas and

Table 5. The ratios of relative concentration of heavy metals in brown rice and the leaves of vegetable species growing in Lung-tang area (affected by acidic rains) and Lung–luan–tang area (non-affected by acidic rains) from 1996 to 1997 in Taiwan (Chen et al., 1998).

Rice and vegetable species	acid rain/non-acid rain affected area (sampling number)	Ratio in acid rain/non-acid rain area Cd	Cu	Pb	Zn
	Rice				
Rice, (*Oryza sativa* Linn.)	24/15	1.25	1.05	1.09	1.03
	Vegetables				
Sweet potato, *(Ipomoea bataus)*	14/9	1.00	1.45	1.07	1.11
Welsh onion, *(Allium fistulosum*)	10/12	0.89	1.48	3.08	2.03
Pickled cabbage, *(Brassica chineniss*)	3/10	5.03	1.23	—[#]	1.33
Chinese chives, *(Allium tuberosum)*	7/5	4.97	0.70	0.08	1.56
Mustard, *(Brassica juncea*)	2/4	—	1.59	—	2.19
Lettuce, *(Lactuce sativa*)	6/8	3.73	1.87	1.00	1.97
Chickweed, (*Alsine media*)	3/1	—	2.40	—	0.36
Garlic, *(Allium sativum*)	6/7	0.85	2.44	—	4.64
Kohlrabi, *(Brassica campestris*)	1/1	2.00	2.00	—	5.50
Cabbage, *(Brassica oleracea*)	2/1	—	1.99	—	3.06
Tassel flower, (*Amaranthus caudatus*)	6/2	0.97	2.23	—	1.47
Celery, *(Apium graveolens*)	2/1	—	—	—	1.55
Spinach, (*Spinacia oleracea*)	2/1	—	0.75	0.80	0.42
Coriander, (*Coriandrum stivum*)	1/4	8.02	5.01	—	1.80
Basil, (*Ocimum basilicum*)	1/3	—	8.05	—	0.36
Radish, (*Raphanus sativus*)	4/2	—	2.76	—	1.08
Pepper, (*Capsicum frutescens*)	3/4	1.97	2.04	3.92	0.88
Kidney bean, (*Phaseolus vulgaris*)	3/10	2.07	1.78	1.09	1.44
Water convolvulus, (*Ipomoea aquatica*)	6/3	0.28	1.97	3.50	0.66

[#] The ratios of relative concentration can not be calculated because the heavy metal contents of rice or vegetables growing in an acidic rain area or in a non-acidic rain area is lower than the method detection limit (MDL) of heavy metals.

non-affected areas. The data indicated that the ratios of relative concentration of Cd, Cu, Zn in brown rice and 19 vegetable species growing in an acid rain area (Lung–tang) and growing in an acid rain non-affected area (Lung–luan–tang) sampled from 1996 to 1997 are almost higher than 1, or higher than 3, except for Pb (Table 5). These results suggested that biogeochemical accumulation of heavy metals in brown rice seems not affected by long-term acid rains but on the contrary for vegetables species in northern Taiwan. Therefore, these accumulations are dangerous for humans eating the vegetables produced in acid rain affected area.

Table 5 also reveals that the mean concentration of Pb in brown rice and leaves of 19 vegetable species from acid rain affected areas and non-affected areas are almost the same. On the other hand, the ratio is close to 1. This result indicated that acid rain does not influence the biological accumulation of Pb in brown rice and leaves of vegetables species sampled in Taiwan. Some studies have indicated that concentration of Pb in the crops was only affected when the concentration of Pb in the soils is higher than 500 mg/kg (Kabata–Pendias and Pendias, 1992). Sloan et al. (1997) also indicated that the relative bioavailability of biosolids-applied heavy metals in agricultural soils was Cd $\gg$ Zn $>$Ni $>$Cu $\gg$ Cr $>$Pb, for the soils 15 years after biosolids application. It is quite consistent with the results achieved by research of Chen et al. (1998). Thus, the phyto-availability of heavy metals caused by acid deposition followed the trend: Cd $>$Zn $>$Cu $\gg$ Pb.

Finally, this determines the exposure pathways and environmental risk values to human beings.

CHAPTER 18

TRANS-BOUNDARY HM AIR POLLUTION

Pollution of the environment by heavy metals is the subject of concern of a number of national and international bodies. In 1998 a number of Parties to the Convention on Long-Range Trans-boundary Air Pollution (hereinafter the Convention) signed the Protocol on Heavy Metals (Protocol). The aim of the Protocol was to control atmospheric emissions of toxic metals (lead, cadmium and mercury). In accordance with the Protocol the Co-operative Program for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe (EMEP) provides assessments of pollution levels of heavy metals in the European region. Measurements of heavy metal concentrations in the air and precipitation are carried out at the EMEP monitoring network. Along with that the Meteorological Synthesizing Centre-East (MSC-E) performs model assessments of depositions and air concentrations of heavy metals throughout the European region as well as trans-boundary fluxes between the European countries (http://www.msceast.org/reps). In 2003 the Protocol on Heavy Metals came into force, and at present the second priority metals (As, Ni, Cr, Zn, Cu) are under pollution assessment. In order to correlate the existing pollution levels with the environment risk to human and ecosystem health, they are compared with scientifically sound critical loads, developed by the Working Group on Effects (WGE). The environmental risk of heavy metals is related to various sources, and the trans-boundary pollution plays a very important role for the European region.

1. MONITORING OF HEAVY METALS IN EUROPE

1.1. Emissions of Heavy Metals in Europe

The resulting maps of the spatial distribution of lead, cadmium and mercury anthropogenic emissions in Europe in 2002 are presented in Figures 1–3 respectively (Ilyin et al., 2004). According to the available data the most significant sources of lead emissions are located in Central Europe (Poland, Germany), Southern Europe (Italy, Croatia, Serbia and Montenegro, Romania, Greece) and Eastern Europe (Russia). In contrast, emissions of cadmium are distributed more or less uniformly over Western, Central and Southern Europe except Poland, where emission levels are significantly higher. Low emissions are in Northern Europe and in some countries of Eastern Europe (Belarus, Ukraine). The most significant emissions of mercury are also located in Western, Central and Southern Europe. The total emission of lead, cadmium and mercury in Europe in 2002 amounts to 8,003 t/yr, 257 t/yr and 180 t/yr respectively.

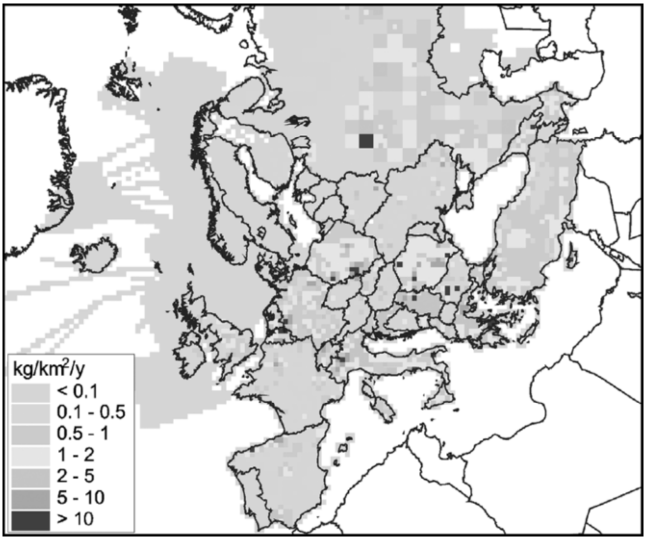


Figure 1. Spatial distribution of lead anthropogenic emission in Europe in 2002.

Apart from anthropogenic emissions, heavy metals enter the atmosphere of Europe due to re-emission of previously deposited substances and from natural sources. These types of sources are taken into account on the basis of expert estimates made in MSC-E (Ryaboshapko and Ilyin, 2001; Travnikov and Ryaboshapko, 2002).

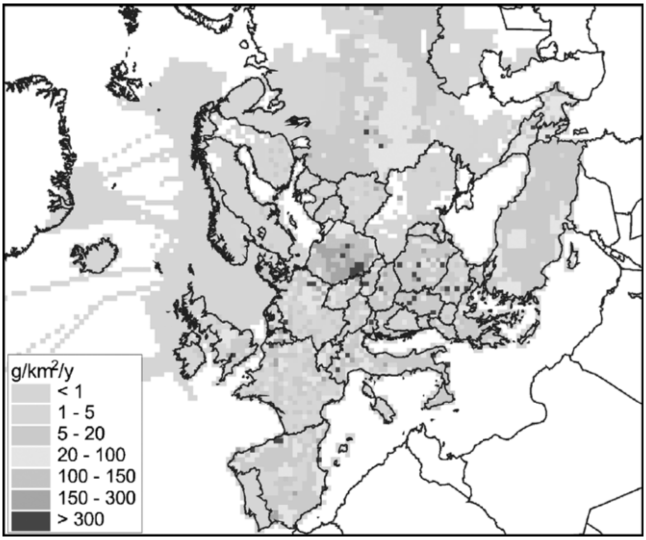


Figure 2. Spatial distribution of cadmium anthropogenic emission in Europe in 2002.

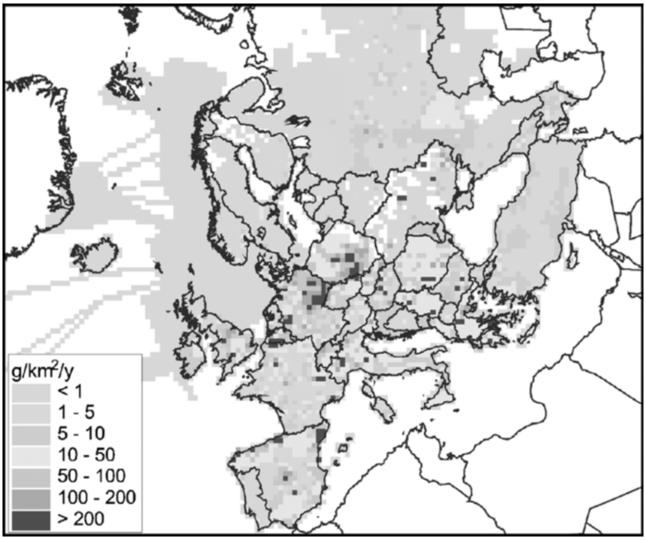


Figure 3. Spatial distribution of mercury anthropogenic emission in Europe in 2002.

1.2. Re-emission of Mercury

Natural emission and re-emission processes are particularly important for the mercury cycle in the environment. The distribution of mercury re-emission from soil in Europe is illustrated in Figure 4. The most significant re-emission fluxes are in Central Europe

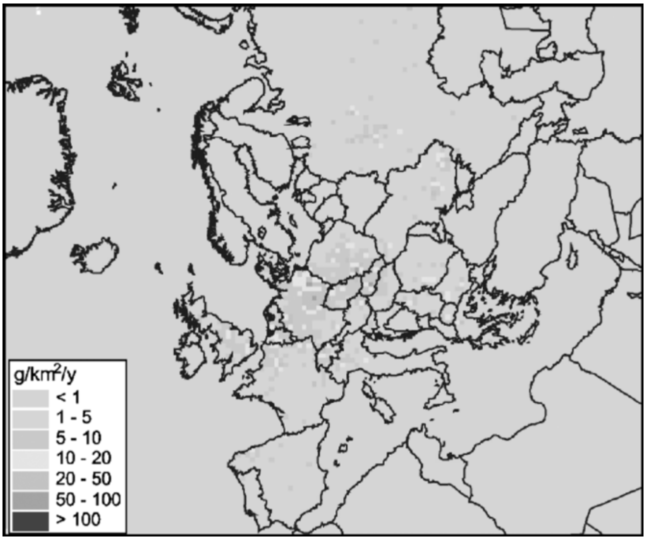


Figure 4. Spatial distribution of mercury re-emission from soils in Europe.

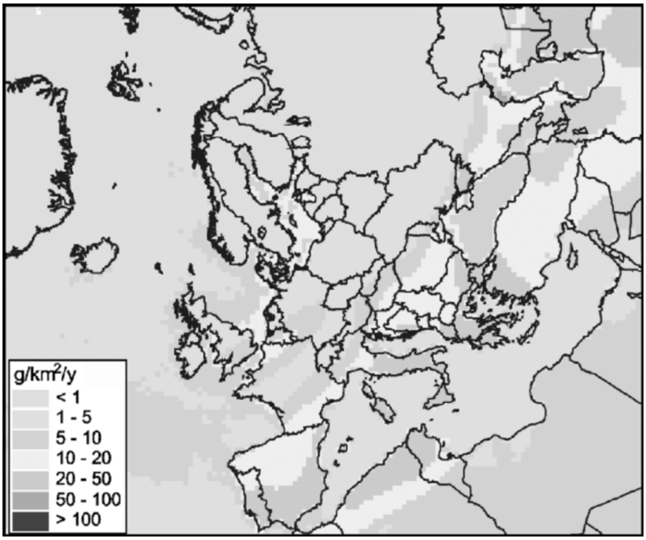


Figure 5. Spatial distribution of mercury natural emission in Europe.

in the regions where intensive depositions have been observed for a long time. The spatial distribution of estimated natural emission of mercury in European region is shown in Figure 5. Rather high emission fluxes are from soil of the geochemical belt in the south of Europe and from coastal seawater with intensive primary carbon production. According to these estimates the total annual emission of mercury from natural sources and re-emission from European soil and marginal seas are 100 and 50 tons respectively (Ilyin et al., 2004).

2. MODELING OF HM CYCLING

As a rule, simulations consider emissions of heavy metals from anthropogenic and natural sources, transport in the atmosphere and deposition to the underlying surface (Figure 6). It is assumed that lead and cadmium are transported in the atmosphere only as a part of aerosol particles. Besides, chemical transformations of these metals do not change removal properties of their particles-carriers. On the contrary, mercury enters the atmosphere in different physical and chemical forms and undergoes numerous transformations during its pathway in the atmosphere (Ilyn et al., 2002; 2004; Ilyin and Travnikov, 2003).

2.1. Atmospheric Transport

The transport of heavy metals in the atmosphere is described by means of a monotone version of Bott's advection scheme. Pressure-based s-coordinate in the vertical makes possible to take into account an effect of the underlying surface elevation. Vertical eddy

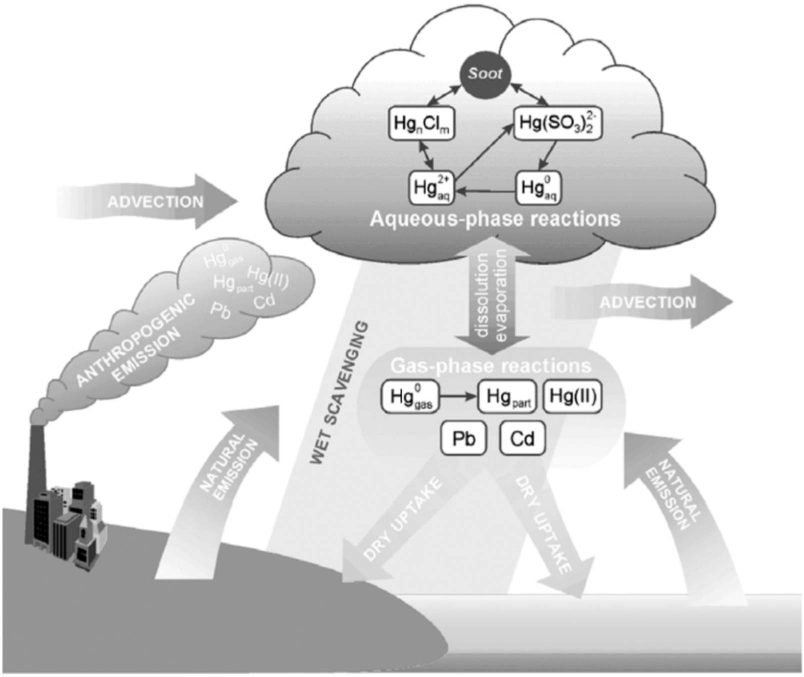


Figure 6. The model scheme of heavy metal behavior in the atmosphere (Ilyin et al., 2004).

diffusion is described in the models to consider air mass mixing in the atmospheric boundary layer.

2.2. Mercury Transformation Scheme

Both models apply the same chemical scheme of mercury transformations. It is assumed that mercury occurs in the atmosphere in two gaseous forms—gaseous elemental Hg0, gaseous oxidized Hg(II); particulate oxidized Hgpart, and four aqueous forms—elemental dissolved Hg0 dis, mercury ion Hg^{2+}, sulphite complex $Hg(SO_3)_2^{2-}$, and aggregate chloride complexes HgnClm. Physical and chemical transformations include dissolution of Hg0 in cloud droplets, gas-phase and aqueous-phase oxidation by ozone and chlorine, aqueous-phase formation of chloride complexes, reactions of Hg^{2+} reduction through the decomposition of sulphite complex, and adsorption by soot particles in droplet water.

2.3. Removal Processes

Heavy metals are removed from the atmosphere by means of surface uptake and precipitation scavenging. The ecosystem-specific dry deposition scheme is based on the resistance analogy approach and distinguishes 16 land use types. Wet removal by precipitation considers both in-cloud and sub-cloud scavenging.

2.4. Model Development

The following modifications of the models have been conducted this year:

The advection scheme of the regional model is improved to take into account the surface orography. Terrain following vertical structure of the model domain with higher resolution was incorporated. Wet removal of heavy metals from the atmosphere was enhanced by developing new parameterizations of precipitation scavenging. Both in-cloud and sub-cloud wet removal were modified on the basis of the up-to-date scientific literature data.

The general structure of a low-resolution multi-compartment model of mercury circulation in the environment was formulated. The atmospheric part of the model was developed and tested.

3. TRANS-BOUNDARY AIR POLLUTION BY LEAD, CADMIUM AND MERCURY IN EUROPE

Assessments of atmospheric pollution have been made by the regional (MSCE-HM) and the hemispherical (MSCE-HM-Hem) transport models developed in MSC-E (Ilyin et al., 2004). The regional model covers the EMEP region (European domain) with the spatial resolution of 50 × 50 km; the hemispheric model describes the atmospheric transport within the Northern Hemisphere with the spatial resolution of $2.5' \times 2.5'$. The main outputs of the modeling include data on heavy metal concentration in the air and precipitation as well as levels of deposition to the surface. Since the negative impact of heavy metals on human health and biota is mainly attributed to their long-term accumulation in environmental media, particular attention has been given to the assessment of their depositions from the atmosphere.

3.1. Pollution Levels in Europe

Depositions and concentrations of lead, cadmium and mercury were evaluated on the basis of emissions and meteorological data for 2002.

Lead

In 2002 anthropogenic emissions of lead in Europe amounted to 8×10^3 tons per year (kt/yr). This is about 11% less than in 2001. In addition, natural emissions and re-emissions made up 1 kt/yr. The total depositions to Europe in 2002 were 6.7 kt.

Spatial distribution of lead depositions in Europe varies to a large extent. A detailed pattern of the spatial distribution is given in Figure 7. In the central and southeastern parts of Europe, e.g. in Belgium, Poland, Italy, Serbia and Montenegro, depositions are the highest and can exceed 2 $kg/km^2/yr$. Similar values of depositions are characteristic of the central region of Russia. These high depositions are caused by the significant emission sources located in these regions. Atmospheric pollution in different countries can be illustrated by deposition fluxes averaged over the country area, and Serbia and Montenegro are characterized by the highest averaged deposition flux of lead (about 1.5 $kg/km^2/yr$). High deposition fluxes are also obtained for

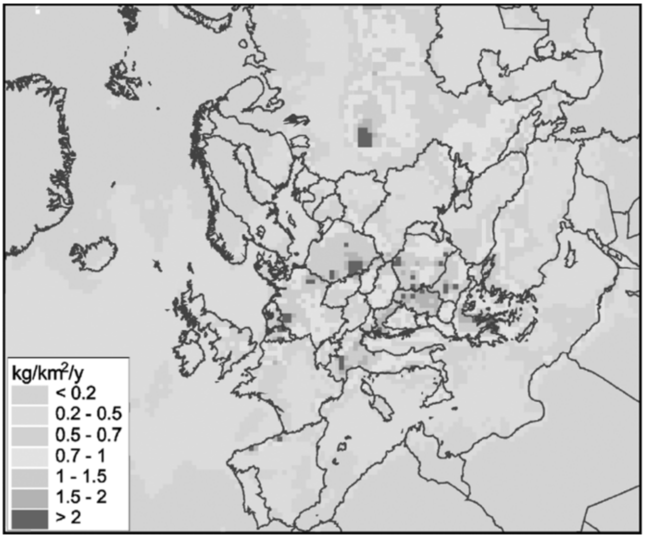


Figure 7. Spatial distribution of lead depositions in Europe in 2002 (Ilyin et al., 2004).

other countries in the south-east of Europe: Croatia, Bulgaria, Greece, and Romania. As for the central and western European countries high depositions are noted for Poland and Belgium. These countries are also characterized by relatively high emissions. The lowest flux was obtained for Scandinavian countries: Norway, Iceland and Sweden.

A significant part of depositions over each country is caused by trans-boundary transport from external sources. In 2002 the contribution of external European anthropogenic sources to depositions over different countries ranges from 5 to 85% (Figure 8). The highest contribution was obtained for the Former Yugoslav Republic of Macedonia and Monaco. In 20 countries of Europe the external European anthropogenic sources contribute more than 50% of total deposition. In addition to individual

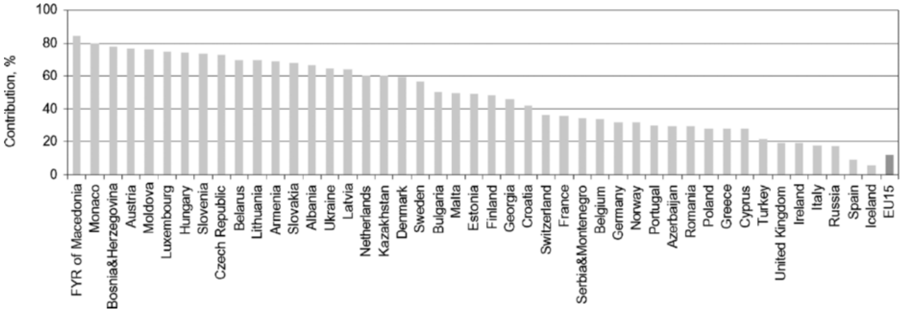


Figure 8. Relative contribution of external anthropogenic sources to lead depositions in European countries in 2002.

European countries, source–receptor relationships were evaluated for the "composite" region: the European Union—EU15). The contribution of external anthropogenic sources to EU amounted to 12%.

A significant amount of lead emitted in a country is transported beyond the national borders contributing to the trans-boundary transport. In 2002 as much as 4.8 kt (around 60% of total anthropogenic emission) of atmospheric lead, emitted in Europe were involved in transport across state borders. Absolute magnitudes of lead transported outside countries vary substantially from country to country. It was calculated as difference between national emission and deposition to the country. This magnitude depends on national emission, size of the territory, climatic conditions and spatial distribution of emission sources within the country.

The highest amount of lead transported across the state borders, is coming from Russia, followed by Turkey and Italy. This can be explained mainly by the significant absolute values of lead atmospheric emissions in these countries. About 1500 t of lead was transported from the European Union. It should be noted that more than 75% of lead mass involved in the trans-boundary transport is emitted by 10 major countries-contributors.

Cadmium

In 2002 anthropogenic emission of cadmium in Europe amounted to 257 t/yr that is 5% lower than in 2001. Emission caused by natural processes (natural emission and re-emission) add up 55 t/yr. Depositions to Europe in 2002 were 240 t/yr. Spatial distribution of cadmium deposition in Europe is shown in Figure 9. The regions

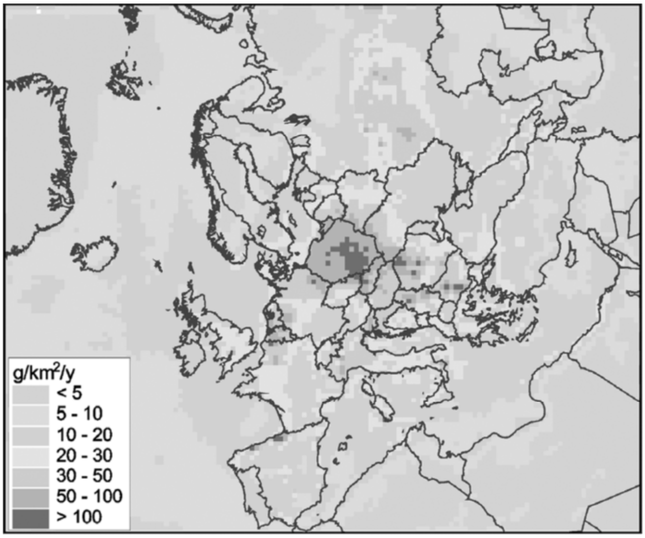


Figure 9. Spatial distribution of cadmium depositions in Europe in 2002 (Ilyin et al., 2004).

with relatively high depositions are Poland with surrounding countries, the south-east of Europe and the area around Belgium. Deposition fluxes in these regions exceed 30 g/km^2/yr. In the northern part of Europe deposition fluxes are below 10 g/km^2/yr.

The spatial pattern of national emissions and atmospheric transport from neighboring countries causes high variability in depositions to different countries. The highest deposition flux of cadmium averaged over the country area is noted for Poland (almost 100 g/km^2/yr), followed by Slovakia, Belgium, and Bulgaria. The lowest average deposition flux is in Finland and Norway.

The contribution of the external European anthropogenic sources to cadmium depositions in Europe in 2002 varies from 4 to 75%. In 17 countries it exceeded 50%. The countries most affected by the trans-boundary transport of cadmium are Belarus, Ukraine, Lithuania, and Czech Republic. These countries are located close to Poland, which is a significant emitter of cadmium. Similar to lead, the lowest contributions are observed in Spain and Iceland. The contribution of the trans-boundary transport to pollution of the European Union with cadmium is about 15%.

Each country is not only a receptor but also a source of the trans-boundary transport. As much as 153 t (60% of anthropogenic emission in Europe) of cadmium, emitted in Europe, leaves the territory of the counties and is involved in the long-range transport. The highest absolute value—30 t/yr—of cadmium transported across national borders was obtained for Poland. The significant "exporters" of cadmium are Spain, the Russian Federation, Romania and Italy. Nearly 40 t of cadmium is transported outside the European Union. Besides, only nine countries control more than 75% of cadmium trans-boundary transport.

Mercury

Mercury emissions from European anthropogenic sources in 2002 totaled 180 tons; this is 11% lower than those in 2001. The input from natural emission and re-emission from European soils and the marginal seas is estimated at about 150 tons. More than 65% of emitted mercury was transported beyond the boundaries of Europe. The total mercury depositions to Europe were about 100 tons. Of this amount, 50 tons originated from anthropogenic sources of European countries; the rest was the input from natural sources, re-emission and global anthropogenic sources.

The spatial distribution of mercury depositions over Europe is shown in Figure 10. The highest deposition fluxes are observed in Central and Southern Europe in the countries with significant anthropogenic emissions and their neighbors. In these countries the annual mercury depositions can exceed 30 g/km^2/yr. The lowest depositions were in Scandinavia and in the northern part of Russia (lower than 5 g/km^2/yr). Levels of mercury deposition vary from country to country appreciably.

As was mentioned above the most significant depositions are in Central and Western European countries—Poland, Belgium, Germany, Slovakia, Check Republic, Hungary, etc.—where average deposition levels exceed 15 g/km^2/yr. In most of these countries the average anthropogenic emission flux is 2–3 times higher. This means that the greater part of mercury emitted in these countries is transported across the

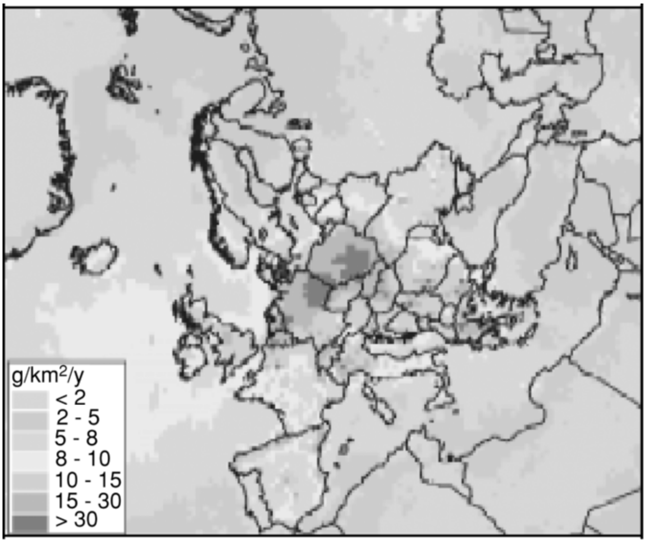


Figure 10. Spatial distribution of mercury depositions in Europe in 2002 (Ilyin et al., 2004).

boundaries. On the contrary, there are countries, such as Macedonia, Croatia, Norway, Sweden, etc., where the average deposition flux significantly exceeds that of national anthropogenic emission.

Contribution of the trans-boundary flux from external (European) anthropogenic sources to mercury deposition in European countries is significant. More than half the total mercury deposition to such countries as Chech Republic, Slovakia, the Netherlands, Macedonia and Belarus was determined by external anthropogenic sources. This fact can be explained by the proximity of these countries to significant emission sources in Poland and Germany. The lowest contribution of external sources was in countries located at the periphery of Europe: Ireland, Spain, Iceland, etc. Deposition of mercury from external sources to the European Union did not exceed 7% of total value.

The role of different European countries in the trans-boundary transport of mercury in Europe is different. The largest contributors to the trans-boundary transport in Europe were Germany, Spain and Poland. Transport beyond the boundaries of these countries amounts to 23 t/yr, 22 t/yr and 18 t/yr, respectively. Besides, nine major countries-contributors determined more than 75% of mercury involved in the Trans-boundary transport. The total transport from the European Union exceeds 85 t/yr.

3.2. Depositions to Regional Seas

Atmospheric loads to seas surrounding Europe are of great importance for environmental risk assessment. In 2002 the highest average deposition flux of lead was obtained for the Black and Azov Seas (Figure 11). This is caused by atmospheric

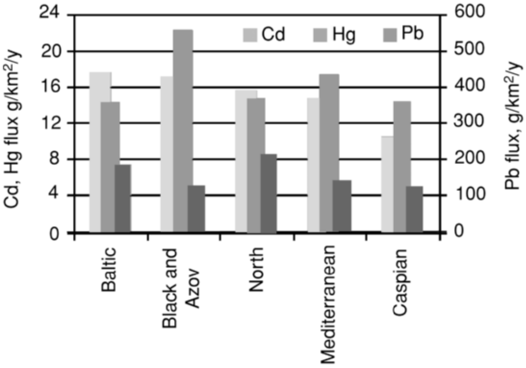


Figure 11. *Averaged deposition fluxes of lead, cadmium and mercury to regional seas in 2002 (Ilyin et al., 2004).*

transport from the countries that are significant emission sources of lead such as Romania, Turkey, Russia and others. The highest deposition flux of cadmium takes place in the Baltic Sea, but the difference in fluxes to other seas is not large. The most significant depositions of mercury occur over the North Sea, the lowest—over the Black and Azov Seas. The highest contribution of anthropogenic sources is observed in the Baltic and Azov Seas. Normally the contribution there exceeds 70%.

High contributions of these sources are also experienced in the Baltic, Aegean and Adriatic Seas. Relatively low contributions were obtained for the northern part of the North Sea and the southwestern part of the Mediterranean Sea. This is caused by remoteness of the main anthropogenic sources. However, it should be noted that depositions from anthropogenic sources to the Mediterranean Sea are most likely underestimated because the anthropogenic emission sources in northern Africa and the Middle East were not taken into account.

For each sea the contribution of various emission sources to atmospheric depositions was assessed. It is obvious that the countries with high emissions, located close to the seas, make the highest contributions to anthropogenic depositions. For example, the most significant contribution to the North Sea comes from the United Kingdom (28%) and Germany (16%). The main anthropogenic contributor to the Caspian Sea is Russia (46%), followed by Azerbaijan (22%) and Turkey (12%). Similar information is also available for cadmium and mercury.

4. ASSESSMENT OF HEAVY METAL POLLUTION IN THE NORTHERN HEMISPHERE WITH PARTICULAR ATTENTION TO CENTRAL ASIA

The assessment of air pollution in the Central Asian region is of great significance for environmental risk estimates. Case study countries, Kazakhstan and Kyrgyzstan are located in Central Asia and have long boundaries with China, the Asian part of Russia, Uzbekistan and Tajikistan. Emissions from these countries as well as the long-range transport from the whole Asian region can significantly affect pollution levels in Kazakhstan and Kyrgyzstan.

Therefore data on anthropogenic and natural emissions in the Asian region are necessary for the assessment of heavy metal pollution in these countries. Pollution of Kazakhstan and Kyrgyzstan by mercury and lead has been initially assessed by means of hemispheric modeling using the available global emission inventories of the considered heavy metals. The outcomes of the assessment are presented in this section.

4.1. Mercury

Anthropogenic emission of mercury to the atmosphere in the considered countries and in the Northern Hemisphere as a whole is assessed with the global emission inventory for 1995 (Pacyna et al., 2003). According to these data the total anthropogenic emission of mercury in the Northern Hemisphere was about 1900 t/yr, the emissions of mercury in Kazakhstan and Kyrgyzstan were 49 and 2.6 t/yr, respectively. Figure 12 illustrates the spatial distribution pattern of anthropogenic emission of mercury in the Northern Hemisphere as well as in Kazakhstan and Kyrgyzstan. The highest density of emission sources of the Northern Hemisphere is in South-Eastern Asia, Europe, and the eastern part of North America (Figure 12(a)). Emission fluxes in the countries of concern (Figure 12(b)) are relatively low in comparison with those in European and Eastern Asian countries. Mercury emissions from natural sources were considered using the parameterization developed in (Travnikov and Ryaboshapko, 2002).

The calculated maps of the annual mercury deposition in the Northern Hemisphere and over the considered countries are shown in Figure 13. A high transport ability of mercury enables it to be transported in the atmosphere over long distances. A significant part of mercury emitted in the polluted regions is deposited far from major

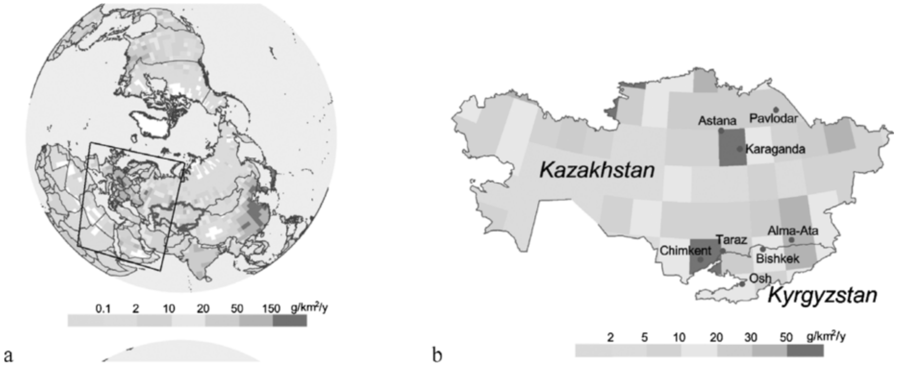


Figure 12. Spatial distribution of mercury anthropogenic emission in the Northern Hemisphere (a) and in Kazakhstan and Kyrgyzstan (b) in 1995. Black line in the left figure delineates the EMEP region (Ilyin et al., 2004).

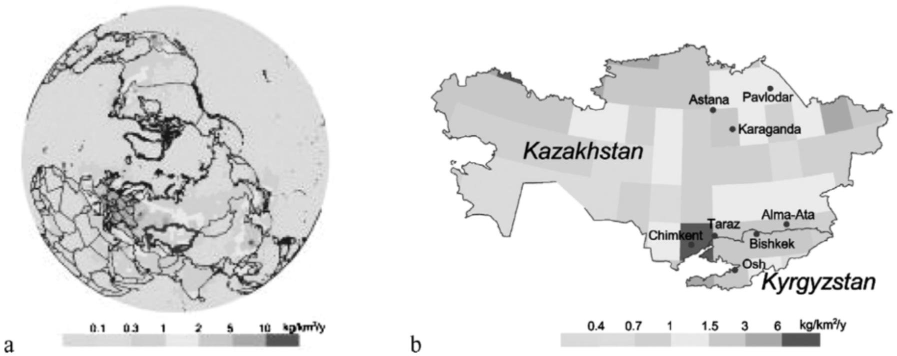


Figure 13. Spatial distribution of annual mercury deposition in the Northern Hemisphere (a) and in Kazakhstan and Kyrgyzstan (b) in 1995 (Ilyin et al., 2004).

emission sources (e.g., in the Central Pacific). On the other hand, national emissions of short-lived mercury forms are responsible for local depositions of this pollutant in a country. Thus, mercury contamination in Kazakhstan and Kyrgyzstan is caused both by national and by remote sources. The highest depositions of mercury in the considered countries are in the areas with intensive emissions located in Northern Kazakhstan near the border between these two states.

The contribution of different regions and countries of the Northern Hemisphere to mercury deposition to Kazakhstan and Kyrgyzstan is illustrated in Figure 14. In the analysis Russia and China are separated from Europe and Asia as the most important neighbors of the considered countries. As seen from the diagram 14a the most significant depositions of mercury to Kazakhstan are from national sources (35% of the total). Russia contributes about 14% of the total deposition that is equal to the joint contribution of the rest of Europe and Asia. On the contrary, national sources contribute only 10% to the total mercury deposition to Kyrgyzstan (Figure 14(b)).

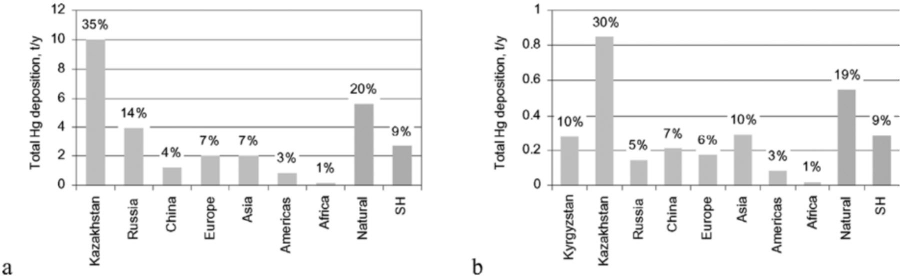


Figure 14. Contribution of different regions and countries of the Northern Hemisphere to the total annual mercury deposition to Kazakhstan (a) and Kyrgyzstan (b) in 1995. The last column of the chart—contribution of the Southern Hemisphere (Ilyin et al., 2004).

About one third of the total deposition is from Kazakhstan and 10% is from other Asian sources. In both cases about 20% is contributed by natural sources. The total annual deposition of mercury to Kazakhstan amounts to 28 t/yr and to Kyrgyzstan—2.9 t/yr.

4.2. Lead

The assessment of lead contamination in Kazakhstan and Kyrgyzstan is based on the global lead emission inventory for 1990 (Pacyna et al., 1995), the only available dataset at the moment. Despite the fact that lead emissions have considerably changed worldwide in the last fourteen years, the outcomes of the assessment can illustrate the general character of the long-range trans-boundary lead pollution in the countries under consideration.

The spatial distribution of lead anthropogenic emissions in the Northern Hemisphere and particularly in Kazakhstan and Kyrgyzstan in 1990 is shown in Figure 15. As is seen the major emission sources were located in Europe. Some significant emissions were also in Eastern Asia and in North America. The total anthropogenic emission of lead in the Northern Hemisphere was about 146 kt/yr, the emissions of lead in Kazakhstan and Kyrgyzstan were 5.8 kt/yr and 0.7 kt/yr, respectively.

Figure 16 shows the calculated maps of the annual lead deposition both in the Northern Hemisphere and in the countries of concern in 1990. Lead is characterized by significantly lower ability to the long-range trans-boundary transport as compared with mercury and for the most part it determines regional pollution. As seen from Figure 16(a) the most significant depositions of lead occurred in the regions with high emission intensity—Europe, Eastern Asia and North America, where deposition fluxes can exceed 10 kg/km^2/yr. Depositions in Kazakhstan and Kyrgyzstan were significantly lower and mostly did not exceed 3 kg/km^2/yr (Figure 16(b)). Higher depositions were observed in the northern part of Kazakhstan because of the trans-boundary transport from the Russian Federation as well as near the boundary between Kazakhstan and Kyrgyzstan, where significant emission sources are located. The total

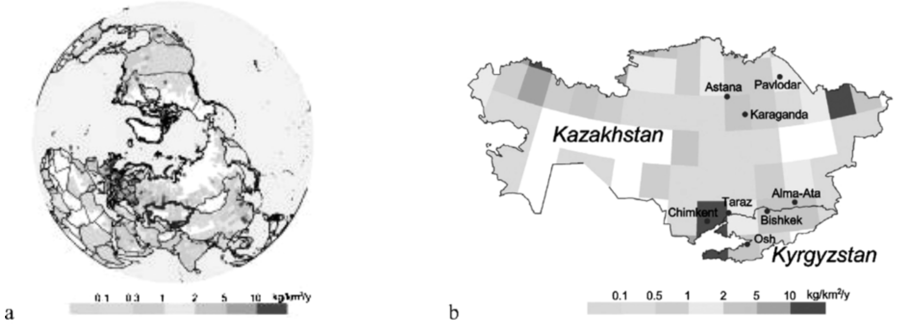


Figure 15. Spatial distribution of lead anthropogenic emission in the Northern Hemisphere (a) and in Kazakhstan and Kyrgyzstan (b) in 1990 (Ilyin et al., 2004).

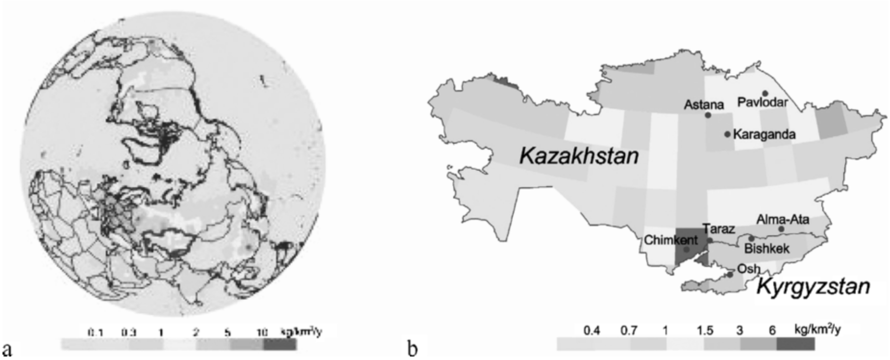


Figure 16. Spatial distribution of annual lead deposition in the Northern Hemisphere (a) and in Kazakhstan and Kyrgyzstan (b) in 1990 (Ilyin et al., 2004).

deposition of lead to Kazakhstan and Kyrgyzstan amounted to 3.5 kt/yr and 0.43 kt/yr, respectively.

The contribution of different regions and countries of the Northern Hemisphere to the total annual deposition of lead to Kazakhstan and Kyrgyzstan is shown in Figure 17. National sources made the most significant contribution to lead deposition to Kazakhstan (38% of the total). Russia was the most important contributor among external sources. It contributed about 27% of the total deposition. The contributions of other European and Asian countries were 15% and 18%, respectively. Depositions of lead over Kyrgyzstan were mostly determined by Asian sources (more than 70%). Among them the greatest contributor was Kazakhstan (40% of the total deposition). The contribution of the national Kyrgyz sources did not exceed 17%.

4.3. Impacts on the European Ecosystems

The following issues are here discussed in depth: ecosystem-dependent depositions, speciation of mercury depositions, mercury concentrations in precipitation. One of the

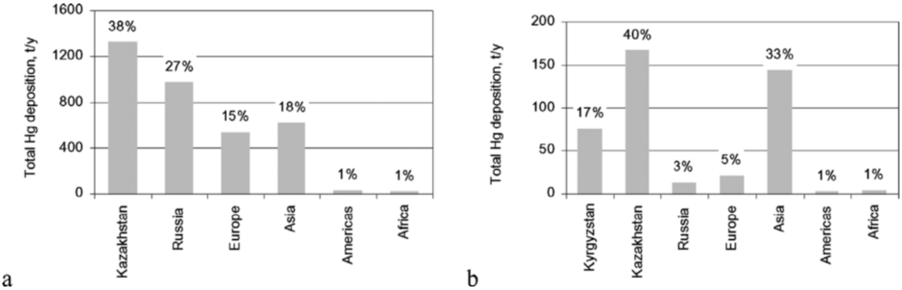


Figure 17. Contribution of different regions and countries of the Northern Hemisphere to the total annual lead deposition to Kazakhstan (a) and Kyrgyzstan (b) in 1990 (Ilyin et al., 2004).

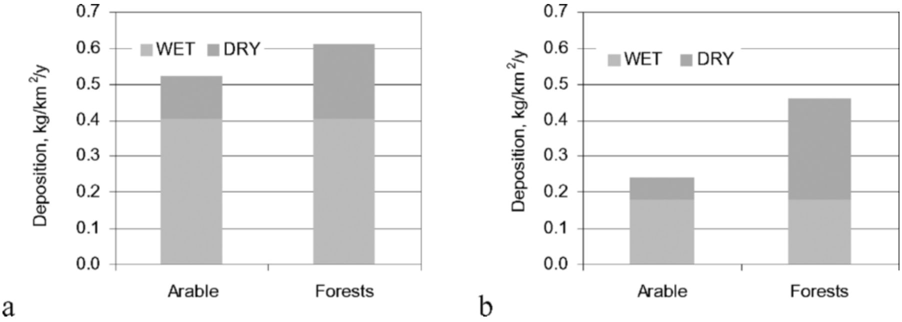


Figure 18. Dry and wet deposition fluxes of lead to arable lands and forests in southern Norway (a) and central Spain (b) in 2002 (Ilyin et al., 2004).

most important types of information is ecosystem-dependent atmospheric depositions. The method to estimate critical load is based on the balance of a metal in soil. Atmospheric deposition is one of the important components of this balance. For each ecosystem critical load is calculated separately (see Chapter 3). Atmospheric deposition, in its turn, also depends on the characteristics of the underlying surface. For example, dry deposition to the areas covered by forests can be significantly larger than that to grasslands or arable lands. That is why it is necessary to differentiate deposition fluxes between land-cover categories (ecosystems). It is especially true for the areas with relatively low precipitation amounts.

To confirm this idea two examples are given in Figures 18(a) and (b): ecosystem-dependent depositions of lead in South Norway and in Central Spain in 2002. Depositions are split in wet and dry. Wet deposition fluxes are assumed to be the same for different types of ecosystems. Annual precipitation amounts in these regions are about 1,400 (Norway) and 510 (Spain) mm. In the Norwegian region dry deposition to forests is higher than that to arable lands. However, due to the large amount of precipitation, wet deposition prevails and total deposition (sum of wet and dry) does not differ much between forests and arable lands.

In Spain the situation is opposite. Dry deposition to forests is higher than that to arable lands as much as 4.5 times. Moreover, unlike Norway, at this station dry deposition to forests is significantly higher than wet deposition. The total deposition fluxes to arable lands and to forests also differ almost twofold. Similar effects are also observed for cadmium and mercury.

Variable geographical conditions and distribution of emission source causes highly uneven distribution of ecosystem-specific deposition patterns across Europe. From the viewpoint of the adverse effects it appears that the most interesting ecosystems are forests, arable lands, grasslands, and freshwaters. In Figure 19 depositions of cadmium to forests and to arable lands are exemplified. As seen, in areas where there are both forests and arable lands, deposition fluxes to forests are substantially higher than to arable lands.

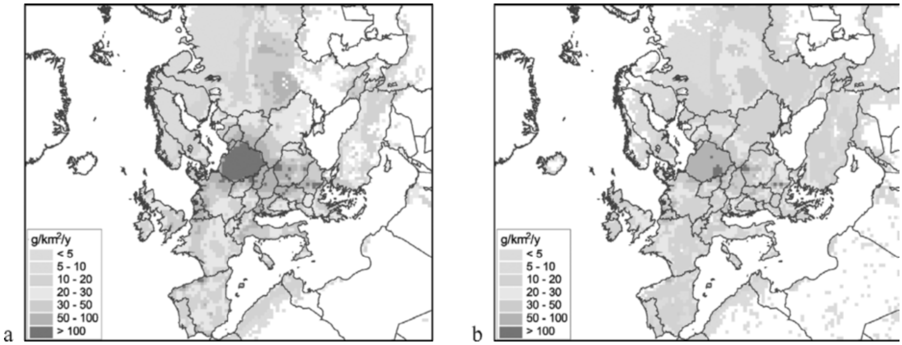


Figure 19. Deposition flux of cadmium to areas covered by forests (a) and to arable lands (b) in 2002 (Ilyin et al., 2004).

Similar information is also available for lead and mercury, and not only for forests and arable lands, but also for other land-cover categories. This information is presented on the Internet [*www.msceast.org*].

5. BIOGEOCHEMICAL CASE STUDIES

5.1. South Sweden, Baltic Sea region

Annual emissions of heavy metals from the anthropogenic sources of HELCOM countries significantly decreased during the period of 1990–2001. In particular, annual emissions of cadmium decreased by 45%, whereas lead and mercury emissions reduced by 60%. Following this reduction and also due to the changes of heavy metals emissions in other European countries the level of atmospheric depositions to the Baltic Sea has also significantly decreased (Figure 20). Compared to 1990

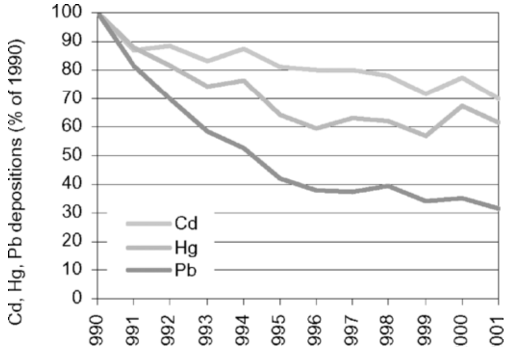


Figure 20. Decrease of cadmium, mercury, and lead depositions to the Baltic Sea in 1990–2001 (Ilyin et al., 2004).

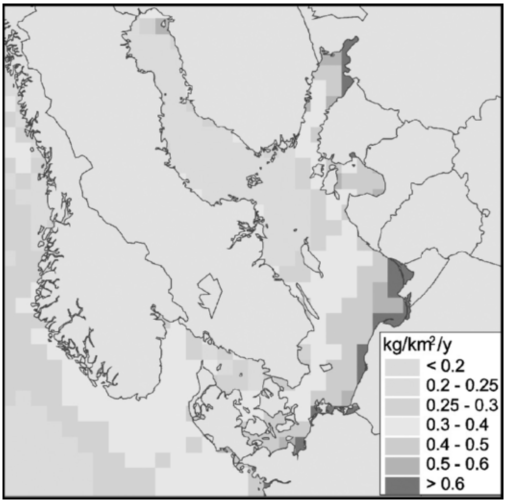


Figure 21. Total annual lead depositions to the Baltic Sea in 2001 (Ilyin et al., 2004).

atmospheric depositions to the Baltic Sea in 2001 are lower by 70% for lead, by 40% for mercury, and by 30% for cadmium.

The highest depositions of heavy metals over the Baltic Sea can be noted in the south-western part of the Baltic Sea within the Baltic Sea and the Baltic Proper sub-basins (Figure 21). Significant levels of lead and cadmium depositions can also be noted in the Gulf of Riga. The total contribution of HELCOM countries to the heavy metals deposition over the Baltic Sea in 2001 amounts to 40%.

The relative partitioning of the HELCOM countries' national emissions of lead, cadmium and mercury deposited to the Baltic Sea is shown in Figure 22.

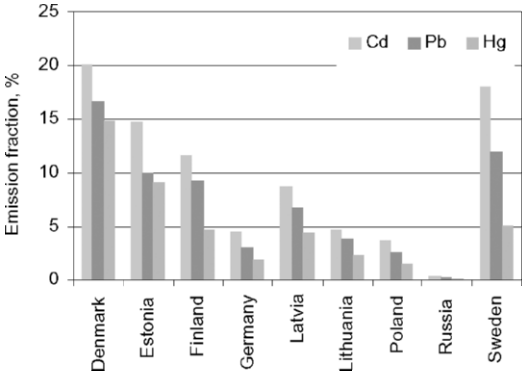


Figure 22. Fractions of the HELCOM countries' emission of lead, cadmium, and mercury deposited to the Baltic Sea (mean values for years 1990, 1995 and 2000).

Catchments Study

Small catchment study of biogeochemical mass balance of mercury was carried out in southern Sweden in early 1990s. The fluxes of methyl Hg (Hg_m) and total Hg (Hg_t) were monitored (Figure 23).

Much of the Hg_t pool was found in the upper part of the soil, which is rich in organic matter. This pattern is likely due to an elevated atmospheric deposition of Hg_t over the extended period and immobilization of mercury by organic functional groups and accumulation of organic matter as part of the soil-forming process. The retention of mercury in the mor humus layer was almost complete due to the very strong association between Hg_t and humic substances.

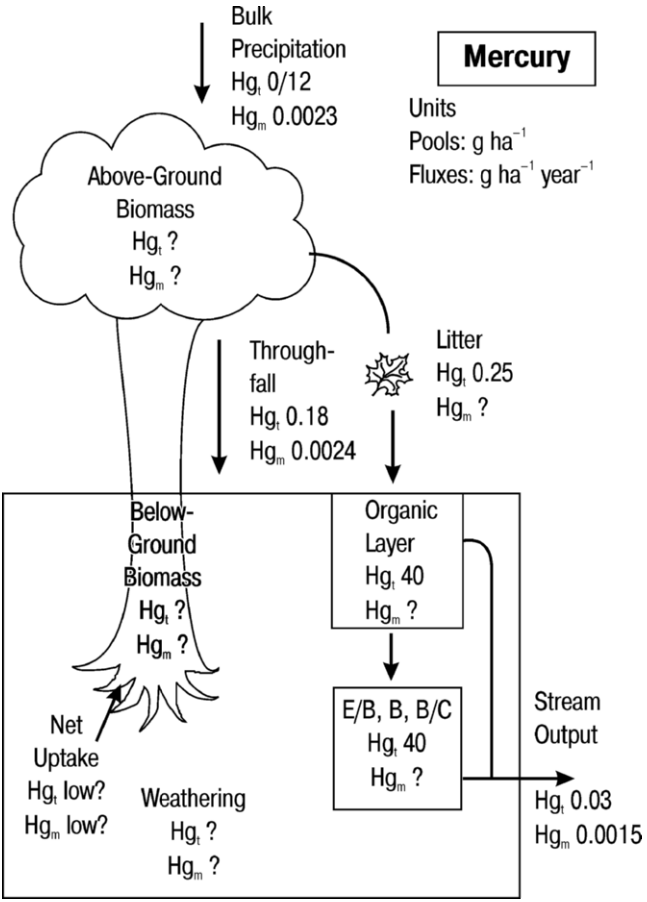


Figure 23. Biogeochemical mass budget of mercury in the experimental forest catchment in South Sweden. The fluxes of methylmercury (Hg_m) and total mercury (Hg_t) are shown in g/ha/yr (Driscoll et al., 1994).

The runoff export was about 0.03 g/ha of Hg_t per year. This value lies within the range of 0.008 to 0.059 g Hg/ha/yr, derived from a number of catchment studies in Sweden. The output of methylmercury from catchment area was 0.0015 g/ha/yr of Hg. This is substantially lower than the input to the catchment. There appears to be an ongoing net accumulation of Hg_m in the terrestrial ecosystems, similar to the pattern previously shown for the total mercury.

There exists evidence of a coupling between the total and methyl-mercury concentrations in surface runoff water. The concentration of methylmercury in surface runoff is of special interest, since this pathway is a major component of the total mercury loading from drainage terrestrial Forest ecosystems to the aquatic ecosystem of a lake. Moreover, methylmercury is the form of Hg that is enriched in the aquatic biogeochemical food wed and subsequently transferred to the human population through fish consumption. A close correlation was found between the water color (i.e., dissolved humic substances) and the concentration of methylmercury and total mercury. This supports the assumption that the transport of dissolved organic matter from the soil with drainage water is regulating the flux of both Hg_m and Hg_t from the terrestrial to the aquatic ecosystem.

Driscoll et al. (1994) have studied the mercury species relationships among water, sediments, and fish (yellow perch) in a series of Adirondack lakes in New York state, USA. In most lakes, approximately 10% of the total mercury loading was in the form of $C_2H_5Hg^+$. Mercury concentrations increased as pH fell, but the best correlation was found between [dissolved Al] and [dissolved Hg] suggesting that the same factors are responsible for mobilizing both these metals. Methylmercury concentrations correlated strongly with the dissolved organic carbon content in the water. Fish muscle tissue was analyzed for mercury and showed an increase with age. However, the study was unable to resolve the question of whether the principal source of mercury to these lakes was atmospheric deposition or dissolution from bedrock due to acid rains.

5.2. Hubbard Brook Experimental Forest, USA

The input of airborne lead to the Forest ecosystems has been studied at the Hubbard Brook Experimental Forest in New Hampshire. The small catchment approach has been used to study the lead biogeochemical cycle since 1963 (Likens et al., 1977; Driscoll et al., 1994). By monitoring precipitation inputs and stream output from small watersheds that are essentially free of deep seepage, it is possible to construct accurate lead mass balance. The detailed study of soil and soil solution chemistry and forest floor and vegetation dynamics supplemented the deposition monitoring.

The biogeochemical mass balance of lead is shown in Figure 24.

The atmospheric deposition of lead was 190 g/ha/yr and this value was connected with declining of leaded petrol use in USA from 1975. The mineral soil and forest floor were the major pools of Pb in the ecosystem. Mineral soil pools (<2 mm size fraction) are generally the largest element pools for the HBEF, however this includes relatively unreactive soil minerals. Deposition and accumulation of Pb in the forest floor have been the focus of a number of investigations. It has been shown that at

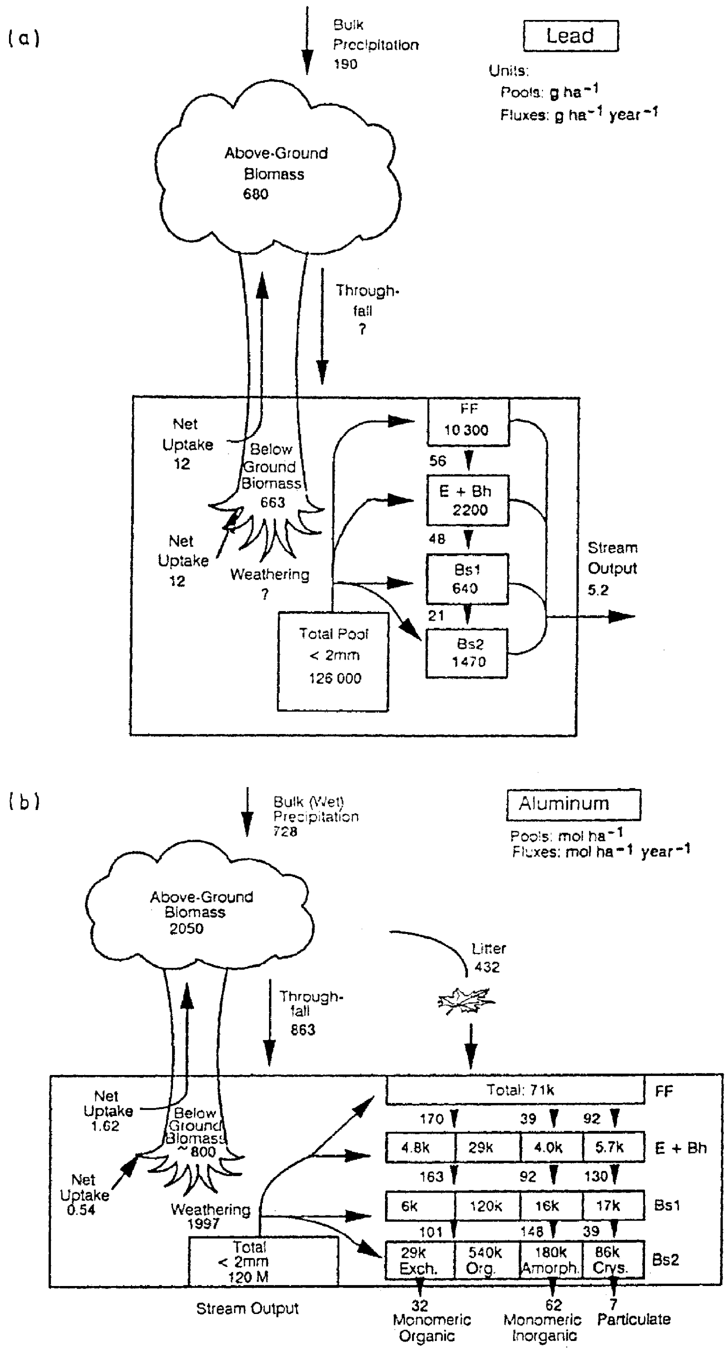


Figure 24. Biogeochemical mass balance of lead in Forest ecosystems of Hubbard Brook Experimental Forest, USA (Driscoll et al., 1994).

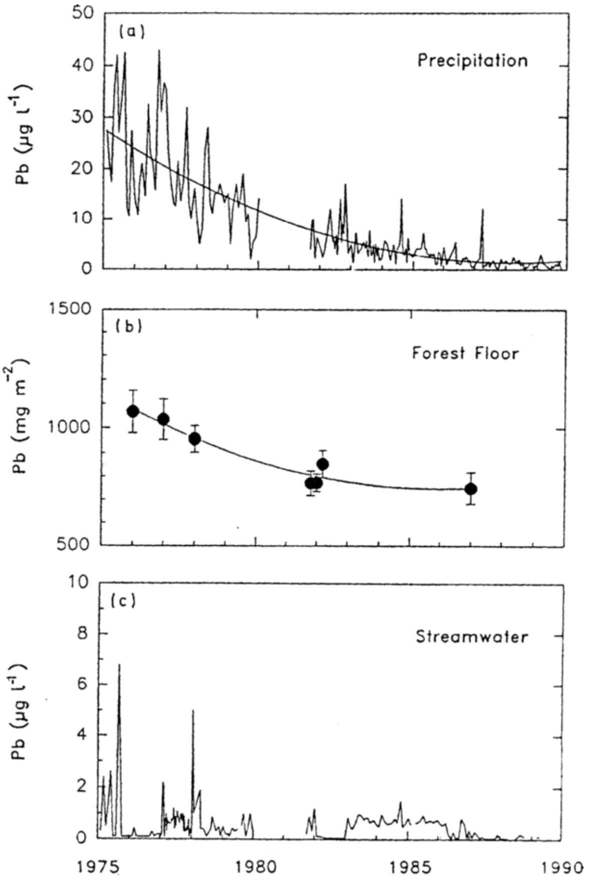


Figure 25. Temporal pattern of the concentration of Pb in the biogeochemical reference watershed at the Hubbard Brook Experimental Forest, NH, USA: (a) bulk precipitation; (b) the forest floor; (c) stream water (after Driscoll et al., 1994).

HBEF, much of the lead entering the ecosystem from the atmosphere appears to be retained in the forest floor. Concentrations and fluxes of lead in bulk deposition are much greater than in Oa horizon leachate. Solution concentrations and fluxes of Pb decrease through the soil profile and losses in stream water are low. There was a strong correlation between concentrations of Pb and dissolved organic carbon (DOC) in soil solution and stream water at Hubbard Brook Driscoll et al., 1994, 1998).

Pools and uptake of lead in vegetation at Hubbard Brook were insignificant. Lead is not a plant essential nutrient and therefore it is not surprising that uptake was low.

The calculated weathering release of lead at HBEF is negative (–174 g/ha/yr). This pattern is likely due to changes in mineral soil lead pools over the study period. There has been a marked decline in lead concentration of the forest floor; concurrently with a decline in atmospheric inputs during 1975–1990 (Figure 25).

These long-term small catchment study results suggest that stream water concentrations are very low and not a water quality concern. In addition, a study of lead in soil solution and stream water following a commercial whole-tree harvest at Hubbard Brook showed that Pb was not released to drainage waters from clearcutting activities (Fuller et al., 1988).

CHAPTER 19

TRANS-BOUNDARY POP TRANSPORT

Persistent organic pollutants, POPs, are a wide class of chemical species with different physicochemical properties and toxicology. Here we will consider the following priority list of POPs: 1,1,1-trichloro-2,2-bis (4-chlorophenyl) ethane, DDT; hexachlorocyclohexanes, HCHs; hexachlorobenzene, HCBs; polychlorinated dibenzo-*p*-dioxins and dibenzofurans, PCDD/Fs; polychlorinated biphenyls, PCBs; polycyclic aromatic hydrocarbons, PAHs. Environmental pollution by persistent organic pollutants, POPs, is one of the global problems that is drawing attention at national and international levels. The trans-boundary aspects of POPs transport and pollution of various environmental media require studying the relevant effects on human health and the environment, including quantification of those effects. In accordance to Protocol on POPs to the UN ECE Convention on Long-Range Trans-boundary Air Pollution entered into force in October 2003, the Parties to the Protocol shall encourage research, development, monitoring and co-operation related, in particular, to an effects-based approach which integrates appropriate information on measured or modeled environmental levels, pathways, and risk to human health and the environment.

1. EVALUATION OF POPS DEPOSITION IN THE EUROPEAN COUNTRIES

1.1. Modeling of POPs Cycling

For the evaluation of long-range atmospheric transport and deposition of POPs, a multi-compartment transport model EMEP/MSCE-POP is used (Mantseva et al., 2004). It includes such media as the atmosphere, soil, seawater and vegetation (Figure 1). A multi-compartment approach is conditioned by the ability of POPs to be accumulated in soil, seawater and vegetation with subsequent re-emission. Apart from atmospheric transport the model also takes into account the transport of pollutants by sea currents.

At present there exist two versions of MSCE-POP model: a regional version elaborated for the EMEP region with spatial resolution 50 × 50 km and 150 × 150 km, and a hemispheric version with spatial resolution 2.5 × 2.5°. Modelling of POP transport requires information on the physical-chemical properties of considered POPs, their emissions and also meteorological and geophysical data. The model output data are calculated fields of depositions and concentrations in the main environmental media with different spatial resolutions and long-term trends of contamination by various

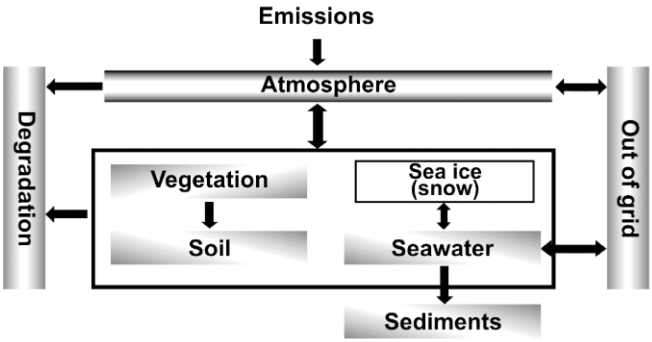


Figure 1. General scheme of MSCE-POP multi-compartment model (Mantseva et al., 2004).

species of POPs. Besides, POP distribution between different environmental media and source–receptor relationships are also evaluated. More detailed information on the structure of the model and parameterisation of the media processes can be found in the EMEP/MSC-E technical reports (Shatalov et al., 2003; Dutchak et al., 2004) and on the Internet (http://www.msceast.org).

1.2. POPs Emissions in Europe

In the EMEP region within the period from 1990 to 2001 emission reduction took place for all POPs under consideration. In particular, during the considered period emissions of B[a]P were reduced by 25%; emissions of PCDD/Fs and PCBs—more than by half and emissions of γ-HCH—almost twice. As an example, temporal trends of total European emissions of PCDD/Fs and γ-HCH for the considered period are presented in Figure 2. For preparation of the data used in calculations available official information supplemented by expert estimates where necessary are used. As a whole a considerable reduction of POP emissions are also characteristic of the most part of Eastern European countries.

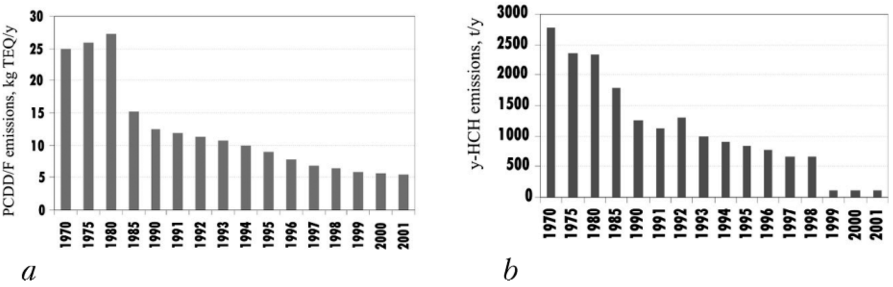


Figure 2. Temporal emission trends of PCDD/Fs (a) and γ-HCH (b) in Europe (Mantseva et al., 2004).

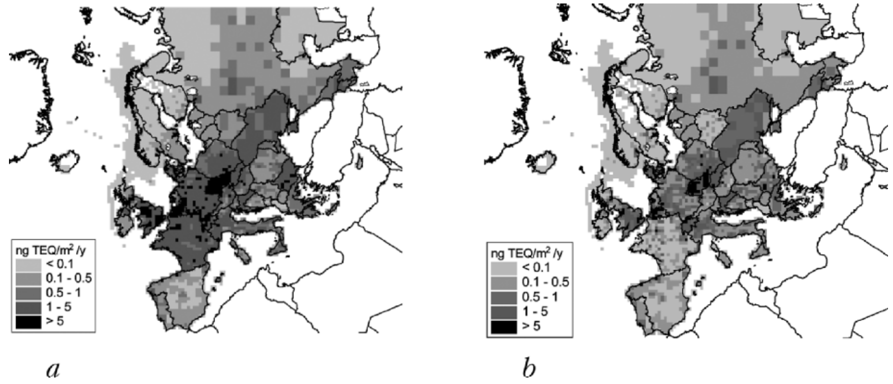


Figure 3. Spatial distribution of the total emissions of 17 toxic congeners of PCDD/Fs in 1990 (a) and 2001 (b) Europe (Mantseva et al., 2004).

On the basis of obtained national totals, spatial distributions of emissions for all years from 1990 to 2001 were prepared. These data allow us to point out the following changes in emission spatial distribution patterns during the considered period. For example, during this period the decrease in emissions of PCDD/Fs was observed in all Eastern European countries (Figure 3). The most substantial reduction can be noted for Belarus, Bulgaria, the Czech Republic, Lithuania and Republic of Moldova.

1.3. POPs Deposition in Europe

One of model's main results is spatial distribution of POP depositions and air concentrations. Calculated fields of depositions and concentrations give the opportunity to assess the changes in atmospheric contamination and deposition of POPs and to select "hot spots" of contamination. As an example, the spatial distribution of PCDD/Fs depositions to the EMEP region, calculated for the beginning and the end of the considered period, is given in Figure 4. "Hot spots" are particular cells of the EMEP

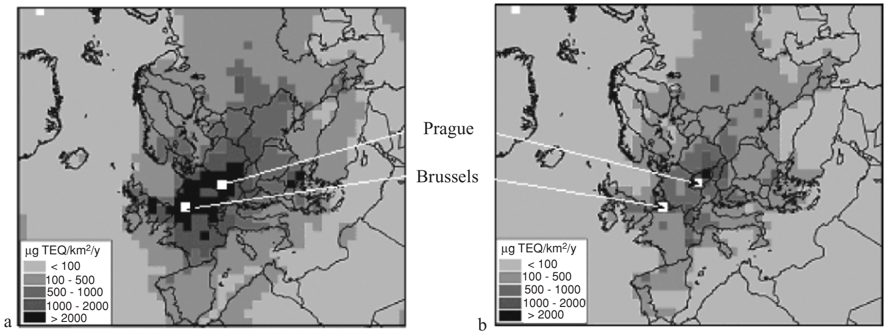


Figure 4. Spatial distribution of PCDD/Fs depositions, 1990 (a) and 2001 (b) (the arrows show "hot spots") (Mantseva et al., 2004).

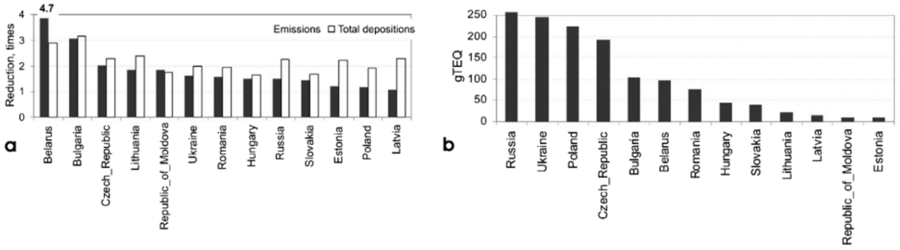


Figure 5. Relative reduction of PCDD/Fs emissions and total depositions (a) and absolute reduction of total depositions (b) in Eastern European countries (http://www.msceast.org).

grid characterized by the highest values of PCDD/Fs deposition fluxes in both years (marked by arrows). As seen from the data presented, deposition fluxes over the European countries decreased substantially. PCDD/Fs deposition at one “hot spot” near Prague (the Czech Republic) decreased more than two times. Such calculated fields of depositions for other considered POPs are also available on the Internet (http://www.msceast.org).

On the basis of calculations the reductions of depositions and air concentrations of all selected POPs in each particular European countries are evaluated. The relative and absolute reduction of PCDD/Fs deposition over Central and Eastern European countries in comparison with relative emission changes is given in Figures 5(a) and (b). For the considered period the maximum relative decrease in PCDD/Fs depositions was obtained for Bulgaria and Belarus (about 3 times) (Figure 5(a)). At that the character of relative decrease in PCDD/Fs total depositions did not completely coincide with that of emissions. It can partly be explained by the influence of trans-boundary transport of PCDD/Fs and by the impact of re-emission flux in these countries. The highest absolute reduction was observed in Russia, Ukraine and Poland (Figure 5(b)).

1.4. Spatial Pattern of PCDD/Fs Contents in Various Environmental Compartments

For PCDD/Fs the spatial distribution of concentrations in air in comparison with that for soil concentrations in 2001 is shown in Figure 6. Note that significant differences in the spatial distribution of air and soil concentrations in most European countries are observed. This fact can be explained by the long-term accumulation of PCDD/Fs in soil and relatively low degradation rates in this medium in combination with changes in the emissions during a long time period.

To take into account the effect of accumulation of POPs in different environmental compartments (soil, seawater and vegetation) the modelling of their long-range transport was performed for a more prolonged period of time (1970–2001). In general, the trends of PCDD/Fs content in air and seawater followed the emission variation. The trend of PCDD/F accumulation in soil was strongly different from that of emissions. Emissions began to reduce in 1980, whereas the decrease in soil contamination started in 1990. The rate of the soil content decrease is much lower. This causes substantial

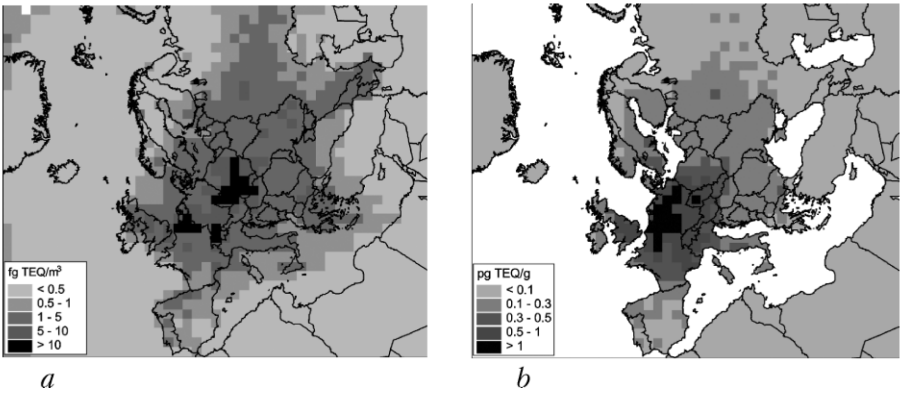


Figure 6. Spatial distribution of PCDD/Fs concentrations in the (a) air and (b) soils of Europe in 2001 (Mantseva et al., 2004).

PCDD/F re-emission flux from soil, which slows down the tendency for a decrease in PCDD/F content in the atmosphere.

The distribution of the annual emissions of PCDD/F in the atmosphere of the EMEP region in 2001 as compared with their distribution between different environmental compartments by the end of the calculated period is presented in Figure 7. Only 1% of the annual PCDD/F emissions remains in the atmosphere; about 56% are deposited to other media. However, the distribution between media after a long time period is not directly determined by PCDD/Fs depositions in 2001. To a great extent it results from their long-term accumulation in the environment (1970–2001). For example, the annual contribution of PCDD/Fs total emissions to soil is about 47%. However, after a long time period the most part of the total PCDD/Fs content in the environment (about 95%) accumulated in soil due to relatively low degradation rates for this medium. Thus, soil is the main "medium-accumulator" of PCDD/Fs.

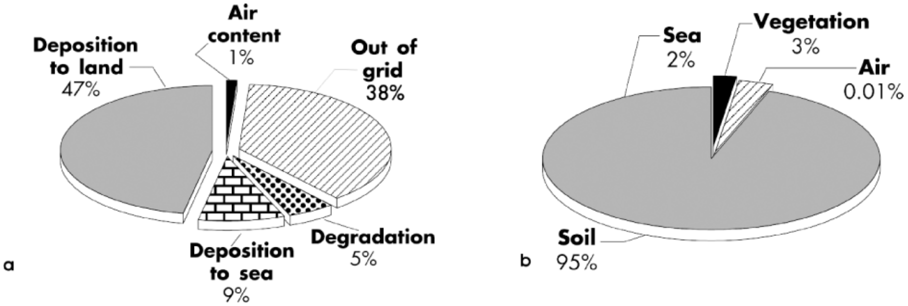


Figure 7. Distribution of annual emissions of the mixture of toxic PCDD/F congeners in the atmosphere (a) and environmental content between different environmental compartments (b) in 2001 (Shatalov et al., 2004).

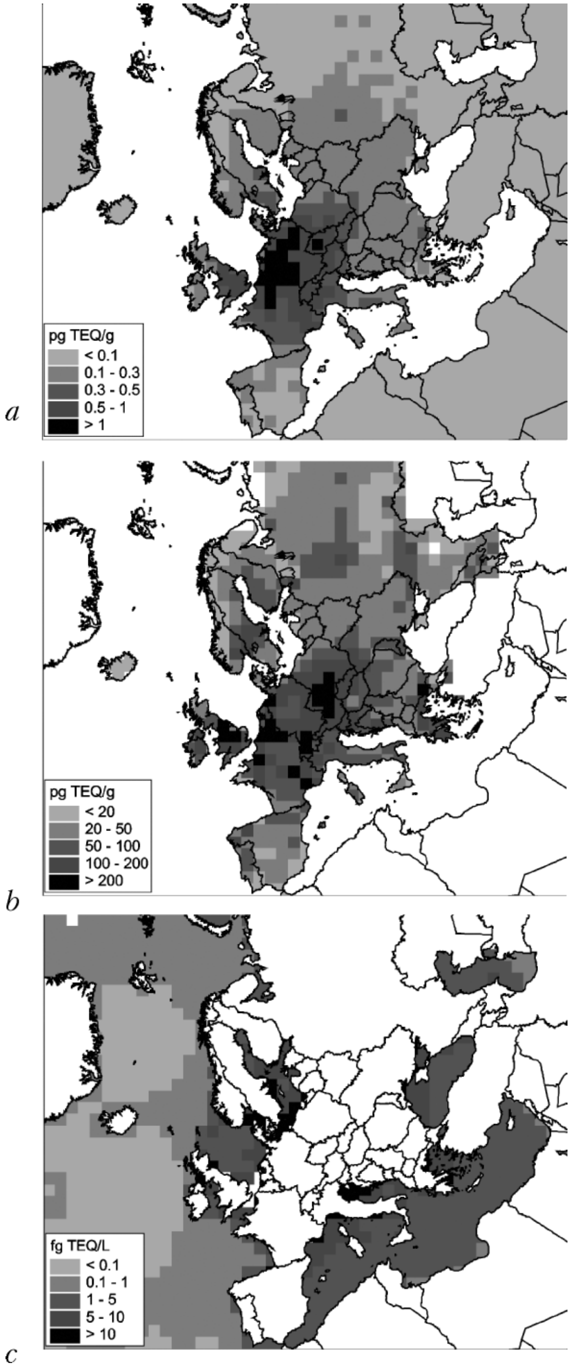


Figure 8. Spatial distribution of PCDD/Fs concentrations in soil (a), vegetation (b) and seawater (c) in 2001 (Mantseva et al., 2004).

Re-emission of toxic congeners from soil to the atmosphere can affect the levels of PCDD/F air pollution.

Such pollutants as PAHs and PCBs also tend to be accumulated in the terrestrial environment but HCB and γ-HCH in the marine ones. Thus, this information gives us an idea of the POPs exposure pathways to human beings.

To identify the areas and regions which were the most polluted by the considered POPs, the preliminary model results on the spatial distribution of their concentrations in different environmental media of the EMEP region were obtained. As an example, the spatial distributions of PCDD/F concentrations in soil, vegetation and seawater with a spatial resolution of 50 × 50 are presented in Figure 8.

1.5. Trans-Boundary Pollution in the European Domain

Model calculations allow one to evaluate POP trans-boundary transport between European countries. The contributions of external sources to PCDD/Fs air concentrations in some European countries including Eastern European countries (given in black) are shown in Figure 9(a). In spite of the general decrease of contamination in Europe, the role of trans-boundary transport is yet essential. The fraction of air concentrations caused by external sources amounts approximately to 60% for Hungary, Romania and Slovakia. As it was mentioned above air contamination by PCDD/Fs is partly explained by accumulation in media with subsequent re-emission. The fraction of concentrations caused by this process can reach 10–15% in some countries (Figure 9(b)).

Figure 10 presents calculated values of trans-boundary depositions of B[a]P from Eastern European countries, that is, depositions outside a country due to national emission sources. For some countries these depositions can reach 2–5.8 tons per year.

Model calculations can provide more detailed information on trans-boundary transport for a particular country. Contribution of European countries to B[a]P depositions to Hungary (import) and distribution of B[a]P depositions from Hungarian sources over European countries (export) are presented in Figure 11. Such information

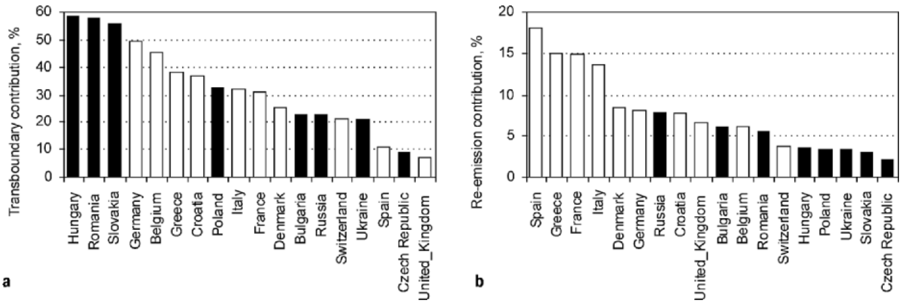


Figure 9. Contributions of trans-boundary transport (a) and re-emission (b) to the POPs air pollution in some European countries in 2001 (data on Eastern European countries are given in black).

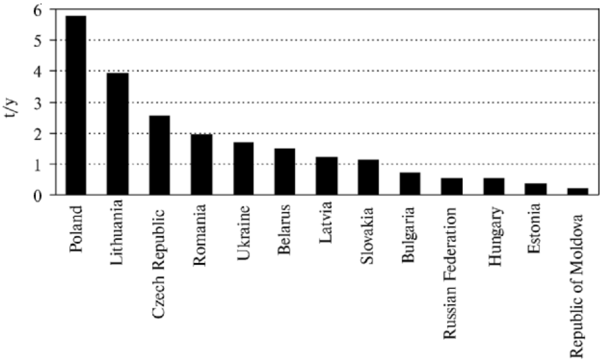


Figure 10. Contributions of Eastern European countries to B[a]P trans-boundary depositions for 2001.

on the environmental risks due to trans-boundary pollution for other countries is also available (http://www.msceast.org).

1.6. POPs Transport in the Northern Hemisphere

To evaluate the long-range transport ability of the considered POPs, the amount of each of these pollutants emitted in Europe and transported outside the EMEP region (outflow) was estimated. For the considered POPs the percentage ratio of outflow to annual emissions range from 20% to 80%. For pollutants with the highest long-range transport potential, such as PCBs, HCHs and HCB, calculations on the hemispheric scale were made. To evaluate the importance of intercontinental transport for these pollutants, calculations of their transport from different groups of sources such as

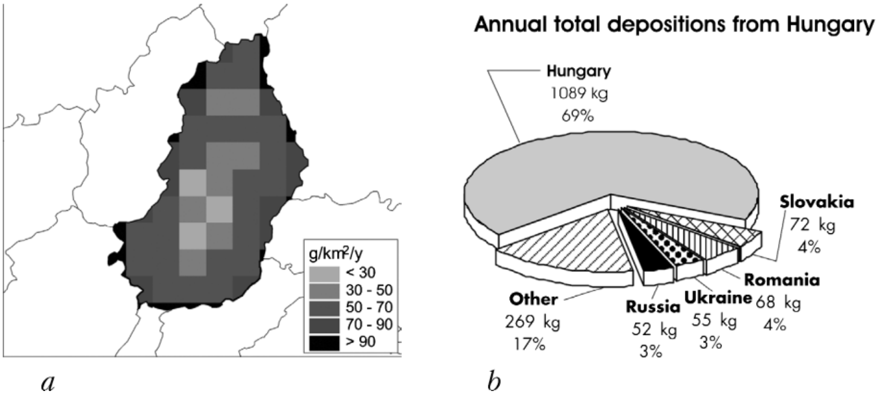


Figure 11. Contribution of European countries to B[a]P depositions to Hungary (a) and distribution of B[a]P depositions from Hungarian sources over European countries (b).

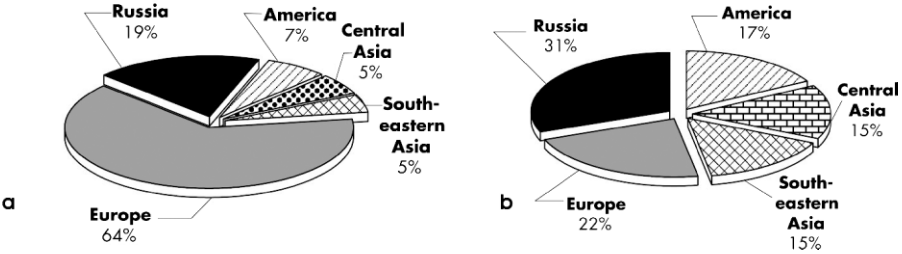


Figure 12. Contributions of emission sources located in the Northern Hemisphere to depositions of HCB over Europe (a) and the Arctic (b), 2000.

European, American, and so on were carried out. To make these calculations tentative hemispheric emission data for these pollutants were used.

On the basis of calculations made contributions of different groups of emission sources located in the Northern Hemisphere, for instance, to HCB depositions over Europe and the Arctic were evaluated (Figures 12(a) and (b)). The contributions of remote source groups in the contamination of these regions are essential. Contributions of Russian emission sources to the European and Arctic contamination amount to about 19% and 31%, respectively. The relevant sum values of Canada and USA are 7% for the European domain and 17% for the Arctic.

At present evaluation of POP depositions to various types of the underlying surface are under investigations. The spatial distribution of PCB-153 depositions to areas covered with forests, soil and seawater in 2000 is demonstrated in Figure 13. Depositions of this pollutant to forests, soil and seawater were estimated using different parameterizations of dry deposition velocities for different types of underlying surfaces. This resulted in considerable differences in depositions to the considered areas. As seen from the maps, the highest levels of PCB-153 depositions were characteristic of forested areas (Dutchak et al., 2004).

2. SIMULATION OF POPS BEHAVIOR IN SOIL COMPARTMENT

To make adequate environmental policies concerning a reduction of the emission of POPs, the risks resulting from the deposition of POPs should be estimated. For that purpose some models to assess the risks of POPs in terrestrial ecosystems have been created (Bakker et al., 1998). The most important step of the approaches is developing models for computation of POP concentrations in soil from the data of their load on the land surface (see section 1). Based on these results, the estimating environmental risk from POPs accumulation in the soil compartment was carried out (Vasilyeva and Shatalov, 2004).

2.1. Priority POPs and Their Permissible Levels in Soil

During the latest decade several international working groups indicated priority classes of POPs, some representatives of which are shown on Figure 14. They are

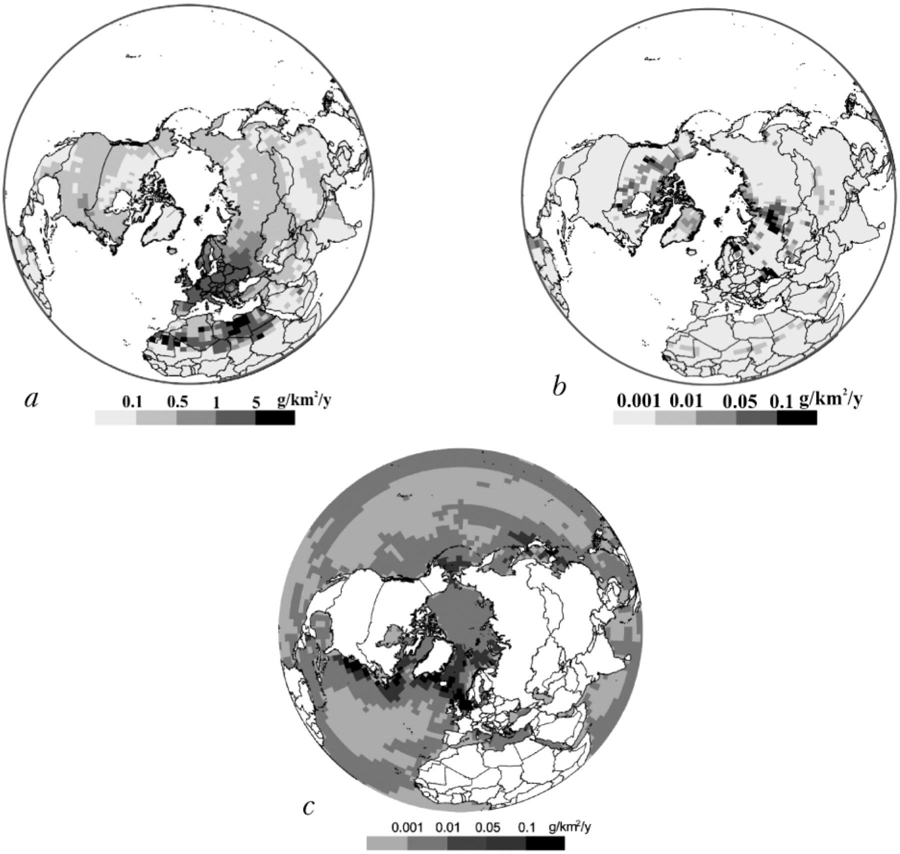


Figure 13. Spatial distribution of PCB-153 depositions on forests (a), soil (b), and sea (c) in 2000 (Mantseva et al., 2004).

several chlorinated pesticides (including DDT, lindane and hexachlorobenzene), dioxins (including 75 congeners of polychlorinated dibenzodioxines and 135 polychlorinated dibenzofuranes), polychlorinated biphenyls (totally 209 congeners) and polycyclic aromatic hydrocarbons (including benz(a)pyrene and others).

Current characteristic of POP levels in background soils are considerably different (Table 1). In some soils their concentrations exceed their permissible levels, which also deviate substantially depending on country and land use.

2.2. POP Transformations in Soil Compartments

The concept of equilibrium distribution of organic chemicals between medium components is widely used for the mathematical description of their degradation and migration processes in soil and other environmental compartments. This is also useful

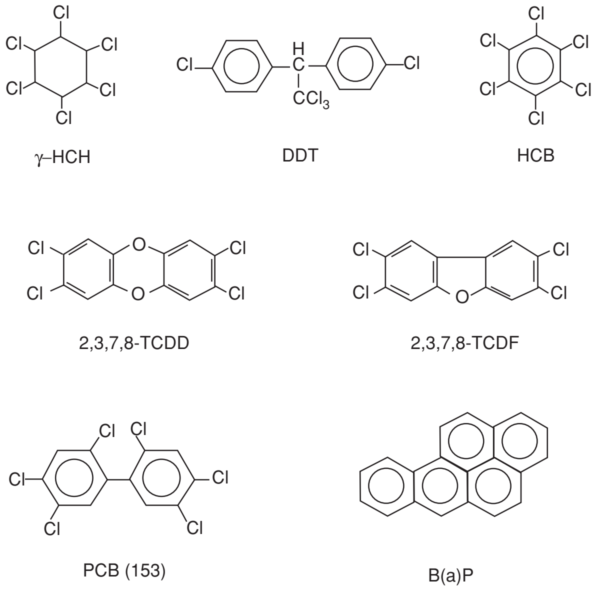


Figure 14. Some representatives of priority POPs.

for environmental risk assessment. The equilibrium distribution means the reversible partitioning of the chemicals at equilibrium conditions between the components. Distribution of a chemical in soil is described with the help of partition coefficients, i.e., the ratios of equilibrium concentrations in soil air, soil solution and solid matrix. It

Table 1. Intervals of POP concentrations in modern background soils (mkg/kg) and their Maximum Permissible Concentrations (MPC) or Interim Acceptable Levels (IAL) in soil accepted in various countries.

POPs	Concentrations in background soils (Vasilyeva and Shatalov, 2004)	MPC or IAL (Bakker et al., 1998)
Total PAHs:	2–186,000	1,000–200,000
Including B[a]P	1–130	2.7–50,000
Total PCBs	0.1–1,000	10–10,000
Total DDT	n.d.*–70,000	10–100
Total (α, β, γ)HCH	n.d.–1,000	5–100
HCB	0.01–10	1.2
Total PCDD/Fs	0.0001–6	0.004

*n.d.—not detectable

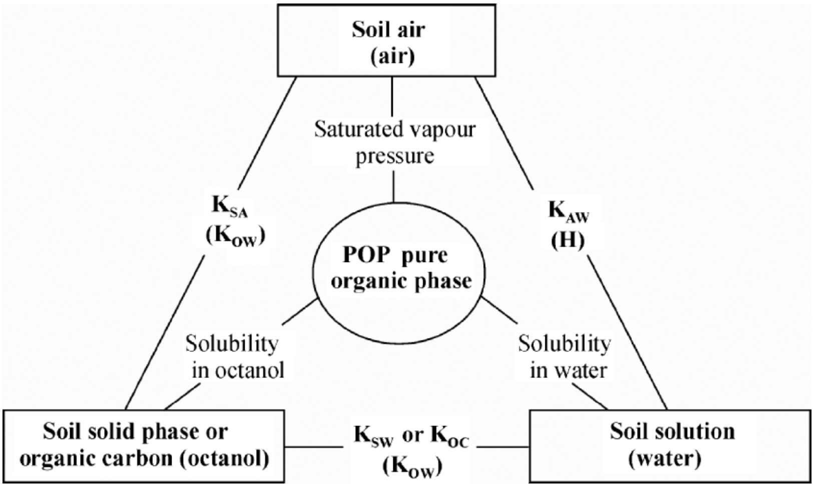


Figure 15. The diagram represents relation of partition coefficients describing POP partitioning between main soil components and respective physical-chemical properties of the chemicals given in brackets (Vasilyeva, Shatalov, 2004).

is also assumed that the equilibrium is set up immediately. Figure 15 represents a diagram of the relationship of partition coefficients of an organic pollutant between three soil phases: gaseous, liquid and soil organic matter (the principal indicator of the chemical distribution in the soil matrix) and associated physicochemical properties of the pollutant.

The following physical-chemical properties and related partition coefficients affect the distribution of a persistent organic chemical in soil:

- Saturated vapor pressure of a pure solid substance (P_S) or of its subcooled liquid (P_L) is an indicator of the substance volatility. These and other physical-chemical properties and distribution coefficients can be found in the handbook (Mackay et al., 1992b).
- The indicator of volatility from the water surface is Henry's law constant (H) or the coefficient of air–water distribution K_{AW} determined as a relationship of concentrations in air and water ($K_{AW} = C_A/C_W$). This coefficient is connected with H by the equation: $K_{AW} = H/RT$, where R is the gaseous constant ($R = 8.314$ Pa m^3/mol K) and T is the temperature (K).
- Partition coefficient between *n*-octanol and water (K_{OW}) is an indicator of a compound hydrophobicity and its capability to be accumulated in natural organic phases (soil organic matter, microorganisms, algae, plants and higher organisms). It is shown that living and nonliving organic matter has similar sorption properties relative to non-polar organic pollutants and very similar absorption capability with

octanol. In spite of low content of the specific organic matter in the majority of soils, the soil organic phase exhibits high specific storage capacity for hydrophobic organic contaminants.

- Partition coefficient between octanol and air (K_{OA}) is determined by the relationship of chemical concentrations in octanol and air ($K_{OA} = C_O/C_A$). The K_{OA} is directly connected with the soil–air partition coefficient of pollutant K_{SA} which is determined as the ratio of solid phase to air concentrations ($K_{SA} = C_S/C_A$) or through other constants ($K_{SA} = K_{SW}/K_{AW}$).
- The linear relationship between the K_{OW} and partition coefficients of a great range of organic contaminants between solid and liquid phases of soil (K_{SW}) is established. It is determined as the relationship of POP concentration in the solid phase and soil solution ($K_{SW} = C_S/C_W$) or through the equation $K_{OC} = K_{SW}/f_{OC}$. The K_{OC} can be determined experimentally or estimated from K_{OW} by a regression equation: $K_{OC} = 0.4^* K_{OW}$ (Karikhoff et al., 1979; Seth et al., 1999) with scattering of K_{OC} is within 2.5 orders of magnitude.

Thus, in according to the concept of equilibrium distribution, the relation of an organic pollutant concentration in the soil solid and liquid phase is constant at any moment (Vasilyeva and Shatalov, 2004). The example of such an approach application for assessing exposure pathways of POPs to living biota is shown in Box 1.

Box 1. Numerical experiments for assessing exposure pathways (Vasilyeva and Shatalov, 2004)

Two new mechanisms of POP adsorption to soil organic matter have been revealed, which influence migration and accumulation of these chemicals in soil and determine the exposure pathways to living organisms. They are: 1—POP adsorption to the dissolved organic matter and 2—dividing of a POP adsorbed by soil organic matter to equilibrium and non-equilibrium fractions or to readily and potentially available ones respectively. Some numerical experiments were carried out to demonstrate the importance of these processes in modelling the pollutants transport and accumulation in soil. These experiments have been given more in detail in (Vasilyeva and Shatalov, 2002).

Exposure pathways were estimated using the modified soil module of the MSCE-POP model (http://www.msceast.org). At present the scheme is complemented with the fraction of dissolved organic matter (f_{DOC}) and with the fraction of the chemical non-equilibrium adsorbed by solid phase ($f_{\text{non-equil}}$) or low available with individual degradation rate. The scheme of a pollutant distribution between different soil components is shown in Figure 16.

The share of a substance adsorbed by DOC is calculated by the partition coefficient of equilibrium partitioning between DOC and the dissolved phase $f_{DOC}K_{DOC}$. In this context it is assumed that the DOC fraction is 1% of total organic matter in soil

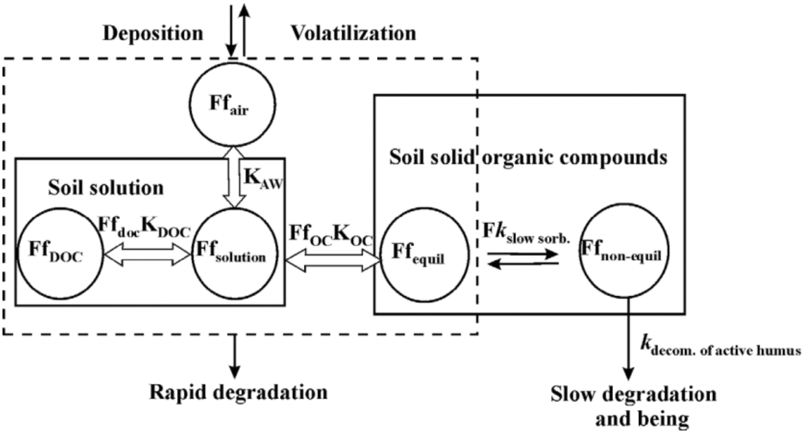


Figure 16. Model realization of POP partitioning between soil components and its degradation.

$f_{DOC} = 0.01 f_{SOM}$. K_{DOC} is assessed through the dependence given earlier (Vasilyeva and Shatalov, 2004). Note that the pollutant associated with DOC is transported with the soil solution.

According to model assumptions the solid non-equilibrium adsorbed (potentially available) fraction of POP is adsorbed by 70% of soil organic matter. The rest of the organic chemical (readily available) is equilibrium adsorbed by the remaining 30% of soil organic matter. This ratio was obtained by M. Krauss et al. 2000 for characteristic congener PCB-153 while investigating urban and rural soils in Germany. The exchange between these phases takes place according to the first order kinetic equation with characteristic time $T_{\text{non-equil},50} = 1$ year. It is also assumed that the non-equilibrium adsorbed fraction degrades "slowly". Its degradation practically coincides with the degradation rate of humus itself with half-life 25 year. It corresponds approximately to the half-life of SOM in soils of temporal climate (Vasilyeva and Shatalov, 2002). A pollutant equilibrium adsorbed by SOM is "rapidly" degraded with a constant rate depending on an individual pollutant.

Following the scheme used, the pollutant migration over the soil horizon is conditioned by diffusion processes in the liquid and gaseous phase and by the transport of the real dissolved and adsorbed to DOC fractions of a pollutant together with the liquid flow J_w. The vertical soil profile is represented by 5 calculation layers with boundary on (from top to bottom) (1) 0.01, (2) 0.05, (3) 0.2, (4) 0.8 and (5) 3 cm.

The general formulation of the numerical problem was as follows. PCB-153 was selected as a characteristic POP, which physical-chemical properties were used in the experiment. This is due to the fact that the properties of this indicator congener are often used for calculations of the long-range transport of PCB mixture (Pekar et al., 1998). Besides it was demonstrated that soil is the most important accumulating compartment in calculations of PCB transport. Physical-chemical properties of

PCB-153 at temperature 25 °C can be found in (Shatalov et al., 2001). Modeling was performed at soil organic carbon content $f_{OC} = 5\%$ typical of usual chernozem. The wet precipitation flux was assumed equal to $J_w = 10$ cm/yr.

In calculations two periods were considered—the accumulation time (5 years), during which PCB atmospheric concentration was 1 ng/m^3 and the clearance interval with air concentration assumed equal to zero. It was considered that pollutant input to soil takes place only due to gas exchange with the atmosphere. The calculations resulted in the profile of pollutant vertical distribution. This profile allows drawing conclusions about the penetration depth variation.

2.3. *Evaluation of POP Accumulation and Clearance in Soil*

Using the proposed algorithm of POP simulation, the assessment of the most important effects related to presence of dissolved organic carbon, DOC, was studied on POP transport, and the calculation results with and without consideration of DOC adsorbed fraction are considered below. The comparison of the curves depicted in Figure 17 indicates that the consideration of DOC phase increases the pollutant concentration in soil as much as 1.8 times during 5 years, and the difference remained during the clearance period. It is explained by more intensive transport of DOC adsorbed pollutant together with the water flow.

Besides, introduction of DOC phase increases the depth of POP penetration down to soil profile. By the 5th year at the stage of accumulation as well as of clearance, the POP concentration in the deeper soil layers is up to 5 times higher than that obtained without DOC phase.

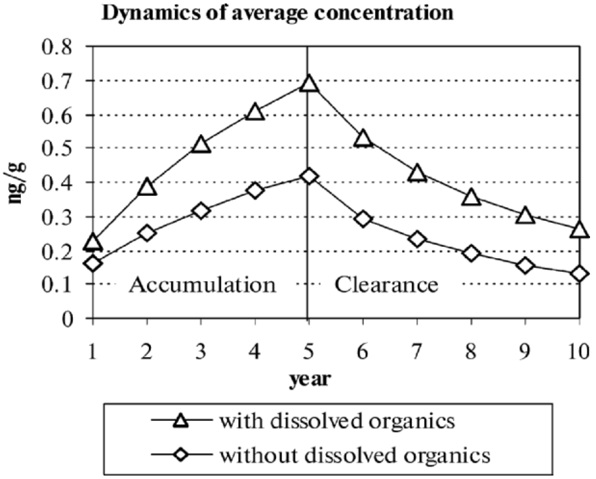


Figure 17. The comparison of average concentration of the POP in soil during 5-year periods of accumulation and clearance calculated with and without DOC consideration (Vasilyeva and Shatalov, 2004).

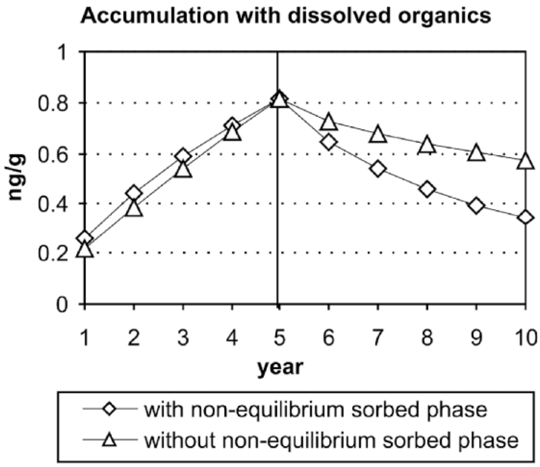


Figure 18. The comparison of average concentration of PCB-153 in soil accumulated during 5-year periods of accumulation and clearance calculated with and without consideration of non-equilibrium adsorbed POP fraction (DOC participation was also taken into account (Vasilyeva and Shatalov, 2004).

Another mechanism of POP transport is connected with adsorption processes. The relevant calculation results, with and without consideration of fraction of non-equilibrium adsorbed POP, are presented in Figure 18.

The figure shows that during a 5-year accumulation period of PCB-153, with the consideration of this fraction in the beginning of experimental time, the process proceeds slower but by the end of the period it is slightly accelerated. An additional calculation run of PCB-153 accumulation a during 20-years period shows that the consideration of the low available fraction leads to a tangible increase of soil capacity resulting from the low intensity of degradation processes in this phase. As to the clearance period the consideration of the non-equilibrium sorption leads to slower decline of the pollutant concentration. In particular, by the end of the period the difference reaches 1.7 times. The consideration of this fraction also increases the pollutant vertical penetration in soil.

Thus the consideration of kinetics of POP sorption by particulate soil organic matter appreciably changes the pollutant vertical distribution, particularly during the clearance period, which increases this period substantially. Accordingly, this is of great importance to environmental risk assessment of POPs exposure to living organisms.

3. EXPOSURE PATHWAYS OF DIOXINS AND DIOXIN-LIKE POLYCHLORINATED BIPHENYLS TO HUMAN

3.1. General Description of Dioxins

In this section we will consider the exposure pathways of POPs to human beings on the example of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans

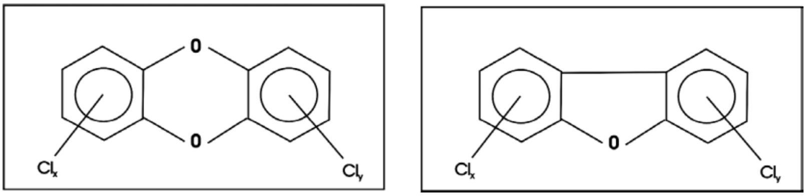


Figure 19. General formulas of polychlorinated dibenzo-pdioxins, PCDDs (left) and polychlorinated dibenzofurans, PCDFs (right).

(PCDD/ PCDFs), often called just “dioxins”. These species consist of two groups of tricyclic aromatic compounds with similar chemical and physical properties. The number of chlorine atoms in each molecule can vary from one to eight. The number of chlorine atoms and their positions are of utmost importance for the toxicological potency of each congener. PCDD/PCDFs have never been produced intentionally, except for pure substances used as references in analytical and toxicological research, and have never served any useful purpose, unlike many other POPs such as polychlorinated biphenyls (PCBs) and DDT. PCDD/PCDFs are formed as unwanted by-products in many industrial and combustion processes. They have also been shown to be formed in the environment by forest fires and volcanoes, and also via enzymatically catalysed processes. The natural formation is in general of less importance compared to the anthropogenic. The general formulas of these compounds are shown in Figure 19.

Primary sources of environmental contamination with PCDD/PCDFs in the past were the production and use of organic chemicals containing chlorine. PCDFs were formed as inadvertent by-products in the production and use of PCBs and, in combination with PCDDs, in such high-temperature processes as waste incineration, the metal industry, home heating and other energy production processes.

PCDFs are also found in residual waste from the production of vinyl chloride and the chlor-alkali process for chlorine production. Factors favourable for the formation of PCDD/PCDFs are high temperatures, alkaline media, the presence of ultraviolet light, and the presence of radicals in the reaction mixture/chemical process (Fiedler, 1999; Hutzinger and Fiedler 1993).

Previous production of pentachlorophenol, as well as the bleaching process in pulp and paper mills, has been shown to be a major source. Changes in industrial processes have resulted in a reduction of PCDD/PCDFs concentration in products. Whereas in the past the chemical industry and, to a lesser extent, the pulp and paper industry were considered to be the main sources of PCDD/PCDFs (and also the cause of many of today’s contaminated sites in several industrialized countries), today’s dioxin input is mainly due to thermal processes. There is still a considerable focus on waste incineration but, owing to requirements for dioxin reduction in stack gases set by several national authorities, the importance of this category has declined during the last years. Examples can be seen especially in the European emission inventories

Table 2. Sources of emission of PCDD/PCDFs.

Stationary sources	
Waste incineration	Municipal solid waste, clinical waste, hazardous waste, sewage sludge
Steel industry	Steel mills, sintering plants, hot-strip mills
Recycling plants	Non-ferrous metals (melting, foundry Al, Cu, Ptx, Zn, Sn)
Energy production	Fossil fuel power plants, wood combustion, landfill gas
Diffuse sources	
Traffic	Cars
Home heating	Coal, oil, gas, wood
Accidents	PCB fires, fires in building, forest fires, volcanic eruptions

Source: Fiedler, 1999

(Fiedler 1999). An overview of combustion sources known to generate and emit PCDD/PCDFs (Fiedler, 1999) is presented in Table 2.

PCDD/PCDFs are found not only in stack gases but also in solid residues from any combustion process such as bottom ash, slag and fly ash. With advanced technology and better burnout of the ashes and slag (characterized by a low content of organic carbon), PCDD/PCDFs concentrations have declined (Fiedler, 1999).

Secondary sources of PCDD/PCDFs, their reservoirs, are those matrices where they are already present, either in the environment or as products. Product reservoirs include PCP-treated wood, PCB-containing transformers and sewage sludge, compost and liquid manure, which can be used as fertilizers in agriculture and gardens. Reservoirs in the environment are, for example, landfills and waste dumps, contaminated soils (mainly from former chemical production or handling sites), and contaminated sediments (especially in harbours and rivers with industries discharging directly to the waterways).

Although these reservoirs may be highly contaminated with PCDD/PCDFs, the chemical and physical properties of these compounds imply that dioxins and furans will stay adsorbed to organic carbon in soils or other particles. On the other hand, mobilization can occur in the presence of lipophilic solvents (leaching into deeper layers of soils and/or groundwater) or in cases of erosion or run-off from topsoil (translocation into the neighbourhood). Experience has shown that transport of PCDD/PCDFs due to soil erosion and run-off does not play a major role in environmental contamination and human exposure (Fiedler 1995, 1999).

The polychlorinated biphenyls (PCBs) have been used commercially since 1929 as dielectric and heat exchange fluids and in a variety of other applications. The presence of PCBs in human and wildlife tissues was first recognized in 1966. Investigations in many parts of the world have since revealed widespread distribution of PCBs in the environment, including remote areas with no PCB production or use. There is evidence that the major source of PCB exposure in the general environment is the redistribution of PCBs previously introduced into the environment. It is believed that large bodies of water, such as the Baltic Sea and the Canadian Great Lakes, may release significant amounts of PCB residues from previous uses into the atmosphere. The fact that PCB levels seem to decline in a similar way at different latitudes indicates that primary sources may play still an important role. The amount of dioxin-like PCBs might vary in the environment but the sources, transport and distribution, as well as persistence, show similarities with the general properties of PCBs.

3.2. Potential for Long-Range Trans-Boundary Air Pollution

PCDD/PCDFs are very persistent compounds; as their Kow and Koc are very high, they will intensively adsorb on to particles in air, soil and sediment and accumulate in fat-containing tissues. The strong adsorption of PCDD/PCDFs and related compounds to soil and sediment particles means that their mobility in these environmental compartments is negligible. Their mobility may be increased by the simultaneous presence of organic solvents such as mineral oil. The air compartment is probably the most significant compartment for the environmental distribution and fate of these compounds.

Some of the PCDD/PCDFs emitted into air will be bound to particles while the rest will be in the gaseous phase, which can be subject to long-range transport (up to thousands of kilometers). In the gaseous phase, removal processes include chemical and photochemical degradation. In the particulate phase, these processes are of minor importance and the transport range of the particulate phase will primarily depend on the particle size. PCDD/PCDFs are extremely resistant to chemical oxidation and hydrolysis, and hence these processes are not expected to be significant in the aquatic environment. Photodegradation and microbial transformation are probably the most important degradation routes in surface water and sediment.

The number of chlorine atoms in each molecule can vary from one to eight. Among the possible 210 compounds, 17 congeners have chlorine atoms at least in the positions 2, 3, 7 and 8 of the parent molecule and these are the most toxic, bioaccumulative and persistent ones compared to congeners lacking this configuration. All the 2,3,7,8-substituted PCDDs and PCDFs plus coplanar PCBs (with no chlorine substitution at the *ortho* positions) show the same type of biological and toxic response.

PCDD/PCDFs are characterized by their lipophilicity, semi-volatility and resistance to degradation. The photodegradation of particle-bound PCCD/PCDFs in air was found to be negligible (Koester and Hites, 1992). These characteristics predispose these substances to long environmental persistence and to long-range transport. They are also known for their ability to bioconcentrate and biomagnify under typical environmental conditions, thereby potentially achieving toxicologically relevant concentrations. The tetra–octa PCCD/PCDFs have lower vapour pressures than PCBs and are therefore not expected to undergo long-range transport to the same extent (Mackay et al., 1992); nevertheless there is evidence for deposition in Arctic soils and sediments (Brzuzy and Hites, 1996; Oehme et al., 1993; Wagrowski and Hites, 2000).

Persistence in Water, Soil and Sediment

Owing to their chemical, physical and biological stability, PCDD/PCDFs are able to remain in the environment for a long time. As a consequence, dioxins from so-called “primary sources” (formed in industrial or combustion processes) are transferred to other matrices and enter the environment. Such secondary sources are sewage sludge, compost, landfills and other contaminated areas (Fiedler, 1999).

PCBs and PCDD/PCDFs are lipophilic (lipophilicity increases with increasing chlorination) and have very low water solubility. Because of their persistent nature and lipophilicity, once PCDD/PCDFs enter the environment and living organisms they will remain for a very long time, like many other halogenated aromatic compounds. As log K_{OW} (typically 6–8) or log K_{OC} are very high for all these compounds, they will intensively adsorb on to particles in air, soil and sediment. The strong adsorption of PCDD/PCDFs and related compounds to soil and sediment particles causes their mobility in these environmental compartments to be negligible.

Their mobility may be increased by the simultaneous presence of organic solvents such as mineral oil. The half-life of TCDD in soil has been reported as 10–12 years, whereas photochemical degradation seems to be considerably faster but with a large variation that might be explained by experimental differences (solvents used, etc.). Highly chlorinated PCDD/PCDFs seem to be more resistant to degradation than those with just a few chlorine atoms.

Bioaccumulation

The physicochemical properties of PCBs and their metabolites enable these compounds to be absorbed readily by organisms. The high lipid solubility and the low water solubility lead to the retention of PCCD/PCDFs, PCBs and their metabolites in fatty tissues. Protein binding may also contribute to their tissue retention. The rates of accumulation into organisms vary with the species, the duration and concentration of exposure, and the environmental conditions. The high retention of PCDD/PCDFs and PCBs, including their metabolites, implies that toxic effects can occur in organisms spatially and temporally remote from the original release.

Gastrointestinal absorption of TCDD in rodents has been reported to be in the range of 50–85% of the dose given. The half-life in rodents ranges from 12 to 31 days except for guinea-pigs, which show slower elimination ranging from 22 to 94 days. The half-life in larger animals is much longer, being around 1 year in rhesus monkeys and 7–10 years in humans.

Monitoring

PCCD/PCDFs have been found to be present in Arctic air samples, e.g. during the winter of 2000/2001 in weekly filter samples (particulate phase) collected at Alert in Canada. PCDD/PCDFs have been monitored since 1969 in fish and fish-eating birds from the Baltic. The levels of PCDD/PCDFs in guillemot eggs, expressed as TEQ, decreased from 3.3 ng/g lipids to around 1 ng/g between 1969 and 1990. Since 1990, this reduction seems to have levelled off and today it is uncertain whether there is a decrease or not. Fish (herring) show a similar picture.

Thus both physical characteristics and environmental findings support the long-range transport of PCCD/PCDFs and PCBs. There are differences, however, both between and within the groups regarding ability to undergo LRTAP.

3.3. Pathways of LRTAP-Derived Human Exposure

For decades, many countries and intergovernmental organizations have taken measures to prevent the formation and release of PCDD/PCDFs, and have also banned or severely restricted the production, use, handling, transport and disposal of PCBs. As a consequence, release of these substances into the environment has decreased in many developed countries. Nevertheless, analysis of food and breast-milk show that they are still present, although in levels lower than those measured in the 1960s and 1970s. At present, the major source of PCB exposure in the general environment appears to be the redistribution of previously introduced PCBs.

Significant Sources and Magnitude of Human Exposure

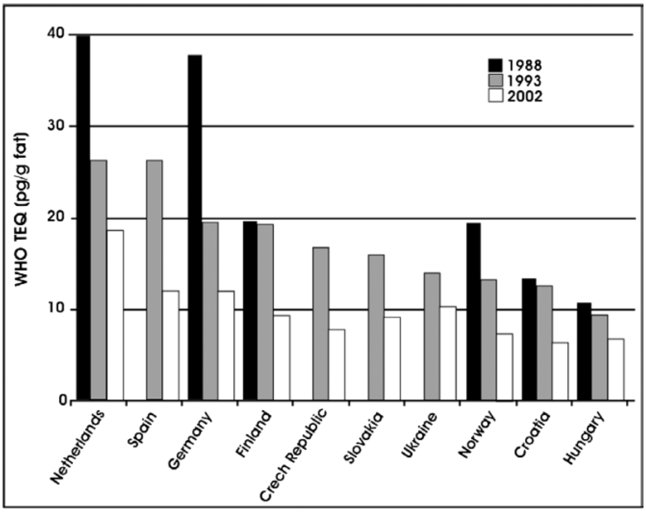
PCDD/PCDFs are today found in almost all compartments of the global ecosystem in at least trace amounts. They are ubiquitous in soil, sediments and air. Excluding occupational or accidental exposures, most human background exposure to dioxins and PCBs occurs through the diet, with food of animal origin being the major source, as they are persistent in the environment and accumulate in animal fat.

Importantly, past and present human exposure to PCDD/PCDFs and PCBs results primarily from their transfer along the pathway: atmospheric emissions → air → deposition → terrestrial/aquatic food chains → human diet. Information from food surveys in industrialized countries indicates a daily intake of PCDD/PCDFs on the order of 50–200 pg I-TEQ/person per day for a 60 kg adult, or 1–3 pg I-TEQ/kg bw per day. If dioxin-like PCBs are also included, the daily total TEQ intake can be higher by a factor of 2–3. Recent studies from countries that started to implement measures to reduce dioxin emissions in the late 1980s clearly show decreasing PCDD/PCDF and PCB levels in food and, consequently, a lower dietary intake of these compounds by almost a factor of 2 within the past 7 years.

Biota from the Baltic have, however, not shown any clear trend for dioxins or PCBs since 1990. Occupational exposures to both PCDDs and PCDFs at higher levels have occurred since the 1940s as a result of the production and use of chlorophenols and chlorophenoxy herbicides and to PCDFs in metal production and recycling. Even higher exposures to PCDDs have occurred sporadically in relation to accidents in these industries. High exposures to PCDFs have occurred in relation to accidents such as the Yusho (Japan) and Yucheng (Taiwan) incidents, involving contamination of rice oil and accidents involving electrical equipment containing PCBs.

Exposure Levels in Adults

PCDD/PCDFs accumulate in human adipose tissue, and the level reflects the history of intake by the individual. Several factors have been shown to affect adipose tissue concentrations/body burdens, notably age, the number of children and period of breastfeeding, and dietary habits. Breast-milk represents the most useful matrix for evaluating time trends of dioxins and many other POPs. Several factors affect the PCDD/PCDFs content of human breast-milk, most notably the mothers age, the duration of breast-feeding and the fat content of the milk. Studies should therefore ideally



Source: van Lee uwen et al. 2002.

Figure 20. Temporal trends in the levels of dioxins and furans in human milk in various countries participating in consecutive rounds of the WHO exposure study (Alcock and Bashkin et al., 2003).

be performed on samples from a large number of mothers, taking these variables into account.

The WHO Regional Office for Europe carried out a series of exposure studies aimed at detecting PCBs, PCDDs and PCDFs in human milk. The first round took place in 1987–1988 and the second in 1992–1992. In 2001–2002, a third round was organized in collaboration with the WHO Global Environmental Monitoring System/Food Contamination Monitoring and Assessment Programme (GEMS Food) and the International Programme on Chemical Safety (IPCS) (van Leeuwen and Malisch, 2002). Results are currently available from 21 countries. Figure 20 presents the temporal trends of levels of PCDDs and PCDFs expressed in WHO-TEQ for those countries participating in all three rounds or in the last two rounds of the WHO study. A clear decline can be seen, with the largest decline for countries originally having the highest level of dioxin-like compounds in human milk.

The general population is mainly exposed to PCBs through common food items. Fatty food of animal origin, such as meat, certain fish and diary products are the major sources of human exposure. Owing to considerable differences in the kinetic behaviour of individual PCB congeners, human exposure to PCB from food items differs markedly in composition compared to the composition of commercial PCB mixtures.

PCB levels in fish have been decreasing in many areas since the 1970s, but the decrease has levelled off during the last couple of years. Today, the daily PCB intake is estimated to be around 10 ng/kg bw for an adult. More information on human exposure to PCBs is given in (Health risks . . . , 2003).

Exposure Levels in Children (Including Prenatal Exposure)

Once in the body, PCBs and PCDD/PCDFs accumulate in fatty tissues and are slowly released. Lactation or significant weight loss increases the release of the substances into the blood. PCBs can cross the placenta from mother to fetus, and are also excreted into the breast-milk. PCB and PCDD/PCDF concentrations in human milk are usually higher than in cow's milk or other infant foods. As a result, breastfed infants undergo higher dietary exposure than those who are not breastfed. This concerns particularly breastfed infants of women exposed to high levels of PCBs, including Inuit and women whose diet is mainly based on fish from highly contaminated rivers and lakes, such as the Great Lakes and the Baltic Sea. Time-trend information suggests that PCDD/PCDF and PCB concentrations in human milk have decreased significantly since the 1970s in countries that have taken measures against these substances. However, the decrease has leveled off during the last couple of years. Therefore, current fetal and neonatal exposures continue to raise serious concerns regarding potential health effects on developing infants.

Compared to adults, the daily intake of PCDD/PCDFs and PCBs by breastfed babies is 1–2 orders of magnitude higher. A recent field study showed higher mean levels of PCDD/PCDFs and PCBs in human milk in industrialized areas (10–35 pg I-TEQ/g milk fat) and lower levels in developing countries (<10 pg I-TEQ/g milk fat). Very few studies have been performed on Arctic populations with respect to the exposure of children to these substances. It is likely, however, that the differences in exposure between children and adults demonstrated in many industrialized regions also exist in Arctic regions.

Potential for High Exposure Situations

It has been shown that these substances, and especially PCBs, can occur in elevated concentration in Arctic fauna. As the diet of many Arctic populations relies to a vast extent on marine mammals that represent high trophic levels, human exposure has been shown to be considerably high compared to industrialized areas.

Significance of LRTAP as a Source of Total Exposure

There are clear connections between food habits and the levels of different POPs, including PCCD/PCDFs and coplanar PCBs, found in humans. The current substances, especially PCBs, have been shown to be capable of transport over long distances. Indigenous people who rely heavily on marine mammals will therefore face a comparably high exposure to different POPs, and atmospheric transport is likely to play an important role in the presence of these animals in remote areas.

3.4. Health Hazard Characterization

Toxicokinetics

The physicochemical properties of both PCDD/PCDFs and coplanar PCBs enable these compounds to be readily absorbed by organisms. The high lipid solubility and low water solubility of all congeners lead to the retention of the compounds in fatty tissues. Once absorbed, the compounds are readily distributed to all body compartments, where the storage rate is proportional to the fat content of the organ. The metabolism and excretion of 2,3,7,8-substituted PCCD/PCDFs and PCBs is very slow.

The main route of excretion is via the faeces (biliary excretion), urine and breast-milk. Excretion through breast-milk results in transfer to breastfed infants, who therefore are highly exposed. There is also transfer across the placenta, thus causing fetal exposure. Perinatal exposure is a major concern with regard to human health effects, even at present background exposure levels.

Effects on Laboratory Animals and the TEF-Concept

As 2,3,7,8-substituted PCDD/PCDFs and coplanar PCBs are believed to act through a common toxicological mechanism, a toxic (or TCDD) equivalency factor (TEF) concept has been established. The concept is based on the observation that, even if the current substances act via a common mechanism, they do so with varying potency. A couple of different schemes have therefore been proposed whereby the toxic potencies of all substances are related to the most potent substance of the group, TCDD. The toxicity of TCDD is set to 1.0 and all the other substances are given individual toxicity factors, which are fractions of 1.0. Thus, the combined toxicity of all congeners in a sample, expressed as a toxic equivalent (TEQ) can be calculated by multiplying the amount or concentration of the individual substances with the respective TEF and adding the products.

The TEF concept has gained wide acceptance and many different schemes have been proposed. Nowadays, the use of the TEFs for dioxins, dibenzofurans and PCBs for humans and mammals suggested by WHO is often recommended (van den Berg et al., 1998). The TEF scheme includes a kind of safety factor, as the TEF values are rounded upwards.

However, no studies on fetal exposure are available for setting TEFs. Thus there is a need for dose–response studies of the critical effects, based on synthetic mixtures reflecting the human exposure situation. The WHO TEFs for dioxins, dibenzofurans and PCBs for humans and mammals are given in Table 3.

Non-Cancer Endpoints

A plethora of effects have been reported from multiple animal studies following exposure to PCDDs, PCDFs and PCBs. The most extensive data set on dose–response effects is available for 2,3,7,8-TCDD; less information is available for the other dioxin-like compounds. Therefore, the focus of the evaluation of the animal data is on the effects of 2,3,7,8-TCDD.

Among the most sensitive endpoints (on a body burden basis) are: endometriosis, developmental neurobehavioural (cognitive) effects, hearing loss, developmental reproductive effects (sperm counts, female urinogenital malformations) and immunotoxic effects, both adult and developmental. The most sensitive biochemical effects are CYP1A1/2 induction, hepatic retionid depletion, EGF-receptor down-regulation and oxidative stress.

Table 3. WHO TEF values for human risk assessment.

Congener	TEF value	Congener	TEF value
DibonzO'P' dtoxim		*Non-ortho PCB*	
2.3.7.8-TCDD	1	PCB77	0.0001
1.2.3.7,8-PnCDD	1	PCB81	0.0001
1.2.3.4,7,8-HxCDD	0.1	PCB126	0.1
1.2,3.6,7,8-HxCDD	0.1	PCB169	0.01
1.2,3.7,8,9-HxCDD	0.1		
1.2,3.4,6,7,8,-HpCDD	0.01		
OCOD	0.0001		
Dibonzofuram		*Mono-Oftho PC8*	
2.3.7.8-TCDF	0.1	PCB105	0.0001
1.2,3.7,8-PnCDF	0.05	PCB114	0.0005
2.3,4.7,8-PnCDF	0.5	PCB118	0.0001
1.243.4,7.8-HxCDF	0.1	PCB123	0.0001
1.2,3.6,7.8-HxCDF	0.1	PCB156	0.0005
1,243.7,8.9-HxCDF	0.1	PCB157	0.0005
2.3,4.6,7.8-HxCDF	0.1	PCB167	0.00001
1.243,4,6.7,8-HpCDF	0.01	PCB189	0.0001
1.243,4.7.8,9-HpCDF	0.1		
OCDF	0.0001		

Source: Van den Berg et al., 1998.

Carcinogenic Effects

2,3,7,8-TCDD has been shown to be carcinogenic in several long-term studies at multiple sites in several species and in both sexes. Short-term studies observed a lack of direct DNA-damaging effects, including covalent binding to DNA by TCDD, which underscores that TCDD does not act as an initiator of carcinogenesis. However, secondary mechanisms may be important in the observed carcinogenicity of TCDD and related dioxin-like compounds. Several PCDDs, PCDFs, non-ortho and mono-ortho PCBs have also been shown to be tumour promoters. The LOAEL of TCDD in the Kociba study was the development of hepatic adenomas in rats at an intake of 10 ng/kg bw per day, and the NOEL was 1 ng/kg bw per day. At the NOEL, the body burden was 60 ng/kg bw (Alcock and Bashkin et al., 2003).

TCDD also causes thyroid tumours in male rats. This has been shown to proceed through a mechanism that involves altered thyroid hormone metabolism and consequent increases in feedback mechanisms, TSH (thyroid stimulating hormone), which results in a chronic proliferative stimulation of thyroid follicular cells.

Health Effects in Humans

There are many studies on the carcinogenicity of 2,3,7,8-TCDD in accidentally exposed workers. Epidemiological studies on people exposed in connection with the accident in Seveso have generated valuable information. Excess risks were observed for ovarian and thyroid cancers and for some neoplasia of the haematopoi-etic tissue; these results were, however, based on small numbers. Epidemiological studies on the cohorts most highly exposed to 2,3,7,8-TCDD produced the strongest evidence of increased risks for all cancers combined, along with less strong evidence of increased risks for cancers of particular sites. The relative risk for all cancers combined in the most highly exposed and longer-latency sub-cohorts is 1.4 (Bertazzi et al., 1998).

Studies of non-cancer effects in children have indicated neurodevelopmental delays and neurobehavioural effects, including neonatal hypotonia. In children in Seveso who were highly exposed to TCDD, small, transient increases in hepatic enzymes, total lymphocyte counts and subsets, complement activity, and non-permanent chloracne were observed. Also, an alteration of the sex ratio (excess female to male) was observed in children born to parents highly exposed to TCDD.

Critical Outcomes and Existing Reference Values

During the last two decades, a number of different risk assessments of dioxins and related compounds have been performed. Since the mid-1990s, coplanar PCBs have often been included in the assessments. In 1997, WHO established an expert group on dioxins and related compounds.

It proposed, based on the TEF scheme shown in Table 3, a TDI for dioxins and related compounds. The proposal was based on kinetic calculations of doses to body burden and vice versa. The body burden approach resulted in a reduced need for a safety factor for extrapolation between species. The two most important studies for estimating LOAEL were both published by Gray et al. (1997a, 1997b). The WHO expert group calculated that a reliable LOAEL probably could be found in the range of 14–37 pg/kg bw per day. By applying a safety factor of 10 to this range, it proposed a TDI of 1–4 pg/kg bw. The group emphasized that the TDI represents a tolerable daily intake for lifetime exposure, and that occasional short-term excursions above the TDI would have no health consequences provided that the averaged intake over long periods was not exceeded. In addition, it recognized that certain subtle effects may be occurring in some sections of the general populations of industrialized countries at current intake levels (2–6 TEQ/kg bw per day), but found it tolerable on a provisional basis since these reported subtle effects were not considered overtly adverse and there were questions as to the contribution of non-dioxin-like compounds to the observed effects. The group therefore stressed that the upper range of the TDI of 4 pg TEQ/kg bw should be considered a maximum tolerable intake on a provisional basis, and that the ultimate goal was to reduce human intake levels to below 1 pg TEQ/kg bw per day. In 2001, the European Commission and the Scientific Committee for Food proposed a temporary TWI of 14 pg/kg bw for 2,3,7,8-PCDD/PCDFs and dioxin-like PCBs.

3.5. Human Health Implications Relative to LRTAP

It has been demonstrated that dioxins and many PCBs resist degradation, bioaccumulate, are transported through air, water and migratory species across international boundaries, and are finally deposited far from the place of release where they can accumulate in terrestrial and aquatic ecosystems. The clearest evidence for this long-range transport derives from the levels of PCDD/PCDFs and PCBs measured in the Arctic. Owing to long-range trans-boundary transport, these substances are nowadays ubiquitous contaminants of the ecosystem and are also present in the food chain. Therefore, most of the human population is exposed to PCDD/PCDFs and PCBs. Moreover, since dioxins and PCBs pass from mother to fetus through the placenta, and from mother to newborn through breastfeeding, infants are at risk of harmful effects in the most critical period of their development. There are just a few reports of dioxins in humans from Arctic regions, but there are plenty of animal samples analyzed for dioxins and PCBs that give information on human exposure through food. As many people living in the Arctic still practice hunting and fishing for an important part of their diet, their exposure to dioxins, PCBs and other contaminants could be elevated compared to people living in industrialized parts of the world (Alcock and Bashkin et al., 2003).

CHAPTER 20

TRANSBOUNDARY GAS AND OIL PIPELINES

Natural gas exploration and transition are accompanied by emission to the atmosphere of various pollutants and first of all, species of nitrogen, carbon, sulfur and some heavy metals. This is connected with different impacts on the surrounding ecosystems in local, regional and continental scale depending upon the areas of exploration and pipeline nets. The extent of impacts is a matter of probability since many uncertainties in both ecosystems properties and impact characteristics are still exist. Accordingly the ERA process is of importance for such activities.

1. OIL AND GAS PIPELINE NETS

1.1. Russian Pipeline Nets

Natural gas and petroleum pipelines play a crucial role in Russia's economy, both in distributing fuel to domestic industrial consumers and in supporting exports to Europe and countries of the Commonwealth of Independent States (former USSR). Their complex network connects production regions with virtually all of Russia's centers of population and industry. Pipelines are especially important because of the long distances between Siberian oil and gas fields and Russia's European industrial centers as well as countries to the west.

In 1993 Russia had 48,000 kilometers of pipeline carrying crude oil, 15,000 kilometers for petroleum products, and 140,000 kilometers for natural gas. In recent decades, the natural gas lines have expanded at a much faster rate than the crude oil lines. The main natural gas pipeline, one of the Soviet Union's largest international trade projects, connects the natural gas fields of northern Siberia with most of the countries of Western Europe. Completed in 1984, the line passes nearly 4,000 kilometers across the Ural Mountains, the Volga River, and many other natural obstacles to connect Russian lines with the European system.

Also completed in the early 1980s, the Northern Lights natural gas line runs from the Vuktyl field in the Republic of Komi to Eastern Europe. The Orenburg pipeline was built in the late 1970s to bring gas from the Orenburg field in Russia and the Kara Chaganak field in northern Kazakstan to Eastern Europe.

Many of Russia's major oil pipelines parallel gas lines. A trunk oil line runs eastward from the Volga-Ural fields to Irkutsk on Lake Baikal, westward from those fields into Ukraine and Latvia, and southwest to connect with the North Caucasus oil fields and refineries; the line is joined by a line from the oil center at Surgut in the West Siberian Plain.

1.2. American Pipeline Nets

Crude oil, also referred to as petroleum, is a resource that is drilled for throughout the world. When refined and processed, crude oil provides the energy resources we have come to depend on in modern society. Crude oil provides the foundation for many products including plastics and petrochemicals in addition to the fuel for our cars and heating oil for our homes. Each day, the United States uses billions of gallons of crude oil to support our daily lives. While many forms of transportation are used to move this product to marketplaces, pipelines remain the safest, most efficient and economical way to move this natural resource.

This is especially important because often times crude is produced in areas far away from major marketplaces where population and manufacturing centers are located. Pipelines permit the movement of large quantities of crude oil and products to these areas with little or no disruption to communities everywhere.

Many people are familiar with the Trans Alaska Pipeline System (TAPS). It is the most photographed pipeline as it, unlike most pipelines, has significant portions of the system above ground. Crude oil is produced in Alaska, moves south on TAPS and then moves by tank ship to the West Coast. From the tank ship, the crude again moves by pipeline to refineries along the west coast of the U.S.

The network of crude oil pipelines in the U.S. is extensive. There are approximately 55,000 miles of crude oil trunk lines (usually 8–24 inches in diameter) in the U.S. that connect regional markets. The map below shows some of the major crude oil trunk lines in the U.S. (Figure 1).

Natural gas, unlike oil, is delivered directly to homes and businesses through local distribution lines. Large distribution lines, called mains, move the gas close to cities. These main lines, along with the much smaller lines to homes and businesses, deliver natural gas under streets in almost every city and town and account for the vast majority of pipeline mileage in the U.S.—1.8 million miles.

2. NATURAL GAS MAIN PIPELINE “YAMAL–WEST EUROPE”

2.1. Critical Load Approach for Assessing Environmental Risks

The most serious concern is related to sulfur and nitrogen species due to acid and eutrophication effects on terrestrial and aquatic ecosystems. Accordingly the critical load approach and relevant methods should be applied for the EIA and ERA during construction of gas pipelines and the production stage when the emission of pollutants occurs due to accidental causes and permanent release due to processing of gas pumping stations. These stations are usually constructed along pipelines through every 70–120 km in order to support the required gas pressure in the pipe (Chernyaev et al., 1991). To a great extent these impacts are along transcontinental gas pipelines up to 3–5 thousands km long, which are common in North Eurasia where at present

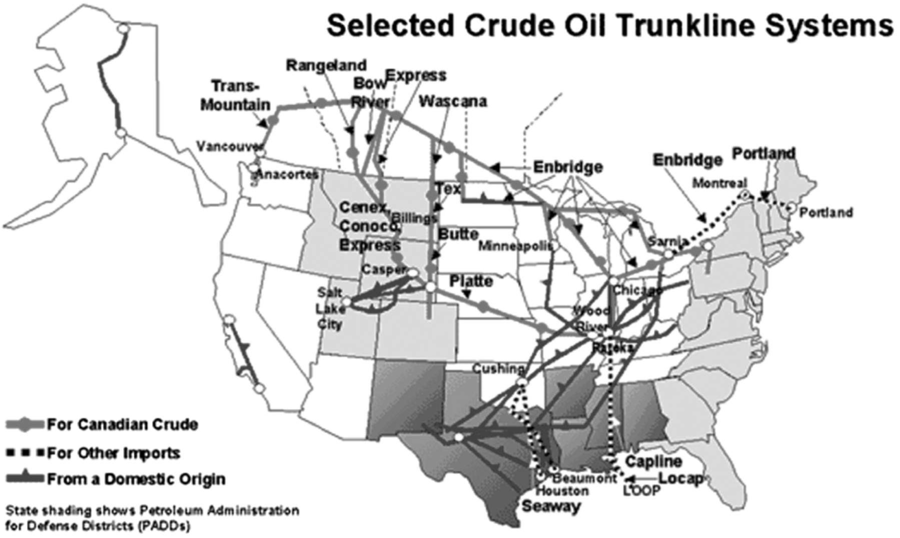


Figure 1. Selected crude oil trunkline systems in the USA.

the most explorations are placed in West Polar Siberia and shelf areas in the Arctic Ocean.

Our previous research has shown that application of the critical load technique allows the researcher to carried out the quantitative estimate of potential loading of atmotechnogenic pollutants due to gas pipeline work at different ecosystems in the boundaries of vast areas in north and central Eurasia (Bashkin et al., 1999, 2002).

This study aims to calculate the critical loads of acidity, eutrophication and heavy metal (Pb, Cd) compounds in the vast area of Eurasia along the natural gas pipeline "Yamal–West" and quantitatively estimate the environmental risk at the surrounding ecosystems. The relevant research was conducted during 1994–2000 for total pipeline length ($>$3,000 km) including 21 gas pumping stations, from the northernmost part at the Yamal peninsula (north of West Siberia) up to the central western part of European Russia.

The area of potential impact due to pollutants emission from gas pumping stations (GPS) was determined using the relevant models (Bashkin et al., 1999). This area is about 900,000 km^2 for each station in the region. However, due to the relatively close placement of neighboring GPSs, the impacted areas are subject to emissions of at least two or even more stations. Such an overload is accompanied by enforced inputs of airborne pollutants on ecosystems and human health.

The technical approach to calculate critical loads used in this research was similar to that described earlier (Posch et al., 1999; Bashkin et al., 2001a). Different biogeochemical data were used for the calculation and mapping of critical loads for acid forming and eutrophication compounds (SO_2, NO_x). These data were monitored

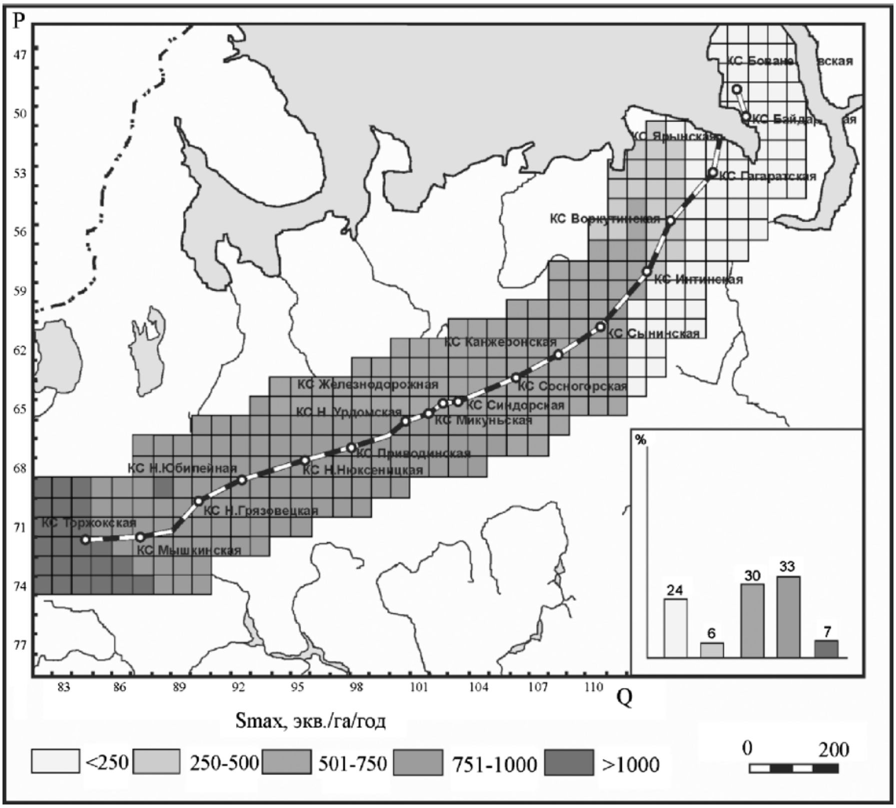


Figure 2. Critical loads of Smax in impact area of trans-continental gas pipeline Yamal–West Nnutr.

during experimental case studies on different sites where construction of GPSs has been planned. Based on experimental results, the calculations were carried out for 332 PQ cells of EMEP grid along the gas pipeline.

2.2. Critical Loads of Pollutants

Acid-Forming Compounds

The values of critical loads for acid forming sulfur species in the region of potential impact for natural gas pipeline "Yamal–West" are calculated to be from 160 up to 1,446 eq/ha/yr. The spatial distribution of these values is shown in Figure 2. One can see that the minimal values, and, accordingly, the minimal sustainability to acid pollutants are monitored for the northernmost tundra ecosystems. In accordance to the previous results, the maximal input of acidity to these tundra ecosystems will not have to exceed 200–250 eq/ha/yr (Bashkin et al., 1996b, 2001b). The forest tundra and taiga forest ecosystems occur in the more south and south-western areas and

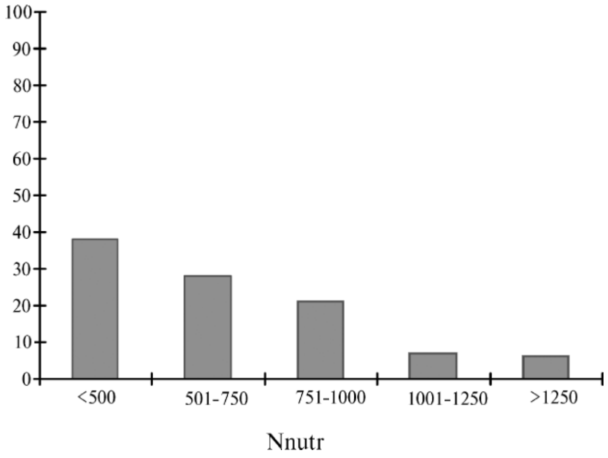


Figure 3. Statistical distribution of nitrogen critical loads on ecosystems in impact area of trans-continental gas pipeline Yamal–West.

these are characterized by the higher values of critical loads for sulfur. In forest tundra and north taiga forest ecosystems the calculated critical loads are in the limits of 300–650 eq/ha/yr, and in middle and south taiga forest ecosystems, 750–1,200 eq/ha/yr. The taiga forest ecosystems are predominant in the area of potential impact and accordingly for >60% of ecosystems the CL(S) are 500–1,000 eq/ha/yr.

The calculation of critical value for nitrogen was conducted to determine the deposition rates, which will induce neither acid nor eutrophication changes in studied ecosystems. This value corresponds to the nutrient nitrogen critical load (CLNnutr). The calculated CL(Nnutr) values are in limits of 301–1,776 eq/ha/yr. This wide range is related to the great variety of natural ecosystems and their biogeochemical cycling conditions in the studied region. Spatial distribution of calculated values showed that the most sensitive ecosystems (minimal values of CLNnutr) occur in the middle part of a gas pipeline. This corresponds to north- and middle taiga forest landscapes with coniferous ecosystems on typical podzolic soils and illuvial-ferrous or illuvial-humic podzols. The maximal values are characteristic for the south-western part of the impacted area where soddy-podzolic soils and mixed forest ecosystems are predominant. The statistical histogram showed (Figure 3) that ecosystems with CL(Nnutr) values <750 eq/ha/yr are predominant, and >50% have critical loads <500 eq/ha/yr (Figure 3).

Heavy Metals

Spatial distribution of critical load values for studied heavy metals (Pb and Cd) is different but the general southward tendency to the increasing values of critical loads in the impacted ecosystems is clear. The calculated values of critical loads for lead are 5–6 times higher than similar values for cadmium. The minimal values of lead

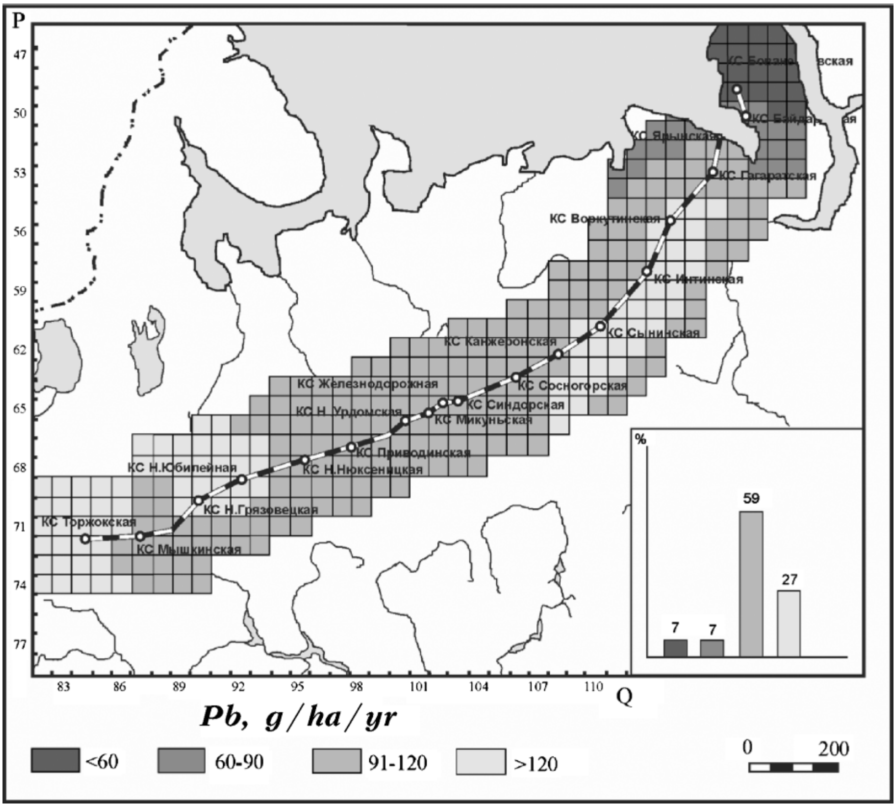


Figure 4. Critical values of lead for the impact zone ecosystems of main natural gas pipe line "Yamal–West" (g/ha/yr).

are calculated for the most northern tundra ecosystems of the Yamal peninsula, and the maximal ones are shown for south-taiga ecosystems of Central European Russia (Figure 4).

The minimal and maximal values of CL(Pb) differ by the rank of 2. The ecosystem areas with CL(Pb) equal to 90–120 g/ha/yr are predominant.

The spatial distribution of critical load values for Cd are shown in Figure 5. The predominant numbers are 16–20 g/ha/yr. The minimal sustainability is characteristic for the northward ecosystems and the mountain ecosystems of the Ural are more sustainable due to relatively high runoff values.

2.3. Exceedances of Critical Loads of Pollutants in the Ecosystems Surrounding Gas Pipelines

The calculated values of critical loads for acid forming species of sulfur, and eutrophication and acid forming species of nitrogen, as well as species of heavy metals (Pb and Cd) characterize the sustainability of natural ecosystems surrounding the main

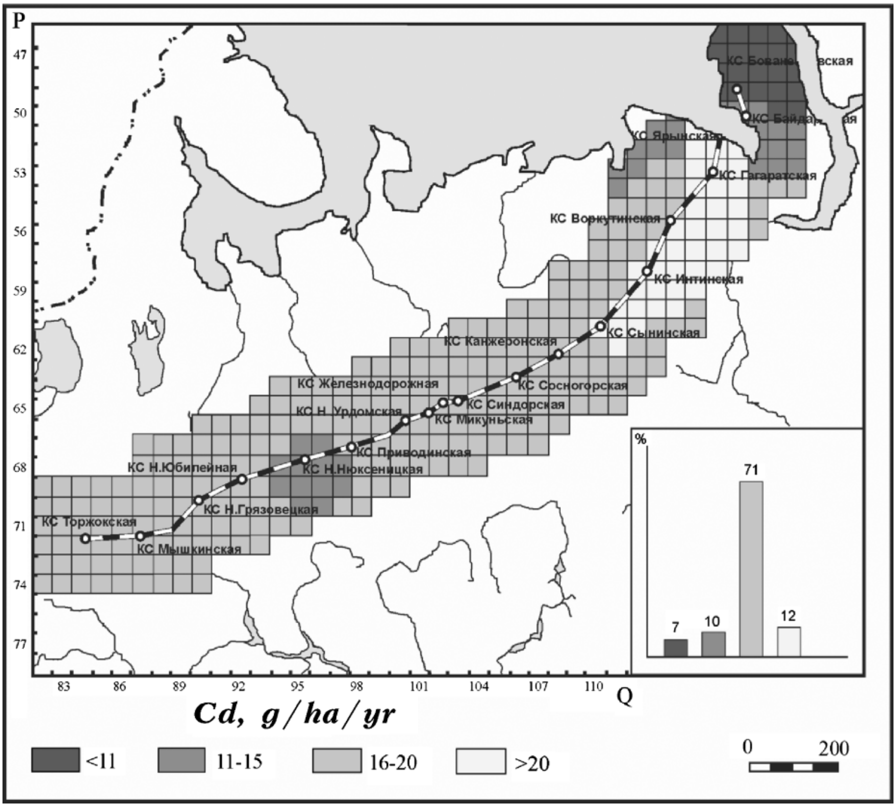


Figure 5. Critical values of cadmium for the impact zone ecosystems of main natural gas pipe line "Yamal–West" (g/ha/yr).

gas pipeline "Yamal–West Europe". These values are of importance for assessing the permissible anthropogenic impact due to pollutant emissions. When this impact is below the critical loads there is no needs to reduce the emissions and v/v the emissions must be reduced when they exceed the calculated critical loads. The reduction of emissions aiming to achieve the critical load values will accordingly decrease the probability of environmental risk (Bashkin et al., 2002).

Since the composition of atmospheric deposition always includes specific amounts of base cations, in addition to critical loads it is necessary to calculate the actual acidifying effect of depositions. For the quantitative assessment the latter effect the "critical deposition" values should be estimated using the following formulas for sulfur and nitrogen:

$$\mathrm{CD(S)} = \mathrm{Sf}^{*}\ [\mathrm{BCdep} - \mathrm{BCu} + \mathrm{CL(A)}],$$
$$\mathrm{CD(N)} = \mathrm{Nu} + \mathrm{Ni} + (1 - \mathrm{Sf})^{*}\ [\mathrm{BCdep} - \mathrm{BCu} + \mathrm{CL\ (A)}],$$

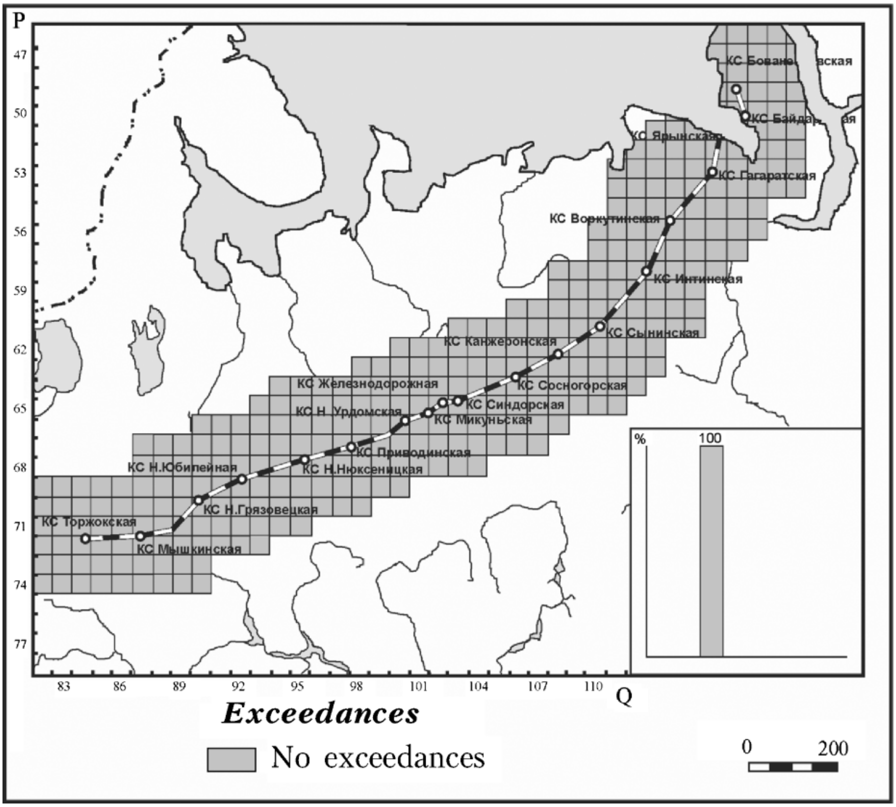


Figure 6. Map of calculated exceedance for critical loads on the ecosystems surrounding the main natural gas pipeline "Yamal–West Europe".

where BCdep is the base cation content in the atmospheric deposition, Sf is sulfur fraction in the atmospheric deposition, BCu is the base cation uptake by annual NPP.

See also Chapter 4 for other parameters.

Using these formulas the exceedance values can be calculated as

$$\mathrm{Ex(S)} = S_{\mathrm{dep}} - \mathrm{CD(S)},$$
$$\mathrm{Ex(N)} = N_{\mathrm{dep}} - \mathrm{CD(N)},$$

where Ex(S) and Ex(N) are the values of excess of inputting acidifying sulfur and nitrogen oxides above their critical depositions (Bashkin, 2002).

Such values are of importance for creation of optimization models and separate emission reduction strategies for both sulfur and nitrogen. When both species must be reduced, the approach described in Chapters 4 and 17 is used.

The calculation of exceedances testifies to the absence of excessive input of acidity for ecosystems surrounding the main natural gas pipeline "Yamal–West Europe" (Figure 6).

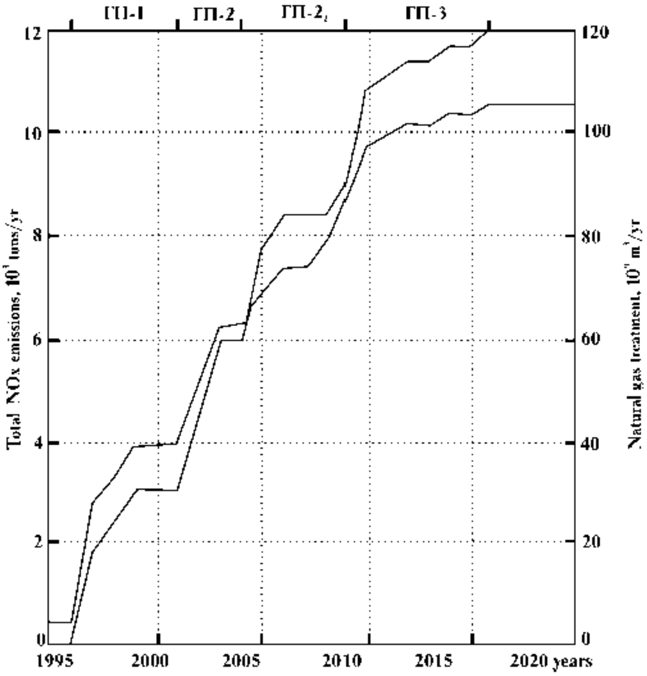


Figure 7. Prognosis of natural gas treatment volume and NO_x *emissions (Bashkin et al., 2002).*

Accordingly, the values of critical loads can be applied for estimation of permissible emission both for a single GPS and for the whole pipeline. Moreover, these values can be also used for the input data in ecological-optimization models for planning of other anthropogenic loading especially in the areas of the center of the European Russia.

For quantitative prognosis of emission rate from natural gas pipeline "Yamal–West" both emission from possible accidents and stationary sources were taken into account (Chernyaev et al., 1991).

Table 1. Forecast for exceedance of critical loads for nitrogen in accordance with planned increase of gas production.

Period	Gas production, billion cubic meter/yr	Total NO_x emission, ton/yr × 10^3	N deposition rate, kg/ha/yr	CL exceedance, kg/ha/yr
2000	30	3.6	2.8	−8.94
2005	78	7.7	4.9	−7.65
2015	115	10.3	14.85	3.11

In accordance with the production plans (Odisharia et al., 1994), the increase of emission rate for nitrogen oxides (NO_x) in the area of Bovanenkovo gas exploration in Yamal peninsula will be during 2000–2015 (Figure 7). Emission of sulfur oxide will be practically permanent and will amount to about 470,000 tons per year. These data indicate also the growth of deposition rate for acid forming and eutrophication compounds in comparison with the present period (Table 1).

Table 1 shows also that at planned volume of gas production of 115 billion cubic meters per year, the critical loads for nitrogen will be exceeded and this exceedance will be about 3 kg/ha/yr or about 200 eq/ha/yr in year 2015.

Under planned sulfur emissions, the exceedances of sulfur critical values will not be achieved before year 2015.

One should note that at present most ecosystems in the studied region are nitrogen deficient. The increasing deposition rates will stimulate bioproductivity but simultaneously decrease the species biodiversity of natural ecosystems.

3. BIOGEOCHEMICAL STANDARDS FOR EXPOSED AREAS

Critical load calculation and mapping of S and N acidity and eutrophication compounds in the vast area of Eurasia along the natural gas pipeline “Yamal–West” were conducted to estimate the environmental risks due to pollutant emission. The taiga forest ecosystems are predominant in the area of potential impact and accordingly for >60% of ecosystems the CL(S) are 500–1,000 eq/ha/yr. Ecosystems with CL(Nnutr) values <750 eq/ha/yr are predominant, and >50% have critical loads <500 eq/ha/yr.

At planned volume of gas production of 115 billion cubic meters per year, the critical loads for nitrogen will be exceeded and this exceedance will be about 200 eq/ha/yr in year 2015. No sulfur exceedances will be projected at planned natural gas production.

The following critical loads values can be considered as the ecological (biogeochemical) standards for the impact zone of this pipeline at 95% of ecosystem protection: CLminN—160–1,230 eq/ha/yr; CLmaxN—774–2,636 eq/ha/yr; CLnutrN—301–1,776 eq/ha/yr; CLmaxS—160–1,446 eq/ha/yr; CL(Pb)—60–135 g/ha/yr, and CL(Cd)—10–25 g/ha/yr.

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