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For Lithuania and its people

Preface

Changes in Earth's biosphere as civilization has developed, its increased technogenic load, and reduced overall resources of resistant stability spur the natural and technological sciences to properly concentrate on the possibilities of interaction between sustainable human activity and natural ecosystems. Trees are a primary focus. Natural tree ecosystems (forests), in terms of the overall mass of the biosphere, have been devastated, in the majority of cases by human activity. Humans also have intensively utilized the energetic, biological, and recreational resources of trees throughout their life cycles. The involvement of industrial society in large-scale applications of fossil fuels along with the rapid development of industry has resulted in the urgent current issue of widespread pollution of the ecosphere and the threat of global warming.

The use of trees in ecological technologies is based on their unquestioned importance in maintaining stability in the biosphere as well as on their presence in a number of Earth's biomes and its ecosystems, particularly those of Scots pine growing in urbanized territories and zones affected by pollution sources. This aspect in particular creates favorable conditions for using trees as bioindicators for establishing the properties and levels of contamination and, in some cases, as a measure for reducing pollution. Because the consequences of negative changes occurring in nature can only be minimized once their essential character is understood, this book focuses mainly on trees as biogeochemical objects and discusses a mechanism by which heavy metals enter into trees, the impact of biotic stressors as determinants of entry, the specificity of metal accumulation in certain species of trees and their parts, the biophilicity of heavy metals, and other aspects of biogeochemistry.

Considering the extent of the life cycle of the tree and with respect to wood as an industrial material and an agent for the sequestration of atmospheric carbon dioxide, investigations into thermally treated wood products and the efficiency of their application in the field of environmental protection engineering are presented. Greater focus is shifted to the properties of biochar and to defining its advantages as a packing material of the filters.

Exhaustive treatment of the versatile role of trees in environmental protection technologies is hardly possible without specifically applied research methods. Thus, investigation into heavy metal concentrations and their distribution in tree rings has assisted in advancing technology for wood sampling and evaluating their representiveness. To assess the eco-technological aspect of using trees in environmental protection technologies, a method of dynamic factors that maximizes the elimination of the impact of local environmental geochemical features on the element uptake evaluation has been developed. As an effective method for examining various ecological aspects, a mathematical simulation of the processes of contaminant transport in the environment, including the original models developed by the authors of the book, has been applied.

The novelty of the book is its explication of the sustainable role of the tree in environmental protection technologies, and the book includes reviews, research, and an evaluation of the use of trees.

This publication is dedicated to scientists and experts in the field of environmental protection. Would-be scientists – Ph.D. and M.A. students – may refer to the study as a source of scientific knowledge in the field of environmental protection technologies.

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Contents

Introduction

It is quite natural that the tree is treated in this book as an important part of nature and the environment in which humans live. With respect to form and functions, trees are sacral objects for people. It should be noted that, though the main functions of trees have not changed, different ways of perceiving them through our senses have developed in humans. The cult of the Tree of Life as a worldwide symbol developed in tribal systems based on using such wooden cult objects as totems and considering a tree as an abode of ghosts. The mythological World Tree was the key artifact promoting the formation of a mythological space concept. According to this concept, the World Tree grows in the center of the universe and forms the axis connecting the sky, Earth, and the underground kingdom. The top of the World Tree supports the sky, its branches embrace the whole world, and its roots reach Earth's depths.

In discussing the modern forms of perceiving the functions of the tree, some well-known feature films are worth mentioning. Thus, in the movie Avatar, directed by James Cameron in 2009, the so-called soul (also native or sound) tree plays the lead and most mystical role and is vitally important for the native people of the fantastic planet Pandora. The 3-D version of Star Wars features Endor, a mystical moon covered with gigantic trees, while the Lord of the Rings features a race of creatures similar to trees called Ents.

In our own day, when the problem of sustainability of various processes and objects is under extensive discussion and debate, the sustainability of trees and their functions has become much more important if we consider their life cycle in areas receiving technogenic pollutant loads. The deterioration of the state of Earth's ecosystemss, the growing concentration of greenhouse gases in the atmosphere, and predictions of climate change are also cause for concern. The sustainability of trees in the context of long-term development is primarily associated with maintaining the geochemical status of the carbon cycle and such dangerous products of technogenesis as metals found in the biosphere, which are strongly affected by human activities.

The life of trees and usage of their products are actually closely connected with their life cycle stages, while their functions confirm the sustainability of trees with respect to their use in environmental protection technologies, which can be attributed to their long life and long-term effects.

Two main areas of environmental protection, where the role of trees is particularly important, are associated with the stage of their life and the stage involving the use of their products. In the first stage, the functions of trees are based on their use in ecotechnologies, while the second stage is closely connected with their use in environmental protection engineering. These two stages are related by the use of trees in environmental protection technologies both as animate and inanimate objects. The major stages of a tree's life cycle include the extraction of nutrient materials from the environment (resources) as raw materials and energy (***Stage A***), the processing of resources (***Stage B***), the manufacture of products (***Stage C***), the use of those products (***Stage D***), and waste utilization (***Stage E***) (Fig. 1).

At ***Stage A***, resource materials are considered to be inorganic environmental resources used by trees to support their vital functions. Trees use inorganic materials, assimilating CO_2 from the atmosphere and nutrient materials from soil for synthesizing biomass and developing their compartments while taking an active part in the biogeochemical cycle (Chap. 1). In polluted territories, these processes

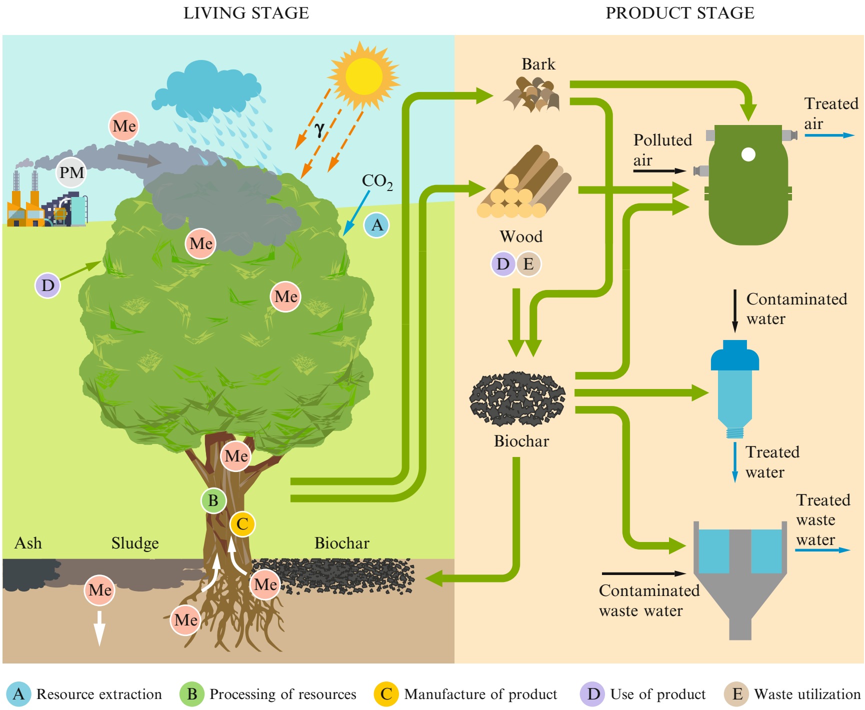

Fig. 1 Major stages of a tree's life cycle

of ecosystems related to trees depend on the type of pollution (Chap. 2) and the transport of pollutants to them. The role of trees as sustainable functional units in areas covered by forests has become particularly important owing to their active participation in biogeochemical carbon circulation in the biosphere. Trees assimilate carbon dioxide from the atmosphere, thereby reducing its concentration as a causal factor of the greenhouse effect. The sustainability of trees is also associated with their role in removing such pollutants as metals from the surroundings and accumulating them in their systems, thereby limiting their mobility and possible negative effects on ecosystems for a long time.

The function of trees associated with stabilizing metals is discussed in Chap. 3, which also partially describes ***Stage B*** of the tree life cycle (resource processing), dealing with the transport of metals and their transformation and accumulation in trees, though in these cases, processes can be strongly affected by biotic factors.

Stage C is associated with the manufacture of the product of biomass synthesis and its increase in the tree's life cycle. In a technogenic environment, a growing tree is subjected to aerogenic and edaphic pollution, causing both quantitative and qualitative changes in biomass properties. The biogeochemical properties of trees are associated with qualitative changes, while functional characteristics determine their qualitative changes (Chap. 4).

At ***Stage D***, relating to the use of the product, a wider range of application of trees besides biomass their use is discussed. In ecotechnologies, these are the functions of bioindication and phytoremediation, involving relatively cheap and effective innovative technologies, which take advantage of the environment's capacity to reduce pollution and risks over the long term (which represents the main sustainable development principles). In environmental protection engineering, the natural and processed products of trees are used. Mathematical models of these processes have become tools that are extensively used in practice (Chaps. 5–7).

At ***Stage E***, the waste materials of trees, including both natural (e.g., bark, wood shavings) and processed (e.g., ashes, biochar, wood fibers) products, which can be practically used, are categorized with waste products. In most cases, these products meet the needs of a specific application and satisfy technical requirements. Their market is being expanded, which helps to avoid negative impacts on the environment and human health. Thus, natural resources are managed in a sustainable way, and materials recovered from trees are used more efficiently (Chaps. 6 and 7).

This monograph aims to demonstrate the links between trees' functions and sustainable development at each stage of the tree's life cycle. The use of trees in environmental protection technologies confirms the ability of humans to expand their knowledge of nature, to have respect for it, and to better understand the role of trees in their lives. Besides the well-known ecological significance of trees, we would like to mention that the role of trees has increased through extensive use of environmental protection technologies. The areas of practical application of trees are as follows: (1) the use of trees and their products in ecotechnologies and the development of predictive models of processes and (2) the evaluation of practical applications of wood products in environmental engineering systems.

The description of the environmental protection role of trees at various stages of their life cycle presented in this book aims to emphasize their ability to improve the state of the environment from both ecological and environmental protection engineering perspectives. Trees can reveal changes taking place in the environment, stabilize the spread of pollution, and protect the environment. When a tree completes the stage of its existence as a living organism, the period of its indirect participation in engineering environmental protection solutions follows.

The present work links nature and technology, ecology and engineering, principles for knowing the world and the application of knowledge, and discusses implications and benefits because, in nature as in life, everything makes sense, while, according to Barry Commoner, everything is connected to everything else.

About the Authors

Edita Baltrėnaitė Doctor of Sciences in the scientific field of environmental engineering and landscape management, Associate Professor, acting professor at Vilnius Gediminas Technical University, Department of Environmental Protection, obtained diploma of Bachelor and International (in English) Master of Sciences at Vilnius Gediminas Technical University. In 2007, she defended her thesis titled *Investigation and Evaluation of the Transfer of Heavy Metals from Soil to the Tree*. Since 2007, Edita has been a scientific secretary of the international *Journal of Environmental Engineering and Ecological Science*, a member of the editorial board of a journal published by Romanian Academy of Science, *Annals—Series on Chemistry Sciences*, a member of the Environmental Institute of Scientific Networks (EISN-Institute), and a representative for Lithuania in the EU research programs COST859: *Phytotechnologies to Promote Sustainable Land Use Management and Improve Food Chain Safety*, COST FA0905: *Mineral-Improved Crop Production for Healthy Food and Feed*, and COST TD1107: *Biochar as an Option for Sustainable Resource Management*.

Areas of interest: application of biogeochemical processes to environmental protection technologies, evaluation of metal transport in the ecosphere and thermal processing, and the application of lignocellulosic products in environmental protection engineering.

E. Baltrėnaitė gives lectures to master's students about environmental protection technologies, anthropogenic impacts on the environment, waste utilization, soil recovery technologies, clean technologies, and soil remediation technologies and supervises doctoral students. She is also a member of the Committee for the Research Area of Environmental Engineering and a chair or member of committees for seven defended theses.

E. Baltrėnaitė was a supervisor of studies of 24 bachelor's and 12 master's degree students as well as Erasmus trainees from Finland, Italy, and Latvia. She also lectures at Helsinki University (Finland), Valencia Polytechnic University

(Spain), Aalto University (Finland), and Southern Denmark University. She has made research visits to the Norwegian University of Life Sciences, the Jozef Stefan Institute in Slovenia, and the Latvian State Wood Chemistry Institute. She maintains close ties and with high schools in Europe and other countries around the world, such as State Montclair University (USA), Swiss Federal Technological Institute in Zurich, Illinois Institute of Technology (USA), Helsinki University (Finland), Tomsk State University (Russia), Barcelona University (Spain), and Ancona University (Italy).

Major publications: author or coauthor of 92 papers (27 of which are published in Web of Science refereed journals with citation index), the author of the textbook *Manufacturing Industries and Environmental Impact*, chapters in the books *Phytoremediation: Management of Environmental Contaminants*; *Plants, Pollutants and Remediation* published by Springer, and *Plant Production Technologies* published by Elsevier.

She is a reviewer of papers for international journals, such as the *Journal of Environmental Management*, *Environmental Science and Pollution Research*, *Environmental and Experimental Botany*, and *Dendrochronology*.

In 2013–2014, Edita Baltrėnaitė was granted a young researcher grant for the work *The Evaluation of Heavy Metals' Stability in Biochar* and, in 2007, a prize for the work *Investigation and Evaluation of the Transfer of Heavy Metals from Soil to the Tree* by the Lithuanian Academy of Sciences.

Pranas Baltrėnas Professor, Dr. Habil, Director of the Environmental Protection Institute of Vilnius Gediminas Technical University (VGTU), a member of three international Academies of Sciences, chief editor of the international *Journal of Environmental Engineering and Landscape Management*, ISSN 1648-6897, a member of the editorial boards of five international journals, chief editor of the *Proceedings of the Conference for Junior Researchers* based on the material of the annual conference *Science—Future of Lithuania*, chair of the organizing committee for the *Environmental Engineering* conference, chair of the Committee of Doctoral Studies in the scientific field of environmental engineering, head of the Public Environmental Protection Commission in the Vilnius City Council, member of the Council of the Union of Lithuanian Scientists, chair of the Environmental Protection Committee No. 36 of the Lithuanian Standardization Department, member of the Noise Prevention Council at the Public Health Ministry, and project evaluation expert on the Research Council of Lithuania. His areas of research include complex theoretical and experimental studies of the technosphere, process modeling and the development of environment protection technologies, including regulation of stationary and mobile air and soil pollution sources and waste and effluents, the investigation of noise sources and electromagnetic fields, and the development of pollution-reducing technologies and equipment. He established the Department of

Environmental Protection, the Institute of Environmental Protection, and the laboratory of the Environmental Protection and Work Conditions in VGTU and pioneered the field of environmental protection engineering in Lithuania. P. Baltrėnas has conducted research visits to Weimar and Mikkeli universities and to Rostock (Germany), Dresden (Germany), Hamburg–Harburg (Germany), Lulea (Sweden), Illinois (USA), and Ancona (Italy) universities and is a Lithuanian representative (coordinator) of international programs such as COST, INTERREG, Seventh Framework, BPD, MUNDUS, and TEMPUS.

Under Prof. Baltrėnas' supervision, 19 doctoral theses have been defended. In 1994, P. Baltrėnas was the winner of the Lithuanian Republic prize for achievements in research, and in 2000, he was awarded the medal of M. Lomonosov and in 2003 awarded an honorary doctorate at the Saint Petersburg Academy of Sciences. In 2007, he was awarded the World Intellectual Property Organization (Geneva, Switzerland) Award Certificate in recognition of his outstanding achievements as an author of inventions.

Prof. Baltrėnas is the author or coauthor of 625 publications, including 15 monographs, 3 textbooks, 26 analytical and review methodological works, and 345 research papers, including 60 papers published abroad and 92 certificates and patents.

Arvydas Lietuvninkas Doctor of physical sciences (volcanology and petrology), professor. His life and work (1956–2006) were associated with scholarship and, later, with Tomsk State University (Russia, West Siberia). A. Lietuvninkas was born when his father, a peasant, was in exile. He completed secondary school in exile in the Krasnoyarsk region with a silver medal and graduated from Tomsk State University, Faculty of Geology and Geography, with honors. He began his career at Tomsk State as a junior researcher, then Lecturer, Assistant Professor, Vice Dean, Chair of the Department of Mineralogy and Geochemistry, and Professor.

A. Lietuvninkas published 5 monographs, 13 teaching aids and textbooks, and authored or coauthored more than 160 papers. He is also an honorary research worker in the Russian system of higher professional education and has received several medals and prizes for his achievements in research and pedagogy.

A. Lietuvninkas has been living in Lithuania since 2006. Currently retired, he collaborates with colleagues from the Department of Environmental Protection of Vilnius Gediminas Technical University in areas of his research interests. Additionally, he is a member of the editorial board of the *Journal of Environmental Engineering and Landscape Management*.

Basic research interests: metamorphism and metamorphic rock, geology of sources of minerals and geochemical methods of their exploration (1961–1988), ecological geochemistry and application of its methods to evaluating the ecological state of ecosystems and their components, and the spread of pollutants in the environment and their accumulation in geochemical barriers.

Areas of activity: practical application of university-level methods, introduction of information technologies and ISO 9001 quality standards at Tomsk State University, application of geochemical methods to the evaluation of ecosystems and their components' ecological state, spread of pollutants and their accumulation in the air, water, and soil, theory and practice of geochemical anomalies in soil, snow cover, and biological objects, application of advanced technologies to environmental protection, and preservation of Earth's mineral wealth.

His major works include *The Stages of Postmagmatic Formation of Minerals*. Tomsk, Tomsk State University, 1977, 110 pp.; *The Stages of Hydrothermal Mineral Formation*. Tomsk, Tomsk State University, 1999, 216 pp.; *Technogenic Pollution and Children's Health*. Tomsk, Tomsk State University, 1993, 92 pp., *The Environmental Problems of the Western Industrial Tomsk Region and Ways to Their Solution*. Tomsk, Tomsk State University, 1994, 260 pp. (with co-authors); *Anthropogenic Geochemical Anomalies and the Environment* (teaching aid). Tomsk, a publishing house of scientific and technical literature, 2002, 290 pp. (2nd edition, 2005); *Geochemistry of the Environment* (textbook). Vilnius. Technika, 2012, 312 pp.

Chapter 1
The Tree in Earth's Terrestrial Ecosystems

This chapter briefly reviews the main functions of the tree in Earth's ecosphere and analyzes the overall geological carbon cycle, rates of Earth's biogeochemical circulation, the main reservoirs of carbon in the lithosphere and ecosphere, and the assessed expected carbon leakage to the stratosphere. Approximately 90 % of the world's carbon (900 Gt) accumulated by terrestrial vegetation is absorbed by forest ecosystems, which represent a short-term reservoir of the world's terrestrial carbon and serve as an additional means of preventing the accumulation of CO_2, a component of the greenhouse effect in the atmosphere. Without going into a detailed description of forest functions, which are discussed thoroughly in specialized works, attention should be paid to the three closest topics of the book: the phytoremediation function of forests, the ecological soil protection function of forests, and the use of wood and wood products as structural materials and fillers in modern air and water treatment equipment. The life cycle of the tree is analyzed as a universal tool for assessing the impact of manufactured products and technologies. The chapter presents a technological scheme for afforestation, which is the remediation of soil contaminated with metals, a comparison of phytoremediation costs and environmental protection benefits for forests, and a summary diagram evaluating the costs and benefits of the life cycle of the tree as applied to forests planted for the purposes of phytoremediation and biochar production.

The sustainable role of the tree in environmental protection technologies is based on at least three essential aspects of using them: reforestation, which actually entails the transfer of a part of atmospheric CO_2 to biomass (wood) and the pedosphere, i.e., the stabilization of carbon in the atmosphere; the long-term stabilization of atmospheric carbon accumulated by wood in biochar as a soil amendment; the use of wood, which is a natural, durable, and ecological material used in construction, ornamentation, and interior decorating, and therefore its wide application in this particular field may cause a substantial leakage of carbon dioxide into the technosphere and, with regard to resources, in part should replace some intensive materials, for example, metal, concrete, plastic, and glass.

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1.1 Functions of the Tree in the Biogeochemical Cycle of Materials

The chapter briefly reviews the basic functions of the tree in Earth's ecosphere and describes changes in conditions for implementing them in the context of modern civilization.

The Carbon Cycle

The tree, as one of the most important components of the present biosphere that carry out biogeochemical metabolism, constitutes a considerable part of Earth's so-called living matter (Lietuvninkas 2012). On the other hand, the existence and evolution of such matter can be characterized by its permanent renewal and improvement as evidenced by the generational changes occurring under conditions of nature and interspecific competition. From the point of view of biochemistry, a change in organisms when they are alive or when they are free following their demise is accompanied by the uptake and release of chemical elements from the environment, which is one of the methods of migration of elements in the biosphere – more precisely, biogeochemical migration. Typically, migration, like the generational change in organisms themselves, is cyclical. In terms of tree, such cycles of migration take place in *tree–soil* space and are known as Liebich biogeochemical cycles of migrating substances or the biological cycle of chemical elements, frequently referred to as the biogeochemical cycle. Because "*everything is related to everything else*" in nature (B. Commoner), the biological cycle of metabolism extends beyond the aforementioned range, affecting the adjacent spheres of Earth, including the hydrosphere, atmosphere, and lithosphere, and forms a geological material cycle (also known as a biogeochemical cycle) (Fig. 1.1).

The activity of tree involved in the biological cycle shows up in their periodical annual changes in separate organs (e.g., leaves, fruit) in deciduous tree and some conifers when biogeochemical migration includes an impressive mass of chemical elements. In the majority of cases, these are biophilic elements –the main chemical elements making up the biomass of terrestrial vegetation in the process of photosynthesis: carbon (C), hydrogen (H), nitrogen (N), calcium (Ca), potassium (K), magnesium (Mg), sulfur (S), phosphorus (P), chlorine (Cl), and sodium (Na). The overall mass of mineral macrocomponents included in biogeochemical migration is close to 8 billion tons, i.e., approximately three times higher than the ionic continental runoff of these macrocomponents, valued at 2.54 billion tons. Thus, terrestrial vegetation annually absorbs approximately 3.1 billion tons of Ca, 2.4 billion tons of K, 0.6 billion tons of Mg, 0.4 billion tons of P, and 0.2 billion tons of Na, which corresponds to 20–26 tons of K and Ca and 3.3–4.6 tons of P and Mg in a land area of 1 km^2. As a matter of fact, along with chemical elements, different

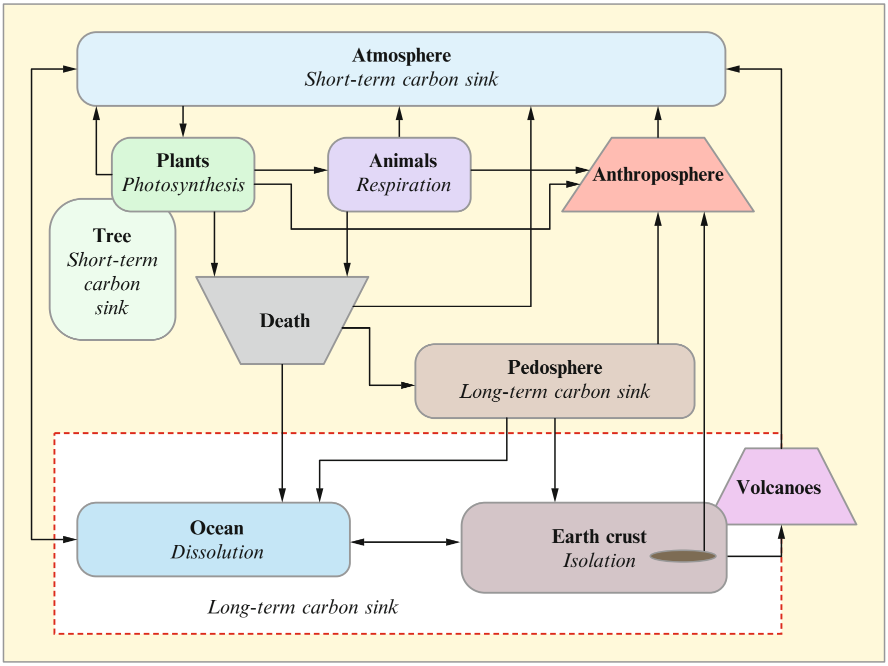

Fig. 1.1 Simplified scheme for geological carbon cycle

microelements, including some metals hazardous to life, are introduced into biological circulation (Table 1.1).

With the help of solar energy, the reaction of photosynthesis to organic compounds causes a bond of carbon dioxide (CO_2) and water. If the overall annual biomass created by the producers (producents) of the organisms of Earth's biosphere makes up 910 billion tons of organic material (430 billion tons of live weight on land and 480 billion tons in the ocean), annual photosynthesis processes remove 125 billion tons of carbon as a component of CO_2 from the atmosphere (Dobrovolsky 2008), including more than 80 billion tons of terrestrial vegetation.

Figure 1.1 shows that, following the destruction of organisms, some free carbon finds its way to natural reservoirs in various ways and remains for a longer or shorter period of time in another form of existence. Earth's atmosphere, the world's oceans, and Earth's crust, its stratosphere in particular, are the well-known global natural reservoirs of carbon.

The general indexes of biochemical circulation on Earth show (Table 1.2) that the regeneration of the largest part of carbon existing in the form of CO_2 in Earth's atmosphere is stimulated by photosynthetics within a period of 5.5 years. As for the world ocean, where the mass of carbon, mainly in the form of HCO_3^-, dissolved in water is at least 55 times greater than that in the atmosphere, the carbon regeneration cycle is substantially longer, as can be observed in the atmosphere, and takes approximately 300 years. However, it is far shorter than the of carbon in an inactive

Table 1.1 Biological accumulation of chemical elements of terrestrial vegetation and their annual uptake according to Dobrovolskii (2008) (Clark values of Earth's crust according to Solovov et al. 1990)

Chemical element	Clark value of Earth's crust (g/t)	Coefficient of biological accumulation	Uptake by annual increment of phytomass	
			Throughout terrestrial area (thousand tons)	1 km^2 (kg)
Mn	770	6.86	41,400	276.00
Zn	76	19.60	8626	57.50
Sr	290	3.48	6900	46.00
Cu	46	9.09	1725	11.50
Pb	16	3.73	431.2	2.87
Ni	58	1.54	345.0	2.30
Cr	99	1.03	310.5	2.07
V	110	0.39	258.8	1.73
Co	23	2.74	172.5	1.15
Mo	1	9.23	103.5	0.69
As	1.7	1.58	60.37	0.40
U	3	0.15	5.18	0.035
Hg	0.08	7.58	2.16	0.014
Cd	0.2	0.63	0.86	0.006

Table 1.2 General indexes of biogeochemical cycle on Earth (the value of number *n* from 1 to 9) (Lietuvninkas 2012)

Primary production of living matter On Earth In ocean	910×10^9 t/year 430×10^9 t/year 480×10^9 t/year
Total living mass on Earth	6500×10^9 t
Regeneration of biomass on Earth Including xylem Herbaceous plants Plankton in ocean	7.2 years $n \times 10$ years *n* years 0.0*n* years
CO_2 regeneration in atmosphere	5.5 years
Regeneration of CO_2 dissolved in ocean	300 years
Water splitting into O_2 and H_2 in hydrosphere	4×10^6 years
Regeneration of total O_2 in atmosphere	3800 years
Water transpiration carried out by Earth's vegetation	$(5–8) \times 10^{13}$ t/year
CO_2 uptake	430×10^9 t/year
Water splitting into H_2 and O_2	340×10^9 t/year
Segregation of free O_2	320×10^9 t/year

form of migration, which remains in Earth's crust in the form of natural gas, oil, and brown/coal as well dispersed carbon (e.g., bitumoides, amorphous carbon, shungite, graphite) in various rocks from solids containing sludge with organic substances and nonlitificated sedimentary rocks (e.g., clay, silt, sand) to shale, marls, dolomite,

Table 1.3 Main reservoirs of carbon in ecosphere and Earth's crust (Dobrovolskii 2008)

	Carbon mass	
Carbon reservoirs	Gt	%
Atmosphere	700	0.04
Terrestrial area of world		
In biomass of plants up to human impact	1150	
In biomass of today's natural plants	900	
Pedosphere	2500	
Ocean		
In biomass of photosynthetics	1.7	
In biomass of users	2.3	
In dissolved and suspended organic matter	2100	
In ions of hydrocarbonate dissolved in water	38,500	
Earth's crust		99.96
Stratisphere		
Organic carbon	15,000,000	
Carbon in carbonates	81,000,000	
Granite layer of block of continents		
Organic carbon	4,000,000	
Carbon in carbonates	18,000,000	

limestone, sandstone, various metamorphic rocks, and even granite. In such a case, carbon from various original reserves becomes isolated from the biosphere for hundreds of thousands, millions, or even over a billion years.

The aforementioned global and other natural reservoirs of carbon greatly differ in their capacities (Table 1.3). Table 1.3 shows the reservoirs whose major amount of carbon is accumulated in Earth's crust, making up 99.96 %. The total carbon in the reservoirs of the ecosphere (in the atmosphere, terrestrial vegetation, pedosphere, and different forms of carbon in the ocean) makes up less than 0.04 % of the carbon sequestered in the ecosphere and Earth's crust. Moreover, carbon is distributed very unevenly within the boundaries of the ecosphere – almost 91 % of carbon is located in the world ocean, where the form of hydrocarbonate dissolved in water makes up more than 86 % of the total carbon in the ocean, and the overall biomass of photosynthetics and users accounts for only around 0.01 %. The biomass of living organisms in the ocean (4 Gt) is presented in Table 1.3 and can be regarded as an optimistic figure because other evaluations – just 3 Gt – have also been made (Schimel et al. 2000).

Carbon is distributed in the reservoirs of terrestrial areas in as follows: 5.6 % in the pedosphere and approximately 2.0 % in the phytomass of terrestrial areas. The total content of carbon in Earth's atmosphere (700 Gt) makes up less than 1.6 % of the total carbon in the ecosphere. This is carbon in the form of dioxide, with the content and concentration of which in the atmosphere the greenhouse effect is related, thus serving to monitor Earth's climate. And this makes up only 0.00059 %, which is a 6×10^{-6} part of the total content of carbon in all reservoirs presented in

Table 1.3. As for carbon reservoirs in the continental biosphere, it is worth emphasizing that an approximate evaluation shows that the present phytomass of Earth's forests makes up around 30 % of the overall terrestrial biomass, while the mass of the pedomass of forest ecosystems makes up approximately 38 % of the mass of the terrestrial pedosphere.

One would expect that, over a long period of evolution, the biogeochemical cycle of substances in the biosphere would be perfectly balanced, i.e., the synthesis of organic matter and its decomposition would take place at very similar rates. However, looking at the Earth in general, it is clear that the biosphere, as one of the planet's shells and as a system, is not closed – it rather actively exchanges materials with deeper geological layers of Earth such as the lithosphere and mantle. Without going deeper into all the aforementioned aspects of the geological evolution of the planet, it is worth recalling that hydrogen and various carbon compounds (e.g., methane, hydrocarbons, CO) constantly enter the biosphere from the depths of the Earth. Thus, the annual flow of methane can reach 2.5–3 Gt (Syvorotkin 2001), while the total content of carbon transferred from the mantle at the developmental stage of Earth's biosphere can reach 96×10^{15} tons (Dobrovolsky 2008). The biosphere, in turn, permanently loses a part of the organic carbon present in sedimentary rock, massive accumulations of Ca, and a smaller content of Mg in the form of carbonates. Subsequently accumulated sediments insulate organic carbon present in sedimentary rocks from the biosphere.

Hence, bituminous shale and sandstone, limestone, dolomite, marl, and other carbonaceous sedimentary rocks, as well as shale oil along with coal, oil, and natural gas fields, are widely dispersed in Earth's stratosphere. The total content of the carbon that "escapes" from the biosphere is enormous – the stratosphere alone may contain approximately 96×10^{15} tons of it (Table 1.3). Nevertheless, the overall leakage of carbon from the biosphere to the stratosphere is difficult to assess – it could amount to approximately 150–200 million tons a year, i.e., the occlusiveness of the carbon cycle in the biosphere can be around 0.14–0.17 % (Lietuvninkas 2012). It is assumed (Bashkin 2004) that for the last 570 million years (the Phanerozoic), approximately 71.3×10^{15} tons of carbon as a component of carbonates and 8.1×10^{15} tons of carbon dispersed in the content of organic matter "leaked" from the biosphere to the stratosphere together with sedimentary rock.

Recently, the urgent issue of global warming brings to mind allegations that, in Earth's distant past, warming waves often coincided with volcanic reactivation and an increase in the emissions of carbon dioxide into the atmosphere (Dobrodeev and Suetova 1976; Bashkin 2004). Under conditions of a milder climate, widely spread forests bound a significant part of the CO_2 in the atmosphere into the biomass of xylem and in the soil humus. As a result, CO_2 concentration in the atmosphere decreased and ended in climate cooling, ice spread, and deforestation.

Forests in the Ecosphere

As for already apparently ongoing climate changes, one can nostalgically recall that before the Industrial Revolution, CO_2 concentration in Earth's atmosphere was only 280 ppm. However, since then, the emission of gases (primarily CO_2) causing the greenhouse effect has been constantly increasing and is mostly linked with fossil fuel combustion and cement production. CO_2 concentration in the atmosphere increased and, on 13 May 2013, reached a symbolic point of 400 ppm, following which maintaining a climate warming level of 2 °C on Earth has become increasingly difficult (Carbon Dioxide 2015). Not so long ago, the world reached another milestone: in February 2015, Mauna Loa Observatory in Hawaii recorded an average CO_2 concentration of 400.26 ppm in the atmosphere. In the same month a year earlier, it was lower, at 397.91 ppm (Trends in Atmospheric 2015). Recall that the observatory started functioning in 1958, and then recorded CO_2 concentrations of 85 ppm lower, i.e., during that period of time, concentrations rose by approximately a quarter, which is 1.55 ppm per year on average. In recent years, growth has been significantly higher at 2.75 ppm annually (Global Climate Change 2015).

In recent decades, global CO_2 emissions have grown on average by 45 % at an acceleration of every 20 years (Fig. 1.2).

Yet in 2014, autumn forecasts predicted that global CO_2 emissions would reach 40 Gt in 2014 (Global carbon budget 2014). In reality, it was lower, just 32.3 Gt. Officially, the achievement can be seen as a success on the part of the world in reducing CO_2 emissions rather than a casual fact related to the economic recessions of the early 1980s, in 1992, or 2009 (Rost global'nyh… 2015). The International Energy Agency (IEA) explains the halt to growth in emissions with reference to changes in energy consumption patterns in China and International Economic Co-operation and Development (OECD) countries. In 2014, China increased its production of electricity on the basis of renewable sources. OECD countries have made progress in fostering sustainable growth, including the production of renewable energy and increasing consumption efficiency.

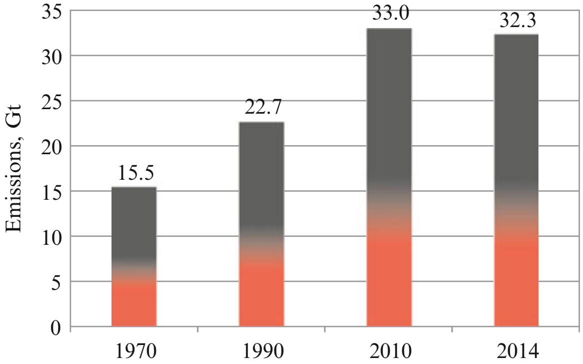

Fig. 1.2 Global CO_2 emission for period 1970–2014

Without going deeper into the problems of CO_2 emissions and balance in the biosphere, as well as possible solutions to them, attention will be focused on **the tree** as the main object of our research and as potential participants in the fighting for the viability of the biosphere. According to data provided earlier by Dobrovolsky, terrestrial vegetation worldwide has accumulated approximately 900 Gt of carbon (Table 1.3), 90 % of which is contained in forest ecosystems. Therefore, forests can be seen as a short-term reservoir of global terrestrial carbon (Fig. 1.1), into which, according to different sources, as part of the process of the synthesis of new biomass, 35–60 Gt of carbon (130–220 Gt of CO_2 in the atmosphere) is annually absorbed from the atmosphere (Isaev et al. 1995; Dobrovolsky 2008). It is assumed that the pure primary output of forest ecosystems accounts for approximately 60 % of the total terrestrial biological output. Almost half of the primary output consists of the biomass of grass, branches, shrubbery, and leaves whose amount covers only approximately 10 % of the total biomass accumulated by forest ecosystems. According to Dobrovolsky, the annual mass of litterfall in terrestrial areas can account for approximately 40 Gt, while the content of carbon on the forest floor comes to 60 Gt (Bashkin 2004). Another version of carbon accumulation in the forests worldwide is presented in Fig. 1.3.

Carbon in leaves, blossoms, fruits, and roots go back only a few years, whereas that in wood charcoal originated approximately 50 years ago (average rate of destruction of wood in the forest). Following the destruction of phytomass, carbon passes into litterfall and then to the forest floor. The average decomposition time of the latter is 1.5–2 years and is highly dependent on specific geochemical conditions of the landscape. As a summarizing index, Glazovskaya proposed a coefficient of litterfall, K_{np}, which can be understood as the ratio of forest litter to the mass of litterfall in a certain area (Glazovskaya 1988). Under conditions favorable for microbiological activity (optimal humidity and higher temperature), falling objects are rapidly decomposed on the forest floor (humid tropical forests $K_{np} = 0.1–0.2$); under less favorable conditions, the process slows down (oak wood $K_{np} = 4$, juniper groves in alluvial landscapes of the southern taiga $K_{np} = 10$); under unfavorable conditions, the process is slow (alluvial landscapes of boreal forests $K_{np} = 10–20$); and under extremely unfavorable conditions, the process is slower still (alluvial landscapes of tundra shrubs $K_{np} = 90–100$, superaqual $K_{np} = 150–3000$).

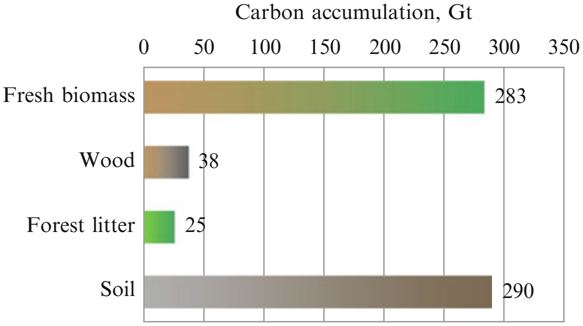

Fig. 1.3 Carbon accumulation in forests worldwide (WHO Global Forest… 2005)

Table 1.4 Carbon found in soil of forests worldwide and in phytomass (according to Olsson 2012)

Biomes	Area (million ha)	Accumulated carbon (Gt)		
		Soil	Phytomass	Total
Boreal forests	1509	**625**	78	**703**
Tropical forests	1756	216	**159**	375
Temperate forests	1040	100	21	121

Maximum values

This means that, for example, the forest floor in humid rainforests may not be formed at all because falling objects mineralize faster than they form. In contrast, in cold climates in the gleyed environment of water-logged forests, the organic matter of falling objects decomposes very slowly, creating favorable conditions for peat formation. The total global stock of peatland carbon is 165 Gt (Bashkin 2004). Moreover, the end of the last century witnessed, in the course of warming, the ecosystems in Alaska and Russia being transformed from carbon sinks into harmful sources of carbon emissions (Oechel and Vourlitis 1994; Zamolodchikov et al. 1997).

The distribution of carbon content in the forests of different biomes is presented in Table 1.4.

Because of the rapid decay of phytomass in tropical forests, soil and the forest floor have accumulated a relatively small amount of carbon, 216 Gt in total. Meanwhile, the soil and forest floor of boreal forests of a similar area (even 16 % less than that of tropical forests) have accumulated 625 Gt of carbon, which is almost three times greater than the level in tropical forests. Naturally, carbon accumulation in the phytomass of forests has the opposite relationship – it is twice as high in tropical forests. Table 1.4 provides a general answer to the question of how carbon distribution and accumulation will change in case of warming in boreal forests, which serve as an important reservoir in terrestrial areas. Under rapid mineralization of the organic matter of falling objects at higher temperatures, carbon accumulation in soil will substantially decrease, i.e., part of the carbon, in the form of CO_2 will "evaporate" into air, further enhancing factors in warming. A similar process, including as a result of fires, has been found to be taking place, for example, in boreal forests in Canada (Juday et al. 2005; Kelman et al. 2009).

However, the tree, as the core component of forest biocenosis in the biosphere and humans, is very valuable as an absorber of carbon from the atmosphere and as a temporary carbon reservoir stabilizing the circulation of gases, primarily CO_2 and O_2, in the ecosphere. Tree-covered terrestrial areas, i.e., forests, are considered in connection with at least three aspects of their importance, generally understood as the ecological, social, and economic functions of forests (Table 1.4).

Without going into the details of numerous and accurately described functions of forests presented in specialized works, only three of those strongly related to the topic of this book will be paid extra attention. Once again, returning to the biosphere function of stabilizing the climate, discussed previously, seems to make no sense.

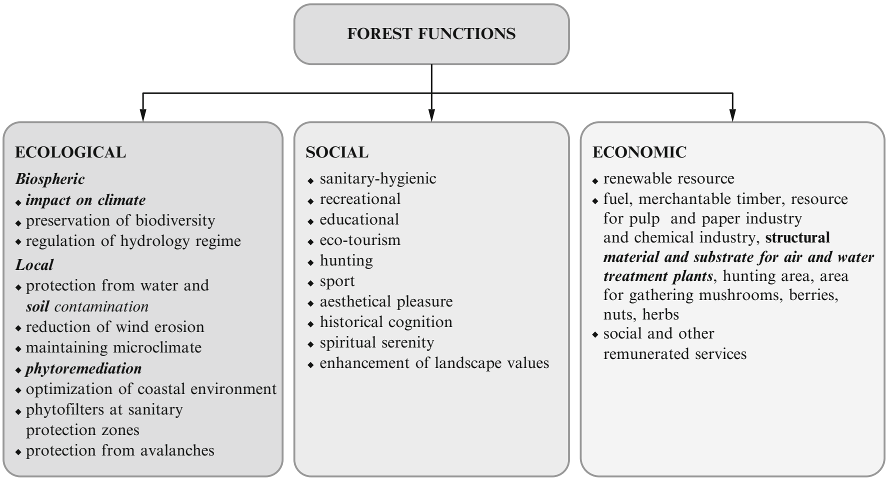

Fig. 1.4 Main functions of a forest

The first *phytoremediation function of the forest* (Fig. 1.4) can be seen as a local ecological function. The tree, as long-lived plants, accumulates in their own biomass, primarily in stems and roots of wood, not only biophilic macroelements but also larger or smaller quantities of microelements. The latter contain microelements important for trees' physiological functions and toxic chemical elements polluting the environment, including metals that are particularly stable contaminants over time. Because soil, as a source of nutrients for the tree, simultaneously acts as a geochemical barrier and an accumulating reservoir for the tree along the pathway of migrating heavy metals, this creates the best conditions for using the tree to extract chemical elements that are harmful to humans and the environment and to temporarily stabilize them in biomass (the aforementioned wood and roots). A similar isolation of metals from such human-affected components of the natural environment as air, water, and soil is also beneficial. Thus, the essence of the question tends more toward assessing this method for the recovery of soil contaminated with metals insofar as may be practical, effective, and economical. Moreover, this is one of the fundamental aspects regarding the sustainable use of the tree in environmental protection technologies.

The second of the three previously mentioned more extensively discussed ecological functions of the tree is as a protector of *soil from pollution*. This function occupies an intermediate position and is a tool for carbon sequestration in soil and a way of improving it. In this case, biochar introduced into soil enriches it with carbon for quite a long time, i.e., it improves the ecological value of soil as a reservoir of carbon. On the other hand, biochar, as an effective sorbent of metals in contaminated soils, decreases their acceptance by plants, i.e.,with respect to hygiene, it improves the quality of agricultural production.

The third of the aforementioned functions of the forest, to put it more precisely, wood as a basic forest product, requires additional attention and is u*sed as a structural material or filler in modern air and water treatment plants.* Because of their individual specific morphological structures, physical properties, and chemical composition, individual wood tissues or products, including wood processing waste such as bark, sawdust, or fiber, can be used as a valuable material in various biofiltration systems for eliminating environmental pollutants. Biochar, as a widely available and cost-effective material, can be successfully employed as a packing material of filters.

Forests in the European Union and Lithuania

Forests in the European Union (EU) cover 159 million ha, composing 4 % of the world's forest area. The total forest coverage in the EU is 38 %. Approximately two-thirds of the forest area of the EU belongs to six member states (in thousands of hectares), including Sweden (28,605), Finland (22,084), Spain (18,173), France (15,954), Germany (11,076), and Poland (9319). The largest single area of a country covered by forests can be found in Finland, Sweden, and Slovenia – more than 60 %. Forests cover 11 % of the areas of the Netherlands and United Kingdom. A fact sheet on the European Union-2015 (Bendra žemės ūkio politika... 2015) states that forests occupy an area of 2,165,000 ha (34.5 %) in Lithuania. Moreover, woodland covers another 84,000 ha. Unlike in the major parts of the world, during the last 60 years, forest areas in the EU have steadily increased, and within the period from 1990 to 2010 alone, they rose by approximately 11 million ha, i.e., 0.4 % annually. Along with woodlands in the EU, forests cover approximately 176 million ha, which accounts for 42 % of EU territory.

On the Web site of the European Parliament, *The European Union and Forests* reviews the status and condition of the forests in the EU, identifies a variety of threatening factors affecting forests, and describes the increased challenges regarding climate change (Bendra žemės ūkio politika... 2015). Fires, particularly in the area of the Mediterranean Sea, droughts, storms, and air pollution caused by emissions from road transport vehicles are highlighted among the abiotic factors affecting forests. Forest biodiversity is under the threat of forest parceling as a result of transport infrastructure elements. Animals (insects, deer) and diseases are mentioned as biotic factors having a negative impact. It is supposed that approximately 6 % of European forests have been infected by at least one of these biotic factors.

Climate change will also bring significant challenges. It is likely that forests will be affected differentially depending on their geographical location. The rate of forest growth, the spread of forests and some of their parasites (probably will move to the north), and the intensity and repetition of extreme meteorological events will vary. As mentioned previously, the situation may change so that boreal forests, particularly important with respect to atmospheric carbon leakage, may become a source of its emission. It is believed that such a critical threshold would be reached at a warming level of 3–5 °C (Olsson 2012). Forest adaptation to a rapid pace of climate change and human assistance (extensive use of renewable energy sources and the employment of wood as a building material) as well as participation in the fight against such developments are identified as two critical tasks.

The Rio+20 Earth Summit took place in June 2012. The conference reviewed major changes having a direct impact on the forest sector over the last 20 years: 300 million ha of forests were lost, CO_2 emissions to the atmosphere increased by 36 %, biological diversity decreased by 12 %, the human population on the planet increased by 26 %, and the prices of raw materials rose by 47 % (Jasinevičius 2012).

Although the EU has no common forestry policy, many initiatives and areas of its plan affect the forests that are not part of its territory. In September 2013, the European Commission adopted a new EU Forest Strategy [COM(2013)659], the main principles of which provide sustainable forest management, the promotion of its multifunctional role, the efficient use of resources, and the responsibility of the EU for the world's forests. Also, strategic guidelines on the actions for the European Commission and its member states have been submitted. A number of actions affect forests in the EU, for example, allocations from the European Agricultural Fund for Rural Development to forests, marketing control over forest reproductive material, maintaining the plant health regime and combating the spread of forest pests (a provision that, by 2020, should make renewable energy resources 20 % of consumed energy), forest fire prevention, the implementation of national plans for sustainable forest management by 2020, creating the European Forest Fires Information System (EFFIS), promoting the ecological public procurement of sustainably harvested wood, and aid in cases of major disasters (storms, forest fires).

The EU is actively involved in a number of international processes exerting a positive impact on forests (e.g., Kyoto Protocol). *Forest Europe* further remains the main initiative related to forests. According to the climate policy, different forest-related initiatives are implemented and include, for example, *The Green Paper on Preparing Forests* for climate change [COM(2010)66] considering the role of forests in connection with international obligations of the EU in the fight against climate change [COM(2012)93], support for actions that will lead to a halt in worldwide deforestation by 2030 and a reduction in tropical deforestation by at least 50 % by 2020 [COM(2008)645], reducing the content of emissions adversely affecting Asian, African, and Latin American forests (Bendra žemės ūkio politika... 2015).

On 1 January 2014, the forested area composed 2177 thousand ha in Lithuania and occupied 33.3 % of the country. For the last 11 years, this area has increased by 131,000 ha and woodedness by 2.0 %. Based on the occupied land area, stands in Lithuanian forests are distributed in the following way: softwood 56.0 %, soft hardwood 40.3 %, and solid hardwood 3.7 % of all forests. According to the species of tree prevailing in stands, the most widespread woods are those of pines (35 %), birches (22.4 %), spruce (20.9 %), black alders (7.1 %), and gray alders (6.2 %) (Lietuvos miškų... 2014).

The total volume of wood in Lithuanian forests amounts to 521.3 million m^3, including 216 million m^3 of pine wood, 85.9 million m^3 of spruce wood, and 88.5 million m^3 of birch wood. The average volume of wood in forests increased from 226 m^3/ha in 2003 to 249 m^3/ha in 2014. According to this index, forests in Lithuania take 9th place in Europe and 14th worldwide. The most productive forests worldwide are those in New Zealand; their annual increment accounts for 430 m^3/ha of wood. The top-producing forests in Europe grow in Switzerland (345 m^3/ha/year).

Forests in Lithuania are cut in a very moderate way and rationally enough – only 1.5 % per year, i.e., much more moderately than in Portugal, India, or Ireland, where 4–7 % of annual wood resources are cut down. Similarly to some other European countries (Latvia, Switzerland, Germany, Austria), approximately 80 % of round wood products suitable for industrial processing are prepared from the wood cut down in Lithuania (Žvilgsnis… 2012).

As shown earlier, the forest performs very important and varied functions in the ecosphere (Fig. 1.4) whose relative values are difficult to compare. However, it can be done. The recently conducted economic and social evaluation of sustainable forest management in Lithuania has shown that the structure of the value of functions looks as follows: economical: 41.1 %, ecological: 37.6 %, social: 21.3 % (Fig. 1.5). A sociological survey among Lithuanians revealed a similar result: economical: 39 %, ecological: 32 %, social: 29 % (Mizaras and Mizaraitė 2014). Now, a specific consumer of forest goods in a particular area may disagree with such a generalized assessment of forest functions at the national level considering the assessment of functions in terms of Earth's current biosphere or at the discretion of the population of the countries having different levels of economic development. In terms of the progress of national economies, the importance of criteria for such an evaluation steps outside the normal sequence of *economy—social value—ecology* and moves from a "for me today" mentality toward a more relevant "for the community tomorrow" one.

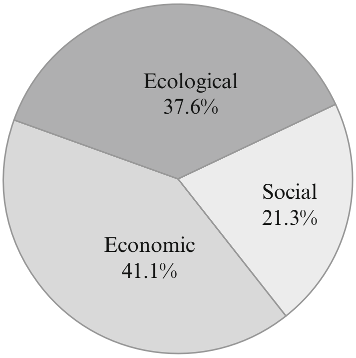

Fig. 1.5 Structure of the value of the functions of Lithuanian forests (according to Mizaras and Mizaraitė 2014)

1.2 Life Cycle of the Tree

Life cycle analysis is known as a versatile and reliable instrument for assessing manufactured products and the impact of technologies on the environment. Detailed analysis provides an opportunity to tangibly and quantitatively compare a few alternative methods for manufacturing and using a product, to identify its strongest and weakest links with respect to environmental protection and to reasonably accept the options of making the selected process more advanced. An important point is that such analysis covers the entire life cycle of the product from its "birth" until expiry. In classic cases, similar stages entail raw material extraction, transportation and processing, and product manufacturing, including byproducts and processes, production waste removal or use in other processes, product application comprising product-related costs, and removing the depreciated product or its residues when its secondary use or recycling are irrational. The general scheme for life cycle assessment is well known and shown in Fig. 1.6.

Life cycle assessment is one of the environmental management methods regulated by the standard series ISO 14000. Although the requirements determined by the system are flexible and adaptable to different types and profiles of companies and organizations, they are based on a common concept of continuous improvement and provide for the optimal use of natural resources, reduction in generating waste produced in technological processes, a decrease in energy consumption and the promotion of more efficient processes, thus involving renewable resources. To apply the set requirements to the main object of this book – a tree in the

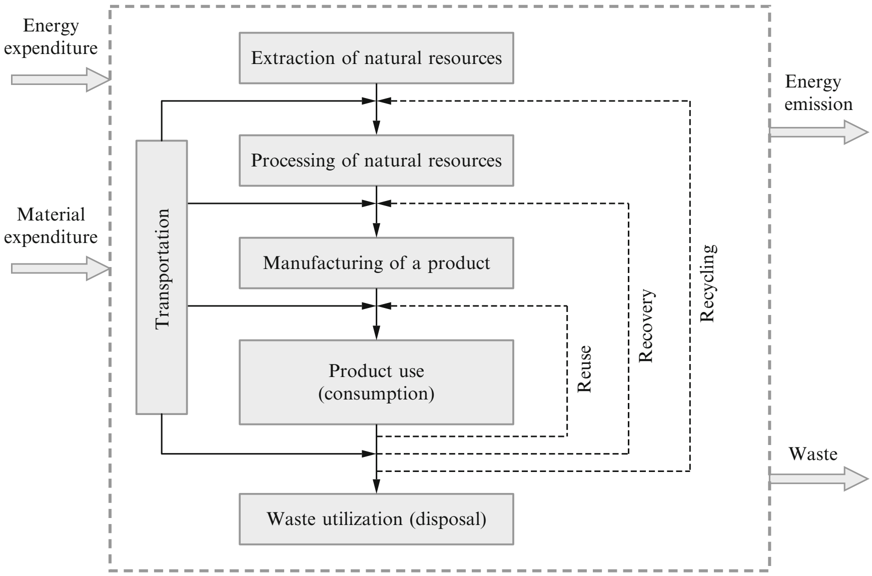

Fig. 1.6 Principal scheme for life cycle assessment (according to ISO 14000)

environment and its protective functions – it is worth emphasizing that, in this case, the requirements for the aforementioned standards involve the complex and incompletely analyzed *tree–environment* system and the uncertainty of its basic functional unit and boundaries.

For example, the main functional unit of the analyzed life cycle is a tree. The question is: is this a tree that is a "consumer" of carbon dioxide and an inhibitor of warming effects (holistic approach), a tree that is an extractor of metals from contaminated soil and the main factor in phytoremediation (local aspect), a tree that is a raw material for biochar and an amendment of soil affected by technogenesis, or, finally, only a raw material used as packing material (biochar and wood fiber) of filters? However, at the moment, there is no way to combine all the foregoing aspects into a single cycle in terms of methodically and minimally required data.

In this case, the word "tree" is used to summarize the concept of "a number of tree" because a single tree cannot perform any of the aforementioned functions. Thus, a discussion should involve the forest as an absorber of carbon dioxide from the atmosphere, as a member of the phytoremediation process taking place in soil, and as a raw material used for other previously mentioned purposes. Hence, it is worth recalling that, in our case, a functional unit of the life cycle is the *afforestation of 1 ha of land contaminated with metals and dominated by pine tree*. The plan is mainly aimed at the remediation of the contaminated soil, which will result in the usage of the polluted wood as the waste of the phytoremediation process. The product developed in the course of the phytoremediation process will be soil purified (at least partially) from dangerous substances. A principal scheme for the general system of these products is presented in Fig. 1.7.

For analyzing the efficiency of phytoremediation as a product of environmental improvement, the input data presented in Table 1.5 will be used. However, the figures do not provide for a real assessment of the value of the recultivated land

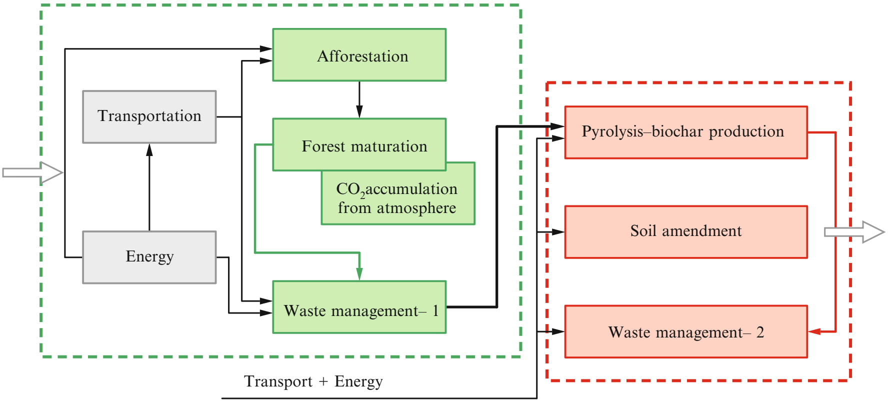

Fig. 1.7 Principal scheme for the system of analyzed products (*green*: phytoremediation, *red*: soil remediation using biochar)

Table 1.5 Main input parameters for assessing tree life cycle

Input parameter	Meaning of parameter	Source
Average volume of stand (m^3/ha)	230	Žvilgsnis į Lietuvos… (2012)
Pine wood moisture (%)	38	Aleinikovas (2010)
Density of dry pine wood (t/m^3)	0.52	Medienos masė… (2015)
Density of freshly cut pine wood (t/m^3)	0.86	
Carbon concentration in dry wood (%)	46	
Coefficient of converting carbon into CO_2	3.67	
Charge for 1 kg of CO_2 emitted to environment (EUR)	0.04058	Lietuvos Respublikos… (2011)
Charge for 1 t of particulate matter emitted into environment (EUR)	61.74	Lietuvos Respublikos mokesčio… (1999)
Amount of dust suppressed by forests per year (t/ha)	30–35	Žvilgsnis į Lietuvos… (2012)
Cost of 1 t of biochar (EUR)	350	
Afforestation of 1 ha of land (EUR)		
Preparing a planting site	75.07	
Price for 5000 pine seedlings	150.14	Žemės ūkio paskirties žemės… (2015)
Planting 5000 seedlings	125.22	
Stand maintenance and protection for first 5 years after planting	735.65	

area, as in the case of possible harm to the environment if soil-contaminating metals are dispersed in the hydrosphere, in the soil of agricultural land, and in soils used for growing nutrient or forage feed plants. Such an evaluation would be very inaccurate and far removed from the boundaries related to aspects of the sustainable role of a tree in environmental protection technologies. Thus, we will mainly focus on the interaction between the tree and the introduced technologies. A general technological scheme for rehabilitating land (afforestation) contaminated with metals is presented in Fig. 1.7.

For example, pine tree planted in contaminated soils will grow for 25 years. Thus, at the end of this period, they could accumulate approximately 34 t of carbon in a 1 ha area containing 230 m^3 of wood. To achieve this result, the growing tree should absorb at least 125 t of carbon dioxide from the atmosphere, i.e., on average 5 t annually. Taking into account current prices for compensating harm caused by components emitted into the atmosphere and global warming (Table 1.5), a total value of carbon in CO_2 equivalent accumulated by tree in wood within the 1 ha area should come to more than 5000 EUR. In cases where felling residues (tree tops, branches with needles, stem losses) should be used for biochar production, the latter figure should increase by approximately one-third, i.e., up to 6500–6600 EUR.

Coniferous tree are known as efficient filters and cleaners that remove particulate matter from the air. It has been reported that 1 ha of forest can annually remove up to 30–35 t of dust from the air (Žvilgsnis į Lietuvos... 2012). From an ecological point of view, such a fact can be interpreted variously. On the one hand, removing particulate matter present in air facilitates improvement in environmental sanitation and promotes hygienic living conditions. It is because of the harmful effects on human health and the environment in general of particulate matter that a fixed charge has been imposed on their emissions (Table 1.5). On the other hand, huge amounts of dispersed particulate matter are emitted by volcanoes into the atmosphere and act as a global cooler of Earth's climate. The particulate matter of anthropogenic origin emitted into the atmosphere acts in a similar way. Nevertheless, among the latter, many of the so-called "black particles" or simply soot may act in a converse way to the aforementioned factors, i.e., they do not make air cooler but warm it by absorbing solar radiation (Skėčio poveikis... 2015). Still, a lack of information on particulate matter, taking into account that its quantities can be projected up to 25 years ahead, means that this aspect of a potential impact will be left to future researchers. Next, we will return to the aforementioned first impact, which is a sanitary-hygienic one.

The translation of 30–35 tons of dust eliminated from air by forests into a charge for particulate matter emitted into the atmosphere above established limits is not an easy task.

First, Lithuanian and EU legislation sets threshold concentrations of particulate matter in ambient air rather than their load per unit of ground surface area, which is expressed in kilograms per square kilometer per day. Thus, defining the content of particles "beyond normative limits" captured by forests is practically impossible. For simplicity's sake, it should be accepted that their entire content is beyond normative limits.

Second, a mature forest annually precipitates 30–35 tons of dust from the air, whereas we discuss afforestation that results in a 20–25 year mature forest. Naturally, young pine saplings precipitate a significantly smaller amount of dust than a mature forest. Therefore, the effect of dust precipitation has been chosen in proportion to the height of the tree depending on their age. Perhaps this is not a very correct decision, but any other choice adopted a priori without specific measurements would also be open to criticism.

Third, the previously mentioned forest can remove 30–35 tons of dust from air if it occurs in sufficiently large quantities. The latter aspect will not be discussed in detail (note that the figures were taken from a publication prepared by the Ministry of the Environment of the Republic of Lithuania (Žvilgsnis į Lietuvos... 2012).

Thus, it is assumed that, for a period of 25 years, afforested pine wood can remove from the atmosphere up to 210 tons of particles present in the air, for the over normative emissions of which the owner should be required to pay a fee of up to 13,000 EUR.

Next, afforestation, forest maintenance, protection, cultivation, and, finally, felling and waste disposal costs will be briefly discussed (Fig. 1.8). The costs of pine seedlings and planting them in an area of 1 ha, land preparation, the maintenance of planted seedlings and stands, as well as expenses for protecting them within the first 5 years after planting, should come to approximately 1400 EUR

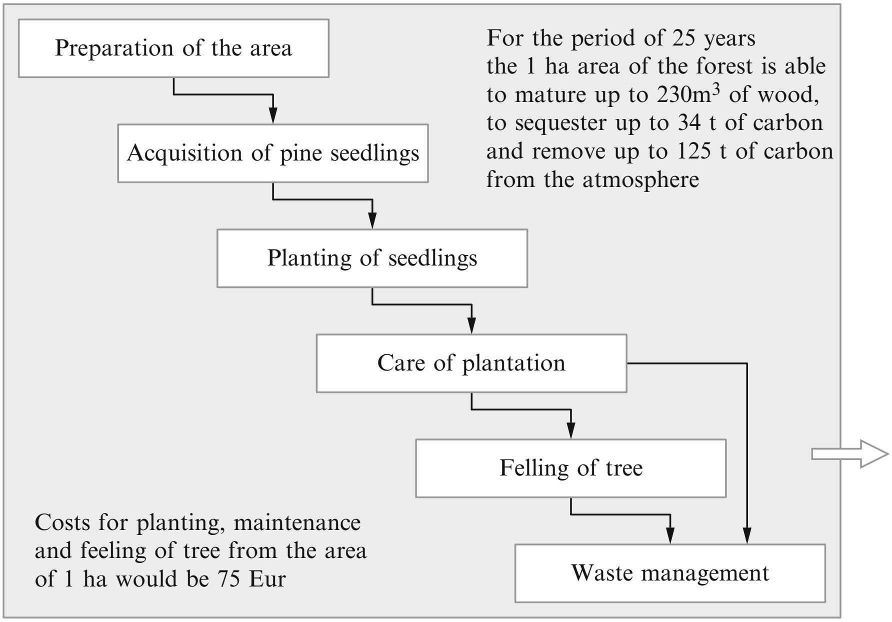

Fig. 1.8 Technological scheme for rehabilitation of land (afforestation) contaminated with metals

(Žemės ūkio paskirties... 2015). The price of the land is not included in the costs of afforestation because it is contaminated and unsuitable for other agricultural uses.

Cutting down a forest (wood production), and hauling the prepared timber in particular, would be highly dependent on specific inventory conditions.

Considering the average cost of operations, their general costs come to approximately 5900 EUR. Processing felling residues/waste (approximately 110 m^3), pulling them close to roads, and transporting them by dumpers would cost 2100 EUR, i.e., the total costs for cutting down forest and waste management would amount to around 8000 EUR.

A concluding diagram illustrating the cost of sales of phytoremediation as the product of the analyzed life cycle is shown in Fig. 1.9.

As mentioned earlier, because of the complexity of the phytoremediation system and separate processes related to it, the obtained result of uncertainty is not accurate, the "green" part of the diagram in particular. Rather, these are focused figures approximately reflecting only two aspects of the same process – the price we pay for the environment and the benefits we receive from it. It could be easily envisaged that a notional and really intangible benefit of the environment for an ordinary user of the Earth is twice as great as the general fair price for it, which is 9300 EUR for 1 ha of land previously violated by humans and now returned to nature. However, this is far from everything that is recovered by both nature and humans from such a piece of land.

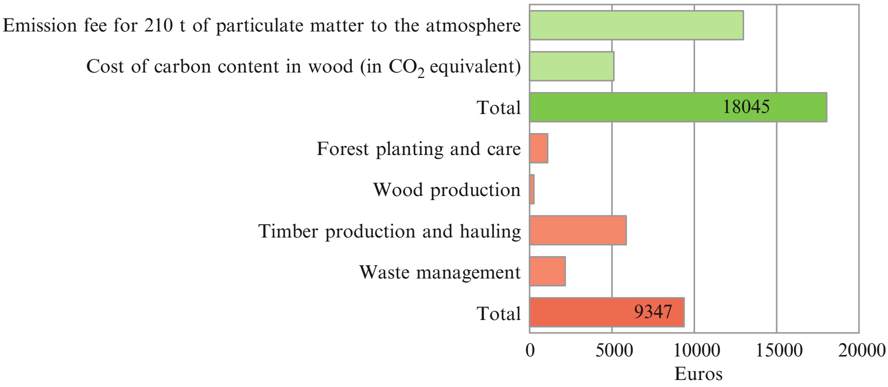

Fig. 1.9 Comparison of costs for phytoremediation and environmental benefits derived from forest in 1 ha area contaminated with metals

The previously presented Fig. 1.5 shows the structure of the value of Lithuanian forest functions where the economic function accounts for 41.1 %, the ecological function 37.6 %, and the social function 21.3 %. The consumption value of CO_2 in the composition of the ecological function of forests comes to approximately 42 % (Mizaras and Mizaraitė 2014). Therefore, it is easy to calculate that, in our case, for the period of 25 years, 1 ha of afforested land may have an integrated value of approximately 25,000 EUR (including taxes for particulate matter removed from the air). Under the same assumptions, its social value integrated within the 25-year period may be equal to a sum of 13,000 EUR (excluding the value of mushrooms, berries, and herbs collected in the infected area). Since the wood of such a forest can be viewed as the waste of a phytoremediation process, those economic benefits will be neglected in this particular case.

Land rehabilitation employing biochar as an element of the life cycle of the tree is aimed at increasing its general economic value, thereby using pine tree wood more or less contaminated with metals as a raw material for producing biochar. On the other hand, carbon present in biochar as a basis for forming CO_2 is stabilized if wood is treated, for example, as a fuel. Because biochar, as a soil amendment, can survive without being affected by oxidation for several hundred years, the responsiveness of soil, as a reservoir of carbon in the land area, can be substantially increased. Thus, it seems illogical to view this feature of biochar as the additional sequestration of carbon in the life cycle of the tree because appropriate contents of carbon removed from air by tree have already been included in the cyclical element of phytoremediation (Figs. 1.7 and 1.9). Hence, in this case, it is possible to discuss only the stabilization of carbon in soil for a longer period of time.

A technological scheme for soil remediation using biochar as an element of the life cycle of a tree (Fig. 1.10) shows that a raw material source of biochar production is wood obtained in deforested phytoremediation fields.

Next follow the stages of wood preparation for pyrolysis, the process of pyrolysis itself, biochar milling and packing, warehousing and storing in warehouses,

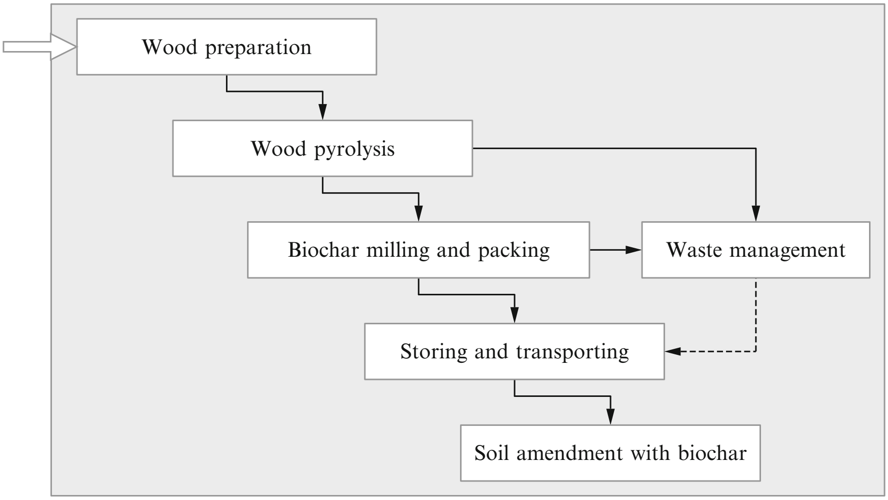

Fig. 1.10 Technological scheme for soil remediation using biochar as an element of the tree life cycle

Table 1.6 Costs for energy and other resources to produce 1 t of biochar from wood (Lehmann and Joseph 2010)

Stage of cycle, type of resource	Costs, EUR
Wood preparation for pyrolysis (growth, transportation, assessment of employee salaries)	11.57
Wood pyrolysis (preparation of device, capital, and energy production costs calculated for 20-year life expectancy of equipment)	115.5
Biochar milling and packing	10.15
Storage, transportation	52.87
Soil amending	1.54
Waste treatment	9.71
Total	201.42

delivering to the end user, and, finally, amending the soil with biochar. Input costs for energy and used materials are displayed in Table 1.6. Costs for wood pyrolysis make up the biggest part, which is more than 57 %.

Wood grown in a 1 ha area allows for producing 34 t of biochar. Thus, taking into account that, in our case, the functional life cycle unit is a pine-dominated forest afforested in a 1 ha area of land contaminated with metals, it can be proposed that costs for producing 34 t of biochar should come to approximately 6868 EUR: preparing wood for pyrolysis: 395, wood pyrolysis: 3940, preparing biochar for land reclamation: 2150, soil amending with biochar residues/waste: 53, waste treatment: 330. These are approximate costs; actual costs should depend also on biochar pyrolysis, a technological scheme for preparing it for use in agriculture,

Table 1.7 Application of biochar economy for growing wheat in the USA (Kulyk 2012)

	Preferred scenarios		
Estimated cost/benefit	Pessimistic	Most likely	Optimistic
Cost of biochar[a]	15,306	26,785	38,265
Cost of application	503	503	503
Price for suppressed content/scenario of CO_2[b]	8296	27,804	44,845
Value of crop (wheat) yield	1741	1741	1741
CBA total costs	15,809	27,288	38,768
CBA total benefits	10,037	29,545	46,586
CBA total profit	−5772	2257	7818

[a] Cost for biochar $200/t, $350/t, and $500/t considering "pessimistic," "most likely," and "optimistic" scenarios, respectively

[b] Prices for suppressed CO_2 using biochar $37/t, $124/t, $200/t considering "pessimistic," "most likely," and "optimistic" scenarios, respectively

established norms for soil amending with biochar and the amount of waste formed during these processes, and regulations for managing them.

The efficiency of employing biochar in agriculture is presented with reference to an example from the USA where wheat is grown in soil amended with biochar (Table 1.7). In the case of using the "pessimistic" biochar application scenario and a biochar price of $200/t, the price of compensating for carbon suppression in soil amended with biochar comes to only $37/t. To improve the soil, 76.53 t of biochar is used in the 1 ha area. Thus, the losses incurred by the farmer should total $5772, which comes with the proviso that the wheat harvest increased from 3924.44 to 6219.44 kg/ha, i.e., 58 %, and the price for wheat will be $0.28/kg of net weight. Only in the case of significantly higher prices for CO_2 sequestered with biochar in reclaimed soil rather than the "most likely" and "optimistic" scenarios may the farmer expect some profit. So far, no similar experiments have been conducted in Lithuania.

With reference to data on the "most likely" scenario (Table 1.7), the final results of the earlier described life cycle of the tree will be provided (Fig. 1.11).

While employing all the aforementioned conditions for phytoremediation, biochar production and its application for improving soil, the general result of activity within such boundaries of the life cycle of a tree is positive – the planned revenues of individual cycle stages are in excess of the incurred costs, which comes to 31,680 EUR, i.e., approximately 153 % taking into account expenditures. The highest revenues (38,860 EUR, i.e., over 68 %) are derived from economic activity that involves soil amendment with biochar. Note that these are estimates based on the duration of the life cycle of the tree, i.e., in our case, 25 years. Biochar insignificantly changes in soil for the period of time given earlier, and costs for additionally acquiring it and introducing it into the soil are not provided.

The remaining revenues relate to the ecological function of a forest planted in an area contaminated with metals – both contaminated soil and air polluted with particulate matter. This function of the forest makes up 32 % of the calculated revenues.

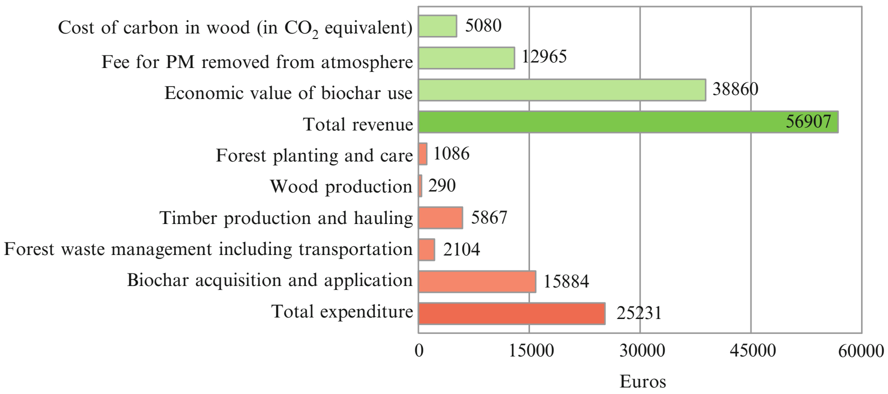

Fig. 1.11 A summary diagram illustrating costs for life cycle of the tree and received benefits, applied in 1 ha land area and used for phytoremediation and biochar production in the planted forest

The most significant costs analyzed in the life cycle of the tree are calculated in the processes of biochar acquisition and using it for improving agricultural soil (63 %), cutting down the forest grown in the phytoremediation area, and hauling the timber close to transportation routes (23.3 % of all costs). Together with operations on forest waste management and transportation, this should come to approximately 7970 EUR (31.6 % of costs).

As mentioned earlier, to assess the costs for amending the soil with biochar in the course of economic activity, an example is given of a biochar economy for growing wheat, i.e., the "most likely" scenario was chosen (Kulyk 2012). The latter scenario suggests a price of biochar of $350/t. Meanwhile, Table 1.6 shows that the price corresponding to costs comes to 201.42 EUR ($225.59). Therefore, a summary diagram of the life cycle of a tree (Fig. 1.11) shows that the costs of acquiring and using biochar are lower than those expected from the version presented in Table 1.7 according to the "most likely" scenario.

Finally, Kulyk (2012) focuses on another very important aspect, which is the selection of a better crop (crop species more profitable than wheat, including vegetables) in soils amended with biochar. It should be rational and obviously boost farming profits. Effective measures, including those in terms of metals and active radionuclides formed after the Chernobyl disaster, must be put in place to ensure biochar quality.

1.3 Benefits of the Tree in Environmental Protection Technologies

The environment can be understood as the totality of natural objects and phenomena changed by human existence and human activity along with the social sphere created by human beings. Environmental protection can be defined as a system of measures supported by the state and society and ensuring harmonious and long-lasting development of society and nature – their coevolution. The latest summary report produced by the European Environment Agency (EAA 2015) indicates that a rational and sustainable use of natural resources set within ecological limits seems to be among the most important measures mentioned earlier. An old primitive sustainable concept of saving natural resources with a focus on underground and biological resources of the biosphere are not the only issues considered in the report. Industrial development, an increasing human population, the rapid urbanization of individual regions and countries have resulted in a mature approach to other natural resources that are extremely important to human existence, including, for example, the preservation of a clean environment, biological diversity, natural climate changes not provoked by human development, and the protection of the planet's ozone shield. These problems have become global ecological issues, and some of them are closely related to the main topic of analysis in this book –a tree in the human environment and biosphere.

The carbon of woody terrestrial vegetation accumulated in biomass represents a significant share of carbon stock reserved for land areas that comprise one third of that carbon stock, while the general content of carbon in the biomass of terrestrial vegetation and the pedosphere is five times greater than its amount in the atmosphere (Table 1.3). CO_2 concentration exceeding 400 ppm in the atmosphere is adding further weight to the warming problem and is forcing people to search more intensively for new methods of getting a large part of the carbon in CO_2 that is present in the atmosphere at least into its main natural reservoirs on land – biomass and the pedosphere – instead of emitting it into the stratosphere, where it arrived as a result of human activity. In this case, afforestation represents one of the main and successfully implemented tasks in Europe – in the context of this book, *the stabilization of atmospheric carbon in the biomass of tree*.

The second previously emphasized aspect is *the permanent stabilization of atmospheric carbon accumulated by wood in biochar as a soil amendment*. Though this sequestration method for atmospheric carbon is not cheap (Table 1.6) and not always economically profitable (Table 1.7), under certain conditions, it can be profitable and attractive (Fig. 1.11). In our case, another point is worth drawing attention to. According to data provided by the Ministry of the Environment of the Republic of Lithuania, annually, approximately 2.5 million m^3 of logging residues form in Lithuanian forests. Their natural degradation and burned carbon as CO_2 reenter the atmosphere (approximately 2.5 million tons). Natural degradation should take place over a period of from 2 to 5 years (e.g., leaves, needles, small branches) or from 50 to 60 years (tree tops, small trunks, the above-ground part of stumps, trimming stems, large branches). Different sources report that up to 40 % of felling residues can be removed from a forest and used in the public interest, for example, for producing biofuel or biochar, without any harm to the environment. However, if only 50 % of felling residues that are allowed to be removed from a forest is converted into biochar introducing the latter into soil, 100,000 to 120,000 t of that carbon would reenter the atmosphere probably a few hundred or may be a thousand years hence. *This should represent an additional transfer of carbon eliminated by the forest from the atmosphere to soil, its long-term terrestrial reservoir.*

Both industrial and municipal *waste* represent one of the most difficult issues to be resolved worldwide. The EU Waste Framework Directive requires following a waste hierarchy, giving priority to waste prevention and reuse, recycling, and recovery, whereas waste emissions are seen as the least desirable option. In accordance with these provisions, tendencies toward waste generation and management in European countries are positively evaluated. Thus, the formation of waste ES-28 (with no mineral waste) per person was reduced to 7 %, i.e., from 1943 kg to 1817 kg. With reference to the data provided by the EU's statistics agency, in 2012, a single EU resident produced 492 kg of municipal waste, 42 % of which was recycled. For the period 2004–2010, the EU-28, together with Iceland and Norway, reduced the amount of waste removed from rubbish dumps from 31 % to 22 % (excluding mineral, combustion, animal, and vegetable waste). Improved waste management allowed for a dramatic reduction in harmful factors, for example, pollution, that are related to incineration and landfills as well as to the extraction and processing of new resources (EAA 2015).

Unlike other industries, for example, metallurgy, chemistry, oil refining, and mining, in many cases, wood waste preparation is not toxic, its utilization does not require high energy consumption, and natural decomposition does not result in the formation of hazardous chemical compounds in the environment, which requires special attention. In the worst case, carbon oxidation takes place within the process of wood decomposition, and greenhouse gases, usually $CO_{2,}$ removed by the tree from the atmosphere are emitted within the process of photosynthesis. In this regard, wood represents an effective, environmentally friendly construction, design, finishing, and carving material. Recently, it has been increasingly replaced by metal, concrete, plastic, glass, and other longer-lived, more technologically advanced, or more hygienic materials that, unfortunately, are not often ecologically rational, because in some cases their production requires disproportionately high energy costs (metals, cement), whereas in other cases large amounts of scarce natural resources (water in the organic chemical industry) or unjustifiably high operational energy costs (numerous glass on construction sites and space-conditioning costs) are required. Moreover, the extraction of such materials, unlike wood maturation in forests, is associated, in a hidden way, with the production of large quantities of CO_2, including from the use of fossil fuels in metallurgy, the cement industry, electricity generation, and CO_2 released from decomposed carbonates of heating cement clinkers.

Thus, *wood and its products, with respect to protecting the environment, are significantly superior to the aforementioned prevailing industrial materials.*

Another serious and well-known ecological problem facing humanity is *the deterioration of the quality of life and the spread of ecological diseases*, particularly in densely populated urban agglomerations, industrial centers, and countries where, because of the general level of development in those places, economic indicators are far more important than the status of the environment in the given country or region (Reimers 1994; Baltrėnas and Ščupakas 2007). Certainly, the tree or the forest itself cannot solve all problems, but some of the problems can be significantly mitigated, in particular those related to, for example, food and fuel, jobs and employment for local residents, timber as a raw material of industry and handicrafts, a more favorable microclimate, and "green" air pollution filters. Looking more globally and deeply, we see how forests are connected to the regulation of the hydrological regime, the prevention of soil water and wind erosion, the uptake of atmospheric CO_2 mitigating the impact of the greenhouse effect on Earth's climate, and negative acidification after-effects on global ocean ecosystems.

Natural wood as a material, unlike many artificial human environment and housing materials, is not allergenic. Today, this characteristic of wood seems particularly important because allergies are often referred to as a twenty-first-century disease affecting almost one-fourth of Earth's inhabitants. Allergens have spread so widely that it would be difficult to find a place where they might not be found in one form or another in the more densely populated parts of the planet. And this is not surprising, because allergologists have found them, for example, in food, beverage, popular cosmetics, personal-hygiene and widely used chemical household products (e.g., creams, lotions, soaps, detergents, disinfectants), food supplements, clothes, toys, synthetic home materials, furniture, and bedding. For example, the modern furniture industry uses a variety of harmful substances resulting in the extensive release of formaldehyde – a colorless, unpleasant, odorous gas that is hazardous to human health. Although formaldehyde emissions are regulated and must comply with E1 standards in many developed countries, beyond, particularly in developing countries, these levels may be two or even more times greater. Furniture, wood chips, hardboard, and plywood are used for manufacturing urea-formaldehyde glues and resins and represent potential sources of allergy stimuli. In contrast, natural wood and its products, in this case, are not dangerous. In addition, on the inside of furniture, for a number of years (for decades, and even for centuries if under proper supervision) they "preserve" carbon absorbed by the tree from the atmosphere.

In this way, not only is wood as a construction, decoration, and interior design material environmentally friendly and durable, but its wide use in these areas will entail considerable leakage of atmospheric carbon dioxide into the technosphere (more precisely to its noocenosis) and can partially replace some resource-intensive materials.

While facing the global stability crisis of ecosystems under the growth of their technogenic load and a deteriorated quality of life, particularly in the concentrated centers of urban and industrial enterprisers, under the pressure of environmental protection authorities, various technologies for reducing a negative impact of the technosphere on the environment are experiencing increased demand. Taking into account the specificity of environmental protection technologies, four groups can be distinguished, including those with the following aims: Group 1: a decrease in the production of waste and emissions harmful to the environment and human health, thereby improving manufacturing processes (e.g., low waste, no waste, rational, reuse); Group 2: saving natural resources (more precisely, saving resources and energy); Group 3: developing treatment based on removing atmospheric pollutants and harmful substances emitted to the environment; and Group 4: implementing the most advanced measures, principles, and technologies for assessing the after-effects of measures taken to ensure environmental quality and reduce pollution.

In the context of this monograph, the focus will be on the last two technologies corresponding to the practical application of the tree and its products. For the removal of harmful compounds from the air, a few modifications of biofilters where wood products are used as packing material have been made (Baltrėnas and Ščupakas 2007). This would be one of the successful applications of wood-based materials in environmental protection technologies in the discussion of which emphasis should be placed on the tree, which function generously and independently as a mechanical, sedimentary, and adhesive geochemical barrier of particulate matter (dust) flowing in the air (Lietuvninkas 2012). Tree can be purposefully used, for example, to create "green barriers" around businesses that produce increasing emissions of particulate matter, close to busy highways, or on the edges of industrial urban functional areas. The ability of the forest to serve as a geochemical mechanical barrier along the pathways of distant transfers of aerosols and to filter the air, removing its aerosol component to forest soil, is presented next (Chap. 2).

The summary report prepared by the European Environment Agency (EAA 2015) highlights that the most important form of capital (productive, human, social, and natural) is natural capital that creates the conditions for basic human existence, covering "fertile soil, multifunctional forests, fruitful land and seas, good quality fresh water and clean air." It also embraces services such as pollination, climate regulation, and protection against natural disasters. In addition, natural capital sets the ecological boundaries of socioeconomic systems and is limited and vulnerable (EAA 2015).

This extremely valuable, limited, and yet vulnerable natural capital must be provided a developed and regularly applied system for monitoring, detailed analysis, assessing changes in dynamics, and implementing prevention measures for negative after-effects. A similar system is in line with the concept of monitoring in ecology. On the other hand, this is Group 4 of the previously mentioned environmental protection technologies implementing "the most advanced measures, principles and technologies for assessing the results of environmental quality and its contamination." The tree represents not only a passive observer of a *monitoring–analysis–assessment–prevention* system. The tree and its separate parts can be used as bioindicators of the dynamics of environmental state and changes taking place within it (e.g., morphological characteristics of leaves or needles, the degree of crown defoliation, the presence of dry tree tops, and dendrochronological and dendroindicational research), as a biogeochemical research object (e.g., micronutrient composition of leaves, needles, and bark), and as an instrument for use in the phytoremediators of contaminated soil. In this case, only an environment contaminated with chemical substances is considered.

In reality, the tree (and the forest as its ecosystem) involves a significantly wider scope of functioning for the prevention of negative environmental changes, a general view of which, in the form of tree functions in the biosphere, was presented earlier (Fig. 1.4).

Undoubtedly, the tree and the forest, a multifaceted ecosystem, in different biomes of the Earth are not only historically important elements and creators of the biosphere; they are also extremely accurate indicators of its deteriorating condition and, perhaps, its guardian angels.

Chapter 2
Contamination Features of Ecosystem Components in a Forested Surrounding Environment

One expert in environmental protection has suggested that a number of direct and indirect links can be found between trees and the chemical composition of other components of an ecosystem, which makes it possible to assess the importance of trees in the active soil–plant–atmosphere system of pollutant transfer 'and evaluate the significance of trees as a means of reducing and stabilizing environmental pollution as well as an indicator of environmental quality. This capability of trees has been established by the well-known interaction between trees and the surrounding environment as one of the main expressions of ecogeochemistry laws, taking into account that the chemical composition of trees as components of an ecosystem directly depends on the geochemical status of the ecosystem.

This chapter reviews the pollution of the components of a tree-based ecosystem in terms of long-term contaminants such as metals. Among other things, the use of trees in ecological technologies is based on their prevalence in both hemispheres of the Earth (e.g., Scots pine is remarkably widespread), including urban areas, zones of impact of pollution sources, and roadsides. Thus, defining the character and extent of the pollution of tree surroundings has emerged as a relevant issue in establishing environmental degradation, identifying the pathways of contamination transfer, and assessing the load of pollution on ecosystems. Special attention is given to metals that are well known for their durability and longevity. The properties of the media transferring and accumulating metals determine the variety of the forms of metals and thus their impact on the environment and human health, which are important parts of the same environment. The chapter focuses on the principles use to assess areas contaminated with metals, determine the pollution caused by metals of aerogenic origin, and quantitatively evaluate the risk level of environmental pollution. The concentrations of metals in surface runoff are described to introduce the load of metals of aerogenic origin in urbanized areas, where a large part of contamination is absorbed by urban forested areas.

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2.1 Edaphic Contamination and Its Ecogeological Evaluation

According to contamination inherence in the general sense, contaminated sites are divided into:

- Urbanized territories,
- Roadsides of roads and railways,
- Agricultural areas,
- Sites in zones affected by industrial enterprises,
- Landfills and sites affected by them.

The sources of concentrated contamination that cause pollution in contaminated sites pose a real threat to the quality of groundwater, air, soil, and local foodstuff. According to the Lithuanian Geological Survey (LGS), 349 sources of concentrated contamination in Lithuania have already been registered in the sanitary protection zones of water bodies.

Early in the period 2000–2007, the LGS took an inventory of geological environment contamination sources in more than ten administrative districts in Lithuania, which included a preliminary assessment of their hazards to geological environments (surface water, groundwater, and soil). During the inventory, potential sources of environmental contamination were attributed to a certain type of contamination:

- Type 1: *objects of industry, energy, transport, and other service providers*;
- Type 2: *objects of accumulation and regeneration of contaminating substances*;
- Type 3: *cattle-breeding objects.*

The experience with the inventory performed by the LGS shows that the potential objects of contamination based on contamination type are as follows:

- Objects of industry, energy, transport, and services comprise 31 %.
- Cattle-breeding objects comprise 30 %.
- Objects of accumulation and regeneration of contaminating substances comprise 39 %.

A total of 5763 pieces of inventory data about 5190 potential sources of contamination were entered into a database of geological contamination sources (Fig. 2.1). That number comprises only about one-fifth of the potential objects of environmental contamination that exist (or may exist) in the territory of Lithuania.

There is only a small number of clean objects, where the values of chemical components do not exceed the allowed levels, i.e., approximately 15 %. The economic activity of another approximately 22 % of objects shows an increase in the general indicators of organic substances and concentrations of individual compounds. This situation is characteristic of new objects, usually found in lowly urbanized sites and used in accordance with environmental regulations.

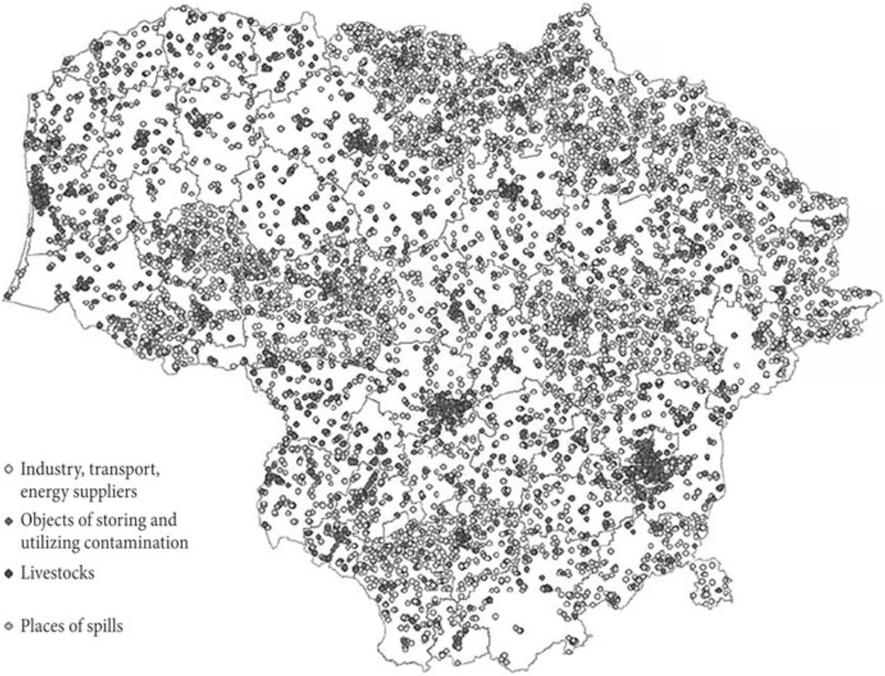


Fig. 2.1 Location scheme of potential sources of geological environmental contamination (LGS Annual Report 2006)

Contamination by hazardous substances (oil hydrocarbons, metals) is observed in almost half of the objects (46 %). Oil hydrocarbons have polluted the groundwater of approximately 33 % of objects: approximately 15 % of the objects show a small or average level of contamination and approximately 18 % show high or very high levels of contamination. These are mainly objects with a heritage of "historical" contamination, where the sources of oil products have penetrated the ground. Although the concentration of oil compounds (mostly benzene) observed in most such objects has a general decreasing tendency, their concentration remains far above legal limits. The highest level of contamination with both oil products and metals is found in railway objects and oil product storage facilities, while the lowest level is found in automobile disassembly and oil extraction sites. Boiler houses and fuel stations are objects of medium contamination. Virtually no contamination by oil products is present in new fuel stations, or the contamination level is low; however, high concentrations of chlorides, sometimes sulfates in groundwater show a negative effect of economic activity.

In all countries, managing contaminated sites consists of several stages (Fig. 2.2). These are inventorying, which in most countries also includes the initial investigation of contamination (e.g., soil, soil + water), preliminary investigation of risk (preliminary risk assessment), and detailed investigation of risk (detailed risk

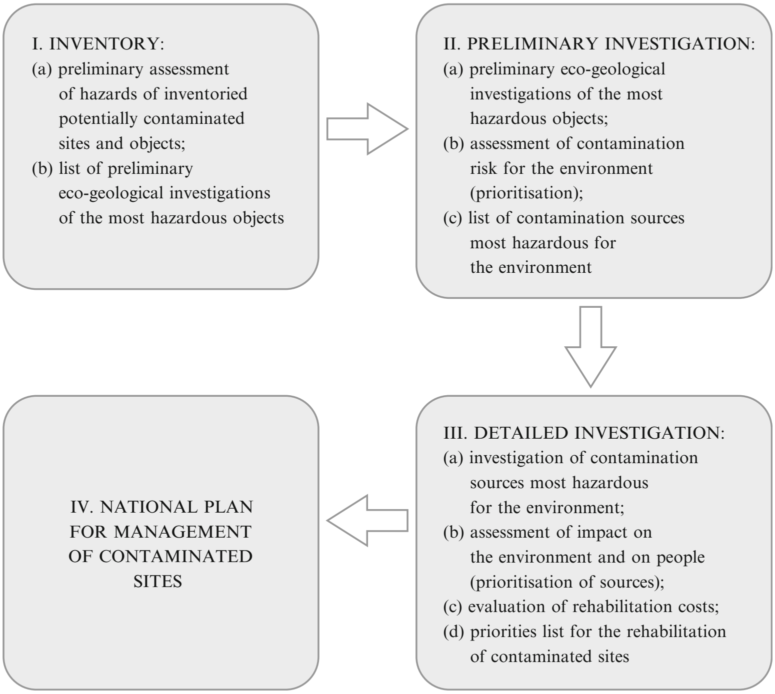


Fig. 2.2 Scheme of management of contaminated sites

assessment). A plan for the management of contaminated sites in a country can be prepared only after the aforementioned stages are completed.

Persons indicated in Order D1–230 of the Ministry of the Environment of the Republic of Lithuania of 30 April 2008, “On approval of the environmental protection requirements for the management of sites contaminated with chemical substances” (henceforth the Requirements) (i.e., persons engaged in economic activities that operate objects in the energy industry, oil, fuel storage facilities; metal production and processing; mineral resources; chemical industry, waste management, wastewater, and others, as indicated in the Requirements) or who perform activities indicated in the aforementioned order and use chemical substances indicated in Annex 3 to the Requirements, as well as territory owners or users in whose territory the activities indicated in Annex 1 to the Requirements were performed, must perform a preliminary ecogeological investigation according to the requirements of the Regulation on Ecogeological Investigations in the following cases:

- If the purpose for using a given territory (land-use method) is changed and the territory is in a group of territories more vulnerable to contamination (Annex 2 of the Requirements), an investigation must be conducted by the time the change is scheduled to take place;

- If activities are planned or changed (Annex 1 to the Requirements), an investigation must be conducted within 2 years of starting certain types of activities or of changes in those activities;
- If the LGS assessment conclusions, prepared according to the results of groundwater monitoring or other investigations, about the need to perform a preliminary or detailed ecogeological investigation are known, an investigation must be conducted within 2 years of the date such conclusions were presented.

A detailed ecogeological investigation in accordance with the requirements of the Regulation on Ecogeological Investigations must be conducted if, during a preliminary ecogeological investigation or groundwater monitoring performed according to the Procedure for Monitoring the Groundwater of Economic Entities, it is established that the concentration of chemical substances in soil or groundwater exceeds the limit value (LV) of chemical substances indicated in an annex to the Requirements and the results of the preliminary ecogeological investigation show that the contamination of soil or groundwater may pose a risk to the environment or people and that is indicated in the LGS's investigation assessment conclusions on the preliminary ecogeological investigation report.

During a detailed investigation it must be established whether contamination, with regard to the use of the territory, poses a risk to human health. Such risk is assessed by the use of risk assessment procedures taking into account the qualities and functions of soil, type and concentration of chemical substances, preparations, organisms and microorganisms, the possibilities of their risk and dispersion according to the Description of the Procedure of Selection of Environmental Rehabilitation Means and Obtaining Prior Approval. Contamination risk must be assessed according to analytical calculations in accordance with the Regulation on Ecogeological Investigations or the models derived using software designed for assessing contamination risk. When assessing the contamination risk, it is necessary to take into account the planned change in the purpose of use of the territory under investigation, if one is aware of such a change before starting a detailed ecogeological investigation.

After performance of a detailed ecogeological investigation on the territory, the established LV of chemical substances in soil is adjusted by calculating the adjusted limit value (LVa) of chemical substances according to Eq. (2.1), and the calculated values are compared to LVs displayed in Table 2.2:

$$\mathrm{LVa} = \mathrm{LV} \times \frac{A + (B \times [\mathrm{CL\_\%}]) + (C \times [\mathrm{OM\_\%}])}{A + (10 \times B) + (3 \times C)}, \tag{2.1}$$

where LVa is the adjusted limit value of chemical substances (mg/kg), LV is the limit value of chemical substances (mg/kg), and CL (%) is the quantity (%) of clay particles (smaller than 0.002 mm) in the investigated soil. In cases where the established quantity of clay particles in soil is more than 50 % or less than 10 %, the values added to the equation are 50 or 10 %, respectively; OM (%) is the soil organic matter content (%). In cases where the established soil organic matter content is more than 10 % or less than 3 %, the values added to the equation are 10 or 3 %, respectively. *A*, *B*, and *C* are coefficients whose values depend on an individual metal (Table 2.3).

The aim of establishing an LVa is to adjust LVs taking into account the quantity of organic matter and clay particles in the soil under investigation. LVa does not apply to underground water. The established LVa are to be referred to when preparing project documentation for the management of a site contaminated by chemical substances, performing such management, or performing control.

Considering that land use should be the main criterion describing LV, and to ensure that territory-sensitivity categories used in legal acts HN 60:2004 and LAND 9-2002 will be applied to the legal act upon assessment of contaminated territories, LV could be applied to these land-use types (Table 2.1).

When establishing the LV for metals in soil for land-use type I, it was considered that the LV was equal to the background concentration of a metal in soil (*X*) plus two to three standard deviations (*S*). The LV of metals in groundwater for land-use type I was established based on the 99th percentile of background values (Table 2.2). This method was applied only to those metals for which reliable statistical information was available. Information on regulating other hazardous substances is presented in annexes to the Requirements.

Table 2.1 Four land-use types of varying sensitivity to contamination for the purposes of assessing contamination risk and for selecting different limit values

Land-use type I	**Land-use type II**
• Strict regime, contamination restriction, and bacteriological contamination restriction strips of sanitary protection zone (SPZ) of potable and natural mineral groundwater sources, established according to Lithuanian Hygiene Standard HN 44:2006 • Protection zones of surface water body coasts • Protected territories • Other territories of similar type indicated in territory planning documents of a municipality (city)	• Farming sites • Forest territories • Other territories of similar type indicated in territory planning documents of a municipality (city)
Land-use type III	**Land-use type IV**
• Territories for residential, recreational purposes • Sanitary protection zone (SPZ) of potable and natural mineral groundwater sources • Surface water body protection zones • Territories for commercial purposes (e.g., shopping centers) • Other territories of similar type indicated in territory planning documents of a municipality (city)	• Territories for industrial use • Motorways with protection zones • Oil extraction (oil well) sites, etc. • Oil and liquid oil products storage, processing and loading places (e.g., storage facilities, fuel stations, terminals) • Railroad • Territories of oil pipeline pump stations • Other territories of similar type indicated in territory planning documents of a municipality (city)

Table 2.2 Limit values (LVs) for metals

	Soil				Groundwater	
	Category of territory sensitivity to contamination					
	I	II	III	IV	I	II, III, IV
Indicator, mg/kg DW	mg/kg DW				μg/L	
Arsenic (As)	5	10	20	50	10	50
Tin (Sn)	4	10	10	170	20	1000
Barium (Ba)	500	700	1000	1500	700	2000
Beryllium (Be)	10	10	100	800	5	50
Boron (B)	40	50	200	400	1000	5000
Chrome (Cr)	50	50	100	300	25	100
Zinc (Zn)	100	300	600	1200	300	1000
Mercury (Hg)	0.3	0.6	1.5	5	1	1
Cadmium (Cd)	0.8	1	3	12	1.5	6
Cobalt (Co)	10	30	150	250	25	100
Manganese (Mn)	1000	1500	2000	10,000	N/A	N/A
Molybdenum (Mo)	2	5	100	200	250	400
Nickel (Ni)	30	75	150	250	20	100
Selenium (Se)	N/A	5	10	15	10	100
Silver (Ag)	0.2	2	10	20	10	40
Stibium (Sb)	5	10	10	40	5	20
Lead (Pb)	40	100	300	550	25	75
Uranium (U)	5	5	15	200	2	15
Vanadium (V)	80	150	150	250	100	200
Copper (Cu)	25	100	200	200	60	2000

Note: *N/A* not applicable

Soil Contamination by Metals in Lithuania and Its Risk Assessment

Lithuanian soils are not contaminated with metals because the country does not have developed industries that contaminate soil very much – metallurgy, mining, or the manufacture of heavy machinery. There are several usual ways to contaminate soil with metals, each of which is more or less specific for individual land-use types. But there is also a common, permanent source of soil contamination—transfer of aerogenic air pollutants from various local sources of contamination and their long-distance cross-border transfer (Table 2.3).

Additional loading of the soil of agricultural land with harmful substances is related both to agrogenic (e.g., soil cultivation, use of standard mineral fertilizers and typical soil amendments, and pesticides) and to frequent agro-technogenic means (use of household, industrial, and cattle-breeding complex waste for fertilization or land improvement, use of contaminated water for irrigation) applied for

Table 2.3 *A*, *B*, *C* values (nondimensional values) for establishing adjusted limit values (LVa) for metals

Metal	*A*	*B*	*C*
Arsenic	15	0.4	0.4
Barium	30	5.0	0.0
Beryllium	8.0	0.9	0.0
Cadmium	0.4	0.007	0.021
Cobalt	2.0	0.28	0.0
Copper	15	0.6	0.6
Chrome	50	2.0	0.0
Lead	50	1.0	1.0
Mercury	0.2	0.0034	0.0017
Nickel	10	1.1	0.0
Tin	4.0	0.6	0.0
Vanadium	12	1.2	0.0
Zinc	50	3.0	1.5

intensive land use. River floodplain soils that are frequently used for vegetable growing receive additional loads of metals and other contaminants during floods with contaminated river sediments. In addition, components that are both soluble and insoluble in soil solutions, washed out of watershed and slope soils, and transported here to river floodplain soils (surface and lateral soil filtration) can accumulate in them.

Additional technogenic loads of soils with metals in urbanized and industrial areas and their impact zones depend largely on the characteristics of the relevant areas, for example, whether they are urban residential functional zones (traditional old zones or new city districts), industrial zones (and the profile of the specific industry), or whether they are in zones of impact of transport arteries and transportation hubs or recreational zones and natural elements. In all cases, the composition of such soils usually varies significantly in terms of metals.

The additional loading of soils with metals in forested areas is mostly related to various agrogenic and agrotechnogenic means applied to them and the application of technologies that exploit forest resources.

In the latest assessment report on strategic consequences for the environment of the EU Structural Assistance Action Programme 2014–2020, it is officially stated that it is still rather difficult to objectively assess soil quality and tendencies in its change owing to insufficient and inconsistent previous investigations. It is also emphasized that the most urgent problems of soil quality are currently related to contamination with chemical substances, soil erosion and soil acidification, and the leaching of nutrients and microelements from the soil. It is indicated in the discussion of aspects of management of contaminated sites that contamination with metals is characteristic of cities, particularly industrial sites where soil can be contaminated up to a dangerous level.

The Geochemical Atlas of Lithuania (Lietuvos geocheminis atlasas), prepared by V. Kadūnas and co-authors (Kadūnas et al. 1999), stands out both for its scope (2395 samples) and for the level of generalization among previous researches on the

Table 2.4 Concentration of metals in Lithuanian soils (mg/kg) (Kadūnas et al. 1999)

Type of soil	Indicator	Co	Cr	Cu	Mn	Ni	Pb	V	Zn
Sandy	X	3.5	6.5	25.1	405	9.4	15.5	26.1	22.2
	V,%	36.8	49.3	36.5	58.8	35.5	32.9	37.1	50.1
Sandy-loamy	X	5.0	9.6	35.7	449	13.8	14.9	37.8	28.9
	V,%	30.9	28.1	28.1	43.0	35.0	28.2	32.0	44.9
Loamy-clayey	X	6.4	6.4	44.0	451	18.0	15.3	49.3	35.7
	V,%	36.1	36.1	29.1	46.4	36.9	28.7	42.1	45.5
Peaty	X	3.6	10.6	21.2	384	12.1	36.2	31.1	39.9
	V,%	69.4	101.5	59.7	197	64.3	73.8	76.9	169.4
All types	**X**	**4.7**	**9.5**	**31.7**	**423**	**13.3**	**16.6**	**36.2**	**31.5**
	V,%	**47.1**	**59.5**	**44.4**	**73.0**	**47.1**	**47.7**	**50.2**	**87.3**

Note: *X* concentration (arithmetic mean) (mg/kg), *V,%* coefficient of variation

distribution of metal concentrations in Lithuanian soils. According to the atlas's data, the background concentrations of metals in Lithuanian soils depend on their granulometric composition and usually increase as the dispersity of the soil mineral components increases (Table 2.4). The largest concentrations of most metals have been established in loamy-clayey soils, whereas those of Pb and Zn are found in peaty soils. Judging from the variation coefficients of distribution of the chemical elements given in Table 2.4, their distribution is rather even – the variation coefficients usually do not exceed 50 %. Unevenness of distribution is observed only in peaty soils enriched with organic matter – in this case, the variation coefficient can exceed even 100 % (Mn, Zn, Cu). Such a quality of these soils is related to an uneven sorption distribution of geochemical barriers in them (Kadūnas et al. 1999).

The aforementioned researches have also established minor regional differences in terms of metals in soil, related to both the age and genesis of parent rocks and to potential long-distance cross-border transport of metals of aerogenic origin (Kadūnas and Radzevičius 2003). The effect of the latter factor is likely seen mostly in coastal soils, which are marked by increased concentrations of Pb, Zn, and Cu. Indirect proof of this assumption could be an increase in the total dustiness of the district, a higher quantity of metals in solid atmospheric fallout (Gregorauskienė and Kadūnas 1998), and significantly higher annual flow of metals with forest litter (Miško ekosistemų 2006).

Certain differences in the concentration of metals in soils depending on land-use type have also been established (Table 2.5).

The concentrations of metals in arable fields and soils of fallows and meadows are close irrespective of soil type; however, they differ significantly from those in forest soils. In addition, such a difference is not single-valued: metal concentrations in sandy and sandy-loamy forest soils are higher (the only exception is Pb concentration in sandy soils of fallows and meadows) but smaller in loamy-clayey soils than in arable fields and soils of fallows and meadows. For the purpose of quantitative interpretation of this fact, we will use a coefficient we call the *forest barrier accumulation coefficient* K_{for}:

Table 2.5 Concentration of metals in Lithuanian soils of different land uses (mg/kg) (Kadūnas et al. 1999)

Type of soil	Land use	Co	Cr	Cu	Mn	Ni	Pb	V	Zn
Sandy	Forest	4.9	34.5	9.3	457	13.4	14.9	37.0	28.0
	Arable field	3.8	27.9	7.5	397	10.2	14.8	28.1	22.7
	Fallow, meadow	3.9	28.0	3.9	429	10.5	15.2	29.4	24.5
Sandy-loamy	Forest	6.4	43.7	11.3	473	17.8	15.4	48.8	35.2
	Arable field	5.2	37.2	9.8	449	14.3	14.9	38.5	28.7
	Fallow, meadow	4.9	35.1	9.6	441	13.6	15.1	37.7	30.1
Loamy-clayey	Forest	2.8	16.3	9.0	322	9.8	20.5	25.5	33.8
	Arable field	6.4	44.1	11.1	434	18.0	15.2	48.6	35.1
	Fallow, meadow	6.5	44.1	11.9	460	18.1	15.4	50.6	36.8

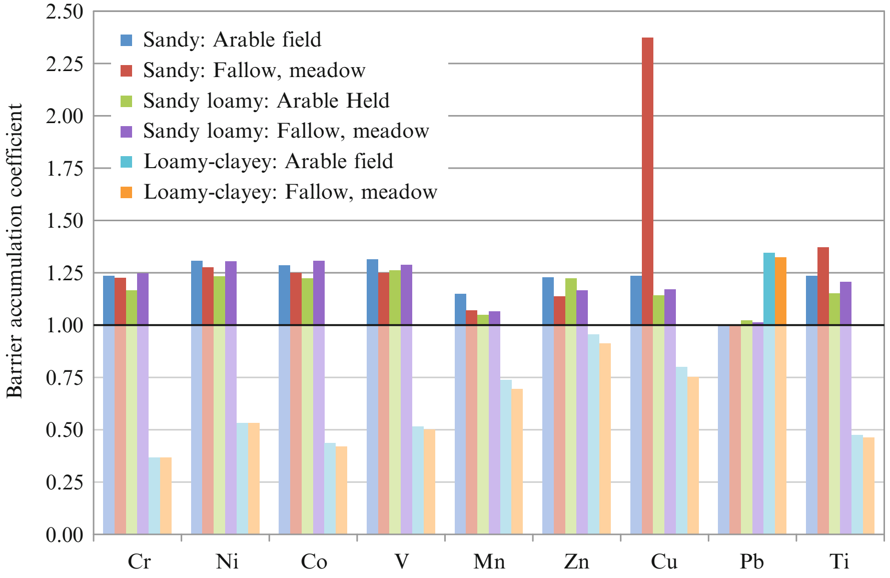


Fig. 2.3 Values of forest barrier accumulation coefficients K_{for} in Lithuanian soils

$$K_{\text{for}} = C_{\text{for}} / C_{\text{j}}, \tag{2.2}$$

where C_{for} is the concentration of investigated chemical element in forest soil (mg/kg), and C_{j} is the concentration of the chemical element in the compared soil of land-use type j (mg/kg).

The diagram in Fig. 2.3 presents the values of the forest barrier accumulation coefficient. The first feature to note in Fig. 2.3 is the appearance of titanium (Ti) in the diagram. Here titanium is one of the chemical elements forming continental aerosols, with particularly small values ($K_a < 1$) of the aerosol accumulation coefficient (Lietuvninkas 2012) and used as a special marker of aerosol fallout. It can be stated that, unlike many other chemical elements, titanium is transported by air masses mostly in the form of solid particles. Meanwhile, such metals as Pb, Zn, Cu, Ni, Cr, and particularly Cd and Hg have aerosol accumulation coefficient values ranging from 10–50 to 50–100 and higher, and a significant part of them in the atmosphere is in the form of vapor – gas.

The second feature related to the interpretation of the diagram in Fig. 2.3 can be called *the accumulative function of a forest on the basis of aerodynamic sedimentary and adhesive geochemical barriers*. Both these barriers, with examples of their activity, are described in the works of one of this book's coauthors (Lietuvninkas 2002a, b, 2012). Their essence is that forest, as an aerodynamic geochemical barrier, changes the properties of land surface interaction with air masses, significantly increasing its "roughness" and reducing the speed of air mass transfer, which is a basis of the aerodynamic sedimentary barrier. On the other hand, this enables more active interaction of air masses and aerosols in them with contact objects, including tree needles and leaves, large and small branches, and trunk bark –the essence of the geochemical adhesive barrier. In this way, a forest affects aerosols, which are in air flows, as a complex geochemical barrier, inducing the mechanical sedimentation of their components, mainly in tree crowns. Naturally, the fallout accumulated in tree crowns later gets into soil – —it is washed down by rain or comes down with litterfall.

The aerosol "catching" mechanism that always operates in forests has clear consequences. The regular monitoring of annual metal fluxes that find their way into forest litter on soil, together with litter in Lithuanian integrative monitoring stations (IMSs) in Upper Lithuania (Aukštaitija) and Lower Lithuania (Žemaitija) regions, shows that they are different. According to data from this source, the annual metal flux into forest litter in the CMS of Upper Lithuania in 2012–2013 was approximately as follows (g/ha): Zn: 250; Pb: 4.5; Cu: 13; Cd: 1.1; Mn: 2500; Cr: 2.1. The annual flux of many metals in the CMS of Lower Lithuania was three to four or more times greater (g/ha): Zn: 280; Pb: 17; Cu: 18; Cd: 7.8; Mn: 11,150; Cr: 6.2. Without going into a deep analysis of the reasons for this fact, we would like to point out two things.

The CMS of Lower Lithuania occupies a mostly frontal position with respect to the transfer flows of long-distance cross-border air masses crossing Lithuania. For this reason, the forests of Lower Lithuania filter air that contains more aerosols, losing a part of them owing to the aforementioned geochemical barriers. For this reason, also owing to a relatively larger part of needles in the fallings of fir forests covered by the CMS of Lower Lithuania (77 % vs. 55 % in pine forests covered by the CMS of Upper Lithuania), the metal fluxes into forest litter are significantly greater.

Second, according to Lithuanian geochemists (Gregorauskienė and Kadūnas 1998; Kadūnas et al. 1999; Radzevičius and Kadūnas 2006), the increased quantity of metals in soils of Western Lithuania and significant anomalies of some of them (Ag, Pb, Zn, Sn) can be explained by larger loads of snow dust and higher levels of their metallization (by up to 65 % vs. the average in Lithuania). The geochemical qualities of aerogenic fallout (increased quantities of Ag, Pb, Zn, Sn, and correlations and associations of chemical elements), which are reflected both in the composition of raised-bog peat and in soils of different compositions, show that at least some of them are related to regional and long-distance cross-border transfer of organic fuel combustion products, which has been ongoing since the beginning of the industrial era some 200 years ago. Acid rain, which is harmful to nature, is only one of the aspects of the "activities" of cross-border air flows, transporting not only around 70 % of S and N compounds to Western Lithuania (Motuzas et al. 2009) but also a significant part of the aerogenic fallout of metals.

Thus, going back to Fig. 2.3, we may conclude that siderophilous chemical elements in Lithuanian sandy and sandy-loamy soils (Cr, Ni, Co, V, to a lesser degree Mn) in forest soils, compared to their analogs in arable fields and in fallows and meadows, accumulate much like Ti, i.e., their concentrations in forest soils are always higher, by up to 25–32 %, than in the soils of arable fields and in those of fallows and meadows. We find the converse situation in the case of loamy-clayey soils – the concentrations of these chemical elements in forest soils are lower by up to two to three times than in the soils of arable fields and of fallows and meadows. Chalcophiles Zn and Cu are distinguished by their more even distribution in soils of different compositions – their concentrations in forest sandy and sandy-loamy soils are higher than their analogs in the soils of arable fields and of fallows and meadows, and in forest soils of loamy-clayey type their levels are just 4–8 % (Zn) or 20–25 % (Cu) lower. The distribution of Pb is unique: in sandy and sandy-loamy soils of all land-use types its concentrations differ by just 1–3 %, and in forest soils of loamy-clayey type they are greater by as much as one-third than in the soils of arable fields and of fallows and meadows.

Such a varied distribution in the concentrations of metals in different soils, which became apparent when analyzing large-scale representative samples (almost 2400 samples), calls for an explanation.

Forest soils of sandy and sandy-loamy types, compared to soils of other analyzed land-use types, obviously accumulate siderophiles Cr, Ni, Co, V, less Mn, with the help of aerodynamic sedimentary and adhesive geochemical barriers. Additionally, it is possible that such accumulations can be influenced by a biogeochemical barrier – the accumulation of metals by leaves and needles that form the basis of forest litter. In the case of arable fields and fallows and meadows, the said geochemical barriers are ineffective.

And what about loamy-clayey forest soil, where concentrations of siderophiles are smaller than in analogous soils of another land-use type? The answer is not easy and it is hard to explain why. In general, the concentration of metals in soil is the result of an equilibrium in geochemical processes of inflow and outflow (leaching, in the case of agricultural land, as well as removal with harvest) established therein.

In sandy and sandy-loamy soils, distinguished by a limited cation exchange capacity, in forests, owing to more effective activity of aerodynamic sedimentary and adhesive geochemical barriers, the accumulation of chemical elements of aerogenic origin dominates in the short term. In the case of arable fields and fallows and meadows, the inflow of metals-aerogens is not that great; therefore, the aforementioned equilibrium of geochemical processes here moves toward their leaching. In agricultural land it is also reinforced by the removal of metals with the harvested biomass.

In soils of the loamy-clayey type, distinguished by a significantly higher capacity of their sorptive cation exchange complex, the conditions for metal accumulation are more favorable. Natural leaching processes here depend mostly on the pH of the soil solution and the composition and quantity of organic acids. Fir forests are common in loamy-clayey soils, which often acquire the qualities of podzol, with acidic forest litter being characteristic of such forests, and a poor eluvial (humus-type) horizon, i.e., conditions that are very favorable for the dissolving and leaching of metals. The equilibrium of geochemical inflow–outflow processes here clearly moves directly toward the leaching of cations. In fallows and meadows, grass plants dominate, and there are many gramineous plants, which ensure both a higher ash content of fallout and a higher content of Ca. The soils here are richer in humus than in forests with a significantly higher-capacity sorptive cation exchange complex. Therefore, it is no surprise that soils of fallows and meadows of the loamy-clayey type accumulate microelements better and that the concentration of the latter is statistically greater than in their forest analogs.

The chalcophiles Zn and Cu migrate better in the environment than the aforementioned siderophiles. In aerosols, they are mostly in a vapor-gas state – the aerosol accumulation coefficients reach 10–50. In general, the distribution of their concentrations in Lithuanian soils is close to that of chemical elements of the siderophile group. Perhaps one of the most significant differences is a slightly smaller contrast between sandy–sandy-loamy and loamy-clayey soils (Fig. 2.3).

Lead distribution is unique compared to all the previously analyzed chemical elements, i.e., the largest values of the forest barrier accumulation coefficients K_{for} are characteristic of loamy-clayey soils (Fig. 2.3). It is obvious that, unlike Zn and Cu, lead is not a biophilic chemical element, it is less mobile in the environment, and it tends to accumulate less in alluvial (clayey) soil horizons, its aerosol accumulation coefficient is even higher than that of Zn or Cu (reaching up to 50–100), and it is among those microelements that accumulate most in snow dust (concentration coefficient: 18.5) in Lithuania (Kadūnas et al. 1999), but it is not clear why in clayey soils it accumulates better in forests than in fallows and meadows or in arable fields. A number of assumptions could be made here, but they are just as easily dismissed.

Soils in Lithuanian cities and industrial zones have significantly higher concentrations of microelements, which depend on many factors: as mentioned previously, in cities they depend on the functional purpose (residential, recreational, transportation, or industrial) of their relevant zones, the duration of soil contamination development, the effectiveness of their self-purification processes, and other factors. In industrial zones, the greatest influence is exerted by the activities of companies in the zones and the range of chemical elements emitted by them into the environment, the sustainability of the technologies used, the capacity of the companies concerned, the work culture, and conformity of the companies' policies to advanced management principles. Information on the soil of some Lithuanian cities is given in Table 2.6. The distribution of metals in urban areas is very uneven and their largest concentrations often considerably exceed the arithmetic means presented in Table 2.6. For example, the largest concentration of Zn in the soil of the Šnipiškės subdistrict in the city of Vilnius amounts to 9950 mg/kg, in the soil of

Table 2.6 Concentration of metals in soils of Lithuanian cities (mg/kg) (Kadūnas et al. 1999)

City, district	Cr	Ni	Co	V	Mn	Zn	Cu	Pb
Vilnius, Žirmūnai	29.3	14.1	3.88	27.4	470	108	23.8	54.4
Vilnius, Žvėrynas	40.9	15.1	3.80	30.6	535	211	25.7	53.7
Vilnius, Šnipiškės	38.5	14.7	3.64	27.3	481	270	37.7	58.2
Šiauliai	88.5	19.6	5.51	33.7	525	70.3	23.5	31.3
Panevėžys	55.5	30.0	5.05	41.1	431	197	86.7	151
Alytus	62.8	40.7	3.91	29.0	392	120	24.4	28.2

the city of Alytus it is 12,000 mg/kg, and in the soil of the city of Panevėžys it is 27,792 mg/kg. The largest concentration of Pb found in the soil of Vilnius is 1140 mg/kg (Šnipiškės), whereas in Panevėžys it is 90,690 mg/kg. But that is within the limits of the so-called city geochemical anomalies. The association of technogenic chemical elements most often detected in urban soil is Pb-Zn-Cu-Sn-Cr-Ni-Co-Mo-Ag. Technogenic anomalies with the greatest contrast are found in the soils of the territories of metal-processing and motor-transport enterprises and boiler houses (Kadūnas et al. 1999).

In Lithuania, the contamination of soil with hazardous substances is regulated by Lithuanian hygiene standard HN 60:2004, "Maximum allowable concentrations of hazardous chemical substances in soil," approved by Order V-114 of the Minister of Health of the Republic of Lithuania, dated 8 March 2004. This hygiene standard sets the maximum allowable concentrations of 77 hazardous chemical substances, including metals, in soil, which do not cause harm, directly or indirectly (through plants, air, or water), to human health or the health of future generations. It is applicable to the soil of residential and recreational areas and soil used in agriculture and is mandatory for entities whose activities are directly or indirectly related to soil use, its possible chemical contamination, change in sanitary conditions, and possible impact on human health, as well as for authorities that perform soil contamination monitoring and regulation functions.

The legal act provides a soil contamination assessment methodology and describes actions that must be taken when hazardous substances exceed the values indicated therein. The approved assessment scale is described in more detail in Sect. 2.3.

2.2 Aqueous (Surface Runoff Water) Contamination Patterns in Urban Areas

With the introduction of the EU Water Framework Directive (2000\60\EC), member states are required to estimate the concentrations and loads of contaminants entering surface waters and to adopt the methods for maintaining an acceptable ecological status of surface water bodies to which surface runoff water is released. Surface runoff water (SRW) from impervious surfaces can be considered a non-point source of water pollution (NPSWP). Emissions from motor transport and

Table 2.7 Comparison of atmospheric metal deposition in wet and dry conditions (Sabin et al. 2005)

	Annual metal flux (range), μg/m^2/year	
Metal	Wet conditions	Dry conditions
Cr	18 (0–45)	440 (250–620)
Cu	200 (0–520)	3211 (1800–4600)
Pb	29 (0–74)	2000 (390–3600)
Ni	38 (0–96)	1300 (0–2700)
Zn	1500 (0–3900)	13,000 (4900–22,000)

railways, industry and energy objects, and the erosion of building materials are among the main sources of pollutants in SRW (Sabin et al. 2005; Milukaitė et al. 2008). SRW is being recognized as a leading source of pollutants to surface water bodies (Shaw et al. 2006). Washings from the atmosphere, transport vehicles, and building materials are considered the main artificial sources of metals in SRW. Metals in atmospheric air can directly affect the total concentrations of metals in SRW. In the case of atmospheric metal deposition into surface water catchment areas, Sabin et al. (2005) determined that wet deposition washes out of the atmosphere approximately 1–10 % of all annual quantities of metals that reach the surface of Earth (in wet and dry conditions). The quantities of metals in atmospheric precipitation are given in Table 2.7.

In urban areas, SRW represents a major environmental issue because it can be affected by elevated concentrations of metals (e.g., Cd, Cu, Ni, Pb, and Zn), deteriorating the quality of water bodies (Tiefenthaler et al. 2008). The contamination of surface water bodies caused by SRW is significant. Table 2.8 presents concentrations of metals in SRW, in raw sewage, and in treated wastewater for comparison.

Of the metals typically found in SRW, Cd, Cu, Pb, and Zn are the major concern (Weiss et al. 2006). Various studies identified the corrosion of galvanized steel roofing materials and metal drainage elements (e.g., gutters, downspouts, and steel sheets) as a main source of Cd, Pb, and Zn in SRW from roof surfaces (Ogburn et al. 2012).

Vehicle exhaust emissions and wear and tear from tires, brakes, and other car parts are the primary sources of Cd, Cr, Cu, Pb, and Zn in SRW from road surfaces (Rule et al. 2006b).

Many parameters affect metal concentrations, speciation, and solubility in SRW. Differences in land use and surface characteristics (e.g., surface roughness or surface materials) result in a variety of metal concentrations and metal speciation in SRW (Wicke et al. 2012). The distribution of metals among speciations is also influenced by precipitation pH and runoff residence time (Sansalone and Ying 2008). Precipitation intensity and volume are important factors influencing the washing of metals from impervious surfaces (Sansalone and Ying 2008). According to Pitt et al. (1995), the distribution of organic and inorganic pollutants depends on the area characteristics, pollutant washout potential, and precipitation characteristics.

Municipalities should define and adopt the best available techniques (BATs) in order to minimize metals' and other pollutants' input to receiving surface water

Table 2.8 Metal concentrations in different wastewaters

Source	Average total metal concentration (μg/L)								Remarks	Reference
	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn		
Raw sewage	–	38.0	173.0	226.0	101.0	0.6	120.0	723.0	–	USEPA (1982)
	–	0.8	12.4	77.8	25.3	0.5	14.2	155.4	–	Rule et al. (2006a)
Wastewater from wastewater treatment plants	–	1.5	20.0	33.0	27.0	–	430.0	270.0	–	Karvelas et al. (2003)
Stormwater	3.0	0.5	4.6	12.0	12.0	0.2	5.4	73.0	Residential area	Pitt et al. (2008)[a]
	2.4	0.9	6.0	17.0	18.0	0.2	7.0	150.0	Commercial area	
	4.0	2.0	14.0	22.0	25.0	0.2	16.0	210.0	Industrial area	
	2.4	1.0	8.3	34.7	25.0	–	9.0	200.0	Motorway	
	4.0	0.4	5.4	10.0	10.0	–	–	40.0	Open space	
	22.3	2.6	23.5	157.4	189.4	0.9	47.0	717.4	–	UKWIR (2002)[b]
	–	2.3	16.0	48.0	118.0	–	22.6	275.0	–	Brombach et al. (2005)[c]

[a] Median metal concentrations (no evidence of state of metal concentrations)
[b] Average value of previous studies (no evidence of state of metal concentrations)
[c] No evidence of state of metal concentrations

bodies. To identify possible pollutant reduction measures or better treatment management, it is necessary to define the sources, load, and behavior of priority pollutants that reach surface water bodies. The assessment of metals partitioning between solid and liquid phases is an important factor in assessing the fate and bioavailability of metals (Ciffroy et al. 2003). Regarding the toxicity of a metal, its bioavailability is more important than its total concentration.

Given the fact that chemical species (speciation) of metals affect the bioavailability and, hence, toxicity of a metal, it is important to determine the concentration of free metal ions, inorganic and organic complexes, and organometallic compounds in SRW. For example, at the same concentration of Cu, Cd, and Pb, the uncomplexed ionic forms are much more toxic than the complexed ones. To determine the bioavailable forms of metals, the speciation modeling of metals should involve the determination of the metals' concentrations together with the water's physicochemical properties (e.g., major ions, organic-metal complexing agents, pH) (Peijnenburg and Jager 2003). According to Comber and Georges (2008), the bioavailability of Cu and Zn depends on pH, Ca concentration, and the presence of dissolved organic matter (DOM). If the water's physicochemical properties are not determined, the evaluation of metal bioavailability and toxicity is hard to define. Compared to the extensive literature on metals in SRW from roof and road surfaces, the presence of Ca^{2+}, K^{+}, and Mg^{2+} ions has been poorly investigated (Göbel et al. 2007).

To our knowledge, only Milukaitė et al. (2010) investigated concentrations of metals (e.g., Cd, Cu, Pb, Zn) in SRW and their distribution among SRW phases in the area of Vilnius.

Chemical Properties of Surface Runoff Water

The maximum allowable concentrations (MACs) of metals in the environment are provided for in Order D1-236 of the Minister of the Environment of the Republic of Lithuania of 17 May 2006, "On the Approval of the Wastewater Management Regulation," and its subsequent amendments. Because of the ongoing restructuring of the water policy of the European Community, the Lithuanian Wastewater Management Regulation was amended several times. As for metals, Order D1-416 of the Minister of the Environment of the Republic of Lithuania of 18 May 2010 conforms to Directive 2008/105/EC. Metals (e.g., Cr, Cu, and Zn) that are not in the list of Directive 2008/105/EC have MAC limits that are set by Lithuanian law.

The problem of contamination of SRW examined in this chapter is discussed by analyzing SRW sampled from three different types of surfaces in the largest and most urbanized city in Lithuania – Vilnius. An urbanized area not far from a heavily industrialized zone, it probably was and continues to be affected by metals of aerogenic origin, falling on area surfaces as atmospheric depositions in wet and dry conditions. In 2000, road transport was the largest source of emissions into atmosphere generated by mobile pollution sources in Lithuania (Baltrėnas et al. 2004a, b, c). Milukaitė et al. (2008) observed a close relationship between Cd, Cu, Pb, Zn, and oil products in atmospheric depositions, inferring that traffic represents the major source of pollution affecting the chemical composition of air in Vilnius. In the street zone, the deposition of Cd, Cu, Pb, and Zn was calculated to be around 20, 40, 29, and 25 % of the total quantity of metals deposited yearly in the city.

The sampling sites were situated in the northwestern section of the city on the banks of the river Neris (54°41′0″ N, 25°14′23″ E). Soil in the area consists of Holocene alluvial deposits of fine sands (Zinkutė et al. 2011). SRW was sampled from three different urbanized surfaces. The first surface was a galvanized metal roof on M.K. Čiurlionis Street (house No. 100), not far from the amphitheater in Vingis Park. The building was just a few years old. The second surface was a pedestrian path (pavement) in the park zone, near an intersection with M.K. Čiurlionis Street. No other potential sources of pollution were identified. The third surface was the roadway of M.K. Čiurlionis Street, where traffic intensity is low, but the road is located on the overpass that crosses over Geležinio Vilko Street, which is among the busiest streets in Vilnius, with a measured transport flow of around 140,000 vehicles per 24 h (Jarašiūnienė 2010).

The SRW sampling was conducted during a downpour event on 19 July 2012; samples were grabbed directly from the flow (Spurlock 1999). In each sampling site, one composite sample was formed out of five samples. Sampling principles, strategy, and preservation of the samples were according to the requirements of ISO 5667–1*: Water quality – Sampling – Part 1: Guidance on the design of sampling programmes and sampling techniques*, and ISO 5667-3: *Water quality – Sampling – Part 3: Guidance on the preservation and handling of water samples*.

Flow rate measurements were made using the volumetric–time based Bucket method (Spurlock 1999). The flow rate in the three sampling sites was different: 0.42 L/s from the pathway, 0.25 L/s from the road, and only 0.05 L/s from the roof.

As data in Table 2.9 show, the length of the dry period was too short for ample dry deposition of atmospheric pollutants.

To express the distribution of metal i concentrations between the dissolved form and solid phase, the partition coefficient $K_{\mathrm{d,i}}$ calculated according to the following Eq. (2.3) was used:

$$K_{\mathrm{d,i}} = \frac{C_{\mathrm{i,s}}}{C_{\mathrm{i,w}}}, \tag{2.3}$$

Table 2.9 Precipitation volumes on 13–19 July 2012 (data of Lithuanian Hydrometeorological Service, the meteorological station in Trakų Vokė)

Date	13 July 2012	14 July 2012	15 July 2012	16 July 2012	17 July 2012	18 July 2012	**19 July 2012**
Daily precipitation (mm)	0	1.3	0.2	0	7.1	3.4	**6.6**

Note: The sampling date and the precipitation volume on that date are in bold.

Table 2.10 Concentration of dissolved metals (μg/L) identified in SRW samples from roads, roofs, and pathways, compared to maximum allowable concentrations of metals in environment (μg/L) according to Order D1-236 of Minister of the Environment of the Republic of Lithuania of 17 May 2006, "On the Approval of the Wastewater Management Regulation," and its subsequent amendments, based on Directive 2008/105/EC (*nd* means that a value is under the detection limit)

Metal	Maximum allowable concentration (MAC) in the environment (μg/L)	Maximum allowable concentration (MAC) for acceptor water body (μg/L)	Sampling site		
			Road (μg/L)	Roof (μg/L)	Pathway (μg/L)
Cr (total)	500	10	nd	nd	nd
Cu	500	10	3.2	nd	nd
Zn	400	100	54.33	72.56	131.9
Ni	200	10	nd	nd	nd
Pb	100	5	4.57	2.85	5.76
Cd	40	5	4.64	2.72	2.06

where $C_{i,s}$ is the concentration of metal i in the SRW solid phase, normalized according to the dry weight of the solid particles (mg/kg); $C_{i,w}$ is the concentration of metal i dissolved in SRW (mg/L).

Compared to the MACs in the environment, the concentrations of dissolved Cd, Cr, Cu, Pb, Ni, and Zn did not exceed the allowable values in any of the SRW samples from the three sites (Table 2.10). In the study of Milukaitė et al. (2010), chemical analysis of SRW from several areas of Vilnius revealed low quantities of metals (Cd, Cu, Pb, Zn) in dissolved form, with only Zn and Cu exceeding the limits set for acceptor water bodies in a few samples. With regard to the quality of SRW acceptor water bodies, in the Neris River, metal (Cd, Cu, Pb, Zn) concentrations were found to be far lower than the MAC limits (Dudutytė et al. 2007).

Table 2.11 presents average values of suspended solids (SSs), dissolved organic carbon (DOC), electric conductivity, and pH from three sampling sites. The measured pH was in the range of 6.9–8.1 in the samples taken from the roof and road surfaces. This is pH range is similar (7.0–8.5) to that reported in Pitt et al. (1995) after analysis of SRW from different surface types. This almost neutral to slightly alkaline medium reduces the concentration of free metal ions in SRW, inhibiting their desorption from SSs (Milukaitė et al. 2010). The sidewalk SRW analysis showed concentrations of DOC twice as high as in the case of other surfaces. Such a difference possibly originated from the surrounding forest area, which enriches the SRW with various particles of biologic origin rich in organic carbon. The average concentration of SSs in SRW samples from the roof was 0.038 g/L.

The SRW sampled from the rooftop produced the lowest concentration of SSs, being from 2 to 4 times lower than that detected in the pathway and road SRW. This can be explained by the low roughness and comparatively greater inclination of the zinc sheet roof surface. Therefore, the particles that were on the roof could easily have been washed off this surface during previous precipitation events. The fact that the SS concentration in SRW samples from the road was much lower than the average values reported in the scientific literature may be due to regular street

Table 2.11 Average values of suspended solids (SSs), dissolved organic carbon (DOC), electric conductivity (EC), and pH in SRW samples at urbanized sites: from roof, pathway, and medium-intensity traffic street (M.K. Čiurlionis Street) in Vilnius

	pH	Electric conductivity (μS/cm)	Dissolved organic carbon (mg/L)	Suspended solids (g/L)
Road	8.1	75.30	3.86	0.135
Roof	6.9	22.70	3.36	0.038
Pathway	7.3	124.3	6.40	0.074

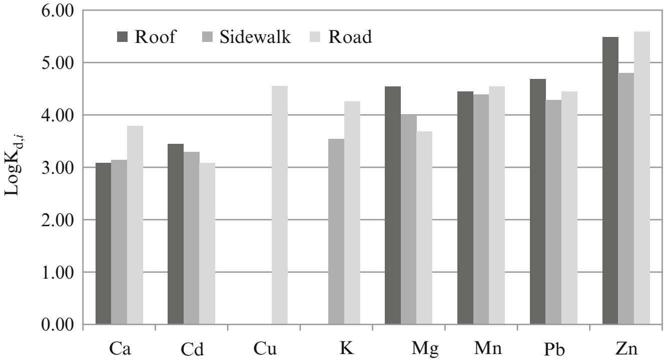


Fig. 2.4 Partition coefficients (log $K_{d,i}$) calculated for macro elements (Ca, K, Mg) and metals (Cd, Cu, Mn, Pb, Zn) in urban stormwater runoff samples from road, roof, and pathway surfaces

cleaning and washing. In addition, it rained each day for a couple of days before sampling (Table 2.9).

In all the investigated sites, the soluble concentrations of metals were much lower than the insoluble concentrations, i.e., as part of SSs (Fig. 2.4). Analyses of metals both in SSs and in dissolved form showed the predominance of the SS-bound fraction of all the detected elements (more than 80 % of the total amount measured), irrespective of the water characteristics (e.g., pH, DOC, SSs, and types of surface area). These results harmonized with the observations reported by Milukaitė et al. (2010) for SRW in Vilnius. They reported that especially Pb and Cd were mostly in insoluble form (more than 90 % of the total amount measured).

Figure 2.4 displays values of the partition coefficient log $K_{d,i}$ of the investigated elements in stormwater runoff from different surfaces. The highest log $K_{d,i}$ values were observed for Zn (4.9–5.6), followed by Cu, Mn, and Pb, reflecting the high affinities of these metals to SSs. The lowest log $K_{d,i}$ values were found for Cd (3.1–3.5).

The values of the partition coefficient log $K_{d,i}$ of Cu, Cd, Pb, and Zn are consistent with values reported for surface waters (Allison and Allison 2005). As for metal partitioning in the SRW from roof surfaces, there was a discrepancy between our findings and those reported in the study of Lamprea and Ruban (2008).

They found that Cd, Cu, Pb, and Zn were in the dissolved phase more because of low pH values (5.1–5.8) and low SS concentrations (3.0–7.7 mg/L). According to Herngren et al. (2005), the reduced solubility of metals in SRW and insignificant release from SSs can be related to the high pH and low DOC concentration. In addition, in our case, possibly smaller dispersity of solid particles and the basis of their lithogenic nature could also have some influence.

Figure 2.5 presents concentrations of investigated metals in dissolved and solid forms from three sampling sites.

Figure 2.5a shows that the concentrations of soluble metals in all the samples from the investigated sites decreased in the following order, with Cu* detected only in the road SRW:

$$\mathrm{Zn} > \mathrm{Mn} > \mathrm{Pb} > \mathrm{Cd} > \mathrm{Cu}^*$$

The concentration of metals (mg/kg DW) in the insoluble form (Fig. 2.5b) in the SRW from the different sampling sites decreased in the following order, with Ni* detected only in the pathway SRW:

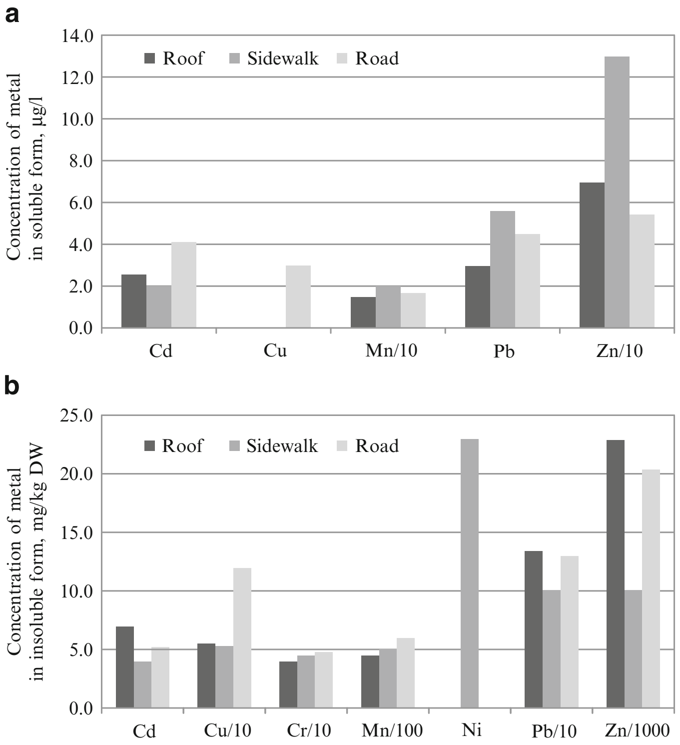


Fig. 2.5 Average concentration of metals detected in soluble (μg/L) (**a**) and insoluble (mg/kg of dry weight) (**b**) forms in urban stormwater runoff samples from road, roof, and pathway surfaces

$$\mathrm{Zn} \gg \mathrm{Mn} > \mathrm{Pb} > \mathrm{Cu} > \mathrm{Cr} > \mathrm{Ni}^{*} > \mathrm{Cd}$$

.A comparison of concentrations of metals in SRW and concentrations of the same metals in snow cover shows a similar tendency. The concentration of metals in snow dust decreases in the following order (Geochemical Atlas of Lithuania, Žirmūnai subdistrict in Vilnius) (concentrations of metals are given by subscripts, mg/kg):

$$\mathrm{Mn}_{470} > \mathrm{Zn}_{108} > \mathrm{Pb}_{54.4} > \mathrm{Cu}_{23.8} > \mathrm{Cr}_{29.3} > \mathrm{Ni}_{14.1} > \mathrm{Cd}_{0.21}$$

.According to Taraškevičius et al. (2008), Zn and Pb were among the main contaminants identified in the topsoil in Vilnius city recreational areas. Based on wet and dry atmospheric deposition analyses, Milukaitė et al. (2008) identified Zn as the metal with the highest annual flux to the ground surface of Vilnius.

The SRW samples from the pathway surface exhibited the lowest concentrations of Zn, Pb, Cu, and Cd bound to SSs, as expected for typical pollutants associated with vehicular traffic (Göbel et al. 2007), that were investigated in the SRW from a car-free pedestrian zone. Conversely, a road SRW analysis showed a high concentration of Zn, Pb, Cu, Cr, and Mn in SSs. In a study of metal concentration in SRW from the Vilnius district, the highest concentrations of Cu, Mn, and Zn were reported to be in the range 0.4–2.0, 1.3–5.1, and 0.9–12.4 mg/L, respectively (Vaitkutė et al. 2010). According to Göbel et al. (2007), metals coming from traffic activities are mainly found as part of SSs in SRW. Wear and tear from tires and the corrosion of vehicle parts are the primary sources of Zn (Rule et al. 2006b); vehicle exhaust gas, especially at braking, is the major source of Cu, Cr, and Pb (Adachi and Tainosho 2004). Strong correlations among metals in SSs, such as Cd ($p < 0.05$), Cu ($p < 0.01$), and Pb, as well as between Cu and Mn ($p < 0.01$), were found.

It was found that the soluble concentration of metals such as Mn, Pb, and Zn was the highest in the SRW samples from the pathway in the pedestrian zone. This is because of the higher concentrations of DOC compared to those measured in the SRW samples from the road and roof surfaces (Fig. 2.5). The metal speciation results reported below confirmed higher Mn, Pb, and Zn complexation to fulvic acids in the modeling of SRW from the pathway versus the road and roof runs, whereas the fractions of Mn-FA complexes were higher in the road runs than the pathways.

It is unclear why Ni was found only in the SRW from the pathway and only bound to SSs (22.19 mg/kg DW), whereas the concentration of Ni in the samples from the other sites was under the detection limit.

It is noteworthy that considerable amounts of metals were detected in the SRW from the pathway but no point sources of metal pollution were identified near this sampling site. Therefore, atmospheric deposition related to the general level of pollution in the city is supposed to be the main source of metal pollution for the area of Vingis Park.

The tendencies of concentrations of metals in the residential site in Vilnius were similar to those mentioned in the work of Milukaitė et al. (2008). They suggest the fact that atmospheric deposition plays an important role in pollutant build-up on the investigated surfaces.

In addition, a strong relation was noticed between SS-bound metals such as Cu ($p < 0.01$) and Cd ($p < 0.01$) detected in the SRW from the roof and road surfaces as well as between Zn ($p < 0.01$) and Pb ($p < 0.01$) detected in the SRW from the road and the pathway surfaces.

For the insoluble form of metals such as Cd, Pb, and Zn, the highest concentrations were measured in the SRW from the roof and road surfaces. This is related to the presence of galvanized steel materials, such as gutters, downspouts, and steel sheets, that have been identified by many authors as being among the primary sources of Zn in roof and road SRW (Lamprea and Ruban 2008). Metals such as Cd and Pb are minor constituents of galvanized steel (Ogburn et al. 2012). Correlations ($p < 0.01$, $p < 0.05$) were found among the concentrations of the metals in SS detected in the SRW from the road (e.g., Pb, Cd) and roof surfaces (e.g., Zn, Cd), between Zn and Cd in the SRW from the roof, and between Cd and Pb in the SRW from the road.

A prolonged contact time with water can increase weathering and deterioration of metal materials (Ogburn et al. 2012). Building materials may certainly represent an important local source of metals in SRW from roof and road surfaces. Prolonged wet weather conditions alternating with dry conditions may promote erosion and weathering phenomena.

Assessment of Metal Speciation in SRW Using Windermere Humic Aqueous Model

For each of the sampling sites, metal speciation in SRW was simulated using the chemical speciation program WHAM/Model VII based on WHAM (Windermere Humic Aqueous Model) (Tipping 1994). WHAM, designed to determine chemical species of chemical substances in water, includes different submodels such as the humic acid-ion binding submodel Model VII; a surface complexation submodel simulating ion binding to oxides of aluminum, iron, manganese, and silicon; a submodel for inorganic solution chemistry speciation; and a submodel for modeling cation exchange on clay particles. WHAM assumes that metal species are at chemical equilibrium, and it does not consider kinetically controlled reactions. WHAM is based on electrostatic interactions of protons and of metals with humic substances; in describing binding sites for metals the model adopts a distributional approach.

The speciation of the detected metals (Cd, Cu, Mn, Pb, and Zn) and macro elements (Mg, K, and Ca) in SRW was calculated using WHAM VI (Tipping et al. 2011) for water. The program input data are presented in Table 2.12. The concentration of metals in SRW (filtered through a filter with 0.45 μm pore size)

Table 2.12 WHAM model input data: pH (pH), dissolved organic carbon (DOC), suspended solids (SSs), and metal concentration in SRW

	Roof	Sidewalk	Road
$[Mg]_{tot\_diss}$, M	4.06×10^{-6}	2.62×10^{-5}	2.44×10^{-5}
$[K]_{tot\_diss}$, M	–	4.53×10^{-5}	1.24×10^{-5}
$[Ca]_{tot\_diss}$, M	2.86×10^{-4}	1.68×10^{-4}	3.57×10^{-5}
$[Mn]_{tot\_diss}$, M	2.71×10^{-7}	3.84×10^{-7}	3.39×10^{-7}
$[Cu]_{tot\_diss}$, M	–	–	5.04×10^{-8}
$[Zn]_{tot\_diss}$, M	1.11×10^{-6}	2.02×10^{-6}	8.31×10^{-7}
$[Cd]_{tot\_diss}$, M	2.4×10^{-8}	1.87×10^{-8}	4.09×10^{-8}
$[Pb]_{tot\_diss}$, M	2.9×10^{-3}	5.8×10^{-3}	4.6×10^{-3}
pH	6.9	7.3	8.1
DOC, mg/l	3.36	6.40	3.86
SS, g/l	0.038	0.074	0.135

determined by flame atomic absorption spectroscopy (FAAS) or graphite furnace atomic absorption spectrophotometer (GFAAS) analysis was identified as total dissolved metal concentration. A temperature of 15 °C and no CO_2 partial pressure were set for SRW from surfaces of all types.

Metal binding to DOM in WHAM assumes binding of metal to humic acids (HAs) and fulvic acids (FAs). It is assumed that the DOM has the binding properties of "default" FA and that the DOM is composed of 50 % carbon. DOM is considered colloidal (Dwane and Tipping 1998) and is assumed to consist of a fraction of 50 % active FA (% aFA) for proton/metal binding and a fraction of 50 % that is inert with respect to ion binding. The calculated metal concentrations being in "aqueous phase," as defined in the model, are reported as soluble. This includes metals in true solution and metals in the diffuse layer of the colloidal phase (in this case, FA).

The Debye–Hückel equation for metal activity correction in the case of solution equilibrium calculation and stability constants in the program database were adopted.

WHAM outputs were analyzed in connection with these parameters for each investigated surface type and each metal: the ratio of free ions to the total dissolved metal concentration, the fraction of truly dissolved metal,) and the fraction of metal bound to colloids (in this case, to FAs).

WHAM modeling results showed a variability in the speciation behavior of metals (Cd, Mn, Pb, and Zn) among the investigated sites, whereas major cations (Ca, Mg, and K) speciation were not substantially affected by the different SRW types (Fig. 2.6).

In all the analyzed SRW types, major cations (Ca, Mg, K) were characterized by the predominance of free metal ions, with a value of free ion activity calculated in a range of 89–99 % of the total dissolved elements (Fig. 2.6). It was determined that Pb and Cu were similar in their ability to form complexes. In all the analyzed SRW types, the predominant Pb species (with more than 90 % of the total dissolved Pb) is the Pb-FA complex. In addition, compared to the total dissolved concentration, the free Pb^{2+} ion activity is negligible. In road SRW modeling, Cu-FA complexes were found to amount to around 99 % of the total dissolved Cu.

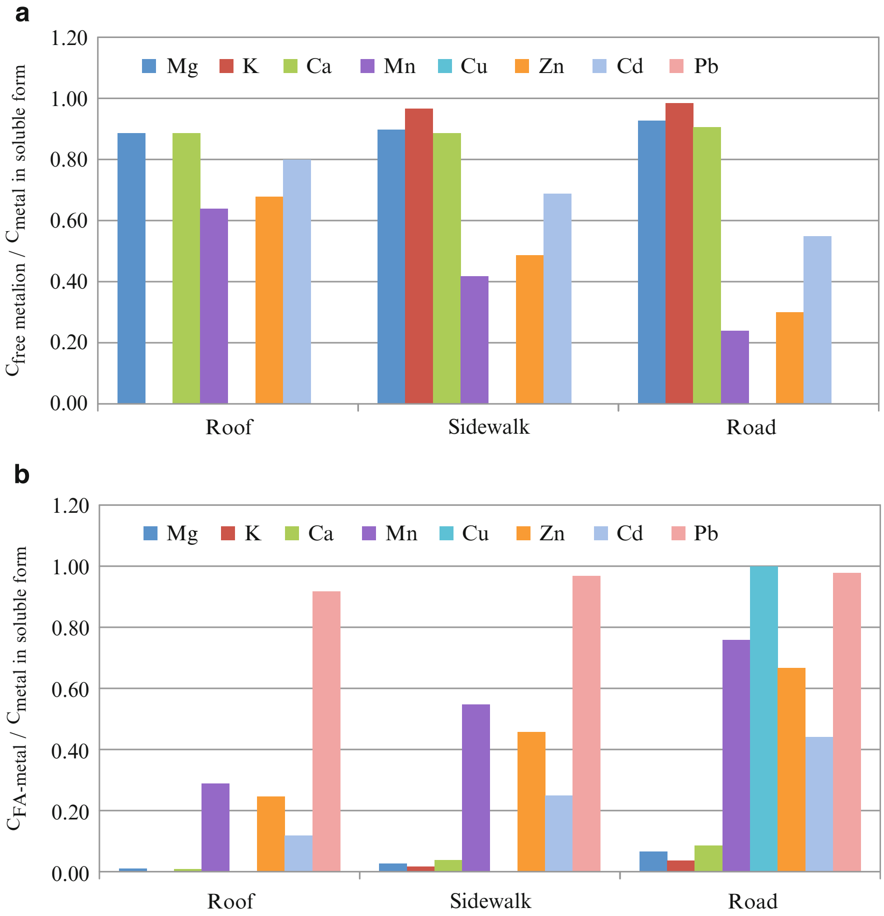


Fig. 2.6 Free ion activity and fraction bound to colloid (FA) of metals (Cd, Cu, Mn, Pb, Zn) and macro elements (Ca, K, Mg) in urban stormwater runoff (SRW) from different surfaces were calculated using WHAM7. *Roof*, *Road*, and *Pathway* refers to sites where the SRW samples were taken. [FA-M], the concentration of M, metals (Cd, Cu, Mn, Pb, Zn), and macro elements (Ca, K, Mg) bound to FA. Total concentration of dissolved micro elements and macro elements in total water

Of all the modeled water types, road SRW showed the highest ratio between the free major cation activity and total dissolved concentration; however, it showed the lowest ratio of free Cd^{2+} and Zn^{2+} ion activity with a value of 55 and 30 % of total dissolved Cd and Zn, respectively. Roof SRW modeling showed the highest ratio of free Mn^{2+}, Zn^{2+}, and Cd^{2+} ion activity with values of 64, 68, and 80 % of total dissolved metals, respectively. The highest fraction of Pb and Zn bound to FA was found in the SRW from the pathway. The Pb-FA and Zn-FA complexes were calculated to be from 19.6 to 52.3 % and from 41 to 70.3 % higher than Pb-FA and Zn-FA complexes in the road and roof SRW modeling, respectively. Mn-FA complexes were 62 % higher in the modeling of metal species in the SRW from the pathway compared to the roof and 18.6 % less compared to the road runs. Comparisons of SRW modeling results showed that the SRW types characterized by a higher pH and DOC concentration produced a higher fraction of metals bound to FA. It was calculated that the fractions of Cd (38.8 %), Mn (62 %), Pb (52.3 %), and Zn (70.3 %) bound to FA were higher in the modeling of SRW from the pathway compared to the roof runs. The road SRW exhibited a higher pH and DOC concentration (by about 47 %) than the roof SRW. In the road SRW modeling, the Cd-FA, Mn-FA, Pb-FA, and Zn-FA complexes were about 40–80 % higher than those calculated in the roof runs. SRW from the road had a higher pH (about 14 %) and an almost equal DOC concentration compared to that from the roof. Investigating the complexation of Cd, Ni, and Zn as a function of DOC concentrations in groundwater for a range of pH values, Christensen and Christensen (2000) found that DOC-metal complexing increased with increasing pH.

2.3 Aerogenic Contamination and Its Evaluation on Ecosystem-Based Approach

Role of Deposit Media in Ecosystems with the Load of Aerogenic Contaminants

The composition of ambient air is constantly changing; therefore, monitoring of the ambient air quality for the purpose of detecting the changes caused by aerogenic (transported by air) pollutants constitutes the essential part of environmental monitoring (at the regional, state, and enterprise levels). However, the currently used system of monitoring air quality, closely associated with the long-term pollution caused by aerogenic contaminants, has a number of drawbacks: (1) the state network of ambient air monitoring stations is not sufficiently large if we take into account the complicated structure of anthropogenic air pollution; (2) at the municipal level, air quality monitoring is usually fragmentary and limited because of the lack of financing and is performed only in areas where large enterprises are located; (3) monitoring of the ambient air quality in the vicinity of large enterprises, which is required by law, is often subjective and superficial; (4) in the case of pollution by metals, which are persistent environmental pollutants, the monitoring of only one of them, lead (Pb), is provided for by the 2008/50/EC. Unfortunately, other important pollutants, e.g., chrome (Cr), copper (Cu), nickel (Ni), and zinc (Zn), which belong to the second toxicity class, are not considered in that document. Changes in the concentration of these metals in potentially polluted areas have already been evaluated in various parts of the biosphere. For example, the concentration of Zn, four times as high as the background concentration, was found in wood samples taken from pine trees growing near a shooting range (Butkus and Baltrėnaitė 2007a, b; Markert et al. 2012). The concentration of Pb, Cr, Cd, and Zn in a Scots pine forest, which exceeded background values by about 1.5 times, was found on a site of a former television manufacturing plant (Pundytė et al. 2011a, b).

Striving to solve problems associated with pollution, monitoring and evaluation of ambient air quality and long-term pollution by metals may be performed while analyzing deposit media such as soil, snow cover, epigeic mosses, and pine bark (Markert 2007; Butkus and Baltrėnaitė 2007a, b; Butkus et al. 2008; Baltrėnaitė et al. 2010; Baltrėnas and Vaitkutė 2011). *Snow cover* is known to be an almost ideal short-term deposit medium for evaluating aerogenic contaminants found in atmospheric precipitation (Lietuvninkas 2012). Ambient air impurities (e.g., dust, soot, gas components) are partially removed when it snows. Naturally, they accumulate on earlier formed snow cover, which is being constantly renewed by falling snow. Snow is an inertial medium onto which pollutants do not migrate vigorously. They accumulate in snow in large amounts because snow represents an aerodynamic barrier to particles suspended in air. In areas with natural background conditions, the concentration of such metals as Pb, Cd, Ni, Zn, Mn, and Cu in snow cover is not high. Therefore, a higher concentration of these metals is a reliable indicator of possible air pollution. With regard to *topsoil* pollution, it may be noted that aerogenic pollutants are not the only contaminants retained by topsoil, though topsoil is the alternative deposit medium to snow cover, occupying the largest area in warm seasons. Soil surface, unlike a relatively passive snow cover, accumulating airborne pollutants, is a geochemically active deposit medium that changes the state of pollutants (particles–solutions), and redistributes them with the help of soil solution both in its profile and among the elementary geochemical landscapes. A certain amount of pollutants in dissolved form are completely removed from topsoil. For this reason (in fact, as a result of the self-purification of topsoil), the pollution levels of topsoil and snow cover often vary, this difference being particularly large in the case of geochemically more mobile chemical elements found in topsoil (this is characteristic of the metals Cu and Zn) and in forest zones (Lietuvninkas 2012; Krastinytė et al. 2013).

The active surface area of epigeic *mosses* is comparable to that covered with tree leaves. Mosses, belonging to evergreen perennial plants, lack true roots. Taking up chemical elements directly from the air and assimilating them, mosses are, in fact, reliable passive biomonitors (Steinnes et al. 1992). *Tree bark* is also known to be a widely used passive biomonitor because, owing to its damp, rough, and charged surface, it can retain suspended particles that sorb metals (Panichev and McCrindle 2004).

Assessing the dynamics of the pollution of territories (ecosystems), the emphasis should be placed on the relationship between the level of the pollutants' accumulation by a deposit medium and air pollution level and its risks to the environment. The relationships between the accumulation of pollutants in soil, snow dust, epigeic mosses, and tree bark, as well as the risk level of pollution, have been discussed in the scientific literature, while the values of the concentrations of metals in soil and the loads of snow dust are already included in current pollution regulations. The present work offers a complex evaluation of aerogenic pollution in the area of oil refinery influence. The level of pollution is evaluated by considering the main deposit media of metals – snow cover, topsoil, epigeic mosses, and pine bark.

Principles of Deposit Media Analysis: Analysis Strategy, Methods of Physical and Chemical Analysis

The AB ORLEN Lietuva Co. (56°23′15″ N; 22°10′34″ E), situated in northwest Lithuania, is a typical complex oil refinery. It is the only oil refinery in the Baltic States (Baltrėnas et al. 2011a, b). The plant was constructed in 1980. It annually refines approximately 15 million tons of crude oil (about 315,000 barrels) a day and, therefore, belongs to a group of big oil refineries (McCoy et al. 2010).

The enterprise is not far from the Latvian border, being 9.5 km from Mažeikiai to the northwest. In the eastern part of the enterprise territory, there is the Juodeikiai pond, while 2 km further east, the Venta River flows in the same direction. About 10 km to the south of the refinery is the Šerkšnė Hydrographic Reserve. The main sources of metals associated with oil refineries are the production processes causing the release of solid particles, which adsorb metals, into the environment. Solid particles released by AB ORLEN Lietuva are generated by primary oil recovery, fuel burning and oxidation, elimination of gases by burning, vacuum distillation of black oil and tar, and tar viscosity breaking, hydrocleaning, coke firing, fluid catalytic cracking, steam generation for thermoelectric power station generators, and welding. AB ORLEN Lietuva makes around 92 % of the total amount of these particles emitted in the region (Institute of Environmental Protection 2011).

The meteorological data used in the present investigation were taken from the Mažeikiai ambient air quality monitoring station. In 2009–2012, the average temperature in the considered territory in the cold season was around 0 °C, while in the warm season, it reached 17 °C; the wind speed was 1.46 and 1.26 m/s, air humidity was 83 and 74 %, while air pressure was 1007 and 1006 hPa, respectively. In winter, thesoutheast wind blew, while in summer, the southwest wind prevailed.

The places where the samples of snow, epigeic mosses (*Hylocomium splendens*), pine (*Pinus sylvestris* L.) bark, and soil were taken are shown in Fig. 2.7. Sampling was made in the area where the refinery exerted an influence. It was divided into four zones, taking into account the direction of the prevailing wind.

Snow cover sampling is described in detail in the paper by Krastinytė et al. (2013). Snow-cap composite samples were taken from the undisturbed snow cap in the middle of February 2011. The temperature was −3 °C without snow. The snow cap had not increased for 1 month. Each composite sample consisted of 14–28 subsamples taken using a snow sampling tool (Fig. 2.8). The snow sampling tool was developed at the Department of Environmental Protection of Vilnius Gediminas Technical University (Lithuania). The dimensions of the tool were 1 m in length, with an internal diameter of 12 cm and external diameter of 5 mm.

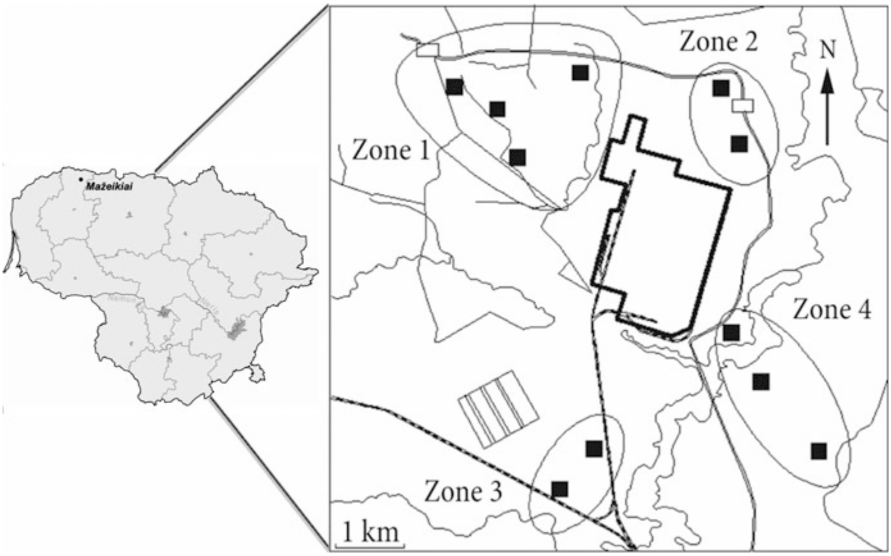
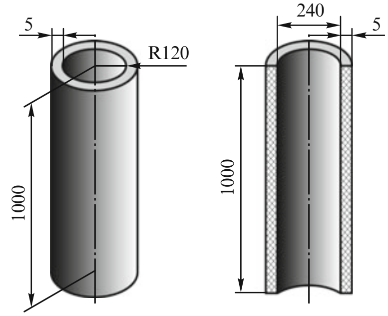


Fig. 2.7 Places in territory affected by AB ORLEN Lietuva where snow, soil, moss, and bark samples were taken. The control area was chosen 10 km to the west of the area affected by the company (not shown here)

Fig. 2.8 Snow sampling tool (mm)



The samples were taken through the entire layer of the snow cap, and the mass of the samples was approximately 10–20 kg each.

Soil samples (composite samples 2 kg each) were taken at three different depths (0–10, 10–30, and 80–100 cm) using a soil drill. A composite sample consisted of four samples taken from the soil around a pine tree in the four cardinal directions.

Outer *bark* samples of the *Scots pine* (*Pinus sylvestris* L.) (2–3 mm) were taken from three pine trees growing not far from each other at 12 different locations. Pines of the same age were chosen, and their height and trunk diameters at a height of 1.5 m were recorded. Mosses and lichens found on the bark were removed from it. Bark samples were taken from the trunk in the four cardinal directions with a stainless steel knife (Odukoya et al. 2000).

The samples of epigeic glittering wood moss (lat. *Hylocomium splendens*), as a typical representative of bryophites, which are known as biological indicators of the contamination by metals (Steinnes et al. 1992), were taken in May 2012. Moss sampling was performed in compliance with the international practice of biogeochemical sampling (Čeburnis et al. 2002). The samples were taken in places that were at least 300 m from the local sources of pollution (e.g., roads, railways, residential buildings). Mosses were gathered from exposed locations on the forest floor. A composite sample was made of 8–10 samples in a 20 × 20 m area. It consisted of an upper green layer of 3-year-old *Hylocomium splendens*, while the lower moss layer, which became brown, as well as needles, leaves, the remaining grass, and mineral soil particles, was removed. The samples were placed in disposable bags (the people taking the samples were wearing disposable latex gloves with no talcum powder) and stored in tight freezing boxes during the field work.

The *physical and chemical* treatment of snowmelt water and mineral snow dust is discussed in the paper by Krastinytė et al. (2013). Snowmelt water was filtered through glass fiber borosilicate nonashen filters, and the filters were dried in a clean drying chamber on fresh sheets of paper to determine the daily load of dust and to measure the concentration of metals. Fifty milliliters of snowmelt water was mixed with 5 mL HCl to determine the concentration of metals. The total concentration of metals was determined after the digestion process. Each sample was mixed with 3 mL HNO3 (65 %) and 9 mL HCl (37 %), poured into special vessels, and then placed into an ETHOS (Milestone, Inc., Shelton, CT, USA) digester and heated for 42 min (Butkus and Baltrėnaitė 2007a, b; Pundytė et al. 2011a, b). The solution was then poured into a 50 mL flask and diluted with deionized water to reach a level of 50 mL. The total concentrations of elements within the samples were determined by FAAS. A graphite furnace (GFAAS) was employed to determine the metal concentrations when they were too low to detect accurately by FAAS (Butkus and Baltrėnaitė 2007a, b; Baltrėnaitė et al. 2010).

Moss and bark samples were dried at room temperature and then fired at 450 °C until they were ashed. Ash samples of 0.2 g were mineralized in a Milestone ETHOS mineralizer (Baltrėnaitė and Butkus 2007a, b, c).

Soil samples were dried at room temperature in the laboratory for 24 h and then passed through a sieve with a 2 mm mesh. Each 0.2 g sample was mineralized in the Milestone ETHOS mineralizer (Baltrėnaitė and Butkus 2007a, b, c).

The concentrations of metals in the specimens of deposit media were investigated using a Buck Scientific (Norwalk, CT, USA) 210 VGP atomic absorption spectrophotometer, employing FAAS. When metal concentrations were very low, GFAAS was used.

Statistical Data Processing and Quality Assurance

The samples were prepared in duplicates. Five blank samples were prepared for each analysis. To ensure the accuracy of analysis, certified reference materials, *BAM-U*110 (*contaminated soil-trace elements*) and *ERM*®*-CD*100]*trace elements and pentachlorophenol* (*PCP*) *in wood*], were used. To obtain the calibration curves, standard solutions were used. The statistical data analysis was performed using *Excel* and *STATISTICA* 8.0 programs. The arrays of the initial data were evaluated using a 3D criterion. Graphically presented results include mean values with standard deviations (SDs).

Evaluating the Pollution of Deposit Media

(a) Calculations of the *daily load of mineral snow dust* were made using Eq. (2.4):

$$A_{\mathrm{n}} = \frac{D}{S \cdot T}, \tag{2.4}$$

where A_{n} is the daily load of mineral snow dust (mg/m^2), D is the weight of the mineral snow dust taken from the filtering surface (mg), S is the area where the snow sample was taken (m^2), and T is the period in which snow fell before the sample was taken (days). To determine the level of area pollution against the scale presented in Table 2.13, the daily snow dust load was calculated for each sample.

The data presented in Table 2.13 are based on the results obtained in long-term research conducted by Russian geochemists (Moscow Institute of Mineralogy, Geochemistry and Crystallography of Rare Elements). The collaborating geochemists, physicians, hygienists, environmentalists, botanists, and soil scientists investigated all pollutant deposit media (contaminants), including snow cover, soil, bottom sediments in ponds and rivers, and biomarkers (mainly hair) of children and adults, as well as the media that transport pollutants – air, river water, and suspensions. The chemical composition of waste products of various industrial enterprises was also analyzed. The evaluation scale presented in Table 2.13 takes into account the state of children's and adults' health and diseases, as well as frequency and duration of disease.

Table 2.13 Pollution level based on daily mineral snow dust load A_{n} (Saet et al. 1990)

Pollution level	Average daily load of mineral snow dust (A_{n}, mg/m^2)
Average, hazardous	250–450
High, hazardous	450–800
Very high, highly hazardous	>800

(b) To assess snow dust load and pollution by metals, taking into account the different wind directions with respect to the considered enterprise, the *ratios* of anthropogenic load were calculated. The values of various pollution parameters for zones located at the same distance from the enterprise were calculated as follows:

$$K_{a-b} = \frac{A_\mathrm{a}}{A_\mathrm{b}}, \tag{2.5}$$

where $K_{a–b}$ is an anthropogenic load coefficient, A_a is the parameter of pollution in Zone a with respect to the enterprise, and A_b is the parameter of pollution in Zone b with respect to the enterprise.

(c) According to the Lithuanian Hygiene Standard (HN 60:2004) currently in force in Lithuania, which conforms to EU requirements, if soil is contaminated by more than one metal, the contamination level is evaluated based on the *total contamination factor* Z_d, which is equal to

$$Z_\mathrm{d} = \sum^{n} K_{\mathrm{k,i}} - (n-1), \tag{2.6}$$

$$K_{\mathrm{k,i}} = \frac{C_\mathrm{i}}{C_\mathrm{f}}, \tag{2.7}$$

where Z_d is the total contamination factor calculated based on the considered metals with $K_{\mathrm{k,i}} \geq 1$, $K_{\mathrm{k,i}}$ is the concentration coefficient of metal i, n is the number of metals with $K_{\mathrm{k,i}} \geq 1$, C_i is the metal concentration in the considered soil sample (mg/kg DW), and C_f is the background metal concentration (mg/kg DW). Based on the Z_d value, the degree (level) of soil contamination is determined based on the total contamination factor (Table 2.14).

(d) According to Lithuanian Hygiene Standard HN 60:2004 (in compliance with EU requirements), the *coefficient of soil contamination* K_0 by a particular metal is found using Eq. (2.8):

$$K_0 = \frac{C_\mathrm{i}}{\mathrm{DLK}}, \tag{2.8}$$

while the contamination hazard level is assessed based on the data presented in Table 2.15 where C_i is the metal concentration in the considered soil sample (mg/kg DW) and DLK_i is the highest allowable concentration of metal i in the soil (mg/kg DW).

If the soil contamination level estimated using both classification methods (Tables 2.14 and 2.15) is not the same, then the higher estimated value is accepted.

(e) Based on the *geoaccumulation index* $I_{\mathrm{geo,dt}}$ (dt denotes the selected deposit medium, i.e., epigeic mosses or pine bark in this case), the pollution of the territory by metals is classified according to the metal concentration in the pine bark and epigeic mosses (Müller 1981):

Table 2.14 Evaluation of soil contamination based on total contamination factor Z_d (HN 60:2004)

Soil contamination (category-degree)	Z_d	Changes in the state of health of inhabitants living in the territories with contaminated soil
I. Allowable	<16	Lowest sickness rate and minimal functional disorders among children
II. Moderately hazardous	16–32	Increasing sickness rate among children and adults
III. Hazardous	32–128	Increasing general rate of sickness of children and adults and number of children suffering from chronic diseases and functional cardiovascular disorders
IV. Highly hazardous	>128	Increasing child sickness rate, more frequent female reproductive system disorders (intoxication during pregnancy, premature births, stillborns, hypotrophy in newborn children)

Table 2.15 Evaluation of hazard level of soil contamination by a particular metal, according to Lithuanian Hygiene Standard HN 60:2004, using coefficient K_0

Soil contamination (hazard level)	K_0
Allowable	$K_0 < 1$
Moderately hazardous	$1 < K_0 < 3$
Hazardous	$3 < K_0 < 10$
Extremely hazardous	$K_0 > 10$

$$I_{\mathrm{geo,dt}} = \log\left(\frac{C_{\mathrm{i}}}{1.5 \cdot C_{\mathrm{f,i}}}\right), \tag{2.9}$$

where C_i is the metal i concentration in the bark or moss sample (mg/kg DW), $C_{f,i}$ is the metal i background concentration in bark or moss samples (mg/kg DW), and the coefficient 1.5 shows the variation in background concentrations due to lithogenic variations. Based on the calculated values of the geoaccumulation index $I_{geo,dt}$ for pine bark and moss, territorial pollution is grouped in a special class (Table 2.16).

(f) The *total contamination index* (TCI_{dt}) (with dt denoting the selected deposit medium, i.e., epigeic mosses or pine bark in this case) (Tomlinson et al. 1980) is used to determine the impact caused by several types of pollutants found in epigeic mosses or pine bark within a given area:

$$\mathrm{TCI}_{\mathrm{dt}} = (C_{\mathrm{f,1}} \cdot C_{\mathrm{f,2}} \cdot \ldots \quad \cdot C_{\mathrm{f,i}})^{\frac{1}{n}}, \tag{2.10}$$

where $C_{f,i}$ is the contamination index, i.e., metal concentration in the sample (mg/kg DW) divided by the metal i background concentration in the sample (mg/kg DW) and n is the number of metals considered with $C_f \geq 1$.

Table 2.16 Values of geoaccumulation index $I_{\mathrm{geo,dt}}$, pollution classes, and levels (Müller 1981)

Geoaccumulation index ($I_{\mathrm{geo,dt}}$)	Pollution class	Pollution level
<0	0	Background level
0–1	1	Background level to moderately polluted
1–2	2	Moderately polluted
2–3	3	Moderately polluted to strongly polluted
3–4	4	Strongly polluted
4–5	5	Strongly polluted to extremely polluted
>5	6	Extremely polluted

(g) To describe the quantitative differentiation of metals in a soil profile, the radial differentiation coefficient is used. The *radial differentiation coefficient* K^i_{rd} shows the accumulation level of a metal in parent rock of the corresponding soil horizon (Lietuvninkas 2012) and is calculated using Eq. (2.11):

$$K^i_{\mathrm{rd}} = \frac{C^i_{\mathrm{dir},j}}{C^i_{\mathrm{uol}}}, \tag{2.11}$$

where $C^i_{\mathrm{dir},j}$ is the mean concentration of metal i in the jth soil horizon (mg/kg DW) and C^i_{uol} is the concentration of metal i in soil-forming rock (mg/kg DW).

Use of Deposit Media for Evaluating Level of Ecosystem Contamination

Snow Dust Load

The average load of snow dust (with mineral particles) in the area affected by the enterprise was calculated using Eq. (2.4). It ranged from 24.4 to 45.8 mg/m^2/day. This load corresponds to a **lower than average hazard** level (average daily load of 250–450 mg/m^2) of pollution according to the scale presented in Table 2.13. The largest snow dust load per day (45.8 mg/m^2) was found in Zone 1, while the smallest (24.4 mg/m^2) was found in Zone 4 (Fig 2.9). Comparing snow dust loads in the downwind (Zone 1) ($A_1 = 45.8$ mg/m^2) and upwind (Zone 4) ($A_4 = 24.4$ mg/m^2) areas with respect to the AB ORLEN Lietuva Co., the snow dust load in the downwind area is **twice** as large as that in the upwind area. Therefore, it may be argued that the refinery contributed to the increase in daily snow dust load (Krastinytė et al. 2013).

The data obtained by calculating the coefficients $K_{a\text{–}b}$ (Eq. 2.4), determining daily snow dust loads in various zones using Eq. (2.5), show that the largest snow dust load is typical of northern zones of the territory affected by the company. The values of snow dust load coefficients in these zones are as follows: $K_{1\text{–}4} = 1.88$,

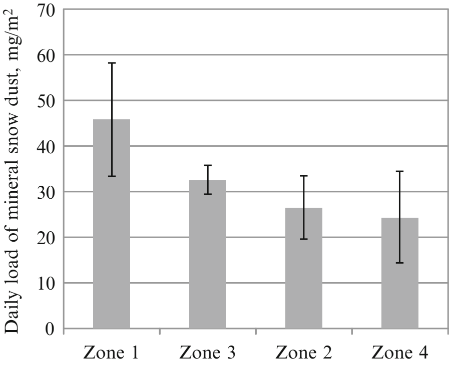


Fig. 2.9 Daily snow dust load A_n (mg/m^2) in various zones of the territory affected by AB ORLEN Lietuva

$K_{1-2} = 1.72$, $K_{1-3} = 1.40$ (Krastinytė et al. 2013). The values of these coefficients confirm that solid particles are transported in the direction of the prevailing winds, i.e., that the impact of company activities ($K_{a-b} > 1$) is real.

Metal Concentration in Snowmelt Water and Snow Dust

The concentrations of metals in snow cover were determined by analyzing the metals that had accumulated in snowmelt water and in snow dust. These concentrations varied depending on the distance (0.2–3 km) of the location where samples were taken from the AB ORLEN Lietuva Co. In many cases, the concentrations of metals in snow dust were considerably larger than the respective concentrations in snowmelt water (Figs. 2.10 and 2.11).

The highest Mn concentrations in mineral snow dust were found in Zone 1, while those of Cu, Cr, and Cd were found in Zone 2 and those of Pb in Zone 4. The highest Mn concentrations in snowmelt water were observed in Zone 3, while those of Cu, Pb, Cd, and Zn were found in Zone 2. Though the highest concentrations are variously distributed with respect to particular zones, the highest increase in metal concentration both in snow dust and snowmelt water are typical of the northern part of company territory (Figs. 2.10 and 2.11). The concentrations of the considered metals in mineral snow dust in the northern part of the territory are twice and in snowmelt water from 1.5 times (Cd and Zn) to 7 times (Pb and Cu) as high as those in the southern part of the territory.

A comparison of the data obtained in similar research carried out in this territory in 2004 revealed a similar trend in metal concentration in *snow dust* in the northern part of the territory. Thus, according to the data obtained in 2004, Cu concentration reached 45 mg/kg, Pb concentration reached160 mg/kg, and that of Cr amounted to 86 mg/kg (Kadūnas et al. 2004), while according to the present research, the average concentrations reached 48 mg/kg (Cu), 158 mg/kg (Pb), and 77 mg/kg (Cr). Comparing these results with the monitoring data obtained for snow cover contamination in 2010 (Cr: 1.4–21.4 mg/kg, Pb; 8–226 mg/kg, Cu: 25–146 mg/kg, Cd: 0.2–2.04 mg/kg) (UAB “Ingeo” 2011), the average concentrations of metals in

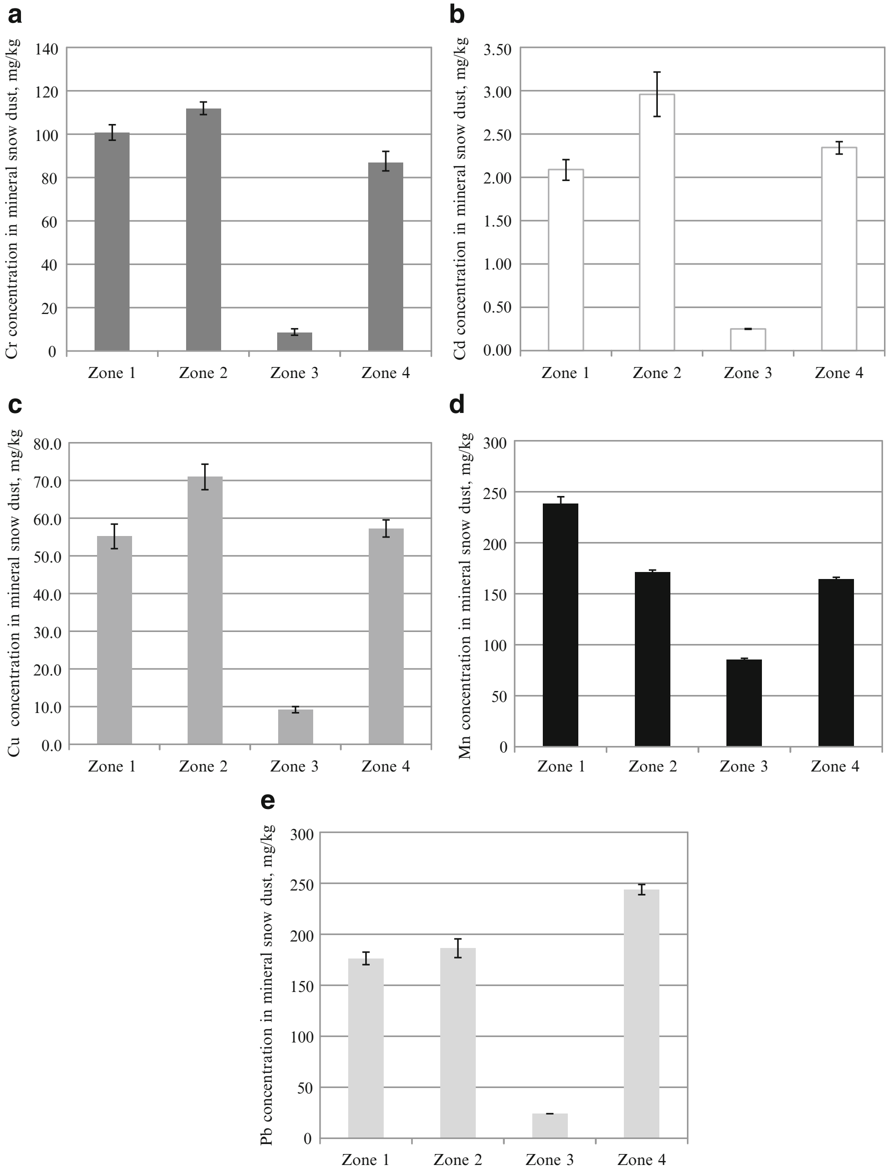


Fig. 2.10 Concentration of metals (mg/kg) in snow dust in zones of the territory affected by AB ORLEN Lietuva. Cd*10 means that Cd concentration was increased tenfold to show the obtained results more clearly. (**a**) Cr, (**b**) Cd, (**c**) Cu, (**d**) Mn, (**e**) Pb

snow dust were found to be similar, except for Cr (according to the data for 2011, its concentration was about four times as high).

The ratios of metal concentrations in snow dust are given in Table 2.17. The highest concentration of most of the considered metals is typical of Zone 1, which

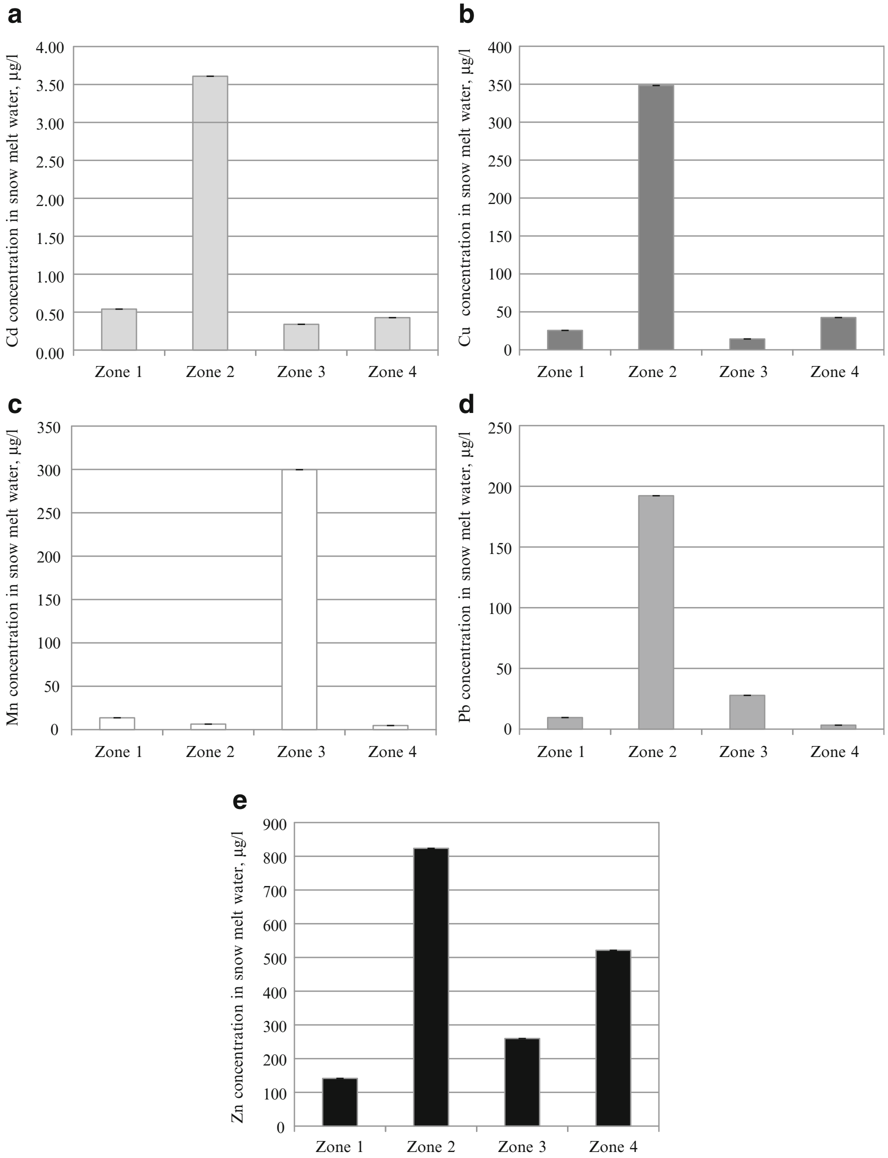


Fig. 2.11 Concentration of metals (µg/L) in snowmelt water in zones of the territory affected by AB ORLEN Lietuva. Cd*50 means that Cd concentration was increased 50-fold, while Zn/10 denotes that Zn concentration was decreased tenfold to show the obtained results more clearly. (**a**) Cd, (**b**) Cu, (**c**) Mn, (**d**) Pb, (**e**) Zn

may be viewed as a trend if we compare it with other zones. The concentration level of the considered metals in Zone 1 was around 3.13 times the level observed in other zones. In the eastern part of company territory (Zones 1 and 3), the concentration of metals in snow dust was around 1.76 times that in the western part (Zones

Table 2.17 Ratios K_{a-b} of metal concentration in snow dust in various zones

K_{a-b}	Cd	Cr	Cu	Mn	Pb	Zn
K_{1-2}	0.70	0.90	0.78	**1.39**	0.95	**1.07**
K_{1-3}	**8.90**	**11.46**	**6.05**	**2.82**	**7.42**	**7.97**
K_{1-4}	0.89	**1.15**	0.96	**1.45**	0.72	0.74
K_{2-3}	**12.65**	**12.74**	**7.78**	**2.03**	**7.85**	**7.41**
K_{2-4}	**1.26**	**1.28**	**1.24**	**1.05**	0.77	0.68
K_{3-4}	0.10	0.10	0.16	0.52	0.10	0.09
$K_{1,2-3,4}$	**1.96**	**2.21**	**1.90**	**1.65**	**1.36**	**1.30**
$K_{1,3-2,4}$	0.44	0.55	0.50	0.96	0.47	0.49

Note: Values in bold are greater than one.

Table 2.18 Ratios K_{a-b} for concentrations of metals in snowmelt water

K_{a-b}	Cd	Cu	Mn	Pb	Zn
K_{1-2}	0.15	0.08	**1.99**	0.05	0.17
K_{1-3}	**1.60**	**1.63**	0.05	0.36	0.55
K_{1-4}	**1.24**	0.60	**2.39**	**2.57**	0.28
K_{2-3}	**10.75**	**21.60**	0.02	**6.80**	**3.17**
K_{2-4}	**8.34**	**7.97**	**1.20**	**47.99**	**1.58**
K_{3-4}	0.78	0.37	**51.35**	**7.06**	0.50
$K_{1,2-3,4}$	**5.40**	**6.26**	0.07	**6.27**	**1.24**
$K_{1,3-2,4}$	0.22	0.11	**24.42**	0.20	0.30

Note: Values in bold are greater than one.

2 and 4). The considered concentration in the northern part of the territory (Zones 1 and 2) was around 1.73 times that in the southern part (Zones 3 and 4).

The ratios of the concentrations of metals in the liquid state in snowmelt water are given in Table 2.18. The trend of having the highest metal concentration in Zone 2 (versus other zones) can be observed. In the western part of company territory (Zones 1 and 3), the concentration of metals was found to be 5.05 times that in the eastern part (Zones 2 and 4), while in the northern part of the territory (Zones 1 and 2), it was around 3.85 times that in the southern part (Zones 3 and 4).

Metal Concentration in Topsoil

Soil contamination by metals is usually evaluated based on the contamination of topsoil (0–10 cm) since topsoil (plant cover and humus) acts as an effective geochemical barrier, accumulating metals and reducing their migration.

Two methods were used to assess the contamination of the topsoil layer by metals. The first method involves the coefficient of soil contamination (K_0) by a particular metal i (Fig. 2.12) and the other uses the total soil contamination factor (Z_d) (Fig. 2.13), which integrates the impacts of several metals. The latter index evaluates soil contamination more accurately, provided that a sufficient number of

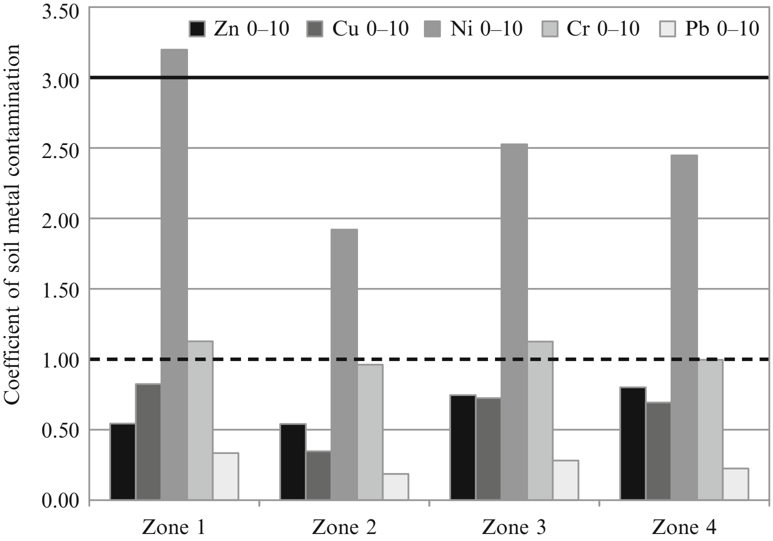


Fig. 2.12 The coefficient K_0 for topsoil (0–10 cm) metal contamination in various zones of territory affected by AB ORLEN Lietuva

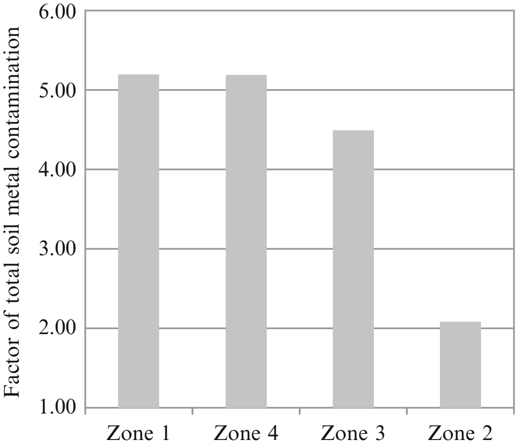


Fig. 2.13 Values of factor Z_d for total soil metal contamination in various zones of territory affected by AB ORLEN Lietuva

metals mentioned in the Lithuanian Hygiene Standard HN 60:2004 is included in the analysis.

As can be seen from Fig. 2.12, Zone 1 is characterized by *hazardous* soil contamination by Ni ($3 < K_0 < 10$), while Zones 2–4 are characterized by *moderately hazardous* contamination by Ni ($1 < K_0 < 3$). Zones 1 and 3 are characterized by *moderately hazardous* soil contamination by Cr. The coefficient K_0 for other metals (Zn, Cu, and Pb) was less than one. In other words, their concentration did not exceed the maximum permissible concentration (MPC).

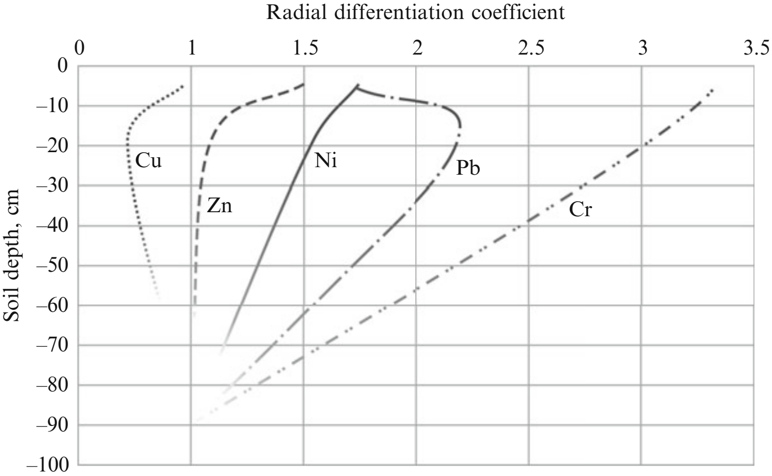


Fig. 2.14 Variation in radial differentiation coefficient (K^{i}_{rd}) values for metals in soil profile of area affected by AB ORLEN Lietuva

The values of the factor Z_{d} for total soil metal contamination are shown in Fig. 2.13. The maximum values of the factor ($Z_{\mathrm{d}} = 5.2$) were obtained for Zones 1 and 4, i.e., zones aligned with the axis of the prevailing wind direction. According to the classification provided in the Lithuanian Hygiene Standard HN 60:2004, when $Z_{\mathrm{d}} < 16$, the area is considered to be *less than moderately* contaminated. However, it should be noted that this is an approximate evaluation of the contamination level since a more accurate evaluation of topsoil contamination requires analyzing more metals (as stated in the Lithuanian Hygiene Standard HN 60:2004, **Pb**, **Zn**, Sn, **Cu**, Ag, Hg, **Cd**, **Ni**, **Cr**, Mo, **Mn**, V, Co, U, Ga, Sc, Be, Yb, and W should be included in the analysis of environment pollution caused by power plants).

The radial differentiation of metals in the soil profile at depths of 0–10, 10–30, and 80–100 cm is presented in Fig. 2.14. When $K^{i}_{\mathrm{rd}} > 1$, this signifies metal accumulation. Otherwise, when $K^{i}_{\mathrm{rd}} < 1$, it is indicative of metal washout in the corresponding layer of soil. In this respect, metals analyzed in the study may be divided into two groups based on their behavior. The first group comprises metals that accumulated in the soil of the area affected by the company (Zn, Ni, Pb, and Cr), while the second group consists of metals washed out from the soil (Cu). Based on metal accumulation in the soil, metals may be arranged in descending order as follows: Cr > Pb > Ni > Zn > Cu.

Figure 2.15 demonstrates the variation in metal concentration in the topsoil layer (0–10 cm) with changes in the distance to the company (in areas downwind and upwind to company territory). Concentrations are expressed by the coefficient $K_{\mathrm{k,i}}$, showing the increase in concentrations with respect to the background territory (Eq. 2.7). It should be noted that, in the downwind direction at a distance of 3.5 km from company territory, metal concentration values exceeded background values

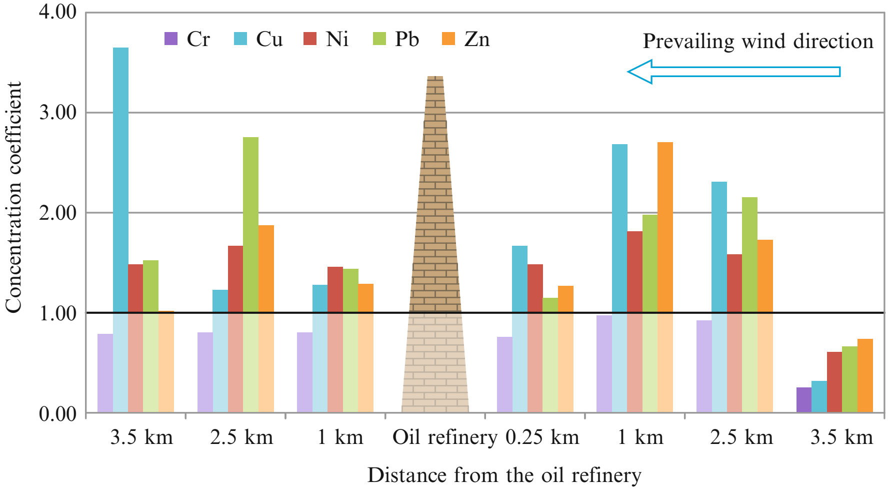


Fig. 2.15 Coefficient $K_{k,i}$ for metal concentration in topsoil layer (0–10 cm) in prevailing wind direction (in areas downwind and upwind relative to company territory) based on distance to refinery

Table 2.19 Values of ratios K_{a-b} for metal concentrations in topsoil layer of various zones

K_{a-b}	Cr	Cu	Ni	Pb	Zn
K_{1-2}	**1.17**	**2.42**	**1.66**	**1.76**	**1.01**
K_{1-3}	**1.01**	**1.15**	**1.27**	**1.23**	0.75
K_{1-4}	**1.13**	**1.20**	**1.31**	**1.57**	0.69
K_{2-3}	0.86	0.47	0.76	0.70	0.74
K_{2-4}	0.97	0.50	0.79	0.89	0.69
K_{3-4}	**1.13**	**1.05**	**1.03**	**1.28**	0.93
$K_{1,2-3,4}$	0.99	0.83	**1.03**	**1.08**	0.72
$K_{1,3-2,4}$	**1.15**	**1.51**	**1.31**	**1.51**	0.96

Note: Values in bold are greater than one.

by around 3.5 times, the quantity by which the concentration values exceeded the background values in the upwind direction at the same distance. The largest values of metal concentrations in the topsoil layer were determined at these distances: at 2.5 km for Zn, Ni, Cr, and Pb and at 3.5 km for Cu (in both cases, in the downwind direction) as well as at a distance of 1 km from the company for Zn, Cu, Ni, and Cr and 2.5 km for Pb (in both cases, in the upwind direction).

The values of ratios for metal concentrations in the soil are given in Table 2.19. One can see that the highest metal concentration is in Zone 1, in accordance with the trend revealed earlier. The concentration level of the analyzed metals in Zone 1 was on average 1.29 times that in other zones. Metal concentration in the soil of the western part of company territory (Zones 1 and 3) was 1.29 times that in the eastern part (Zones 2 and 4). In the northern part of company territory (Zones 1 and 2), only the concentrations of Ni and Pb were higher than in the southern part (Zones 3 and 4).

Metal Concentrations in Bark of Scots Pine

As mentioned earlier, the bark of Scots pine (*Pinus sylvestris* L.) is considered to be a passive biomonitor and is widely used in the analysis of ambient air quality (Saarela et al. 2005).

As shown in Table 2.20, the concentrations of Ni, Pb, and Cu metals (especially Ni) in the bark of pine trees growing in the area affected by AB ORLEN Lietuva activities are higher compared to the background concentrations of these metals in Lithuania and other countries or in the territories of a similar source of contamination. Ni is known to be one of the metals most frequently released into the air by oil refineries.

Müller (1981) suggested using geoaccumulation index $I_{\mathrm{geo,dt}}$ (Eq 2.9) to evaluate the quality of ambient air based on the concentration of individual metals in the biological environment. To determine the level of contamination by several metals based on their quantities in a deposit medium, Tomlinson et al. (1980) proposed to use the total contamination index TCI_{dt} (Eq 2.10). Guéguen et al. (2012) recommend using these indices to evaluate ambient air pollution based on metal concentrations in tree bark and mosses. The present study analyses metal concentrations in the bark of Scots pines (*Pinus sylvestris* L.). These are the most common trees in Lithuania and are not known as effective contamination barriers, since it has been determined that Scots pines, unlike birches and black alders, tend to accumulate metals (especially, in a polluted territory) (Baltrėnaitė et al. 2012a, b).

Figure 2.16 presents the results obtained from an evaluation of the ambient air quality based on the quantities of metals accumulated in the bark. A higher metal concentration was detected in the pine bark from Zones 1, 2, and 4. Zones 1 and 4 are characterized by a higher Ni concentration, while Zone 2 shows a higher Cr concentration. The pollution is considered to be *mild* or *moderate* because $0 < I_{\mathrm{geo,b}} < 1$ (Table 2.17) (Guéguen et al. 2012).

The total ambient air pollution by metals based on their quantities in the pine bark and expressed as the total metal contamination index TCI_{b} is given in Fig. 2.17. According to the obtained TCI_{b} index values, higher pollution was observed in Zone 4, followed by Zones 1, 2, and 3.

It was determined that the greatest difference between the obtained metal concentration values and the background concentration values is at these distances: at 2.5 km for Ni and Cr, at 3.5 km for Zn, Cu, and Pb (in both cases, in the downwind direction), at 0.25 km from the company for Cu and Ni, at 1 km for Zn, and at 3.5 km for Pb and Cr (in all cases, in the upwind direction) (Fig. 2.18). This allows us to assume that there is a connection between the transfer of Ni and Cu and coarse particles of aerogenic pollutants, while the transfer of Zn, Cu, and Pb is associated with fine particles and their gas phase (Saet et al. 1990; Lietuvninkas 2012).

The values of the ratios for metal concentrations in the bark of Scots pines are presented in Table 2.21. The highest metal concentration, in agreement with the trend revealed earlier, was found in Zone 1. It was about 1.14 times that in other

Table 2.20 Metals in bark of *Pinus sylvestris* L. trees growing in Lithuania and other countries

Territory	Average concentration (mg/kg DW)						Reference
	Zn	Mn	Ni	Pb	Cr	Cu	
Paaliosios village (Vilnius district)[a], Lithuania	15.2	70.6	0.868	1.26	0.092	1.99	Baltrėnaitė and Butkus (2006)
1.5–2 km in vicinity of AB ORLEN Lietuva Co.	32.9	nd	5.39	10.9	252	571	Baltrėnaitė et al. (2014a, b, c)
Territory of Mažeikiai district (background concentration)	39.3	nd	3.61	10.1	184	743	
Alytus Region, Lithuania	nd	30.3	1.22	1.34	1.21	nd	Butkus and Baltrėnaitė (2007a, b)
Territory of Ruklos military shooting range (Kaunas district), Lithuania	198	81.4	1.76	0.770	0.230	1.39	Butkus and Baltrėnaitė (2007a, b)
Relatively unpolluted area in Finland	13.6–45.0	29.2–432	0.54–1.71	1.00–2.10	nd	267–340	Harju et al. (2002); Saarela et al. (2005)
Territory of Sweden	83.0	nd	0.80	2.50	1.80	6.00	Nehrenheim and Gustafsson (2008)
Harjavalta territory (Finland) 6 km from Zn smeltery	4.3	71.0	18.0	9.10	nd	89.0	Saarela et al. (2005)
Territories of Bulgaria, Germany, Norway, Poland, and Russia	4.50–189	nd	0.01–8.20	1.70–61.2	0.50–10.4	1.00–36.0	Schulz et al. (2000)

[a] The wood was infected by rotting caused by *H. annosum* fungus, *nd* no data available

Fig. 2.16 Positive values of geoaccumulation index $I_{\mathrm{geo,b}}$ for metals in pine bark from various zones of territory affected by AB ORLEN Lietuva

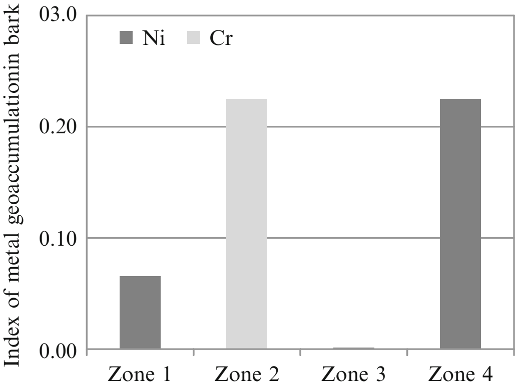
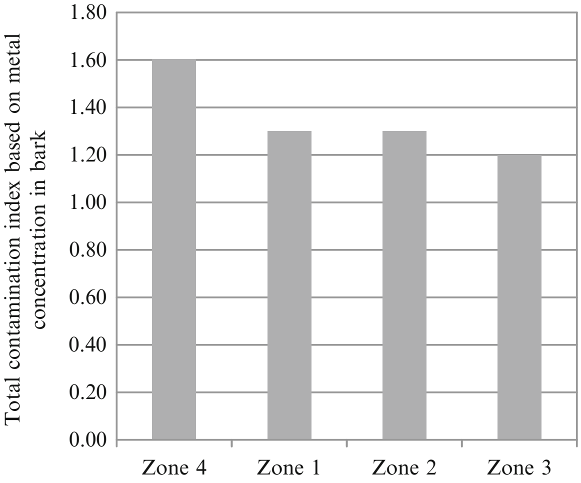


Fig. 2.17 Values of total metal contamination index TCI_{b} based on metal concentrations in pine bark from various zones of territory affected by AB ORLEN Lietuva



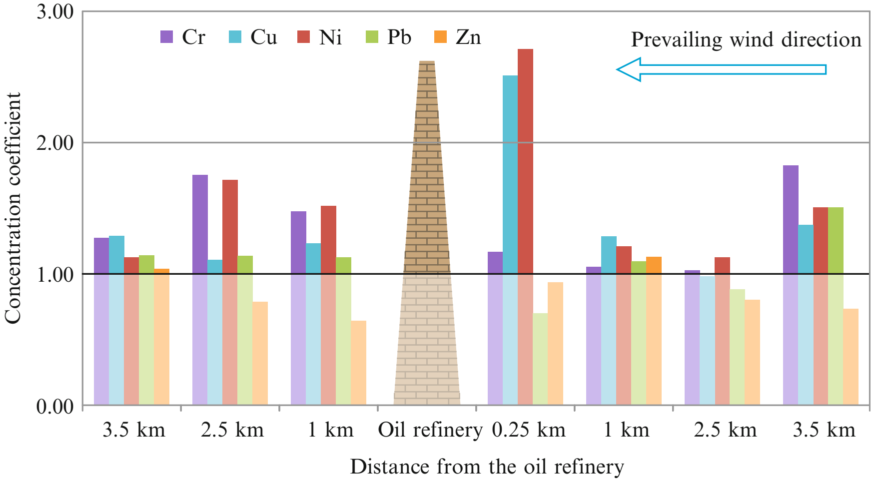


Fig. 2.18 Values of coefficient $K_{\mathrm{k,b}}$ for metal concentration in pine bark determined at various distances from territory affected by the company in prevailing wind direction

Table 2.21 Values of ratios K_{a-b} for metal concentrations in bark of Scots pines (*Pinus sylvestris* L.) from investigated zones

K_{a-b}	Cr	Cu	Ni	Pb	Zn
K_{1-2}	0.72	**1.10**	**1.15**	**1.37**	**1.78**
K_{1-3}	**1.17**	**1.04**	**1.46**	**1.22**	0.92
K_{1-4}	**1.00**	0.78	0.87	**1.33**	**1.22**
K_{2-3}	**1.64**	0.95	**1.28**	0.90	0.52
K_{2-4}	**1.39**	0.71	0.76	0.97	0.68
K_{3-4}	0.85	0.75	0.60	**1.09**	**1.32**
$K_{1,2-3,4}$	**1.29**	0.85	**1.02**	**1.10**	0.82
$K_{1,3-2,4}$	0.77	0.90	0.83	**1.22**	**1.51**

Note: Values in bold are greater than one.

zones. The western part of the territory affected by the refinery (Zones 1 and 3) had higher concentrations of Pb and Zn than the eastern part (Zones 2 and 4), while the northern part of the territory (Zones 1 and 2) had higher concentrations of Ni, Cr, and Pb compared to its southern part (Zones 3 and 4).

Metal Concentrations in Epigeic Mosses

In general, bryophytes (which include mosses) have the ability to accumulate persistent atmospheric pollutants and are widely used in biomonitoring to evaluate metal concentrations. Technologies based on epigeic mosses (*Hylocomium splendens*) are often used in the analysis of metal deposition on a regional scale and on a local scale (Steinnes et al. 1992).

Table 2.22 provides the research data of Lithuanian and foreign scientists on metal concentrations in epigeic mosses with the aim of comparing metal concentrations on the local and regional levels as well as from areas with similar sources of contamination. The highest concentrations of Zn (93.4 mg/kg) given in the present paper are higher compared to its concentrations in areas affected by emissions produced by oil burning (67.7 mg/kg) or the value obtained for Mažeikiai district (46.8 mg/kg). The highest obtained Cu concentration values (10.5 mg/kg) are similar to the data obtained for a zone affected by an oil-fired boiler (13.7 mg/kg) and approximately 1.5 times that of the background concentrations in mosses in Lithuania. The highest Ni concentration values (10.4 mg/kg) are close to the data obtained in similar research performed within the territory of Mažeikiai district in 2004 (14.5 mg/kg). The highest Pb concentration values are approximately one-fourth the values produced in similarly affected zones. Lastly, the highest concentration values for Cr, Cd, and Mn (6.68, 0.69, and 382 mg/kg, respectively) are higher than the expected values for the zone affected by the oil industry.

Equations (2.9) and (2.10) were used to estimate the level of environmental contamination by metals based on their concentrations in mosses and metal concentrations in bark. The calculated values of $I_{\text{geo,m}}$ and TCI_{m} are given in Figs. 2.19 and 2.20. *The average* contamination by Ni, Pb, and Cr, based on epigeic mosses, was determined for Zone 1, *the average* contamination by Ni and Pb was

Table 2.22 Metal concentrations in epigeic mosses (*Hylocomium splendens*) in Lithuania and other countries (*nd* no data available)

Territory	Concentration, mg/kg DW								Reference
	Zn	Cu	Ni	Pb	Cr	Cd	Mn	V	
Territory affected by AB ORLEN Lietuva oil refinery and a power plant	26.4–93.4	6.34–10.5	2.79–10.4	0.47–2.45	1.45–6.68	0.08–0.69	382	nd	Baltrėnaitė et al. (2014a, b, c))
Territory of Mažeikiai district	45.3	6.17	1.52	0.51	1.49	0.57	32	nd	
Zone in Mažeikiai district affected by a boiler	nd	nd	2.37–21.4	nd	nd	nd	nd	5.90–59.3	Čeburnis et al. (2002)
Zone in Italy affected by an oil-fired boiler	67.7	13.7	3.83	8.90	4.08	0.32	68.0	4.30	Genoni et al. (2000)
Territory of Lithuania (mean value for years 1990, 1995, and 2000)	38.8	6.29	1.63	nd	1.25	nd	nd	3.79	Harmens et al. (2007)
Zone affected by an oil refinery and a boiler	46.8	7.20	14.5	8.08	2.13	nd	nd	23.4	Kadūnas et al. (2004)
Territory of Mažeikiai district	18.9–65.3	4.1–10.2	0.99–37.29	3.15–11.53	0.63–5.42	nd	nd	1.8–112	
European countries	29.8–50.2	3.90–9.13	1.47–3.86	14.0–20.0	1.33–4.88	0.09–0.36	nd	2.00–9.60	Rüling (1994)

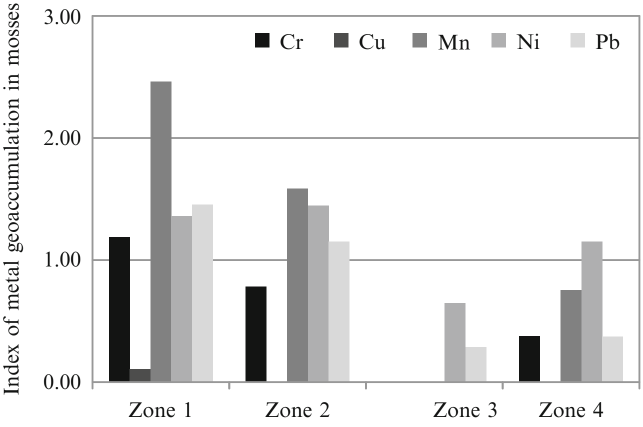


Fig. 2.19 Geoaccumulation index $I_{geo,m}$ for metals in epigeic mosses (*Hylocomium splendens*) from various zones of territory affected by ORLEN Lietuva

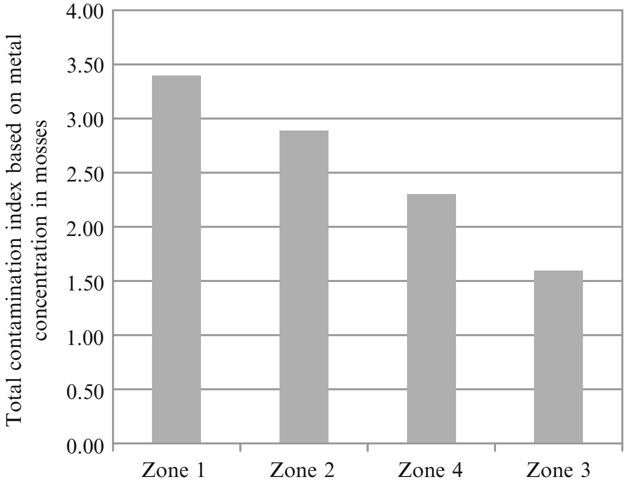


Fig. 2.20 Values of total metal contamination index TCI_m based on metal concentrations in epigeic mosses (*Hylocomium splendens*) from various zones of territory affected by AB ORLEN Lietuva

determined for Zone 2, and *the average* contamination by Ni was determined for Zone 4. Based on metal concentrations in epigeic mosses, Zone 3 can be considered *mildly* or *moderately* polluted territories.

The values of the index TCI_m for various zones, similarly to the values of $I_{geo,s}$, are arranged in descending order as follows: Zone 1 > Zone 2 > Zone 4 > Zone 3.

All things considered, it can be stated that the highest concentrations of most metals (including Zn, Cu, Cr, Mn, and Ni, not Cd) in epigeic mosses were

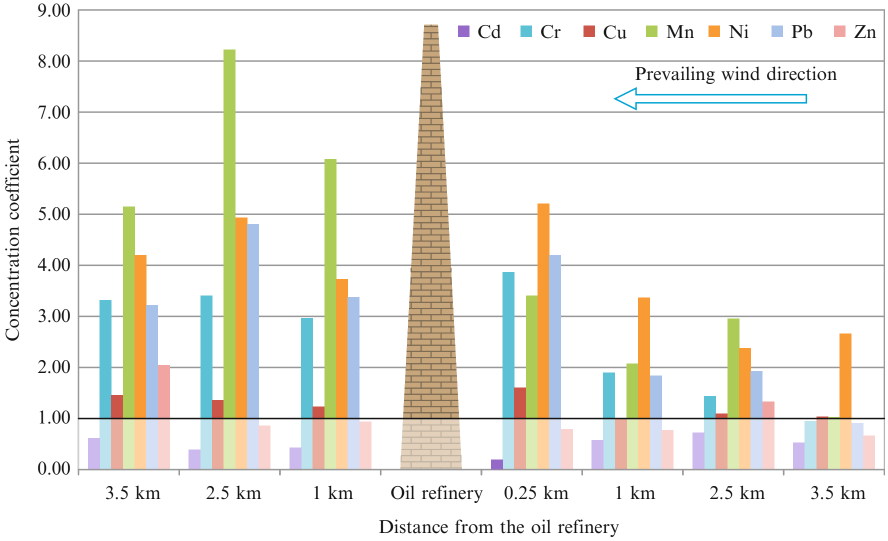


Fig. 2.21 Values of coefficient $K_{k,m}$ for metal concentration in epigeic mosses (*Hylocomium splendens*) determined at various distances from territory affected by the company in prevailing wind direction

determined for the territory of Mažeikiai district situated north of the company (Zn, Cu, Cr, Mn in Zone 1, Ni in Zone 2) (Fig. 2.20).

It was determined that the greatest difference between the obtained metal concentration values and the background concentration values is at these distances: at 2.5 km for Ni, Pb, Mn, and Cr, at 3.5 km from the company for Zn, Cu, and Cd (in both cases, in the downwind direction), at 0.25 km for Ni, Pb, Mn, Cr, and Cu, and at 2.5 km from the company for Zn and Cd (in both cases, in the upwind direction) (Fig. 2.21).

In the downwind zone, at a distance of 2.5–3.5 km from the refinery, the difference between the metal concentrations in epigeic mosses and the background concentration values is greater than the corresponding difference in the upwind zone ($K_{k,m}$ in the area downwind relative to company territory is about twice that in the upwind area). This proves the total effect of the refinery on the geochemical state of the environment.

The ratios for metal concentrations in epigeic mosses are given in Table 2.23. Metal concentration in accordance with the trend revealed earlier was the highest in Zone 1. It was about 1.72 times that in other zones. Metal concentrations in bark from the western part of the territory affected by the company (Zones 1 and 3), on average, are 1.23 times that in the eastern part (Zones 2 and 4). The same metal concentrations in the northern part of the territory (Zones 1 and 2) are about 1.53 times those in its southern part (Zones 3 and 4).

Table 2.23 Values of ratios K_{a-b} for metal concentrations in epigeic mosses (*Hylocomium splendens*)

K_{a-b}	Cd	Cr	Cu	Mn	Ni	Pb	Zn
K_{1-2}	**2.16**	**1.23**	**1.19**	**1.95**	0.87	**1.19**	**1.51**
K_{1-3}	0.89	**1.96**	**1.47**	**5.34**	**1.22**	**2.12**	**1.31**
K_{1-4}	**1.45**	**1.70**	**1.18**	**2.75**	**1.21**	**1.83**	**1.50**
K_{2-3}	0.45	**1.59**	**1.24**	**2.73**	**1.40**	**1.78**	0.87
K_{2-4}	0.67	**1.38**	0.99	**1.41**	**1.39**	**1.54**	0.99
K_{3-4}	**1.67**	0.87	0.80	0.52	**1.00**	0.87	**1.15**
$K_{1,2-3,4}$	0.81	**1.65**	**1.20**	**2.75**	**1.31**	**1.81**	**1.16**
$K_{1,3-2,4}$	**1.84**	**1.08**	0.99	**1.36**	0.92	**1.06**	**1.33**

Note: Values in bold are greater than one.

Based on the results obtained in evaluating the accumulation of aerogenic pollutants in natural objects and the response of the most sensitive deposit media to this process, the considered territory was included in areas of ***mild or moderate* pollution level**. The largest *daily snow dust* load (45.8 mg/m^2) was found in Zone 1, situated to the northwest of the company AB ORLEN Lietuva. Being lower than 250–450 mg/m^2/day, it did not exceed the corresponding daily snow dust load considered to be *moderately hazardous*. The greatest *values* of the *total* topsoil (0–10 cm) *contamination* ($Z_d = 5.2$) based on the considered metal concentrations were found in Zones 1 and 4, situated in the prevailing wind direction. According to the classification presented in Lithuanian Hygiene Standard HN 60:2004 (complying with EU requirements), a territory is considered *lower than moderately* polluted if $Z_d < 16$. It should be noted that the aforementioned pollution level value Z_d is the smallest possible value because not all metals listed in the considered standard were analyzed. According to the concentration of particular metals in the soil and the requirements of HN 60:2004, *hazardous* soil contamination by Ni ($3 < K_o < 10$) is characteristic of Zone 1, while the soil in Zones 2–4 has *moderately hazardous* contamination by Ni ($1 < K_o < 3$). *Moderately hazardous* soil contamination by Cr is characteristic of Zones 1 and 3. The determined metal concentration in epigeic *mosses* allowed the considered territory to be included among those areas of *mild* or *moderate* pollution level ($0 < I_{geo,m} < 1$). Higher contamination by metals is characteristic of Zones 1, 2, and 4. In Zones 1 and 4, higher contamination by Ni was found, while in Zone 2, contamination by Cr was higher. *Moderate* moss contamination by Ni, Pb, and Cr was found in Zone 1, contamination by Ni and Pb was found in Zone 2, and contamination by only Ni was observed in Zone 4. Based on the evaluation of metal concentrations in pine *bark*, the territory was grouped among areas of mild or moderate pollution ($0 < I_{geo,b} < 1$). In Zones 1 and 4, higher contamination by Ni was found, while in Zone 2, pollution by Cr was higher.

On the downwind side of the territory with respect to the oil refinery, the anthropogenic load of metals on deposit media is about 1.5–2 times that on the upwind side. According to the level of anthropogenic loading of deposit media, they can be arranged in the following order: snow cover > epigeic mosses > topsoil > pine bark. The preceding order is explained by the fact that a higher load of metals is in deposit media more closely associated with airborne pollutants than with the lithosphere (snow cover and epigeic mosses). Environmental processes of self-purification practically do not affect metals deposited in the considered media. Metals that accumulate in bark and soil are subject to the action of abiotic and biotic factors associated not only with accumulation but also with self-purification of the medium. Therefore, the accumulation of metals is not as prominent in them as in snow or epigeic mosses.

The most prominent increase in metal concentration in natural objects located in the downwind zone with respect to the refinery was observed within the territory 3.5 km from it, while in the upwind zone, it was found within the territory approximately 1 km from the refinery. This can be accounted for by the formation and release of gases by the oil refinery and specific distribution patterns of solid particles having various dispersities. In the upwind direction, the effect of coarse particles and metals transported by them is stronger, while in the downwind direction, the effect of gases, as well as fine particles, is greater.

Thus, concentrations and chemical species of metals in urban stormwater runoff from different sites are related to nonpoint sources of pollution, e.g., atmospheric deposition, and local sources of pollution – for example, industrial, energy, transport, and other enterprises, highways and parking lots, municipal infrastructure, and the erosion of building materials. The reason for the high concentrations of Cd, Pb, and Zn in urban stormwater runoff from roof and road surfaces may be the corrosion of galvanized steel products (e.g., steel sheets, gutters, downspouts, and safety barriers). Strong correlations ($p < 0.01$) between Pb and Cd in SSs in stormwater runoff from roads and between Zn and Cd from roofs were found.

The investigations of metal concentrations in SSs and in dissolved form show that with all investigated metals, the largest concentration is found in SSs—over 80 % of the total quantity, disregarding the water pH, dissolved organic acid, feculence, and type of surface area. The metals coefficient of partition (log K_d) between the total concentration of metals (on the basis of dry weight) and metals dissolved in water decreases in the following order: Zn > Cu ≈ Mn ≈ Pb > > Cd.

The concentration of dissolved metals (Cd, Cr, Cu, Pb, Ni, and Zn) in all the urban stormwater runoff samples does not exceed the limits of the maximum allowable concentration for acceptor water bodies.

Adapted to real circumstances, WHAM modeling revealed a variety of distributions of metals (Cd, Mn, Pb, and Zn) among chemical species in the investigated sites in cases where the speciation of the main cations (Ca, Mg, K) was not essentially affected by the stormwater runoff from different urbanized sites. The free metal ion form characteristic of Ca, Mg, and K was in the range of 89–99 % of the total dissolved elements. In urban stormwater runoff, which typically has higher values of pH or DOC concentration, the fraction of metals forming complexes with FA was higher. The fractions of Cd, Mn, Pb, and Zn bound to FA were higher by 38.8, 62, 52.3, and 70.3 %, respectively, in the modeling of stormwater runoff from the pathway compared to roof runs. In stormwater runoff from the road, Cd, Mn, Pb, and Zn tend to form complexes with FAs 40–80 % more than in stormwater runoff from roofs.

As the investigated metals were mostly related to SSs, the removal of SSs can be an efficient method of reducing metal concentration in urban stormwater runoff.

As in stormwater runoff from roofs, the largest fraction of Zn and Cd is in SSs (up to 1.5 times more than in cases of roads and pathway), and the activity of Zn and Cd free ions is high (68 and 80 % of the total quantity, respectively); therefore, the alteration of water chemical properties such that metals are released from SSs can result in increased contamination risk.

The largest daily mineral dust deposition on snow cover in the zone affected by AB ORLEN Lietuva *did not exceed* values characteristic of *average hazard rates*; based on the concentration of typomorphic Ni and Cr of AB ORLEN Lietuva in the soil and according to the requirements of HN 60:2004 in different sectors of the zone affected by the company, soil contamination ranged from *medium hazard* to *hazard*; according to metal accumulations in moss and bark, the site is within a territory of *low or medium* contamination. Following the principles of biogeochemistry and sanitary-hygienic principles, an integrated assessment of site contamination, in which the general site contamination level is linked to the reaction of the most sensitive depositing media, shows that the site is in a *low to medium* contamination area, except for Zone 1, where *soil contamination by Ni is at the hazardous* level.

Though the contamination of snow cover in the zone affected by AB ORLEN Lietuva, as an indicator of the state of its air, *does not exceed average hazard* values, in media depositing aerogenic pollutants, such as glittering woodmoss (*Hylocomium splendens*), pine bark, and soil, the contamination level was assessed as ranging from low (glittering woodmoss, pine bark) to medium hazard (glittering woodmoss, pine bark, soil) and hazard (soil). This means that the *aerogenic load of a relevant site exceeds the possibilities of natural self-purification of the said depositing media* (*technogenic load > natural self-purification*), which creates possibilities for a gradual increase in the site's general contamination level.

From the point of view of a human consumer of biological products at the top of the ecological pyramid and taking into account the biomagnification principle in ecology, *the increased pollution of deposit media by materials dangerous for humans is undoubtedly harmful*, especially if these materials are metals (as in the case considered here), which are persistent and not biodegradable. The geochemical condition of natural elements and pollution level in the ecosystems in the area affected by the refinery *are associated* with an anthropogenic load generated by the company. Therefore, taking into account the long period of operation of the oil refinery and its emission of harmful substances into the air, which is a pollutant-transporting medium, there is no doubt that the company affects its surroundings and the living conditions of local residents.

The current monitoring of environmental aerogenic contamination, oriented only toward analyses of the composition of the surrounding air, is very limited.

There is considerable need for thorough monitoring of ecosystems and the depositing media that characterize them. To perform monitoring of such scope, it is realistic not only to assess the conditions of the depositing media and determine the site’s aerogenic contamination level, but also to forecast the long-term development of ecosystem components and the impact of their condition on the quality of human life.

Chapter 3
Biogeochemical Aspect of Metal Uptake by Trees

The This chapter discusses the access of metals to ecosystems and mechanisms for entering trees. The transfer of metals from soil (also owing to an aerogenic load of metals) to trees should be steady; however, external or internal factors determine the investigated system. Environmental pollution, in terms of trees, acts as a stressor as it is classified as an external, ecological, and abiotic factor. Tree diseases are a no less important example of biotic factors and are among the consequences of climate change, attracting attention to the sustainability of forest management. This chapter deals with examples of abiotic and biotic factors, discusses the biological uptake of metals in wood, and examines the differences and peculiarities of metal bioavailability, bioaccumulation, and biophilicity in trees.

3.1 Entering Entrance of Metals into Forest Ecosystems

A discussion about the entrance of metals into trees will emphasize the fact that it is important to understand the methods of uptake of metals by forest ecosystems. The major part of metals enters forest ecosystems from the atmosphere. The intensity of metal emission to the atmosphere determines the concentration of these microelements in the layers of the troposphere. When they enter the stratosphere, metals (usually during volcanic eruptions) become a part of the global cycle. The particulate matter containing metals inside and moving in the troposphere is conveyed by circulation until it is precipitated to the ground (Cawse 1982). The main methods for removing microelements from the atmosphere include wet deposition (with precipitation) and dry deposition (as sedimentation). The latter highly depends on the size of the particulates carrying microelements, meteorological conditions, and the depositing surface structure (Merian 1991). The wet deposition of microelements is mainly conditioned by the intensity of precipitation. The vast majority of metals amassed in the atmosphere are bonded to dust particles. However, dustlike metals vary in

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size. Fine particulate matter of less than 0.1 μm in diameter is also referred to as Aitken nuclei and most frequently forms in the processes of gas combustion and changes in state from gas to solid. Pb, Cd, Zn, and other appear in a state of fine particulates that either quickly coagulate or are incorporated into clouds, and their lifetime in the atmosphere is less than 1 h. Particulate matter of a medium size in diameter ranging from 0.1 to 2.5 μm relates to Cr, Ni, V, and others and is formed from the particulates of a small fraction within the processes of coagulation and condensation on their surfaces. Middle-size particulate matter remains in the atmosphere longer and therefore can be transferred further from the sources of contamination (Schroeder et al. 1987). Fe, Si, and other microelements are most frequently found as large particulates (more than 2.5 μm in diameter) in atmospheric air. Similar particulate matter forms within mechanical processes such as the decomposition of soil or the incomplete combustion of fuel. They fall from the atmosphere as dry deposition. Their lifetime in the atmosphere may vary from several minutes to a few hours (Merian 1991). Because the size of particulates is the crucial factor making an impact on the rate of deposition of microelements, the relative rate, compared to the total deposition, is higher near emission sources. Wet deposition is the main method for removing particulates of less than 1 μm in diameter from the atmosphere in remote areas (Berg 1993).

Metals, like other chemical elements in the ecosystems of forests, are involved in biogeochemical cycles (Steinnes 1992) (Fig. 3.1). The cycles of the elements and changes in forest ecosystems are affected by the long-distance transfer of contaminants.

The atmosphere serves as a medium for transferring large amounts of metals from the sources of contamination. They precipitate on trees and later are washed out by rain on the forest floor together with litter from trees. The dust of the forest floor affected by wind can put metals back onto the surface of trees, where they are washed by precipitation again, or, together with litter, fall on the forest floor. Metals can be further washed out into deeper layers of soil. Metals may cause a decrease in nutrients absorbed by plants owing to their ability to change them in soil or, because of their toxic effect on soil microorganisms, slow the processes of mineralization. Macronutrient cations are leached out more easily from the root zone. The great majority of metals, particularly Cu and Ni, restrict nutrient uptake because they weaken the functions of tree roots because of which the growth of the above-ground parts of trees become suppressed, which leads to a reduction in the efficiency of external nutrient transfer and a decrease in organic matter that gets to the forest floor with falling objects. However, despite the aforementioned fact, large quantities of objects accumulate in soil litter because of the sharp weakening of the mineralization process.

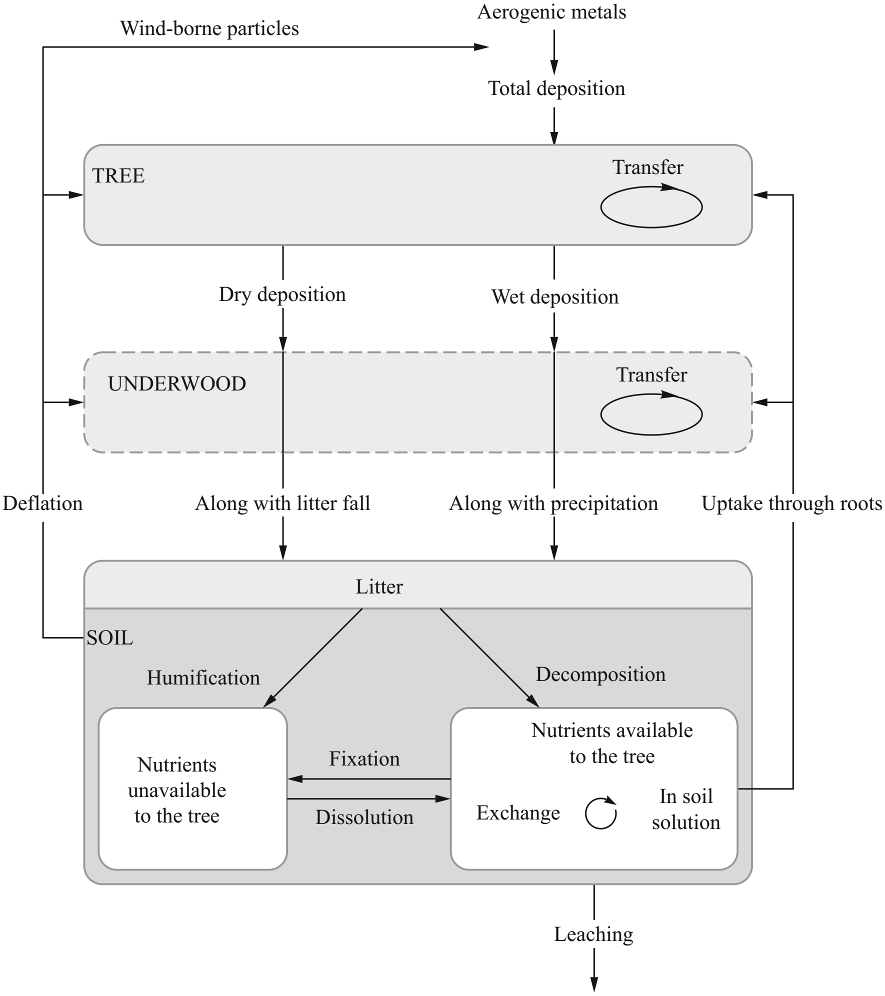

Fig. 3.1 General model for metal cycle in forest ecosystems (according to Nieminen 2005)

3.2 Metals in Tree Rhizospheres, Uptake and Bioaccumulation in Trees

The uptake of metals by trees involves several stages of metal transfer: metals in soil ⟶ metals in the rhizosphere zone ⟶ metals transferred through coating tissues in roots through bark and wood tissues ⟶ metal translocation in above-ground parts of tree. Next, the main metal transfer processes in soil and trees are discussed.

Metal uptake by plants is based on their solubility in the soil solution. Then, along with nutrients, metals easily make their way through the roots of plants and

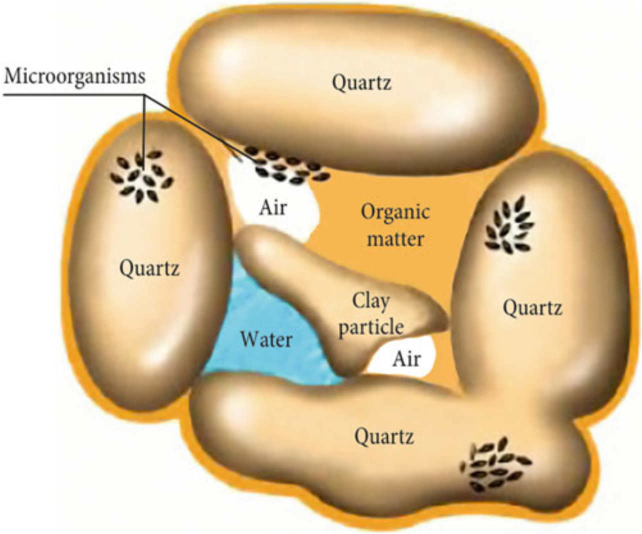

Fig. 3.2 Main components of soil (Maier et al. 2000)

are further transferred to the other above-ground parts of plants. Metal solubility is greatly affected by the type of soil (clay content in soil), pH, organic matter content, and the amount of Al, Fe, and Mn oxides in soil (Narwal and Singh 1998; Lietuvninkas 2012).

Metals' interaction with the main components of soil (Fig. 3.2) involves different processes (McBride 1989), including dissolution, sorption, formation of complexes, migration, precipitation, diffusion (into minerals), making compounds with an organic material, sorption to living matter, and evaporation.

Metal toxicity and biological uptake directly depend either on free metal ions or on metal labile forms in soil solutions (Neal and Sposito 1986). This confirms the *free metal ion* hypothesis proposing that a part of biologically absorbed metals largely depends on the number of free metal ions in soil (Lund 1990).

Organic matter has an impact on metal biological uptake subject to whether or not it is soluble. For example, the uptake of Cu^{2+} and Pb^{2+} by plants is impeded under the formation of stable complexes of insoluble organic matter (Almås and Singh 2001) as these complexes are composed of metals that cannot get to roots by diffusion. On the other hand, soluble organic matter makes soluble organometallic complexes and thus may increase the capacity of transferring metals through the soil solution (McBride et al. 1997) because large quantities of dissolved organic matter may lead to metal adsorption on the surface area of plant roots. Plant roots affect the release of metals from dissolved organometallic compounds when these enter the area of plant roots. The stability of the introduced organometallic complexes can be explained by the relationship of metals with organic matter. Cu and Pb make stable complexes with dissolved organic matter, and only a small part of these metals is available in the form of hydrated metal ions when the soil is not strongly acidic (Sauve et al. 1997). Zn and Cd are less likely to form such stable complexes with organic matter (Holm et al. 1995) and, therefore, are more prevalent in the free form of hydrated metal ions.

It has been noticed that *soil temperature* increases the quantity of metals adsorbed by soil particulates and the adsorption rate (Almås et al. 2000). Also, it has been discovered that an increase in soil temperature results in a higher uptake of metals by plants (Pinamonti 1998). Thus, temperature causes ongoing metal inhibition in soil, which does not necessarily set limits on metal uptake by plants. This can be explained by the fact that the growth of roots can be restricted by either a very high or very low soil temperature. The activity of roots increases where the temperature of the soil increases until the optimal size (Singh and Subramaniam 1997). Huang et al. (1991) found that an optimal soil temperature for winter wheat roots is 25 °C.

Soil pH is one of the most important factors in maintaining control over metal transfer from soil to trees. Moreover, it impacts other factors of soil, for example, organic matter, and therefore it is difficult to distinguish a separate effect of these two factors on the biological assimilation of metals. Gupta et al. (1987) suggest that, under an alkaline medium of soil, metal concentration in the soil solution decreases, whereas under neutral and acidic media of soil, metal concentrations in soil solutions are determined by adsorption processes. Singh and Abrol (1985) discovered that the most active metal adsorption processes took place when the soil medium was below pH 6.0, while in a range of 6.0 to 7.9, metal concentrations in the solution of soil are affected not only by adsorption processes but also by metal precipitation. Under natural conditions, pH values vary from 5 from 7, and those of the oxidation-reduction potential (Eh) range from 220 to 400 mV, except for reduction conditions or wetland soils. The properties of metal ions depend on the specific metal, while the influence of soil pH on metal precipitation varies. Nevertheless, the most mobile metals are expected under the lowest values of pH and Eh (Fig. 3.3) (Kabata Pendias 2011). The diagram shows a clear trend as long as metals are in the form of ions in soil solutions. However, in case of complex ions, such as molybdenum, the situation changes as Mo better migrates in an alkaline medium. Other chemical elements forming compounds (e.g., V^{5+}, W^{6+}, As^{5+}, Cr^{6+}, Se^{6+}) behave in a similar way. Even a more difficult task is to evaluate the possibilities of metal migration in soil solutions under higher concentrations of organic acids and with reference to the formation of soluble complex organic compounds in a less acidic environment (Lietuvninkas 2012).

Al, Fe, and Mn hydroxides in soil make hydroxyl groups that, in an acidic medium, can adsorb metals. It is assumed that Zn adsorption on the surface of soil particles may have an impact on its dissolution (McBride and Blasiak 1979).

Clay particles are a component of soil and adsorb metals onto their surface. Metal adsorption on the surface of clay particles is affected by the soil pH and their mineral composition (Lietuvninkas 2012).

Metal solubility strongly depends on the development of *metal compounds with inorganic ligands* in the soil solution (Mattigod and Sposito 1977). Because of the ligands that form compounds, metal suspension and mobility may increase.

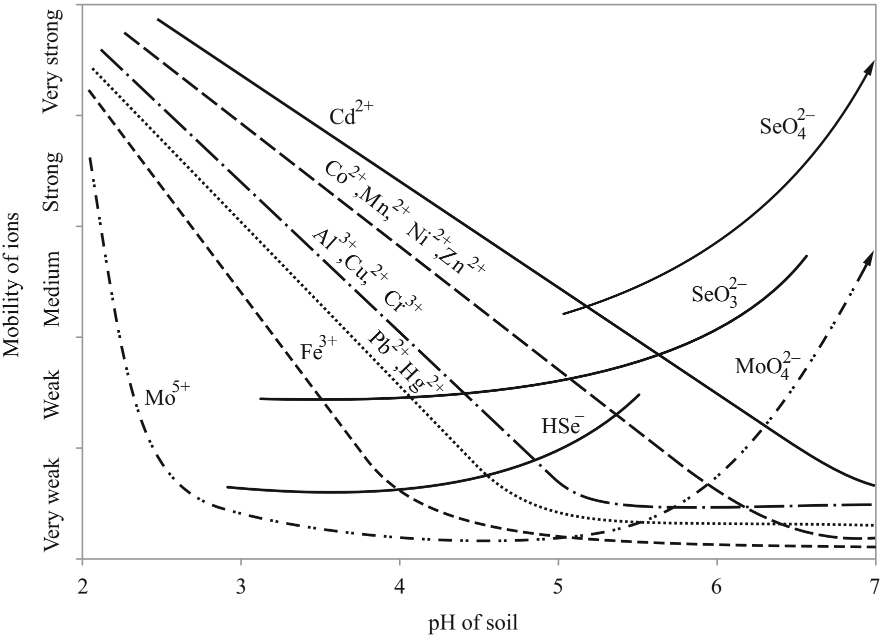

Fig. 3.3 Impact of soil pH on mobility of metals (Kabata Pendias 2011)

Inorganic ligands most frequently forming compounds with metals are SO_4^{2-}, Cl^-, OH^-, PO_4^{3-}, NO_3^-, and CO_3^{2-}. Of these, chlorides are extremely mobile and therefore form compounds with metals and increase the mobility of metals in soil. Chloride compounds with Cd, Hg, Pb, and Zn are particularly durable (Hahne and Kroontje 1973). Cases are known where chlorine compounds are produced with Ni, Cu, and Cd. Because of the presence of chlorine compounds, the concentrations of Pb and Cd in soil solutions increase; however, no effect has been noticed in cases of Zn, Cu, and Ni (Usman et al. 2005).

Cation exchange capacity (CEC) in soil can be defined as the ability of the soil solid phase to exchange cations with the soil solution. This quality of soil is important for the metabolism of chemical elements in soil. CEC influences the solubility of metals and, therefore, affects metal adsorption (Brigatti et al. 1996; Lietuvninkas 2012). Different types of soil have diverse values of CEC that often vary from 1 to 100 meq/100 g of soil. The particles of the soil solid phase with a large surface area (usually clay minerals) can be characterized by high metal values and a large capacity of adsorption and buffering capacity. [In this case, the soil buffering capacity is defined as its capacity to preserve an unchanged chemical composition under the influence of the flows of natural and anthropogenic materials (Lietuvninkas 2012).]

Metal competitiveness in the processes of adsorption. It has been noticed that metals compete with each other in these processes (Tyler and McBride 1982). The adsorption of ions is highly influenced by their potential, for example, ions having a longer radius are best adsorbed among the ions of the same valence, i.e., having a lower potential of the ion. The main reason for this dependence is that ions almost always hydrate in aqueous solutions, and their hydration shell considerably limits the electrostatic interaction between the sorbed ions and a polar sorbent. Thus, the higher the potential of the ion, the thicker the hydration shell, and therefore the sorption of the hydrated ion is weaker. Because of the increasing ability to sorb in aqueous solutions, monovalent and divalent cations take the following sequence (the value of the cation radius in angstroms is shown in parentheses) (Lietuvninkas 2012):

$$\mathbf{Li}^{+}(0.68) < \mathbf{Na}^{+}(0.98) < \mathbf{K}^{+}(1.33) < \mathbf{Rb}^{+}(1.49) < \mathbf{Cs}^{+}(1.65)$$

$$\mathbf{Mg}^{\mathbf{2}+}(0.74) < \mathbf{Ca}^{\mathbf{2}+}(1.04) < \mathbf{Sr}^{\mathbf{2}+}(1.20) < \mathbf{Ba}^{\mathbf{2}+}(1.38)$$

Metal concentrations in soil fertilized with sewage sludge. Because of the huge amount of phosphorus, nitrogen, and organic carbon, sewage sludge is useful for the enrichment of soil with nutrients required for the growth and development of cultural, nutritious, and other plants (Sommers et al. 1976). This has led to the use of sewage sludge as a fertilizer in agricultural fields and forests or their logging sites. Nevertheless, because of high metal concentration in sludge, its use may be limited due to the fact that, upon uptake by the soil solution, metals can be easily transferred to plants or reach groundwater (Planquard et al. 1999). Through herbivorous animals, metals can be further transported via food chains and thus pose a risk to human health. Increased concentrations of Zn, Cu, and Pb can be frequently observed in sewage sludge (Table 3.1).

When sludge is spread across soil, metal quantity in soil increases notably, thus causing groundwater contamination risk, increasing the mobility of toxic metals (for example, by the formation of metal compounds with organic matter), and raising the toxicity and contamination of plants through food chains (Mikac et al. 1998).

Researchers have investigated metal migration from sludge to deeper layers of soil and found that metal concentration in layers of soil deeper than 30 cm, compared to background concentration, was not that severe. Migrating metals become less soluble and produce insoluble compounds (Planquard et al. 1999).

Ni concentration increases slightly based on soil depth and is highly dependent on the amount of clay: a higher content of clay results in a higher concentration of Ni (Abdel-Sabour 1991).

With reference to data provided by Sims and Patrick (1978), the solubility and mobility of Zn and Pb are affected by pH, organic matter, and the type of soil. Owing to a higher content of organic matter (approximately 26 %) and an acidic medium (pH 4.8), Pb solubility and leaching from soil increase. Compared to Zn, organic matter is more important for adsorbing Pb, but clay minerals have more weight to adsorb Zn. Changes in Zn concentration in soil fertilized with sludge is similar to that of Pb. The largest metal deposits in soil fertilized with sludge form at

Table 3.1 Concentrations of metals (mg/kg) in sewage sludge and highest allowable metal concentration in sludge used for agricultural purposes according to LAND 20–2005

Metal	Bozkurt (2003)	Saet et al. (1990)[a]	VPIRG (1999)	Gasco et al. (2004)	Shomar et al. (2005)	Usman et al. (2005)[b]	Katinas et al. (2002)	Highest allowable metal concentration in sludge used for agricultural purposes according to LAND 20–2005
Mn	270	n.d.	n.d.	n.d.	188–273	n.d.	224–572	n.d.
Zn	1807	3200	995	984	1820–2527	4500	383–538	2500
Cu	271	2610	784	268	220–304	2000	118–161	1000
Ni	64	625	35	172	21–28	442	33–45	300
Cr	99	2635	59	330	68–111	n.d	60–100	400
Cd	2.1	44	6	6.5	1.5–2.2	77	n.d.	20
Pb	n.d.	218	112	297	111–156	1650	597–1421	750

n.d. no data

[a] Average concentration of mechanical engineering, chemical, and light industrial sewage sludge in the city

[b] Metal concentration in soil when sewage was spread 50 years ago

depths of 40–50 cm (Shomar et al. 2005). In case of contamination, the tendency for metal concentration to increase along with the amount of clay in soil becomes particularly relevant (Navas and Machin 2002).

Metals in the Rhizosphere

The rhizosphere is a zone that includes plant roots and complex relationships between plants, soil organisms, and the soil itself. Plant roots and the related biolayer may affect chemical processes taking place in soil, particularly the soil pH and nitrogen transformations (Heckman and Strick 1996). The rhizosphere has a width of about 1 mm and covers the epidermis, producing root hair and border cells of mycorrhiza. The rhizosphere and surrounding soil are rich in a variety of constantly changing microorganisms (Shigo 1996).

Plant roots absorb nutrients in the form of cations and anions. The differential uptake of these ions affects the pH of the rhizosphere. Nitrate (NO_3^-) or ammonium (NH_4^+) ions are among the basic ones. The uptake of ammonium ions may release hydrogen ions (H^+) and thereby reduce the soil pH in the rhizosphere. Hydroxide ions (OH^-) are released during the uptake of nitrate ions, which increases the pH of the rhizosphere. The introduced variations in pH arise only in the root zone and do not affect the overall pH of the soil medium (Heckman and Strick 1996).

It is common that the loss of trees depends on the processes occurring in the rhizosphere. Trees can result in death for the following three reasons: the depletion of nutrition stocks (when a reduction in nutrients necessary for the tree may result in diseases or loss of the tree), dysfunction (when a malfunction of one or another part of a tree may result in the disruption of the normal development and functioning of the tree), or the disturbance of natural growth processes of the tree (tree injury, breaking, mechanical damage) (Heckman and Strick 1996).

Biological uptake of metals and toxicity depend on the reactions taking place in the rhizosphere and include not only the exchange reaction between the tree and soil but also the activity of microorganisms (mycorrhiza) (Schützendübel and Polle 2002). Under natural conditions, the roots of many plants, especially those of trees, are related to the symbionts of mycorrhizae. Fungi prevail in mycorrhizae in acidic forest soils and actively participate in the destruction of falling objects from coniferous trees. Organic acids produced within this process make soil even more acidic. Saprophytic bacteria predominate in mycorrhizae in deciduous forests where the pH of soil solutions is close to neutral values (Afanaseva and Berezina 2011).

Mycorrhizae are useful for plants because they increase the suction surface of roots and, therefore, assist in the more efficient uptake of nutrients. Moreover, symbiotic mycelium protects plant roots from disease-causing fungi. The mycelium of root cortical cells receives high-energy compounds (e.g., carbohydrates). Moreover, the respiration of mycorrhizal plant roots becomes two to four times more intense than that of plants that do not have similar symbiosis, in which case, owing to the activities of fungi, morphological changes in tree roots occur and variations in the structure of the membrane of root cortical cells can be observed (Bonfante-Fasolo and Scannerini 1992). Some of the results of the conducted research have disclosed that the impact of mycorrhizae on both the morphology and organisms of roots can reduce the uptake of some nutrients; however, in the case of mycorrhizae, nutrients along with metals migrate and accumulate in the biomass of fungi (Richards 1987). Symbionts can change the reaction of trees to the impact of metals (Jantschje and Godbold 2000). The findings of the research carried out by Schützendübel and Polle (2002) have revealed that, without mycorrhizae, pine seedlings that grow in soil with an increased concentration of Cd (≥ 15 μM) accumulate biomass that is 35 % less compared with similar control saplings in terms of Cd. In contrast, no decrease in biomass has been noticed in saplings whose roots were in symbiosis with the fungus *Paxillus involutus*.

Higher activity of microorganisms in the rhizosphere affects metal uptake by plants in two ways. First, for decomposing large organic metal compounds, microorganisms can release them. Second, compound components secreted by roots can increase the uptake of contaminants in plants (McLaughlin et al. 1998). The excretion of organic compounds into the rhizosphere zone has been found to be greater, and, as the rhizosphere contains more microorganisms (Barber and Martin 1976), it is assumed that the uptake of metals by plants will also grow.

Chelates are water-soluble complex chemical compounds in which a metal ion is tightly bound to an organic molecule with the help of multiple chemical bonds. Chelates are made of metals in contact with humic substances. Metal in such substances appears in the anionic part of the compound, and therefore can be involved in exchange reactions (such reactions take place much slower). Thus, conditions for metal migration are ensured, because metal is protected against sorption and precipitation (Lietuvninkas 2012). This is particularly relevant under conditions of high pH values. According to R. Brooks, the stability sequence of the cation chelates of divalent metals is as follows (Lietuvninkas 2012):

$$\mathrm{Hg} > \mathrm{Cu} > \mathrm{Ni} > \mathrm{Co} > \mathrm{Pb} > \mathrm{Zn} > \mathrm{Cd} > \mathrm{Fe} > \mathrm{Mn} > \mathrm{Ca} > \mathrm{Sr}$$

Chemical substances excreted by plant roots change metal solubility in the rhizosphere. Thus, Fe is one of the most common metals in soils (3.0–3.5 %). Nevertheless, Fe comprises only a minor part of soil solutions (10^{-8} M) and creates Fe deficiency. Meanwhile, the average Fe concentration in plant tissues is about 10^{-6} M, i.e., 100 times more. To fulfill their physiological needs for Fe, plants have developed a special uptake mechanism that becomes active under a severe lack of Fe. Hence, monocotyledons excrete special materials called phytosiderophores (nonprotein amino acids) to properly chelate metals. For other metals such as Cu, Zn, and Mn, the process of uptake takes place in a similar way. Kupčinskienė (2011) provides a similar mechanism for Fe uptake with respect to poaceae plants.

Metal Transfer Through Root Tissues

The main transfer of mineral matter and water to trees takes place through roots (Fig. 3.4). Water with minerals, including metals, from root hair enters bark cells, then to root vessels, and finally to wood vessels.

Roots have the strongest contact with the nutrients present in soil. Roots, as the main segment of a tree, are most adapted to the required food absorbed by the tree. Roots also provide mechanical support for the tree, accumulate energy resources, and transport water, dissolved substances, and those substances that regulate the growth of the tree, for example, amino acids and vitamins. The surface layer of roots adsorbs metals, and nutrient ions are replaced by H^+, OH^-, and HCO_3^- ions emitted by tree roots.

Metals, along with nutrients, approach the roots of a plant in two ways (Williams et al. 2000) (Fig. 3.5):

- *Apoplastic transfer (active transfer)*. Either as a result of diffusion or because of passive water inflow, metal ions enter the walls of root cells and space between cells up to the Casparian strip in the root endodermis. Woody cell walls in this particular location of the root are water resistant, and therefore further transfer is blocked, but metals with nutrients can be transferred through cell membrane to the cytoplasm.

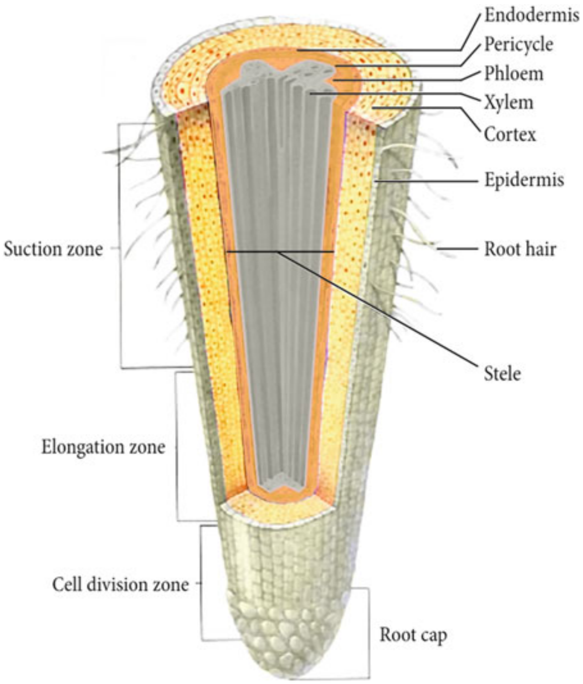

Fig. 3.4 Root structure of a woody plant (Mader 1998)

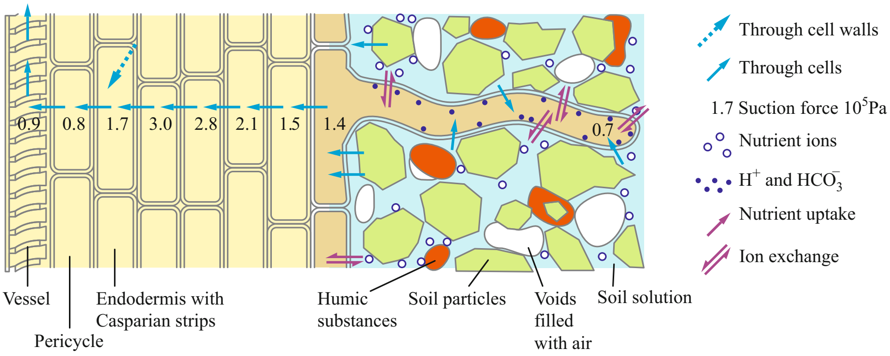

Fig. 3.5 Transfer of nutrients and water through a root (Heinrich and Hergt 2001)

- *Symplastic transfer (passive transfer).* This type of transfer of metals and nutrients takes place through the cytoplasm up to the vascular tissue. Metals and nutrients are distributed in the plant with transpiration flow.

Cd, Cu, and Ni ions most frequently undergo active transfer; however, they are prevented by the ions of K, Ca, and Mg. Passive transfer is often used for transporting the ions of Sr, Ba, Co, Ni, Cu, and Cd. So-called calcium channels help with the motion of these cations through the membranes of the root cells that also transmit and monovalent cations. It has also been established that Cu and Ni can be transmitted through passive transfer to the roots of the fir tree (Godbold 1991).

Metals in Tree Crowns

Investigation into metal concentrations in tree crowns has disclosed that metal concentration in needles and leaves depends on the conditions of the habitat (soil, geographical location, contamination load), the seasons of the year, and individual properties of the tree (age of the tree and crown, light, and decay rate) (van den Driessche 1974).

Because environmental pollution affects the distribution of nutrients and pollutants in needles (Shaw and McLeod 1995), they are used for environmental protection purposes to monitor the level of contamination (Dmuchowski and Bytnerowicz 1995). It is supposed that the concentration of mobile Zn, Ni, and Mn (Kabata Pendias and Pendias 1993) in needles can be related to the accumulation of these metals and transfer from the soil (Helmisaari 1992). Metal accumulation in needles can be affected by aging processes when, along with a reduction in water content, a decrease in the amount of metals transferred through water is produced (Zelawski 1967). Al concentration in soil may have an impact on metal accumulation in needles. Under an acidic soil pH, the content of Al^{3+} that is available but toxic to plants grows (Kabata Pendias and Pendias 1993).

It has been found that birch leaves can accumulate an extremely high content of Mn (Zyrin et al. 1985), which can be under the influence of the acidic medium of soil and therefore under an increase in the content of mobile Mn (Hrdlicka and Kula 1998).

Cu concentration in needles has been found to sharply increase after the roots of the pine tree were saturated with this metal. A direct correlation between Cu concentration in needles and their surfaces has been established, which indicates that Cu accumulation in needles is affected by Cu that is transferred through atmospheric air and precipitates on the surface of needles (Mulgrew and Williams 2002). Such a phenomenon can be defined as an adhesive mechanical barrier frequently described as deposited media of solids covered with aerosol particles (and together with metals that are transported with aerosols) (Lietuvninkas 2002a, b).

Pb is one of the major pollutants emitted from transport vehicles (Loppi and Pirintsos 2003). As Pb most frequently falls into ecosystems in the form of fine particulates (Rizzio et al. 1999), leaves are the main tree segments preventing contamination by metals (Wagner 1993). Significant amounts of Pb are formed from natural sources. A content of 75 ppm Pb has been found to accumulate in the needles of coniferous trees growing in uncontaminated soil, while only 1/18 part of Pb uptake from the atmosphere to soil is absorbed by plants (Mažvila 2001). About 64 % of the total Pb content (14 ppm) in plants (besides Pb concentration in roots) accumulates on the surface of leaves and can be washed out by precipitation. Pb concentration of the leaves themselves, in the majority of cases, is accumulated in cell walls (Schwedt 1997). The biggest part of Pb (approximately 80 %) can be extracted using hydrochloric acid. About 3 % of Pb is concentrated in cellular organelles, whereas 5 % form compounds with soluble proteins in a vacuolization liquid. These compounds have a detrimental effect on enzyme activity and the processes taking place in membranes (Schwedt 1997). Metal concentration in fir needles may vary from 0.32 to 1.40 mg/kg (Kadūnas 1998).

Zn is another important pollutant emitted by transport vehicles (Loppi and Pirintsos 2003). Experimental research has revealed (Bargagli 1990) that a part of Zn enters lichens growing on the trunks of trees from tree bark. Nriagu (1979) identified that even about 20 % of Zn emitted to the atmosphere was removed from trees.

A number of researches focus on the use of sludge for soil fertilization and metal transfer from sludge to plants. Sewage sludge, apart from beneficial nutrients for plants and a high content of organic matter, contains large quantities of metals that often are mobile in sludge and therefore, when in contact with soil, easily migrate into the deeper layers of soil or are absorbed by plants together with the soil solution. The use of sewage sludge for soil fertilization has resulted in a significant rise in the concentration of Mg, Fe, Mn, and Zn in apple-tree leaves, whereas that of Cu, Ni, Cr, and Cd has varied only to a small extent (Bozkurt 2003). Sewage sludge has caused an increase in the trunk biomass and height of apple trees and has accelerated the growth of twigs (Bozkurt 2003). An increase in the concentrations of Zn, Cu, Cd, and Cr in plant tissues after fertilizing soil with sewage sludge has also been reported by other authors (Pinamonti et al. 1997).

Not all plants equally absorb metals from sludge. For example, willow (*Salix viminalis*) and birch (*Betula pendula*) growing in sludge-fertilized soil accumulate higher amounts of Zn than ash trees (*Fraxinus excelsior*) or alder (*Alnus incana*) (Rosselli et al. 2003). Although, in the cases of willows and birches, the coefficient of Zn transfer is higher than that of the ash tree or alder; however, it does not exceed 1.0. Moderate amounts of Cu in the investigated trees may occur for several reasons. Cu is known to form stable compounds with the components of soil (Turner and Dickinson 1993). Moreover, Cu is kept in the roots of trees (Khan 2001). There is evidence that Cu is barely mobile in plants because it is retained in wood (Nissen and Lepp 1997). High Cu concentrations have been established in different species of birch (Kozlov et al. 1995) and the roots of willows (Punshon and Dickinson 1997). The the case of birch and willow cannot be explained by the fact that the plants quickly absorb metals (Kopponen et al. 2001); however, compared to other species of trees, they can be employed for biological extraction thanks to their ability to transfer relatively large quantities of metals to above-ground structures. The ash tree (*Fraxinus excelsior*) can be grouped with those species of trees not absorbing metals (Rosselli et al. 2003) and may have a special mechanism preventing the uptake of metals, thus keeping them in the rhizosphere or roots (Blaylock and Huang 2000).

Metal Transfer to and Accumulation in Stemwood

Upon entering the tree, metals have several ways of migrating inside it (Fig. 3.6):

- together with water and dissolved minerals, from soil through roots into the trunk, shoots, leaves, and needles;
- together with organic matter in the trunk and leaves toward roots.

The gradients of concentration and electrical potential affect the entrance of metals and nutrient solutions into plants (Heinrich and Hergt 2001) (Table 3.2).

Changes in soil moisture affect the transfer of the solution to roots: owing to a decrease in moisture, a reduction in diffusion and mass flow rate can be observed though the concentration of exchangeable cations in the soil solution increases (Nye and Tinker 1997). Under natural conditions, the impact of changes in soil moisture can be even more complex because significant variations in moisture and soil microflora can result in physiological and morphological changes in the root system (Smucker and Aiken 1992; Russell 2001).

Trees growing in temperate climates and during a change in seasons have the ability to shape the annual layers of wood – annual rings. Coniferous tree rings are extremely bright. The multielemental analysis of annual rings has been found to provide information on variations in atmospheric pollution and acid rain. Annual

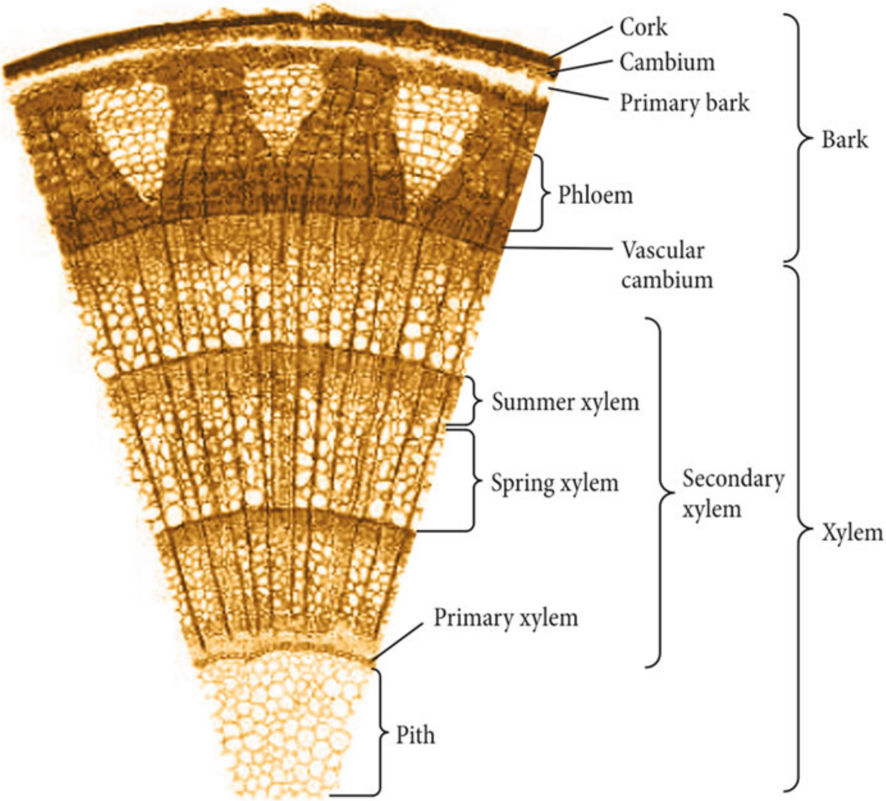

Fig. 3.6 Structure of trunk of a woody plant (Borusas et al. 1990)

Table 3.2 Electrochemical potential of metals (mV) in aqueous medium (pH 7.0; 25 °C, according to Weast 1984)

Metal ion	Oxidation-reduction potential (mV)
Zn^{2+}	−1.18
Cd^{2+}	−0.82
Ni^{2+}	−0.65
Pb^{2+}	−0.55
Cu^{2+}	−0.26
Fe^{2+}	+0.35
Hg^{2+}	+0.43

rings are used, for example, for monitoring changes in climate, identifying environments contaminated with metals, determining the relationship between conditions for tree growth and atmospheric pollution, relating tree growth to acid rains, and establishing ambient temperature in the past (Ozolinčius 2004).

A high correlation between metal concentration in later-formed tree rings and that in soil has been established (Larsson and Helmisaari 1998). Scientists investigated metal accumulation in wood near industrial companies extracting fossil fuels and concluded that an increase in metal concentration in wood was affected by the wet and dry deposition of combustion products on trees (Baes and McLaughlin 1984). The research disclosed that increased Pb concentration in annual rings was related to transferral of the metal through the atmosphere from car emissions (Latimer et al. 1996). Background quantities of Mn in the trunk of *Pinus sylvestris* L. are larger in older wood rings than in newly formed ones. Higher contents of Ni have been found in trees growing in heavily contaminated sites (Larsson and Helmisaari 1998). Radial transfer of metals from previously formed annual rings to newer ones is not clear, though a similar tendency has been established in the case of Mn (Baes and McLaughlin 1984).

Researchers at the Department of Environmental Protection of VGTU conducted research to determine the concentrations of metals in wood rings at sites of increased pollution such as military grounds (Rukla–Gaižiūnai and Kairiai) and longstanding industrial district in Alytus. Two pine trees were observed in Rukla–Gaižiūnai military ground (1P and 2P), one pine tree on the Kairiai military grounds (3P), and a pine tree and a birch at a distance of 10 km from the south of Alytus.

Metal concentrations in wood have been assessed with reference to long-term observations based on background, deficit, surplus, and phytotoxic metal concentrations in plants (Table 2.10) (Kabata Pendias and Pendias 1992).

Table 3.3 shows the characteristics of five studied trees that grew in regions of increased contamination.

Figure 3.7 shows the concentrations of Cr, Cu, Ni, Mn, Zn, and Pb of four pine trees (1P, 2P, 3P, and 4P) and one birch (B) in annual rings within the period from 1978 to 2001.

Metal concentrations in all investigated trees exceeded neither phytotoxic nor excessive concentrations of metals (Table 3.4). The concentrations of Cr, Ni, Mn, and Zn were close to background ones. Pb concentration (<3.5 mg/kg) was lower than background Pb concentration in trees, while Cu concentration (<3.0 mg/kg) was close to the considered deficiency concentration of Cu in plants (Table 3.4). Lower than background and deficiency concentrations of Cu and Pb were determined in pine trees growing on military grounds. Moderately higher Pb concentration was found in the pine tree and birch that grew close to the industrial city (Alytus); however, it did not exceed background Pb concentrations in trees (Table 3.4).

Cu concentrations were similar in the trees of all investigated places within the period 1978–1988. Higher Ni concentrations were discovered in the annual rings

Table 3.3 Main characteristics of surveyed trees

Tree	Tree species	Height (m)	Age (years)	Diameter (at a height of 1.3 m)
1P	*Pinus sylvestris*	16	44	0.40
2P	*Pinus sylvestris*	15	31	0.35
3P	*Pinus sylvestris*	15	32	0.30
4P	*Pinus sylvestris*	30	55	0.40
B	*Betula pendula*	28	51	0.41

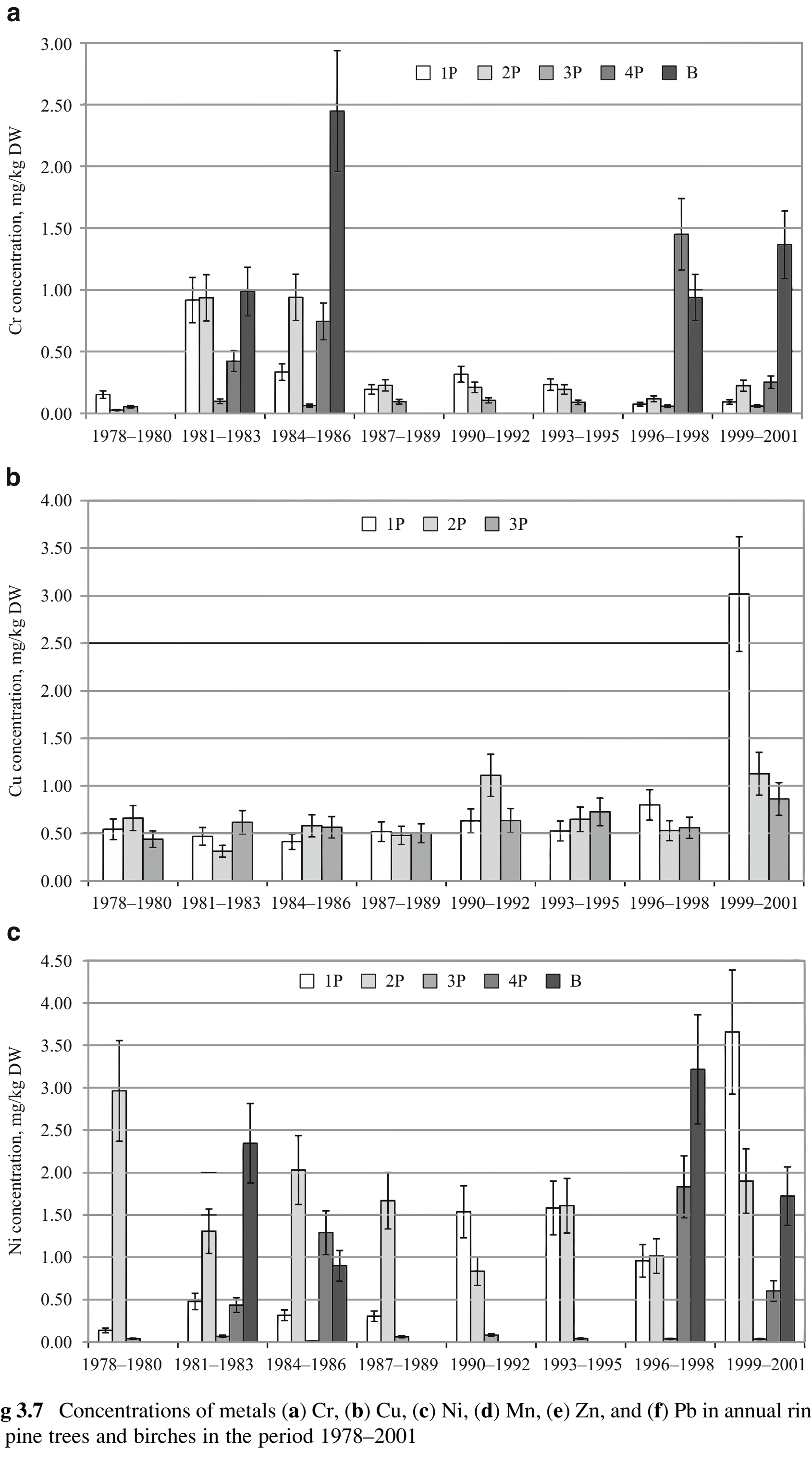

Fig 3.7 Concentrations of metals (**a**) Cr, (**b**) Cu, (**c**) Ni, (**d**) Mn, (**e**) Zn, and (**f**) Pb in annual rings of pine trees and birches in the period 1978–2001

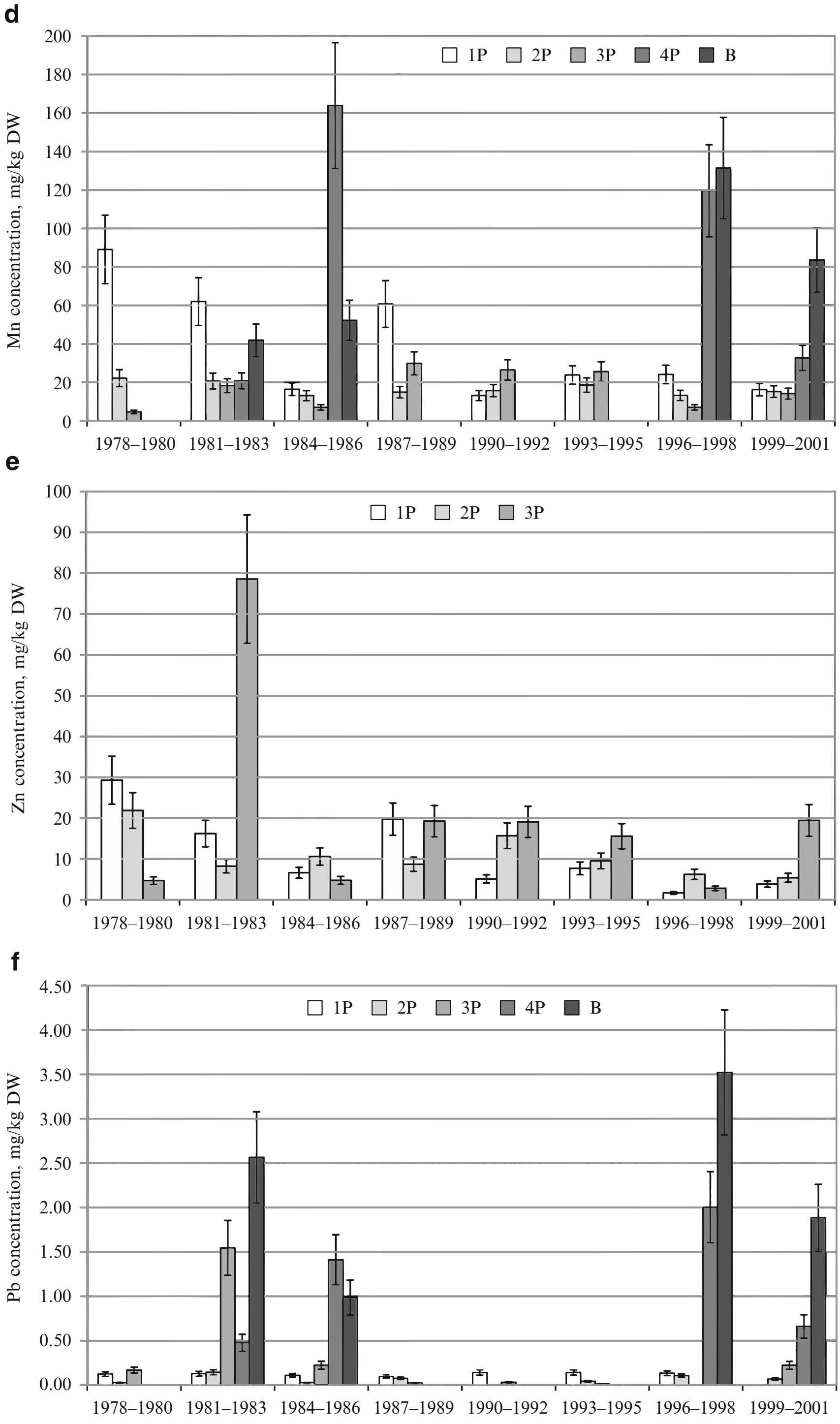

Fig 3.7 (continued)

Table 3.4 Background, deficiency, excessive, and phytotoxic concentrations of metals in plants (mg/kg) (Kabata Pendias and Pendias 1992)

Metal	Background concentration	Deficiency concentration	Excessive concentration	Phytotoxic concentration
Ni	0.1–5	n.d.	10–100	100
Cr	0.1–0.5	n.d.	5–30	75–100
Co	0.02–1	n.d.	15–50	50
Mn	20–300	15–25	300–500	1500–3000
Cd	0.05–0.2	n.d.	5–30	n.d.
Pb	5–10	n.d.	30–300	100–400
Zn	27–150	10–20	100–400	70–400
Cu	5.1–30	2–5	20–100	60–125

n.d. no data

(in the period 1978–2001) of the pine tree (2P) growing on the Rukla–Gaižiūnai military grounds and, starting from 1990, in the pine tree growing near the shooting range on the Kairiai military grounds. An increase in the concentrations of Cr, Ni, Mn, and Pb in wood has been observed within two periods:, 1981–1986 and 1996–2001. Significant variations have not been observed in the concentrations of Cu and Zn in the rings for the period 1978–2001.

Higher concentrations of Cr, Mn, and Pb have been noticed in older rather than in younger trees. Considering their age, the investigated trees can be arranged in the following descending order: 4P > B > 1P > 3P > 2P. A similar decrease in the order varies in some average concentrations of metals in wood: Mn—4P (84.22 mg/kg) > B (77.28 mg/kg) > 1P (38.19 mg/kg) > 2P (16.69 mg/kg); Cr—B (1.433 mg/kg) > 2P (0.359 mg/kg), and Pb—B (2.23 mg/kg) > 3P (0.319 mg/kg) > 2P (0.070 mg/kg).

Metal concentrations in birchwood have been found to be higher than those in pinewood and in Cr around 4 times, in Ni around 2 times, in Mn around 2 times, and in Pb around 1.5 times. Moreover, higher concentrations of Cr, Ni, Zn, and Mn have been discovered in the annual rings of pine trees that grew on military grounds when the growth and augmentation of the trees were at their most intensive one, i.e., 15–30 years old (Stravinskienė 2002) (Table 3.5). This tendency has not been observed in trees growing in the city of Alytus.

Figure 3.8 provides the values of the metal transfer coefficient (TC_i) calculated according to Eq. (3.1) considering the metal concentration at a particular depth i of the soil profile and the metal concentration in the latest-formed tree ring:

$$\mathrm{TC}_i = \frac{C_{\mathrm{metal}} \cdot P_i}{D_i \cdot 100}, \qquad (3.1)$$

where C_i is the concentration of metal formed in the ring within the period of recent years (mg/kg dry mass); D_i is the concentration of metal at soil depth i (mg/kg dry mass); P_i is root mass fraction (%) at soil depth i considering the total mass of roots.

Table 3.5 Annual rings with highest established concentrations of metals

Metal	1P	2P	3P	4P	B
Cr	1981–1983	1984–1986	1990–1992	1996–1998	1984–1986
Cu	1999–2001	1999–2001	1999–2001	*n.d.*	*n.d.*
Ni	1999–2001	1978–1980	1990–1992	1996–1998	1996–1998
Mn	1978–1980	1978–1980	1987–1989	1984–1986	1996–1998
Zn	1978–1980	1978–1980	1981–1983	*n.d.*	*n.d.*
Pb	1993–1995	1981–1983	1981–1983	1996–1998	1996–1998

Gray periods denote most intensive periods of growth (15–30 years)
n.d. no data

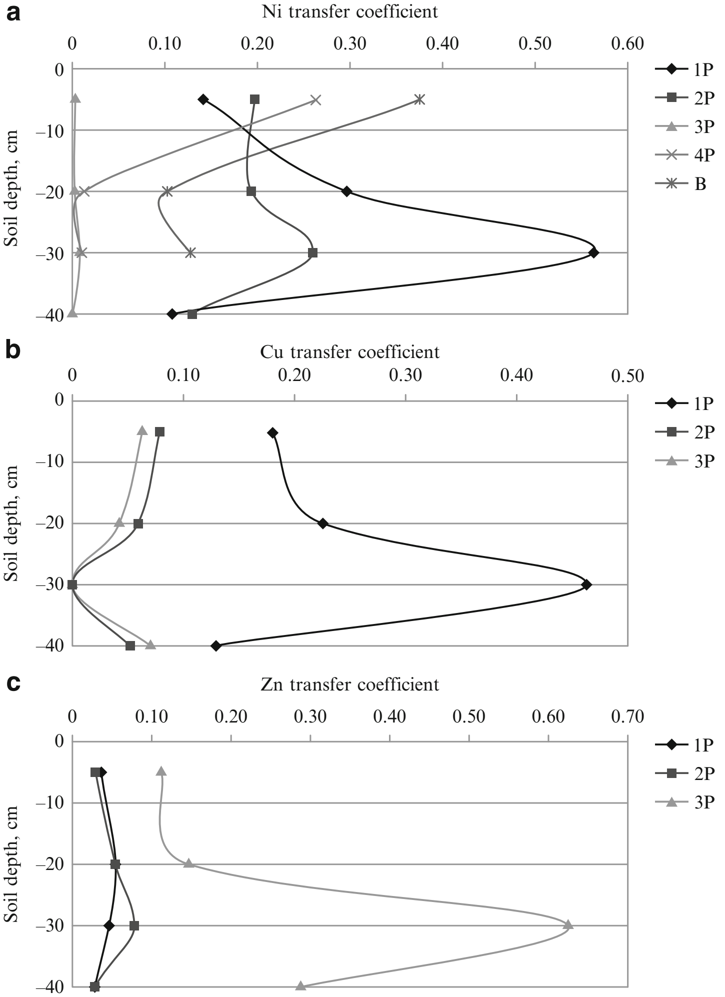

Fig. 3.8 Coefficients of metal transfer from different layers of soil to wood of recently investigated last annual rings of trees for the period 1999–2001

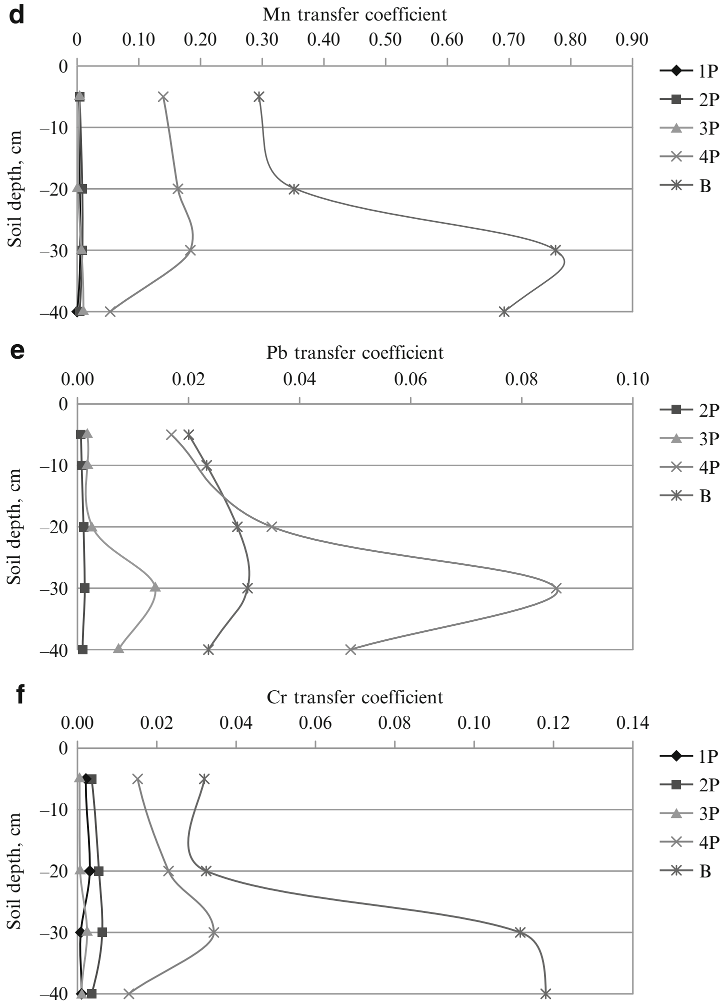

Fig. 3.8 (continued)

TC has been calculated with reference to different soil depths and the mass of tree roots at a particular soil depth. The established TC values fluctuated as follows: Ni—from 0.001 to 0.55; Cu—from 0.04 to 0.45; Zn—from 0.03 to 0.6; Mn—from 0.001 to 0.75; Pb—from 0.002 to 0.085 and Cr—from 0.005 to 0.11; however, none of the investigated metals exceeded 1.0.

Table 3.6 shows the sequences of trees according to the highest TC values. A massive transfer of Mn, Cr, and Pb to the pine tree and birch was observed close to the city of Alytus and a less immense transfer of Ni, Cu, and Zn to pine trees was observed on military grounds. A much greater transfer of Mn, Cr, and Pb to the birch was determined than to the pine tree. The highest transfer of Zn to the pine

Table 3.6 Sequence of investigated trees according to highest values of transfer factors

Metal	Sequence of investigated trees
Ni	1P, B > 2P > 4P > 3P
Cu	1P > 2P, 3P
Zn	3P > 2P, 1P
Mn	B > 4P > 3P, 2P > 1P
Cr	B > 4P > 2P > 1P > 3P
Pb	B, 4P > 3P > 1P, 2P

Table 3.7 Soil depths (cm) at which the transfer coefficient of metals were the highest

	Metal					
Tree	Ni	Cu	Zn	Mn	Pb	Cr
1P	20–30	20–30	10–20	20–30	n.d.	10–20
2P	20–30	0–10	20–30	20–30	20–30	20–30
3P	20–30	30–40	20–30	30–40	20–30	20–30
4P	0–10	n.d.	n.d.	20–30	20–30	20–30
B	0–10	n.d.	n.d.	20–30	20–30	30–40

n.d. no data

tree (3P) was discovered to be close to the shooting range and was seven times stronger than to pine tree 1P and about six times stronger than to pine tree 2P.

High values of the Ni transfer coefficient to pine tree 1P were found. The object was close to a water body used by military transport (the transfer was 1.5 times greater than that to 2P, about 7 times greater than to 3P, about 2 times greater than to 4P, and about 1.4 times greater than to the birch). A similar tendency also characterized Cu in pine tree 1P, which was four times higher than that to pine trees 2P and 3P (Table 3.7).

Table 3.7 provides data on the layers of soil whose calculated TC values were the highest. The cases where TC values of a layer at a depth of 20–30 cm were the highest have been highlighted. The most important factors are characteristic of Pb and Mn at a depth of 20 to 30 cm. The highest TC values of this layer were calculated in pine trees growing on military grounds.

Figure 3.9 shows metal concentrations in soil regarding the pine tree 1P (Rukla–Gaižiūnai military grounds), pine tree 3P (Kairiai military ground), and pine tree 4P (Alytus region) in the directions of the prevailing winds (southwesterly and westerly winds, respectively). A decrease in metal concentration was observed in the leeward side of the trunks in relation to the windward side. This tendency is particularly strong for Cr in pine trees 1P and 3P (decrease reached 1.5 times), for Ni in pine tree 3P (up to 1.4 times), for Mn in pine trees 3P and 4P (up to 2.5 times), and for Zn in pine trees 1P and 3P (up to 1.2 times) in the soils of pine trees.

Figure 3.10 shows differences in metal concentrations at a different height of the pine tree trunk. The concentrations of Cr (2P), Cu (1P), Ni (1P, B), Zn (1P and 2P), and Pb (B) were noticed to have gradually decreased from the bottom part of the trunk toward the top of the tree. Cr concentration in the upper part of the tree (two-thirds of the trunk height) was around 3.5, that of Cu around 1.2, that of Ni

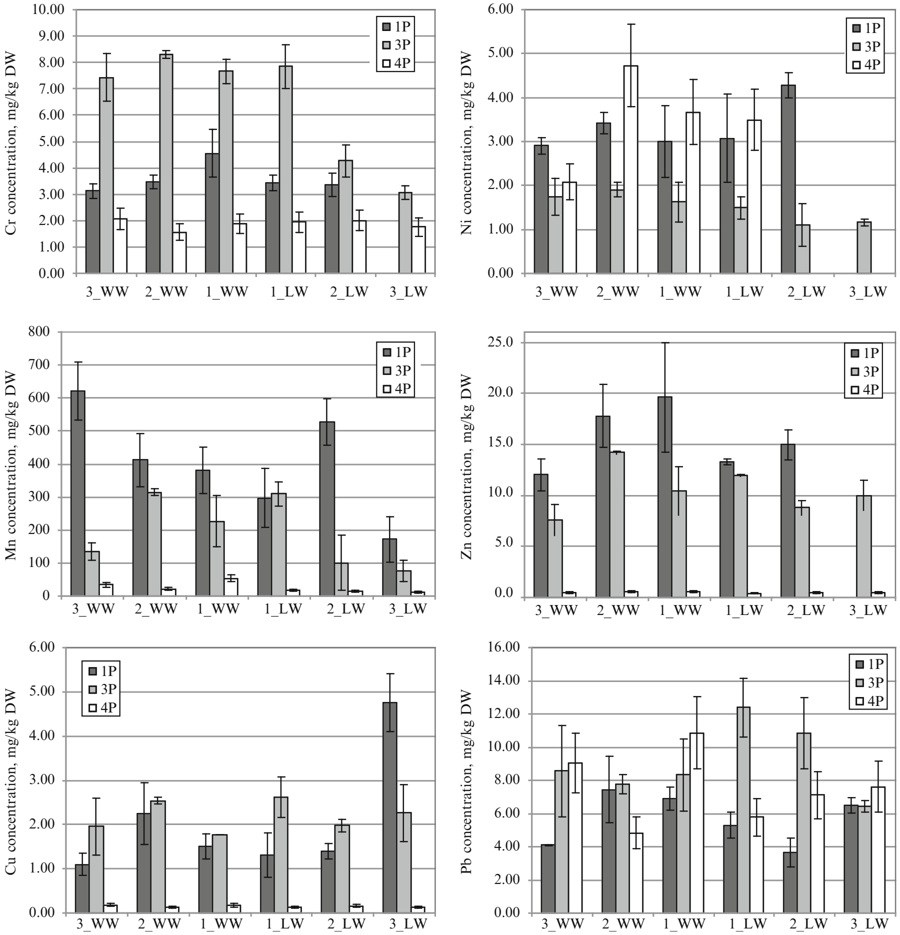

Fig. 3.9 Variations in concentrations of metals in soil under pine tree crown [*WW* windward side of trunk, *LV* leeward side of trunk; 1, 2, 3: distance (m) from trunk]

from 3.4 (1P) to 4.6 (B), that of Zn from 1.7 (2P) to 5 times (1P), whereas that of Pb, in the case of the birch, was 5 times less intensive than the concentration in the lower part of the trunk (at a distance of 1 m from the stump).

A tendency toward an increase in the concentration along the trunk toward the top has been observed in the cases of Cr (3P, 4P), Cu (2P and 3P), Ni (3P, 4P), Zn (3P), Pb (3P and 4P), and Mn (4P, B) and for Cr was from 1.6 (3P) to 8 (4P), for Cu on average 1.4, Ni from 1.9 (3P) to 5 (4P), Zn 4, Pb from 1.3 (3P) to 7 (4P), and Mn from 1.3 (B) to 6.5 (4P) times, respectively.

A comparison of metal distribution along the trunks of the pine and birch trees growing in the same soil reveals that Ni and Pb concentrations, unlike those of the pine tree, decreases toward the top. Mn variations are similar in both trees, i.e., concentrations increase toward the top.

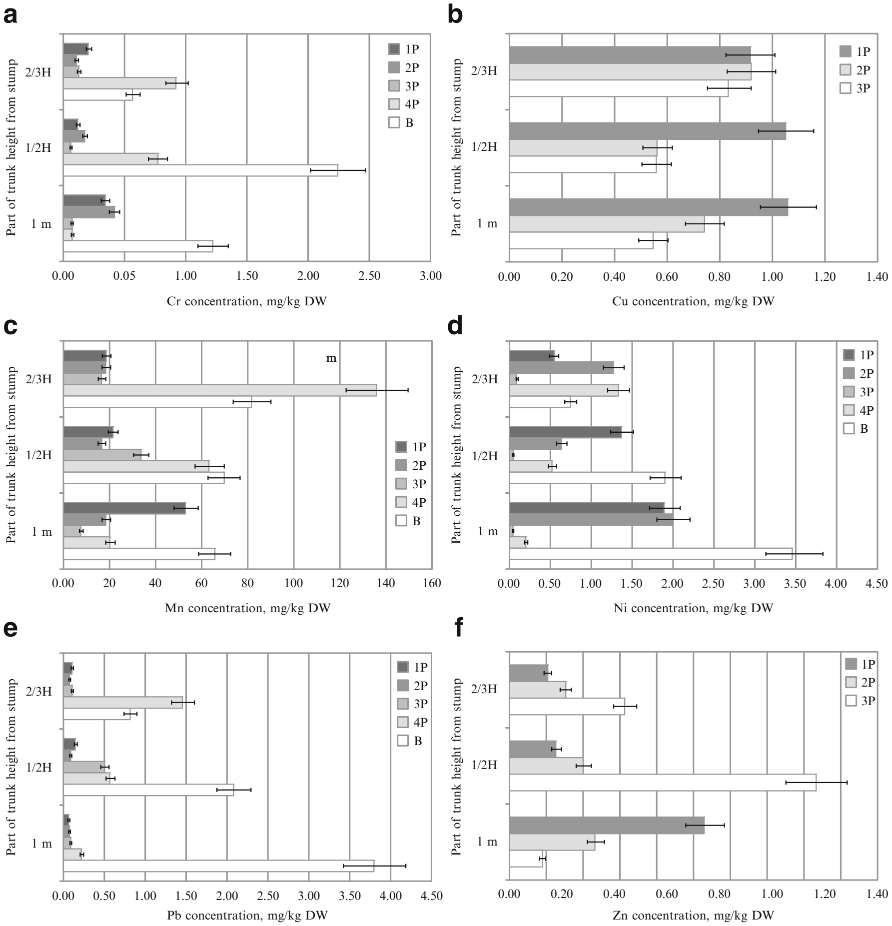

Fig. 3.10 Distribution of metal concentrations at different heights of tree trunk (at a height of 1 m, ½*H* in the middle of the trunk, 2/3*H* at a height of 2/3 of the trunk, *H* trunk length)

Metal concentrations in the annual rings of the investigated trees varied not only among the tree species but also among the trees growing at different sites of the investigation. The established differences could be affected by complex natural processes operating with each other between biotic and abiotic factors and wood properties. The fact that metal concentrations are not high in trees shows that metal transfer is not very active at relatively contaminated sites. Relatively low concentrations of Pb and Cu in wood reflect a slow metal transfer and can be interpreted with reference to metal characteristics: Pb is not an essential element for plants, and Cu transfer to the above-ground parts of a tree is limited by a mechanism by which Cu accumulates in tree roots (Marschner 1995).

A tendency by which the annual rings (in the period 1987–1996), compared to the rest of the period, of pine trees growing on military grounds contained concentrations of Cr, Mn, Pb, and Ni that were two times lower has been observed. For the period from 1986 to 1995, under favorable climatic conditions for tree growth (Stravinskienė 2002), lower metal concentrations were observed, which can be explained by a favorable climatic impact on wood formation and the bioaccumulation of materials as well as by a greater increment that causes a decrease in metal concentration in the tree ring. Higher concentrations of Cr, Mn and Pb (about 4.4; 3.4 and 9.9 times respectively), compared to trees on military grounds, were found in the wood of trees near Alytus and are related to the long-term transfer of these metals from industrial companies situated in the city of Alytus.

Higher concentrations of Mn, Cr, and Pb found in older rather than in younger trees for the same period point to the ability to accumulate higher metal content and perhaps more intense metal radial transfer between adjacent annual rings. Along with time, an increase in Mn on foliage has been established by Kavvadias (Kavvadias and Miller 1999). Mn can be characterized by higher runoff from crown to soil, and therefore the possibility arises of an increase in the concentration in the soil under the crown. On the other hand, Cr, Zn, Ni, and Mn are nutrients important for plants (Schützendübel and Polle 2002), and, along with time, large resources of these metals are accumulated.

Birches are grouped with trees sensitive to air pollution, and the waxy layer that covers their leaves is able to detain twice as much Cu and Zn and about 1.5 times more Ni than the leaves of other trees (Kadūnas 1998). Moreover, the birch has about 1.7–4 times more fine roots that are particularly important for the uptake of nutrients from soil and about 2.2 times more large roots than pine tree (Danusiavichius'ius 1994). These findings support the results indicating an enhanced transfer of metals to birch than to pine trees.

TC helps with a comparison of the rate of uptake by trees of metals from different soil profiles. It was determined that, in the case of Zn, TC values were about three times lower than the background transfer of Zn to trees (when $TC = 1.0–2.0$), and in the case of Pb and Cu, the estimated TC values were only slightly higher than background transfer (Korentejar 1991). None of the cases of the investigated tree exceeded a TC value of 1.0. On the other hand, the concentrations of some metals found in trees make it possible to group them with species accumulating metals rather than with metal-excluding plants. This idea was supported by individual research carried out by Nieminen (2005). Higher TC values of Ni, Cu, and Zn discovered in pine trees growing on military grounds had links to higher concentrations of metals in the environment of habitats. Pine tree 3P was growing close to a shooting range at a distance of 1 m from the bullet area where Zn concentration in soil was 2.8 times higher than average on the site (4.54 mg/kg) (Baltrėnas et al. 2005a, b). Zn is one of the main components of bullets used in military activities in Lithuania (Baltrėnas et al. 2005a, b). Higher TC values of Ni and Cu to pine tree 1P are related to activities of military transport and thus to an increase in metal concentrations in the water body close to the site. On the basis of previously conducted research, Cu concentration in the water body near the habitat of the pine tree exceeded the background concentration of metals in water by

19 times (<5 μg/L), and the allowable concentration of Ni in drinking water surpassed it by 22 times (Baltrėnas et al. 2005a, b). In the past, the water body was obviously extensively used for military training purposes. The emission-transferred metals could access wood through the soil and, on the basis of the geochemical filtration barrier, when, upon precipitation of metals on the crown, part of the metals was transferred from the crown to wood through the bark of trees. The latter proposition about the uptake of metals by wood from air through bark justifies the obtained results showing that Cu concentration (1.75 mg/kg) in the bark of pine tree 1P was found to be 1.3 times higher than average of wood, and Ni concentration exceeded the mean by approximately 2 times (4.56 mg/kg).

The TC values for Mn and Cr were respectively 14 and 10 times higher in the birch than in the pine trees growing in similar conditions. This can be explained by a greater uptake of elements from soil to the birch owing to a larger mass of fine roots (from 1.7 to 4 times). High TC values from a soil depth of 20–30 cm (Table 3.7) can be calculated owing to greater root density (Laitakarai 1927) and, therefore, because of a greater density of fine roots (about 97 %) at a depth of 0–30 cm than at a depth of 30–40 cm (Danusiavichius'ius 1994).

It seems that metal distribution in the soil of pine trees at a depth of 0–40 cm is affected by the direction of winds prevailing at a given site (particularly in the case of single trees). Examination of the obtained findings has revealed a tendency, in the leeward direction from the trunk, for the concentrations of Cr, Ni, Mn, and Zn to be lower than those in the windward direction. This ratio varied on average from 1.2 times in the case of Zn up to 2.5 times in the case of Mn. Such metal distribution could be achieved when metals transferred through air and precipitation, in the direction of the prevailing winds, are suppressed by the pine tree crown from which the metals are washed out by precipitation or, together with leaves, enter soil.

Metal distribution in wood along the trunk height is dependent on the capacity of metal transfer from underground to aboveground and from older to younger tissues. Unequal metal distribution along the trunk height of trees has been observed. Along the trunk and up to the top, in the cases of Cr, Ni, and Zn, a downward trend and, in the cases of Pb, Mn, and Cu, an upward trend have been observed. A decrease in concentrations toward the top can be related to metal distribution in the tree at the end of vegetation when, along with organic matter, metals are transferred to roots, where they accumulate maximum energy deposition for spring when, along with birch sap, an explosive transfer of the matter to young tissues occurs. A specific trend was detected for Mg. In both the birch trunk and pine tree trunk the concentration of Mg grows toward the top. A similar trend can be observed not only in older but also in younger trees as well as in plants growing on slightly polluted sites. Mn is known as an extremely important element in physiological processes and promotes the activity of enzymes, proteins, fats, and photosynthesis. Therefore, higher contents of Mn (even up to 6.5 times) can accumulate in the upper parts of trees in the direction of leaves and needles where more intense processes take place. The concentrations of Pb and Mn in wood were much lower (Fig. 3.7) than those naturally detected in plants (5–10 mg/kg and 5.1–30 mg/kg, respectively).

3.3 Impact of Biotic and Abiotic Factors on Metal Uptake by Trees

The condition of trees and their potential lifetime and development, like with every organism, directly depend on environmental factors affecting it. Subject to the nature of those factors and the degree of functioning, the balance between trees and the environment varies, and the metabolism of materials and energy fluctuates, thus determining changes in the growth of trees. The factors influencing changes usually fall into at least two groups. Subdivision into abiotic and biotic factors is based on the impact of the components of the living and nonliving environment. Subdivision into physiological and ecological factors refers to the classification of internal and external factors, respectively (Lietuvninkas 2012). Insufficient or increased actions of the factors disrupt the physiological processes of trees. Pb, Zn, Cu, Cd, Mg, and K are actively involved in all of the aforementioned processes. For example, K controls the stomatal opening and thus regulates photosynthesis. The opening of stomata depends on the biologically available content of K conditioning faster gas exchange (Noland and Kozlowski 1979). Ambient air pollution damages leaves with particulate matter that absorbs metals and thus slows down photosynthesis (Reich 1987). As for the nitrogen assimilation process, Mo-Fe protein is involved in the conversion of N_2 into ammonia, which is further assimilated in the body of the tree in the form of glutamine and other amino acids. Lack of K, Mg, and Ca decreases the loss of epicuticular wax, which limits transpiration, controls gas exchange, suppresses plant minerals, acts as a barrier to air pollutants, and supports agricultural chemicals in entering leaves, fruits, and stems (Kozlowski and Pallardy 1997). Most enzymes important for respiration participate in trees as organic reaction catalysts and can be active only under the presence of Mg, Mn, Cu, Ca, Zn, and K ions (Markert et al. 2012). Air pollutants can damage the layer of leaf wax and increase the amount of leached materials.

Fodor (2002) described the behavior of metals in plants within a five-stage impact model (Fig. 3.11):

- Stage 1. At this stage, metals entering the rhizosphere of a plant interact with other soil components present in the form of ions. Here, metals may form insoluble compounds with anionic ligands or compete with other cations for the places of joints in the material of the cell wall. Another competition takes place between toxic and essential metals for organic chelate compounds (they can be secreted by the roots of a plant or be artificial). This fight ends in the formation of integrated compounds at a different level of stability. Considering that the cellular wall itself is an effective adsorbent with a significant cation exchange capacity, the inhibition or stimulation of cation uptake is inevitably the first effect of metals and determines significant changes in the metabolism of the plant (for example, stress due to lack of Fe). The dysfunction of oxidation-reduction enzymes is caused by metals or occurs because of electron leakage in the walls of cells, which therefore leads to active oxygen species (AOS).

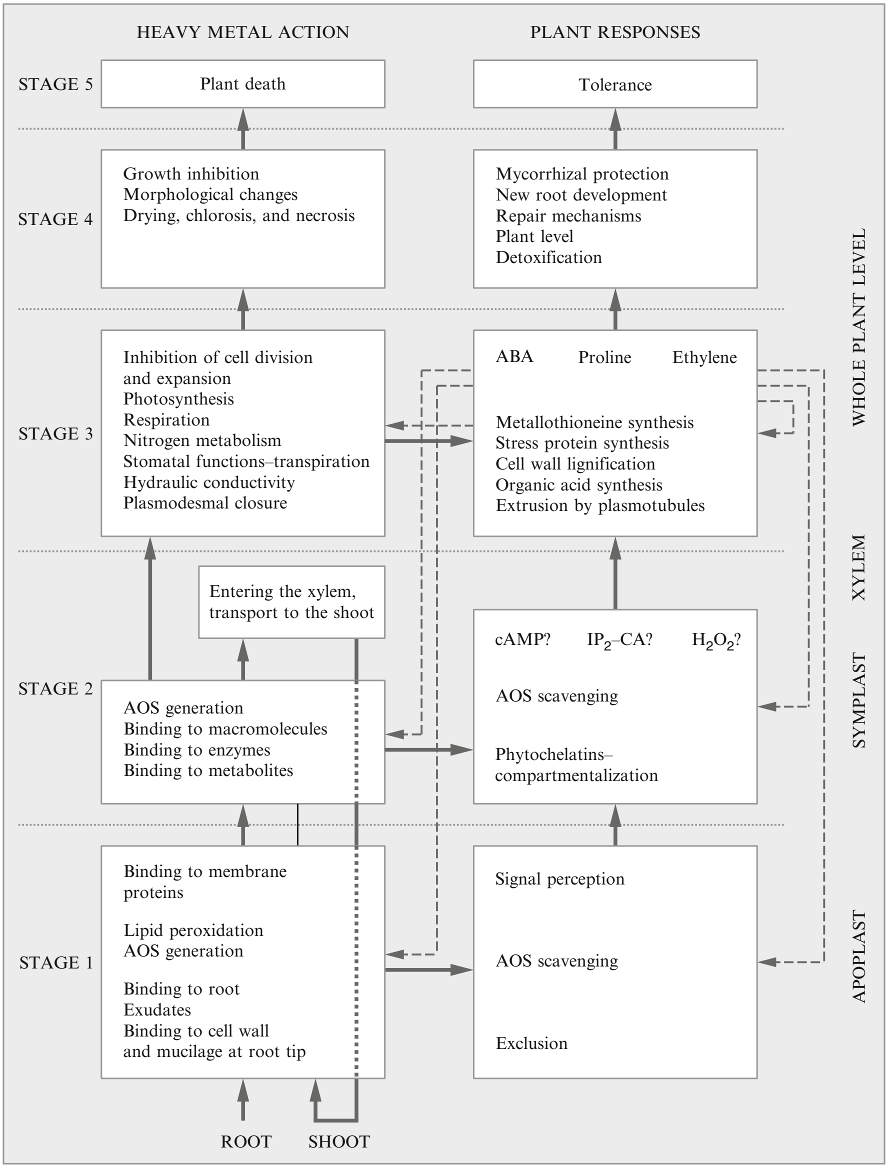

Fig. 3.11 Consistent model of impact of metals on plants (according to Fodor 2002)

Harm caused by Cu, Al, Cd, Zn, and Fe is related to oxidative stress. Moreover, increased Fe concentrations may initiate oxidative harm. Cu, Ni, and Zn, similarly to Al, also cause lipid peroxidation in plasmalemma where active oxygen species (AOS) are involved. These reactions initiate "holes" in the membrane. However, at this stage, the reactions of metals with the proteins of the cell membrane seem to be the most harmful process and inhibit normal processes of transfer through membrane transport or conditions for toxic metals to enter cytoplasm. These events take place in the space of the apoplast (a complex of adjacent cell walls extended along the plant) and therefore have been attributed to the *first* stage of the impact of metals.

- Stage 2 begins when toxic metals reach the symplast where it is bound to proteins, nonenzymatic macromolecules, thus inhibiting a variety of metabolic and regulatory reactions and re-causing oxidative stress. Many questions about how metals reach the vessels of the xylem and then reach leaves through the transpiration stream have not yet been answered. Metals enter apoplasts in the leaf mesophyll again and the *first* and *second* stages of the impact of metals on plants are repeated.
- Stage 3 is the level of vital processes, i.e., transport, metabolism, and homeostasis (the tendency to maintain stability of the inner medium of an organism) negatively affected by metals. It has been found that, owing to the toxicity caused by Al and because of an increase in polysaccharide in plant synthesis, plasmodesmata (narrow tubules operating as intercellular cytoplasmic bridges for transferring relations and materials among the cells of the plant) close. Water entering the plant and its transfer inside it are reduced owing to hydraulic conductivity, pressure in roots, and closing of the stomata, which therefore causes weaker transpiration. This decreases the mineral matter required for the fusion processes of other substances. Nitrogen metabolism drops because of a decline in the reduction of nitrates in leaves. The processes of photosynthesis and respiration are diminished owing to inhibited substance synthesis or the disruption of the photosynthesis mechanism, impeded redox reactions, gas exchange, and oxidative stress-induced damage, and are in addition a result of *inhibited enzymes of glycolysis* and a restriction of the pentose phosphate cycle. Cell division can more or less be negatively affected.
- Visually observed symptoms of the toxic impact of metals on plants can be observed at Stage 4. Leaf chlorosis is one of the first visually observed signs of metabolic stress that makes it possible to make determination about the decrease in the content of chlorophyll and on the relatively increased amount of carotenoids. In acute cases, leaf necrosis occurs owing to the transfer of Fe almost completely inhibited by Cd to shoots and because of the subsequent stress related to a lack of Fe and, finally, because of photoinhibition. Ni toxicity can be expressed in patchy necrosis and in the desiccation in the locations of necrosis. Growth inhibition and morphological changes are conditioned by all the aforementioned negative actions caused by metals.
- All processes lead to the death of a plant, which is Stage 5.

Plants have specific and nonspecific responses to the effects of metals, and these responses become active at different times (Fodor 2002).

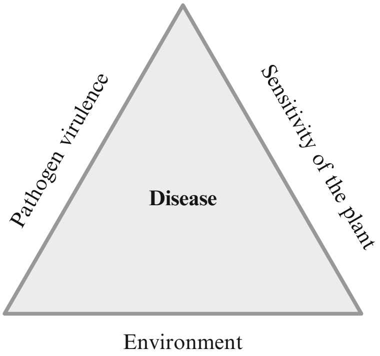

Fig. 3.12 Impact of a disease on a plant depending on pathogen virulence, sensitivity of plant, and environment (according to Poschenrieder et al. 2006)

While one model presents the impact of metals – as an abiotic factor – on plants, the effect of interaction between one abiotic factor (i.e., metal impact) and another abiotic factor (i.e., plant disease) is even more complex.

Trees are constantly affected by biotic factors such as fungi and viruses. To begin the development process in the body of a tree, fungi and viruses have to overcome the protective functions of the tree. The interaction between a tree and a disease can be illustrated by a triangle (Fig. 3.12), where the three sides – pathogen virulence, the sensitivity of the plant, and the environment – are the three major factors affecting the impact of plant disease. The most important environmental factors include local climatic conditions, soil properties, competition with other trees, human activity, and, thus, anthropogenic pollution because of which an even more complex interaction between the pathogen and the tree is expected (Poschenrieder et al. 2006).

A certain concentration of metal in the cells of a plant is necessary for the optimal growth and development of the plant and its pathogens as well as for the protective functions of the plant, and at the same time, for pathogen virulence (Poschenrieder et al. 2006). For example, significant amounts of Zn and Mn are required for larvae eating plant seeds (Morgan et al. 2003); large contents of Fe are important for bacteria that infect organisms (Franza et al. 2005); ATPases that transfer As and Cu are needed for a plant affected by fungal diseases (Cramer and Lawrence 2004); large amounts of protein related to Zn are necessary for rice-destroying fungi to penetrate through plant cuticles; regulating Zn homeostasis is important for the virulence of disease-causing plant bacteria (Tang et al. 2005).

Five types of metal functions protecting plants from biotic factors have been identified:

1. *A sanitary–hygienic effect* manifests itself as the intensive activity of metal ions in soil or on the surface of a plant in the process of eliminating the growth and development of pathogens. For example, copper sulfate was used in the nineteenth century for protecting vineyards against fungal pathogens (Eeva et al. 1998).

2. *The hypothesis of self-protection effect* is based on an assumption that metal accumulation in the tissues of plants can protect against biotic factors. Noret et al. (2005) have concluded that large amounts of Ni, Zn, Cd, and Se in plants helps in protecting plants from fungal diseases and viruses.
3. *The compatibility hypothesis* suggests that metals can save energy-intensive organ-protective functions (Boyd and Martens 1998).
4. *Metal therapy* is based on metals' ability to act as a curative under metabolic disorders. It has also been noticed that hyperaccumulating plants grown in soils with low metal concentration were very sensitive to the impact of biotic factors (Poschenrieder et al. 2006).
5. *The metal-induced amplification hypothesis* is based on data showing that metal ions can produce protective reactions and sometimes cause resistance to pathogens inside conventional plants that are able to accumulate small amounts of metals (Nelson and Citovsky 2005). Metal-triggered reactive oxygen species (ROS) generate protective signals and defensive synthesis of secondary metabolites (Fig. 3.13) (Jonak et al. 2002; Walters et al. 2005).

Metal-induced amplification of the defensive functions of plants is based on the signals and defense mechanisms of metals and biotic factors (Poschenrieder et al. 2006).

When plants receive an environmental impact, they respond to it by resistance and reactions encouraged by that impact. All plants, including those growing in soils with nonbioavailable metals, have special mechanisms for ion homeostasis

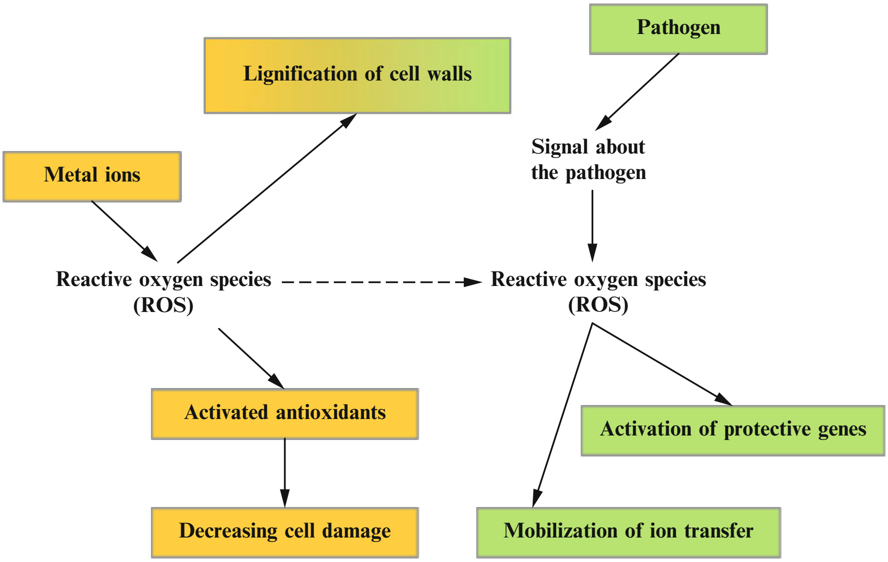

Fig. 3.13 Metal-induced amplification is characteristic of plants having a low degree of metal accumulation (hyperaccumulators) (according to Poschenrieder et al. 2006)

that allow them to deal with a certain limited excess of metal ions (Becher et al. 2004). Metals that are toxic in high concentrations but essential in low concentrations are taken up and distributed in different parts of a plant. To ensure a secure process, the plant releases chelators and specific transmembrane transfers. When the excess of ions affects plants not adapted to this impact, the generation of composite compounds such as phytochelates, metallothioneins, or organic acids increases (Macnair et al. 2000).

A response of plants to an excess of metal ions is similar to reactivated protective reactions caused by pathogens. Signals about the impact of a biotic factor on plants are interrelated with those induced by the impact of metal ions. This mutual interaction is encouraged by certain substances, for example, cytoplasmic Ca^{2+}, ROS, and sulfur-redox production (Glazebrook 2005). Signals about the impact of metal ions and biotic factors in a plant are transferred through the same molecules, and the ability to survive, though under the loss of a high content of glutathione (GSH), seems to be a crucial factor explaining resistance to metals and pathogens (Romero-Puertas et al. 2004).

In what follows, the results and a biogeochemical interpretation on metal content variation in Scots pine (*Pinus sylvestris* L.) affected by a biotic factor (in this case, *Heterobasidion annosum* causing annosum root rot) and an abiotic factor (in this case, the load of metals of aerogenic origin) are presented.

Heterobasidion annosum, which causes annosum root disease and damages pine trees, has been chosen for investigation purposes as a characteristic ecologic (external) biotic factor that has also been used in analyzing the contamination of an anthropogenic source of metals of aerogenic origin. According to Schulze et al. (2005), the first of those is a factor causing stress to a living environment, whereas the second causes stress to a nonliving environment. Both factors can be considered harmful while the first is also classified as having a lethal effect on plants (Kupčinskienė 2011).

Heterobasidion annosum is one of the major fungi severely infecting European, Asian, and North American coniferous forests. The fungus grows in coniferous and mixed forests, mostly in wet, darker fir and pine forests on the roots of coniferous trees, trunk roots, or stumps and sometimes on trunks situated close to the thicker end of the tree. This is a very dangerous fungus that first appears on the live roots of trees and reaches the trunk at a later stage. Damaged trees are killed and fall down (Gricius et al. 1999). Wood losses caused by the fungus in Europe are valued at 800 million EUR each year (Woodward et al. 1998).

Intensive technogenesis increases metal technophilicity (the use of metals in terms of their concentration in the lithosphere), which has a negative impact on forest ecosystems. Evaluation of the impact of biotic and abiotic factors on variations in the concentrations of micro- and macroelements in the soil–pine tree system are discussed.

The habitat of pine trees infected by this biotic factor has been selected as an experimental wooded area (54°53′12″ N, 24°04′33″ S) that earlier was used for agricultural purposes. The loss of agricultural productivity for the period 1959–1963 led to an afforested area. *Pinus sylvestris* L. predominated in the

Fig. 3.14 Pine trees infected by *Heterobasidion annosum*: (**a**) endangered pine crown; (**b**) fruit of pathogenic fungus

territory. Pine trees infected by the biotic factor of *Heterobasidion annosum* were identified by their external appearance. Pine trees negatively infected by the fungus had an extremely poor crown, uneven canopy, a significantly endangered upper part of the canopy (Fig. 3.14a), and yellowish spines; also, the fruits of the fungus were observed on roots (Fig. 3.14b).

The neighborhood close to a former TV factory (55°44′04″ N, 24°23′30″E) in the city of Panevėžys was chosen as the study site of pine trees infected by an abiotic factor. For almost 40 years, the factory produced glass components and color TV tubes. Starting from 1962, the factory was the only industrial unit in the Baltic States (in an area of 9000 m^2). The factory was closed in 2007. The emissions of different substances to the ambient air produced 766 tons of NO_x, 155 tons of carbon monoxide, 46 tons of volatile organic compounds, and about 15 tons of particulate matter a year. Among metals, emissions from that factory typically contained Zn, Pb, Cr, Mn, Co, Sn, Mo, Ni, Ag, As, and V are inherent. With reference to data provided by the Environmental Protection Agency, the factory was a pollution source in 2004. Intensive aerogenic contamination by Pb, Cu, Cd, and Zn made a significant impact on the geosanitary state of the environment (Kadūnas and Radzevičius 2001). The site of the pine trees infected by an abiotic factor was 200 m from the anthropogenic source (company). Southwesterly winds predominate at the site. The control site where *Pinus sylvestris* L. had been present was selected not that far from the habitat of the pine trees infected by the biotic factor.

The sampling procedure was carried out in May, at the beginning of the vegetation period of trees, when physiological processes are at their most active (Hill 2002). To analyze each site, ten similar-age (approximately 30 years) pine trees more than 10 m apart from one another were selected. Wood samples were taken employing a Pressler increment borer (∅ 12 mm) (Baltrėnaitė et al. 2010).

Composite soil samples were taken near each pine tree at a depth of 0–40 cm. Analysis methods such as the preparation of soil and wood samples, the identification of the concentrations of pH and total organic carbon as a form of biologically absorbed metals in soil, and the total concentrations of metal in soil and wood were applied in the work and discussed in detail in articles by Pundytė and coauthors (2011a, b) and Baltrėnaitė and coauthors (2013a, b).

To establish the differences between bioaccumulation and biophilicity, a methodology for calculating dynamic factors was applied, while for assessing the interrelationship between metals, a log-linear correlation was used. A dynamic factor of element bioaccumulation defines the variations in the bioaccumulation of a chemical element under conditions in contaminated compared to background (control) soil. A dynamic factor of element biophilicity reflects changes in the chemical elements involved in the metabolic reactions of the plant. The dynamic factor of element bioavailability expresses variations in the mobile part of the chemical element in soil (thus, a part of the element available for plants). Dynamic factors were calculated with reference to the methodology described in the publication by Baltrėnaitė and coauthors (2012a, b) and discussed more extensively in Chap. 5 of this book.

Metal Concentrations in the Investigated Soils

Metal concentrations in the investigated soils where control pine trees infected by biotic or abiotic factors were growing are presented in Table 3.8.

Data provided in Table 3.8 allow one to observe a trend whereby the total concentrations of metals in the soil of the contaminated site were higher than those in the control site as the coefficients of the concentration of all microelements exceeded 1.0. A particularly striking increase can be observed in cases of Cu and Pb when concentrations in the contaminated site are 2.42 and 6.70 times higher than the background value, respectively. An increase in metal concentrations in soil is determined by the aerogenic emissions of metals from nearby industrial plants.

The concentrations of metals in the soil of the habitats of infected pine trees were lower or varied within the limits of errors compared with concentrations observed in the soil of the control site – all concentration coefficients, without exception, were lower than 1.0. The difference in Mg concentrations between the investigated soils was rather slight, while the concentration of K in soil markedly varied as follows: the soil of the control site > the soil of the contaminated site > the soil of the habitat of the pine tree (Table 3.9).

Table 3.9 shows the concentration of the mobile part of metals compared to the total concentration. Higher concentration values of Mg, K, and Cd in the mobile part under higher pH values are monitored. The mobility of the majority of analyzed metals (except for Cu) is higher in the soil of the contaminated site compared to that of the control site. An increase in the mobile part of the soil of the habitat of the infected pine compared to the control site was also characteristic of all examined metals, except for Cu. In the case of Zn and Cd, which are of high affinity, a tendency for the mobility of Cd to be higher than that of Zn in an acidic

Table 3.8 Total concentrations of metals (mean ± SD) in investigated soils (mg/kg) and concentration coefficients ($K_{k,i}$) (Eq. 2.7)

Site	Parameter	Cd	Cu	K	Mg	Pb	Zn
Soil of control site (pH = 5.3)	Mean ± SD	0.25 ± 0.01	9.58 ± 0.97	1282 ± 486	497 ± 89	3.82 ± 0.63	30.2 ± 18.2
Soil of habitat of infected pine tree (pH = 5.4)	Mean ± SD	0.04 ± 0.02	5.82 ± 0.50	826 ± 271	450 ± 75	3.37 ± 1.65	15.8 ± 5.6
	$K_{k,i}$	0.16	0.61	0.64	0.91	0.88	0.52
Soil of contaminated site (pH = 6.6)	Mean ± SD	0.28 ± 0.04	23.2 ± 3.4	1107 ± 320	498 ± 389	25.6 ± 10.1	36.9 ± 13.6
	$K_{k,i}$	1.12	2.42	0.86	1.00	6.70	1.22

Table 3.9 Concentration of mobile part of metals compared to total concentration (%). Maximum values in the case of each metal are denoted **by italics**

	Cd	Cu	K	Mg	Pb	Zn
Soil of control site (pH = 5.3)	1.60	*0.80*	0.61	0.48	0.20	0.73
Soil of habitat of infected pine tree (pH = 5.4)	2.50	0.02	1.62	0.54	*0.59*	*2.92*
Soil of contaminated site (pH = 6.6)	*3.27*	0.31	*2.21*	*1.70*	0.46	1.39

environment is displayed (Alloway 1995). The exception is the soil of the habitat of an infected pine tree where the mobile part of Zn exceeds the mobile part of Cd by 17 %.

Differences in the Bioavailability of Metals in the Investigated Soils

The index of the investigated bioavailability of metals in the soils of pine tree habitats infected by both abiotic and biotic factors was higher (except from Cu) than that in the control site (Fig. 3.15). This characteristic makes it possible to predict changes (increase) in that part of metal bioavailability in trees that is under the influence of external environmental factors.

Unlike in other studied metals, an increase in the mobile forms of Pb and Zn, compared to controls, is more pronounced in the soil of the habitat of the infected pine tree rather than in the contaminated soil. In the case of K, Mg, and Cd, the trend is the converse, i.e., the biotic factor that infected the pine tree may result in a larger increase in Pb and Zn mobility, while the abiotic factor may result in Mg and Cd in the soil of the pine tree habitat.

Differences in Metal Bioaccumulation in Pinewood Under the Impact of Different Factors

A dynamic factor of metal bioaccumulation in pine trees presented in Fig. 3.16 highlights a few main tendencies. Mg and K bioaccumulation increased in the infected pine trees and those growing in the contaminated site compared to the control pine tree. A rise in the bioaccumulation of Zn and Cu was observed in the infected pine trees, whereas a decrease was observed in those of the contaminated site. As regards Pb, this tendency was the converse. Cd bioaccumulation increased in the infected pine trees while it changed slightly in the contaminated site compared to the control.

K was the element that mostly increased in the infected pine tree wood (about 4.5 times more than in control pine trees) while Pb was prevalent in the pine trees of

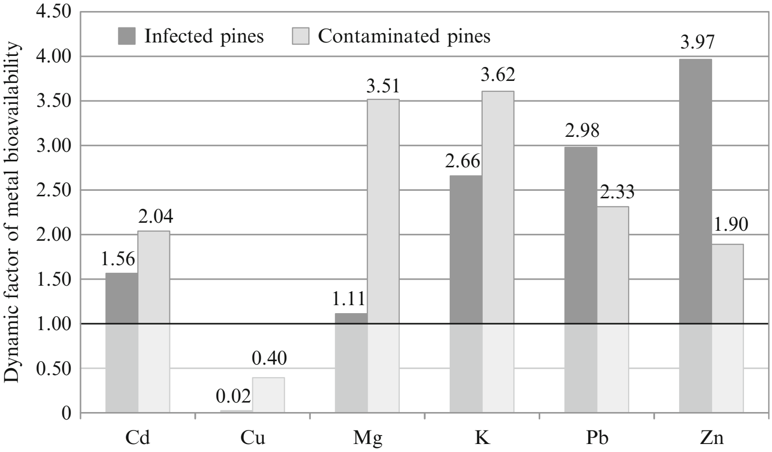

Fig. 3.15 Dynamic factor of metal bioavailability in soils of pine tree habitats

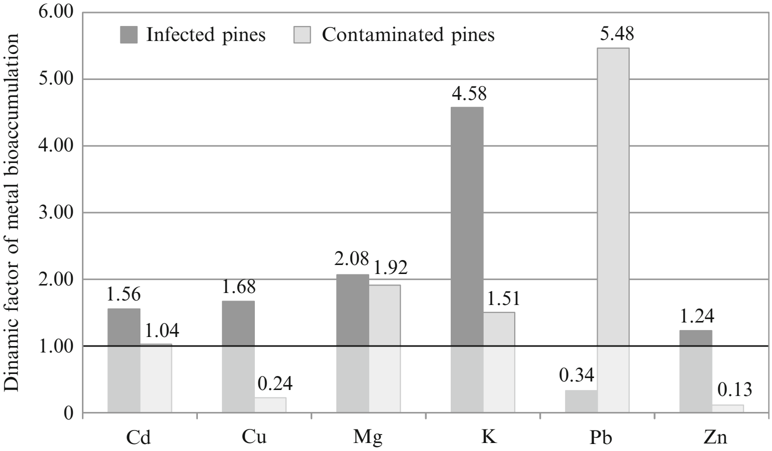

Fig. 3.16 Dynamic factor of metal bioaccumulation in pine trees

the contaminated site (about 4.5 times more than in the control site). Mg bioaccumulation, in the case of both factors, remained similar, though about 2 times higher than in control pines.

Differences in Metal Biophilicity

The dynamic factor of metal biophilicity, unlike that of bioaccumulation, expresses metal variations in wood compared to metal concentrations in soil. This makes it possible to assess variations in metal transfer to trees in a wider biogeochemical

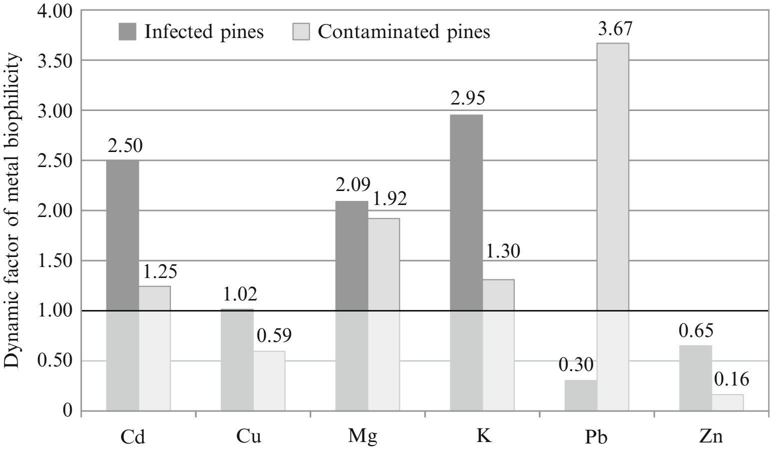

Fig. 3.17 Factor of dynamic metal biophilicity in pine trees

context. In the case of our research, the dynamic biophilicity factor indicated that the transfer of all investigated metals in the infected pine trees and those growing in the contaminated site had become more intensive; however, the most significant trends suggest that Pb biophilicity mainly occurred in the pine trees growing in the contaminated site while K was prevalent in the infected sites (Fig. 3.17).

It can be asserted that biotic factors contribute to a more intensive biophilicity and bioaccumulation of macroelements while pollution promotes a similar biophilicity and bioaccumulation of typical microelements of contamination in pine trees.

Variations in Equilibrium of the Soil–Pine Tree System

Figures 3.18, 3.19, and 3.20 show the interrelationship between metals in different forms or media among the studied sites. It can be proposed that metal concentrations (mobile and total concentration in soil and wood) in the log-scale are arranged in the form of a straight linear dependence, and only relevant factors may determine deviations from linear dependence.

Concentrations have been found to retain a quite noticeable log-linear dependence among the investigated parameters in the mobile form of metals ($R^2 > 0.9$) in terms of the impacts of studied factors, i.e., metal concentration in the mobile form of metals is only marginally infected by abiotic and biotic factors. A slightly different trend is observed in the cases of total metal concentration in soil and wood. As for total metal concentration in soil, Cu “reduces” the evenness of the log-linear dependence, whereas Pb acts in a similar way as regards total metal concentration in wood. These apparent differences are highlighted in the infected site and are likely to express the nature of contamination.

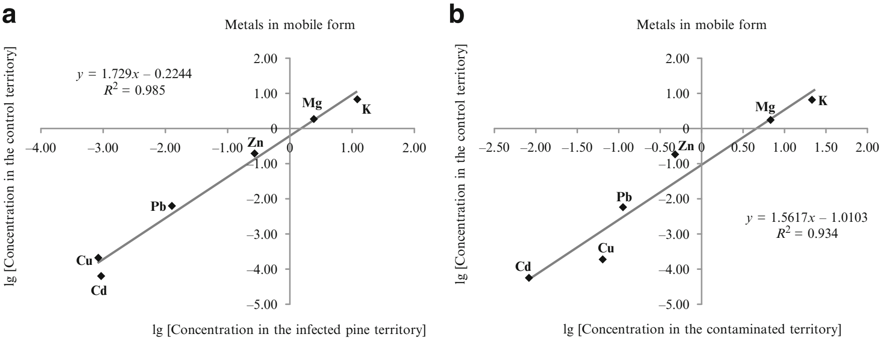

Fig. 3.18 Interrelationship (using log scale) between metals in mobile form in soil at (**a**) control site and infected site; (**b**) control site and contaminated site

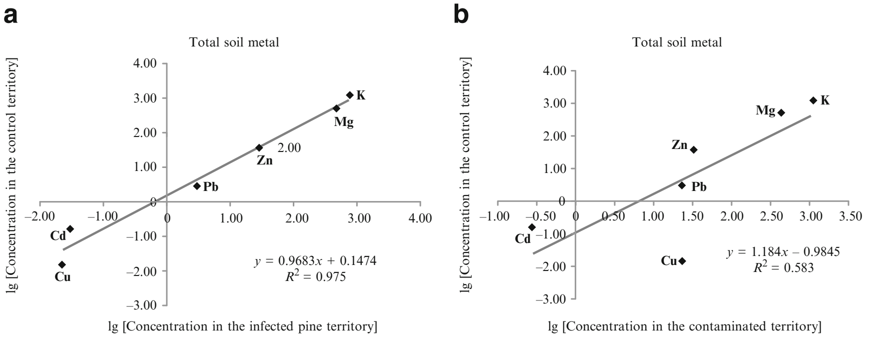

Fig. 3.19 Interrelationship (using log scale) between total soil metals at (**a**) control site and infected site; (**b**) control site and contaminated site

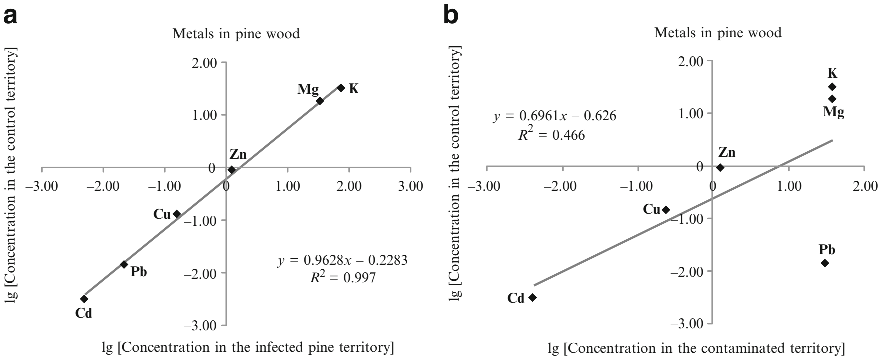

Fig. 3.20 Interrelationship (using log scale) between total concentration of metals in wood at (**a**) control site and infected site; (**b**) control site and contaminated site

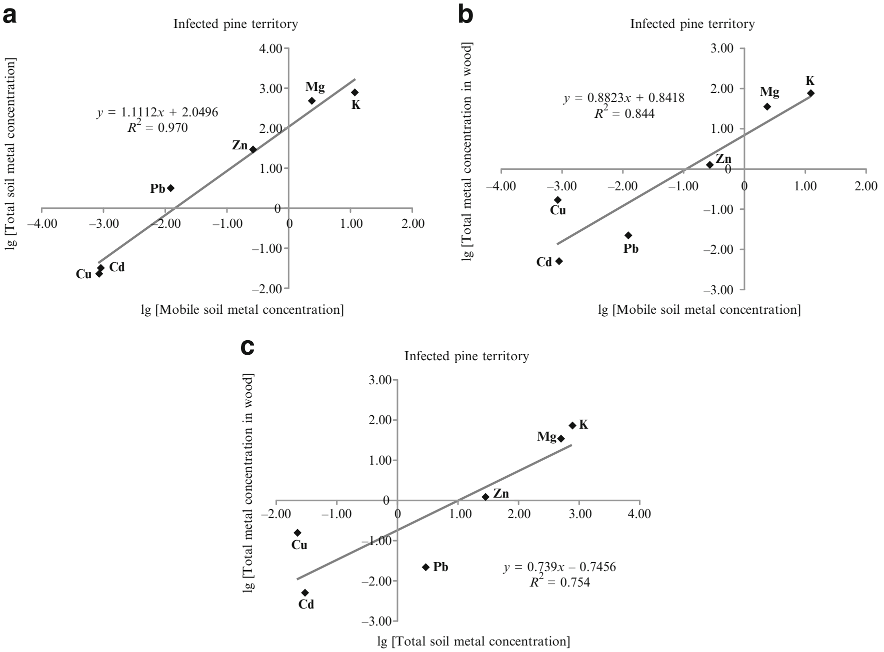

Fig. 3.21 Interrelationship (using log scale) between metal concentrations in different media (**a** total soil metal concentration and mobile metal concentration in soil; **b** total concentration of metals in wood and mobile soil metal concentration; **c** total metal concentration in wood and total soil metal concentration) at infected site

Cu and Pb concentrations in the contaminated site are 2.4 and 6.7 times respectively higher than those in the control site. Although the source (enterprise) of the emission of both metals and the method (aerogenic) of transfer are similar, they have a different impact on the log-linear dependence in different media. It seems that this influence can be determined by the level of contamination, i.e., in terms of the control site, Pb exceeds the allowable limits of concentration by three times. The log-linear dependence in the site infected by the biotic factor remains fairly uniform.

Figures 3.21, 3.22, and 3.23 show the dependence of the correlation of the concentrations of the investigated forms of metals in separate elements of the soil–pine tree system on different factors (biotic and abiotic) infecting pine trees. All situations displayed in the figures are similar in the emergence of a log-linear relationship between mobile and total concentrations of metals, mobile concentrations in soil, and concentrations in wood, as well as total concentrations in soil and concentrations in wood on the sides of the control, infected, and contaminated sites. In these cases, the values of the regression coefficient (R^2) varied within the limits of 0.66–0.99.

The strongest positive correlation, in all cases of the involved factors, occurred between mobile and total concentrations in soil. This tendency, in all cases, was

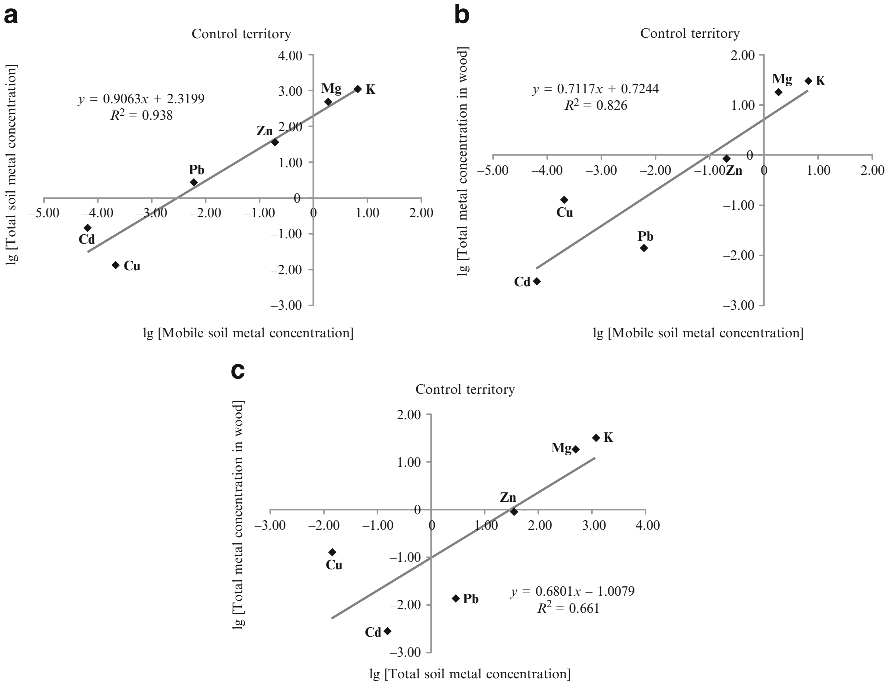

Fig. 3.22 Interrelationship (using log scale) between metal concentrations in different media (**a** total soil metal concentration and mobile metal concentration in soil; **b** total concentration of metals in wood and mobile soil metal concentration; **c** total metal concentration in wood and total soil metal concentration) at control site

confirmed by a regression coefficient that was higher than 0.90. A slightly weaker correlation is that between the concentration of mobile metal concentrations in soil and wood. An even weaker correlation between total metal concentrations can be observed in soil and wood. The strength of the correlation signal is weakened by metals such as Pb and Cu, particularly in the case of the abiotic factor. The weakest positive correlation was established between the concentration of mobile metals in soil and concentration in wood. In that case, it can be observed that the abiotic factor (in our case, based on a higher contamination level of Pb and Cu) may have a greater influence on the relationship of the log-linear dependence between a mobile form of metals in soil and their concentration in wood. A more stable correlation is appropriate considering the effect of the biotic factor and the control site.

Interconnection among metal concentrations expressed in the form of a log-linear dependence points out an important fact that, in the absence of an additional metal load, the investigated metal concentrations expressed in the log form are exactly arranged in a straight line. Under an additional metal load, as observed in the contaminated site, the log-linear dependence breaks down and maximum deviations from the log-straight line are characteristic of newly entered metals. Thus, the major changes in metal concentrations take place in pinewood,

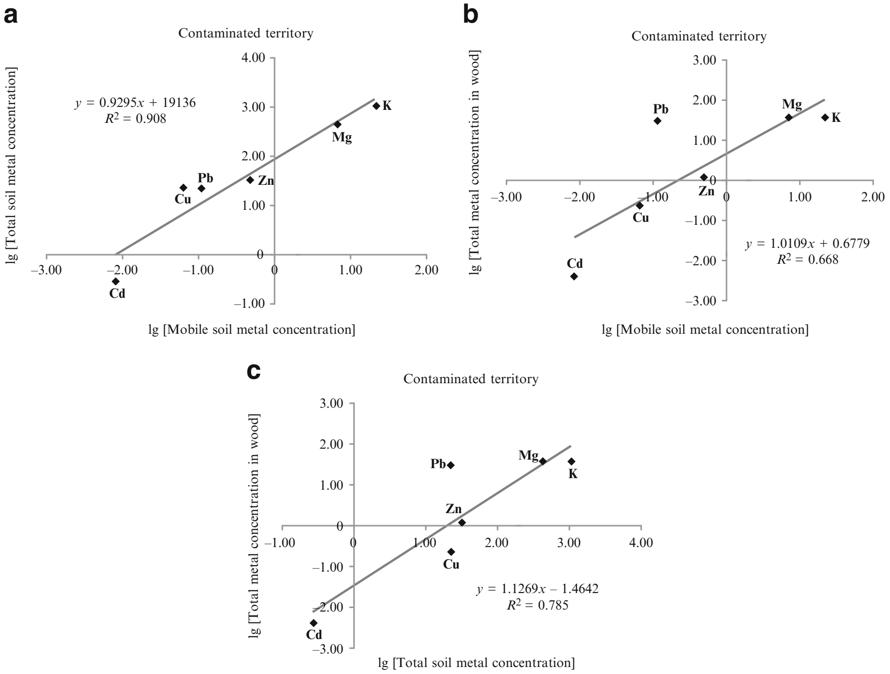

Fig. 3.23 Interrelationship (using log scale) between metal concentrations in different media (**a** total soil metal concentration and mobile metal concentration in soil; **b** total concentration of metals in wood and mobile soil metal concentration; **c** total metal concentration in wood and total soil metal concentration) at contaminated site

less noticeable are the changes in the total metal concentrations in soil, and the smallest changes are those in the concentrations of mobile metals in soil. From a practical point of view, this correlation makes it possible to assess the new elements entering the soil–pine tree system, an anthropogenic source contaminated with metals, or even the nature of contamination. Under the natural state or the impact of an external but natural—biotic—factor, the log-linear dependence among the investigated metals remains extremely strong, particularly between total and mobile metal concentrations in soil, as well as between mobile metals in soil and the concentration in wood.

Both biotic and abiotic factors promote the activation of the protective functions of trees. These are related to chemical protection devices.

A further analysis of the factors affecting the soil–pine tree system has revealed that biotic and abiotic factors determine not only changes in pine trees themselves but also in their habitat soils; however, anthropogenic contamination (abiotic factor) has a stronger influence on an increase in the total microelement concentration, while the biotic factor more strongly influence the growth in the total macroelement concentration. The functioning of the abiotic factor (chemical contamination) has been found to promote an increase in microelement concentration, particularly typomorphic chalcophiles (Pb, Cu) in soil, whereas the biotic factor promotes a rise in the concentration of macroelement lithophile K that is actively involved in suppressing infections caused by the pathogen in pinewood. In parallel, a decrease in the concentration of the biophilic element Zn takes place in the soil of the pine tree habitat in terms of the control soil. A slight variation in the concentration of such a litophilic element as Mg in soil, in terms of the control, has been observed.

The major developments in variations in metal concentrations observed in the contaminated site were as follows:

- Higher concentrations of toxic elements Pb and Cd in the soil of the contaminated rather than in the control site, where the presence of Pb is particularly striking;
- Much higher values of the bioaccumulation and biophilicity of K, Mg, and Cd make it possible to systematically discuss the disorders of pine *photosynthesis*. Cu and Zn are known as essential elements of plants and play a crucial role in inducing reactions of *photosynthesis*. Thus, in our case, a decrease in the bioaccumulation of these elements can characterize a malfunction of photosynthesis (Ayeni et al. 2010).

Owing to an increase in the concentrations of toxic elements Pb and Cd in the environment, a few reasons can cause the malfunction of tree photosynthesis. On the one hand, increased metal concentrations cause an imbalance in carbon dioxide fixation and thus negatively affect gas exchange sites in the membranes of plant tissues. Because of the low rate of photosynthesis translocation, a disruption of starch synthesis occurs (Ericson 1979), and therefore a decrease in the total growth of the tree can be observed. Moreover, contamination with metals causes tree decay processes because of a reduction in the content of chlorophyll, deoxyribonucleic acid (DNA), ribonucleic acid (RNA), and protein weight loss that are together related to a reduction in photosynthesis (Jana and Choudhuri 1982). Metal toxicity is evidenced by their sulfhydryl groups included in proteins and forming compounds, thereby disrupting the activity of proteins, destroying their structure, or causing a deficit in essential elements in proteins (Van Assche 1990). Pant and coauthors (2011) found that growth in the concentrations of Pb, Cd, and As significantly increased the content of *proline*, C_4H_8NCOOH, and ascorbic acid.

Amino acids are known to play a crucial role in the initial metabolism of plants. They are primary products of photosynthesis and nitrogen assimilation processes and therefore represent the most important bond between nitrogen and carbon metabolism. Environmental factors have direct implications for the biosynthesis of amino acids. Thus, they greatly influence the volatility of the accumulation of free amino acids (Durzan and Steward 1983). The facts confirm that increased concentrations of Pb, Cu, and Cd disrupt metabolic processes in trees and activities of enzymes responsible for the biosynthesis of chlorophyll, which is one of the mechanisms (in addition to carbon fixation, stomatal conductance, electron transport, and the enzyme of the Calvin cycle) involved in the process of photosynthesis

(Prasad and Strzałka 2000). Moreover, such a concentration of Cd has no impact on producing the biomass of a plant and decreases the concentration of Mg, Cu, and chlorophyll (Salt et al. 1995).

Changes in metal concentrations also take place in pine trees and the soil of their habitats infected by a pathogenic fungus. Metal concentrations in the soil of the habitats of infected pine trees were lower than those in the control soil; in some cases, the difference was rather substantial. For example, if a slight decrease only in Pb and Mg was observed, Zn, K, and Cu concentrations in the soil of the infected pine trees were 1.5–2 times and Cd concentration 6 times lower than that in the control soil. This makes it possible to draw the conclusion that metal concentrations in soil vary by habitat of infected pine trees owing to changes in metal forms and considering the uptake of metals by pine trees. For example, the mobile part of all investigated metals (except for Cu) in soil has increased compared to the soil of the control site. The effect may be due to the fact that a pathogenic fungus in soil will increase plant availability for metals, thereby extracting carboxyl and amino acids that chelate, first of all, transitional metals related primarily to proteins (Gramss 2010). Our research shows this to be very evident in the cases of Cu and Zn.

Changes also occur in pinewood infected by a pathogenic fungus, which determines variations in metal concentrations. The pathogen, upon entering the wood, is supposed to affect the wood constituent lignin, whose destruction is important because the pathogen could reach the cellulose of cell walls as the latter material is a very important source of energy. The stress caused by the signals of the aforementioned processes triggers the protective properties of wood. Lignin is one of the most common organic polymers in plants and is supposed to be responsible for the protection of coniferous trees against pathogens (Vance et al. 1980). It can be grouped with quantitatively important secondary wood compounds that reduce the decomposition of tree nutrients vitally necessary for pathogens in infected trees.

Numerous phenolic compounds can be found in rich lignin (woody) tissues, for example, ferulic acid or hydroxycinnamic acid involved in forming compounds with cellulose and hemicellulose (Hartley and Ford 1989). Peroxidase is a key enzyme that, upon using phenolic precursors, leads to lignin biosynthesis and acts as one of the proteins whose production is stimulated by infection or slashes (Asiegbu et al. 1994). As a result of intense lignification in the damaged location, an increase in the bioaccumulation of micro- and macroelements is expected. This phenomenon was also observed in our research. Apart from Pb, the bioaccumulation of all other investigated metals (Mg, K, Zn, Cu, and Cd) has increased compared to control pine trees. This can be explained by the role of these metals in the processes of lignification and the fight with the infection. Cu is a constituent part of the enzyme phenol oxidase, which is involved in the production of lignin, i.e., lignification processes (Turvey et al. 1992). Most enzymes are active only under a sufficient concentration of Mg^{2+}, K^{+}, Mn^{2+}, and Ca^{2+} ions.

Cu, Zn, and Fe are known as coenzymes of ferment systems, are included in the composition of enzymes, or make up the so-called prosthetic group. Zn is a cofactor of polymerase and influences the synthesis of enzymes. Under a shortage of Zn, protein synthesis is disrupted, and acids and amides accumulate (Faust 1989). Mg^{2+} (together with Ca^{2+}, Sr^{2+}, Ba^{2+}, NH_4^+) has been found to affect the contents of peroxidase in the walls of cells and is thus involved in monitoring the accumulation of lignin on the walls of cells (Lipetz and Garro 1965). A noticeable increase in K^+ and Mg^{2+} ions in infected wood was established by Johansson and Theander (1974), who explained it as a process inhibiting infectious agents. In our case, K^+ bioaccumulation was the greatest, and the bioaccumulation coefficient was the highest (4.58), compared to other investigated metals. The K^+ biophilicity index (2.95) was the most significant of all the metals studied. The adjustment of Zn homeostasis is important for the virulence of bacteria that cause plant diseases (Tang et al. 2005). Finger-Teixeira and coauthors (2010) explain the impact of Cd in lignification processes by the fact that this metal induces the production of lignin-forming monolignols.

The assessment of variations in the biophilicity and bioaccumulation of the investigated metals points to a clear tendency: biotic factors stimulate more intensive biophilicity and bioaccumulation of macroelements, and contamination is more characteristic of the biophilicity and bioaccumulation of microelements in pine trees. The concentrations of metals (K, Mg, Zn, Pb, Cd, and Cu) organically take a log-linear dependence in the components (wood, soil) of the soil–pine tree system: $R^2 > 0.90$ indicates a *strong* linear dependence between the total and mobile part concentrations of metals in soil, $R^2 > 0.80$ denotes a *sufficiently strong* dependence between the concentrations of the mobile part of metals and concentrations in wood, and $R^2 > 0.60$ indicates such a dependence between total metal concentrations in soil and wood. An external abiotic factor (anthropogenic metals of aerogenic origin) significantly changes the steadiness of the balance of metal concentrations in the soil–pine tree system. The balance between metal concentrations in wood and the concentration of mobile metals in soil is greatly affected, whereas the balance between the total concentrations of metals and the concentrations of the mobile part in soil is only slightly affected, which means that anthropogenic metals of aerogenic origin that enter the system as an additional load supplement the system with the content of metals in quantitative terms and determine variations in the natural balance in qualitative terms. An increase in environmental pollution, as an abiotic factor, leads to higher concentrations, whereas the pathogenic fungus *Heterobasidion annosum* as a biotic factor leads to lower total concentrations of metals in the soil of pine habitats compared to the control site.

Metal concentrations in trees older than 30 years, even in zones of potential pollution, do not exceed phytotoxic and excessive concentrations established in literature sources. The conducted research revealed that, in a temperate climate, the most common conifer *Pinus sylvestris* L. and deciduous *Betula pendula Roth* can be employed as bioindicators in a metal-contaminated environment where lower metal concentrations agree with climatic conditions favorable to tree augmentation and coincide with a decrease in environmental pollution, and vice versa. Higher values of the transfer coefficient from soil to wood in potentially contaminated sites have been characteristic of Ni, Cu, Zn, and Mn (up to 0.45–0.75), while the lowest values are those of Pb and Cr (approximately 0.1). The prevailing direction of winds in a particular area has an impact on the distribution of metals in the soil of pine habitats to a depth of 0–40 cm: a Mn concentration lower, by even 2.5 times, has been discovered in soil at the leeward rather than windward side toward the trunk.

Chapter 4
Biogeochemical and Functional Traits of a Tree in Metal-Contaminated Territory

Long-term biogeochemical processes occurring in nature are usually judged by their outcome, i.e., the products received in the course of certain biogeochemical reactions. Quality assurance of their result depends on mastering methodological and analytical methods. To this end, the chapter starts with an introduction of the methods used for determining metal content in wood. The exact determination of metal concentrations in the components of the soil–tree system forms the basis for identifying the level of contamination in a wood environment and a valid response of the tree to interpreting pollution. Using the method for the functional traits of trees, effective answers to the following (and other) questions can be found: *What is the content of metals accumulated in the biomass of wood? Which morphological part of the tree has the highest content of metals? How does the technological modification of soil change the capacity of the tree?*.

4.1 Methodological Aspects of Metal Content Determination in a Tree

Investigation into metal concentrations in separate rings emphasizes the importance of reducing the possibility of random errors related to sampling. Thus, the most accurate sampling methodology must be chosen.

The literature provides much information about wood sampling for identifying the physical properties of wood (wood moisture, annual ring thickness) to determine dendrochronological and dendroindicational research; however, a lack of extensive examination on the methods for taking samples of tree rings to determine metal concentrations in each ring can be observed.

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A comparison of the measurement accuracy of metal concentrations in the annual rings of pine trees was performed using the following tree-ring-sampling methods (Baltrėnaitė et al. 2010):

- Sampling using a plane,
- Splitting off using common chisels,
- Splitting off using arched chisels,
- Drilling with an increment borer.

The investigated single pine tree (30 m high, 0.4 m thick, 55 years old) was located in southern Lithuania, 10 km from the town of Alytus, Lithuania (E024°02′56.9″ N54°18′33.7″), which is widely known to have had an intense industry when Lithuania was part of the Soviet Union (1940–1991). According to geochemical investigations carried out in 1998–1999, the soils are known to contain dangerously high metal contamination derived from nearby refrigerator and textile factories (Kadūnas et al. 1999). The anthropogenic load to topsoil consists mainly of metals such as Zn, Pb, Cu, Cd, Ni, Cr, Hg, Ag, Sn, and Mo (Kadūnas et al. 1999). Soil in the investigated area is sandy loam with a mean pH of 5.5. The terrain is hilly with an inclination of 3–5°. Forest litter thickness varies from 4 to 5 cm; the mean annual temperature is around 6.0 °C. Southwesterly wind with a speed of 4.2 m/s prevails in the region. The mean annual precipitation is 619 mm. Pines prevail in the Alytus region and cover 70–80 % of the investigated forest area. A single pine tree was randomly selected from a group of pines growing in the vicinity of the exposed industrial zone. Permission was granted to fell but was restricted to one tree. This was sampled at the beginning of the vegetation period in late April.

Sampling Using Common Chisels

During separation of the annual rings using common chisels (Fig. 4.1(1)), the wood roll is split off in the tangential direction according to the boundaries of the rings (Fig. 4.2).

Sampling Using Arched Chisels

In terms of splitting off annual rings, arched chisels for (Fig. 4.1(2–4)) are similar to common chisels, except for their different forges. Thus, they are more easily applied to the boundaries of the circles of concentric rings (Fig. 4.2). Arched chisels are developed to separate tree rings of wooden plants 10–80 years old. A flat chisel is used to remove bark and separate rings from rolls larger than 500 mm in diameter. To reduce the risk of higher random errors, the height of a roll cannot exceed 5 cm. Chisel blades were extended by welding plates onto their surface produced from particularly hard steel that is resistant to long-term use and deformation. The

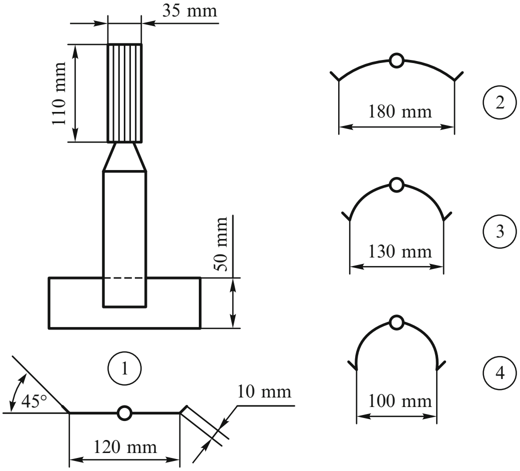

Fig. 4.1 Equipment for sampling annual rings of wood: (*1*) common chisel, (*2–4*) arched chisels having a different bend radii

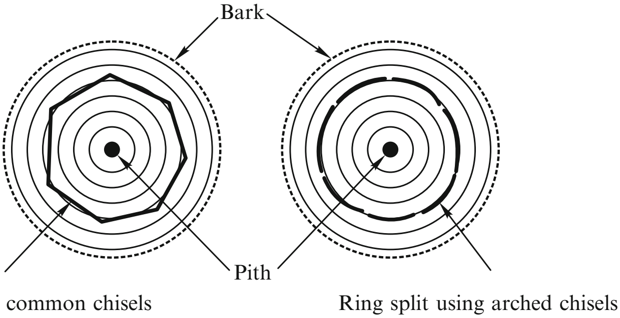

Fig. 4.2 Scheme for splitting off annual rings using common and arched chisels

leaning angle of the blade was 25° and the height of the sharpened blade was 10 mm. A number of differently arched chisels were produced to fit the ring curvature and reduce the risk of sampling error during the ring separation procedure. Chisel blades were extended with 10 mm of length-limiting extensions, perpendicular to the blade, which do not allow rings to deviate and produces ring samples of a more accurate shape. Later rings should be sampled with chisels of larger diameter and smaller arch, and rings close to the pith should be separated using chisels of a smaller diame-ter and higher arch.

Sampling Using a Plane

Separate ring samples were formed out of chips after planing away separate rings. The mass of one-specimen samples using common and arched chisels and a plane was in the range of 200–300 g.

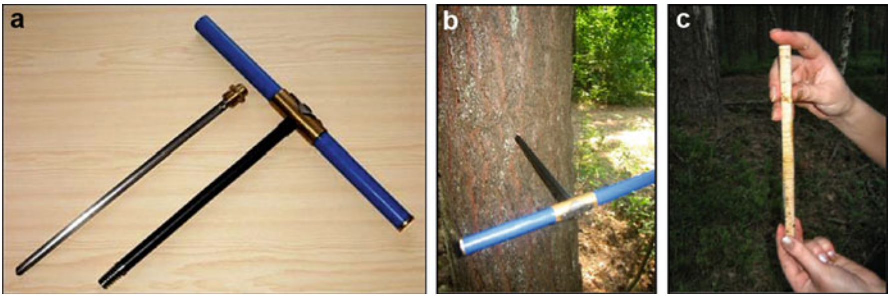

Fig. 4.3 An increment borer and a sampling procedure for tree rings: (**a**) increment borer 300 m long and 300 m in diameter, (**b**) a borer bored into a tree, (**c**) wood sample sampled using increment borer (Baltrėnaitė et al. 2010)

Sampling with an Increment Borer (Lithuanian Patent 5325)

The borer was used to obtain a cylindrical wood bore made of a number of tree rings (Fig. 4.3) from which separate rings were split off by applying a thin saw blade about 0.5 mm thick and cutting through the middle of the ring tag, which was thoroughly granulated. The mass of a similar ring sample was about 0.10 g. To make a single sample of an annual tree ring, three drilling sessions were required. The drilling process took place at the same height above the stump. Annual rings were split off from several drilled wood samples, and the tree ring samples of the same year were mixed, producing a composite sample.

For further investigation, 32 specimens of wood rings were formed (8 for each sampling method). In addition, nine wood specimens were prepared (three with masses of 0.10, 0.15, and 0.20 g) to compare metal concentrations in wood samples of different masses.

After dissection the wood samples were ground with a Retsch grinding machine RM 200 to 3–5 mm particles and prepared for metal analysis by digestion. Wood samples 0.5 g each were taken and mixed with 8 mL HNO_3 (65 %) and 2 mL H_2O_2 (30 %). Then they were poured into specific vessels and put into a Milestone ETHOS microwave digester to be digested for 31 min. The solutions were poured into 50 mL flasks and diluted with deionized water to a mark of 50 mL. A parallel procedure was used for the five blanks. The total concentration of metals was determined by flame atomic absorption spectrophotometry (FAAS). When they were below detection limits, a graphite furnace atomic absorption spectrophotometer (GFAAS) was employed. Detection limits of Mn, Ni, Zn, Pb, Cu, and Cr were 2.0, 90, 0.5, 10, 1.0, and 3.0 (μg/L) by FAAS and 0.01, 0.1, 0.001, 0.05, 0.02, and 0.01 (μg/L) for GFAAS (Baltrėnaitė et al. 2010).

A one-way analysis of variance was performed so as to simultaneously compare the mean values of metal concentrations obtained employing all four methods. To apply a certain method of analysis, a significance level of $p = 0.05$ was chosen. The values of the calculated and critical criterion F are presented in Fig. 4.4, whereas

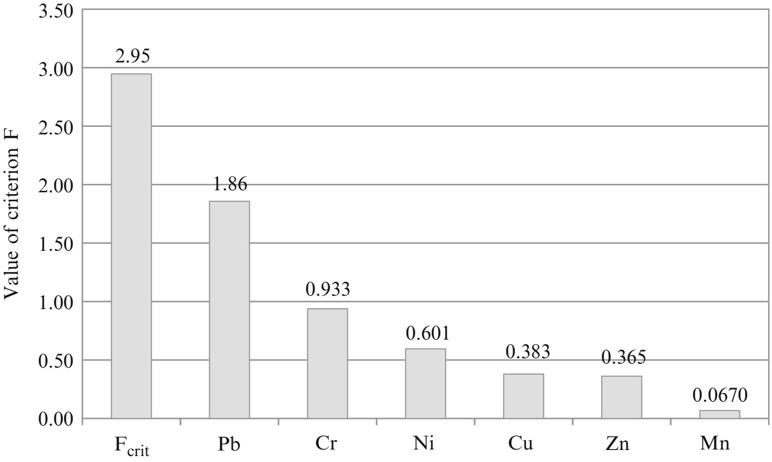

Fig. 4.4 Values of criterion *F* comparing metal concentrations applying four methods (common chisels, planing, arched chisels, and an increment borer) in wood samples

Table 4.1 Mean concentrations of metals in wood rings applying separate sampling methods and mean concentration (mg/kg DW)

Metal	Common chisels ($n = 8$)	Planing ($n = 8$)	Arched chisels ($n = 8$)	Increment borer ($n = 8$)	Mean concentration
Cr	0.220 ± 0.103	0.156 ± 0.057	0.134 ± 0.033	0.268 ± 0.032	0.195 ± 0.031
Cu	0.591 ± 0.306	0.419 ± 0.118	0.508 ± 0.097	0.346 ± 0.034	0.466 ± 0.053
Mn	23.6 ± 7.7	23.6 ± 10.9	26.87 ± 6.89	27.0 ± 1.1	25.3 ± 0.9
Ni	0.495 ± 0.277	0.285 ± 0.089	0.246 ± 0.045	0.272 ± 0.032	0.324 ± 0.057
Pb	1.32 ± 0.42	0.588 ± 0.272	0.911 ± 0.457	0.231 ± 0.039	0.761 ± 0.231
Zn	6.79 ± 2.09	8.45 ± 5.41	11.5 ± 3.2	7.96 ± 1.05	8.68 ± 1.01

the mean metal concentrations obtained from the samples of wood rings using different methods and the mean metal concentrations established employing all methods are shown in Table 4.1 (Baltrėnaitė et al. 2010).

The results of the variation analysis showed that the difference in the mean metal values determined in wood sampling methods is not statistically significant because in all cases of metals, the calculated F values were lower than $F_{\text{critical}} = 2.95$ (Fig. 4.4). Thus, it can be concluded that to define metal concentrations in wood rings, *all the aforementioned methods can be used.*

On the other hand, the mean squared deviation of metal concentrations in wood samples taken with the help of the increment borer was the smallest compared to other investigated methods (Table 4.1). Hence, this method is *more reliable* than other techniques for sampling and examining metal concentrations. The values of a standard deviation taking tree rings using arched chisels were higher than those using the increment borer. However, the values were lower compared to the remaining methods (except for Pb and Zn). Cu, Cr, and Ni concentrations had the highest calculated values of a standard deviation and were established in the samples taken employing common chisels while those of Mn and Zn were obtained in the planing process. These are not very accurate sampling methods, because common chisels are straight and not adapted for the curves of tree rings. Therefore, under the split-off of the annual tree ring, the probability that the sample will take a part of the wood of another tree ring increases.

Practical Comparison of Methods

A tree must be cut down by taking samples of tree rings using a chisel and plane. Research on low metal concentrations of trees where their concentrations are not high and where high variation of results is expected points to the necessity to investigate the maximum possible number of trees. Nevertheless, it is not appropriate or reasonable to cut down a huge number of trees for research that applies to only a few rolls cut out of the tree trunk. Thus, the first three methods can be used when clear cutting, stepwise cutting, and selective logging (for example, some trees are damaged by a pathogen) are carried out, i.e., cuttings may be taken not only for research purposes but also taking into account requirements for forestry. In this respect, the application of an increment borer has a big advantage, because the investigated tree is not cut down, and a hole 12 mm in diameter, which represents the remainder of the trunk, is sealed up with a cut-off tree branch, thereby reducing the danger that might be caused by pathogens entering the wood.

Tree ring splitting techniques are critically assessed with respect to time of delay. In the cases of the chisels and planers that were used here, the tree is chopped down, rolls are cut out, and only then are annual rings split off. Just cutting down trees and cutting out rolls can frequently take up to a few hours depending on where the tree is growing (by itself or in a forest), the number of people involved in the process, and other factors. Splitting off annual tree rings from planing a single roll or employing chisels takes at least 1 h.

Due Owing to the complexity of the sampling method, the expected errors of application length may affect the quality of the obtained results. Cutting down a tree requires not only time but also technical preparation, labor, and skills. Additionally, a saw, at least one assistant, and skills at cutting down trees are necessary. To drill a tree, no special training is needed. The application of any method rather than drilling requires physical power. A comparison of tree species shows that pinewood is softer than birch and therefore can be more easily drilled.

Wood samples for cutting off tree rings should often be taken from three heights of the trunk: a lower part (at a height of 1 m above the stump), the middle part of the stump, and the upper part of the stump (at a height of three-fourths of the trunk length from the ground surface). Thus, metal concentrations at different heights of the tree can be compared, or more homogenous wood specimens taken from tree rings at different heights can be formed for establishing the metal concentrations more precisely. To take such samples, a tree must be cut down, and to cut off tree rings, all the previously discussed methods can be used.

Arched chisels have been produced such that to cut off tree rings, the curves of concentric circles that significantly differ in the upper and lower parts of the trunk can be more accurately replicated. In this respect, arched chisels are far superior to common ones because, at the time of cutting off of the tree ring, the probability of cutting off a part of the wood of other tree rings decreases. Hence, more accurate information on metal concentrations in an individual annual tree ring is obtained. When tree rings are cut off with a jigsaw in a wood borehole, the error probability decreases even more because the width of the tool (0.5 mm) is less than the thickness of the annual ring.

Sampling is directly related to the processing and preparation of samples. Therefore, an important point in this case is that it should not complicate further work. Having applied all methods for splitting off annual rings, shredding or burning is required. Only the volume of wood sometimes differs: the use of chisels and planers makes it possible to obtain a 300 g specimen from three rolls, whereas the application of a borer produces only 0.3 g. To mineralize wood, only 0.1–0.5 is needed. Thus, in the first case, producing several samples is very practical, while in the second case, there should be enough wood for only two additional investigations. However, even in this particular case, the statistical requirements are met.

Comparison of Mass of Wood Samples Applying the Method of Dispersive Analysis

Figure 4.5 shows the results of dispersive analysis (ANOVA) obtained comparing metal concentrations in specimens of wood rings having a different mass and taken employing the increment borer.

The conducted dispersive analysis reveals that, in the cases of Ni and Cr (5.62 and 6.86 respectively), the calculated F values (Fisher criterion) were higher than the value of F_{crit}, which indicates that the difference between the mean metal concentrations in the samples of different masses was statistically significant, i.e., determined not only by a randomness factor. Moreover, Cr and Ni concentrations in the samples having mass $m = 0.10$ g were 1.5 times higher than those in the samples of other masses.

As for the remaining cases of metal, no significant deviation between concentrations in the samples of a different mass has been established. Thus, the concentrations of Cu, Mn, Pb, and Zn can be defined in wood samples having a mass of even up to 0.10 g because statistically the deviation is not significant (Baltrėnaitė et al. 2010).

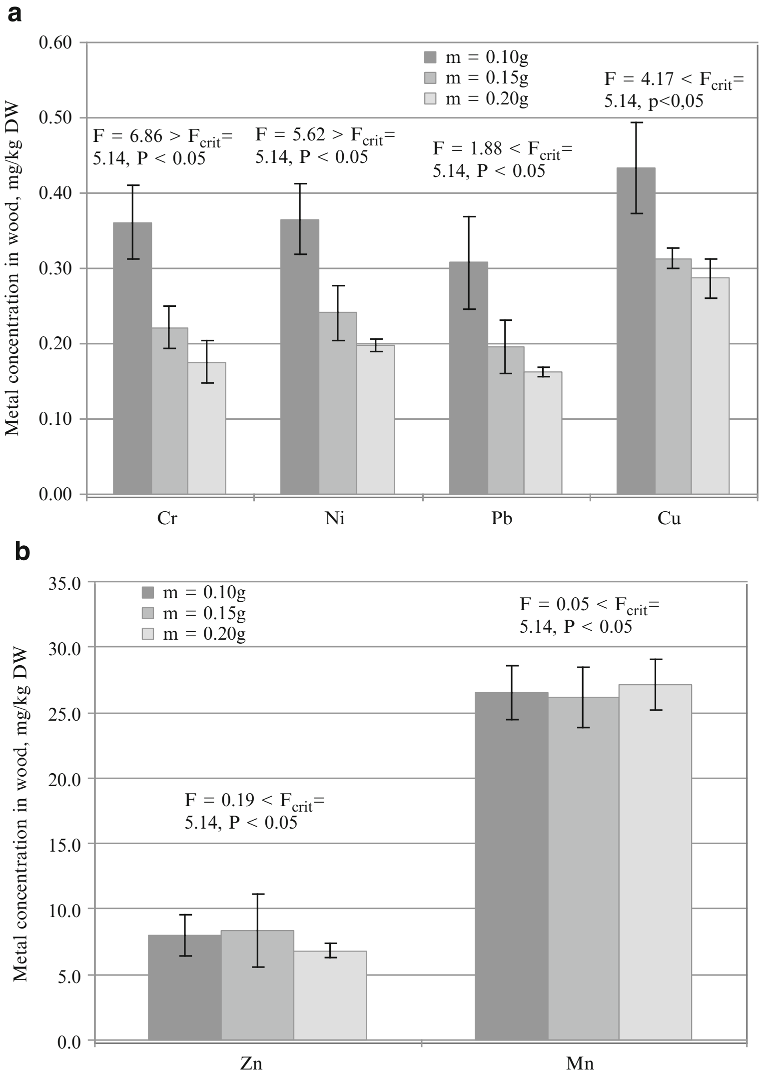

Fig. 4.5 Concentrations of Cr, Ni, Pb, Cu (**a**) and Zn and Mn (**b**) (mg/kg DW) in wood taking wood samples of a different mass using increment borer

4.2 Biogeochemical Traits of Trees in Metal-Contaminated Territory

Numerous discussions about the possibility of using sewage sludge as a fertilizer in forestry have been taken place (Hermle et al. 2006). Deforested soils usually lack nutrients, are mostly acidic, particularly in peaty areas. Sewage sludge is made of components that may be useful for soils (for example, organic matter, P, N, Ca, and Mg). However, wastewater can have high concentrations of metals, particularly Cd, Pb, Cu, and Zn, which usually come from industry. High metal concentrations can be phytotoxic and inhibit the growth of trees (Kabata Pendias and Pendias 2001). The ions of toxic metals in subsoil can have a harmful effect on trees and their roots and prevent water from entering and nutrients getting to the upper part of the plant.

Metal distribution and mobility mostly depend on soil properties controlling the mobility of metals in soil and uptake by trees. Specific soil properties (pH, varying acidity of H^+ and Al^{3+}), soil moisture and texture, along with organic matter, are the major factors describing soil quality and growth conditions for trees (Global Forest Resources Assessment 2005).

The metal uptake rate of a tree is related to phytotoxicity and mostly depends on tree species. For example, it is supposed that *Betula* and *Salix* tolerate metals and accumulate them (Kahle 1993). Research on two clones of *Salix* has disclosed that, upon entering, metals should prevent trees from growing further (Vandecasteele et al. 2004). Nevertheless, another investigation demonstrated that the growth of *Salix viminalis* in acid subsoil decreased having accumulated a higher content of Zn and Cd (Hermle et al. 2006). However, visual examination of the birch and pine tree on a site treated with industrial wastewater sludge (Taruškų forest, Lithuania) established no negative impact on the aforementioned tree species (Baltrėnaitė and Butkus 2007a, b, c).

Other researches indicate that the above-ground biomass of birch in soil contaminated with metals has decreased (Bojarcuk et al. 2002). A large part of the biomass of the silver birch (*Betula pendula Roth.*) growing in contaminated soil is spread in roots (60 % compared to 30–40 % on the control site). Still, when fertilized with sewage sludge mostly made of organic nutrients, trees can grow faster.

Further, differences between the biogeochemical traits of *Pinus sylvestris* L. and *Betula pendula* when grown in soil amended with industrial sewage sludge are discussed.

Experimental trees were growing in a formerly forested area (Gitėnai forest, Taruškos Forest Management Unit, Panevėžys region, North Lithuania, E024°34′38.8″, N55°43′31.6″), where in 1998 part (2 ha) of the territory was amended with wastewater sludge having elevated concentrations of metals (Table 4.2).

The chosen control site was situated at a distance of more than 200 m from the treated site. A year after the sludge amendment, the site was planted with *Pinus*

Table 4.2 Mean concentrations of metals in sewage sludge and industrial background concentrations of metals in soil of area before amendment with sewage sludge (Katinas et al. 2002)

Metal	Background concentration (mg/kg)	Concentrations in sewage sludge (mg/kg DW)
Cu	3.1–9.9	291
Pb	11.0–15.0	1456
Cd	2.2–5.0	6.2

sylvestris L and *Betula pendula*. Under natural conditions, the site was overgrown with *Alnus glutinosa*. Wood and soil samples were taken in the contaminated and control sites. Twelve randomly selected trees (*Pinus sylvestris* L. and *Betula pendula*) were sampled. Composite soil samples at soil depths of 0–10 and 0–30 cm in the habitat of each tree were taken.

Soil Properties

Soil moisture was higher at the contaminated than at the control site (Table 4.3). The soil moisture of the control site varied significantly ($p < 0.05$) and was higher in the upper than in the deeper layer of the soil; also, the values of moisture in these places varied widely ($p < 0.05$). The upper layer of soil and subsoil were more acidic ($p < 0.05$) than those of the contaminated site (Table 4.3). Exchangeable acidity at the contaminated site varied to a lesser extent than at the control site (Table 4.3).

The level of varying acidity in the different layers of the soil of the contaminated site was not that high ($p > 0.05$), whereas it was very pronounced at the control site ($p < 0.05$). A comparison of both sites shows that the difference in this parameter was not that large ($p < 0.01$) in both investigated layers of soil. Variations in the concentration of total carbon at both sites were similar: the concentration of total carbon at both investigated sites was higher at 0–10 cm than at 20–30 cm (Table 4.3). Nevertheless, comparison of both sites shows that a considerable difference ($p < 0.05$) has been established in the soil layer at 20–30 cm.

Soil is important to plants as a nutrient and water source that can resist (remains stable) against ambient pressure and recover after it (Griffiths et al. 2005). Conditions for growing plants depend on a number of soil properties, including pH, soil texture, moisture, and the content of oxygen. Soil moisture, the content of total carbon, exchangeable acidity, and pH are important indexes to growth conditions. Soil moisture has an impact on transferring soil solutions through roots. In the studied sites, higher moisture content was observed in the contaminated soil, which means that sludge helps with retaining moisture.

Table 4.3 Main properties of soil ($n = 6$, mean ± SD) in control and contaminated sites

Site	Depth of soil (cm)	Moisture %*	pH*	Exchangeable acidity (cmol/kgH**)	Total carbon (mg/kg)
Control	0–10	1.87 ± 0.79	3.15 ± 0.07	1449 ± 85	5.35 ± 0.97
	20–30	0.50 ± 0.14	3.69 ± 0.11	1100 ± 76	1.33 ± 0.27
Contaminated	0–10	3.49 ± 0.44	6.27 ± 0.17	61.3 ± 22.6	5.03 ± 0.90
	20–30	6.79 ± 0.32	6.13 ± 0.41	73.3 ± 39.6	3.45 ± 0.56

*$p < 0.05$, **$p < 0.01$

Variations in the concentration of total carbon in soil affect the physical properties of soil (Denef et al. 2001), and thus, owing to a higher content of carbon, soils are more stable (Sort and Alcaniz 1999). Regarding the investigated case, the content of total carbon in soil was higher than that found in the soil of the contaminated control site. Although the content of total carbon was similar in the surface layer of the soil of both sites, the content of carbon in the deeper layers of the soil of the contaminated site was higher than that at the control site.

Exchangeable acidity is one of the three main types of acidity governing the overall acidity of soil (the other two are pH and residual acidity) and is related to exchangeable aluminium-hydrogen ions attached to colloidal clay particles (as opposed to exchangeable acidity, the pH value does not assess the ions adhering to colloidal clay ions, only hydrogen ions in the soil solution). The evaluation of exchangeable acidity partially makes it possible to assess the extent of aluminum ions. Higher values of similar acidity refer to wider Al^{3+} bioavailability. Al^{3+} prevents root development and reduces the uptake of nutrients (for example, Ca and Mg) (Kupčinskienė 2006). Because of the low pH of soil, the mobility of toxic metals and their bioavailability increase (Kabata Pendias and Pendias 2001). The soil of the investigated control site is more acidic, and exchangeable acidity (Al^{3+}, H^+) shows high Al^{3+} concentrations (Sparks 1995). High aluminum concentration (in such a case, soil pH is less than 5.5) makes a toxic impact on plants: immature root fibers get thicker, nutrients from the soil are less intensively absorbed, and the development of plants is slowed (Goransson and Eldhuset 1995; Bojarszuk et al. 2002).

Both investigated sites were found to differ in the important soil properties of vegetation development. H^+ ion concentration of soil solutions at the contaminated site was 40–100 times lower than that at the control site, which contains 2.59 times more organic carbon in deeper layers of soil and 1.9–13.5 times more moisture. The contaminated site also has lower values of exchangeable acidity, which reach 24 times in the upper layer of soil and 16 times in lower layers of soil. In such a case, the spread of sewage sludge (excluding technogenic contamination with metals) improves the overall soil properties that are important to the viability of vegetation.

Differences in Metal Concentrations in Soils of Investigated Sites

The spread of industrial sewage sludge in soil had an impact on the increase in the concentrations of total metals. The total concentration of Cu at the contaminated site was higher than that at the control site (Table 4.4). Differences in the total concentration of Cu between the layers of soil were not significant ($p > 0.05$).

The total concentration of Cd in the soil of the contaminated site was significantly higher than that at the control site ($p < 0.05$) (Table 4.4). Cd concentration

Table 4.4 Total concentrations of Cu, Cd, and Pb and ratio of concentration of these metals in mobile form to total concentration (%) (mean ± SD, $n = 6$) in two different soil layers of investigated sites (0–10 and 20–30 cm), *$p < 0.05$

Site	Soil depth (cm)	Cu		Cd		Pb	
		Total* (mg/kg DW)	Mobile (%)	Total* (mg/kg DW)	Mobile (%)	Total* (mg/kg DW)	Mobile (%)
Control	0–10	4.00 ± 1.04	4.4	0.85 ± 0.11	36.1	24.78 ± 0.63	1.6
	20–30	4.53 ± 1.92	2.5	0.75 ± 0.07	47.5	23.00 ± 1.18	1.6
Contaminated	0–10	9.9 ± 0.07	2.1	1.33 ± 0.18	13.8	38.83 ± 8.72	0.7
	20–30	9.35 ± 4.41	1.5	1.15 ± 0.24	18.7	42.92 ± 2.42	0.6

between different layers of soil varied ($p > 0.05$) at both sites. Pb concentration at the contaminated site was notably higher ($p < 0.05$) than that at the control site. Pb concentration in the different layers of soil did not differ significantly ($p > 0.05$). The ratio of mobile metals, in terms of total concentration, was higher in the control site than at the contaminated site. According to the ratio of the mobile form to total concentration, the metals are as follows: Cd > Cu > Pb (Table 4.4). The obtained results point to a lower content of Pb in the mobile form, which is different from other investigated metals, whereas the major part of soluble Cd was observed in deeper soil layers of the contaminated and control sites. Moreover, the soluble part of metals is related to soil pH and has an impact on the migration of metals (Perelman 1961; Lietuvninkas 2002a, b).

Metals present in sewage sludge can prevent the development of tree biomass. For example, because of only 0.005 mg/kg Cd in soil, the root elongation of the spruce decreased, and 0.005 mg/kg of Cu dissolved in the soil solution may result in a lower growth of pine biomass (Arduini et al. 1998). It has been found that the content of Cd entering plants was 0.16 mg/kg in soil enriched with sewage sludge, which could have a negative impact on the development of pine tree roots (Arduini et al. 1998). Pb is not very mobile and therefore can only be available to plants in acidic soils. Moreover, soluble Pb in soils enriched with sewage sludge totalled ≤0.3 mg/kg, which is much less than 18 mg/kg, i.e., it did not reach a concentration limiting the growth of trees (Breckle and Kahle 1991).

The concentrations of the aforementioned Cu, Pb, Zn, and Cd present in pine and birch trees grown on the control site and that contaminated with sewage sludge are presented in Table 4.5.

Because the introduced trees are not considered to be among those that concentrate metals or exclude them, nothing special can be observed in their concentrations. The highest concentrations of metals in each tree are shown in the following table in **bold** type. As indicated, all the metals in both the contaminated and control site are found in the two upper lines of Table 4.5, i.e., in the needles (leaves) of trees and shoots. Only minor differences between the contaminated and control sites can be observed: five positions out of eight, i.e., 62.5 %, are taken from branches indicating maximum concentrations in the contaminated territory while the control site contains less, only 4 (50 %). Thus, it can be asserted that all the aforementioned

Table 4.5 Concentrations of metals in different compartments of pine tree and birch (mg/kg DW)

	Cu		Pb		Zn		Cd	
Compartment of tree	Pine	Birch	Pine	Birch	Pine	Birch	Pine	Birch
	Site contaminated with sludge							
Needles/leaves	1.17	**5.30**	0.25	0.32	23.58	61.75	**1.84**	**1.88**
Shoots	**4.89**	4.93	**0.58**	**0.59**	**42.71**	**154.70**	0.78	1.52
Stem	0.82	2.71	0.05	0.33	6.14	82.25	0.32	0.89
Roots	1.31	2.78	0.09	0.49	7.79	54.76	1.10	1.26
	Control site							
Needles/leaves	2.61	**5.57**	**0.72**	0.33	18.45	29.48	**1.78**	**4.31**
Shoots	**3.70**	3.62	0.31	**1.40**	**27.17**	**122.46**	0.63	1.34
Stem	3.58	2.88	0.18	0.38	21.02	113.94	0.48	0.68
Roots	1.19	3.33	0.11	0.88	8.53	39.65	0.66	1.07

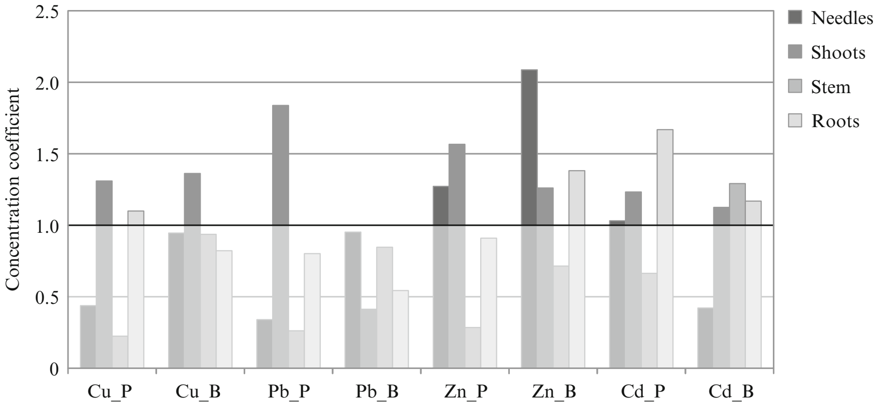

Fig. 4.6 Concentration coefficients $K_{k,i}$ of Cu, Pb, Zn, and Cd in different parts of a pine tree and birch growing on site contaminated by sewage sludge; values $K_{k,i} \leq 1$ are shown in a *darker background*

metals found in the pine and birch tree indicate a typical basipetal distribution (Kovalevsky 1987).

Differences in metal distribution in separate compartments of trees in the contaminated and control sites are better observed in Fig. 4.6, which shows the values of the concentration coefficients $K_{k,i}$ of certain metals, i.e., a concentration ratio of the *contaminated* to the *control* site. Values $K_{k,i} \geq 1$, i.e., higher on the contaminated site (a part of the diagram above its darker square), account for approximately 44 % of all possible cases (14 out of a possible 32), which generally means metals are not exposed to fast accumulation at the polluted sites. In this case, the analysis of the separate parts of the trees demonstrates that most frequently this is characteristic of their shoots (88 %) and roots (50 %), less frequently of needles and leaves (38 %) and extremely rare of stem wood (13 %). Strictly speaking, anomalous metal concentrations of tree organs (parts) at the contaminated site, when $K_{k,i} \geq 1.5$ (Lietuvninkas 2012), are rare, which includes only Pb and Zn concentrations in the shoots of the pine tree, Zn concentrations in birch leaves, and Cd concentration in pine roots.

Figure 4.6. presents another fairly significant implication: according to the frequency of the values of the coefficients of metal concentration $K_{k,i} \geq 1$ in the trees, metals are generally positioned in descending order Cd (6) > Zn (5) > Cu (3) > Pb (1) (the frequency of such situations is shown in parentheses). This largely agrees with the value ratio Cd > Cu > Pb of the mobile forms of metals in the soil of the contaminated site (Table 4.4).

Thus, as for the Gitėnai Forest area contaminated with sewage sludge, the investigated Cu, Pb, Zn, and Cd mainly tend to accumulate in the roots and shoots of trees. Metal concentration in tree wood, particularly in the pine tree, is frequently lower than that at the control site by two times or even more ($K_{k,i} \leq 0.5$).

Back Returning to metal distributions in the compartments of trees, their basipetal and acropetal forms, attention should be focused on Fig. 4.7, which illustrates how the distribution changed after the site was amended with metal-contaminated sludge. The translocation factor TF more frequently exceeds a value of TF = 1 at

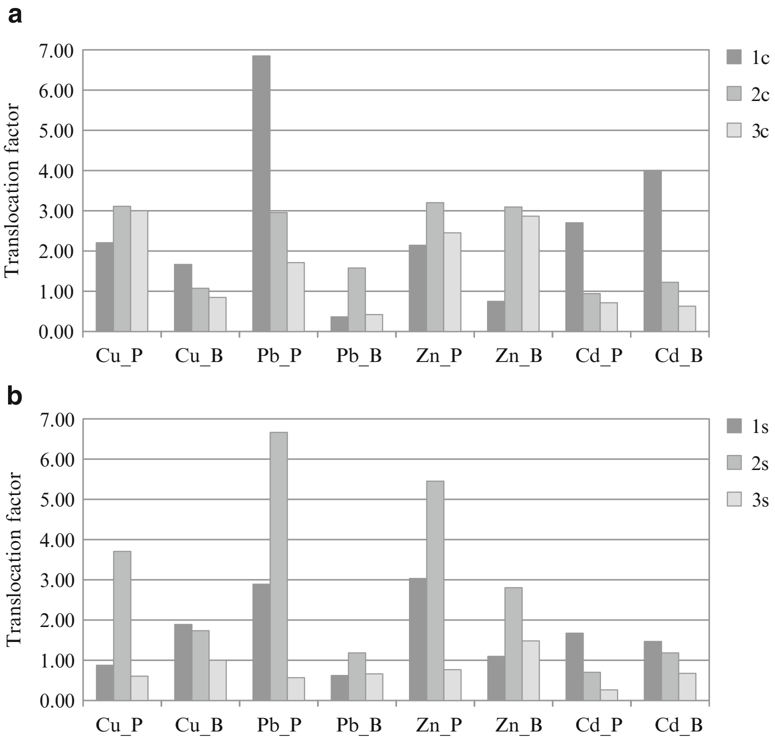

Fig. 4.7 Translocation factor (TF) as an index of basipetal distribution of Cu, Pb, Zn, and Cd in pine tree (P) and birch (B) at control site (**a**) and contaminated site (amended with sludge) (**b**)

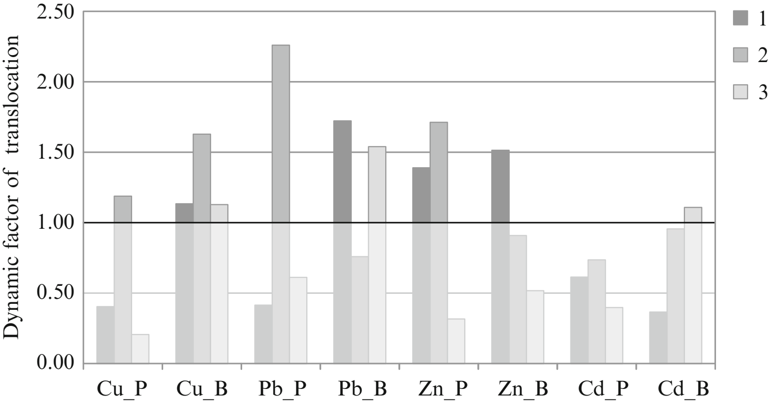

Fig. 4.8 Dynamic factor of translocation (TF_{dyn}) as an expression of metal translocation in trees growing on contaminated site [MC]_B refers to metal in birch, [MC]_P refers to metal in pine

the control site (71 %) than at the site contaminated with sewage sludge (58 %), i.e., in this case, the aforementioned four metals more actively accumulate in the above-ground parts rather than in roots. The values of the translocation factor (expressing the basipetal distribution) in the sequence *needles/leaves—shoots—stem wood* systemically reduce only in less than half of the possible cases: Cu decreases in birch, Pb decreases in pine trees growing on the control site, and Cd decreases in the pine tree and birch of both sites. In a number of other cases, the basipetal distribution of metals in the tree compartments is more complex, but, as mentioned earlier, the contaminated rather than control site can be characterized by a higher basipetal distribution of metals in the shoots.

The peculiarities of metal translocation in trees growing on the control site and on the site contaminated with sewage sludge can be more easily explained through *a dynamic index of translocation factor* (TF_{dyn}) (Fig. 4.8.) expressed as

$$TF1_{dyn} = \frac{TF1_g}{TF1_c}, \tag{4.1}$$

$$TF2_{dyn} = \frac{TF2_g}{TF2_c}, \tag{4.2}$$

$$TF3_{dyn} = \frac{TF3_g}{TF3_c}, \tag{4.3}$$

where $TF1_{dyn}$, $TF2_{dyn}$, and $TF3_{dyn}$ are the dynamic factors of metal translocation in needles/leaves (1), shoots (2), and stem wood (3); $TF1_s$, $TF2_s$, and $TF3_s$ are the values of the translocation factor of metals in needles/leaves (1), shoots (2), and stem wood (3), respectively; $TF1_c$, $TF2_c$, and $TF3_c$ are those values at the control site.

In Fig 4.8 the cases for which $TF_{dyn} \leq 1$, implies that metal translocation in the contaminated site takes place slower than that in the control site. The investigated site in Gitenai forest there were many of trees of such a type (54 %). Moreover, indexes $TF_{din} \leq 0{,}5$, i.e., when metal translocation in the contaminated site takes two and more times longer than that in the control one, can be also observed in quite a few situations: Cu and Pb—in the needles of the pine tree and stem wood, Zn—in the stem wood of the pine tree and Cd—in the stem wood of the pine tree and birch leaves. On the other hand, the opposite situation when metal translocation occurs two and more times effectively in the contaminated rather than in control site, i.e., $TF_{din} \geq 2$, is a rare case, as only Pb is found in the shoots of the pine tree (4 %).

Situations where the efficiency of metal translocation to different parts of trees is higher at the contaminated than the control site (area above $TF_{din} \geq 1$) underscore that there are practically equal probabilities of translocation to the leaves or needles of the trees as well as to shoots. All the aforementioned properties of metal translocation involve only the investigated polygon of Gitenai Forest and pine trees and birches growing at the control site and at the one contaminated with sewage sludge.

In general, it is well known that in plant bioindicators, metal concentration more or less reflects the concentration of certain metals in the soil (as in their nutrient medium) (Baker 1981). This clearly cannot be attributed to situations where plants exist in the environment of a higher aerogenic load when a foliar (through leaves and needles) entrance of metals to plants can achieve a high impact (Lukashev and Petukhova 1968). Although softwood, because of an exceptionally large general surface of needles on the basis of which an adhesive geochemical barrier operates (Lietuvninkas 2012), has been found to be remarkably efficient at removing air pollutants, showing that, under conditions of aerogenic air pollution, the concentration of Zn, Cd, and Pb in all parts of hardwoods such as birch and mountain ash can be significantly higher than in pine trees growing at the same site (Fedorova and Odintsova 2005). Metal redistribution from leaves and bark to wood (Pulford and Dikinson 2009) is frequently observed in trees growing in moderately contaminated soils at the end of the vegetation period.

However, the uptake of microelements from soil through plants represents not only their conveyance to biomass because that depends on a number of poorly defined and intricately interacting factors, mainly the composition of soil (e.g., mechanical, organic matter content and their composition, the presence of carbonates, and forms of soluble phosphates), its physical-chemical properties (pH and Eh), the intensity of exchange sorption, aeration and humidity, and temperature. The mobility of metals in soil fertilized with sewage sludge largely depends on the pH values – it increases with a decrease in pH (Antoniadis et al. 2009). The translocation of Fe, Mn, Cu, Zn, Cd, and Co improves in an acidic medium. In this case, attention should be paid to data provided in Tables 4.3 and 4.4 – the values of the soil pH of the site of Gitėnai Forest contaminated with sewage sludge are significantly higher than those of the control site (6.1–6.3 and 3.2–3.7, respectively), while the relative content of the mobile forms of metals is lower by 2–2.5 times.

It is accepted that, in time, the availability of Cd for plants in soil fertilized with sewage sludge may increase because of the mineralization of organic matter carried in by sludge, which results in the more intensive sorption of soil (Hyun et al. 1998). To sum up the issue of the benefit of amending soil with sewage sludge, B. Antoniadi and his colleagues support the idea that metals persist in soil for a long time; however, only additional research can prove the advantage of this process to plants (Antoniadis et al. 2009).

Apart from the aforementioned factors related to soil, the transfer of metals to plants may also depend on the peculiarities of the interaction of chemical elements, i.e., their antagonism or synergism (Antoniadis et al. 2009). The latter are frequently observed when the concentration of one or more chemical elements is 1.3–2 times higher than usual (Sibirkina 2014). A similar interaction of chemical elements may occur not only between individual microelements but also between them and important macroelements of the soil such as Ca, Mg, K, P, and N. The obtained data show that a higher concentration of K and P in soil negatively affects the uptake of Cd (John 1976), Zn can reduce the uptake of Cd and Pb, while Cu and Fe can decrease the uptake of Cd (Siedlecka 1995). Moreover, antagonism or synergism may vary depending on the concentration of chemical elements, their relationship in soil and plant tissues, the pH of the environment, temperature, and plant species (Alekseeva-Popova 1983). Returning to Table 4.4, the total concentration of Cu, Pb, and Cd in the soil of the contaminated site exceeds the concentration of appropriate metals in the soil of the control by 1.5–2 times. On the other hand, as mentioned earlier, differences in the concentrations of the mobile forms of these metals are on the opposite side –concentrations are higher in the control site the portion of metal in mobile form (in relation to the total concentration) is 2–2.5 times higher. Thus, at least nominally, the manifestations of the antagonism/synergism of chemical elements in the processes of the metabolism of trees at the contaminated site and their after-effects concerning metal accumulation and distribution in tree organs can be fully expected.

As discussed earlier, all metals (Cu, Pb, Zn, and Cd) investigated in the Gitenai Forest can be characterized by a basipetal distribution between the organs and parts of the pine tree and birch. In general, it is known that the distribution of metals between the organs and tissues of plants largely depends on the individual properties of metals and plants rather than on edaphic, seasonal, or landscape geochemical factors (Yang et al. 1995).

As regards this particular case, information has been presented in the most recent work by A. Sibirkina (Sibirkina 2014) who thoroughly analyzed the biogeochemical properties of *Pinus sylvestris L.* in relict belt pine forests in Pairtišė, East Kazakhstan. The forests are mostly situated in steppe zones and dry steppes characteristic of their typical soils: different kastanozems and brown desert-steppe soils. In the course of the conducted investigations, 312 specimens of soils and 174,869 specimens of plants (including 875 pine tree specimens and ten specimens of *Betula pendula Roth.*) were studied. The distribution of Zn concentrations in the needles and shoots of the pine tree has been found to depend on their age:

Needles 3 years old > needles 4 years old > needles 1 year old > needles 2 years old.

Shoots 5–7 years old > shoots 3 years old > shoots 1 year old > needles 4 years old > shoots 2 years old.

The distribution of the concentrations of different metals also has its peculiarities (mg/kg DW):

Zn: shoots (30.3) > needles (29.4) > wood (23.7) > cones (18.7).
Cu: shoots (3.47) > wood (3.04) > needles (2.53) > cones (1.37).
Pb: shoots (3.51) > needles (2.77) > wood (2.57) > cones (0.77).
Cd: wood (0.136) > shoots (0.082) > cones (0.056) > needles (0.030).

The presented data show that metals are unevenly distributed in the aboveground parts of pine trees: their concentrations usually decrease within the sequence Zn > (Cu, Pb) > Cd, and, in the case of the concentrations of Zn, Cu, and Pb, the relationship *shoots > (needles, wood) > cones* remains. Cd, as a metal particularly toxic to plants, safely accumulates in wood. A. Sibirkina notes that the basipetal distribution of metals in trees and shrubbery is only characteristic within the range of "low concentrations." As for the range of "high concentrations" in plants, metals tend to show an acropetal distribution of chemical elements.

Thus, to conclude the biogeochemical research on pine and birch trees in the Gitenai Forest and the previously presented similar findings of investigations of other scientists, the main biogeochemical characteristics of pine and birch trees growing in the experimental polygon on Gitenai Forest can be identified.

Trees growing at the site contaminated with sewage sludge do not readily accumulate any of the four examined metals: their coefficient of concentration $K_{\mathrm{k,i}} \geq 1$ has only been established in less than half (44 %) of all possible situations. Most frequently this can be observed in the shoots of trees (88 % of all cases) and roots (50 % of all cases) and most rarely in stem wood (only Cd in birch wood).

Cd, Zn, and, very rarely, Pb (only in the shoots of pine trees) most frequently accumulate in trees growing at the contaminated rather than the control site. The resulting frequency sequence Cd > Zn > Cu > Pb of metal accumulation in trees of the contaminated site matches well with the ratio Cd > Cu > Pb of the values of the mobile forms of metals in the soil of the contaminated site.

Values of $\mathrm{TF_{din}} \leq 1$ of the dynamic factor in metal translocation in trees growing on the contaminated site have been established in 54 % of all possible cases, frequently attaining $\mathrm{TF_{din}} \leq 0.5$. This means that, in this case, metals slowly accumulate in the trees. The possible and defined reasons taken from the previously cited works and concerning this phenomenon may include changes in edaphic conditions at the contaminated site, significantly higher values of soil pH, the concentrations of the mobile forms of the metals (2–2.5 times lower), a soil humidity, a concentration of total carbon higher that is 2.7 times higher in deeper layers of the soil, and the expected manifestation of antagonism and synergism of chemical elements in the environment of the contaminated soil induced by a significant deviation of the environment from the "standard" characteristic of the control site (soil pH, humidity and Eh conditions, concentration of metals and organic materials).

A common characteristic of the accumulation of metals in the organs and parts of the trees growing in the contaminated site includes their basipetal distribution, though this is less expressed than at the control site, and the highest metal concentrations recalculated into a dry mass in the shoots of trees and significantly frequently in leaves (Cu, Cd) or needles (Cd).

A decrease in basipetal metals at the site contaminated with sewage sludge can be related to the aforementioned general deviation from the "standard" for Gitenai Forest, which may bring changes in the peculiarities of metal distributions in trees from basipetal to acropetal.

4.3 Functional Traits of a Tree in Metal-Contaminated Territory

The environmental factors affecting a plant determine the morphological variations in the plant. To evaluate these changes, the so-called *functional traits* were observed (Ryser 1996; Landjeva et al. 2003; Mahmood et al. 2007; Singh and Agrawal 2007). These are indicators of changed environmental conditions of a plant (soil pollution, variations in soil moisture). Functional traits can relate to the entire plant (e.g., a change in the dry biomass of the whole plant) or its parts [e.g., specific length of roots (root length/g root mass), the ratio of roots to the plant mass, the ratio of the stem (trunk) to the plant mass, the ratio of leaves to the plant mass, the ratio of branches to the root mass, the diameter and length of the stem (trunk), the number of branches and roots].

Overall Dry Biomass of Trees and Their Separate Parts

This indicator is one of the simplest and primary indices for conditions affecting the growth of trees. Both the overall and dry biomass of the separate parts of trees were smaller at the contaminated site than at the control site . Deviations (except for the dry biomass of pine roots) were not significant ($p > 0.05$) between contaminated and control sites (Fig. 4.9).

It is assumed that tree biomass at the control site will be smaller than at the site with sewage sludge considering the expected positive impact of sewage sludge on soil properties (Pikka 2005). Poor soil conditions (e.g., varying high acidity and low pH values) suppress the development of the root system (Kupčinskienė 2006) and nutrient uptake, which leads to a lower growth in biomass at the control site and, conversely, a larger biomass of trees in territory that has had sewage sludge spread over it. However, research has revealed that the biomass of trees decreased at the

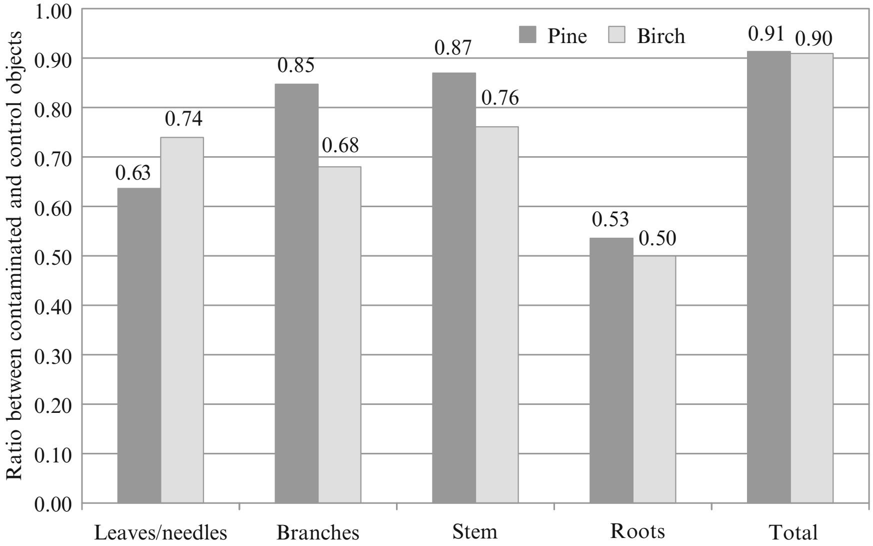

Fig. 4.9 Ratio of dry biomass of pine tree, birch, and separate parts on contaminated and control sites

site with sewage sludge compared with the control site: a larger decrease in the biomass of tree tissues has been observed in pine trees rather than in birch. Also, a remarkable reduction (approximately 50 %) in the root biomass of both species of trees has been observed.

Diameter and Height of Trunk

The diameter of birches and pine trees was measured at a height of 30 cm and was larger at the contaminated site than at the control site; however, a deviation was not statistically significant ($p > 0.05$). A similar tendency is characteristic of the height of the trunk (Fig. 4.10).

Ratio of Mass of Roots to Mass of Shoots

The values of this indicator in both cases, including the pine tree and the birch, were lower at the contaminated site than at the control site, and in the case of the birch, a deviation from this ratio between the investigated sites was statistically significant (Fig. 4.10). Research into a deviation of the ratio of roots to shoots at the contaminated and control sites has revealed that the ratio at the contaminated site compared

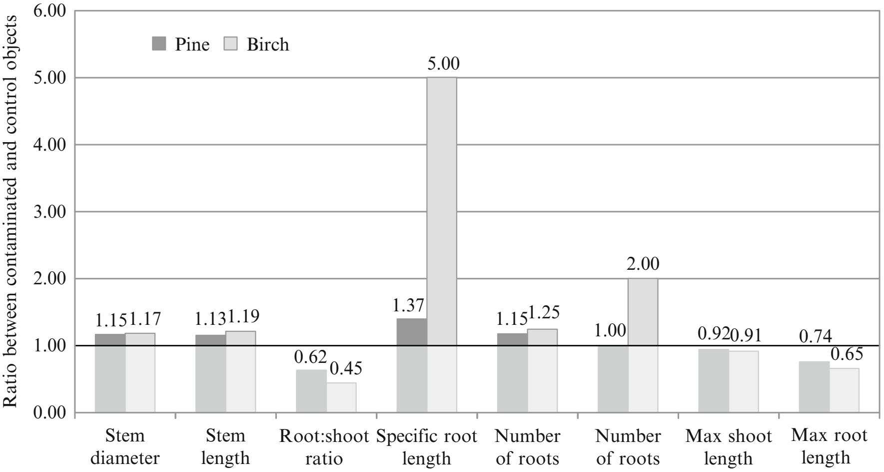

Fig. 4.10 Ratio of functional traits of pine tree and birch on contaminated and control sites. The *shaded* part indicates the zone where the values of the parameters in the modified site are lower than or equal to the parameters of the control site

to the control site has decreased. Thus, the mass of roots vis-à-vis shoots, is much smaller at the contaminated site than at the control site. A smaller biomass of roots at the contaminated than at the control site was discussed earlier in the context of investigating variations in biomass.

Specific Length of Roots

The values of this functional trait of both species of tree were statistically significantly higher at the contaminated vs. the control site ($p < 0.05$). In particular, a notably higher value was obtained in the case of the birch (Fig. 2.31). The specific length of roots indicates the carbon distribution in the root system and makes it possible to consider the level of the nutrient environment in the surroundings of the plant roots. The value of this indicator at the contaminated site was found to be higher than at the control site (particularly in the case of the pine tree), and this suggests a lower root density and a greater ability of tree roots to absorb nutrients (Hartikainen et al. 2001). Higher values of the specific length of roots show that soils are rich in nutrients (Ryser et al. 1996), and higher hydraulic conductivity is characteristic of roots (Eissenstat 1997). The higher the value of the specific length of roots, the more effectively nutrients can reach short roots (Wahl and Ryser 2000).

Maximum Lengths of Roots and Shoots

The maximum lengths of roots and shoots of both investigated tree species were shorter at the contaminated than at the control site (Fig. 4.10). The systems of tree roots in infertile soils are characterized by long, poorly branched surface roots, while roots in fertile soils are well branched (Crow 2005). A similar trend was observed in the investigated case: the number of roots of both the pine tree and the birch was larger at the contaminated site than at the control site, though the maximum length of roots was longer. A similar tendency was characteristic of the shoots.

Number of Roots and Shoots

This functional trait describes the nutrient state of soil in the environment of the tree. In the investigated case, the contaminated site was more favorable in terms of the nutrient environment (Fig. 4.10), which can be manifested by a larger number of roots and shoots in the contaminated site.

A general evaluation shows that, at the site contaminated site with spread sludge polluted with metals, vs. at the control site, excluding a technological load of metals, soil properties had to be more favorable for plants to grow; however, this cannot be proved by general functional traits and biomass qualities characterizing the growth and development of trees. Moreover, significantly lower root biomass draws attention to the potential impact of metals in the contaminated vs. the control site.

Chapter 5
The Role of Trees in Ecotechnologies

This chapter presents the ecotechnological advantages of using trees. In this case, the ecotechnological application of trees is presented as the assessment of the role of trees within their vegetative period in ecosystems using mathematical tools. The chapter describes a method, created by the authors, of dynamic factors to assess biophilicity, bioavailability, bioaccumulation, translocation of chemical elements, and phytoremediation effects. Mathematical models of chemical elements (with a focus on metals) in the transfer system atmosphere–soil–tree–atmosphere–soil provide the possibility of predicting the load of contamination from both stationary and diffuse pollution sources entering the tree environment, the uptake and bioaccumulation of chemical elements in the main morphological parts of a tree, and the potential for using trees in phytotechnologies.

The chapter describes the environmental and economic aspects of using trees in ecotechnologies. The examined aspects are shown to be an effective tool for assessing the role of trees in the framework of sustainable development.

5.1 Bioindication and Phytoremediation: Practical Features of Metal Bioaccumulation in Trees

The complicated mechanisms of the accumulation of chemical elements in plants have been discussed in the literature for at least 60 years now, while their practical application in geochemistry has been going on for more than 70 years. The chemical composition of plants (similar to that of other organisms) depends on three important factors, including their status in the system, the main characteristics of the environment (e.g., the composition of soil, rock), and the individual character of particular organisms (primarily, the stage of their development). Moreover, various organs of plants (e.g., roots, trunks or stems, leaves, seeds or fruits) differ in chemical composition (Lietuvninkas 2012). The main factors relating to the

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concentration of chemical elements in plants are usually divided into internal (physiological) and external (ecological) factors. The main external (ecological) factors are associated with the concentration of chemical elements in the nutrient medium (the soil for plants) and the accessibility of a chemical element to plants. The latter depends on a number of other interrelated factors, such as the chemical and geochemical properties of an element, environmental characteristics (pH, Eh, temperature), the presence or absence of geochemical barriers, as well as, for example, climate and landscape geochemical characteristics.

The bioaccumulation level depends on the amount of light plants receive. The internal (physiological) factors also include specific biochemical barriers characteristic of some plants, the taxonomy of plants, and their vegetative phases and organs (Dobrovolskii 2008).

In recent works, plant tolerance for certain chemical elements is associated with two types of plant behavior: the ability to resist the action of these elements, which leads to their elimination, or resistance manifesting itself as the assimilation of chemical elements and, subsequently, their immobilization in cells together with immobile forms (Prasad 2006). In actual conditions, the problem is more complicated because, under the same conditions, various organs of plants (e.g., roots, trunks or stems, leaves and reproductive organs) accumulate chemical elements in different ways. Therefore, there are two variations of this process, representing acropetal and basipetal accumulation of chemical elements (Kovalevsky 1987), which are not discussed in this section.

We will limit our discussion to the statement that, under certain conditions, plants can accumulate larger or smaller amounts of chemical elements with respect to the background, and this property of plants can be used both for evaluating the environmental conditions (bioindication) and for soil phytoremediation purposes.

Bioindication is the most widely used method of pollution indication in Lithuania and the world. The most commonly used trees for bioindication are *Pinus sylvestris* L., *Betula pendula*, *Fraxinus excelsior*, *Sorbus aucuparia*, *Tilia cordata*, and *Malus domestica* (Kupčinskienė 2011; Butkus and Baltrėnaitė 2007a).

Phytoremediation based on the use of trees for cleaning areas polluted with metals takes advantage of several factors, including a large biomass of trees, their genetic variation, the availability of highly experienced forest rangers and methods for converting biomass to fuel by anaerobic digestion, andfermentation and thermochemical processes, positive attitudes of people to planting trees, and the stability of the forested areas and their resistance to soil erosion caused by wind and water (Pulford and Dickinson 2006).

Summing up, it may be claimed that the methods of bioindication and enhancement of environmental conditions could be more strongly supported by interested stakeholders if their quantitative expression was more convincing.

In this section, a survey of studies performed by Lithuanian researchers investigating the great potential of higher plants based on their chemical composition and a description of a new method of evaluating the transfer of chemical elements from soil to plants and their translocation within plants using the *dynamic factors of* *bioaccumulation, bioavailability, biophilicity, phytoremediation and translocation*, is presented.

Trees are considered to be sensitive indicators of environmental conditions (Cook and Kairiūkštis 1999; Stravinskienė 2002; Kupčinskienė 2011). Ordinary pine trees (*Pinus sylvestris* L.) are the most widespread species of tree. In fact, their habitat includes the entire territory of Lithuania (Navasaitis 2008). Because it is so widespread and because, generally speaking, there are no barriers to the accumulation of most environmental pollutants, *Pinus sylvestris* L. is well suited for observing environmental changes. The academicians Cook and Kairiūkštis (1999) emphasize that dendrochronological and dendroindication methods of environmental research establish a theoretical basis for seeking evaluation criteria on anthropogenic effects on forest ecosystems and tree growth.

An increase in environmental pollution and more comprehensive analyses of the problems created by this process and the problems associated with the effects of xenobiotics on various organisms, as well as the important role of the circulation of pollutants in the nutrient cycle and the use of plants for engineering solutions to environmental problems (phytotechnologies), have caused a growth in importance of such pollutants as metals, which are chemical elements that remain for a long time in soil and plants (with most of them producing harmful effects from a biogeochemical perspective). Much attention has also been paid to metals in the international research programs FA COST Action 859: Phytotechnologies to Promote Sustainable Land Use and Improve Food Safety, COST FA 0905: Mineral-Improved Crop Production for Healthy Food and Feed, which have been discussed at international conferences, as well as by the Society for Environmental Toxicology and Chemistry (SETAC), the International Society of Trace Element Biogeochemistry (ISTEB), and at the International Conference on the Biogeochemistry of Trace Elements (ICOBTE).

In 2001, research on the methods of transferring metals from soil to pinewood was performed in Lithuania at the military training grounds located in Rukla–Gaižiūnai (Jonava District) and Kairiai (Klaipėda District). Several main pathways of transferring metals such as nickel (Ni), copper (Cu), and zinc (Zn) to pine trees, which included air–pine bark, air–soil–pinewood, and soil–pinewood, were investigated. The concentration of zinc (Zn) in wood samples, exceeding the average concentration of this metal by four times, was found in pine trees near the shooting grounds. This can be explained by the fact that Zn concentration in the soil of the shooting ground was three times as high as the average Zn concentration in this area. The concentration of Ni, about five times higher than its average concentration, and Cu concentration, around three times higher than its average concentration in this territory, were found near the water body used for military training purposes. The metals Ni and Cu could permeate the ambient air and be deposited on the bark of pine trees as fuel particles or to seep into the soil with wet deposition and into pinewood through tree roots (Butkus and Baltrėnaitė 2007a). The increase in metal concentration in this locality was also confirmed by the fact that the concentrations of Cu and Ni, exceeding the ultimate concentrations allowed for drinking water by about 19 and 22 times, respectively, were found in the investigated spring

(Baltrėnas et al. 2005a, b). In bark samples of pine trees growing in the investigated area, Cu concentration (1.75 mg/kg) and Ni concentration (4.56 mg/kg) (Butkus and Baltrėnaitė 2007a) were found to have exceeded their average concentration in the examined pines by 1.3 and 2 times, respectively. The ability of pine bark to take up metals in great amounts explains why pine trees are used for bioindication purposes in various countries, such as, for example, Portugal, Jordan, Germany, Finland, Check Republic, and the United Kingdom (Harju et al. 2002). This problem is also being investigated in Lithuania (Butkus and Baltrėnaitė 2007a; Pundytė and Baltrėnaitė 2011).

In 2005, a territory formerly covered with forest was investigated. It was 7 years after the sludge had been spread on the soil in this area and 6 years after it had been planted with trees (*Pinus sylvestris* L.; *Betula pendula*; *Alnus glutinosa*). No metal pollution in the ambient air had been found there, so the researchers expected to see a translocation of metals in the soil–tree system. Indeed, the concentration of copper (Cu), lead (Pb), and nickel (Ni) in the investigated pine were respectively six and four times higher than their concentrations in black alder. The concentrations of Cu, Pb, and Ni in the pine were about 2.5, 4, and 3 times higher, respectively, than those in the birch. The concentrations of these metals in the pine were five times higher than those observed in the control samples. The tests performed allow us to believe that spreading sludge polluted with metals in the soil stimulated the accumulation of these metals in the young plants over the course of the 6 years since they had been planted. The concentrations of Ni, Pb, and Cu in *Pinus sylvestris* L. can be five times higher than the concentrations of these metals in the control trees and three to six times higher than those found in *Betula pendula* and *Alnus glutinosa* (Butkus and Baltrėnaitė 2007b; Baltrėnaitė and Butkus 2007a, b, c).

The obtained results allow us to consider trees to be a good choice for phytoremediation purposes when required to eliminate or stabilize soil pollution. Trees are good bioindicators in the case of low-level pollution. On the other hand, it has been observed that sludge polluted with metals does not stimulate the growth of biomass. Evaluation of biomass growth in the trees on the examined territory 10 years later has shown that the difference in biomass growth between the control pines and other trees and those growing in the soil containing polluted sludge was statistically insignificant. It has also been found that biomass growth in the pine was 87 % higher than that in the birch trees, while the concentrations of Cu, Cd, and Pb in the pine were about 60 % higher than those in the birch. This investigation allowed us to identify two sets of functional traits of an ordinary pine and a birch: better nutrient characteristics of soil are associated with the increase in the specific root length (SRL), a decrease in the root/shoot ratio, and more intense root branching, while the potential effect of metals is characterized by the lower height of trees, smaller trunk diameter, and lower dry biomass amount (Vaitkutė et al. 2010).

The concentrations of Pb, Cu, Zn, K, and Mn determined in the wood of *Pinus sylvestris* L. during the investigation of the formerly highly industrial area (Panevėžys, Lithuania) confirmed the possibility of using pines in phytomonitoring, i.e., regular surveillance of aerogenic metals, in the environment. Compared to the data on the control territories, the concentrations of Cd ($p < 0.05$), as well as Zn ($p < 0.01$), Cu ($p < 0.05$), K ($p < 0.05$), and Mg ($p < 0.05$), in the pinewood were respectively 2, 1.5, 1.3, and 1.9 times higher (Pundytė et al. 2011a, b).

However, trees are affected not only by anthropogenic but also by natural (biotic and abiotic) factors, often acting as stressors. As mentioned earlier, in the process of bioindication, the available data on the relationship between bioindicators and the environment should be considered.

Diseases of trees, as an example of the effect of biotic factors/stressors, as well as the relationship between trees and disease, should be given more attention if we want to more thoroughly understand the natural resistance of trees and the biogeochemical aspects of the considered relationship. For example, *H. annosum* is known to be a dangerous pathogen causing, first, the decay of the main roots and, later, the wood of conifers. In 1999, this pathogenic microorganism damaged about 1,200 ha of conifer forest (Navasaitis et al. 2003). An investigation of the composition of the damaged pine softwood performed in 1959–1960 revealed concentrations of nickel (Ni) and chromium (Cr) in its annual ring that were five times higher than those found in other annual rings of the tree. Based on the micromorphological characteristics of the mycelium found in the pine tree ring, it was the mycelium of the pathogen *H. annosum*.

Higher concentrations of nickel (Ni) and chromium (Cr) in damaged pine can be attributed to its disease tolerance associated with the increase in the concentration of elements required for fighting pathogens causing plant diseases (Poschenrieder et al. 2006). A pathogen that gets into wood destroys lignin, its component, seeking to reach cellulose found in the cell walls, which is a vitally important source of energy. The stress caused by these processes stimulates tree defense mechanisms against pathogens by special signals. It is believed that metals also take part in these defensive reactions.

It is well known that nickel (Ni) improves the metabolism of plants because, when deposited on cell walls, increases their carrying capacity, while chromium (Cr) is needed for glucose production, which is later used for generating glucosides and lignin. These preliminary data allow us to believe that the variation in metal concentrations can help identify biotic and abiotic factors influencing the behavior of plants (Baltrėnaitė and Butkus 2006; Vaitkutė and Baltrėnas 2011).

The effects produced by other types of pollutants on pines and other tree species in Lithuania are discussed in the works of Kupčinskienė (2011), Ozolinčius et al. (2005), Augustaitis et al. (2007a, b), Baltrėnaitė et al (2010), Stravinskienė (2010, 2011), Baltrėnas and Vaitkutė (2011), Pundytė et al. (2011a, b), and Markert et al. (2012).

We will now discuss metals, as well as the ways in which they penetrate into trees and translocate within the tree organism, though the presented evaluation method, which is based on the use of dynamic factors, may be applied to the investigation of any other chemical element and plant.

5.2 Dynamic Factor Method for Evaluation Metal Uptake Processes by Trees

Definition of Dynamic Factors

Determining phytoremediation and bioindication areas required the evaluation of the uptake of metals by plants to compare plants according to their ability to accumulate metals and to evaluate metals according to their ability to penetrate into trees. The different methods of metal uptake in plants, depending on their species and genotypes, have been widely discussed in Prasad (1997) and Brooks (1998). However, a biogeochemical approach to the problem of metal uptake by plants is no less important than a biochemical approach. In the former, emphasis is placed on the relationship between a plant and its environment (primarily, soil).

The relationship between the soil and a plant is most important in determining the peculiar character of the concentration function in plants. On the other hand, it complicates the evaluation. The major soil parameters on which the uptake of metals into plants depends, such as pH, Eh, CEC (cation exchange capacity), the amount of clay particles, and amount of organic matter in soil, as well as the concentration of oxides and hydroxides of Fe, Mn, and Al, the amount and variety of microorganisms, and, finally, the relationship between the mobile forms of metals, vary depending on rock, terrain, type of ecosystem, and soil and determine the uptake of metals by plants.

In addition, an invisible rhizosphere zone, a thin layer of soil full of microorganisms, characterized by high biological activity – and usually ignored by researchers – is found between the soil and plant roots. On the other hand, a rhizosphere zone provides a protective mechanism of plant homeostasis, while being, on the other hand, a well-functioning nutrient processor, where great changes in the existing forms of chemical elements take place (Bais et al. 2006). In recent years, some elements from the soil solution have been deposited (and, thereby, rendered harmless), while others have been dissolved by specific root secretions (exudates) joined together to make chemical compounds and then assimilated by the roots of the plants. Owing to mostly acidic types of root secretion, the amount of mobile forms of metals in the rhizosphere has increased by 1.5–1.7 times (Biriukova 2006). Panin and Biriukova (2003) investigated the rhizosphere of two trees (a pine, *Pinus sylvestris* L., and a birch, *Betula pendula* Roth) and two herbaceous plants (*Artemisia arenaria* D.C. and *Stipa Ioanne* L.), growing in the relic forest in eastern Kazakhstan. According to their data, the total concentration of metals in the rhizosphere is much higher than in the soil: Cu concentration is 1.3 times higher, Zn 1.4–1.9 times higher, Pb 1.3–1.7 times higher, and Cd 1.8–2 times higher than the concentration of these metals in the soil. The concentration of soluble forms of such metals as Cu, Zn, Pb, and Cd in the rhizosphere was 1.5–2, 2–3.5, 2.5–7.5, and 10–13 times higher than in the soil, respectively. It should be noted that the concentration of metals in soil solution in the rhizosphere was 1.8–3 times higher than in the rhizosphere of *Artemisia arenaria* D. C. and *Stipa Ioanne* L.

A widely known type of biological absorption is based on the relationship between a plant and the soil, or, in other words, the coefficient referred to as the index of bioaccumulation (IBA), transfer factor (TF) (Kabata Pendias 2010), transfer coefficient (TC) (Antoniadis et al. 2006), bioaccumulation factor (Prasad 2006), mobility ratio (MR) (Mingorance et al. 2007; Baker 1981; Chamberlain 1983), bioconcentration factor (BCF) (Pulford and Dickinson 2006; Gál et al. 2008; Yoon et al. 2006), and plant–soil coefficient[1] (Kovalevsky 1987) and is expressed by the concentration of metals in a plant with respect to the soil. Thus, it is expressed as the relationship between the concentration of metals in a plant and the soil in which it grows. This relationship is used to determine the ability of plants to accumulate metals (when its value is greater than one, plants are called accumulators, whereas when the relationship value is equal to or around one, they are referred to as indicators, and when this value is less than one, plants are called excluders). The considered relationship is also used for identifying the harmful effect of metals and for determining a risk posed by them to the biota.

In Russia, B. Polynov created and A. Perelman further developed the classification of metals and other chemical elements depending on their bioaccumulation (by arranging them in sequences). According to their uptake, chemical elements have been divided into four groups: elements of vigorous uptake (P, S, Cl, Br, I), strong uptake (e.g., Ca, K, Mg, Zn, Se), medium uptake (e.g., Mn, Ni, Cu, Co, Pb, As, Hg), and weak/very weak uptake (e.g., V, Cr, Sb, Cd). Mingorance et al. (2007) used the term *enrichment factor* to compare the concentrations of metals and other chemical elements in a given soil or plant with those in control objects.

However, the aforementioned factors/coefficients, expressing the concentration of metals in plants compared to that in the soil, have some drawbacks. From a biogeochemical perspective, they reflect the comparison of metal concentrations in various media (plants and soil), but this refers only to a particular area and to particular environmental conditions characteristic of this area in a particular period of time (e.g., 10 years after sludge had been spread over the soil). **First**, from a biogeochemical point of view, comparison of various plants based on the considered factors/coefficients could hardly be accurate because these plants could have been growing in different conditions, different types of soil, and elementary landscape, which could result in different levels of mobility and accumulation of metals (or other chemical elements) in them. **Second**, one must compare not only the concentrations of metals in plants with their concentrations in soil or the control plant but also the differences in the process of metal transfer and its intensity with respect to the control case. This is all the more important because in evaluating a process (transfer of metals in this case), we should compare processes rather than concentrations. **Third**, a numerical value of the relationship between the transfer of metals to the investigated tree and to the control trees, which could facilitate evaluating the variation in metal transfer, is lacking. However, a method based on

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[1] The plant–soil coefficient expresses the relationship between metal concentrations in ash and the soil. In other words, metal concentration in a plant is recalculated in terms of biomass.

dynamic factors can provide it. **Fourth**, it is important that the effect of natural processes influencing the transfer of metals be integrated into the estimate. These objectives could be achieved by introducing higher-order factors[2] calculated by comparing the value of metal transfer factor obtained for the investigated territory with the corresponding value for the control territory.

In this work, third-level factors are referred to as dynamic factors.[3] The authors recommend these factors for describing four types of metal behavior, depending on the changes taking place in the soil. They are referred to as dynamic factors because of their sensitivity to changes in the variables involved in calculations.

The dynamic factor of bioaccumulation ($\mathrm{BA_{dyn}}$) evaluates the physiological sensitivity of a plant depending on a particular metal's concentration in it with respect to the general level of this metal concentration in the soil (Eq. 5.1):

$$\mathrm{BA_{dyn}} = \frac{C^{\mathrm{i}}_{\mathrm{T\_t}} \times C^{\mathrm{i}}_{\mathrm{S\_c}}}{C^{\mathrm{i}}_{\mathrm{S\_t}} \times C^{\mathrm{i}}_{\mathrm{T\_c}}}, \tag{5.1}$$

where $C^{\mathrm{i}}_{\mathrm{T_t}}$ is the concentration of metal i in the biomass ash of the plant in the investigated territory (mg/kg), $C^{\mathrm{i}}_{\mathrm{S_t}}$ is the concentration of metal i in the investigated soil (mg/kg DW), $C^{\mathrm{i}}_{\mathrm{S_c}}$ is the concentration of metal i in the control soil (mg/kg DW), and $C^{\mathrm{i}}_{\mathrm{T_c}}$ is the concentration of metal i in biomass ashes in the control territory (mg/kg).

The dynamic factor of metal translocation expresses the variation in metal translocation a plant's roots to its vegetative organs (Eq. 5.2):

$$\mathrm{TR_{dyn}} = \frac{C^{\mathrm{i}}_{\mathrm{v\_t}} \times C^{\mathrm{i}}_{\mathrm{r\_c}}}{C^{\mathrm{i}}_{\mathrm{r\_t}} \times C^{\mathrm{i}}_{\mathrm{v\_c}}}, \tag{5.2}$$

where $C^{\mathrm{i}}_{\mathrm{v_t}}$ is the concentration of metal i in the vegetative organs of the plant growing on the investigated territory (mg/kg DW), $C^{\mathrm{i}}_{\mathrm{r_t}}$ is the concentration of metal i in the roots of plants growing in the investigated territory (mg/kg DW), $C^{\mathrm{i}}_{\mathrm{r_c}}$ is the concentration of metal i in the roots of plants growing in the control territory

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[2] Several comparison levels of metal concentration in plants may be distinguished in (1) a direct comparison of metal concentrations in biomass (which would be misleading because the respective metal concentrations in the soil as a source of nutrients for plants are not taken into consideration), (2) bioconcentration (bioaccumulation) coefficients (the effect of higher or lower metal concentrations in soil upon their transfer and accumulation in plants is not taken into account), and (3) dynamic bioaccumulation factors taking into consideration the effect of metal concentrations in the soil of the control (background) and polluted territories on their transfer and accumulation.

[3] The definitions and calculations of the dynamic factors are consistent with the data provided in Baltrėnaitė et al. (2012a, b).

(mg/kg DW), and $C^{\mathrm{i}}_{\mathrm{v_c}}$ is the concentration of metal i in the vegetative organs of plants growing in the control territory (mg/kg DW).

The dynamic biophilicity factor of metals ($\mathrm{BF_{dyn}}$) indicates the variation in metal involvement in the metabolism of a plant (Eq. 5.3). In fact, the biophilicity of a metal is the ratio of metal accumulation in live biomass to metal concentration in Earth's crust and, therefore, reflects the involvement of metals in metabolism:

$$\mathrm{BF_{dyn}} = \frac{C^{\mathrm{i}}_{\mathrm{T\_t}}}{C^{\mathrm{i}}_{\mathrm{T\_c}}}. \tag{5.3}$$

The dynamic phytoremediation factor ($\mathrm{FR_{dyn}}$) indicates the variation in phytoremediation effects and the capacity of plants to be used for phytoremediation. It can be calculated by Eq. (5.4):

$$\mathrm{FR}^{\mathrm{i}}_{\mathrm{dyn}} = \frac{C^{\mathrm{i}}_{\mathrm{biomass\_tr}} \times B_{\mathrm{tr}} \times C^{\mathrm{i}}_{\mathrm{soil\_c}} \times \rho_{\mathrm{c}}}{C^{\mathrm{i}}_{\mathrm{biomass\_c}} \times B_{\mathrm{c}} \times C^{\mathrm{i}}_{\mathrm{soil\_tr}} \times \rho_{\mathrm{tr}}}, \tag{5.4a}$$

where B_{t} and B_{c} denote the annual growth of a tree in the control and investigated territories (kg/ha), and ρ_{c} and ρ_{t} are the soil density in the control and investigated territories, respectively (g/cm^3). Usually, $\rho_{\mathrm{c}} = \rho_{\mathrm{t}}$. If Eqs. (5.1) and (5.4a) are rearranged, and the assumption is made that the density of the soil before and after modification does not differ significantly (i.e., $\rho_{\mathrm{c}} = \rho_{\mathrm{t}}$), the relationship between the dynamic bioaccumulation and dynamic phytoremediation factors will be expressed as follows (Eq. 5.4b):

$$\mathrm{FR_{dyn}} = \mathrm{BA_{dyn}} \times \frac{B_{\mathrm{t}}}{B_{\mathrm{c}}}. \tag{5.4b}$$

The dynamic factor of element bioavailability $\mathrm{BIO_{dyn}}$ has been estimated applying Eq. (5.5) and expresses variations in the mobile part of the chemical element in soil (thus, a part of the element available by plants):

$$\mathrm{BIO_{dyn}} = \frac{C^{\mathrm{i}}_{\mathrm{mob\_t}}}{C^{\mathrm{i}}_{\mathrm{tot\_t}}} \times \frac{C^{\mathrm{i}}_{\mathrm{tot\_c}}}{C^{\mathrm{i}}_{\mathrm{mob\_c}}}, \tag{5.5}$$

where $C^{\mathrm{i}}_{\mathrm{mob_t}}$ is the concentration of chemical element i in the soil solution on the treated/affected site (mg/kg), $C^{\mathrm{i}}_{\mathrm{tot_t}}$the total concentration of chemical element i in the soil on the treated/affected site (mg/kg), $C^{\mathrm{i}}_{\mathrm{mob_c}}$ is the concentration of chemical element i in the soil solution on the control site (mg/kg), and $C^{\mathrm{i}}_{\mathrm{tot_c}}$ is the total concentration of chemical element i in the soil on the control site (mg/kg).

In addition to their biogeochemical significance, the dynamic factors have a number of advantages in practical application:

(a) They integrate the information of four various types by combining the data about the amount of metals in two media (or the plant organs) and the data on the control and the polluted (treated) territory into a single value, thereby facilitating the evaluation of metal transfer.
(b) They are nondimensional and, therefore, easy to compare.
(c) They eliminate the risk of systematic errors in the analysis, thus improving the reliability of the obtained results and the quality of evaluation.

Practical Application of Dynamic Factors

The dynamic factors were first tested for practicability in the experimental research carried out on the territory formerly covered with forest (Gitėnai Forest, Taruškos Forest Station, Panevėžys District, Northern Lithuania, E024°34′38.8″, N55°43′31.6″), part of which (2 ha) was amended with contaminated industrial sludge.[4] The selected control area was more than 200 m from the contaminated area. Some years after it had been polluted, this territory was planted with pines (*Pinus sylvestris* L.) and birches (*Betula pendula*). Alders (*Alnus glutinosa*) had naturally spread over this area. Wood and soil samples were taken in the affected and control areas. Six wood samples of various species of trees (*Pinus sylvestris* L., *Betula pendula*, *Alnus glutinosa*) were taken, while one composite soil sample was taken at a depth of 0–40 cm in the area where these trees were growing.

A statistical analysis of the obtained data was carried out using Microsoft Office Excel 2007. An array of the initial data was evaluated based on 3S criteria. The average measurement values were used for calculating the values of the dynamic factors. The dynamic factors describing the translocation (transfer) of metals in pines, birches, and alders are given in Figs. 5.1, 5.2, 5.3, and 5.4. The columns present the values of the dynamic factors, showing the increase/decrease in the metal bioaccumulation intensity compared to the control territory.

The data presented in Fig. 5.1 show that the BA_{dyn} values are greater than one for most metals. Values less than one were found only for the investigated alder and birch. The closest BA_{dyn} values characterizing metal accumulation in various species of trees were found for zinc and nickel. The distribution of BA_{dyn} values characterizing the amount of copper and chromium in trees follows the sequence pine > birch > alder. In general, the pine is characterized by the largest BA_{dyn} values, while, with respect to metals, the highest BA_{dyn} was found for Ni ($BA_{dyn} = 120.8$).

For most of the metals the values of the dynamic biophilicity factors, BF_{dyn} (except for Mn in the alder), were greater than one (Fig. 5.2), which shows that the pollution of the soil with metals had increased their biophilicity, i.e., the

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[4] The data used for dynamic factor calculations was selected from experimentally obtained results by choosing the most pronounced values of metals in soil and plant. Therefore, the metal concentration values from the investigated site that are used in the other chapters may differ.

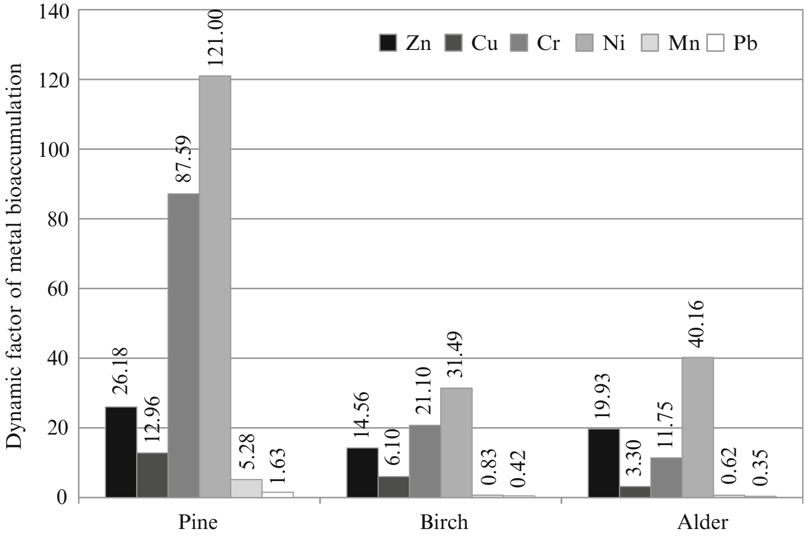

Fig. 5.1 Dynamic factor of bioaccumulation (BA_{dyn}). Values greater than one signify an increase in metal accumulation in the investigated territory compared to control territory; values less than one signify its decrease

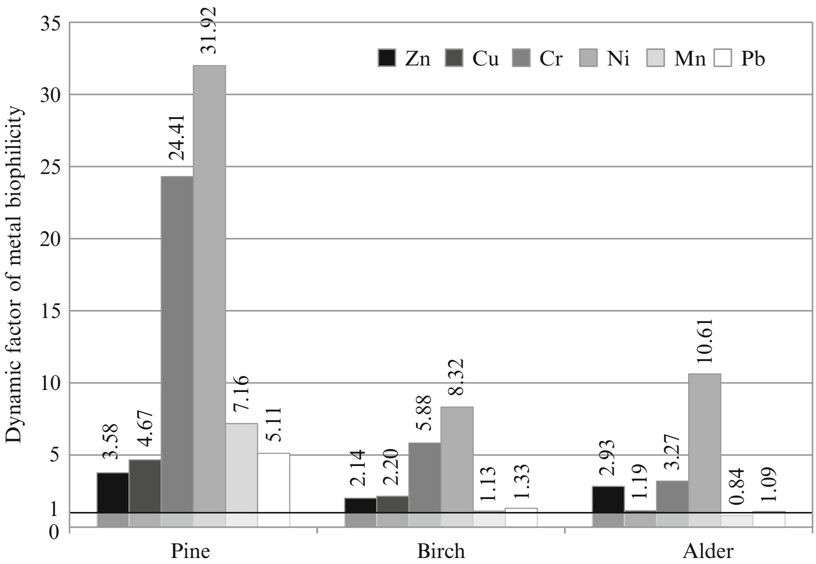

Fig. 5.2 Dynamic factor of metal biophilicity (BF_{dyn}). Values greater than one signify a metal's increase compared to control territory; values less than one indicate its decrease

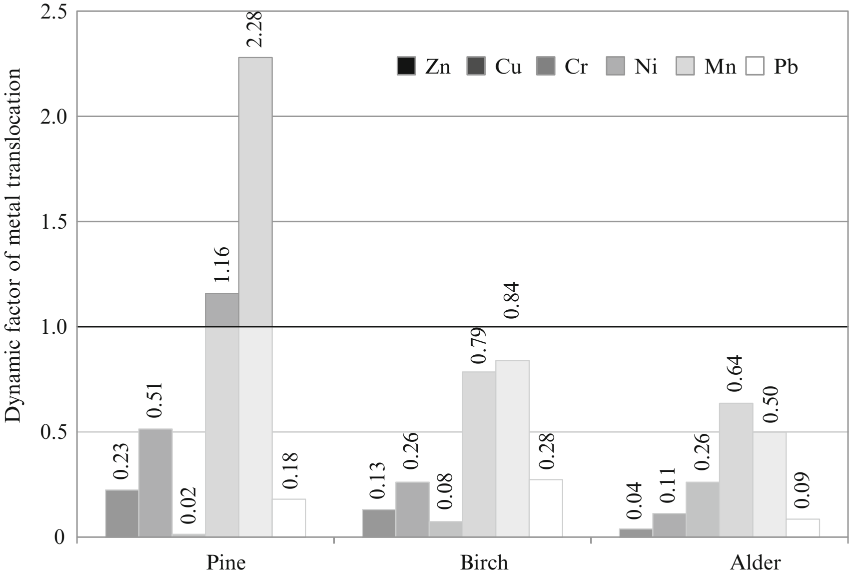

Fig. 5.3 Dynamic factor of metal translocation (TR_{dyn}). Values greater than one show its increase compared with control territory; values less than one indicate its decrease

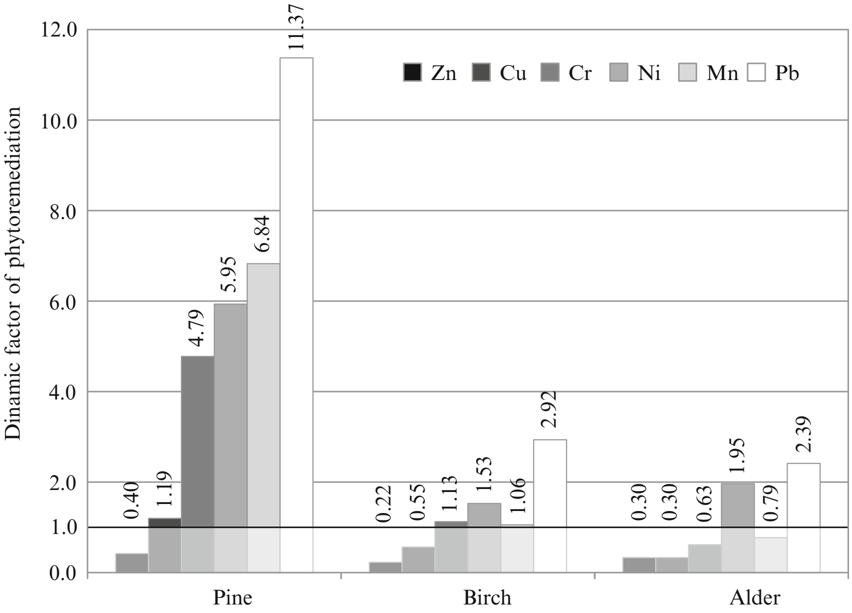

Fig. 5.4 Dynamic factor of phytoremediation (FR_{dyn}). Values greater than one signify an increase in this process compared with control territory; values less than one indicate its decrease

concentration of metals in plants compared to their concentration in the soil. Pines also demonstrated the highest BF_{dyn} values with respect to the considered metals.

The opposite trends could be observed for Mn and Ni, whose TR_{dyn} factor values were greater than one, but only in the case of the alder (Fig. 5.3). For the other metals, this factor indicated a decreased metal translocation in the contaminated territory compared to that found in the control territory.

The dynamic phytoremediation factor FR_{dyn} reflects the individual phytoremediation abilities of the examined trees. The FR_{dyn} value was the highest for the pine and particularly large in the case of Pb (Fig. 5.4).

Advantages of Dynamic Factors

Some advantages of the dynamic factors have already been mentioned. We will now present more factors and give a more detailed description of their application for various purposes.

(a) *Dynamic factors allow us to compare the differences in translocation of metals in various plants (trees), depending on the geochemical properties of the soil in the examined territory.*

Dynamic factors make it possible not only to compare plants according to their ability to accumulate metals but also to assess the changes taking place in metal transfer in the soil that is modified (e.g., by adding sludge to it) compared to soil in the control area, which is similar to it from a geochemical perspective in all respects except for the modification made.

We can see that the investigated pine differs from the other two tree species growing in the soil on whose surface sludge was spread because the translocation of metals in it is more intense than in the birch and alder compared to the control territory. This is indicated by higher values of BA_{dyn}, BF_{dyn}, and FR_{dyn}, which means that, on the one hand, pines accumulate larger amounts of metals than other investigated trees, and this process intensifies with the growth of soil pollution with metals. This fact was also pointed out by Kovalevsky (1987), who studied the mechanisms of the transfer of metals to trees in nonpolluted territories. He reported that nonbarrier accumulation of Pb and Cu is characteristic of pines. On the other hand, more intense metal accumulation by pines could indicate that they have weaker protective functions and lower resistance to environmental pollution than birches and alders.

Less intense photosynthesis and lower resistance of pines to environmental pollution than compared to birches have also been reported by Neverova and Iagodkina (2010). Thus, coniferous trees (as the case study of pines has shown) could be more strongly affected by metal load than deciduous trees.

The analysis yielded the highest TR_{dyn} value for alder with respect to all metals except Pb, for which the TR_{dyn} value was higher in the birch, and Cr was higher for pine. Thus, the translocation of substances (including metals) from a plant's roots to the vegetative organs is more intense in the polluted territory. It is known that deciduous trees transpire more intensively than coniferous trees, and the comparative transpiration intensity of tree vegetative organs (where that of larch is equal to 1) (according to L. Ivanov) decreases in the following sequence: 2.59 for *Alnus glutinosa*, 2.41 for *Betula pendula*, and only 0.6 for *Pinus sylvestris* L. (Zimmermann and Milburn 1982).

(b) *Dynamic factors allow for proper comparison of the modified soil effects on the participation of chemical elements (including metals) in the metabolism of plants (including trees).*

Human activities are considered to be a stress factor acting on plants, while metals are classified as substances that produce harmful effects (Kupčinskienė 2011) on plant metabolism and cause other negative effects. Soil pollution with metal-contaminated sludge is also considered a stress factor, while the participation of the considered metals in the metabolism of trees is reflected in the dynamic factors of biophilicity and bioaccumulation, as well as in the changed biophilicity sequence of metals. Soil modification increases the biophilicity of such metals as Ni and Cr in the analyzed trees because the comparison of our case with the biophilicity sequence in connection with the plant biomass in the world – $\mathrm{Zn}_{\mathbf{19.6}}$ $\mathrm{Cu}_{\mathbf{9.1}}$ $\mathrm{Mn}_{\mathbf{6.9}}$ $\mathrm{Pb}_{\mathbf{3.7}}$ $\mathrm{Ni}_{\mathbf{1.5}}$ $\mathrm{Cr}_{\mathbf{1.0}}$ (Dobrovolskii 2008) – shows that Ni and Cr have "moved" to the beginning of the sequence[5]:

Pinus sylvestris L. : $\mathbf{Ni_{31.94}Cr_{24.41}Mn_{7.16}Pb_{5.11}Cu_{4.67}Zn_{3.85}}$

Betula pendula : $\mathbf{Ni_{8.32}Cr_{5.88}Cu_{2.20}Zn_{2.14}Pb_{1.33}Mn_{1.13}}$

Alnus glutinosa : $\mathbf{Ni_{10.61}Cr_{3.27}Zn_{2.93}Cu_{1.19}Pb_{1.09}}Mn_{0.84}$

In addition, the values of Ni and Cr $\mathrm{BA}_{\mathrm{dyn}}$, as well as $\mathrm{BF}_{\mathrm{dyn}}$, were greater than one for all the trees tested. These metals are known to be active participants in the processes taking place in trees experiencing the effects of stress factors. Jhee et al. (2005) determined that Ni stimulates metabolism and increases the permeability of the cell walls of trees affected by stress factors, while Cr is a stimulator of their lignification. Increased concentrations of Ni and Cr have also been observed in pinewood affected by biotic factors (Baltrėnaitė and Butkus 2006).

(c) *The dynamic factor of phytoremediation helps us to more precisely evaluate its effectiveness.*

$\mathrm{FR}_{\mathrm{dyn}}$ helps us to determine the most suitable plant for phytoremediation purposes. The results obtained in the present research have shown that the investigated pine differed from other trees in its ability to accumulate larger amounts of metals and remove them from the modified soil where they grew.

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[5] The indices found in the biophilicity sequences correspond to biophilicity factors expressing the relationship between the accumulation of metals in living biomass and metal concentration in Earth's crust with respect to world vegetation or soil of particular territories.

Thus, during the year, it removed from 0.07–0.15 % (Cu, Pb, Ni, and Zn) to 0.23–0.29 % (Cr and Mn) of metals accumulated in the upper 40-cm-thick soil layer. At the same time, the effectiveness of purification of sludge-polluted soil by the birch was equal to 0.04–0.07 % (Cr, Cu, Pb, and Ni) and 0.2–0.3 % (Zn, Mn), while the effectiveness of the alder reached 0.01–0.04 % (Cr, Mn, Cu, Pb and Ni) and 0.1 % (Zn). Compared to the data on the control territory, the pine was more effective at accumulating and thereby removing ($FR_{dyn} > 1$) from the polluted soil such metals as Ni, Mn, Cu, Cr, and Pb, while the birch and the alder were more effective at accumulating and removing Pb, Ni, and Cr and Pb and Ni, respectively.

The results on the application of the dynamic factor of bioavailability were presented in Chap. 3.

5.3 Modeling of Metal Transfer in Air–Tree–Soil System

As described in Chap. 3, the vast majority of metals that enter forest ecosystems are bound to particulate matter that are later deposited on the surface by dry or wet deposition. The first two models presented in this chapter were used to evaluate the dispersion patterns of particulate matter and metals carried by these particles from stationary pollution sources.

Results of Modeling the Spread of Particulate Matter

The goal of simulation presented in this work is to assess the distance from the source of pollution (AB *ORLEN Lietuva*) through which particulate matter is transferred. For modeling purposes, two simulation programs for the spread of stiff particles – ADMS4 (Atmospheric Dispersion Modeling System) and AERO2 – were used. ADMS4 has been used to evaluate the spread of the general emission of particulate matter from all sources of contamination, whereas AERO2 allows one to assess the spread of particles from an individual source.

ADMS4 is a model for the dispersion of a close transfer of contaminants and allows one to assess the spread of suspended and passive releases in the atmosphere. This model evaluates the tropospheric layer according to two characteristic parameters – the tropospheric layer and the so called Monin–Obukhov length. The selected distribution of Gaussian concentration is used for assessing the dispersion of contaminants under convective conditions. ADMS4 is suitable for simulating the spread of pollution up to 60 km downwind (Fig. 5.5).

ADMS4 is linked to other programs such as Surfer, ArcGIS, MapInfo, and ArcView GIS (Geographical Information System) that allow one to illustrate the results of simulation or ease data input. ADMS4 is employed for receiving pollution permits, determining the height of a smokestack, assessing environmental impact, and developing plans for safety and accident removal.

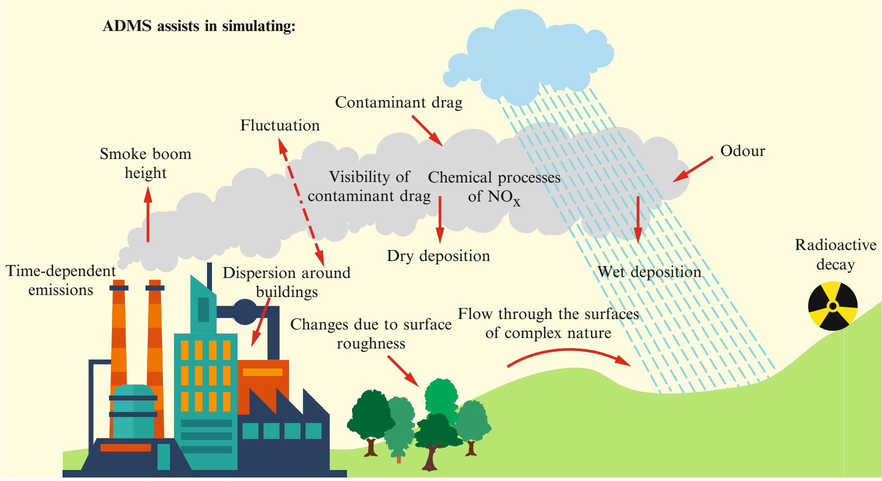

Fig. 5.5 Environmental processes assessed with using ADMS4 model (according to CERS)

The Gaussian plume model is most frequently used for simulating emissions from one or several stationary point sources of pollution. Under convective meteorological conditions, the dispersion of contaminants is more accurately defined by a skewed rather than symmetric Gaussian distribution. One of the preconditions for this model is that, within a short period of time (for instance, several hours), steady air pollution and meteorological conditions are established. Air pollution is represented by the idealized flow removed from a smokestack considering a characteristic height and diameter.

Equation (5.6) presents the field of the concentrations of three dimensions, which is formed from contamination sources under stationary meteorological and emission conditions (Vaitiekūnas and Špakauskas 2003):

$$C(x,y,z) = \frac{Q}{2 \cdot \pi \cdot u \cdot \sigma_y \cdot \sigma_z} \exp\left[-\frac{1}{2}\left(\frac{y^2}{\sigma_y^2}\right)\right] \left\{\exp\left[-\frac{1}{2}\left(\frac{(z-H)^2}{\sigma_z^2}\right)\right] + \exp\left[-\frac{1}{2}\left(\frac{(z+H)^2}{\sigma_z^2}\right)\right]\right\}, \tag{5.6}$$

where C is the contaminant concentration (mg/m^3), Q is the rate of emissions from the smokestack (mg/s), σy and σz are the dispersion of the concentration of a plume in the direction of the y- and z-axes, H is the effective height of the contamination source (m), u is the wind speed (m/s), and z is the altitude of the point from Earth's surface (m), the place where the concentration of contaminants is assessed (if the concentration close to Earth's surface needs to be established, $z = 0$), where y is the spread of the plume in terms of the y-axis.

In the majority of cases, attention is paid to the values of the ground-level concentrations of emissions (Eq. 5.7):

$$C(x,y,z) = \frac{Q}{2 \cdot \pi \cdot u \cdot \sigma_y \cdot \sigma_z} \exp\left[-\frac{1}{2}\left(\frac{y^2}{\sigma_y^2}\right)\right] \exp\left[-\frac{1}{2}\left(\frac{H^2}{\sigma_z^2}\right)\right]. \tag{5.7}$$

The ADMS4 model evaluates the following aspects:

- Concentrations have a characteristic Gaussian distribution under stable and neutral conditions;
- Meteorological conditions such as wind speed, cloudiness, surface heat flow, and the height of the tropospheric layer are taken into account;
- The modules of the ADMS4 program allow one to assess the height of a rising flow, surface roughness of the area, street canyons, noise barriers, and buildings;
- Chemical variations in NO_x (related to NO, NO_2, O_3, LOJ) are thoroughly evaluated. The model also considers changes in the concentrations of primary and secondary contaminants.

The other program, AERO2, was used in the work by Lietuvninkas (2005). The concentration of aerogenic pollutants in air is calculated considering unfavorable meteorological conditions and dangerous wind speeds. The following equations serve as a basis for calculating an algorithm for AERO2:

1. *The highest ground-level concentration of the contaminant* (C_M) (mg/m^3) under unfavorable meteorological conditions and dangerous wind speeds is calculated according to Eq. (5.8):

$$C_M = \frac{A \cdot M \cdot F \cdot m \cdot n \cdot \eta}{H^2 \cdot \sqrt[3]{V_1 \cdot \Delta T},} \tag{5.8}$$

   where A is an index assessing atmospheric stratification (air mass formation in layers); F is a dimensionless index assessing the deposition rate of contaminants in the atmosphere and subject to the dispersivity of particulate matter, usually the efficiency of air treatment equipment (gas pollutants $F = 1$, particulate matter $F = 2$ when the efficiency of treatment equipment exceeds 90 %, $F = 2.5$ when the efficiency of treatment equipment reaches 75–90 %, and $F = 3$ when the efficiency of treatment equipment is less than 75 %); M is the emission of a contaminant per unit of time (g/s); m and n are indexes assessing conditions for the emission of a contaminant; η is a dimensionless index assessing the impact of the local relief (in the investigated case, $\eta - 1$, since at a distance of 1 km the altitude of the relief is lower than 50 m); H is the height of the contamination source (smokestack) (m); V_1 is the content of the gas emitted from the smokestack (m^3/s); and ΔT is the difference between gas emitted from the contamination source and ambient air temperatures (°C).
2. *Dangerous wind speed* (U_M) (m/s), under which the highest ground-level concentration (C_M) of the available contaminants considering specified conditions is

reached, in the majority of cases, depends on the auxiliary coefficient (V_{M}) calculated according to Eq. (5.9):

$$V_{\mathrm{M}} = 0.65 \cdot \sqrt[3]{\frac{V_1 \cdot \Delta T}{H}}. \tag{5.9}$$

If $V_{\mathrm{M}} \leq 0.5$, then the wind speed $U_{\mathrm{M}} = 0.5$ m/s is considered dangerous; if $0.5 < V_{\mathrm{M}} \leq 2$, then $U_{\mathrm{M}} = V_{\mathrm{M}}$; if $V_{\mathrm{M}} > 2$, then the dangerous wind speed (U_{M}) is calculated with reference to a more complex equation.

3. *The distance from the contamination source* (X_{M}) (m) where, under unfavorable meteorological conditions, the highest concentrations (C_{M}) of contaminants form, is calculated according to Eq. (5.10):

$$X_{\mathrm{M}} = \frac{(5 - F) \cdot d \cdot H}{4}, \tag{5.10}$$

where d is a dimensionless index that depends on conditions for the emission of contaminants and the parameters of the smokestack.

4. *The highest concentration of contaminants in the ground-level air,* depending on wind speed (C_{MM}) (mg/m^3), under unfavorable meteorological conditions is estimated according to Eqs. (5.11)–(5.13):

$$C_{\mathrm{MM}} = r \cdot C_{\mathrm{M}}, \tag{5.11}$$

$$r = 0.67 \cdot \left(\frac{U}{U_{\mathrm{M}}}\right) + 1.67 \cdot \left(\frac{U}{U_{\mathrm{M}}}\right)^2 - 1.34 \cdot \left(\frac{U}{U_{\mathrm{M}}}\right)^3, \quad \text{if} \quad \frac{U}{U_{\mathrm{M}}} \leq 1, \tag{5.12}$$

$$r = \frac{3 \cdot U}{U + (2 \cdot U_{\mathrm{M}})}, \quad \text{if} \quad \frac{U}{U_{\mathrm{M}}} > 1, \tag{5.13}$$

where C_{M} is the highest ground-level concentration of the contaminant (mg/m^3) under unfavorable meteorological conditions and a dangerous wind speed U_{M}, and r is a dimensionless index that depends on the ratio of the present wind speed to the dangerous wind speed U_{M}.

In the investigated case, all six stationary point sources of contamination (smokestacks) at AB ORLEN Lietuva – 45, 76, 120 m, with two reaching 180 m but having different parameters and one reaching 205 m in height[6] – were examined. Every source of contamination is described according to its height, the diameter of the exhaust vent in the smokestack, the rate of contamination flow, temperature, and coordinates (x, y).

Data on meteorological conditions (average per hour) were received from the automated air quality monitoring station of the Environmental Protection Agency

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[6] According to the requirements of ADMS4, only pollution sources more than 10 m high were studied.

(Ventos str. 27, Mažeikiai). The oil refinery is localized in an open area and surrounded by fields and meadows, and therefore the coefficient of surface roughness (*P*) is chosen to be equal to 0.16 (Vaitiekūnas and Špakauskas 2003).

The value of the dimensionless index assessing the precipitation rate of contaminants and the efficiency of treatment equipment removing gas through the smokestack (*F*) has been selected to be equal to 2 because the efficiency of air treatment equipment is higher than 90 %. The highest concentration of particulate matter was established under unfavorable meteorological conditions (highest air temperature in summer and a constant atmospheric condition) and dangerous wind speed. The visualization program SURFER was used to show the results of simulating data input.

A smokestack 120 m in height emits the highest content of particulate matter compared to emissions from other sources of contamination. The AERO2 program was used to establish the highest concentration of particulate matter (12 μg/m^3) reached at a smokestack 120 m in height under a dangerous wind speed of 6.4 m/s (Fig. 5.6).

In all cases, the highest concentration of particulate matter in air is achieved under certain speeds of dangerous wind. The highest concentration of particulate matter (12 μg/m^3) is related to emissions from a smokestack 120 m in height and likely at a distance of 2 km from the contamination source (Fig. 5.7). Meanwhile, the highest concentration of particulate matter emitted from the investigated lowest

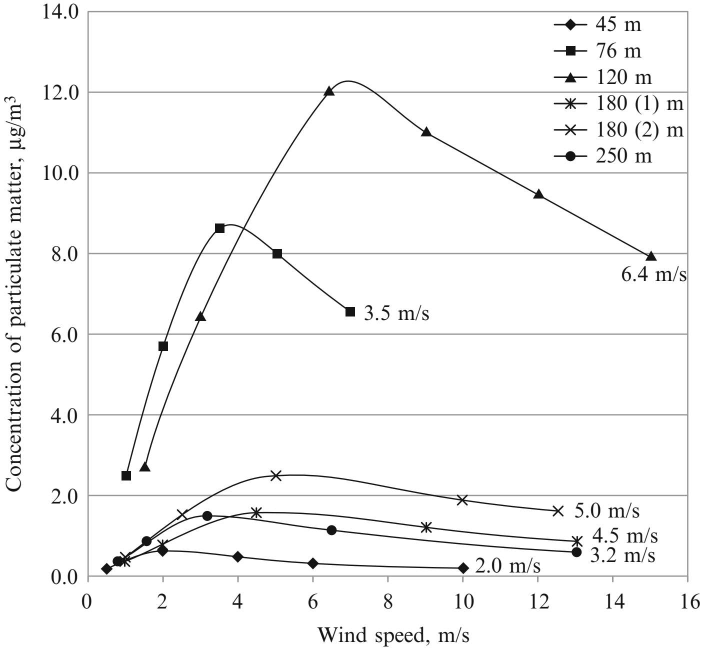


Fig. 5.6 Dependence of highest concentrations of particulate matter and dangerous wind speed, shown in figures in charts, on smokestack height and parameters of emitted contaminants

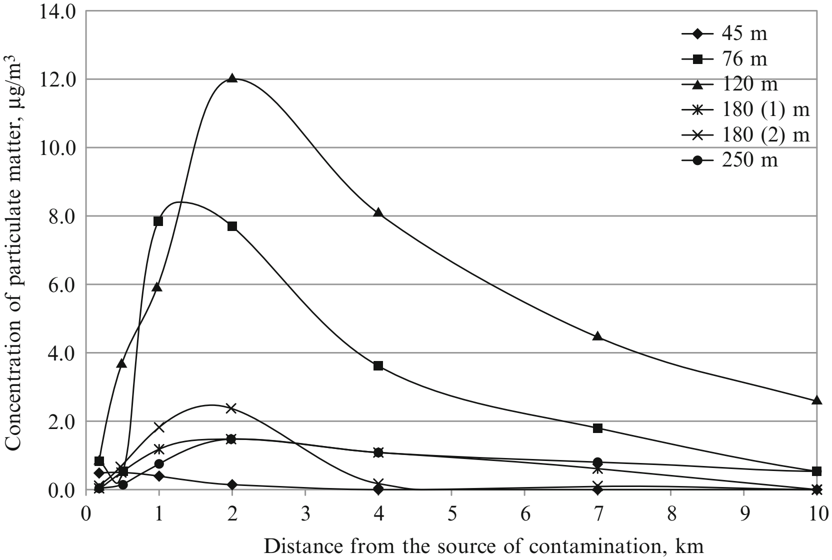


Fig. 5.7 Distribution of concentration of particulate matter as a function of distance from different contamination sources whose height is denoted by conventional signs

smokestack ($H = 45$ m) is probably closest to the source of contamination (up to 0.5 km) compared to other generated pollution sources and maximum concentrations in air (Fig. 5.7).

The greatest concentration of particulate matter (1.5 µg/m^3) from the highest smokestack (250 m) was found at a distance of 2 km from the source of contamination. The general contribution of individual smokestacks to the contamination of ground-level air with particulate matter at different distances from contamination sources is shown in Fig. 5.7.

To define the impact of the height of contamination sources (smokestacks) on the concentration of particulate matter, the concentrations of stiff particles from smokestacks 250 and 120 m in height with the same parameters of emission input were compared. Simulation findings confirmed that a lower smokestack produces the highest concentrations of particulate matter closer to the source of contamination (Fig. 5.8).

Using the ADMS4 program, the dispersion of particulate matter from more than one source of contamination was assessed. The distribution of stiff particles within a day was considered to be 90.4 %. The maximum daily concentration of particulate matter reached 4.5 µg/m^3 and did not exceed the allowed value of 50 µg/m^3.

The hourly concentration also did not exceed the highest allowable value of particulate matter of 40 µg/m^3. The highest concentration of stiff particles per hour was found to be 1.2 µg/m^3. The distribution of daily and hourly concentrations of particulate matter is shown in Figs. 5.9 and 5.10.

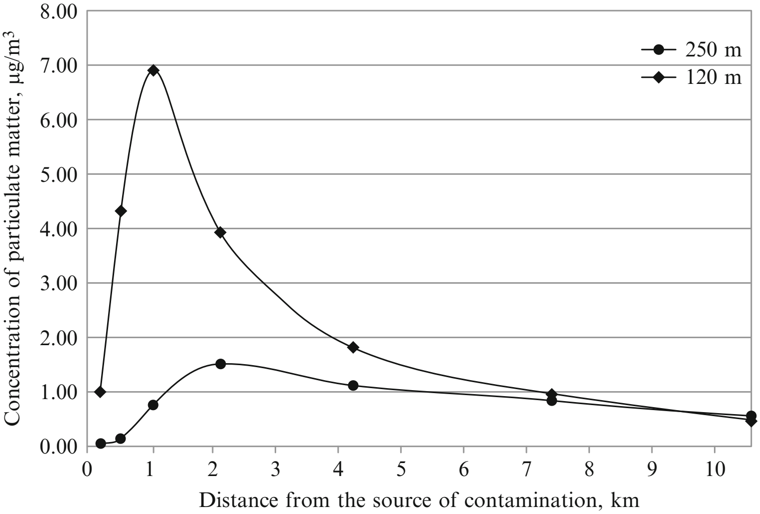


Fig. 5.8 Variations in distribution of concentration of particulate matter depending on the height of the contamination source

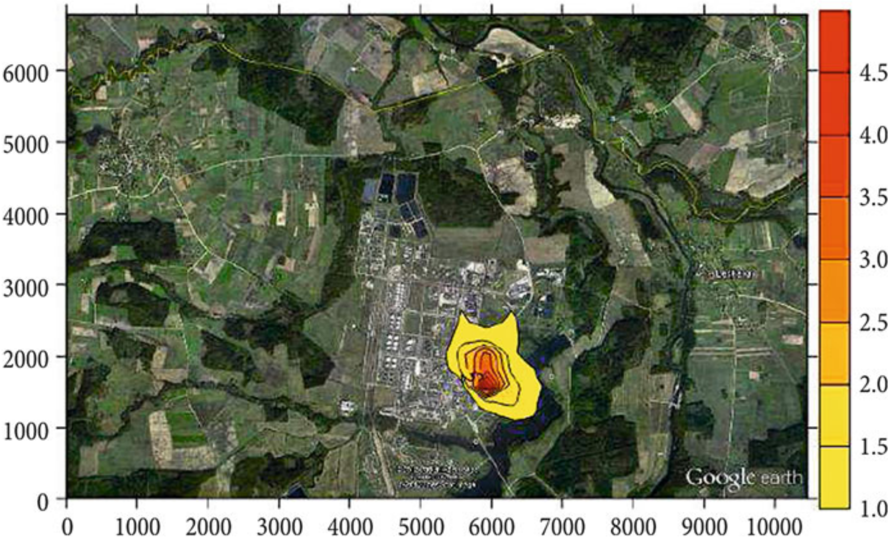


Fig. 5.9 Distribution of daily concentration of particulate matter based on readings of color scale $\mu g/m^3$ (distance in meters is given on ordinate and abscissa axes)

The highest concentration of particulate matter was established at a distance of 1.5–2.2 km from the source of contamination. The ascertained hourly and daily concentrations of particulate matter were found to be lower than the allowable levels, and therefore, it can be asserted that the oil refinery, in terms of concentration, has no significant impact on the quality of ambient air.

Fig. 5.10 Distribution of hourly concentration of particulate matter based on readings of color scale μg/m^3 (distance in meters is given on ordinate and abscissa axes)

To display a pattern in how particulate matter precipitated on the ground surface (snow cover), the results of simulation were compared with a daily snow dust load and insoluble concentrations of metals in snow dust. The highest concentrations of metals in snow dust and the largest snow dust load were established at a distance of 1.5–2 km from the source of contamination, i.e., at a similar distance where the highest concentrations of particulate matter were obtained using simulation software ADMS4 and AERO2.

Modeling the Translocation of Metals in the Soil–Tree System

The translocation of metals from the soil to a tree involves various chemical, physical, and biological processes (e.g., diffusion of metals in soil and trees as well as in the area of the roots and the tree itself, adsorption and absorption in the tree and soil, the growth of the tree and transpiration). Because of the complicated nature of these processes and the action of external factors (e.g., climatic conditions, type of substrate), it is nearly impossible to accurately describe them by mathematical equations.

Therefore, the models found in the literature describing the transfer of pollutants from soil to trees are rather simplified descriptions, usually based on a few transfer coefficients and the evaluation of the transfer of pollutants only to the whole tree organism. To create more complicated models of pollutant translocation, huge computing resources, as well as great amounts of experimental data, making it possible to validate the accuracy of the developed models, are required.

In this subsection, a model showing the transfer of metals from sludge-amended soil that is based on a simplified model of pollutant transfer from soil to plants proposed by Hung and Mackay (1997) is described. This model can be used to evaluate the transfer of pollutants from soil to trees through the stem, from the stem to the leaves, from the leaves to the air, from the air to the leaves, from the leaves to the stem, and from the stem to the tree roots. In this model, penetration of pollutants from soil to plants is based on equilibrium factors describing the distribution of pollutants in various media (e.g., soil, water, transpiration flow), as well as on the rate of metabolism and time of diffusion. The time of the growth of the main plant organs is also evaluated.

Modeling the transfer of metals to plants is a more complicated problem than that associated with the transfer of organic pollutants (e.g., benzopyrene, naphthalene) because, unlike organic pollutants, metals are significant for physiological processes occurring in plants, such as, for example, their growth, metabolism, and fermentation.

Therefore, the distribution of metal concentrations between octanol and water (K_{ow}) is not the only important factor in the accumulation of metals in plants. The coefficients of biological uptake of metals by plants and their translocation are also required for modeling.

The main Eqs. (5.14)–(5.16), giving the concentration of pollutants in leaves (C_{lap}), stem (C_{kam}), and roots (C_{sak}) used in the present model are provided as follows:

$$C_{\mathrm{lap}} = \left(\frac{B_{\mathrm{er}} \cdot B_{\mathrm{rs}} \cdot B_{\mathrm{sl}} \cdot K_{\mathrm{lw}} \cdot C_{\mathrm{dirv}}}{K_{\mathrm{ew}}} + \frac{B_{\mathrm{al}} \cdot K_{\mathrm{lw}} \cdot C_{\mathrm{a}}}{K_{\mathrm{aw}}} \right) \cdot \frac{M_{\mathrm{SM}}}{\rho_{\mathrm{lap}}}, \tag{5.14}$$

$$C_{\mathrm{kam}} = \left(\frac{B_{\mathrm{er}} \cdot B_{\mathrm{rs}} \cdot K_{\mathrm{stw}} \cdot C_{\mathrm{dirv}}}{K_{\mathrm{ew}}} + \frac{B_{\mathrm{al}} \cdot B_{\mathrm{ls}} \cdot K_{\mathrm{stw}} \cdot C_{\mathrm{a}}}{K_{\mathrm{aw}}} \right) \cdot \frac{M_{\mathrm{SM}}}{\rho_{\mathrm{kam}}}, \tag{5.15}$$

$$C_{\mathrm{sak}} = \left(\frac{B_{\mathrm{er}} \cdot K_{\mathrm{rw}} \cdot C_{\mathrm{dirv}}}{K_{\mathrm{ew}}} + \frac{B_{\mathrm{al}} \cdot B_{\mathrm{ls}} \cdot B_{\mathrm{sr}} \cdot K_{\mathrm{rw}} \cdot C_{\mathrm{a}}}{K_{\mathrm{aw}}} \right) \cdot \frac{M_{\mathrm{SM}}}{\rho_{\mathrm{?ak}}}. \tag{5.16}$$

In the model, the achieved level of pollutant concentrations in the leaves, stem, and roots of the plants is evaluated using Eqs. (5.17)–(5.19):

$$A_{\mathrm{lap}} = 1 - \mathrm{e}^{-0.639 \frac{t}{T_{\mathrm{L}}}}, \tag{5.17}$$

$$A_{\mathrm{kam}} = 1 - \mathrm{e}^{-0.639 \frac{t}{T_{\mathrm{K}}}}, \tag{5.18}$$

$$A_{\mathrm{sak}} = 1 - \mathrm{e}^{-0.639\frac{t}{T_{\mathrm{R}}}}, \tag{5.19}$$

where T_{L}, T_{K}, T_{R} are half of the dying-off period of the cells of an ordinary leaf, stem, and roots (h). The variables for equations and measuring units of their values are given in Table 5.1.

Table 5.1 Input and computed parameters to model uptake of metals by young trees

Parameter	Marking	Unit
Leaf surface area	L_{P}	m^2
Transpiration rate	Q	m^3/h
Growth and metabolism		
Growth rate of leaves	τ_{LG}	1/h
Growth rate of stem	τS_{G}	1/h
Growth rate of roots	τR_{G}	1/h
Metabolism rate for leaves	τ_{LM}	1/h
Metabolism rate for stem	τ_{SM}	1/h
Metabolism rate for roots	τ_{RM}	1/h
Density of leaves	ρ_{lap}	$\mathrm{kg/m}^3$
Density of stem	ρ_{kam}	$\mathrm{kg/m}^3$
Density of roots	$\rho_{\check{\mathrm{s}}\mathrm{ak}}$	$\mathrm{kg/m}^3$
Exposure duration of metals	t	h
Molar mass of metal	M_{HM}	g/mol
Concentration of metal in air	C_{a}	$\mathrm{mmol/m}^3$
Equilibrium partitioning coefficients		
Carbohydrate–water	K_{cw}	Dimensionless
Octanol–water	K_{ow}	Dimensionless
Air–water	K_{aw}	Dimensionless
Leaves–water	K_{lw}	Dimensionless
Stem–water	K_{stw}	Dimensionless
Root–water	K_{rw}	Dimensionless
Soil–water	K_{ew}	Dimensionless
Sap–water	K_{xw}	Dimensionless
Octanol–air	K_{oa}	Dimensionless
Diffusion fraction in xylem flow	Φ	h
Characteristic time through cuticle	T_ku	h
Characteristic time through air	$T\_sr.or$	h
Ratios of metal uptake		
From air to leaves	B_{al}	Dimensionless
From leaves to stem	B_{ls}	Dimensionless
From stem to leaves	B_{sl}	Dimensionless
From stem to roots	B_{sr}	Dimensionless
From roots to stem	B_{rs}	Dimensionless
From soil to roots	B_{er}	Dimensionless
Total concentration of metal in soil	C_{soil}	mg/kg

The processes considered in the presented model are not associated with the specific features of pollutants. For example, the solution of a pollutant in a plant was not modeled; therefore, this model can be adapted to modeling the translocation of pollutants from the soil to a tree.

To adapt the considered model to modeling the translocation of metals, it was extended to include:

- A factor characterizing the distribution of metal concentrations between octanol and water (K_{ow});
- A factor characterizing the distribution of metal concentrations between soil and water (K_d), which depends on soil pH and the amount of organic material;
- The coefficient of the metals' solution in water (K_T);
- Correction factors.

The characteristic values of metals and the related references are given in Table 5.2.

Then the transfer of metals from sludge-amended soil to the roots, stems, leaves, and needles of deciduous and coniferous trees was modeled. Since the examined territory was far from the sources of possible aerogenic pollution with metals, it was assumed that metals' concentration in the air was around zero, while the transfer of metals from the air to the leaves and needles and then lower toward the roots was insignificant.

In the process of modeling, wood density was evaluated as follows: 863 kg/m^3 for the pine, 878 kg/m^3 for the birch, and 827 kg/m^3 for the alder (Verbyla 1990), while the average density of sludge was 1520 kg/m^3. During the experiment, the average volume of the roots, stems, and leaves of the young trees was also

Table 5.2 Values and molar masses of metals

Parameter and units	Metal						Reference
	Cu	Ni	Mn	Pb	Cr	Zn	
Molar mass, g/mol	63.5	59	55	207.2	52	65.3	
K_d at pH 4.5–6.0, l/kg	–	12–650	1126–2063	4219–12,904	16.8–360	16–530	Jose and Pillai (1996)
Log K_d for soil, l/kg	0.1–3.6	1.0–3.8	–	0.7–5.0	–0.7 to 4.7	–1.0 to 5.0	Allison and Allison (2005)
K_{ow}	200	120	140	40	200	110	Turner and Mawji (2005)
Concentration of metals in soil amended with industrial sewage sludge, mg/kg	143	46.5	698	1000	107	471	Katinas et al. (2002)

determined: 0.001, 0.002, and 0.00013 m^3 for the examined deciduous trees, respectively, and 0.001, 0.003, and 0.00013 m^3 for coniferous trees.

The rate of metabolism in the roots, stems, leaves, and needles of the trees was assumed to be the rate given in the model because these values were mentioned when physiological processes taking place in maples and translocation of metals in them were considered and evaluated (Tsiros et al. 1999).

In modeling the transfer of metals to young trees, the concentration of metals in soil was assumed to be the same as their concentration in sludge mixed with soil (Table 5.2).

Though the depth of the sludge spread on the soil surface reached 3 cm, the data provided by researchers studying the variation of metal concentrations in a particular territory show that, in a year, the mobile forms of metals penetrated soil in which great masses of roots (particularly fine roots, which play an important role in metal absorption from soil) were concentrated, to a depth of 10–20 cm. When data on the concentration of metals are introduced into the model, the value is multiplied by the mean coefficient of the metals' absorption from the soil solution ($K_{ad} = 0.3$) (Verma et al. 2006). The time of modeling metal translocation in the soil–tree system was 6 years, though emphasis was placed on the setting in of the constant metals' concentration in various parts of a plant, rather than on the time period of modeling (Eqs. 5.17–5.19). The largest amount of metals penetrates into plants during the first years after sludge spreading and planting of young trees.

The modeled values of metals' translocation from sludge-polluted soil to young trees were corrected by applying the correction coefficients and compared to metals' values determined for tree organs in the experimental investigation.

Data on metal transfer from soil to the roots, stems, and leaves or needles of young deciduous and coniferous trees are given in Fig. 5.11. Different concentrations of metals in the young coniferous and deciduous trees may be attributed to a heterogeneous sludge composition, different kinds of young trees, or root systems, for example.

The values obtained for coniferous trees were close to their experimental values and varied within the range of admissible errors. The modeled metals' concentrations in young coniferous trees varied as follows: Zn from 25.9 to 66.5 mg/kg, Cu from 2.22 to 9.59 mg/kg, Mn from 28.8 to 179.1 mg/kg, Ni from 15.9 to 20.9 mg/kg, and Pb from 0.41 to 3.27 mg/kg. A trend of gradually decreasing Pb and Zn concentration in the direction from roots to leaves could be clearly observed. An opposite trend was observed for Mn concentration. The concentration of Ni in the organs of young coniferous trees varied slightly. The highest concentration of Cu was found in the stems of these trees. In modeling metal translocation from the soil to coniferous trees, the correction coefficients were corrected to vary from 1 to 3 for the rate of metal translocation from soil to roots, from 0.1 to 0.6 for the rate of translocation from roots to stem, and from 0.1 to 9 for the intensity of translocation from stem to leaves.

The data obtained in modeling metal concentrations in young deciduous trees differed slightly from the corresponding experimentally obtained values; however, these differences were in the range of admissible errors. The modeled metal

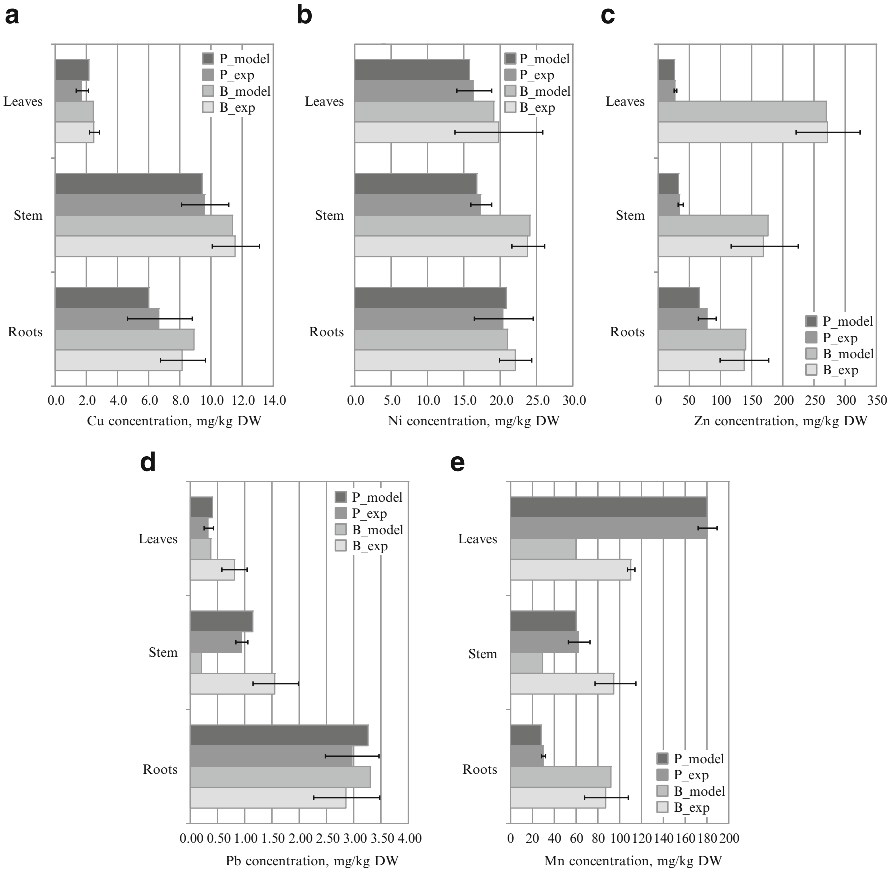


Fig 5.11 Concentrations of metals: (**a**) Cu ; (**b**) Ni; (**c**) Zn; (**d**) Pb; (**e**) Mn in different organs of young coniferous and deciduous trees: the values obtained in modeling are given in *lighter colors*, while the experimental data are shown by *darker colours*; *bars* represent standard error values

concentrations in the young trees were as follows: from 141 to 270 mg/kg for Zn, from 2.51 to 11.45 mg/kg for Cu, from 84.7 to 118.8 mg/kg for Mn, from 19.2 to 24.2 mg/kg for Ni, and from 0.01 to 3.30 mg/kg for Pb.

In the case of Mn and Zn, an increasing trend of their concentration from roots to leaves could be observed. An opposite trend could be observed for Pb concentration. The concentration of Ni in various parts of young deciduous trees varied insignificantly, while in the case of Cu, the highest metal concentration could be observed in the stem.

In modeling metal translocation from the soil to deciduous trees, the correction coefficients were corrected to vary from 1 to 3 for the rate of metal translocation from soil to roots, from 0.25 to 0.35 for the rate of translocation from roots to the stem, and from 0.5 to 4 for the intensity of translocation from the stem to leaves.

The results of modeling have shown that the model used in the investigation may be applied to modeling metal translocation to young coniferous and deciduous trees because, when the appropriate values of the correction coefficients are chosen, the results obtained in modeling are close to the experimental values and vary within the range of standard error values.

To model metal translocation from sludge-amended soil to young deciduous trees in the conditions of our study, the following correction coefficients were used: for translocation from soil to roots, 1.5 (Zn and Cu) and 3.0 (Ni and Mn); for translocation from roots to stem, 0.25 (Pb, Mn, and Cu), 0.35 (Zn), and 0.30 (Ni); for translocation from stem to leaves, 0.5 (Pb), 3.0 (Ni), 4.0 (Mn), and 6.0 (Zn). The correction coefficients for metal translocation in coniferous trees were as follows: from soil to roots, 3.0 (Ni and Mn); from roots to stem, 0.1 (Zn and Pb), 0.25 (Ni), 0.5 (Cu), and 0.6 (Mn); from stem to leaves, 0.1 (Zn, Pb, and Cu), 3.5 (Ni), and 9.0 (Mn).

In using the considered model, the average correlation coefficient value of metal translocation from the sludge-amended soil to the roots of deciduous trees was 2.0, from roots to stem it was 0.28, and from stem to leaves it was 2.9. For coniferous trees these values were 1.8, 0.31, and 2.56, respectively.

Phytotechnologies Involving Pine and Birch: Environmental Protection and Economic Assessment of Efficiency

The Phyto-DSS model is designed for assessing the use of plants in phytotechnologies taking up chemical substances from soil and thus decreasing soil decontamination. The model is used to simulate the transfer of chemical pollutants from soil to plants and for processes having an impact on accumulation in plants: plant growth, the transfer of water flow or a chemical element (e.g., contaminant or nutrients). For an economic assessment of the efficiency of phytoextraction, the model uses a cost–benefit analysis when large areas of vegetation are investigated. A similar simulation will reveal the possibilities, risks, and potential benefits of phytomanagement. The algorithm for the model includes information about climate and the properties of soil and plants. The economical assessment of phytoextraction is carried out making a comparison of phytoremediation costs with inactivity costs and other best alternatives to technologies for soil restoration.

The Phyto-DSS model was created at the Institute of Natural Resources and Agrobiology of Seville, Spain (*Instituto de Recursos Naturales y Agrobiología de Sevilla*). Then it was improved in New Zeeland (HortResearch) and at the Swiss Federal Institute of Technology in Zurich, Switzerland. The model is based on the transfer of chemical substances through transpiration flow, and therefore water transfer through the plant and the solubility of chemical substances in water serves as a basis for the model's algorithm. Thus, an assumption that the content of chemical substances removed from soil through plants is proportional to the speed of transpiration within the investigated period can be made (Robinson et al. 2003):

$$M_{\mathrm{i}} \approx \int_{0}^{t} T\mathrm{d}t, \tag{5.20}$$

where M_{i} is the concentration of chemical substance i in the above-ground part of the plant (mg/kg DW), T is the rate of transpiration flow (L/day), and t is the time (days). The program makes the assumption that the concentration of a chemical substance in the above-ground part is proportional to the concentration of the chemical substance in the soil solution:

$$M_{\mathrm{i}} \approx [C_{\mathrm{i}}], \tag{5.21}$$

where C_{i} is the concentration of chemical substance i in the soil solution (mg/L).

The amount of a chemical substance accumulated in a plant is not necessarily equal to the chemical content of the soil solution calculated with reference to water content transferred through the plant. To reach the above-ground parts of the plant, metal first needs to get to roots either, in the symplastic or apoplastic pathway, based on active and passive filtration, respectively. The ratio of the concentrations of chemical substance i in the xylem of roots to the soil solution is expressed through a dimensionless factor in root absorption (φ_{i}) calculated according to Eq. (5.22):

$$\varphi_{\mathrm{i}} = \frac{C_{\mathrm{i,r}}}{C_{\mathrm{i}}}, \tag{5.22}$$

where $C_{\mathrm{i,r}}$ is the concentration of chemical substance i (mg/L) in the root xylem.

The root absorption factor (φ_{n}) up biogeochemical factors having an impact on the uptake of chemical substances by the roots of plants from the soil. These factors represent rhyzobiological activity, root exudates, soil temperature, humidity, pH, and the concentration of the ions of competing materials. The values of this factor vary subject to the concentration of a chemical substance in the soil solution. This change in the model is characterized by the disproportion constant (K_{i}) and calculated according to Eq. (5.23):

$$\varphi_{\mathrm{n,i}}(C_{\mathrm{i}}) = \frac{\varphi_{\mathrm{n,1}} C_{\mathrm{1,i}}}{C_{\mathrm{1,i}} + K_{\mathrm{i}} \times (C_{\mathrm{i}} - C_{\mathrm{1,i}})}, \tag{5.23}$$

where $\varphi_{\mathrm{n}}(C_{\mathrm{i}})$ is a factor in root absorption of the species of the investigated plant n when the concentration (mg/L) of chemical substance i in the soil solution is C, $\varphi_{\mathrm{n,1}}$ is a factor in the root absorption of the species of the investigated plant n when the concentration (mg/L) of chemical substance i in the soil solution is $C_{\mathrm{1,i}}$, K_{i} ($0 \leq K_{\mathrm{i}} < 1$) is the disproportion constant because $\varphi_{\mathrm{n,i}}$ decreases when a part of soluble chemical substance i in soil (in the of nonbarrier plants) increases, and K_i is the expression for the rate of decrease.

The factor in root absorption ($\varphi_\mathrm{n,i}$) that depends on the species of plant n can be approximately estimated according to the total amount of water consumed by the plant, the above-ground dry weight of the plant, and the concentration of chemical substance i in the soil solution. These values are interrelated in the following way:

$$\varphi_{\mathrm{n,i}} \cong \frac{M_\mathrm{i} \times B_\mathrm{n}}{T_\mathrm{n} \times C_\mathrm{i}}, \tag{5.24}$$

where B_n is the biomass of species n of the above-ground plant (kg) and T_n is the total water consumption of species n of the plant (liters).

The model accepts a precondition that the potential uptake of chemical substance i through the plant of a certain species n depends on the density of the root system. To enter the plant, the concentration (mg/kg) of chemical substance i at depth d of soil changes, and this variation is calculated according to Eq. (5.25):

$$\Delta M_{\mathrm{i},z} = \frac{1}{\rho_z} \int_0^t R_z T C \varphi \mathrm{d}t, \tag{5.25}$$

where ΔM_Z denotes the variations in the concentration (mg/kg) of chemical substance i at soil depth z, ρ_z is the bulk density (g/cm^2) of soil at depth z, t is the time (days), and R_z is a part of the mass of plant roots (mass of root system at soil depth z divided into general mass of root system).

An economic assessment of phytoextraction implementation is carried out comparing the benefits and costs of phytoextraction with the benefits and costs from another technology for removing chemical substances from soil and the benefits and costs of nonactivity, i.e., leaving the area under conditions of natural arbitrariness.

Phytoextraction can be selected in cases that, from a financial point of view, are attractive in the long term. Phytoextraction costs V (EUR) are calculated according to Eq. (5.26):

$$\begin{aligned} V &= A \times \int_0^A (c_1 + c_2 - P_1 \times V_1 - P_2 \times V_2)\mathrm{d}t \\ &+ \sum_{x=1,2,3\ldots t} \int_0^x (c_1 + c_2 - P_1 \times V_1 - P_2 \times V_2)\mathrm{d}t \times \frac{I}{100}, \end{aligned} \tag{5.26}$$

where A is the space of the phytoextraction area (ha), C_1 is the planting costs (EUR/ha), C_2 is the production costs (Eur/ha), P_1 is the content of marketable biomass (t/ha), V_1 is the biomass price (EUR/t), P_2 is the content of the chemical substance recovered with the help of phytoextraction (t/ha), V_2 is the value of recovered chemical substances (EUR/t), and I is the interest rate (%).

Phytoextraction costs can be compared with those of an alternative technology used for recovering soil over the same period. If, in the course of applying the alternative technology, soil was recovered for a shorter period of time, the costs (V_a) of this technology would be covered owing to the increased costs of cleaning up the land, applying Eq. (5.27):

$$V_{\mathrm{a}} = A \times \left(C \times \left(1 + \frac{I}{100} \right)^{t_1} - L \times \left(1 + \frac{I}{100} \right)^{t_2 - t_1} \right), \tag{5.27}$$

where A is the space of the area (ha), t_1 is the time required to recover soil employing a traditional environmental protection technology (years), t_2 is the time required to recover soil employing phytoextraction (years), C is the costs of an alternative technology (EUR/ha), L is the income from the area where soil is recovered (EUR).

Nonactivity (V_{in}) costs, compared to phytoextraction, are calculated according to Eq. (5.28):

$$V_{\mathrm{in}} = (\mathrm{LG} + \mathrm{RP} + \mathrm{LE} + \mathrm{FC}) \times \left(1 + \frac{I}{100} \right)^{t}, \tag{5.28}$$

where LG denotes the costs related to meeting legal requirements (EUR), RP is the costs associated with the loss of reputation (Eur), LE is the loss of revenue from the area (EUR/year), FC is expected costs (EUR), and t is the simulated period.

Restrictions characteristic of the Phyto-DSS model:

- The impact of conditions such as drought on phytoextraction is not considered.
- The accumulation of chemical substances is assessed only in the above-ground parts of plants.
- For practical and facilitation purposes in the model, the assumptions that soil moisture is equally distributed in both the radial and vertical direction are made. In such a case, the restoration period can be shorter that in reality. As for the long-term period, the concentration of chemical substances in plants can be several times higher than under real conditions.
- The model does not provide for simulating a mixed afforestation of the area.

The selected simulation period lasts from the first quarter of 1999 to the first quarter of 2008. The simulated area in the Panevėžys Region covers 1 ha. Information on climatic conditions is obtained by the device for simulating climate. Typical average annual precipitation (672 mm) and the annual content of evapotranspirated moisture (367 mm) have been established in the Panevėžys Region.

The simulated profile of the peat soil at a thickness of 50 cm had a density of 1.6 kg/L (Buivydaitė and Motuzas 2000). A soil humidity content of 5 % was found using the experimental method. It is accepted that precipitation is maximally (100 %) infiltered into soil. Chemical substances, including the metals Pb, Cd, and Cu, were investigated. The conducted experiments revealed that the highest concentration of the introduced metals accumulated at a depth of 10–20 cm.

Two species of tree – *Betula pendula* and *Pinus sylvestris* L. – and their application for phytoextractiion purposes were simulated. With reference to Laitakari (1934), it was accepted that the main biomass of birch roots accumulates at a depth of 15–20 cm.

In the case of the pine, as an evergreen tree, transpiration takes place all year round; the mass of lateral roots is distributed at a depth of 10–15 cm (Laitakari 1934).

The highest initial concentration of metals was introduced into the model and reached 45 mg/kg Pb, 7.3 mg/kg Cd, and 9 mg/kg Cu in the most heavily contaminated part of the soil profile. The background concentrations of these metals reached 12 mg/kg Pb, 2.2 mg/kg Cd, and 3.1 mg/kg Cu (Katinas et al. 2002). The established soluble concentrations of metals were experimentally introduced into the model and reached 6.4 mg/L Pb, 0.23 mg/L Cd, and 0.56 mg/L Cu. According to Pais and Jones (1997) and Kabata Pendias and Pendias (2001), limit concentrations of metals in pine trees contained 30 mg/kg Pb, 5 mg/kg Cd, and 20 mg/kg Cu, while those in birch reached 30 mg/kg Pb, 10 mg/kg Cd, and 30 mg/kg Cu. In the case of Cd and Cu, the latter values are higher in birch than in pine because, in light of the conclusions of Eltrop et al. (1991) and Kahle (1993), birch is more resistant to the negative effects of metals.

A factor in root absorption was calculated according to Eq. (5.22). Data on the concentration of metals in the above-ground part of trees and dry biomass were obtained in the course of the experimental method. The absorption factor of Pb in birch roots (φ_n) was 0.002, that of Cd was 0.22, and that of Cu was 0.29. The absorption factor in pine roots with respect to Pb was found to be 0.0015, that of Cd was 0.16, and that of Cu was 0.14. The absorption of metals through roots was assumed to be equal in all seasons, and therefore $K = 0$. Because higher concentrations of metals frequently accumulate in leaves rather than in stems, the assessment of metal translocation from stem to leaves is of utmost importance, because, along with fallen leaves, metals reach the soil and complement the accumulation of metals in soil. In the case of the birch, the ratio of the concentration of metals in leaves and the stem was 0.9 for Pb, 2.5 for Cd, and 1.9 for Cu, whereas in the pine-tree it was 5.0 for Pb, 5.6 for Cd, and 1.4 for Cu.

The initial (background) concentrations of metals found in trees were introduced into the model and experimentally defined in the trees grown in the control area were found to be 5 mg/kg Pb, 0.05 mg/kg Cd, and 5.1 mg/kg Cu in the pine tree and 5 mg/kg Pb, 0.1 mg/kg Cd, and 5.1 mg/kg Cu in the birch. To assess the area of afforestation, it was assumed that 1 m^2 included 1 birch and 2 pine trees growing in the territory. To determine the wet biomass, dry biomass was added at a rate of 1 kg of birch or 2.5 kg of pine.

The scenario of economic evaluation included phytoremediation and the employment of biomass in energetics. It is assumed that, after 1 year, income from biomass is available; however, in our case, 10 years later, the content of biomass was not enough to produce profit. It was calculated that the area's costs come to US$8000 (7435 EUR); afforestation costs US$4600–5300/ha (4275–4926 EUR/ha) while the value of biomass is US$2000–3000 (1859–2788 EUR). The cost of eliminating soil contamination would reach US$160,000/ha/year (148,699 EUR/ha/year) (Terry and Banuelos 1999).

In the case of nonaction, the costs of the area should cover the loss of capacity, or US$4600–5300/ha/year (4275–4926 EUR/ha/year), loss of reputation at US $1000,000 (929,368 EUR), and costs related to meeting legal environmental requirements (penalties) of US$200,000 (185,874 EUR).

Figures 5.12 and 5.13 show the content of metals in the biomass of the birch and pine tree per hectare. The content of metals in the birch biomass established using

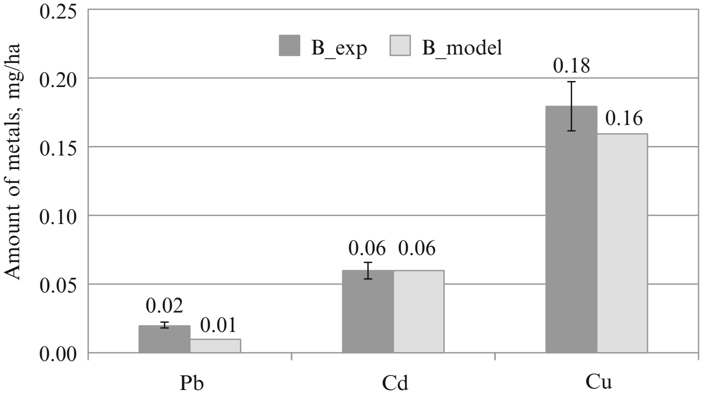


Fig. 5.12 Content of metals in biomass of above-ground part of birch (values established by applying the model and conducting an experiment)

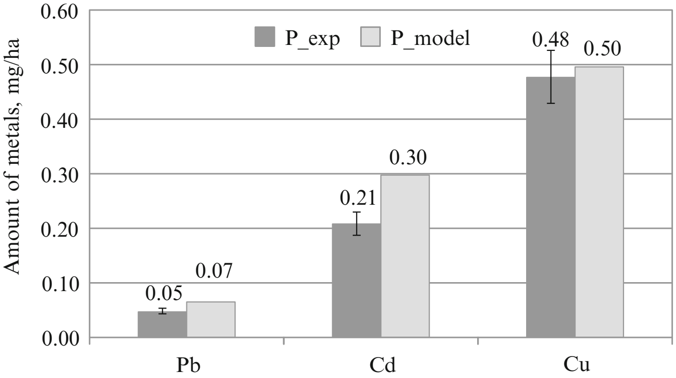


Fig. 5.13 Content of metals in biomass of above-ground part of pine tree (values established by applying the model and conducting an experiment)

the model was found to be lower than that observed during the experiment, but, with respect to the pine tree, these differences were found to be insignificant.

During the investigated period, the measured increment in the mass of birches was 1.12 kg/m^2, a bit smaller than that assessed applying the model (1.20 kg/m^2). As for the pine tree, the estimated increase in mass reached 6.22 kg/m^2 and was larger than that established employing the model (4.2 kg/m^2) (Fig. 5.14).

The estimated costs of phytomanagement were lowest during the investigated period compared to the costs of alternative technology and nonactivity. After 9 years, the costs of the area of afforestation came to 16,728 EUR (Fig. 5.15). Alternative technologies – the prevention of metals from seeping into groundwater – should come to US$180,438 (167,693 Eur) (Fig. 5.16).

In the case of nonactivity, the costs were highest: US$1.8 million/ha (1,672,862 Eur) for 9 years.

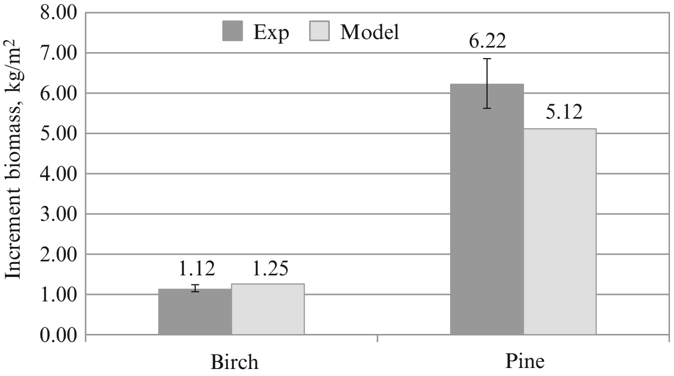


Fig. 5.14 Increment in biomass of birches and pines (values established by applying the model and conducting an experiment) (kg/m^2)

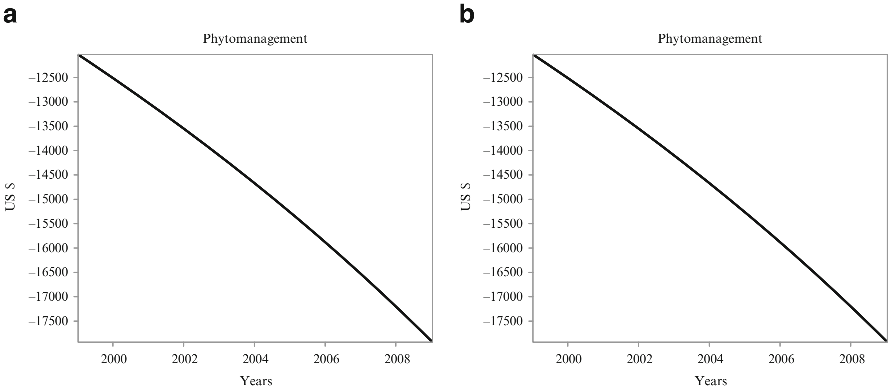


Fig. 5.15 Recovery of soil in area applying afforestation with birches (**a**) and pines (**b**) (US$)

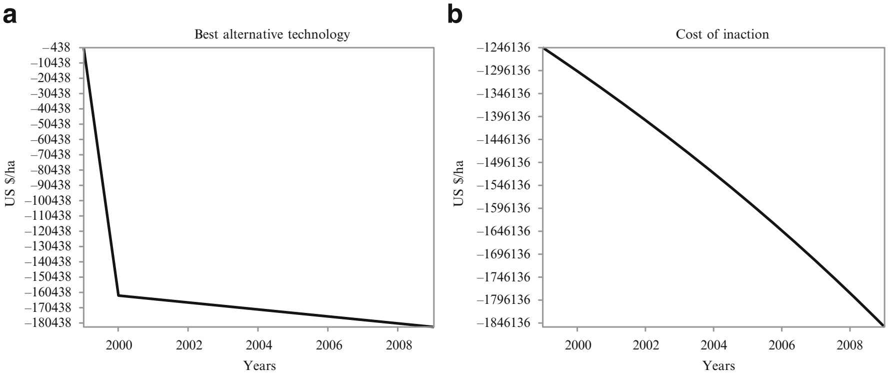


Fig. 5.16 Costs of preventing contaminants from seeping into groundwater (**a**) and nonactivity (**b**) (US$/ha)

The determined values of an increment in biomass using the Phyto-DSS model were similar to the measured values. The concentrations of metals in the biomass of the investigated trees were found applying the model and remained similar to those worked out over the course of the experiment. Cd and Cu concentrations in pine trees were different from the calculated ones by 25 and 4 %, respectively. The estimated concentration of Pb differed from the simulated one by approximately 30 %. As for the birch, the values of Cu and Cd varied slightly, by approximately 11 and 1 %, respectively; however, similarly to the case of the pine tree, in the case of Pb, the biggest difference between the simulated and measured values was observed (about 50 %). In both cases, the experimentally determined values of Pb were higher than the simulated ones. This can be related to the lowest value of the index root absorption in the case of Pb compared to other examined metals. This index was calculated on the basis of the results of our research. It is suggested that this index be calculated under laboratory conditions.

Economic analysis revealed that the application of phytotechnologies can be economically effective. No significant economic difference between the species used in phytotechnologies has been observed. This could be a function of the higher costs of pine rather over birch seedlings or of the greater income in connection with the higher output of the biomass of pines versus birches.

The model is very sensitive to variations in the water regime, and therefore the values of climatic conditions must be chosen to be as close as possible to the investigated area.

Therefore, bioindication and phytoremediation are the practical aspects of chemical elements' translocation from soil to plants. More and more herbs and treelike plants are being studied for their possible use in bioindication and phytoremediation, and the relationships between various media (e.g., soil–plant, plant–air) and between the various organs of an organism are being investigated. When expressed quantitatively, the methods of increasing the efficiency of environmental monitoring, based on the use of plants, should become more popular among the interested parties.

The dynamic factors of bioaccumulation, bioavailability, biophilicity, translocation, and phytoremediation allow us to compare the variation in translocation of metals in different plants (trees), depending on the geochemical properties of the examined area. They help to assess the effect produced by soil modification on the participation of chemical elements in the metabolism of plants (as well as trees), allowing for a quantitative evaluation of phytoremediation effectiveness for any particular period of time. The dynamic factors integrate the internal (physiological) and external (ecological) factors associated with the accumulation of chemical elements in plants.

In the case of trees, dynamic factors help us to identify a number of important trends: (1) the dynamic bioaccumulation factors have shown that in sludge-amended soil, metal translocation to trees increases in the order alder > birch > pine, while the pine has demonstrated the highest metal accumulation with respect to its mass; (2) the dynamic biophilicity factor helps us to observe the tendency of soil polluted with sludge to cause variation in metal biophilicity when the biophilicity of Ni and Cr is significantly increased compared to other metals found in sequence of metals according to their biophilicity values of the biomass of plants around the world; (3) the dynamic translocation factor helps us to determine that metal translocation from roots to vegetative organs increases more in alder than in birch and pine owing to soil pollution with sludge; (4) the dynamic phytoremediation factor has demonstrated quantitatively that the investigated pine is a better remediator of soil polluted with the considered metals than birch or alder.

The maximum daily tropospheric concentration of particulate matter produced by stationary pollution sources of AB ORLEN Lietuva has been assessed applying ADMS4 simulation software and is 4.5 μg/m^3, whereas the hourly concentration is 1.2 μg/m^3, and therefore it does not exceed the established limits. The highest concentrations of particulate matter have been found at a distance of 1.5–2 km from contamination sources. The maximum concentrations of metals in mineral snow dust have been discovered at a similar distance.

The model of pollutants' translocation from soil to plants developed by Hung and Muckay and used in the present work allows us to evaluate the modeled processes and conditions (e.g., various rates of transportation and metabolism in particular tree species, growth rate and density of various tree organs). Given the detailed information about the species of the investigated young trees, including the density and volume of their roots, wood, and leaves, as well as the amounts of water, air, and lipids in their particular organs, we can use the correction coefficients to obtain results that may well agree with the real values characterizing the modeled processes. The results obtained in the present work differ from the data obtained in the experiment carried out in natural conditions as follows: by 6 % in leaves, by 5 % in stems, and by 8 % in roots of the examined trees.

Differences in the transfer of metals found during the experiment and employing the model and the accumulation in the biomass of the trees did not exceed values by 30 %, except for Pb (50 % difference).

Chapter 6
Use of Wood Products for Water and Soil Quality Improvement

This chapter deals with the life cycle of trees where the process of using manufactured wood waste in ecotechnologies takes place, thereby recovering valuable components of a wood product (e.g., biochar) and converting some waste into raw materials (e.g., using ash for reclaiming soil). Two products of the thermal treatment of wood, including a solid product of wood pyrolysis (biochar) and its full oxidation product (ash), as well as their use in environmental protection engineering and agriculture, are examined. Recent years have seen a major increased interest in biochar owing to the greater stability of carbon compounds and characteristics improving the properties of soil and forming the advantages of biochar in light of the problems related to climate change and soil fertility. The assessment of the composition of the different types of wood ash is a separate topic. In the case of fire, ash determines changes in the chemical composition of soil. Along with an increase in the use of biofuel in energetics (in Lithuania in particular), the utilization of combustion products raises environmental concerns. The chapter describes the concentrations of metals in the ash of different trees and environmental risk.

6.1 Biochar from Wood: Properties, Resources, and Applications

The concept of biochar became important when scientists studying rich Amazonian soils called *terra preta* discovered that they had over 70 more times carbon, more nitrogen, phosphorus, potassium, and calcium than the surrounding soils. It is believed that soils of considerably better quality were formed over a long period of time as people living in those places at that time fertilized soil with waste and charcoal, which, as a soil amendment, performed the functions of disinfecting waste and improving the quality of soil (Schmidt 2012).

E. Baltrėnaitė et al., *The Sustainable Role of the Tree in Environmental Protection Technologies*, DOI 10.1007/978-3-319-25477-7_6

Nowadays, the aim is to attain the quality of *terra preta* soil by meliorating common soil, especially one degraded with "black carbon," which comes close to the notion of "biochar." According to the definition given by the European Biochar Foundation (EBC) (EBC 2012), biochar is described as a heterogeneous material rich in aromatic carbon and minerals. It is produced through the pyrolysis of sustainably obtained biomass under controlled conditions and using environment friendly technology. The use of biochar in soil reduces CO_2 emissions and its final use would be for soil melioration.

Biochar creates conditions for carbon-negative technology and can compensate for 0.25 Gt/year of carbon emitted to the atmosphere by 2030 by stabilizing it. And this is only by producing biochar from biomass waste (IBI 2015). Why is biochar negative? In view of climate change, the production and use of biochar not only help to avoid adding carbon to the atmosphere in the form of CO_2, as happens when fossil fuels are burned, or just to maintain the current level of greenhouse gases in the atmosphere, as happens in the case of burning biomass, which is carbon-neutral; it is much more. When biomass is thermally processed using pyrolysis, biomass transforms into (bio)char and carbon becomes more stable, emissions of pollutants into the atmosphere are lower than in the case of combustion, and when biochar is used to meliorate soil, the quality of the soil improves, and the soil becomes an effective reservoir of carbon as a result of increased carbon stability and considerable limitation of CO_2 emissions caused by it. This makes for a "carbon-negative" technology (Glaser et al. 2009).

Carbon stability is reached by way of thermal processing of biomass in the environment where oxygen is limited. During this conversion biomass, turns into products of three states: liquid (bio-oil), solid, and gaseous (Bridgwater and Peacocke 2000). Pyrolysis is attributed to renewable energy creation processes, competing with the burning of nonrenewable sources of fossil fuel (Özçimen and Karaosmanoglu 2004). Traditional pyrolysis conditions, which maximize the formation of solid residue, are an oxygen-free environment and thermal processing of biomass at temperatures of 350–800 °C (Bridgwater 2003).

To quantitatively determine which products of thermal processing of biomass can be considered biochar, Hedges et al. (2000) proposed to compare products of thermal conversion according to the oxygen/carbon (O/C) molar ratio. Products produced during thermal processing include condensates (graphite, soot), i.e., forms of black carbon that do not have the relic structure of the primary biomass, and residues, which retain the relic structure of the primary biomass. In the continuum of conversion products, biochar includes products whose O/C ratio amounts to 0.2–0.6 and the raw material source is exceptionally renewable but not fossil fuel.

Biochar is new in terms of its purpose and application (carbon sequestration). The advantage of biochar in carbon sequestration is that carbon from biosphere accumulation is transformed into a less circular form (i.e., black C), which has the potential to remain stable from 100 to 1000 years (Haberstroh et al. 2006). The biochar stability in soil and its resistance to change is characterized by the

H/C_{org} ratio. When the value of the H/C_{org} ratio is less than 0.7, the organic carbon in biochar will remain stable for over 100 years (Spokas 2010).

Biochar is too valuable for use in meliorating soil right after its production. It should be used for another useful purpose at least once before that, for example, as a storage of nutrients, adsorber, insulating material in the building industry, accumulator of energy, filter in wastewater treatment systems, or feedstock additive. In his publication about the usefulness of biochar, Schmidt (2012) presents 55 ways of using it, including in stock breeding (e.g., as a feedstock additive, in manure composting, for water treatment in fishery farms), in the construction sector (e.g., as insulating material, for adsorbing humidity, protection against electromagnetic fields), in pollution reduction (e.g., as a meliorating substance for restoring soil), in the production of biogas (e.g., as a biomass additive), in wastewater treatment systems (e.g., in filters of activated carbon, in composting toilets), in water preparation systems (e.g., microfilters), in the textile industry (e.g., as a thermal insulating fabric for clothes), and in wellness improvement (e.g., in mattress and pillow ticks).

Potential of Biochar Production from Wood Waste

The most valuable raw material recommended by the EBC for biochar production is lignocellulosic biomass. It is divided into primary biomass (biomass of trees, shrubs, grasses), biomass waste (in agriculture, for example, sugarcane bagasse, in forestry, for example, waste from sawmills and paper factories), and biomass of energy cultures (e.g., Miscanthus varieties).

The EU Biomass Action Plan indicates that the annual resources of energy biomass in Europe amount to about 150 MTOE (million tons of oil equivalent) (European Commission 2005). In 2010–2020 the major part (about 100 MTOE) can be expected from agricultural waste (manure, straw), waste from forestry, wood and paper industries, and household waste. It is forecast that later on (in 2030) more energy potential can be expected from energy plants – up to 142 MTOE. It is planned to grow them in an area of 1.3 million ha in 2030. The total plant biomass fuel potential in Lithuania could amount to 2.02 MTOE (European Commission 2005).

Wood waste potential for the production of biochar consists of wood cutting waste (stumps, bark, tops, with the largest diameter under the bark >5 cm) and small stems and branches (with a diameter under the bark ≤ 5 cm)). Forest cutting waste consists of the part of the tree stump that is above the ground, shredded section wood, tops, branches (except for usable branches), stems of small trees whose diameter at a height of 1.3 m is 5 cm or less, offcuts that appear when cutting tree stems, waste from the cleaning of burning sites, wood chips, wood sawdust, and repeatedly used wood (construction and demolition wood waste, used pallets and other wooden packaging, remnants of furniture and other wooden products). Most solid household waste is also lignocellulosic (Sluiter et al. 2005).

Raw material for the production of biochar from forests and from energy forests can be considered ecologically acceptable, which cannot be said about repeatedly used wood. Compared to forest cutting waste, used wood is drier, more calorific, and denser. Usually such wood is impregnated, painted, or varnished and contains various additives (e.g., metal, glass, plastic); therefore, further processing of such wood is complicated. In the case of thermal processing of such wood (e.g., by use of pyrolysis), emissions are subject to stricter requirements, special technologies for removing contaminants are needed, and smoke cleaning systems are necessary. It is noteworthy that some wood waste is considered hazardous. Often it is wood that contains toxic substances (e.g., nonhalogenated organic wood preservatives, organochlorinated wood preservatives, organometallic wood preservatives, inorganic wood preservatives, other wood preservatives with hazardous ingredients [chromated copper arsenate (CCA); creosote] (Commission Regulation (EC) No. 574/2004).

Forest cutting waste is among the types of wood waste that are most suitable for biochar production. According to data for 2013, wood waste (wood chips, particles, and residues) amounted to 708,000 m^3 in Lithuania, 1,650,000 m^3 in Estonia, 572,000 m^3 in Latvia, 5,500,000 m^3 in Poland, 5,117,000 m^3 in Finland, 4,154,000 m^3 in Sweden, and 3,299,000 m^3 in Germany (State Forest 2015). Lithuania produces about 2.5 million m^3 of such waste per year (State Forest 2015). According to data from different sources, forest cutting waste that can be potentially used in Lithuania amounts to 0.8–1.1 million m^3. One of the most important reasons why forest cutting waste is not used extensively is the large cost of its preparation and the peculiarities of transporting it (Ministry of Environment 2015).

Packaging waste comprises a large part of the flow of household waste. One type of packaging is wood packaging, which accounts for 15 % of all packaging in the EU (Fig. 6.1).

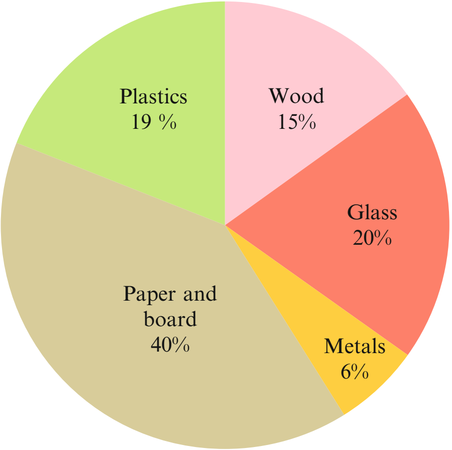


Fig. 6.1 Shares of packaging waste by weight, EU-27, 2011 (*Source*: Eurostat)

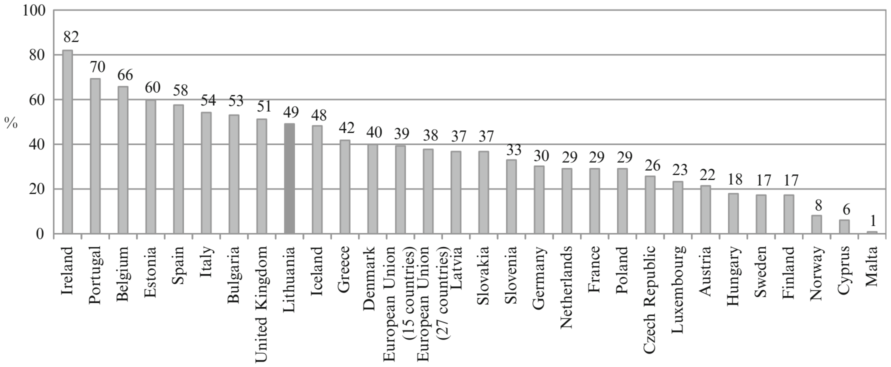


Fig. 6.2 Recycling rate for wood packaging, 2011 (*Source*: Eurostat)

Wood packaging recycling tendencies according to Eurostat are given in Fig. 6.2. Recycling rates achieved in this area of wood waste (wood packaging) are not high in many EU member states, falling even under 40 %. Therefore, it can be said that wood packaging (not contaminated with toxic substances) is a potential raw material for biochar production.

Characteristics of Wood Pyrolysis Process

The chemical composition of raw material (biomass) is important for the production of biochar. Wood and its waste are high-quality raw materials for the production of biochar thanks to their low humidity and a high lignin content. Wood is a complex mixture of natural macromolecular polymers. The most important of these polymers are cellulose (about 50 %), hemicellulose (about 25 %), and lignin (about 25 %); however, depending on the tree type, the ratio of these polymers differs (Drysdale 1985). Unlike synthetic polymers, wood is nonhomogeneous and nonisotropic. Table 6.1 presents differences in the chemical composition of various wood types.

Coniferous trees contain more cellulose, whereas deciduous trees contain more pentosans. Cellulose, which is the principal constituent of all higher plants, is a condensation polymer of hexose sugar, D-glucose, and has a linear structure. This configuration allows molecules to align themselves into bundles (microfibrils) that provide the structural strength and rigidity of the cell walls. The microfibrils are bound together during the process of lignification when the hemicellulose and lignin are laid down in the growing plant (Drysdale 1985). The structure of hemicellulose is similar, based on pentose sugars, but that of lignin is vastly more complex (Greenwood and Milne 1968). Thermogravimetric analysis of the degradation of wood, cellulose, and lignin showed that the constituents decompose to release volatiles at different temperatures, typically hemicellulose at 200–260 °C, cellulose at 240–350 °C, and lignin at 280–500 °C. During pyrolysis most volatiles

Table 6.1 Chemical constituents of some wood types (percentage of the whole mass) (Žurauskienė et al. 2012)

Wood type	Cellulose	Lignin	Pentosans	Hexosans	Ash	Ether-soluble substances	Water-soluble substances
Fir	45.2	29.0	9.3	9.2	0.3	1.5	1.4
Pine	51.9	20.5	11.2	9.3	0.2	2.6	0.6
Oak	38.9	23.8	22.8	6.3	0.3	4.3	1.8
Birch	34.1	21.2	22.0	20.0	0.4	1.3	–
Aspen	52.4	20.3	22.6	0.5	0.2	1.6	2.2
Maple	41.5	23.1	25.6	7.7	0.3	0.3	0.5
Poplar	39.8	18.8	23.5	8.3	0.3	6.8	2.1

in wood are released at a temperature of 600–650 °C. In the case of coal, this maximum is at around 700 °C, whereas in the case of peat, it is at around 500 °C (Roberts 1970). It is believed that lignin is aromatic, whereas cellulose and hemicellulose are heterocyclic compounds. The thermal resistance of compounds depends on their chemical composition. Aromatic compounds are thermally more resistant than heterocyclic ones.

If lignin is heated to temperatures in excess of 400–450 °C, only about 50 % volatilizes, with the balance of the mass remaining as a char residue. If inorganic impurities (e.g., sodium salts) are present, much higher yields are found: for instance, viscose rayon (a fiber consisting of regenerated cellulose and having a relatively high residual inorganic content) can yield over 40 % char (Madorsky 1964). When wood is burned or heated above 450 °C, 15–25 % normally remains as char, much of this coming from the lignin content (up to 10–12 % of the original weight of wood). However, the yield from cellulose (and, presumably, hemicellulose) is variable, depending on the temperature or rate of burning and, more importantly, on the nature and concentration of any inorganic salts that are present. The significance of this is that the nature of the volatiles changes significantly if there is a change in the yield of char. It is known that the rate of decomposition of wood, or cellulose in particular, is very sensitive to the presence of inorganic impurities, such as fire retardants.

Impact of Pyrolysis Temperature and Raw Material (Wood Type) on Qualities of Biochar

Coniferous and deciduous trees are two categories of plants that are widely spread on Earth. The wood of both types of tree have a high potential for biochar production. In what follows, we discuss the characteristic peculiarities of biochar produced from two types of tree – pine and birch, representing both categories of plants, coniferous and deciduous trees, respectively. The morphological, physicochemical, and microbiological differences and similarities of biochar produced at different temperatures are discussed in the following subsections.

(a) *Morphological peculiarities of biochar derived from coniferous and deciduous trees*

During thermal treatment the macro structure of wood barely changes. Pine and birch wood samples used for biochar production were made for SEM photos by splitting wood in the fiber direction or cutting it across fibers.

As seen from the pine (P) micro photo, the structure along the fiber consisted of hollow tracheids, around 40 μm in diameter (Figs. 6.3 and 6.4). The cross section of the tracheids had a rectangular form (Fig. 6.4) and their wall thickness was 3–4 μm. Birch wood is plastic, and when the wood structure was cut crosswise, the surface of small-diameter pores was covered (Fig. 6.5). Photographs of birch wood present pores of larger diameter,

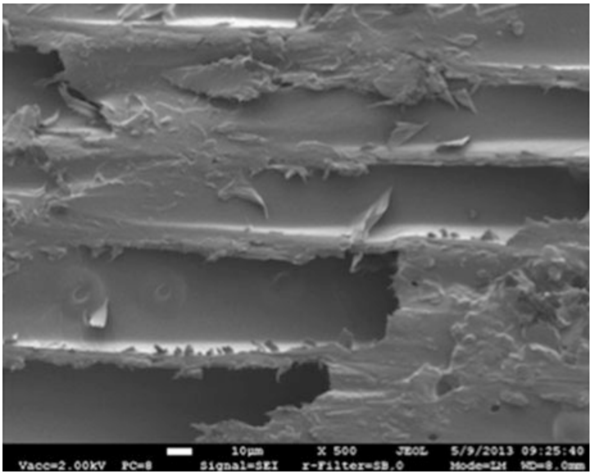


Fig. 6.3 Pine biochar. Section along wood structure. Magnification 500×

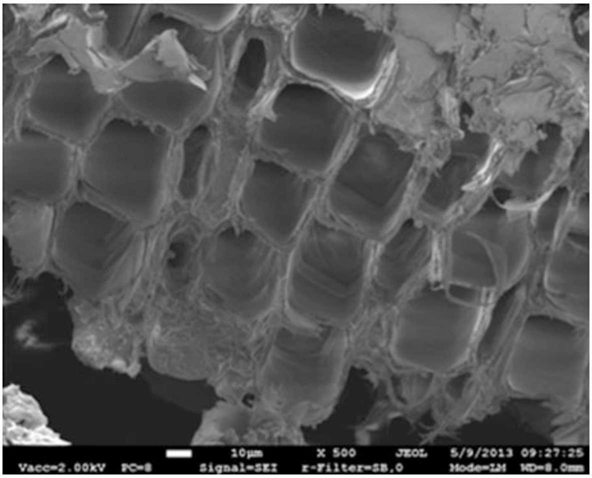


Fig. 6.4 Pine biochar. Section across wood structure. Magnification 500×

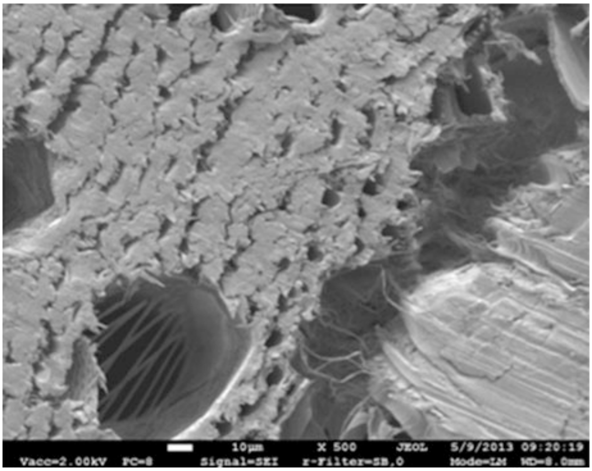


Fig. 6.5 Birch biochar. Section across wood structure. Magnification 500×

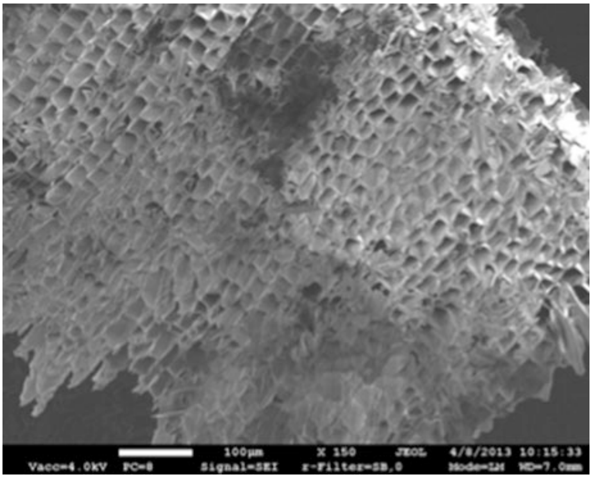


Fig. 6.6 Pine biochar processed at 300 °C. Magnification 150×

50–60 µm, with the specific structure of internal surface, and micropores, which were 3–4 µm in diameter.

The pine and birch wood samples that underwent thermal treatment at 300 °C had low electric conductivity, and therefore, in the case of increased magnification, secondary electrons accumulated on their surface, which reduced the brightness of significantly magnified photographs. Following thermal treatment the wood structure remains unchanged but the rims of pore edges become round (Fig. 6.6 and 6.7). These samples may be considered transition char when wood increasingly undergoes dehydration and depolymerization, but cellulose retains a notable crystallinity (Baltrėnaitė et al. 2015).

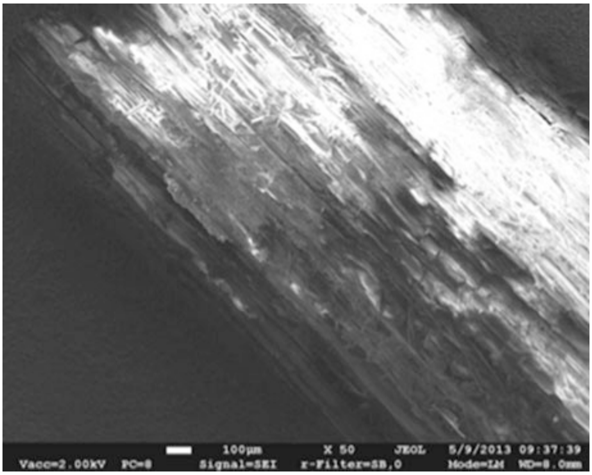


Fig. 6.7 Birch biochar processes at 300 °C. Magnification 50×

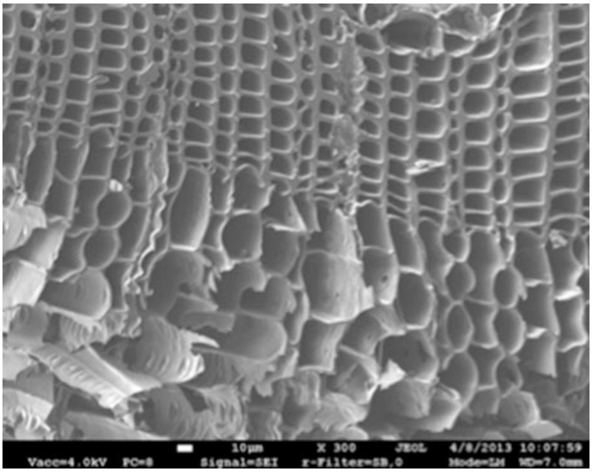


Fig. 6.8 Pine biochar processed at 450 °C. Magnification 300×

A layered structure of a sample comprising pores having smaller, 8–12 µm, and larger, 30–50 µm, diameters was observed perpendicular to pores in the pine sample treated at 450 °C temperature. The surfaces of material breaks were clear and had sharp edges. Minor pores had thicker walls of 3–4 µm, while the walls of major pores were around 1 µm thick (Fig. 6.8). When impacted mechanically, the sample of pine char broke over the layer of large-diameter pores. Since the birch biochar sample treated at 450 °C retained low conductivity, a load accumulated on the sample surface (Fig. 6.9). It had pores of two different diameters. Large pores 50–80 µm in diameter were evenly distributed within an array of small pores. In this case, the walls of small pores were 2–3 µm thick.

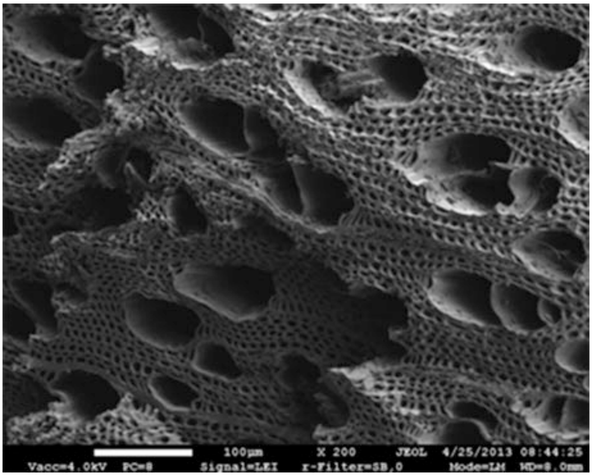


Fig. 6.9 Birch biochar processed at 450 °C. Magnification 200×

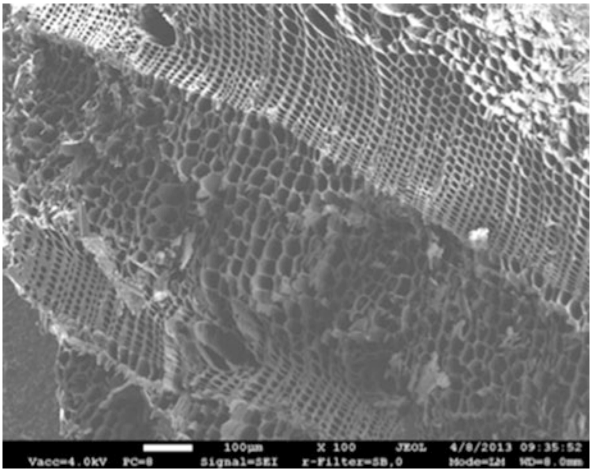


Fig. 6.10 Walls of small pores of pine biochar processed at 750 °C. Magnification 100×

Photos of a pine sample thermally treated at 750 °C are presented in Figs. 6.10 and 6.11. The sample's layered structure, made of 10–15 and 20–30 µm diameter pore layers, remained unchanged. The walls of the small pores were 2–3 µm thick, while those of the large pores—0.5–1.0 µm.

Photos of birch biochar samples thermally treated at 750 °C are presented in Figs. 6.12, 6.13, and 6.14. The break planes of samples perpendicular to pores were equal to 50–80 µm diameter pores located in the array of smaller diameter pores. The length of pores was much greater than their diameter and exceeded 1000 µm (Fig. 6.12). No open pores were visible either in the material's wall (Fig. 6.13) or the inner surface of pores (Fig. 6.14). Observation of B750 samples at larger magnification revealed that birch biochar

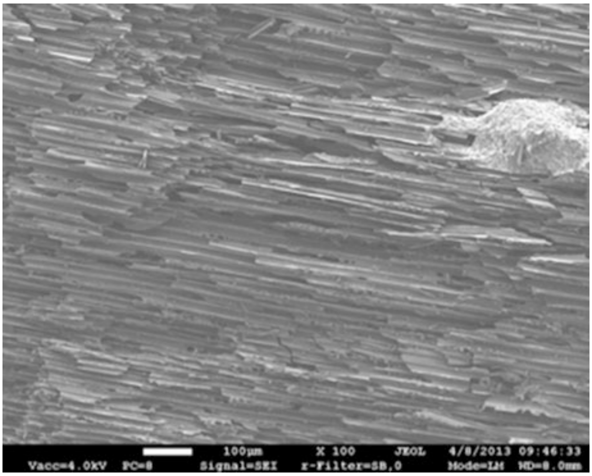


Fig. 6.11 Walls of large pores of pine biochar processed at 750 °C. Magnification 100×

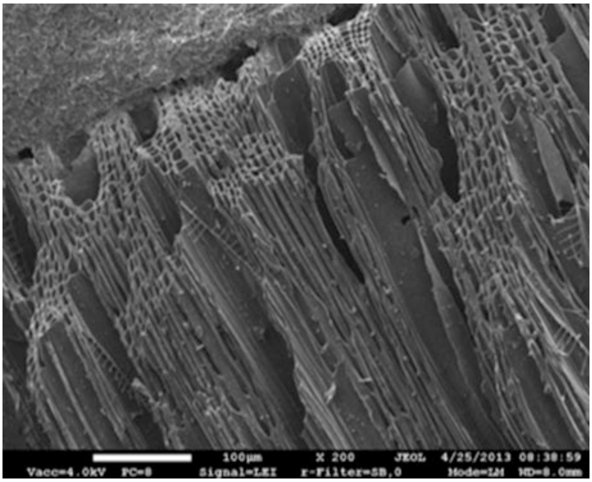


Fig. 6.12 Birch biochar processed at 750 °C. Magnification 200×

consists of turbostratic crystallites while the composition of pine biochar retains pyrogenous amorphous carbon.

Electron microscopy showed that thermally treated wood preserves the initial structure of wood pores. When the treatment temperature was increased, it was possible to observe the structure of the material with ever increasing enlargements. The pine and birch biochar samples analyzed were made up of large 40–80 μm and small 5–10 μm diameter pores that were arranged either in layers (pine) or pores with a large diameter that are within the array of pores of small diameter (birch).

The pore structure of biochar from birch varied with treatment temperature. When wood was treated at 300 °C, the porosity, pore surface area, and pore volume were at their smallest. However, at 750 °C, the porosity and pore

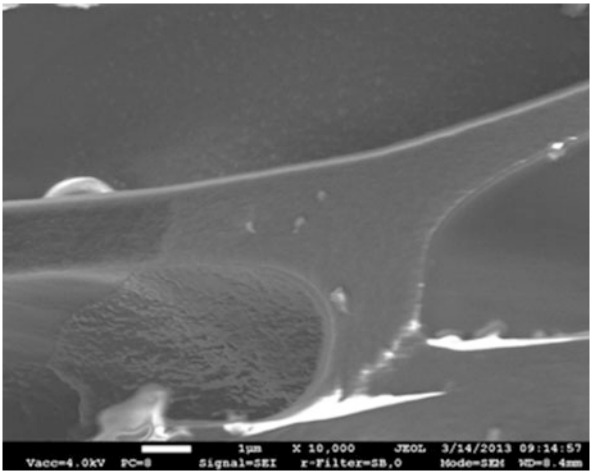


Fig. 6.13 Birch biochar processed at 750 °C. Magnification 10,000×

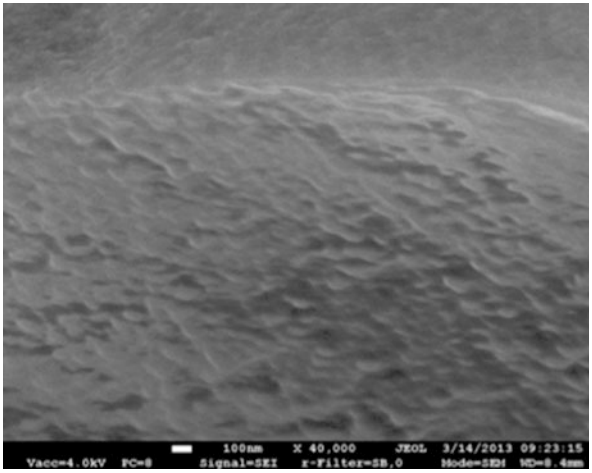


Fig. 6.14 Birch biochar processed at 750 °C. Magnification 40,000×

volume were smaller than at 450 °C. The relationship between the pore volume and the pore diameter of the birch sample is presented in Fig. 6.15. Up to 90 % of the material's pore volume consisted of pores that were 0.5–60 μm in diameter. In sample B 750, mesopores whose diameter was smaller than 0.05 μm took up 1.56 % of the pore volume, in sample B 450 0.9 %, and in sample B 300 0.7 %. The increase in pore amount with increasing treatment temperature had a particularly significant effect on the pore surface of the samples. The relationship between the pore surface area and pore diameter is shown in Fig. 6.16. The pore surface of samples was most influenced by the amount of mesopores, which were 0.05–0.00648 μm in diameter. The mesopore surface in different birch biochar samples was as follows: B 300: 4.68 m^2/g; B 450: 3.97 m^2/g; B 750: 2.59 m^2/g. It is obvious

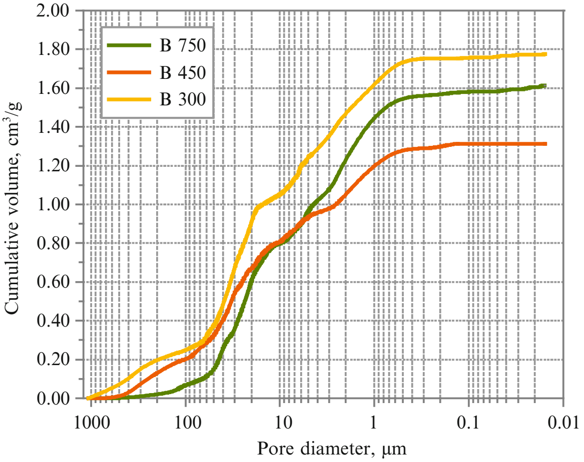


Fig. 6.15 Pore volume distribution by pore diameter of birch biochar with processing at various temperatures

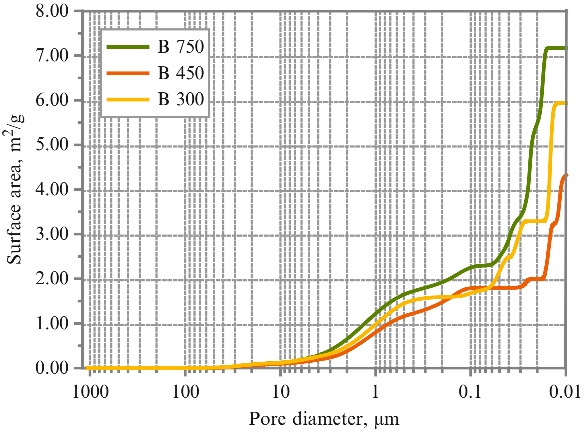


Fig. 6.16 Pore surface area distribution by pore diameter of birch biochar with processing at various temperatures

from the preceding statements that the amount of mesopores decreased when the treatment temperature increases.

The porosity of pine biochar barely depends on the treatment temperature and was slightly greater than that of birch. However, the pore surface area of the pine biochar samples was up to two times larger than that of the birch biochar samples. Also, the pore volume of pine biochar samples was almost twice as large as that of the birch biochar. The relationship between the pore volume and the pore diameter of the pine biochar samples is presented in Fig. 6.17. The pores of the pine biochar samples treated at different temperatures had a 1.04–1.16 cm^3/g higher volume than the birch biochar at all treatment temperatures. Pores 5–30 µm in diameter accounted for the major part of the volume in the samples. In samples P 750 and P 450 the volume of pores of this diameter differed insignificantly, while in sample P 450 the

Fig. 6.17 Pore volume distribution by pore diameter of pine biochar with processing at various temperatures

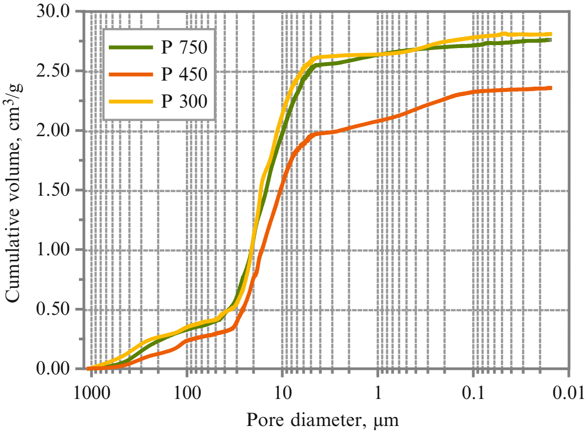
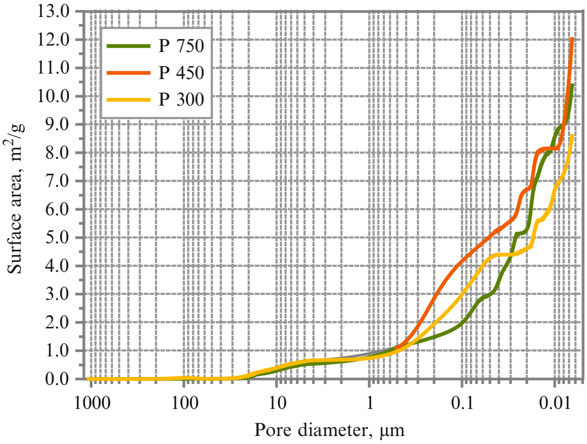


Fig. 6.18 Pore surface area distribution by pore diameter of pine biochar with processing at various temperatures



volume was 0.5 cm^3/g lower. In sample P 750 mesopores smaller than 0.05 μm accounted for 1.25 % of the pore volume, in sample P 450—0.98 %, and in sample P 300—1.08 %. Distribution by pore diameter of the pore surface area of the pine biochar samples treated at different temperatures is presented in Fig. 6.18. In regard to pine biochar, the largest surface area of pores was obtained in sample P 300, which was treated at the lowest temperature. The area of pore surface was also mostly impacted by mesopores taking up a small volume. The mesopore surface of the pine biochar surface in different samples was B 300—7.36 m^2/g, B 450—4.26 m^2/g, and B 750—6.99 m^2/g.

Observation of the birch and pine wood samples pyrolized at a temperature of 750 °C at larger magnification shows that the birch biochar consists of turbostratic crystallites while the composition of the pine biochar retains pyrogenous amorphous carbon (Baltrėnaitė et al. 2015). This implies that at a temperature of 750 °C, the birch biochar reached a crystalline state, i.e., a

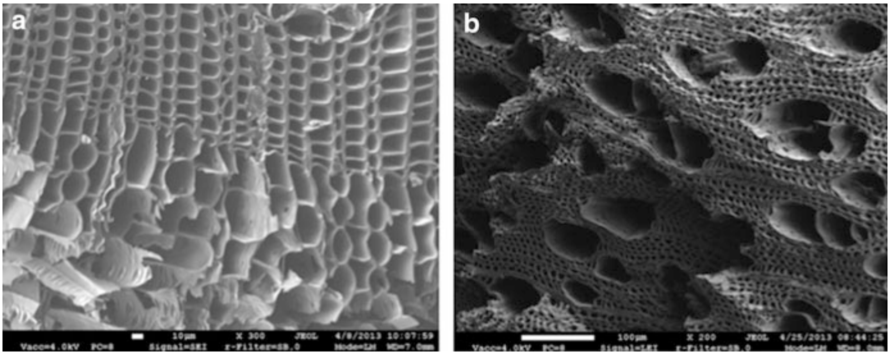


Fig. 6.19 Morphological structure of biochar processed at 450 °C: (**a**) pine (magnification 300×); (**b**) birch (magnification 200×)

more stable form (probably more covalent relations between C atoms) than the pine biochar.

Small pores of the pine biochar processed at a temperature of 450 °C had thicker walls (3–4 μm), whereas large pores had thinner walls (~1 μm) (Fig. 6.19a). There was an opposite tendency in the case of birch: small pores had thinner walls (2–3 μm), whereas large pores had thicker walls (50–80 μm) (Fig. 6.19b) (Baltrėnaitė et al. 2015).

Under the impact of higher temperature, thinner walls started decomposing earlier than thicker ones; therefore, in the case of the birch biochar, when the walls of small pores started decomposing sooner and micropores opened earlier than those of pine, the specific surface area increased sooner than that of pine at a lower temperature. In this way, at a temperature of 450 °C, the values of the specific surface area were higher in the case of the birch biochar than in the case of the pine biochar (which was especially evident when the BET method was used, which helped to evaluate the impact of micropores on the specific surface area more accurately) (Fig. 6.20b).

In the case of the pine biochar these processes were slower, but the temperature of 750 °C caused a sudden increase in the specific surface area, and the value of the latter became close to that of the birch biochar.

Analytically, using the BET method, higher values of the specific surface area were obtained at higher temperatures (750 °C), characterizing conditions of fast pyrolysis, whereas in the case of MIP, they were obtained at lower temperatures (300 and 450 °C), characterizing conditions of torrefaction and slow pyrolysis, respectively. This tendency can be explained by the fact that the structure of micropores has great significance for the size of the specific surface area, and unlike with MIP [a technique that allows one to detect macro- (diameter > 500 Å) and mesopores (20–500 Å)], the BET method makes it possible to evaluate the effect of micropores (with diameter under 20 Å according to the International Union of Pure and Applied Chemistry), as nitrogen gas used in the method can reach micropores more easily. During

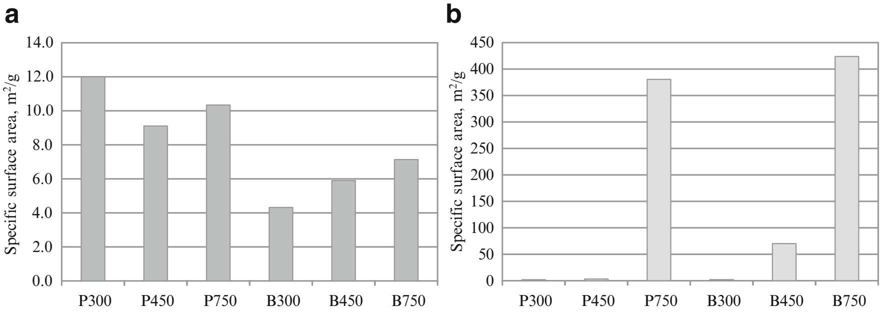


Fig. 6.20 Changes in specific surface area (m^2/g) depending on type of raw material [(*P* pine, *B* birch), pyrolysis temperatures (300, 450, and 750 °C heating temperatures), and research method (*MIP* mercury intrusion porosimetry, *BET* Brunauer, Emmett, and Teller method)

research using MIP, the specific surface area of the pine biochar was larger than that of the birch biochar, as this method evaluates the impact of meso- and macropores on the specific surface area. In the case of pine, the latter was greater because larger pores had thinner walls, which started decomposing earlier than the thick walls of the small pores and the specific surface area started increasing – at the expense of the larger pores.

With regard to temperature, as expected, a significant increase in the specific surface area can be observed at higher temperatures because a rising temperature helps to decompose pore walls: initially thin walls, then thicker ones. This tendency can be well observed in the case of the BET method. At a temperature of 750 °C, the specific surface area of the birch and the pine biochar was at its largest and amounted to about 380–425 m^2/g.

It has been determined that morphological changes in biochar were the result of the interaction of the difference in wood type (biochar feedstock) and the processing temperature (processing conditions). Differences in lignocellulosic raw material were mostly observed at the stage under a temperature of 450 °C, i.e., in the transitional stage, when the raw material loses more of the relic structure of biomass. In this case, we observe results of raw material transformation from relic to nonrelic biomass structure. The morphological differences remaining in biochar in the stage under a t emperature of 750 °C probably resulted mostly from differences in raw material. The biggest differences in raw material (wood type) were observed in biochar processed at a temperature of 750 °C. The specific surface area of the birch biochar (425 m^2/g) was slightly greater than that of the pine biochar (380 m^2/g).

(b) *Physical peculiarities of biochar derived from coniferous and deciduous trees*
According to the lowest ash content values, wood is comparable to fuel oil in the energy sector: the ash content of wood amounts to about 1 % on average, whereas that of fuel oil amounts to 0.3 %. The ash content of other fuels is as follows: peat: 10 %, coal: 10–30 %, shale: up to 60–70 %, brown coal: up to 40 % (Martinaitis and Lukoševičius 2014). Biochar ash content tendencies

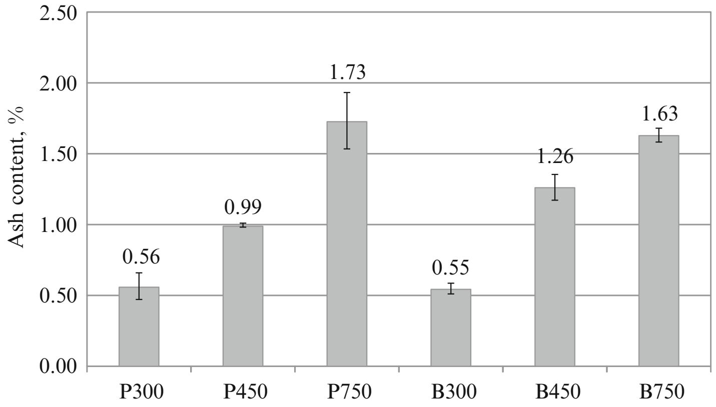


Fig. 6.21 Biochar ash content (%) (mean ± SD) depending on raw material type and pyrolysis temperature (*P* pine, *B* birch, 300, 450, and 750 °C heating temperatures)

were not significantly different in the cases of pine and birch but increased considerably as the temperature increased. Average ash content values of the pine and birch biochar amounted to 0.55–0.56 % at a temperature of 300 °C, 0.99–1.26 % at 450 °C, and 1.63–1.73 % at 750 °C (Fig. 6.21).

As the temperature increases and the quantity of volatile and condensing compounds decreases, the nonorganized biochar structure turns into a relatively organized structure (as crystals, similar to graphite), which causes increases in skeleton (true) density. The density of biochar skeleton most often amounts to 1.5–1.7 g/cm^3 (Oberlin 2002), which was similar to our results. The density of the pine biochar skeleton amounted to 1.21–1.43 g/cm^3, the birch biochar skeleton 1.68–2.14 g/cm^3. The density of the birch biochar skeleton was about 1.5 times more than that of the pine. Jankowska et al. (1991) determined that biochar with a greater skeleton density was characterized by a smaller ash content and smaller quantity of volatile substances whose molecular mass was smaller than that of fixed carbon. This tendency was observed in the case of biochar, processed at a temperature of 750 °C (when most of the volatile substances were released), and it allows us to assume that the quantity of ether-soluble substances, which was twice as big in the birch wood as in the pine wood, can have an effect on the formation of biochar-specific (true) density and its differences in different wood types.

As the heating temperature increases, the apparent (bulk) density decreases (Byrne 1996). This tendency was observed in the present research, too (Fig. 6.22): the apparent density of the pine and birch biochar decreased as the heating temperature increased, and in case of the pine biochar it was about 1.5 times less than in the birch biochar. The apparent (bulk) density is usually smaller than the skeleton (actual) density, as the volume of pores and cavities in a unit of biochar volume are taken into account. In our research this difference was about 2.5 times. As is evident from Fig. 6.22, the apparent (bulk) density of biochar depended more on different raw material than on changes in temperature. There was also a clear tendency for this density to decrease at a higher processing temperature in both the birch biochar and the pine biochar.

Biochar yield decreased as the temperature increased (Fig. 6.23). The largest biochar yield (22–28 %) was achieved after processing at a temperature of 300 °C, whereas the smallest was obtained at 750 °C (9–15 %). The

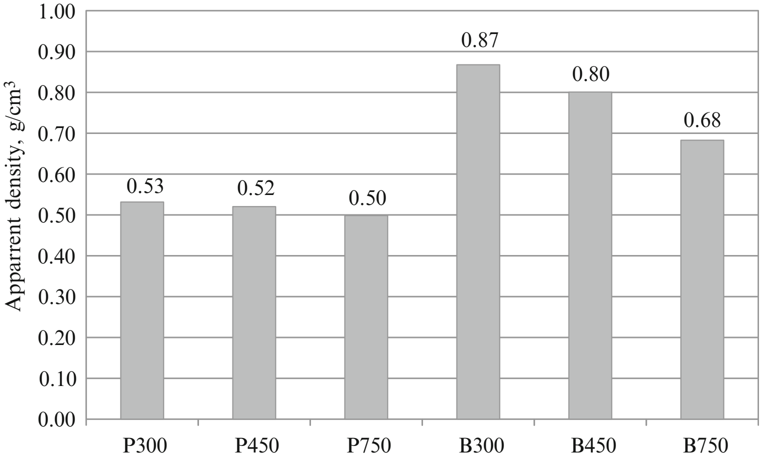


Fig. 6.22 Apparent (bulk) density of biochar (g/cm^3) depending on raw material type and pyrolysis temperature (*P* pine, *B* birch, 300, 450, and 750 °C heating temperatures)

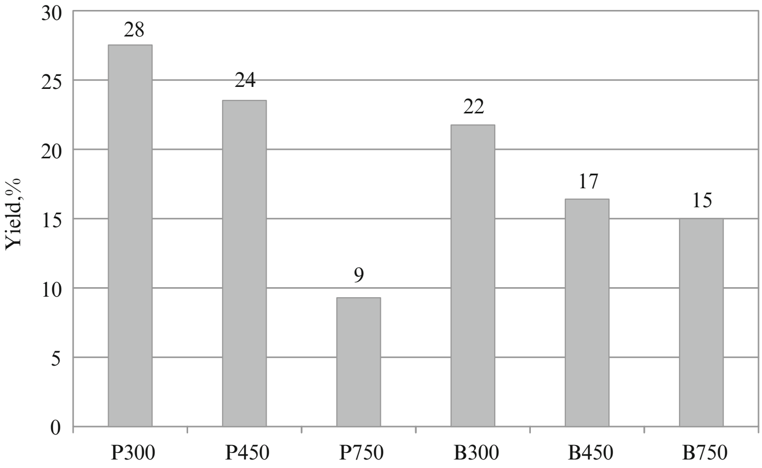


Fig. 6.23 Biochar yield (%) depending on type of raw material and pyrolysis temperature (*P* pine, *B* birch, 300, 450, and 750 °C heating temperatures)

pine biochar yield is slightly more than the birch biochar yield within the limits of 300–450 °C, but about 1.6 times less at a temperature of 750 °C. Biochar yield differences were caused more by different temperatures than by different raw materials.

(c) *Chemical and physicochemical peculiarities of biochar derived from coniferous and deciduous trees*

The pH values of wood biochar increased as the pyrolysis temperature increased. A similar tendency of change and the extent of change was observed in the case of ash content (Fig. 6.21). An increase in pH depends largely on Mg, K, and Na, and especially on Ca, found in ash. The impact of Ca concentration on pH has been determined in the case of our research, too. Ca concentration in the pine biochar processed at temperatures of 300, 450, and 750 °C amounted to, respectively, 751, 2.216, and 2.946 mg/kg, and in the birch biochar it was 770, 2.389, and 3.039 mg/kg of dry matter (data not presented here). Starting at 300 °C, when the heating temperature increased by 150–200 °C, the pH value increased by 1.4–1.5 times. When a different type of wood was heated, the pH values of biochar differed only slightly, but we noticed a tendency, when the temperature increased, for the pH of the pine biochar to increase more than of the birch biochar (Fig. 6.24).

At a pyrolysis temperature of 300 °C, the total carbon content was different in biochar derived from different wood, but at temperatures of 450 and 750 °C the TC content was similar, perhaps because most volatile compounds were emitted up to 450 °C, resulting in mass reduction and formation of an amorphous carbon matrix. The total carbon (TC) content in the pine biochar heated at a temperature of 300 °C was about 17 % higher in comparison to the birch biochar (Fig. 6.25).

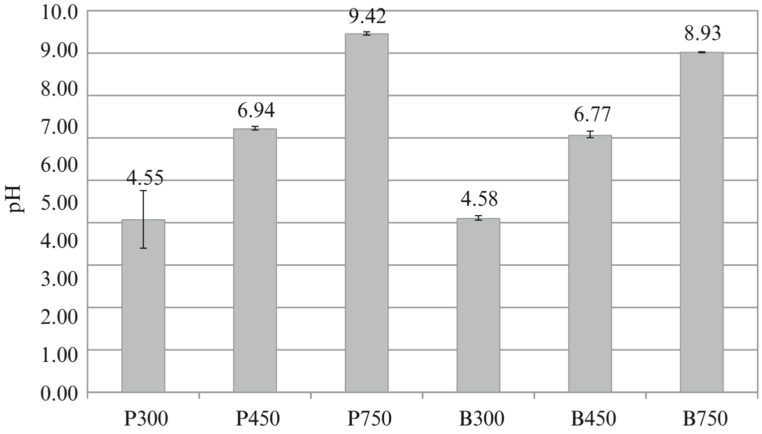


Fig. 6.24 pH values of biochar (mean ± SD) depending on type of raw material and pyrolysis temperature (*P* pine, *B* birch, 300, 450, and 750 °C heating temperatures)

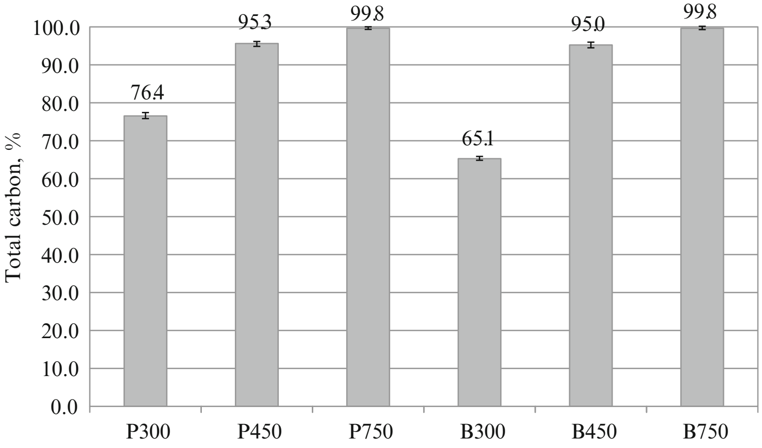


Fig. 6.25 Total carbon in biochar (%) (mean ± SD) depending on type of raw material and pyrolysis temperature (*P* pine, *B* birch, 300, 450, and 750 °C heating temperatures)

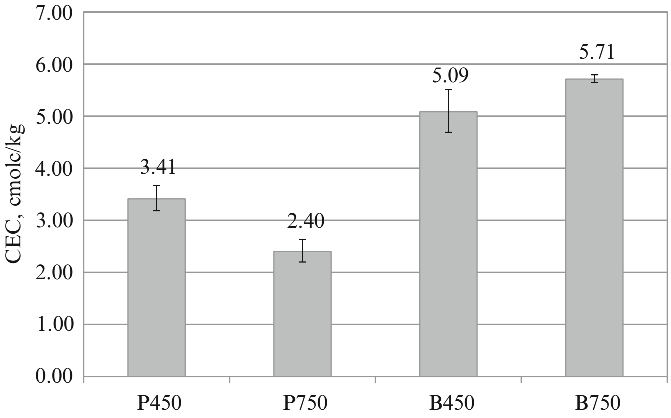


Fig. 6.26 Cation exchange capacity (cmolc/kg) (average ± SD) depending on type of raw material and pyrolysis temperature (*P* pine, *B* birch, 300, 450, and 750 °C heating temperatures)

The cation exchange capacity (CEC) of the pine biochar was less (2.40–3.41 cmolc/kg) than that of the birch biochar (5.09–5.71 cmolc/kg), and different CEC change tendencies were observed at different temperatures: in the case of pine biochar, the CEC was smaller at higher temperatures, in the case of the birch biochar, the converse was true. The impact of temperatures on the biochar CEC changes was not as great as the impact of different wood types (Fig. 6.26).

Concentrations of metals in biochar were different depending on the processing temperature, wood type, and a metal. Changes in Cu, Cr, and Ni concentrations were similar, and their higher concentrations were observed at higher processing temperatures in the case of both wood types. The change in Zn concentrations in biochar was marked by smaller concentrations at higher temperatures in the case of both wood types and can be explained by Zn evaporation quality at a temperature of about 700 °C. Evaporation temperatures of other metals are higher; therefore, the differences in their concentrations in biochar were caused by other factors. Pb and Cd were marked by different dependencies of concentration on temperature tendencies depending on wood type: they were greater in the pine biochar at higher temperatures, whereas in the case of birch biochar they were smaller at higher temperatures. This suggested an effect of the difference in the type of wood (both types of wood were taken from trees that grew in similar conditions, in a relatively clean environment; therefore, the impact of the environment was similar in both trees) (Fig. 6.27).

It was noted that the concentrations of metals, irrespective of wood type and metal, increased by 1.3 times in biochar prepared at a temperature of 450 °C compared to biochar prepared at 300 °C. This tendency is similar to that of ash content and Ca concentration. The increase in concentration of metals in biochar in a range of 450 to 750 °C was not the same: the concentrations of all metals in the pine biochar increased, except for Zn (this metal is volatile at a temperature of about 700 °C), whereas in the case of the birch biochar the concentration of Cu, Cr, and Ni increased, whereas the concentration of Pb, Zn, and Cd decreased.

Metal content in a material limits its uses as an amendment. Table 6.2 presents the concentrations of metals in biochar of various types and the limit values of metals in biochar that can be used in agriculture. The concentrations of metals in wood biochar from trees that grew in relatively clean territories, irrespective of processing temperature, were not above the limit values, and actually they were at least five times (in the case of Cr, up to 37 times) less than the limit values. Biochar produced from sewage sludge from the pulp and paper industry did not exceed limit values, either. Increased concentrations of Cr and Ni were identified in biochar produced from sewage sludge from tannery processors.

(d) *Microbiological peculiarities of biochar derived from coniferous and deciduous trees*

The wood type and temperature at which biochar was prepared influenced the quantity and changes in species of microorganisms developing on it. When comparing different wood types, it was determined that, unlike bacteria and micromycetes, no yeast was found on the birch biochar, no matter what the processing temperature was. The counts of yeast on the pine biochar differed little at different temperatures, meanwhile the counts of bacteria and micromycetes on the pine and birch biochars prepared at different temperatures differed more significantly: the counts of micromycetes decreased as the temperature of biochar preparation increased, whereas, though the number of bacteria decreased on biochar processed at a temperature of 450 °C, it again increased on biochar processed at 750 °C (Fig. 6.28).

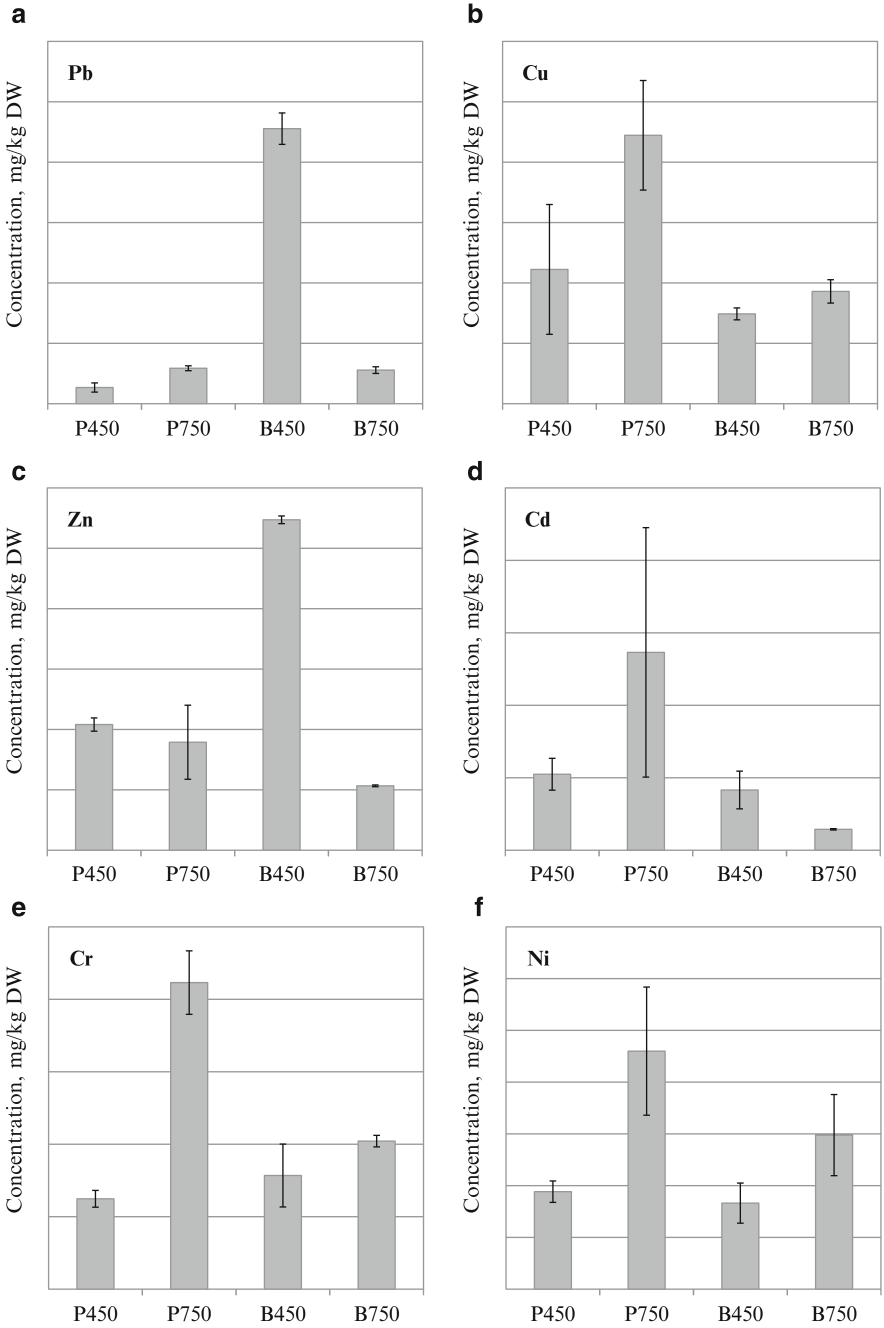


Fig. 6.27 Concentrations (mg/kg DW) of metals in biochar (mean ± SD) derived from different wood types in cases of biochar processing at 450 and 750 °C (*P* pine, *B* birch, 450 and 750 °C heating temperatures)

Table 6.2 Concentrations of metals (mg/kg DW) in (bio)char prepared from sewage sludge and primary wood

Sample type	Pb	Cu	Zn	Cd	Cr	Ni
Biochar from sewage sludge from leather processing industry (at a temperature of 450 °C)	15.9	51.5	96.7	0.45	**803**	**42.5**
Biochar from sewage sludge from wood board industry (at 450 °C)	13.3	36.1	56.8	0.22	64.5	18.8
Pine biochar prepared at 300 °C	0.20	2.92	8.84	0.13	0.57	0.88
Pine biochar prepared at 450 °C	0.26	4.42	20.9	0.05	0.62	0.94
Pine biochar prepared at 750 °C	0.58	8.86	17.9	0.14	2.11	2.30
Birch biochar prepared at 300 °C	2.02	3.14	23.7	0.10	0.91	1.13
Birch biochar prepared at 450 °C	4.55	2.97	54.6	0.04	0.78	0.83
Birch biochar prepared at 750 °C	0.55	3.71	10.7	0.01	1.02	1.49
"Basic" biochar (EBC 2012)	150	100	400	1.50	90	50.0
"Premium" biochar (EBC 2012)	120	100	400	1.00	80	30.0
For ecological marking of materials to meliorate soil	100	100	300	1.00	100	50.0

For comparison, we present limit values of metals according to the limit values of EBC and the EU limit values for substances to mark materials for meliorating soil

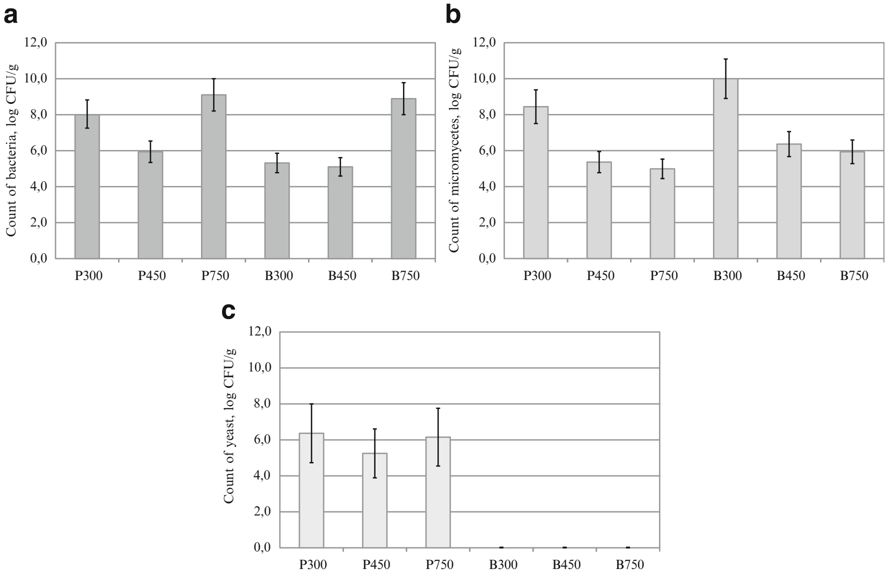


Fig. 6.28 Counts of microorganisms (**a** bacteria, **b** micromycetes, **c** yeast) (log CFU/g ± SD) on biochar prepared at different temperatures 30 days later (*CFU* colony-forming unit) (*P* pine, *B* birch, 300, 450, and 750 °C heating temperatures)

The pine biochar, processed at different temperatures, provided better conditions for the development of various microorganisms, while the birch biochar restricted yeast development. The results confirmed the fact that bacteria and micromycetes were significantly dominant groups of microorganisms. Bacteria are characterized by fast consumption of substrate and fast growth, while micromycetes grow slower but are capable of decomposing more various contaminants and are resistant to unfavorable conditions.

The wood derived from the two types of tree as well as feedstock processing temperatures had an effect on the biochar characteristics. It was noticed that differences in the morphological structure of these tree types had influenced the characteristics of the biochar, namely, the specific surface area, morphological structure of biochar, apparent/bulk density, CEC, and microbiological characteristics. Better development of the microstructure was determined in the birch wood and its biochar, while the development of the meso- and macrostructure was more pronounced in the pine wood and its biochar. The impact of differences in raw material properties on the properties of biochar was revealed better when wood was processed at lower temperatures (up to 450 °C) than at higher temperature (750 °C). The specific surface area of the birch biochar was larger (425 m^2/g) than that of the pine biochar (380 m^2/g) owing to better developed microstructure in birch wood. The morphological differences in wood also remained in the morphological structure of the biochar, and it is probable that they have an effect on the differential characteristics of apparent/bulk density of the birch and the pine biochar: it was lower in pine biochar than in the birch biochar because of the obvious impact of different pore sizes. In addition, at a temperature of 750 °C the formation of a crystal structure in the birch biochar and a pyrogenous amorphous structure in the pine biochar is observed. In addition to the impact of different wood types on biochar qualities, changes in the chemical qualities of the biochar surface should also be mentioned. One of the important results of these changes was the difference in the CEC. CEC values were lower in the pine biochar than in the birch biochar, whereas the impact of temperature on CEC was the converse: the CEC of the pine biochar at higher temperatures was smaller than at lower temperatures, whereas the converse was true in case of the birch. Because of the variety of processes determining different CECs (e.g., isomorphic changes in the structure of silicate minerals, disrupted connections at the edges and outer surfaces of minerals, dissociation of acid functional groups of organic compounds, and easier adsorption of certain organic compounds on surface of particles), it would be difficult to strictly separate factors influencing CEC. Cheng et al. (2006) have determined that CEC increase is affected by the formation of oxidation functional groups on the biochar surface. This may lead to the presumption that more oxidation functional groups form on the surface of birch biochar than on the surface of pine biochar.

Differences in the chemical properties of pine and birch biochars depend more on pyrolysis temperature. If a primary wood is used for the production of biochar, it is important to emphasize the same tree-growing conditions. Ash content, biochar yield, pH, TC, and concentrations of metals should be noted as biochar chemical properties, changes in which depend on temperature more than on wood type. Ash content, biochar yield, pH, and TC were higher at a higher processing temperature and differed according to raw material type only slightly. Having noticed a tendency that at the thermal stage of 300–450 °C, irrespective of wood type (birch or pine), the concentrations of the researched metals (Cu, Cr, Pb, Zn, Cd, and Ni) in biochar increased by 1.3 times on average, whereas at the thermal stage of 450–700 °C there were different tendencies depending on metal and wood type; one might think that chemical reactions of constituent parts of raw materials would depend on temperature.

Prospects of Use of Wood Biochar

When discussing the prospects for using wood biochar, we will perform a closer examination of several ways of using wood biochar in areas related to environmental protection. These include the use of biochar in compost, in meliorating soil, in biofiltration, and in adsorbing contaminants from an aqueous medium. It is noteworthy that a raw material that contains a large portion of lignin (about 2.4 times more than is found in sludge) and little humidity (10–20 %) is particularly important and valuable for biochar production (Gajalakshmi and Abbasi 2008). The properties are particularly characteristic of wood biomass, waste from green areas, or agricultural waste.

For effective biofiltration systems, biochar must meet the requirements of the optimal substrate: a sufficient quantity of inorganic nutrients (nitrogen 0.4 %, phosphorus 0.15 %, potassium 0.15 %), a certain quantity of organic substances as an alternative nutrition source for microorganisms, high water-retention capacity, pH of 6–8, porosity of 40–80 %, large specific surface area, developed system of macropores for the development of microorganisms, mechanical stability, limited degradation, a material that does not cause odors combined with an odor-reduction function, durability (2–4 years), and safe utilization (Devinny et al. 1999). Biochar produced from wood meets requirements for biofiltering substrates, for example, the water-retention capacity of wood biochar is about 1.7 times that of biochar produced from industrial sewage sludge. The concentration of K in pine and birch biochar prepared at a temperature of 750 °C amounts to around 0.07–0.09 %. The pH value of birch biochar prepared at a temperature of 450–750 °C is between 6.77 and 8.93, the specific surface area of birch biochar processed at a temperature of 750 °C is 425 m^2/g, about four times more than that of biochar produced from bones and about 80 times more than that of biochar produced from algae (Baltrėnas et al. in preparation). In addition, wood biochar can cost up to four times less than activated carbon (personal discussions).

Biochar as an adsorbent must be of higher pollutant selectivity, have a large sorption capacity, create favorable conditions for the kinetics and transportation of pollutants, be chemically and thermally stable and not very soluble, retain sorption qualities for a long time, be mechanically resistant and durable, be in a form to facilitate the filling of volumes, be contaminant-resistant in the long term and chemically stable, be capable of regeneration, and be cheap (Seader and Henley 2006). The biochar produced from birch showed better characteristics regarding its use as an adsorbent. The birch biochar was capable of adsorbing more metals (Cu, Zn, Pb, and Cd) from an aqueous medium than the pine biochar (Komkienė and Baltrėnaitė 2015), and this was linked more to the higher CEC value. Moreover, physical adsorption between adsorbed metals and the two types of biochar (Komkienė and Baltrėnaitė 2015) enables an easier regeneration of biochar. Biochar prepared at a temperature of 750 °C has a large specific surface area that facilitates higher retention of contaminants from the aqueous phase and provides a surface area for the development of biomass in a biofiltration system. Wood biochar has high stability and, though the H/C_{org} ratio changes depending on the specific wood type and preparation conditions, an $H/C_{org} < 0.7$ criterion is usually characteristic of wood biochar when processed at a temperature higher than 300 °C for more than 2 h (Krull et al. 2010).

In the case of composting, it is recommended to mix biochar with organic waste because it speeds up the composting process as a result of the temperature, which is around 10 °C higher, promotes faster propagation of microorganisms (Yoshizawa et al. 2007), serves as a favorable medium for microorganisms to exist (Steiner et al 2004), reduces odors (Ogawa 1994), reduces the intensity of greenhouse gas (CH_4, N_2O) emissions, reduces ammonia losses, and is a good structural material of compost. Through the composting process, biochar adsorbs nutrients from waste but does not decompose itself. Biochar might be suitable as a soil-meliorating substance thanks to its large specific surface area, high porosity, ability to increase soil water retention, high CEC, and soil acidity reduction potential. As research has revealed, the pine biochar was a particularly favorable substrate for the existence of various types of microorganisms. Both types of wood biochar processed at 750 °C had alkaline qualities (pH of 8–9) important for reducing soil acidity and rather large specific surface areas (380–425 m^2/g) that greatly affect sorption qualities.

6.2 Wood Biochar as a Sustainable Soil Amendment: Metal Risk Evaluation

Using soil amendments produces both positive and negative effects on soil quality and the sustainability of the environment. The commonly reported positive effects of amendments are associated with improving soil characteristics, increasing soil buffering, and facilitating the availability of nutrients (Glaser 2007). Organic farming has not only been transformed into sustainable farming, whose development cannot be retarded by constantly diminishing resources, but has also been perceived as carbon farming. This type of farming is aimed at restoring the biological life of soil, reducing carbon dioxide emissions into the air, increasing plant biomass, food production, and nutritional value, and reducing water pollution and the consumption of power and fertilizers. It also helps to control pests and increase biodiversity (Glaser et al. 2009). In carbon farming, one can observe a transition from using amendments that are industrial byproducts (e.g., sewage sludge) to the application of technologically designed amendments (e.g., biochar). However, even in this case, the risk of environmental pollution remains. Taking into account the prospects of sustainable development and the existing threat of pollution, the problem of long-term pollution should be given special attention. The threat is associated with both strong and durable pollutants, for example, metals, and the possible stability of metals in biochar (the latter case is not considered here). The threat of long-term pollution, which might be caused by biochar as a relatively new soil amendment, has not yet been thoroughly investigated. It can be accounted for by the lack of data obtained in long-term research. In this case, only predictive pollution evaluation models based on the major mechanisms causing pollution and, thus, risks should be used. These models should be validated in simultaneously performed tests.

A review of the literature on the considered models shows that papers analyzing modeling in the soil–plant–atmosphere system are rare, probably because of the complicated nature of this process and the large amount of variables used. Guala et al. (2010) focus on the model of metal transfer from soil to plants based on the mechanism of physiological absorption of plants, which aims to assess the effect produced by it on their growth. This model is limited to the evaluation of Cd and Ni concentrations in the soil and their effect on two cereal crops (rice, *Lolium perenne* L., and oats, *Avena sativa* L.). The model is based on the physiological mechanisms of metal transfer and the physiological characteristics of plants described by Moreno et al. (2006).

The Phyto-DSS model is a detailed phytomanagement model based on the transpiration mechanism of plants (Allen et al. 1998). It evaluates the influence of climatic conditions, soil characteristics, basic plant parameters, fertilizer characteristics, and economic parameters on the transfer of pollutants from soil to plants and the costs of phytomanagement, which allows us to compare them with other alternatives of soil restoration (Robinson et al. 2000). However, the model does not evaluate natural migration of pollutants in the process of self-cleaning of the soil, which is the main method of their moving away from the system.

The transfer of pollutants in the soil–plant–atmosphere system was modeled by Trapp and McFarlane (1995), who used the PLANTX model for this purpose. This model considers (a) the dynamic transfer of pollutants to plants from the soil solution and air and (b) the metabolism of anthropogenic pollutants and their accumulation in the roots, stem, leaves, and fruits of plants. The model is based on the processes of pollutant diffusion in the soil solution and the soil pores filled with air and roots as well as their transfer to roots by the transpiration stream, the exchange between the ambient air and leaves through their stomata due to diffusion, and the metabolism and distribution of pollutants due to the growth of plants. The model can be used to predict pollutant concentrations in plants; however, it is designed for consideration of organic pollutants. Boersma et al. (1991) integrated the processes of pollutants' transport and transformation into one mathematical model, CTSPAC, combining two submodels representing soil and plant, while Ouyang (2002) discussed the problem of applying the model to 1,4–dioxane transfer to poplars. The model of Hung and Mackay (1997) developed for pollutant transfer from the air and soil to plants and the transfer of inorganic pollutants to higher plant species was discussed by Baltrėnaitė and Butkus (2007a, b, c).

Mathematical modeling of the migration of metals and their concentration in the soil as a heterogenic system of variable composition is challenged by the complexity of these closely connected processes and the respective large amount of input data required for these models. The migration of chemical elements in soil depends largely on the filtration capacity, usually determined by its granulometric composition, as well as on metal sorption, the solid soil phases (e.g., humus, clay minerals, Fe and Mn hydroxides), and possible alkaline, oxidational, reductional, and thermodynamic effects produced by geochemical barriers. Moreover, the migration of pollutants depends on climatic conditions (e.g., soil moisture content), terrain (a particular type of geochemical landscape), the composition of rock elements of the soil, soil solutions and their temperature, the Eh and pH, and the biomass of chemical element absorption (the effectiveness of the biochemical barrier). Given these usually not easily determined parameters required for describing the migration of chemical elements, as well as various soil surface contours, we obtain a set of basic parameters of the modeled chemical elements' migration in a particular soil system that is often incomplete and not sufficiently clear. Therefore, the application of mathematical models to the description of chemical elements' migration and accumulation that does not take into consideration the complicated nature of these processes seems rather limited.

The mathematical model MINTEQA2/PRODEFA2 (Landner and Reuther 2004) used for investigating the interaction between metals and soil may be mentioned as a model of this kind.

In the present study, the BALANS model, based on the concept of a constantly occurring transfer of metals with amendments to the soil as part of the ecosystem and their removal from it, is considered (Fig. 6.29). The concentrations of metals in polluted soil sown with grain crops were estimated taking into consideration the invariable values of background metal concentrations, aerogenic metal load (uptake), and the removal of metals from the soil as a result (consequence) of their natural physicochemical migration and gathering of harvest, i.e., as a result (consequence) of biogeochemical migration.

The uptake of aerogenic metals is evaluated based on the values of the total load of aerogenic aerosols and metal concentration in them. The amount of metals and harvested crops are calculated based on biomass removed with crops and the metal concentrations in it. Evaluation of possibly removing metals naturally as a result of their physicochemical migration in soil is made based on empirical annual migration coefficients corresponding to the respective geographical climatic zone and type of soil, rather than to the many previously mentioned migration/accumulation parameters. This largely facilitates mathematical modeling, as well as increasing

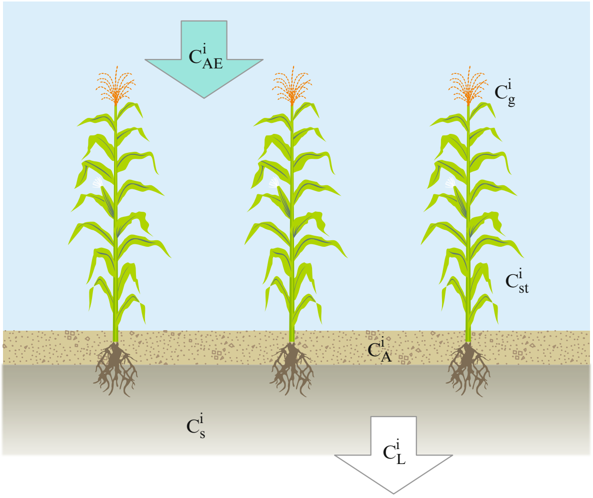


Fig. 6.29 BALANS model based on systemic concept of penetration of metals into soil of area sown by wheat together with amendments and their removal. C^i_{AE} is the concentration of metal i in mineral dust of aerogenic origin; C^i_A is the concentration of metal i in the amendment; C^i_L is the amount of metal i removed as a result of natural migration; C^i_s is the remaining amount of metal i in amended soil; C^i_g is the concentration of metal i in wheat grains; C^i_{st} is the concentration of metal i in wheat straws

the responsibility of an operator for more accurate application of migration coefficient values. The BALANS program uses annual migration coefficients for Cu, Zn, Pb, Co, Ni, Cr, V, and Mo, chosen by default from numerous literature sources, which correspond to the types of soil, such as albeluvisols and podzols, characteristic of southern taiga and mixed forest zones (Malinina 2012). Experienced specialists modeling a particular aspect of migration/accumulation of metals in soil under real conditions can change the values of the migration coefficients as they deem necessary.

The real advantages of this model include (a) the differentiation between the removal of metals by the process of natural physicochemical migration together with harvested crops; (b) determining the balance of metals in the soil–plant–atmosphere system in the long and short terms, which is of particular importance in the context of sustainable development; (c) evaluating the effect of various method of metal uptake by soil (through aerogenic sources and with amendments) and their removal (owing to natural migration and with harvested crops) on the balance of metals in soil; (d) the integration of the principles of acropetal and basipetal distribution of metals in plants into the model of their translocation in the soil–plant–atmosphere system; (e) the influence of complicated processes affecting the system expressed by the coefficients of annual pollutant transfer, thereby creating the conditions for the effective practical use of the model.

The present investigation aims to compare the variation of metal concentrations in the soil in the long term using a predictive model under conditions where the amounts of metals entering into the soil with amendments are close to background or limiting values, specified for such amendments as biochar and sewage sludge.

Modeled object. A territory in the Mažeikiai region in the northwest of Lithuania has been chosen for modeling. The soil in this territory is characterized by higher concentrations of metals (Zn, Cu, Ni, Cr, and Pb) owing to pollution of aerogenic origin produced by the largest oil refinery in the Baltic States (Baltrėnaitė et al. 2014a, b, c). The inhabitants in this area are mainly agricultural workers who grow wheat, which is one of the most popular crops in many European countries.

The BALANS model for describing the self-purification of soil from metals was developed at Tomsk State University (Russia) by Prof. Arvydas Lietuvninkas (2002a, b). The input data of the model's program are as follows:

- The concentration of metal i in the soil of the polluted territory, $C_{\mathrm{s}}^{\mathrm{i}}$ (mg/kg) (Table 6.3);
- The daily load of aerogenic mineral dust in the soil (32.4 mg/m^2 in the examined area) and metal i concentration in it, $C_{\mathrm{AE}}^{\mathrm{i}}$ (mg/kg) (Table 6.3);
- The concentration of metal i in the amendment, $C_{\mathrm{A}}^{\mathrm{i}}$(mg/kg) (Table 6.4);
- The concentration of metal i in crops, i.e., wheat grains ($C_{\mathrm{g}}^{\mathrm{i}}$) and straws ($C_{\mathrm{st}}^{\mathrm{i}}$) (mg/kg) (Table 6.5);

Table 6.3 The concentration of metals in the soil of the examined territory and mineral dust of aerogenic origin (mg/kg)

Metals	In examined soil, $C_{\mathrm{s}}^{\mathrm{i}}$ (at a depth of 0–10 cm) (Baltrėnaitė et al. 2014a, b, c)	In mineral dust of aerogenic origin found in examined territory, $C_{\mathrm{AE}}^{\mathrm{i}}$ (Krastinytė et al. 2013)
Zn	17.5	338
Cu	5.22	48.0
Ni	30.4	88.0
Cr	32.0	77.0
Pb	3.89	158

Table 6.4 Concentrations of metals in biochar used as amendment, $C_{\mathrm{A}}^{\mathrm{i}}$: A denotes biochar obtained from relatively nonpolluted pinewood; B denotes biochar with the highest allowable values of metals (mg/kg DM) (EBC 2012); C denotes Class 1 sewage sludge (86/278/EEC) used as an amendment in agriculture

Metals	A	B	C
Zn	20.9	400	300
Cu	1.47	100	75
Ni	0.94	50	50
Cr	0.21	90	140
Pb	0.760	150	140

Table 6.5 Concentrations of metals in wheat grains and straws (mg/kg DW) (Kabata Pendias 2010)

Metals	Wheat grain, C_g^i	Wheat straws, C_{st}^i
Zn	25.0	10.0
Cu	4.00	11.0
Ni	3.00	1.50
Cr	1.50	7.00
Pb	0.700	0.600

- The amount of soil amendment (biochar and sewage sludge), tons/ha (in our case, 50 tons/ha);
- The density of the soil (assumed to be 1.2 g/cm^3 in the model);
- Annual wheat crop, ct/ha (30 ct/ha);
- Annually formed wheat straw mass, ct/ha (60 ct/ha);
- The portion of wheat straws annually removed from the field, % (60 %);
- The type of microrelief of the field: (a) a strongly pronounced hill (index H), (b) a plain (no index), and (c) a strongly pronounced lowland (index L);
- Annual migration coefficients of the modeled chemical elements, given by default from the database of the program or chosen by the operator;

The BALANS model cannot take into account by default the influence of various forms of metals found in amendments (biochar and sewage sludge) on the geochemical migration intensity in soil. This can be taken into consideration only if an operator inputs the respective data. Unfortunately, this capability of the model has not been used in the experiment.

To model the long-term removal of metals from soil, amendments, including biochar and sewage sludge, were chosen. Several types of amendments were considered: (a) biochar of pinewood, not polluted with metals (Table 6.4); (b) basic biochar with metal concentrations reaching the highest allowable values specified by the European Biochar Certificate (EBC) (Table 6.4); (c) sewage sludge with the highest allowable values of metals (Class 1) in this material that may be used as soil amendment in agriculture (86/278/EEC). The concentrations of metals in amendments are given in Table 6.4.

The concentrations of metals in wheat grains and straws, chosen based on the data obtained from long-term experiments (Kabata Pendias 2010), are given in Table 6.5.

To obtain biochar relatively unpolluted with metals, the wood of Scots pine (*Pinus sylvestris* L.) was used. The pine (about 40 years old and 22 cm in diameter) was chosen and cut down in the Labanoras Forest, Molėtai region (55°12′51″N, 25°42′54″E), where trees are grown according to Forest Stewardship Council (FSC) requirements. The bark of the pine was removed and pinewood specimens of 15 mm^3 were prepared. Then they were dried for 48 h at room temperature. Pyrolysis was performed at 450 °C and lasted for 2 h (Joseph et al. 2009) while the specimens were placed in closed aluminum containers (Saleh et al. 2012) in an E5CK–T muffle furnace under conditions of limited air flow. The methods adapted according to Wong and Li (2004) recommendations were used to detect metals in

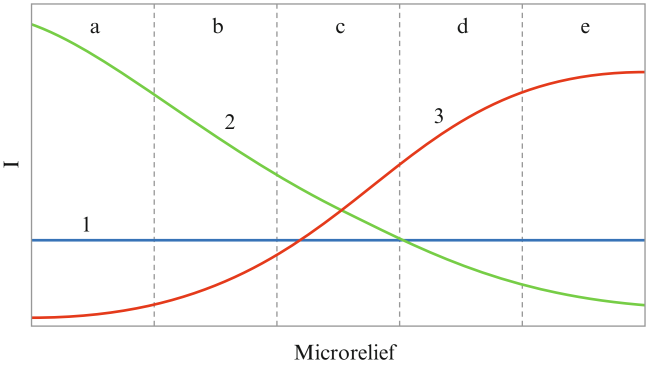


Fig. 6.30 Schematic diagram of BALANS model describing the removal of metals from the soil (*2*) and their concentrations in it (*3*) at a constant load of mineral dust (*1*): *I* is the level of these parameters; the type of the field's microclimate: (*a*) strongly pronounced hill; (*b*) weakly pronounced hill; (*c*) flat surface; (*d*) weakly pronounced lowland; (*e*) strongly pronounced lowland. *Note*: cases (*b*) and (*d*) are not included in the analysis of the investigation results

biochar. The amounts of metals (Cr, Cd, Cu, Ni, Zn, Pb, and Mn) were analyzed using the 210 VGP atomic absorption spectrophotometer (Buck Scientific, Inc., Norwalk, CT) (Baltrėnaitė et al. 2010; Pundytė et al. 2011a, b).

The method takes into account the microrelief of the field where wheat is grown and the load of aerogenic pollutants on which the removal and accumulation of metals in the soil depend (Lietuvninkas 2002a, b). A schematic diagram of self-purification of the soil from metals and their accumulation in the soils, depending on the fields' microrelief, is given in Fig 6.30. The aerogenic load of mineral dust is assumed to be invariable (straight line 1). The removal of metals from soil is closely associated with the microrelief type of the field. This process is much more intense in an autonomous geochemical landscape (a positive type of microrelief, i.e., a strongly pronounced hill) and less intense in a superaquatic geochemical landscape (a negative type of microrelief, i.e., strongly pronounced lowland). It is shown by curve 2 in the figure (not taking into account the extent of the process). Nonuniform removal of metals and the polluted soil manifests itself in their different concentrations. Thus, the soil of the positive microrelief type accumulates a considerably smaller amount of these materials than the soil of the negative microrelief type (Fig 6.30, curve 3), and the purification of soil is more intense in this case. In real conditions, the aforementioned difference depends on the geochemical characteristics of the particular metals and given conditions (e.g., edaphic conditions, including the type and properties of the soil and the level of pollution).

In the present work, the following three types of a field's microrelief are investigated: (a) a strongly pronounced hill (index H), (b) a plain (no index), and (c) a strongly pronounced lowland (index L). The types of microrelief are described in more detail in the book by Lietuvninkas (2002a, b). The predictive values of the amounts of metals are calculated for 200 years into the future.

Ensuring research accuracy and validating the model. To analyze the biochar specimens, their duplicates were prepared and examined. To ensure the proper concentration of metals in the biochar specimens, reference material (ERM®-CD100) was used, while standard solutions were used for developing the calibration curves. Statistical analysis of data was performed using Excel and Statistica 8.0 programs. Graphical presentation of the results obtained in the experiments is based on the mean arithmetic values with the standard deviation (SD).

The BALANS model has not been specially validated because the prediction period of 200 years in the future makes that impossible. The coefficients of annual migration of Cu, Ni, Zn, Cr, and Pb used by default were calibrated several times based on a comparison of the obtained modeling results with data on the primary natural partial self-purification of soil from metals provided in the literature (Glazovskaia 1988; Kabata Pendias and Pendias 1989; Kaigorodov and Ruk 2005; Plekhanova 2009). However, it should be noted that the coefficients of annual metal migration given by default are actually their approximate values.

The output data yielded by the considered predictive model characterize the amounts of metals removed from the soil contaminated with pollutants of aerogenic and edaphic origin during a particular period (up to 200 years in this case). The results of the modeling describe the concentrations of metals in the soil depending on time, as well as the amount of metals removed from it due to natural physicochemical migration and with the harvested crops, the period of time (years) during which the metals' concentration in the soil was reduced by half (i.e., half-life period), the portion of metals removed from the amended soil depending on a particular type of microrelief, and the portion of metals of aerogenic origin influencing the intensity of their leaching from the soil.

(a) *Removal of metals (g/ha) from amended soil by the process of their natural migration during the first year after amendment*

Taking metals out of soil using their natural physicochemical migration is a basic method of purifying polluted soil (Fig 6.29). The extent of this process in the modeled cases is determined by the total concentration of a particular metal in the amended soil and its solubility in the soil solution, as well as by the climatic conditions and soil properties developed under these particular conditions. Therefore, the total amount of metals removed from arable land as a result of their physicochemical migration is directly proportional to their concentration in the amended soil and the migration intensity expressed in the considered model by the annual migration coefficients.

Similar results were reported by Plekhanova (2009), who examined arable albeluvisols polluted with sewage sludge in the Moscow region 12 years ago. The author found that the largest amounts of metals (particularly Cd and Cu), which reached up to 40–47 % of their total amounts, had been lost in the considered period by the most highly polluted soil. It should be mentioned that this refers only to the layer of arable land going down to a depth of 20 cm because at a depth of 30–45 cm considerable amounts of metals (particularly Cd, Ni, and Zn) removed from the upper soil levels were accumulated.

Their evaluation has shown that, actually, at a depth of around 50 cm, the soil lost only up to 22 % Cd, 14 % Zn, and 9 % Cu found in this layer over the 12-year period, i.e., the changes were very slight. Plekhanova (2009) does not jump to conclusions because of the variability of metal quantities and considers the obtained results to be only approximate. However, subsequently, Malinina (2012), studying deeper layers of gleyic albeluvisols found northeast of Moscow, found the same redistribution of metals in polluted soil. According to this author, the concentrations of Cu, Zn, and Ni in the soil at depths of 20–40 cm often largely exceed the maximum allowable concentration (MAC), while the variability of the amounts of some chemical elements (e.g., Mn, Cr, Cu, Zn, and Pb), which could be accounted for by their redistribution after sewage sludge was spread over the soil, was two to three times higher than that of the control field soil.

In the work by Sistani and Novak (2009), metals' migration in soil and their accumulation in the manured Alisoils (referred to as Ultisols in the USA) have been described in detail. According to these authors, the vertical Zn and Cu migration in this type of soil was found only to depths of 30–45 cm and might be considered limited.

The removal of metals from the soil as a result of their natural migration in cases where the soil is amended with biochar, in the presence or absence of aerogenic load, as well as in cases where the concentration of metals does not exceed the limiting value specified for biochar and sewage sludge used for land amendment in agriculture, is shown in Fig 6.31.

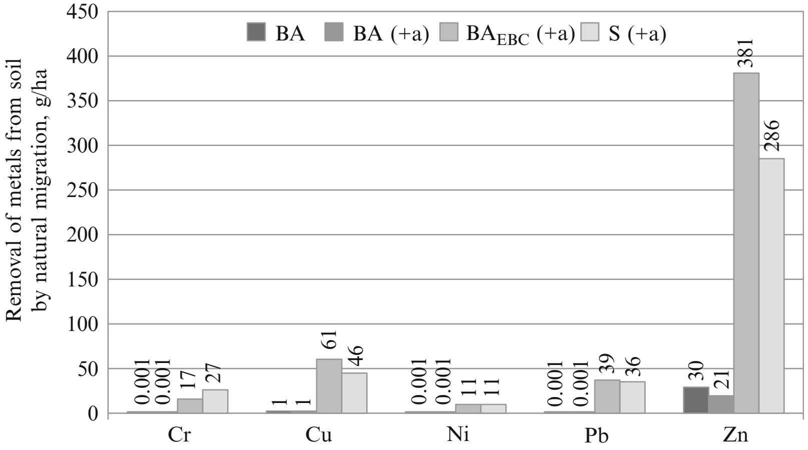


Fig. 6.31 Annual amount of metals, carried from soil amended with various types of amendments as a result of their migration, C_L^i (g/ha) for an area of flat land: *BA* biochar unpolluted with metals, *BA(+a)* biochar unpolluted with metals in area with inflowing metals of aerogenic origin; *BA_{EBC}(+a)* biochar with highest concentration of metals allowed by EBC in area with load of metals of aerogenic origin; S(+a) sewage sludge load with highest metal concentration allowable in agriculture

In general, the largest mass of metals removed as a result of natural physicochemical migration was found for Zn, while for Cu and Pb it was slightly slower, and for Cr and Ni this mass was the lowest. Larger amounts of Zn, Cu, and Pb have been removed from soil amended with biochar having the limiting metals' concentrations, while in the case of Cr, a larger amount of this metal was lost by soil amended with Class 1 sewage sludge. A comparative analysis of the removal of metals from soils amended with various amendments has shown that the metals having the highest concentrations in the soil were removed from it in larger amounts. This is one of the properties of soil self-purification characteristic of the considered model. Moreover, the difference in the proportions between metals in the amendment and their amount removed from the soil has been observed and was accounted for by various intensities of the physicochemical migration of metals.

(b) *Removal of metals (g/ha per year) from amended soil together with the removal of wheat straw and grain*

Figure 6.32 demonstrates the removal of metals from amended soil as a result of biogeochemical migration associated with the removal of wheat grain and straw. The amount of metals removed with harvested crops decreased in the following order: Zn > Cu > Ni > Cr > Pb. From a biogeochemical perspective, this sequence is close to that characterizing the bioaccumulation of metals in living matter (Perelman 1972): $Zn_{19.6}Cu_{9.1}Mn_{6.9}Pb_{3.7}Ni_{1.5}Cr_{1.0}$ [where numerical values show their concentration in the mineral portion of plants (ash) compared to the concentration of metals in soil].

Zn is a metal most intensively removed annually together with wheat crops from amended soil (786 g/ha), and it occurs in amounts 5 times greater than that of removed Cy, about eight times than that of Ni, about 11 times than that of Cr, and about 34 times than that of Pb. For the other metals considered (i.e., Cu, Ni, Cr, and Pb), the respective calculated value was equal to 0.23–1.6 g/ha

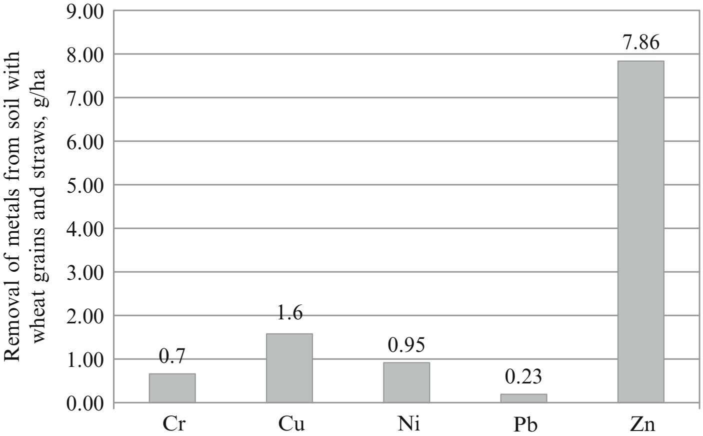


Fig. 6.32 Removal of metals from amended soil per year (g/ha) with wheat grains and straws

per year. The model does not take into account the correlation between metals' concentrations in amended soil and their accumulation in the biomass of plants (wheat grains and straws) because the biochemical migration of metals is not intense (around 2.7 % for soil amended with sewage sludge) compared to their natural physicochemical migration in soil solutions. Evaluating the relatively intense self-purification of the albeluvisols near Moscow polluted with metals, on which sewage sludge was spread, Plekhanova (2009) emphasized that this process was accelerated because fodder crops grown for 12 years in the polluted fields were harvested every year, and a large portion of metals was removed together with their biomass. This is natural because, for example, metal concentrations in the biomass of rye grass (at ground level) growing in polluted soil were higher than those found in the rye grass growing in the control fields. Thus, the concentration of Zn was 4.7 times, that of Pb was 5.2 times, that of Cr was 7 times, and that of Ni was 10 times higher than that in plants growing in the control field soil, while for mangold, this value was 1.5, 7.5, 10.4, and 10 times greater. Unfortunately, however, the author (Plekhanova 2009) did not evaluate the contribution of migration to the self-purification of the soil.

(c) *The influence of metals of aerogenic origin on the self-purification of soil*

In fact, pollutants of aerogenic origin comprise an important and permanent source of pollution in various territories, increasing the load of pollution and slowing down pollutant removal and the self-purification of ecosystems. In Fig. 6.33, two cases representing the concentration of metals in amended soil unpolluted by biochar are compared where the effect of metals (pollutants) of aerogenic origin cannot be observed (e.g., in relatively clean or protected territories) and when it can be observed.

The modeling data reveal a rather uniform concentration of metals in the amended soil without a load of metals of aerogenic origin. However, in the absence of this load, the concentration of metals in the amended soils does not tend to decrease since, because of the relatively low concentration of metals, the sorption of solid metals, which predominate in this type of soil, limits the process of metal removal. Pollution with metals of aerogenic origin plays an active role in the higher or lower accumulation of metals in soil, depending on the extent of aerogenic contamination. The composition of the fallout of materials of aerogenic origin, reaching 32.4 mg/m^2 per day over the period of 200 years, as presented in Table 6.3, can cause an increase in the metals' concentration, reaching 2 % Cr, 3 % Ni, 7 % Cu, 17 % Zn, and even 39 % Pb (Fig. 6.33).

It should be emphasized that the aforementioned dust load (32.4 mg/m^2) is considered a lower than average and less dangerous load (Saet et al. 1990; Krastinytė et al. 2013; Baltrėnaitė et al. 2014a, b, c), though in the long term (after 200-year period), it can cause, in the case of Pb, an increase of up to 39 % in the metals' concentrations in soil. Therefore, larger loads of mineral dust or a higher concentration of metals in it will cause a disproportionately larger load of metals of aerogenic origin. Pollutants of aerogenic origin

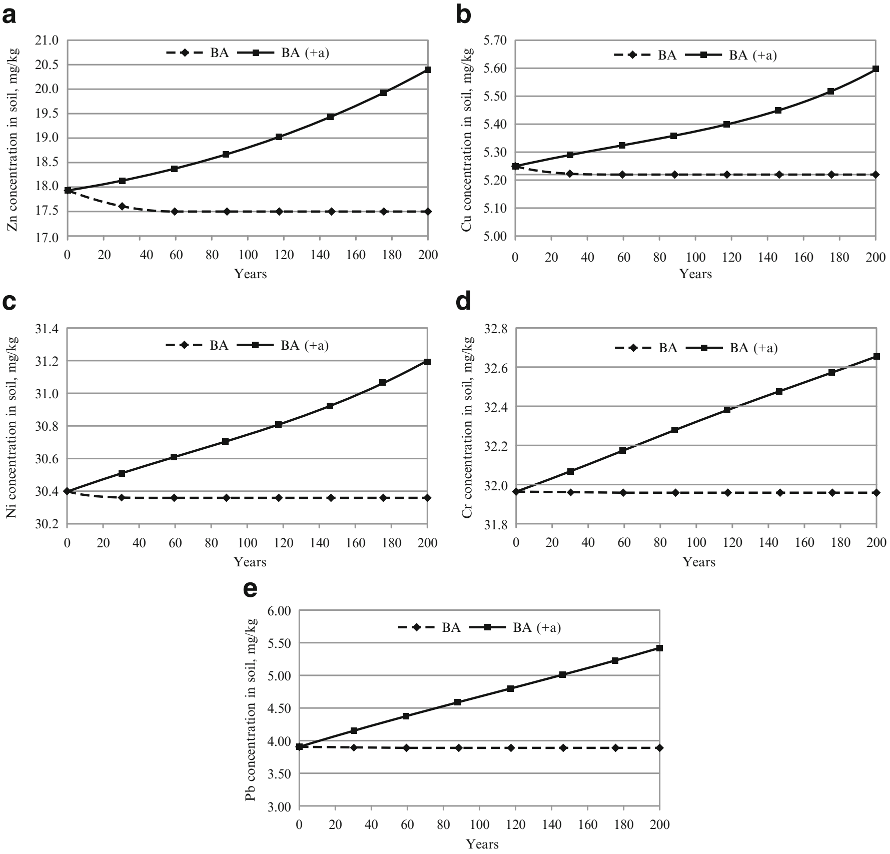


Fig. 6.33 Concentration of metals in soil (mg/kg) amended with relatively clean biochar, which is polluted [BA(+a)] or unpolluted (BA) with metals of aerogenic origin in period of 200 years

(metals) can be found not only close to the source of pollution but also much farther away from it. It is known that the largest amounts of metals of aerogenic origin in liquid form can be found at distances of around three times further from the source of pollution than the highest concentration of nonsoluble (i.e., found in dust) metals (Lietuvninkas 2012). Metals of aerogenic origin, which are typomorphic with respect to the source of pollution, are usually found in higher concentrations in soil.

(d) *The predicted variation of metal concentrations in the soil of a plain (microrelief) amended with various materials over the course of 200 years*
Figure 6.34 demonstrates the accumulation of metals remaining in soil polluted with metals of aerogenic origin, which was amended with various materials, after a long period of time. It can be observed that, at the aforementioned level of aerogenic load, the concentration of metals in the soil amended by various materials varies differently. When highly polluted

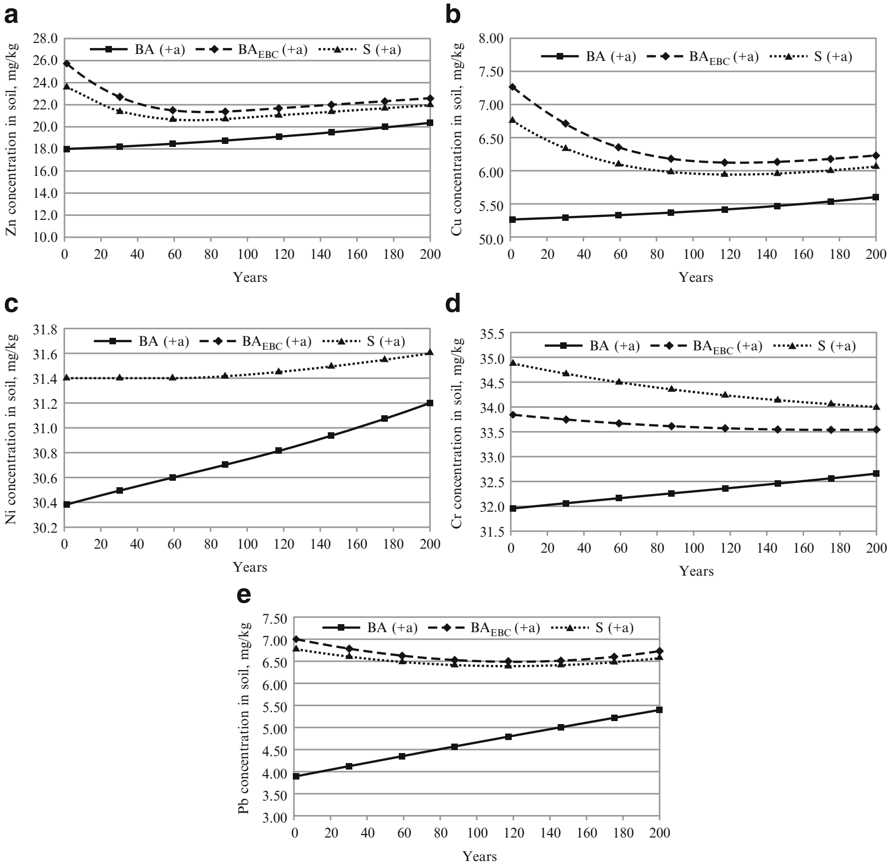


Fig. 6.34 Variation of metal concentration (mg/kg) in the soil of a plane (microrelief) of amended with various materials and polluted with metals of aerogenic origin in a period of 200 years: BA (+a) denotes relatively clean biochar; BA$_{EBC}$ (+a) denotes biochar with highest allowable concentration of metals; S(+a) denotes sewage sludge with highest allowable metal concentrations in agriculture (*Note*: in the case of Ni, the curve characterizing Ni removal from biochar with the highest allowable metal concentrations according to EBC and that characterizing the removal of these metals from sewage sludge with the highest allowable metal concentrations in agriculture match each other and thus overlap)

materials are used in the first period after amending (30–80 years in the case of Zn and Cu and 80 years in the case of the other metals), self-purification processes dominate in the soil, i.e., a decrease in metal concentrations can be observed. A more dynamic process is characteristic of Zn and a less dynamic process characterizes Cu. The removal from the soil of other metals, particularly Cr, was slower. In the later period, when metal concentrations in the soil decreased significantly while their aerogenic load remained the same, self-purification processes slowed down and were gradually replaced by metal accumulation, i.e., became a process of constantly growing soil pollution.

When and how it happens depends on the type of removal of metals of aerogenic origin from soil, their uptake, and its relation to the intensity of metal removal from the soil provided for in the considered model.

When relatively clean biochar is used as an amendment, metal concentration in soil manly depends on the uptake of metals of aerogenic origin as well as on their removal together with crops (grains and straws). As shown by the graphs in Fig. 6.34, the main factor determining the ratio of soil pollution to soil self-purification (with respect to metals) is the load (deposition) of metals of aerogenic origin. It is evident that if a quantitative relation between the aforementioned processes is not taken into account when using unpolluted biochar as an amendment, soil pollution remains at its lowest level.

The graphs presented in Fig 6.34 show the individual geochemical character of metals found in soil where some (Zn and Cu) are more mobile and more dynamic from the perspective of their concentration, while others (Ni, Pb, and Cr) migrate slower and are less mobile. The default mode of the BALANS model does not take into account the effect produced by various forms of metals found in different types of amendments (such as biochar and sewage sludge) on the intensity of their geochemical migration in soil. This can be done only if the data are entered manually by an operator. Unfortunately, it was not done in modeling the situation in question.

(e) *The period of metals' half-life in amended soil and its dependence on microrelief*

The half-life of metals introduced into soil together with amendments entails a reduction of their levels in amended soil by half and indicates the rate of the metals' removal from the soil. As mentioned previously, under the climatic conditions specified in the model, the rate of a metal's removal from soil strongly depends on its position in the soil catena, i.e., in a field's microrelief (Lietuvninkas 2012).

The experimental (modeling) results presented in Fig. 6.35 show that the half-life of metals depends not only on the metals' properties and the additional streams of metals flowing in the soil, but on the type of relief, determining the gradient of metal removal as well. It also determines the rate of decrease in metal concentration in the soil.

The half-life of metals in soil reflects the specific nature of the considered metals. It has been found that, in the investigated case, this period increases for various metals in the following order: Zn < Cu < Ni < Cr < Pb, and, as mentioned earlier, depends on the migration rate of a particular metal, the additional input of metals of aerogenic origin, and lateral differentiation of these metals in the soil, depending on the type of microrelief.

The additional input of metals of aerogenic origin provided for in the considered case can even double the half-life of metals (particularly for Ni and Cr) or, in other words, reduce by half the self-purification rate of the soil (Fig. 6.35). The difference can be more clearly seen in the case of different types of microrelief, for which the removal of metals from the soil is evaluated. In Fig. 6.35, the decreasing order of metals' half-life, when this period

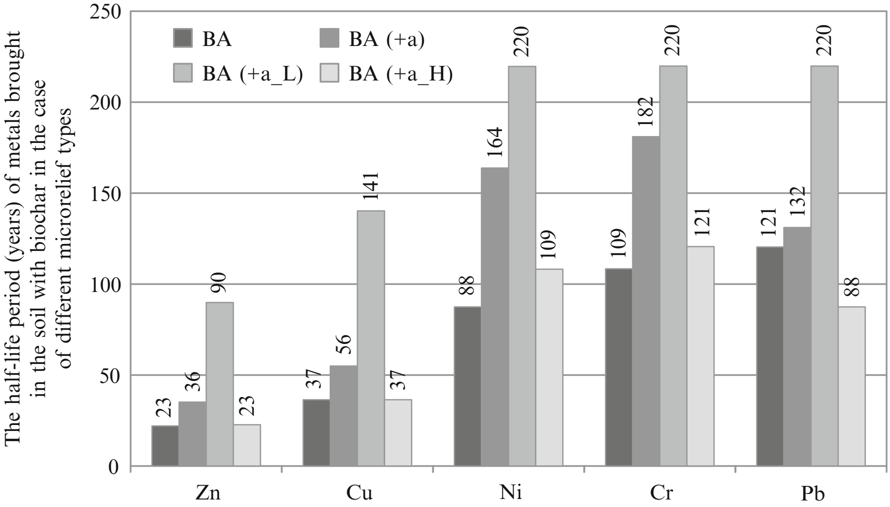


Fig. 6.35 Half-life period of heavy metals brought in soil together with amendments (years): *BA* relatively unpolluted biochar; *BA(+a)* relatively unpolluted biochar in presence of load of heavy metals of aerogenic origin and microrelief of plane; *BA(+a_L)* relatively unpolluted biochar in presence of load of heavy metals of aerogenic origin and microrelief of strongly pronounced lowland; *BA(+a_H)* relatively unpolluted biochar in presence of load of heavy metals of aerogenic origin and microrelief of strongly pronounced hills

decreases with increasing altitude (i.e., when the half-life is largest in the case of the microrelief characterized by a strongly pronounced lowland and shortest in the case of a strongly pronounced hill) can be observed.

If we ignore the influence of relief and the load of metals of aerogenic origin and consider the albeluvisols amended with relatively clean biochar, we obtain the following half-life of the metals (years): Zn: 23, Cu: 37, Ni: 88, Cr: 109, Pb: 121 (Fig. 6.35). But can this be achieved in real-life conditions?

According to Japanese researchers (Jimura et al. 1977), the initial period of a metal's half-life determined using a lysimeter is 70–510 years for Zn, 13–1100 years for Cd, 310–1500 years for Cu, and 740–5900 years for Pb. Plekhanova (2009) assessed the duration of the considered process in a layer of arable land near Moscow consisting of albeluvisols amended with sewage sludge in a different way and provided the following data: 12 years for Zn and Cd, 15 years for Cu, and 20 years for Ni. However, she emphasized that, in that case, the phytoremediation effect, manifesting itself as the removal of metals from soil together with the biomass of fodder crops (e.g., rye grass, mangel-wurzel) grown in fields, could contribute to this process considerably. Therefore, the provided data are rather controversial, reflecting the complicated nature of self-purification of soil and the environmental conditions affecting it, as well as the uncertain role of the physicochemical parameters of metal migration in the soil in particular cases.

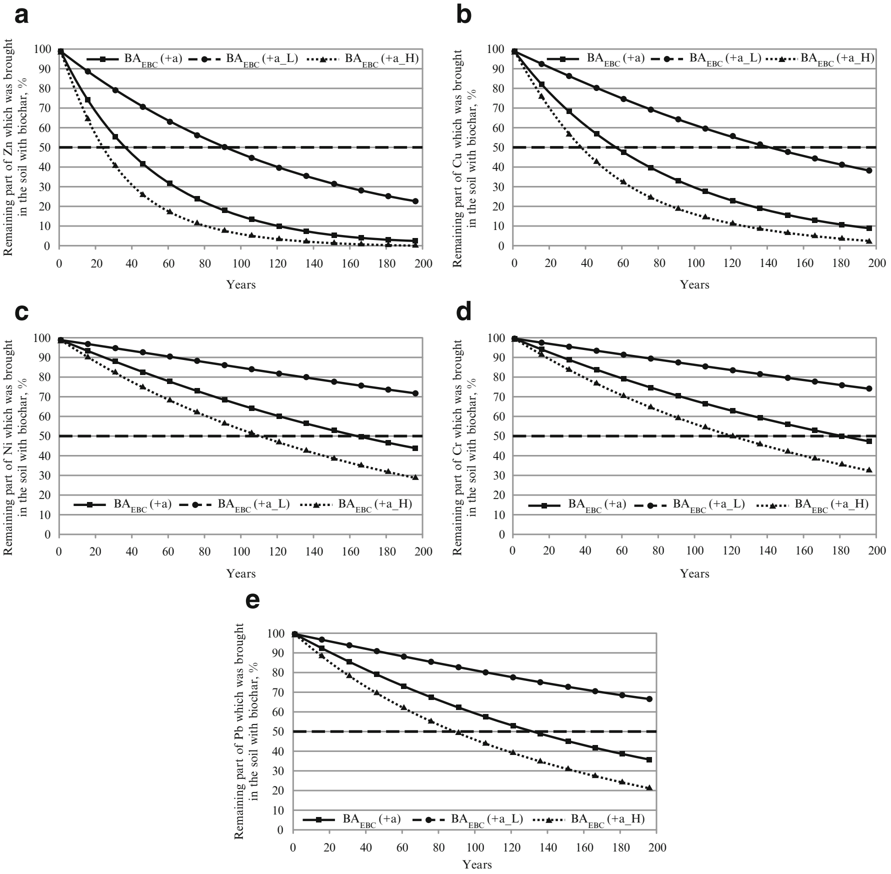


Fig. 6.36 Metals brought in soil together with biochar (having highest concentration of metals according to EBC), which remain in soil over period of 200 years in case of various types of microrelief and pollution of aerogenic origin: *BA_{EBC}(+a)* for a plane; *BA_{EBC}(+a_L)* for strongly pronounced lowland; *BA_{EBC}(+a_H)* for a strongly pronounced hill. *Dotted line*: amount of metals remaining in soil, corresponding to metals' half-life (50 %)

(f) *The amount of metals introduced into soil together with amendments that remain there for 200 years under conditions of different types of microrelief*
Figure 6.36 presents the data related to modeling the removal of metals from soil amended with biochar (and having the highest, according to the EBC, allowable value of metal concentration) in the presence of a load of metals of aerogenic origin over a period of 200 years in the case of three types of microrelief: a strongly pronounced lowland, a plane, and a strongly pronounced hill.

As expected, the results of modeling show that metals are most rapidly removed from soils found in autonomous geochemical landscapes (hills) and most slowly from superaquatic and similar types of soil found in depressions in elementary geochemical landscapes. Based on the analysis of metals, it was found that, on average, the removal of metals from the soil of a plane (as a kind of microrelief) is 1.5–3 times slower than their removal from the soil of a hill, while it is about 2–10 times faster than the removal of metals from lowland soil, keeping in mind the difference in metals' mobility.

It has been predicted that, under the most favorable conditions of soil self-purification (in the case of microrelief characteristic of hills) the amount of Zn and Cu remaining in the soil will be at the lowest levels (not exceeding 5 %) compared to the other examined metals, such as Ni, Cr, and Pb, which could amount to around 20–30 %. In lowlands, the rate of metal removal is slower compared to that in hills: two to three times slower for Ni, Cr, and Pb and around 20 times slower for Zn and Cu. Therefore, in the soils of lowlands, the half-life of Ni, Cr, and Pb before their removal from soil is much more than 200 years, while for Zn and Cu it is around 90 and 150 years, respectively (Fig. 6.36).

6.3 Use of Wood Biochar for Removing Metals from Urban Surface Runoff Water

In urban areas the threat of metal-contaminated water is hidden by the increased (due to urbanization) variety and amount of pollutants transported to receiving waters by surface runoff water (SRW) as a diffuse pollution source. Oil, grease and toxic chemicals, sediments, and road salts are carried off by urban SRW from impervious surfaces (e.g., roads, motorways, pavements, roofed structures, parking lots, airports, and industrial sites) to receiving waters, where pollutants can be toxic (depending on the concentrations) to aquatic life. Usually, an insignificant part of urban SRW is treated before its release into receiving waters (Muthukrishnan 2010). The absence of an urban SRW treatment facility can hardly assure that the maximum metal levels will not be exceeded. Pollutants in urban SRW mainly include suspended solids, metals (e.g., Cd, Pb, Cu, Zn, Hg), hydrocarbons, and bacteria (Hvitved-Jacobsen et al. 2009).

Adsorption is widely used as an effective physical method of separation in order to eliminate or lower the concentration of pollutants (organics and inorganics) in polluted waters by the application of the most common adsorbents, such as silica gel, activated carbon, and aluminum oxide (Lin 1993). The results of various studies on the application of biochar and characteristics such as porosity, high specific surface area, and cation exchange capacity suggest that it would be prudent to develop biochar as an adsorbent material that could be efficiently used in urban SRW treatment for the removal of anthropogenic soluble metals, which would reduce the costs of stormwater treatment by avoiding expensive materials (such as activated carbon, complexing agents the improve removal performance) (Table 6.6) (Downie et al. 2009).

Table 6.6 Physicochemical properties of samples of biochar, mean value ± SD

	Scots pine (*Pinus sylvestris* L.)		Silver birch (*Betula pendula*)	
Physicochemical properties	450 (±5)[a]	700 (±5)[b]	450 (±5)[a]	700 (±5)[b]
Porosity (%)	77.4	77.3	79.2	73.1
Specific surface area[c] (m^2/g)	9.16	10.4	5.92	7.17
Density (g/cm)	0.275	0.279	0.444	0.453
Apparent density (g/cm)	0.520	0.499	0.804	0.682
Bulk density (g/cm)	1.21	1.23	2.14	1.68
pH	8.56 ± 0.02	8.52 ± 0.01	8.69 ± 0.02	9.27 ± 0.01
CEC (cmolc/kg)	3.41 ± 0.24	2.40 ± 0.21	5.09 ± 0.42	5.71 ± 0.07
TC (%)	96.3 ± 0.01	95.8 ± 0.01	95.0 ± 0.01	96.6 ± 0.01

[a] Specific surface area was determined using mercury intrusion
[b] Biochar production process duration was 120 min
[c] Biochar production process duration was 45 min

Table 6.7 Concentrations of metals ions in leaching solutions

Metal ions	Onefold MAC (mg/L)	Twofold MAC (mg/L)	Fivefold MAC (mg/L)
Cd (II)	0.04	0.08	0.2
Pb (II)	0.1	0.2	0.5
Cu (II)	0.5	1.0	2.5
Zn (II)	0.4	0.8	2.0

Figure 6.6 provides data on the physicochemical properties of biochar used for metal adsorption experiments. Wood biochar might be suitable for use as an adsorbent thanks to such properties as a predominant microporosity (10–3000 μm) and the specific surface area (from 5 to 600 m^2/g) of produced wood biochar.

A leaching solution and column test setup were developed for the use of a column test to test metal adsorption by biochar. The leaching solutions used corresponded to compositions with one-, two-, or fivefold values of the MAC for selected metal ions [Cd(II), Pb(II), Cu(II), Zn(II)] in water discharged to receiving waters (Table 6.7) in accordance with the requirements set out in the Water Framework Directive 2000/60/EC. The leaching solutions were prepared by dissolving metal salts [$CdSO_4 \cdot 8/3H_2O$; $Pb(NO_3)_2$; $Cu(NO_3)_2 \cdot 3H_2O$; $Zn(NO_3)_2 \cdot 6H_2O$] into deionized water. The leaching solutions were modeled with 0.1 M NaOH to adjust the pH to 7.5 ± 0.02.

Seven experimental columns in compliance with ISO 21268-3 were made from organic glass with an internal diameter of 56 mm and a height of 50 cm and fitted with plastic filters at the bottom to prevent grains from passing through (Fig. 6.37). In the top part of the column, a thin layer of nonreactive rubber material was applied to ensure proper water flow over the width of the column.

To model the biochar adsorption capacity using an extended Freundlich isotherm and to compare the adsorption capacity among different types of biochar, each column was filled with a different dose of biochar. Different types of biochar fitted bed filled the columns with a biochar mass ratio of 1:2.5:5:10:25:50:100.

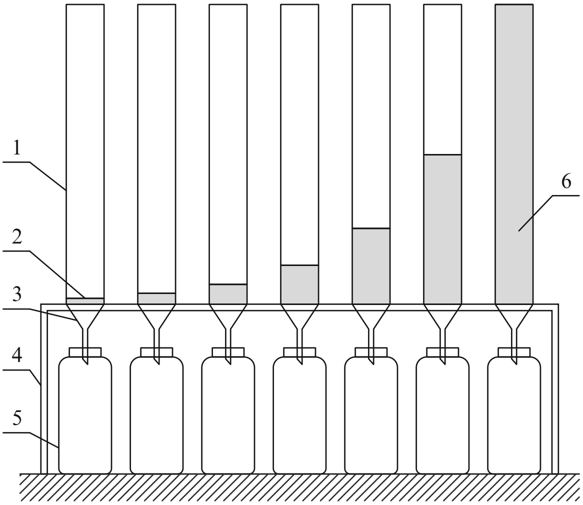


Fig. 6.37 Setup for a column leaching test: (*1*) organic glass cylinder, (*2*) nonreactive material, (*3*) analytic funnel, (*4*) wooden frame, (*5*) 1000 mL HDPE bottle, (*6*) biochar fitted bed

Each of the seven columns was filled with different doses of Scots pine (*Pinus sylvestris* L.) biochar produced under fast pyrolysis conditions (owing to the high specific surface area), and then 1000 mL of leaching solution was applied to each column at a constant pH of leaching solution, temperature (23 ± 2 °C in the laboratory), and contact time. The column experiment was repeated twice with different initial concentrations of metals. Then the columns were filled with the same dose of silver birch (*Betula pendula*) biochar sample produced under fast pyrolysis (owing to the high cation exchange capacity), and the process of filtration was repeated. High-density polyethylene bottles with an appropriate volume of 1 L, and with a screw cap for eluate collection, transportation, and preservation of eluate samples, were used. The leachate solutions obtained were filtered using qualitative filter paper with a particle retention of 5–13 μm. The pH was determined immediately after taking the samples. The concentrations of metal ions (Cd, Pb, Cu, Zn) were determined by flame atomic absorption spectrophotometer (FAAS). The adsorption efficiency was calculated using Eq. (6.1):

$$E = \left(1 - \frac{C_{\mathrm{el}}}{C_{\mathrm{initial}}}\right) \cdot 100\,\% \tag{6.1}$$

where E *is* the adsorption efficiency (%), C_{el} is the concentration of metal in eluate (mg/L), and C_{initial} is the concentration of metal in solution (mg/L).

The adsorption process is mathematically expressed by adsorption isotherms. The adsorption capacity and intensity of pollutants on adsorbents for single-component leaching solutions are evaluated by applying *Freundlich isotherms*. The capacity applying a *Freundlich isotherm* is defined by Eq. (6.2):

$$\frac{X}{M} = K \cdot C_{\mathrm{f}}^{\frac{1}{n}}, \tag{6.2}$$

where X/M is the amount of adsorbed pollutant per unit mass of biochar (mg/g), K is a constant denoting the capacity of the biochar, C_{f} is the pollutant equilibrium concentration (mg/L), and $1/n$ is a function of the adsorption intensity.

To evaluate K and $1/n$, the mass of the removed solute was expressed as the difference between the original and final concentrations, where X is $C_0 - C_{\mathrm{f}}$. After performing a linear regression on the logarithmic data, the intercept K and the slope $1/n$ were determined through the produced equation (Thavamani and Rajkumar 2013).

For multicomponent systems, the extended *Freundlich isotherm* is widely used because of its accuracy and is recommended for most cases of multicomponent adsorption. Freundlich constants were determined using the linear form of the equation for the calculation of the experimental data. The expressions for four-metal adsorption systems are obtained by Eqs. (6.3)–(6.6):

$$q_{\mathrm{Cd}} = \frac{K_{\mathrm{Cd}} C_{\mathrm{Cd}}^{\frac{1}{n_{\mathrm{Cd}}}+\frac{1}{n_{\mathrm{Cu}}}+\frac{1}{n_{\mathrm{Pb}}}+\frac{1}{n_{\mathrm{Zn}}}}}{K_{\mathrm{Cd}} C_{\mathrm{Cd}}^{\frac{1}{n_{\mathrm{Cd}}}} + K_{\mathrm{Cu}} C_{\mathrm{Cu}}^{\frac{1}{n_{\mathrm{Cu}}}} + K_{\mathrm{Pb}} C_{\mathrm{Pb}}^{\frac{1}{n_{\mathrm{Pb}}}} + K_{\mathrm{Zn}} C_{\mathrm{Zn}}^{\frac{1}{n_{\mathrm{Zn}}}}}, \tag{6.3}$$

$$q_{\mathrm{Pb}} = \frac{K_{\mathrm{Pb}} C_{\mathrm{Pb}}^{\frac{1}{n_{\mathrm{Cd}}}+\frac{1}{n_{\mathrm{Cu}}}+\frac{1}{n_{\mathrm{Pb}}}+\frac{1}{n_{\mathrm{Zn}}}}}{K_{\mathrm{Cd}} C_{\mathrm{Cd}}^{\frac{1}{n_{\mathrm{Cd}}}} + K_{\mathrm{Cu}} C_{\mathrm{Cu}}^{\frac{1}{n_{\mathrm{Cu}}}} + K_{\mathrm{Pb}} C_{\mathrm{Pb}}^{\frac{1}{n_{\mathrm{Pb}}}} + K_{\mathrm{Zn}} C_{\mathrm{Zn}}^{\frac{1}{n_{\mathrm{Zn}}}}}, \tag{6.4}$$

$$q_{\mathrm{Cu}} = \frac{K_{\mathrm{Cu}} C_{\mathrm{Cu}}^{\frac{1}{n_{\mathrm{Cd}}}+\frac{1}{n_{\mathrm{Cu}}}+\frac{1}{n_{\mathrm{Pb}}}+\frac{1}{n_{\mathrm{Zn}}}}}{K_{\mathrm{Cd}} C_{\mathrm{Cd}}^{\frac{1}{n_{\mathrm{Cd}}}} + K_{\mathrm{Cu}} C_{\mathrm{Cu}}^{\frac{1}{n_{\mathrm{Cu}}}} + K_{\mathrm{Pb}} C_{\mathrm{Pb}}^{\frac{1}{n_{\mathrm{Pb}}}} + K_{\mathrm{Zn}} C_{\mathrm{Zn}}^{\frac{1}{n_{\mathrm{Zn}}}}}, \tag{6.5}$$

$$q_{\mathrm{Zn}} = \frac{K_{\mathrm{Zn}} C_{\mathrm{Cu}}^{\frac{1}{n_{\mathrm{Cd}}}+\frac{1}{n_{\mathrm{Cu}}}+\frac{1}{n_{\mathrm{Pb}}}+\frac{1}{n_{\mathrm{Zn}}}}}{K_{\mathrm{Cd}} C_{\mathrm{Cd}}^{\frac{1}{n_{\mathrm{Cd}}}} + K_{\mathrm{Cu}} C_{\mathrm{Cu}}^{\frac{1}{n_{\mathrm{Cu}}}} + K_{\mathrm{Pb}} C_{\mathrm{Pb}}^{\frac{1}{n_{\mathrm{Pb}}}} + K_{\mathrm{Zn}} C_{\mathrm{Zn}}^{\frac{1}{n_{\mathrm{Zn}}}}}, \tag{6.6}$$

where q_{Cd}, q_{Cu}, q_{Pb}, q_{Zn} are the amounts of adsorbed metal per unit mass of biochar (mg/g); K_{Cd}, K_{Pb}, K_{Cu}, K_{Zn} are the capacities of the biochar for the metal; C_{Cd}, C_{Cu}, C_{Pb}, C_{Zn} are the pollutant equilibrium concentrations (mg/L); and $1/n_{\mathrm{Cd}}$, $1/n_{\mathrm{Cu}}$, $1/n_{\mathrm{Pb}}$, $1/n_{\mathrm{Zn}}$ are functions of the adsorption intensity.

The effect of initial metal concentrations on the adsorption of metals by two types of biochar is shown in Fig. 6.38.

The temperature, contact time, pH, and dosage of the biochar fixed bed were kept constant. When the concentration of metals increases, available adsorption sites are occupied, and, as a result, a decrease in the adsorption efficiency follows.

Though the specific surface area of Scots pine (*Pinus sylvestris* L.) biochar is 1.45 times higher than that of silver birch (*Betula pendula*) biochar, the higher efficiency of adsorption of metals on silver birch (*Betula pendula*) biochar is easily

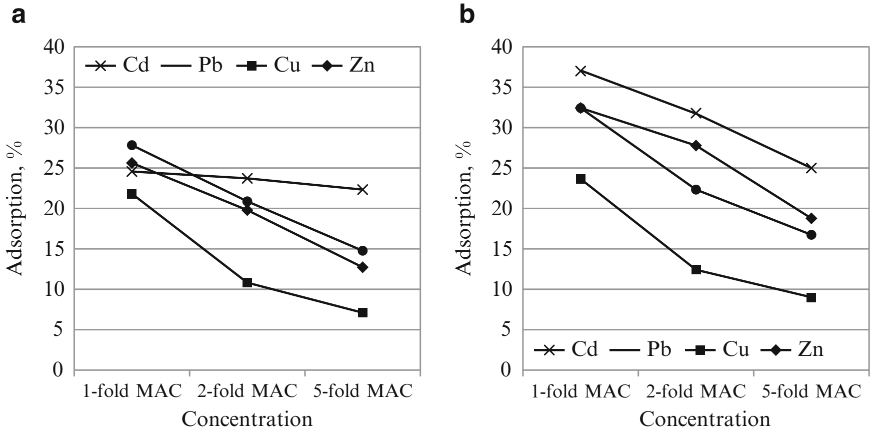


Fig. 6.38 Effect of initial metal concentration on adsorption (%) of metals on (**a**) Scots pine (*Pinus sylvestris* L.) biochar; (**b**) silver birch (*Betula pendula*) biochar

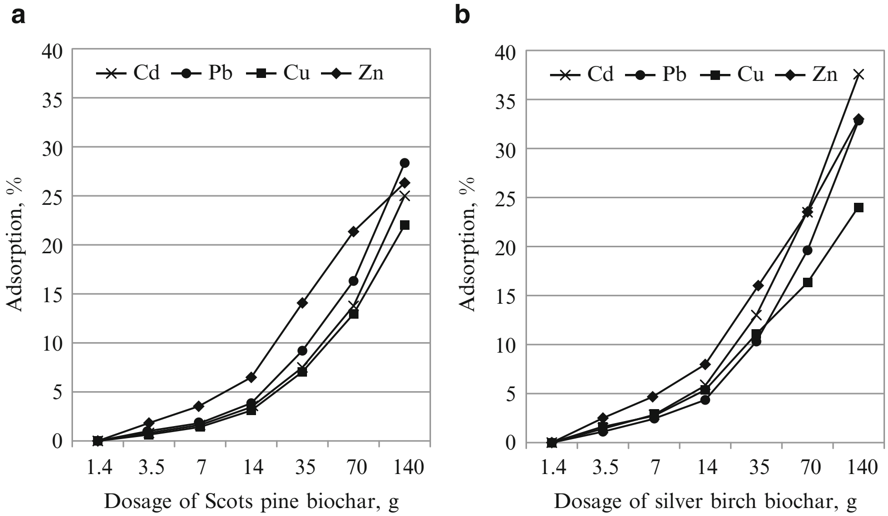


Fig. 6.39 Effects of biochar (produced under fast pyrolysis conditions) dosage on adsorption of metals on (**a**) Scots pine (*Pinus sylvestris* L.) biochar; (**b**) silver birch (*Betula pendula*)

observed. It is possibly due to the 2.38 time higher cation exchange capacity of silver birch (*Betula pendula*) biochar.

The effect of dosages of two different types of biochar on the adsorption of metals by the two types of biochar is shown in Fig. 6.39. The temperature, contact time, pH, and initial concentration of metals were kept constant. The adsorption of metals increases when the dosage of the adsorbent increases. The increase in the specific surface area of an adsorbent is followed by increases in the number of sites available for adsorption.

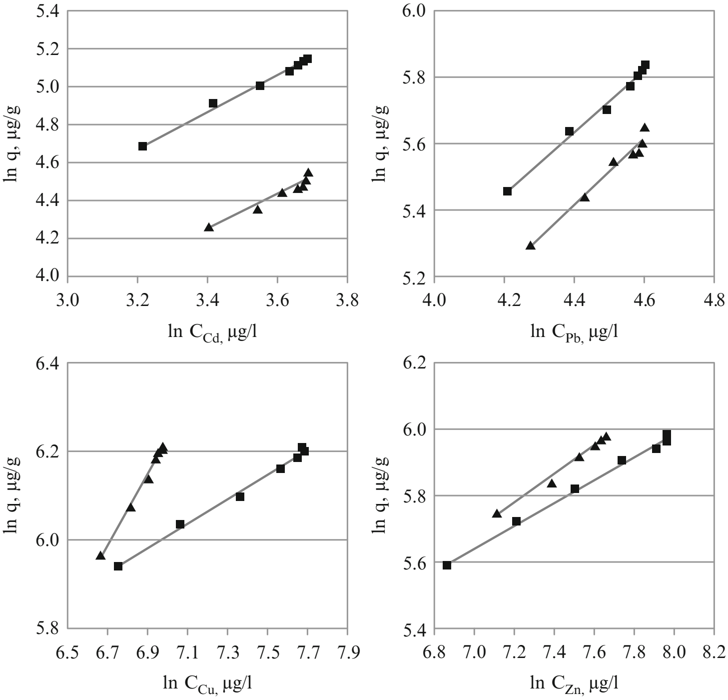


Fig. 6.40 Freundlich isotherms for metal adsorption on silver birch (*Betula pendula*) biochar (*filled square*) and Scots pine (*Pinus sylvestris* L.) biochar (*filled triangle*) when leaching solution composition has onefold value of MAC for selected metals

A Freundlich isotherm was used to represent the adsorption of metals from metal-contaminated solution on biochar. The curvature and steepness of the isotherm is determined by K_f and n (Low and Lee 2000). The affinity of the adsorbent toward the uptake of metal ions is indicated by the value of n (Mohan and Karthikeyan 1997): when $n = 1$, the partition between the two phases is independent of the concentration; when $1/n < 1$, normal adsorption occurs; when $1/n > 1$, cooperative adsorption occurs. When the value of n is in a range between unity and 10, conditions are favorable for adsorption (Goldberg 2005).

All results are presented in Figs. 6.40, 6.41, and 6.42. A linear regression on the logarithmic data produces the equations in the plots (e.g., Eqs. 6.7). Using the equation, the following parameters were calculated:

$$\log q_{\mathrm{Cd}} = 0.9052 \log C_{\mathrm{Cd}} + 1.1783, \tag{6.7}$$

$$\begin{gathered} \ln K = 1.178, \\ K = 3.249, \\ 1/n = 0.905, \\ n = 1.1. \end{gathered}$$

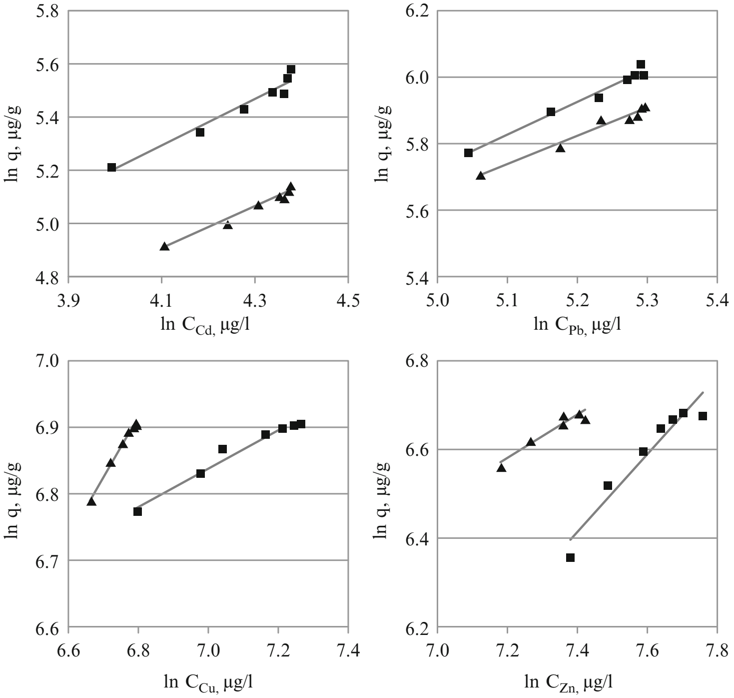


Fig. 6.41 Freundlich isotherms for metal adsorption on Silver birch (*Betula pendula*) biochar (*filled square*) and Scots pine (*Pinus sylvestris* L.) biochar (*filled triangle*), when leaching solution composition is with twofold value of MAC for selected metals

The value $n = 1.1$ indicates the favorableness of adsorption of Zn(II) onto silver birch (*Betula pendula*) biochar.

The approximate indicators of the adsorption capacity K and the adsorption intensity n of all isotherm equations are shown below in Table 6.8.

Values of $n > 1$ indicate the degree of nonlinearity between the solution concentration and adsorption as a physical process (Desta 2013). In all cases, n is between 1 and 10 (Table 6.8), which is favorable for adsorption. R^2 values confirm that the Freundlich isotherms fit the experiments. Comparing the Freundlich equation parameters K and n, silver birch (*Betula pendula*) biochar often has a higher adsorption capacity than Scots pine (*Pinus sylvestris* L.) biochar.

6.4 Wood Ash as Fertilizer: Environmental Problem or Benefit

Huge amounts of wood ash in nature and human environments may occur in two main ways: during forest fires or by the use of wood and its waste as fuel in energetics. The ash resulting in the first case is naturally “realized” in nature – in

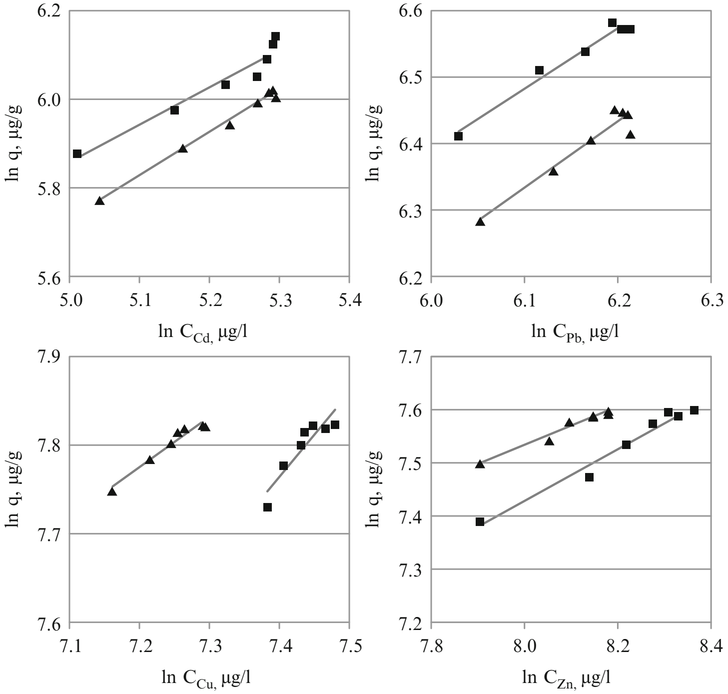


Fig. 6.42 Freundlich isotherms for metal adsorption on Silver birch (*Betula pendula*) biochar (*filled square*) and Scots pine (*Pinus sylvestris* L.) biochar (*filled triangle*), when leaching solution composition is with fivefold value of MAC for selected metals

a forest affected by fire, ash more or less changes the chemical composition, characteristics, and evolution of forest soil. In general, these are not waste in the common meaning of the word. In the second case, when the received ash is accepted as wood waste and its industrial use (burning), the situation changes as ash, in this case, is no more than waste in the true sense of this term. Next, different types of wood ash will be discussed.

Forest Fire Ash

Fire is an important factor in building forest ecosystems worldwide. Fires are a common and widespread phenomenon. Annually, between 200 and 600 fires take place in Lithuania, and the whole fire-damaged area covers 100 to 700 ha (SFSS 2005). Lithuanian forests make up as much as 32.9 % of Lithuanian territory (2.05 million ha) (SFSS 2005). Thus, the fire-damaged areas of forests amount to approximately 0.03 % of the whole area of the country. The number of fires per year depends on meteorological conditions (Marozas et al. 2007). Most fires in Lithuania

Table 6.8 Parameters for plotting Freundlich adsorption isotherms for selected metal adsorption on biochar produced from two types of wood

Concentration of metal ions in leaching solution	Biocha r	Metal ion	Estimated parameters of Freundlich isotherm		
			n	*K*	R^2
Onefold value of MAC	Scots pine (*Pinus sylvestris* L.) biochar	Cd(II)	1.11	3.25	0.947
		Pb(II)	1.01	2.92	0.969
		Cu(II)	1.25	1.86	0.993
		Zn(II)	2.29	14.0	0.987
	Silver birch (*Betula pendula*) biochar	Cd(II)	1.04	4.91	0.991
		Pb(II)	1.07	4.49	0.991
		Cu(II)	3.60	58.2	0.993
		Zn(II)	2.92	25.7	0.995
Twofold value of MAC	Scots pine (*Pinus sylvestris* L.) biochar	Cd(II)	1.27	5.38	0.973
		Pb(II)	1.16	3.77	0.972
		Cu(II)	1.12	2.30	0.987
		Zn(II)	2.10	23.2	0.914
	Silver birch (*Betula pendula*) biochar	Cd(II)	1.13	5.23	0.956
		Pb(II)	1.03	2.37	0.985
		Cu(II)	3.54	128.7	0.969
		Zn(II)	1.16	1.03	0.924
Fivefold value of MAC	Scots pine (*Pinus sylvestris* L.) biochar	Cd(II)	1.01	2.22	0.992
		Pb(II)	1.00	1.29	0.932
		Cu(II)	1.77	41.1	0.950
		Zn(II)	2.80	107.0	0.976
	Silver birch (*Betula pendula*) biochar	Cd(II)	1.18	5.04	0.940
		Pb(II)	1.12	2.85	0.969
		Cu(II)	1.06	2.21	0.832
		Zn(II)	2.05	34.2	0.972

occur within the period from March to August and are infrequent at other times of year (ME 2008). Approximately 84 % of forest fires in Lithuania start in pine areas. The greatest number of fires occur in forest litter (97.3 %), at the tops of trees (1 %), and underground (1.7 %) (Marozas et al. 2007).

Fire affects forest ecosystems in different ways. The characteristic features of fire include its severity, climatic conditions, intensity, temperature span, scope of burning, vegetation type, physical characteristics of fire locality, and soil properties (Gabet and Bookter 2011). The severity of a fire is difficult to determine while the fire is burning. Little information is provided on the impact of fires of different intensities on soil qualities (Shaoqing et al. 2010). According to Pereira and Úbeda (2010), variations in soil temperature affect soil properties in different ways during experimental fires, in terms of fire severity. Fire intensity and severity can be best defined by the extent of damage caused by the fire (Gray and Dighton 2006).

Forest fires cause a decline in organic matter content, and forest litter and falling objects are affected in particular (Odiwe and Muoghalu 2003). Fires have the greatest negative impact in terms of loss of vegetation and forest litter, which reduces the intensity of rain and keeps part of the total amount of precipitation from reaching the hinterland (Gabet and Bookter 2011). The temperature of fires on the surface of forest litter may reach 500–700 °C, and yet at a depth of 5 cm in soil, temperature barely exceeds 150 °C (Prokushkin and Tokareva 2007).

Forest litter acts as an input–output system accumulating nutrients (Dames et al. 2002) and contaminants that are later absorbed by vegetation (Pundytė et al. 2011a, b). The rate of forest litter formation and decomposition determines the energy flow rate, biomass productivity, and nutrient circulation in forest ecosystems (Liao et al. 2006) as well as further vegetation and physiological processes of the trees that survive a fire (Beghin et al. 2011). A thick layer of ash after a fire indicates that the number of elements that can affect soil characteristics may have significantly increased (Ulery et al. 1993): under changes in nutrient metabolism at the time of evaporation, elements could evaporate, be carried away or adsorbed onto particles, or leach down into the soil (Driscoll et al. 1999). Fire affects the nutrient metabolism of ecosystems, destroying part of the undergrowth and forest litter. Under a temperature of 300–400 °C, at the end of a burn (Iglesias et al. 1997), N and S evaporate proportionally to the weight of the lost mass (Gray and Dighton 2006). The interaction of fuel consumption, fire severity (intensity, air content, and frequency), microclimate, the composition and structure of vegetation, the moisture of the burning substrate, and compactness of the substrate influence the loss of nutrients during fire and immediately after it (Wanthongchai et al. 2008).

The impact of fire temperatures on the composition of ash is an important issue. Next, the loss of mass, color, pH, electrical conductivity, and carbon/nitrogen ratio (c/n), as well as variations in the concentrations of Ca, K, S, Na, Fe, P, Mg, and Zn in thermally processed forest litter separately formed from the needles of *Pinus sylvestris* L. and leaves of *Acer platanoides* L. are described. The samples of this type of litter has been heat treated at different temperatures of 150, 250, 350, 450, and 550 °C under monitored laboratory conditions in order to determine the effect of temperature on the dynamics of the properties of forest litter.

Loss of mass. The results of the loss of the mass of a given forest litter, taking into account temperature, are presented in Fig. 6.43, which shows that, at temperatures of 250, 350, and 450 °C, the forest litter has lost slightly more mass than the needle litter. However, at temperatures of 150 and 550 °C, the needle litter loses more mass than the leaf litter.

A comparison of the extent of burning litter (general ability of vegetation to burn) shows that a different temperature more significantly affects leaf litter than needle litter. Bearing in mind that litter is composed largely of falling objects of wood, trends for variations in the loss of mass can be explained by variations in the polymer composition of trees under heat treatment conditions. At the first stage of heating (when the temperature reaches 150 °C), the degradation of hemicellulose and cellulose starts. Because a higher extent of hemicellulose and cellulose is characteristic of pine wood as a representative of softwood rather than of hardwood (in our case, maple tree) (Table 6.9), the loss of mass is more substantial. At a temperature of 250–450 °C, more dramatic losses of the mass of pine wood are

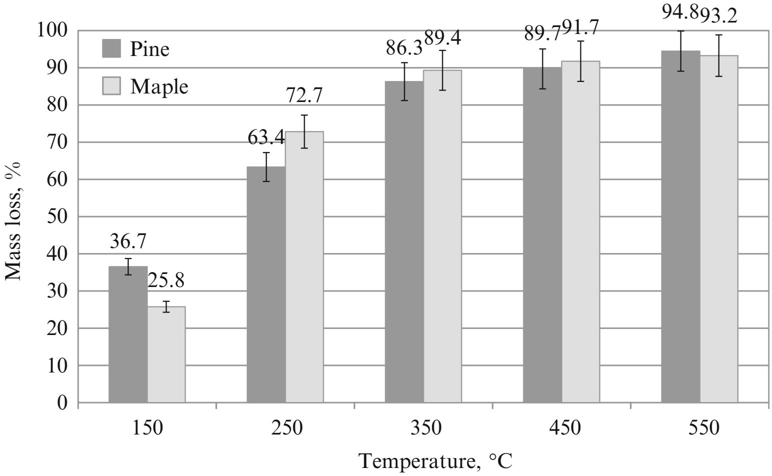


Fig. 6.43 The loss of the mass of *Pinus sylvestris* L. needle litter and *Acer platanoides* L. leaf litter under different heat treatment temperatures (average value ± SD) ($n = 5$)

Table 6.9 Composition of hardwood and softwood, % (mean ± SD) (Drysdale 1985)

	Hardwood	Softwood
Cellulose	42 ± 2	45 ± 2
Hemicellulose	27 ± 2	30 ± 5
Lignin	28 ± 3	20 ± 4
Extractives	3 ± 2	5 ± 3

observed, because at this temperature lignin decomposition starts and becomes pronounced. Lignin makes up a smaller proportion of softwood than hardwood (Table 6.9), and therefore the loss of mass is not that great. It seems to be clear that at a temperature of 550 °C, the loss of the mass of the pine litter increases slightly. This stage of heat treatment involves a large part of decayed polymers, and the difference in mass loss can be attributed to dissimilarities in combustion residues. A higher content of ash is more characteristic of deciduous than coniferous trees, and thus the loss of mass is not that significant.

A discussion on the extent of burning litter reveals that differences in temperature affects leaf litter more than needle litter. In general, the extent to which litter samples burn, and the different temperatures at which they burn, can vary depending on the mass of the litter (Gabet and Bookter 2011). Leaf litter can burn more severely because of the spaces between leaves and better ventilation as oxygen freely circulates (Úbeda et al. 2009). A strong, statistically significant relation between the loss of the mass of the needle litter and heating temperature ($r = 0.91$; $p = 0.01$) as well as between the loss of the mass of the leaf litter and heating temperature ($r = 0.823$; $p = 0.01$) has been established.

The color of ash is an index of fire severity (Bodi et al. 2011); ash can be either black or white (i.e., organic matter is completely burned out). The color of ash is

Table 6.10 Differences in colors of ash of *Pinus sylvestris* L. needle litter and *Acer platanoides* L. leaf litter depending on temperature

Temperature (°C)	Color of litter ash (according to *Munsell's* color value scale)	
	Pinus sylvestris L. needles	*Acer platanoides L.* leaves
150	7.5YR4/6	10YR5/6
250	7.5YR2/0	10YR2/2
350	10YR2/1	10YR2/1
450	10YR3/1	10YR7/2
550	10YR7/2	2.5Y7/2

assessed using *Munsell's* color value scale. The results of laboratory research have revealed that the color of ash in the samples of needles and leaves varied depending on temperature (Table 6.10). With reference to shades, all samples fall into three groups, exactly 2.5Y (5 samples), 7.5YR (10 samples), and 10YR (35 samples). The following groups of colors have been distinguished: brown, brownish-black, black, yellow-orange for the ash of *Pinus sylvestris* L. needle litter and yellowish, brownish-black, black, yellow-orange, and grayish-yellow for the ash of *Acer platanoides* L. leaf litter. Shadows assist in distinguishing one color from another in the system (Yuzer et al. 2004).

The values of the colors of ash increased under rising temperatures and reached their highest values at a temperature of 450–550 °C (ash of *Acer platanoides* L. leaf litter) and 550 °C (ash of *Pinus sylvestris* L. needle litter). At a heating temperature of 150 °C, leaves and needles lost water (Úbeda et al. 2009). The establishment of mass loss point to the same situation. At a temperature of 150–250 °C, ash was brown or yellow, probably from the iron oxides and because of the location of iron oxidation. Ferrum (III) is brown, red, or yellow (Raclavska et al. 2009). The color of ash depends on ferrum oxides whose hydration degree is different (ferrum minerals oxidize at a temperature lower than 300 °C) (Úbeda et al. 2009). At a temperature of 300–400 °C, the ash of burned materials is black because the organic matter of the vegetation is not yet fully oxidized (Zaeni et al. 2010). At a temperature of 350 °C, the color of the ash of both types of litter was black. According to Pino et al. (2008), this may happen because the materials did not burn completely. Moreover, organic matter starts decomposing intensively at a temperature of 200–250 °C and finally burns at a temperature of 460 °C. The organic matter of the ash of the needle litter completely burned at a temperature of 550 °C, and the ash of the leaf litter began getting lighter in color at a temperature of 450 °C. According to Iglesias et al. (1997), completely burned organic matter turns into white ash when the temperature of a fire exceeds 500 °C. As regards the litter of both types, the value correlation between temperature and *Munsell's* color value scale was strong ($r = 0.92$, $p = 0.01$).

Ash pH and electrical conductivity. Litter burns at different temperatures during a forest fire and affects the soil. The pH and number of cations increases immediately following a severe fire and the impact remains for at least 1 year. Ash pH

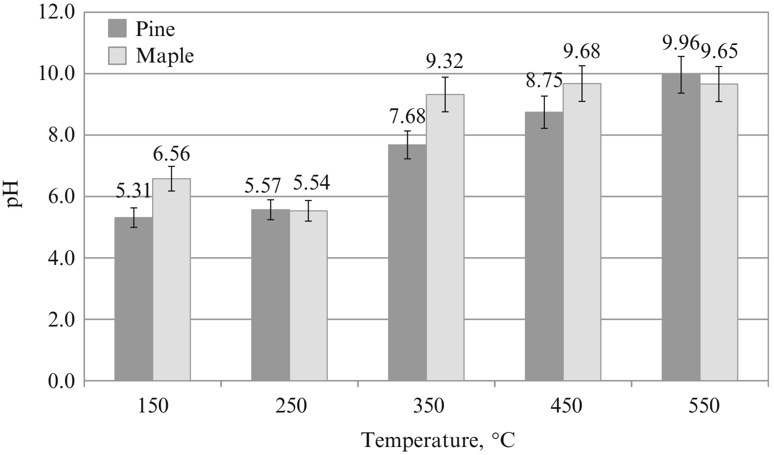


Fig. 6.44 Differences in the ash pH of *Pinus sylvestris* L. needle litter and *Acer platanoides* L. leaf litter depending on temperature (average value ± SD) ($n = 5$)

increases owing to a rise in the concentration of the main cations, for example, Ca^{2+}, Mg^{2+}, and K^+ and the carbonates, oxides, and hydroxides contained in them (Rhoades et al. 2004).

Figure 6.44 shows that variations in the values of ash pH depend on temperature. The ash pH of *Pinus sylvestris* L. needle litter ranges from 5.31 to 9.96 and that of *Acer platanoides* L. leaf litter ranges from 6.56 to 9.65 under increasing temperatures.

As regards this investigation, the values of the ash pH of *Pinus sylvestris* L. needle litter remained almost the same (5.5) up to a temperature of 250 °C, though during burning at a higher temperature of fire (350, 450, and 550 °C), the values of ash pH gradually increased. At temperatures of 150, 250, 350, 450, and 550 °C, the values of the pH of the needle litter were 5.31, 5.57, 7.68, 8.7, and 9.96, and those of the ash of the leaf litter were 6.56, 5.54, 9.32, 9.68, and 9.65, respectively. Under the same conditions, the values of the ash pH of *Acer platanoides* leaf litter (at a fire temperature of 150 °C) increased more dramatically than those of the samples of *Pinus sylvestris* L. litter. Ash can be very acidic (pH 3–4), though usually it is highly alkaline (pH 10–12), because fire forms hydroxides and carbonate salts (Matsi and Keramidas 1999). The highest established value of the ash pH of *Pinus sylvestris* L. needle litter reached 9.96 during the experiment. The conducted research did not find very high values of ash pH, except in cases where temperatures exceed 350 °C, an alkaline pH value was found in all samples of ash. A strong positive correlation between ash pH and temperature values was confirmed: in the case of *Pinus sylvestris* L. needle litter, $r = 0.828$ and $p = 0.01$, and in the case of *Acer platanoides* L., $r = 0.972$ and $p = 0.01$.

Investigation into variations in the electrical conductivity of the ash of needle and leaf litters revealed a tendency similar to that of pH (Fig. 6.45). The value of the electrical conductivity of the ash of *Pinus sylvestris* L. needle litter reached

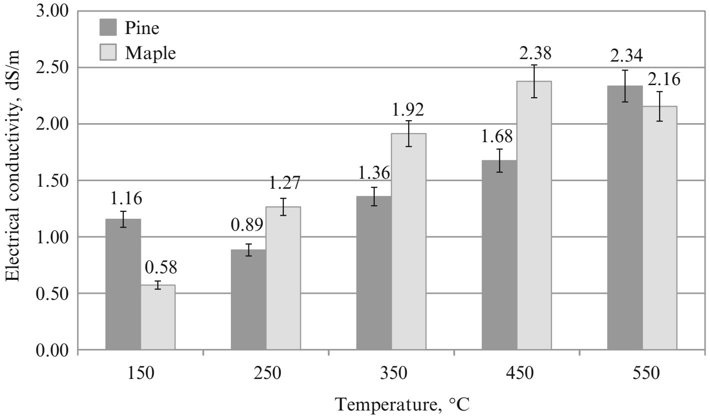


Fig. 6.45 Variations in the electrical conductivity of the ash of *Pinus sylvestris* L. needle litter and *Acer platanoides* L. leaf litter under a rising temperature (average value ± SD) ($n = 5$)

2.34 dS/m at the highest temperature of 550 °C, whereas the electrical conductivity of *Acer platanoides* leaf litter reached its highest value at a temperature of 450 °C. A rise in burning temperature resulted in an increase in the values of the electrical conductivity of the ash of *Pinus sylvestris* L. needle litter from 1.16 to 2.34 dS/m, while the values of the electrical conductivity of *Acer platanoides* leaf litter resulted in an increase from 0.58 to 2.16 dS/m.

The electrical conductivity of the soil solution increases along with a rise in the concentration of Mg, Ca, and K. A strong positive correlation between the electrical conductivity of ash and temperature has been established: in the case of the ash of *Pinus sylvestris* L. needle litter, it reached $r = 0.807$ and $p = 0.01$, whereas in the case of *Acer platanoides* leaf litter, it was $r = 0.836$ and $p = 0.01$.

Concentrations of macroelements in ash. Fire causes changes in the chemical properties of soil as soil temperature increases, forming ash. Because of soil heating up to 100 °C, the concentration of metal ions, for example, those of K, Ca, and Mg, becomes higher in ash (Carter and Foster 2004). As regards the ash of needle litter (Fig. 6.46, a–h), in descending order, macroelements were ranked in the sequence Ca > K > Na > S > Mg > P > Zn > Fe, whereas in the case of leaf litter, the sequence was Ca > K > S > Mg > P > Na > Fe > Zn. Na concentrations have been shown to vary only slightly depending on temperature and the type of litter, while Ca concentrations were rather high in the ash of both types of litter. Greater concentrations of Ca, K, and S have been revealed in the ash of leaf litter than in needle litter. At higher temperatures, higher concentrations of K, Mg, and S have been estimated in the ash of both types of litter.

The correlation between the concentration of macroelements and temperatures has been found to be strong in terms of the following macroelements: Ca ($r = 0.674$), Na ($r = 0.660$), K ($r = 0.872$), S ($r = 0.905$), Mg ($r = 0.776$), and P ($r = 0.736$) with respect to *Acer platanoides* L. and lower but still sufficiently

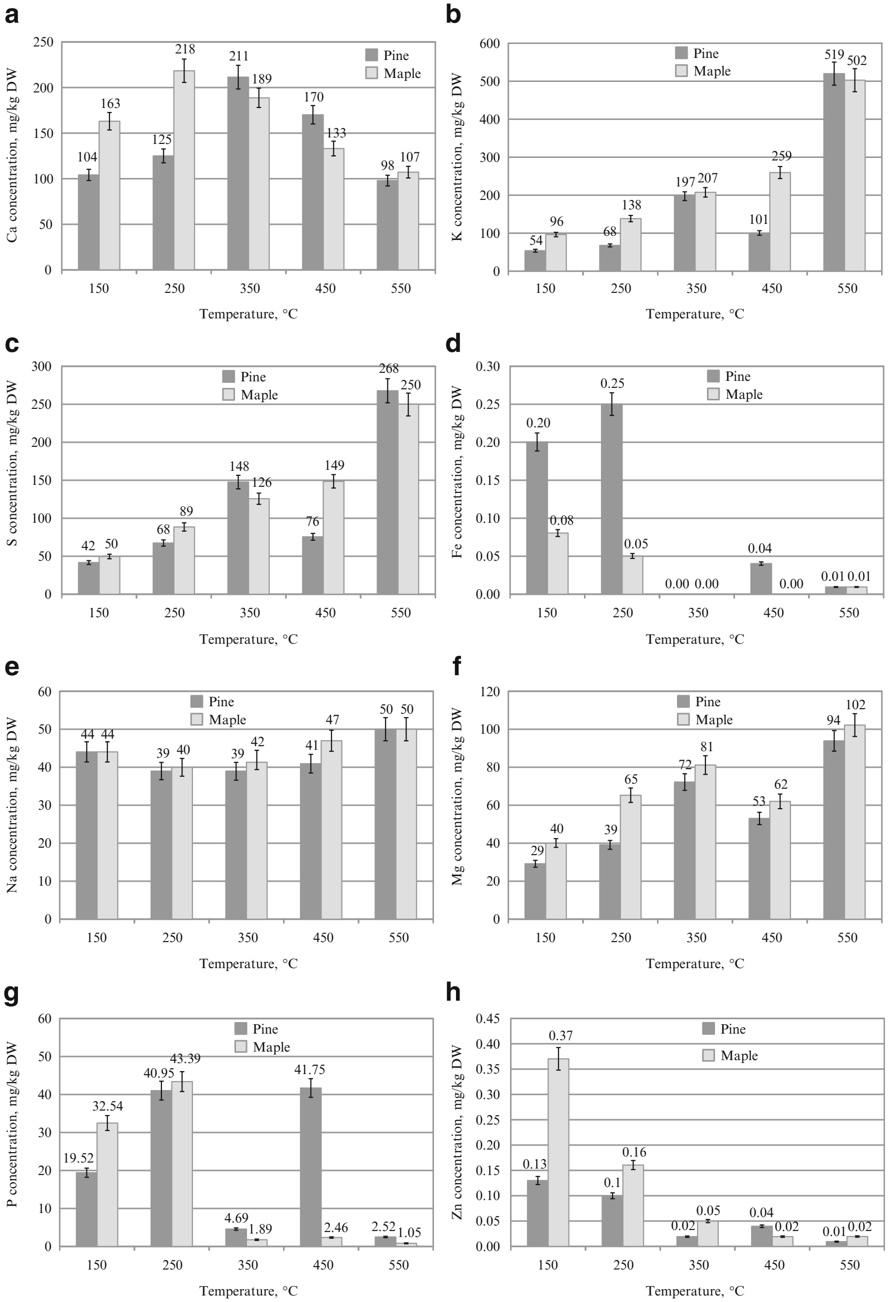


Fig. 6.46 Variations in the concentrations of chemical elements in the ash of *Pinus sylvestris* L. needle litter and *Acer platanoides* L. leaf litter under different burning temperatures (average value ± SD) ($n = 5$)

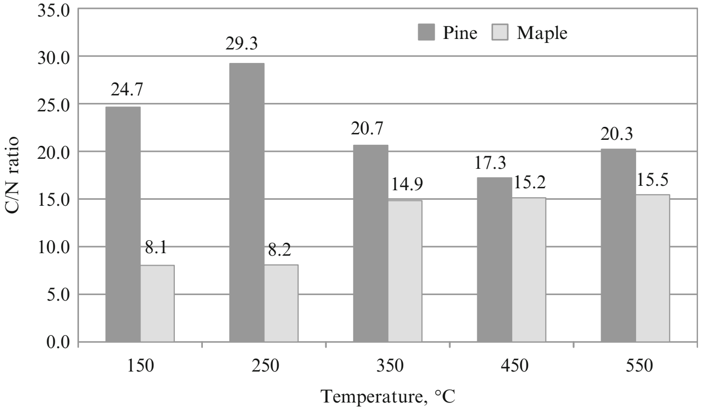


Fig. 6.47 C/N ratio in the ash of *Pinus sylvestris* L. needle litter and *Acer platanoides* leaf litter under a different temperature ($n = 5$)

intense with respect to Na ($r = 0.446$) [only the P correlation was low ($r = -0.273$)] with regard to *Pinus sylvestris* L.

Fire severity affects the balance of nutrient elements in exposed forest soil. If the fire temperature is not high enough to evaporate nutrient elements, their concentration in soil increases. Only a minor part of those vaporize at a temperature lower than 1000 °C. At a temperature of 400–500 °C, C, N, and S evaporate, whereas such elements as P and Ca vaporize at very high temperatures (for example, 774 °C for P and 1484 for Ca). Variations in the concentration of nutrients indicate that the degree of the mineralization of organic matter depends on the fire intensity (Thomas et al. 1999).

C/N ratio. According to Carter and Foster (2004), as a result of fires that take place above the ground, the C/N ratio increases, which slows down the process of N mineralization and, thus, forest growth. The C/N ratio has been found to be higher in the ash of needle litter rather than in that of leaf litter (Fig. 6.47). However, the ratios tended to increase with a rise in temperature.

The values of the C/N ratio of the ash of needle litter varied from 24.7 to 20.3, while that of leaf litter varied from 8.1 to 15.5. The correlation between the C/N ratio and temperature was $r = 0.834$, $p = 0.01$ in the case of needle litter and $r = 0.921$, $p = 0.01$ in the case of leaf litter. The C/N ratio of the ash of *Pinus sylvestris* L. increased along with a rise in temperature and reached a maximum value at 250 °C. At a later stage, the value of the ratio decreased under a rising temperature and was at its lowest at a temperature of 450 °C; next, under a rising temperature, the value of the ratio increased again. The value of the C/N ratio of the *Acer platanoides* L. sample, under a rising temperature, increasing continually, and the largest increase was noticed between 250 and 350 °C, which can be determined by decomposed organic matter that usually starts decaying at a temperature of 200–315 °C (Moreno and Baath 2009).

Laboratory conditions do not fully represent those present during a forest fire; nevertheless, experiments showed that differences in temperatures cause changes in the qualities of ash. It has been established that both fire temperature and the type of litter strongly affect ash properties. Detailed statistical analysis confirms strong links between an increase in fire temperature and the concentration of some elements, pH, electrical conductivity, and a rising C/N ratio.

Ash of Wood and Incineration of Its Industrial Waste

According to data provided in 2007, Lithuanian energy companies burning wood produced 25,000 tons of ash annually (Valuntienė and Paškauskaitė Ž 2007). In 2012, forest-related companies sold 157,000 m^3 of felling residue to private individuals and biofuel producers (Biokuro potencialo 2013a, b), i.e., twice as much as in 2006. It can be assumed that the amount of ash produced had doubled so it could be used for its intended purpose. The total structure of energy wood in Lithuania is shown in Fig. 6.48. With reference to evaluation, for the period 2020–2025, the extent of resources that can be used in the energy sector will reach 8.63 million m^3 of wood (1.5 million tons). An approximate evaluation conducted by scientists from

Fig. 6.48 The structure of energy wood in Lithuania (Kuliešis 2013)

the Institute of Forestry under the Lithuanian Research Centre for Agriculture and Forestry show that, currently, 15–20 % of all felling residues are collected in Lithuania, although without taking into consideration legal requirements in terms of ecological sustainability, 50 % of those residues can be used (Biokuro potencialo 2013a, b). Thus, the total mass of generated ash can reach 45,00 to 50,000 tons.

Even wood ash, much less coal ash, is not a natural product of the creative activity of nature. Therefore, its storage or disposal must inevitably lead to problems proportional to their amount. According to guidelines for the management and disposal of wood waste fuel ash (Medienos kuro 2011), wood ash can be applied as a fertilizer in agriculture and forestry, for the recultivation of disturbed areas (e.g., quarries, unexploitable peatlands, closed landfills, roadbeds), decreasing the pH of sewage sludge, and, in some cases, as a building material or its supplement (substitute), including the construction of roads.

The use of wood waste fuel ash in agriculture and forestry encounters problems related to their composition and properties. Apart from organizational and technological aspects (designing and agreeing on plans for using ash, reports on their management and usage, composition and properties of soil monitoring, complying with the established regulations and rules, acceptance of technology and equipment for ash dispersal), the use of ash as an active soil amendment also requires knowledge of its properties and detailed research into its composition, particularly those that can lead to negative changes in soil with respect to microelements (metals). Information on exactly these properties of wood ash will be provided next.

As a result of the combustion of wood, the formed ash is usually divided into bottom ash (ash residues) and fly ash. Additionally, fly ash can be further subdivided into two groups: coarse particles (particulates several micrometers in diameter) and fine particles (less than 1 μm).

Bottom ash forms on furnace grates. Depending on the composition of biofuel, it mixes with other noncombustible parts of it (sand, stones, pieces of dirt) and, at a lower melting temperature of that kind of mixture, may form slag or cause the aggregation of ash particulates (sintering). Ash dust deposited by *cyclones* (often multicyclones) mainly consists of fine inorganic particulates transferred by flue gas produced within the furnace combustion process. The basis of its composition is *the coarse fly ash fraction*. Apart from multicyclones, bag *filters*, or electrostatic precipitators where the finest gas particles present in the cleaned dust stream settle are usually used in larger boiler houses. This results in filter fly ash that may contain so-called particles of condensed sludge. This part of fly ash makes up their small-scale aerosol fraction (about 10 % of the mass of all ash formed in the combustion process).

Metal concentrations vary significantly in different ash fractions of wood and its waste incineration (Table 6.11).

In ash, the concentrations of chalcophile metals, such as Pb, Cd, and Zn, tend to move relatively easily into the vapor-gas phase and increase in the sequence *bottom ash < cyclone ash < filter ash*. In contrast, the concentrations of siderophile metals Ni, Cr, and V, which have a high melting temperature and are not inclined to enter

Table 6.11 Average concentration of metals in different ash fractions of burning bark, wood chips, and sawdust (Utilizacija zoly 2007) in comparison with maximum allowable concentration in ash (Medienos kuro 2011)

Element	Index	Bottom ash	Cyclone ash	Filter ash	Forest fuel ash of boiler houses in Lithuania (mg/kg[a])	MAC in ash
Cr	*X*	325.5	158.4	231.3	7.6–35.0	100
	SD	383.0	61.0	263.7		
Ni	*X*	66.0	59.6	63.4	7.0–8.6	75
	SD	13.6	19.0	35.4		
Co	*X*	6.5	19.0	17.5	–	–
	SD	190	7.3	5.2		
V	*X*	43.0	40.5	23.6	–	150
	SD	10.0	16.6	9.1		
Zn	*X*	432.5	1870.4	12980.7	4.0–**820.0**	300
	SD	305.2	598.5	12195.9		
Cu	*X*	164.6	143.1	389.2	4.80–24.10	100
	SD	85.6	46.7	246.4		
Pb	*X*	13.6	57.6	1053.3	0.7–40.0	100
	SD	10.4	20.5	1533.0		
Cd	*X*	1.2	21.6	80.7	0.03–**9.60**	3
	SD	0.7	8.1	59.2		

X average metal concentration in ash (mg/kg); *SD* standard deviation from average metal concentration (mg/kg)

[a] According to Kompensuojamojo tręšimo (2011)

the vapor-gas phase following this particular sequence, generally decrease in ash (V, Cr) or vary only slightly (Ni). An exception among siderophiles is cobalt whose concentration, like that of chalcophile metals, is the lowest and characteristic of bottom ash (Co itself, in parallel with the properties of chalcophiles, is a good enough chalcophile). Higher metal concentrations in a tiny fly ash fraction (filter ash) can be explained by absorbing metals from gas and vapor with the help of very dispersed ash particulates. Moreover, some aerosol particles emerge from the condensation of metal vapor in filters or react with other components of flue gas.

As mentioned earlier, the ash of burned wood can be used as a valuable chemical reclamation measure for agricultural and forest soil and to compensate for losses caused by the removal of nutrients (Ca, K, P, Mg) from soil together with crop and wood biomass and to decrease soil acidity. A common application of wood ash for improving soil properties may be restricted by the contents of toxic metals such as, for example, Cd, Pb, Hg, Cu, Zn, and Cr. For this purpose, filter ash is completely inappropriate, as the concentrations of some of the aforementioned metals (Cd, Zn, Pb) may exceed the established MAC by tens or even hundreds of times (Table 6.11). Metal concentration restricted by sanitary-hygienic norms in the mix of bottom and cyclone ash is generally significantly lower, particularly that of chalcophile metals, though in their case, the predicted concentrations of maximum allowable amounts frequently exceed established limits. In this respect, forest fuel ash in boiler houses in Lithuania can be considered ecological enough;

according to data provided in Table 6.11, only the highest concentrations of Cd and Zn exceed the MAC.

Apart from toxic metals, radioactive isotopes of ^{40}K, ^{90}Sr, and ^{137}Cs can be detected in forest fuel ash. The Chernobyl accident (in the former USSR, Ukrainian territory, 26 April 1986) seems to be the most probable source of these isotopes in Lithuanian forests. ^{137}Cs concentration in the forest fuel ash of boiler houses in Lithuania does not exceed 5 kBq/kg (Kompensuojamojo tręšimo 2011). Around 8 % of the total wood fuel ash, based on the level of contamination with ^{137}Cs, cannot be used in agriculture as a soil fertilizer but is suitable for producing construction materials or building roads (Radiacinės saugos 2014). Wood ash as a fertilizer has been used only in experimental studies in Lithuania, although habitable areas with conditions favorable to their use exceed 400,000 ha (Valuntienė and Paškauskaitė Ž 2007).

Variations in the chemical composition of wood ash is a special issue and can be addressed with respect to trees and energy plants growing in contaminated soil, for example, in one fertilized with sewage sludge. In this respect, more detailed data have not been accumulated in Lithuania. Individual data on osier willows fertilized with effluent water sludge indicate that these trees accumulate metals at levels that are 1.5–3.9 times higher (mainly Zn and Cu, with the lowest levels being those of Cr and Ni) than those not so fertilized ones (Jakienė et al. 2013). More fertilizers and a significant increase in the concentration of metals in soil result in an uneven content of the metals in willows up to a certain bioaccumulation level. The major part of metals has been found to accumulate in leaves (50–80 %), a smaller part in roots (15–20 %), and the least in stems (1–25 %). The authors suggest that, taking into account the overall balance of harmful metabolism, metal concentration in the biomass of willows remains insignificant (0.004 % Cd and 0.269 % Zn) and has no practical value. As for the advantages of phytoremediation, the authors emphasize that the species of willows that accumulate metals more intensively have been identified; the ash of willows contains about 150 mg/kg of cadmium, i.e., approximately 10–20 times the average fertilized biofuel ashes. Moreover, the authors note that "a greater part of metals, while combusting biomass, do not remain in ash but are emitted into the atmosphere together with smoke" (Jakienė et al. 2013).

According to data provided by Keller (2009), the highest Zn concentration in *Salix viminalis* grown in the contaminated fields of an experiment performed in Switzerland was found in leaves (475–1700 mg/kg DW) and a lower concentration was found in stems (120–430 mg/kg DW). Cd was distributed in a similar way and had concentrations of 1.5–5.1 mg/kg DW and 1.2–2.3 mg/kg DW, respectively. Cu distribution was more even: 5.6–13.0 mg/kg DW in leaves and 5.1–13.0 mg/kg DW in stems. The author does not indicate the content of ash in the investigated willows, and thus the evaluation of the concentration of the aforementioned metals seems to be a complex issue. Because the content of the ash of stems with willow bark usually amount to around 2 %, metal concentration in their ash should be approximately 50 times higher. Hence, it is easy to estimate that it would exceed the established values of the MAC by at least 10 times (Table 6.11).

Table 6.12 Concentrations of metals in ash of pine and birch wood grown in territory of Gitėnai Forest (northern Lithuania) contaminated with sewage sludge

Chemical element	Concentration (mg/kg)		Ratio pine/ birch	MAC in ash (mg/kg)	Hazard ratio		Ash from forest fuel in Lithuanian boiler houses (mg/kg[a])
	Pine	Birch			Pine	Birch	
Cr	23	36	0.64	100	0.23	0.36	7.6–35.0
Ni	37	14	**2.64**	75	0.49	0.19	7.0–8.6
V	7.8	10.9	0.72	150	0.05	0.07	
Zn	814	1380	0.59	300	**2.71**	**4.60**	4.0–820.**0**
Cu	72	51	**1.41**	100	0.72	0.51	4.80–24.10
Pb	10	6	**1.67**	100	0.10	0.06	0.7–40.0
Cd	50	18	**2.78**	3	**16.67**	**6.00**	0.03–9.60
Hg	4	2.5	**1.60**	1.5	**2.67**	**1.67**	–

[a] According to Kompensuojamojo tręšimo (2011)

Baltrėnas and Čepanko (2009) grew *Salix dasyclados* employing the method of hydroponics in the concentration of waste filtrate. The conducted experiment revealed no significant differences in their ability to accumulate metals in their lower, more woody, middle, and upper parts of foliage. By level of accumulation, the metals can be put in the following order: Pb > Cu > Cr > Zn > Ni. An increase in the concentration of the filtrate reveals that 87 % of plants have a linear decrease in the accumulation of metals under an increase in the concentration of filtrate.

The concentrations of metals in the ash of pine and birch wood that grew in the territory of the Gitėnai Forest (northern Lithuania) fertilized with sewage sludge are presented in Table 6.12. The pine wood ash demonstrates higher concentrations of Cu, Hg, Pb, and, especially, Ni and Cd, whereas birch wood ash showed higher concentrations of Zn, Cr, and V. Often, the concentrations of these metals correspond or are very close to their usual concentrations in ash from forest fuel in Lithuanian boiler houses. But in about 50 % of cases they are obviously higher. First of all, these are Cd and Cu concentrations in both pine and birch wood ash that significantly (by at least twice as much) exceed the highest concentrations of these metals in ash from forest fuel in Lithuanian boiler houses. The concentration of Ni in pine wood ash is also prominent: 37 mg/kg, i.e., 4–5 times higher than its usual concentration in ash from forest fuel in Lithuanian boiler houses. The concentration of Zn in birch wood ash is also abnormally high, exceeding the highest concentration of this metal in ash from forest fuel in Lithuanian boiler houses by about 1.7 times.

The level of contamination of soil and groundwater with metals that is characteristic of Lithuanian territory, including its forests, is generally low. Therefore, it is natural that their concentrations in ash from forest fuel in Lithuanian boiler houses would not be high, at least compared to the concentrations of these metals in ash from forest fuel in foreign boiler houses that we know from sources in the literature (Kompensuojamojo tręšimo 2011). The highest concentrations of Cu that are characteristic of ash from forest fuel in foreign boiler houses exceed the relevant concentrations in ash from forest fuel in Lithuanian boiler houses by as much as 12 times, whereas the concentrations of Cr and Ni exceed them by 6.4–7.4 times.

The aforementioned concentrations of metals in the ash of pine and birch wood from the Gitėnai Forest in many cases do not exceed the established MACs of metals in ash from wood fuel for use in Lithuanian agriculture and forestry and for the rehabilitation of damaged territories (Table 6.12).

The hazard ratios calculated based on the MAC (the ratio between the real concentration of metal in ash and its MAC) usually do not exceed the range 0.5–0.7. The hazard ratios of Hg, Zn, and, especially, Cd are an exception. The concentration of Cd in pine wood ash exceeds the MAC by almost 17 times and in birch wood ash by 6 times. This means that, according to the requirements established in Lithuania (Medienos kuro 2011), such an ash cannot be used directly in agriculture, forestry, for the rehabilitation of damaged territories, in civil engineering, or together with sewage sludge for pH optimization.

Concentrations of metals in wood ash that in individual circumstances exceed the MAC values raise the issue of whether it is generally worth using wood ash as a meliorating material that can optimize the pH of acidic soils and supplement soil with valuable nutrients, i.e., Ca, K, Mg, P. Practice shows that in many cases the concentration of toxic metals in soil is considerably lower than the established limit values of the MAC (Table 6.12). In those cases where wood from contaminated territories is used as fuel in boiler houses, including from forests affected by the Chernobyl disaster, the use of ash must be strictly controlled for its compliance with the relevant regulations.

Thus, two factors – the feedstock and the processing temperature – that affect biochar properties were analyzed in the study. It was determined that the differences in the morphological structure of the tree wood had influenced the characteristics of the biochar, namely, the specific surface area, morphological structure of the biochar, apparent/bulk density, CEC, and microbiological characteristics. Ash content, biochar yield, pH, TC, and concentrations of metals should be noted among biochar's chemical properties, and changes in them depend more on temperature than on wood type. On the current situation in the EU, the wood waste potential for biochar production consists of wood cutting waste, wood chips, wood sawdust, and recycled wood. A large part of wood waste has not been used until now; therefore, it holds great potential as a raw material for biochar production. Only a noncontaminated (without impregnation, paints, metal, galls of plastic additives) wood feedstock could be used in safe biochar production. Because of the advantageous properties, biochar could be further used as an agent in a variety of environmental protection technologies: as a compost additive, an amendment of soil, an adsorber of contaminants and nutrients, and as a biofiltration substrate. The slight difference between biochars produced from decidous and coniferous trees can be mentioned in connection with the proposed application. Pine biochar could provide more advantages than birch biochar in terms of environmental technologies that involve processes of both a living and nonliving nature, for example, biofiltration, composting, and the amelioration of soil. Owing to the advantageous physical and chemical characteristics (such as porous network and cation exchange capacity) of biochar, the interest in adsorption processes and efficiency of various pollutants on different types of biochar has increased in recent years. Current work indicates there are opportunities to treat efficiently metal-contaminated water by the adsorption onto biochars of silver birch (*Betula pendula*) and Scots pine (*Pinus sylvestris* L.).

The pH of eluate resulting from elution through silver birch (*Betula pendula*) biochar increases slightly owing more to its higher biochar pH value compared to that of Scots pine (*Pinus sylvestris* L.). Attention should focus on highly alkaline biochar, which could increase the pH of treating water beyond the established limits. The adsorption efficiency of both types of biochar decreases with increased initial metals ion concentrations. The adsorption of metal ions increases when the dosage of the adsorbent increases. The capacity and intensity with which biochar adsorbs metal ions from leaching solution have been modeled by the application of extended Freundlich isotherms. This reflects the heterogeneous properties of surfaces and a favorable adsorption process. In evaluating the adsorption capacity of both types of biochar, experimental results showed the reliability of extended Freundlich adsorption isotherms (average of statistical reliability $R^2 = 0.96$). Comparing the revealed parameters from the Freundlich equation, the adsorption capacity of silver birch (*Betula pendula*) biochar was higher than the adsorption capacity of Scots pine (*Pinus sylvestris* L.) biochar in 7 of 12 cases.

The BALANS model describes the main inputs and outputs of metals to the atmosphere–plant–soil system as follows: the input of metals of aerogenic origin, the amount of these metals introduced into the soil together with amendments, their natural physicochemical migration beyond a particular layer of soil expressed by the annual metal migration coefficient, the uptake of metals by the biomass of plants grown in the soil, and their removal from the system together with crops (a phytoremediation effect). The BALANS model makes it possible to analyze the effectiveness of soil self-purification processes for different types of field microrelief (i.e., plains, hills, and lowland) in the case of soil solutions and different migration patterns of the considered metals (i.e., different systems of migration and accumulation characterizing the particular types of geochemical landscape). The values determined for the initial period of metal half-life in albeluvisols and podzols using the BALANS model largely depend on the microrelief of the examined field and are often within the limits of the periods of soil self-purification from metals mentioned by soil specialists and environmentalists and published by A. Kabata-Pendias. The empirical coefficients of metals' annual migration, integrating the internal and external factors, and influencing chemical elements' migration make up the core elements of the BALANS model responsible for the accuracy of the final data yielded by this model. These coefficients are well understood by soil specialists and geochemists, who, when using the suggested model, can easily change them as they deem necessary, depending on the particular conditions.

Chapter 7
The Use of Wood Products for Improving Air Quality

This chapter further explores the application of wood waste and recovered products in environmental protection but is more focused on the systems for environmental protection engineering where the use of wood products and waste, with respect to the principles of sustainable development, is more favorable owing to lower costs, greater availability, or even more powerful environmental effects compared to other popular materials.

Tree products and waste can be successfully used for air treatment and removing odors in engineering systems of biotechnology, which is based on the organic nature of wood products and waste, a favorable medium for biological processes, and a competitive price. The chapter presents results using wood-based materials as the main substrate in biofiltration systems and as an additive to mineral substrates.

7.1 Wood Products in Systems for Biological Air Treatment

The contamination of air in living and work environments is a major environmental problem, particularly as it relates to immediate contact with the human organism and other components of the ecosystem. If a general property of all pollutants points to a rising toxic effect on the environment, which increases its concentration, inorganic compounds pose an additional problem of unpleasant odors in the air even, at low concentrations. Areas where the quality of life is affected by odors are often situated close to facilities that manufacture furniture, varnish, paint, food, and plastic, as well as to petroleum refineries. The problem of unpleasant odors is frequently attributed to the presence of such volatile compounds as benzene, toluene, xylene, ethylbenzene, acetone, hydrogen sulphide, and ammonia.

Various biotechnologies are used to deal with the problems of odors and a reduction in the concentrations of the most popular volatile compounds; the

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biotechnologies are based on the ability of microorganisms to decompose compounds. This subsection will further discuss biofiltration, which is one type of system applied to biotechnologies. Unlike the other types of bioreactors, microorganisms in biofilters decompose air pollutants in a porous medium.

The benefits of biofilters include the following: they are highly efficient at removing volatile compounds from the air, the products of the reactions taking place in the device are not dangerous, a wide variety of pollutants are suitable for removal, they have a simple structure, they can use locally available material as biofiltration media, they have considerable longevity (10 years), they require relatively small capital and operating costs, they are highly reliable, their energy requirements are low, and they are easy to maintain and service. Disadvantages include the considerable space occupied by the equipment, more complicated moisture and pH control within the process (Baltrėnas and Vaiškūnaitė 2002, 2003, 2004).

The biofiltration process is widely used in chemical industry, domestic and industrial wastewater treatment plants, composting equipment, timber production, and varnishing and surface coating processes. In the European chemical industry alone, biofiltration is applied by more than 600 chemical companies (Sakuma et al. 2008; Mudliar et al. 2010).

In biofilters, microorganisms grow in a biofilm on the surface of a medium or are suspended in the water phase surrounding the medium particles. The filter-bed medium consists of relatively inert substances that ensure large surface attachment areas and additional nutrient supply. As the air passes through the bed, the contaminants in the air phase sorb into the biofilm and onto the filter medium, where they are biodegraded. Biofilters are not filtration units because they are systems that use a combination of basic processes: absorption, adsorption, degradation, and desorption of gas-phase contaminants (Fig. 7.1).

Microorganisms decompose compounds into odorless and less hazardous substances in biofiltration systems, thereby increasing their biomass. Hydrogen sulfide emits an intense odor and is oxidized by microorganisms (*Thiobacillus* microorganisms are especially active) into odorless compounds (Eq. 7.1):

$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+. \tag{7.1}$$

Water-soluble ammonia is oxidized (Eqs. 7.2 and 7.3) into odorless nitrate (Eq. 7.3):

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-, \tag{7.2}$$

$$2NH_4 + 3O_2 \rightarrow 2NO_3^- + 8H^+. \tag{7.3}$$

Bacteria oxidize volatile organic compounds into carbon dioxide and water (Eq. 7.4):

$$VOCs + O_2 \rightarrow CO_2 + H_2O. \tag*{(7.4.)}$$

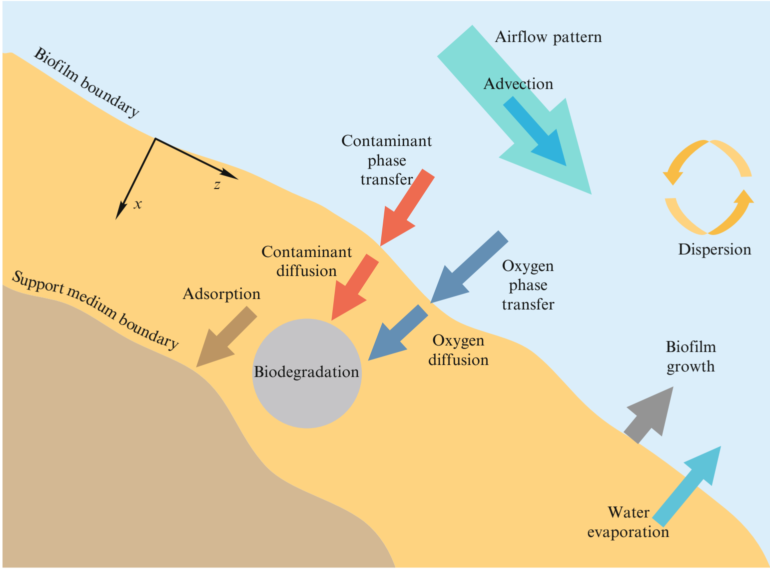


Fig. 7.1 Processes taking place in biofilter (according to Devinny and Ramesh 2005)

Table 7.1 Biological conversions in biofiltration of odorous compounds and bacteria responsible for the process in aerobic or anaerobic conditions (McNevin and Barford 2000)

Transformation	Typical operating bacteria	Conditions
Organic carbon oxidation VOC → CO_2, H_2O	Chemoheterotrophic bacteria	Aerobic
Nitrification $NH_4^+ \rightarrow NO_2^-$, NO_3^-	Nitrifying bacteria	Aerobic
Sulfide oxidation $H_2S \rightarrow S^0$, SO_4^{2-}	Sulfur oxidizing bacteria	Aerobic
Denitrification $NO_3^- \rightarrow N_2$	Denitrifying bacteria	Anaerobic

The efficiency of the biological air treatment process depends on the medium of the proliferating cultures of microorganisms. The most frequently found strains include *Arthrobacter*, *Acinetobacter*, *Pseudimonas*, *Bacillus*, *Flavobacterium*, *Mycobacterium*, *Micrococcus*, and *Rhodococcus*. Carbohydrates are broken down by more than 70 strains of microorganisms (Lugauskas et al. 1997; Liu et al. 2005).

Contaminants in biofiltration systems are actively decomposed by fungi and bacteria. Table 7.1 presents several transformation processes of typical bacteria and contaminants in which they are present under aerobic and anaerobic conditions.

The removal of contaminants with the help of a biofiltration method can be applied at different concentrations of pollutants (from 0.01 to 10 g/m^3). From an economical point of view, in pollutant concentrations of up to 1 g/m^3, a biological air treatment can be employed in a more rational way.

A biofiltration medium must have the following key physical features: a large surface area and a porous structure required for the proliferation of microorganisms, cost efficiency, a low mechanical load necessary to avoid excessive pressures, beneficial moisture-sorption properties, homogeneity of the packing material allowing moisture to be evenly distributed over the whole surface area of the packing material, and a longer effective duration of use (Wani et al. 1998; Shareefdeen et al. 2003).

The biofilter bed may consist of packing material of different origins. As products develop in increasingly environmentally friendly ways, natural substrates are becoming ever more popular. Frequently, substrates include various organic waste and natural products processed applying different means. For substrates of extremely small capacity, compost, soil, moss, wood shavings (Mohseni and Allen 2000), and activated pine bark (Baltrėnas and Vaiškūnaitė 2003) are used. The materials most frequently used for biological air treatment removing organic and inorganic chemical pollutants include peat, soil, compost, and their mixtures (Delhomenie et al. 2002). For example, the treatment efficiency of a biofilter with peat packing material at removing hydrogen sulfide from air reaches 97–99 % (Hartikainen et al. 2002). Air can also be purified using packing materials made of cellulose beads and coconut shavings (Shareefdeen et al. 2003). Also, wood sawdust, bark, and various types of shredded waste, as well as sewage sludge, are widely used (Shareefdeen et al. 2003). The majority of packing materials are efficiently used from 2 to 5 years (Tymczyna et al. 2004). To extend the lifetime for the effective operation of biofilter packing materials, inorganic materials are used. To ensure high treatment efficiency and the sustainability of the device, organic and inorganic materials such as perlite or polyurethane are mixed in. Inorganic materials are employed to reduce a drop in pressure. Zeolites, classified with frame aluminosilicates whose crystalline structure is composed of apex-joined tetrahedrons $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$, are quite widely used. Alkali and alkaline earth metal cations, ammonium, water molecules, and others are located in the pores and canals of such an openwork frame composing up to 50 % of the volume of the metal; for example, the composition of clinoptilolite can be described by the formula $(K_2Na_2Ca)_3[Al_6Si_{30}O_{72}] \bullet 20H_2O$. Zeolites are frequently classified according to the ratio of $SiO_2{:}Al_2O_3$: the higher it is, the more resistant is the zeolite to acids (Baltrėnas and Paliulis 2002).

The efficiency of biofiltration systems is quantitatively characterized with reference to several parameters. The productivity of biofilters is expressed through the parameter of the elimination capacity of pollutant *I* (Rahul and Balomajumder 2013) applying Eq. (7.5):

$$\mathrm{EC}^{\mathrm{i}} = \frac{\left(C_{\mathrm{Gi}}^{\mathrm{i}} - C_{\mathrm{Go}}^{\mathrm{i}}\right)Q}{V_{\mathrm{f}}}, \tag{7.5}$$

where EC^{i} is the elimination capacity of gas pollutant i (g/m^3/h), C_{Gi} is the concentration of the inflow of gas pollutant i (g/m^3), C_{Go} is the concentration of the outflow of gas pollutant i (g/m^3), Q is the discharge of gas flow with pollutant i (m^3/h), and V_{f} is the volume of the packing material of the biofilter (m^3).

The treatment efficiency (RE^{i}, %) of the biofilter from which pollutant i is removed (Bohn 1992) is calculated according to Eq. (7.6):

$$\mathrm{RE}^{\mathrm{i}} = \frac{\left(C_{\mathrm{Gi}}^{\mathrm{i}} - C_{\mathrm{Go}}^{\mathrm{i}}\right)}{C_{\mathrm{Gi}}^{\mathrm{i}}} \times 100. \tag{7.6}$$

Contact time for the polluted airflow in a biofilter and the packing material (EBRT, s) (Devinny et al. 1999) is calculated according to Eq. (7.7):

$$\mathrm{EBRT} = V_{\mathrm{f}} \cdot Q. \tag{7.7}$$

A volumetric load of gaseous pollutant i in the biofilter (A^{i}, g/m^3/h) (Devinny et al. 1999) is calculated according to Eq. (7.8):

$$A^{\mathrm{i}} = \frac{Q \cdot C_{\mathrm{Gi}}^{\mathrm{i}}}{V_{\mathrm{f}}}. \tag{7.8}$$

In biodegradation, VOCs are aerobically degraded to CO_2 and water by microorganisms and exploited as a carbon source for microbial growth. Thus, the CO_2 production rate may provide valuable information about the activity of microorganisms in a biofilter. The term *carbon recovery* is used to assess the amount of carbon utilized by microorganisms and is calculated using Eq. (7.9) (Singh et al. 2010a, b, c):

$$C_{\mathrm{R}} = \frac{n_{\mathrm{p}}^{\mathrm{CO_2}}}{n_{\mathrm{c}}^{\mathrm{C}}}, \tag{7.9}$$

where C_{R} is the carbon recovery (%), $n^{\mathrm{CO2}}{}_{\mathrm{p}}$ is the mole of CO_2 produced, and $n^{\mathrm{C}}{}_{\mathrm{p}}$ is the mole of C in pollutant consumed.

Under aerobic conditions, O_2 serves as the primary electron acceptor for VOC oxidation and biomass growth. Williamson and McCarty proposed a relationship for determining whether the reaction within a biofilm is flux-limited by a substrate or by O_2 (Williamson and McCarty 1976a,b) (Eq. 7.10). The O_2 limitation within the biofilm will occur if

$$C_{\mathrm{s}} > \frac{D_{\mathrm{o}} \nu_{\mathrm{m}} M_{\mathrm{m}}}{D_{\mathrm{m}} \nu_{\mathrm{o}} M_{\mathrm{o}}} C_{\mathrm{o}}, \tag{7.10}$$

where C_{o} and C_{m} are concentrations of O_2 and the medium material in the liquid film or at the biofilm surface, D_{o} and D_{m} are the diffusion coefficients of O_2 and the medium material in the liquid phase or in the biofilms, v_{o} and v_{m} are the stoichiometric reaction coefficients, and M_{o} and M_{m} are the molecular weights of O_2 and the medium material. Assuming Henry's law applies at the liquid–gas interface and

Table 7.2 Types of biofilter media used for biofiltration (McNevin and Barford 2000)

Type	Qualities
Bark compost, wood chips	Low pressure drop, removes volatile organic compounds
Sewage sludge, compost	Removes hydrogen sulfide
Perlite, crushed oyster shells, compost	Removes aromatics, hydrogen sulfide
Sod-peat nodules, extruded peat granules	Low pressure drop, removes hydrogen sulfide, methyl mercaptan
Sieved compost and chaff	Removes triethylamine, chaff reduces pressure drop
Compost, wood chips, bark mulch	Removes odor from sludge composting facilities
Compost, perlite, zeolite, oyster shells	Removes ammonia, volatile organic compounds

under ideal gas conditions, this criterion for O_2 limitation within the biofilm in a gas phase biofilter can be related to Henry's constant as (Zhu et al 2004) (Eq. 7.11)

$$P_{\mathrm{s}} > \frac{10^3 D_{\mathrm{w,o}} \nu_{\mathrm{s}} \mathrm{RT}}{D_{\mathrm{w,s}} \nu_{\mathrm{o}} MW_{\mathrm{o}}} C_{\mathrm{w,o}} H, \tag{7.11}$$

where p_{s} is the VOC partial pressure in the gas phase (ppmv), $C_{\mathrm{w,o}}$ is the O_2 concentration in the liquid film or at the biofilm surface (mg/L), $D_{\mathrm{w,o}}$ and $D_{\mathrm{w,m}}$ are the diffusion coefficients of O_2 and the VOC in the liquid phase or in the biofilms, H is the dimensionless Henry's constant of the VOC, R is the ideal gas law constant (0.082 L atm/mol · K), and T is the absolute temperature (K). This criterion can help to assess the possibility of O_2 limitations in a biofiltration system.

Table 7.2 lists biofilter-bed media types for the removal of odorous compounds using biofiltration. Typical materials used as a biofiltration medium include soil, peat, compost, bark mulch, perlite, sewage sludge, and combinations of these. Multiple layers of biofilter media have been recommended by some manufacturers.

Table 7.3 presents specific packing materials used in biofiltration systems for removing acetone, ammonia, and xylene from airflow and presents the parameters of biofilter efficiency. Higher removal efficiency is reached by applying organic substrates because they create more favorable conditions for the survival and proliferation of decomposing microorganisms. To remove the aforementioned pollutants from airflow, in the case of an inorganic packing material (e.g., perlite pellets), an efficiency of 50 % can be reached (productivity of around 330 g/m^3/h), whereas when the packing material is organic (stabilized compost), efficiency reaches up to 99 % (productivity of over 800 g/m^3/h).

Advancements in biofiltration systems have led to making the biofiltration process more efficient, reducing capital and operational expenses, using more effective and cheaper packing materials, assessing the local availability of these materials, and creating structures of biofiltration systems such that the surface area and the time of contact between the pollutant and packing material are increased.

Table 7.3 Examples of packing materials of biofilters, maximum elimination capacity (EC_{max}, g/m^3/h), removal efficiency (RE, %), contact time between a pollutant and packing material (EBRT, s)

Medium	Pollutant	EC_{max} (g/m^3/h) or RE (%)	EBRT (s)	Reference
Polyurethane foam	Acetone	(>95 %)	30	Lee et al. (2013)
Perlite beads	Acetone	325.9 g/m^3/h (54 %)	17,1	Rene et al. (2010)
Polyurethane foam	Ammonia	(>95 %)	30	Lee et al. (2013)
Perlite beads	Ammonia	(>95 %)	30	
Stabilized compost	Ammonia	836 g/m^3/h (>98.8 %)	86	La. Pagans et al. (2005)
Mixture of pig manure and sawdust	Xylene	130 g/m^3/h (>95 %)	180–270	Gallastegui et al. (2011)
Aerated peat	Xylene	236 g/m^3/h (66 %)	68	Jorio et al. (2002)
Mixture of compost and sawdust	Xylene	73 ± 14	60	Torkian et al. (2003)
Mixture of peat and mineral additives (at mass ratio of 70:30)	Xylene	61 g/m^3/h (93 %)	150	Elmrini et al. (2004)
Mixture of pig manure, forest soil, and polyethylene	Xylene	80 g/m^3/h (96 %)	132	Wu et al. (2006)
Pressed bagasse	Xylene	67 g/m^3/h	42	Saravanan and Rajamohan (2009)
Sawdust with introduced fungi	Xylene	77 g/m^3/h (53 %)	59	Jorio et al. (2009)
Sawdust with introduced bacteria	Xylene	58 g/m^3/h (49 %)	59	

The physicochemical properties of the majority of wood products are beneficial for biofiltration systems owing to the favorable medium for the survival of microorganisms as a backup food source for microorganisms. As a result of the developed morphological structure, effective moisture-support materials available from local sources are conditionally cheap and relatively durable, and their use agrees with the main principles of sustainable development. For example, because of the employment of local materials, the amount of CO$_2$ removed within transportation vehicles and wood waste products suitable for packing materials is decreased. Thus, their application in the biofiltration process reduces waste generation and promotes the reuse of waste and the turning of waste into products. Some of these wood products, as alternatives to biofiltration systems, are described in this chapter.

The use of wood biochar in biofiltration packing material is based on its low price, local availability, stability of about 5–8 years (Schmidt 2012), and a relatively high surface area (300–400 m^2/g) (Lehmann and Joseph 2010) that is larger than that of the majority of inactive and natural substrates applied in biofilters (1–10 m^2/g) (McNevin and Barford 2000). It is a favorable medium for the adsorption of gas contaminants from polluted air and for thriving organisms that decompose pollutants. As stated in the European Biochar Certificate (EBC 2012): "Biochar is a heterogeneous substance rich in aromatic carbon and minerals. It is produced by pyrolysis of sustainably obtained biomass under controlled conditions with clean technology and is used for any purpose that does not involve its rapid mineralization to CO_2 and may eventually become a soil amendment." Most times, biochar produced from different types of feedstock is not fully carbonized; therefore, biomass-derived black carbon is denominated biochar instead of charcoal (Chen et al. 2008). Biochar is often referred to as carbon used for improving the properties of soil, particularly for stabilizing carbon compounds in soil and reducing the processes determining climate change. However, bearing in mind that biochar is too expensive to improve soil qualities once it has been produced (Schmidt 2012), its application in a biofiltration system may be part of an intermediate stage before soil reclamation. In all cases, before the entrance of biochar into soil, an environmental protection factor must be assessed.

Table 7.4 gives values of the principal structural and physicochemical parameters of several types of biochar. Four different types of biochar, which differ by the raw material used for biochar production, were selected for comparison purposes. The first two were lignocellulose biochar from pine and birch wood that contains a high content of carbon; the third biochar was from algae, and its carbon content was significantly lower and it was widely used in environmental protection technologies (e.g., in waste treatment, bioremediation of territories affected by anthropogenic activities); the fourth was bone biochar, with a typically low content of carbon, formed on a calcium-phosphate basis, and was used as a mineral fertilizer for soil. The principal properties of substrates given in Table 7.4 allow for evaluating the efficiency of pollutant adsorption and biodegradation processes. The largest BET surface area of pine biochar signifies a larger pollutant adsorption capacity. A slightly larger micropore volume in birch biochar than in pine biochar could result

Table 7.4 Principal properties of pine (*Pinus sylvestris* L.) biochar and other selected chars in relation to biofiltering purpose (*nd* no data)

Properties	Pine biochar (*Pinus sylvestris* L.)	Birch biochar (*Betula pendula*)	Green tide algae (*Ulvaflexuousa*) biochar (Bird et al. 2011)	Bone char (Ip et al. 2010)
BET surface area (m^2/g)	380	291	1.15–4.26	107
Micropore volume (mm^3/g)	78.7	119	nd	0.0
Micropore volume percentage	42	77	nd	nd
Ash content (%)	1.73 ± 0.2	nd	26.5–31.0	nd
Loss on ignition (LOI), 700 °C (%)	89.4 ± 2.12	nd	30.1	nd
pH	9.42 ± 0.04	9.27 ± 0.004	10.1	nd

in a higher retention of gaseous pollutants in micropores, as larger molecules (0.4–0.6 nm) of the researched gaseous pollutants are better retained in narrower pores (the average diameter of micropores according to IUPAC is about 2 nm) (Ip et al. 2010). But a smaller ratio of micropore volume to the volume of all pores in pine biochar than in birch biochar would create conditions for more efficient pollutant biodegradation processes, when the average size of microorganisms participating in the biofiltration systems is 1–3 μm; therefore, microorganisms can exist in pores that are larger than 1 μm. In such a case, it will be more difficult for microorganisms to reach pollutants adsorbed in micropores and mesopores of a substrate (Ip et al. 2010). This means that a smaller micropore volume percentage, as in the case of pine, was preferred.

The ash content of pine biochar was less than that of mineral-based algae biochar, partially indicating a more mechanically stable substrate structure. Higher values of loss on ignition in pine biochar than in algae biochar are partially related to a higher organic content, which is more favorable for the development of microorganisms. Insignificant pH differences are characteristic of all the compared biochar types.

Activated Carbon

Granular activated carbon has been used as a biofilter medium for quite a long time. It worked well for the full-scale treatment of petroleum hydrocarbons from refineries and from a soil vapor extraction project. It can be used as a standalone or as a bulking agent mainly to attenuate pollutant fluctuations. It has good resistance to crushing and a substantial water-holding capacity and provides a good surface for microbial attachment. While its adsorptive capacity in a biofilter is reduced by the water and biomass on its surface, it is still much higher than that of other media. Activated carbon must be prepared for use in a biofilter. Nutrient amendment and microbial inoculation are usually required, and some carbons are strongly basic and must be neutralized to provide a suitable pH. Its primary disadvantage is its high cost (Devinny et al. 1999).

Wood Chips and Bark

Wood chips or bark are commonly used in various proportions as bulking agents, but in some cases it was reported the use of wood chips alone as medium. In this case, regular nutrient supply is needed. Common particle sizes are 1–5 cm. In addition to preventing bed compaction and allowing for homogeneous airflow, wood chips or bark constitute a reservoir of water that may in some case attenuate fluctuations in packing moisture content due to poor reactor control or excessive heat generation (Devinny et al. 1999). In works of used spruce wood chips and bark (Baltrėnas and Zagorskis 2007a, b) or pine bark (Baltrėnas and Vaiškūnaitė 2003; Vaiškūnaitė and Baltrėnas 2007).

Wood Products as the Bulk of Biofilter Packing Material

A number of organic materials (including wood products) possess the required structure and properties important for ensuring an effective biofiltration process. Nevertheless, organic materials can frequently be characterized by a short operating time of approximately 2–5 years (Tymczyna et al. 2004). Thus, to ensure higher treatment efficiency and equipment sustainability, mixtures of organic and inorganic materials used in the packing materials of biofilters are formed (Aizpuru et al. 2003). US researchers used mixtures of wood chips and compost for removing ethyl acetate and toluene from the air. Also, to decrease the pressure drop conditioned by packing materials and to prolong the life of the packing material, wood chips with polystyrene beads were added (Deshusses and Cox 1999). To reduce the pressure drop in such composite substrates, the prepared inorganic materials take on the forms of the sphere or cylinder. Under such circumstances, the inoculation of microorganisms seems to be the best option.

Inorganic materials can help with reducing the operational costs of biofiltration because of the properties allowing biological processes to maintain the required moisture content that is particularly important to maintaining biological processes in the biofilter (Jankevičius and Liužinas 2003). This is determined by the capillary structure of materials, which creates conditions for producing a capillary effect (liquid rather than vapor molecules attract those of the material surface more strongly, and thus the emergence of tension forces results in a rise of liquid to the top). Hence, the solution saturated with biogenic elements rises through substance capillaries, humidifying the packing material itself and performing the functions of the biomedium carrier.

Baltrėnas et al. (2015a, b) investigated biofiltration systems made of mixed nonwoven caulking material and wood fiber and examined the efficiency of removing volatile compounds from the air. Some properties composing the packing material of the biofilter are presented in Table 7.5.

Heat-treated birch wood fiber granules were fitted from both sides of a solid, polymer wavy lamella. Heat treatment of the birch wood fiber was imperative for maintaining its longevity. Birch wood fiber was obtained by treating birch wood cuttings with heat in a steam explosion reactor at 32 bar pressure and 235 °C.

With reference to data provided by a scanning electron microscope, the major part of the nonwoven caulking material was made of small filaments with a thickness of 15 to 25 μm. The set spaces between the filaments were found to be from 5 to 10 times larger than the thickness of the filaments (Fig. 7.2).

Table 7.5 Selected physical properties of materials used in biological air treatment equipment

Name of substance	Relative moisture of material (%)	Absolute moisture of material (%)	Porosity (%)	Density (g/cm^3)
Nonwoven material	3.1	8.4	89.2	0.13
Birch wood fiber	10.6	13.3	72.0	0.14

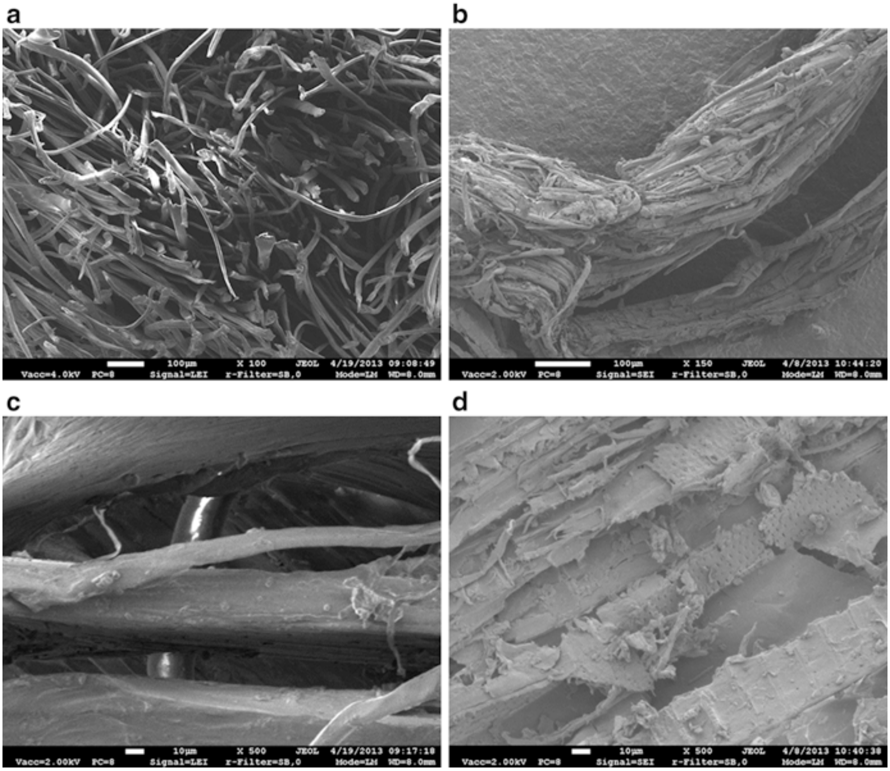


Fig. 7.2 Micromorphological structure of materials: (**a**) nonwoven caulking material (magnified 100×), (**b**) birch fiber (magnified 150×), (**c**) nonwoven caulking material (magnified 500×), (**d**) birch fiber (magnified 500×)

It is likely that such an arrangement of filaments makes it possible to make a biofilm, thereby avoiding anaerobic zones harmful to microorganisms.

The chaotic distribution of the filaments allows one to increase the specific surface area of the material and the volume of the biomedium in the material. The image of the material magnified up to 500 times allows one to monitor filaments of 120–180 µm thickness, which makes for capillaries 10–30 µm thick (Fig. 7.2c). The heat-treated birch fiber also had an irregular surface, a porous structure, and, hence, a larger specific surface area (Fig. 7.2b). The capillary structure of wood fiber was uneven with a width varying from 10 to 50 µm (Fig. 7.2c).

The structure of the fiber surface allows the biomedium to nestle to the material and to form a biofilm the microorganisms in which could be absorbed organic carbon in the birch fiber.

Zeolite is another popular inorganic material used in biofilters; it has a uniform pore size, a large specific surface area (600–800 m^2/g), and high thermal stability. Like synthetic zeolites, they are characterized by molecular sieve properties, high sorption at low pressures, and power that does not depend very much on the temperature range of 10–105 °C (Baltrėnas and Paliulis 2002).

It has been found that wood chips mixed with zeolite increase the performance of the biofilter and improve moisture retention in the medium. The microorganisms accumulated in the biofilm formed on the surface of zeolite granules efficiently decompose organic pollutants adsorbed in zeolite pores. To retain moisture in the packing material, wood chips can be mixed with a material having a larger sorptive area such as foam rubber. In this case, the packing material can be characterized by even better properties of moisture retention, a large specific surface area, low density, and greater economy.

7.2 Physicochemical Properties of Wood Products Used in Systems for Biological Air Treatment

The choice of materials for biofiltration systems should be based on a number of criteria, such as inorganic nutrient content, organic content, chemical and inert additives, water content, pH, sorption characteristics, porosity, bacterial attachment, mechanical properties, odor of filter bed, filter bed cost and lifetime, and filter bed disposal. Several properties of tree-derived media and changes in them over the lifetime of the biofilter operation are discussed in what follows.

Specificities of Changes in Moisture, Porosity, Durability, and Pressure of Packing Material in Biofiltration Systems

A comparison of different mixtures of organic (wood chips, bark) and inorganic (zeolite, foam) materials shows that the highest moisture content (75 %) has been found in packing material consisting of wood chips, bark, and foam cubes. Zeolite pellets mixed with wood chips and bark have resulted in a moisture content of 40 % for a period of 100 days. The moisture content of packing material made of wood chips and bark has been found to be slightly lower (70 %). The moisture content of wood chips and bark is affected by their porosity, i.e., the ratio of pore volume and cavities to the total volume of the material. Wood chips and bark have a structure of communicating pores, which increases moisture retention. The moisture content of packing material has been found to increase over time. Under a biofilter operating for 900 days, the moisture content of all investigated packing materials increases by around 10 % compared with 100 days of operation (Fig. 7.3).

The moisture content of the packing material of the biofilter can increase owing to the reduced porosity. After 900 days, the porosity of wood chips mixed with bark decreased from 55 to 40 %. The maximum decrease in porosity was recorded in packing material consisting of wood chips, bark, and a foam mixture. The porosity of this packing material decreased from 75 to 59 % for a period of 900 days of use. The reduced porosity of the packing material raises its moisture content and thus its

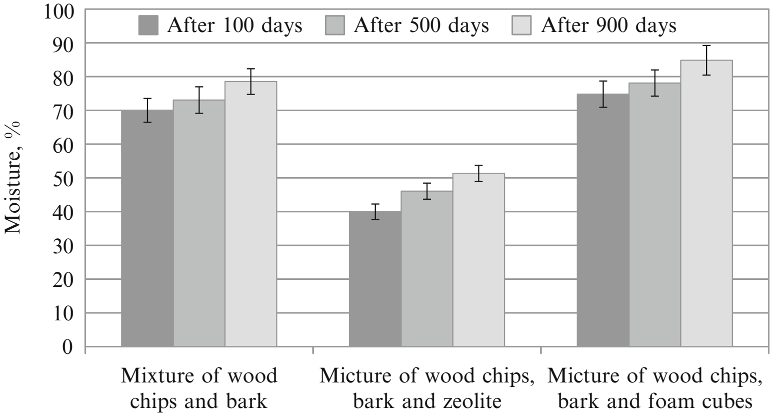


Fig. 7.3 Dependencies between moisture of different packing materials used in biofilters and biofilter life span

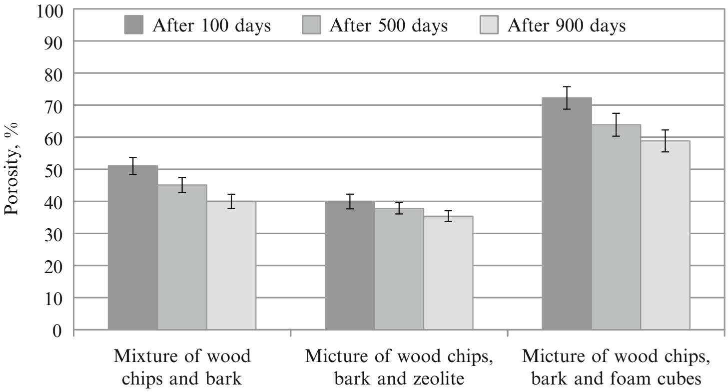


Fig. 7.4 Dependence of porosity of packing materials of biofilter on performance of biofilter

pressure drop. The moisture content of the mixture of wood chips, bark, and zeolite grew from 40 to 51 % over the 900 days it was used. Meanwhile, for the same period, the porosity decreased from 42 to 35 %. Zeolite pellets have been shown to be more resistant to environmental conditions and microbial processes, and therefore the degradation of wood chips and bark had a greater impact on changes in the porosity (Fig. 7.4).

The pressure drop in packing material varies and thus affects the performance of the biofilter. At the beginning of testing, the pressure drop in the packing material of the biofilter reached 950 Pa (under an airflow rate of 0.3 m/s). After the biofilter was tested for 100 days, this value was 1005 Pa, while after 900 it was 1221 Pa (Fig. 7.5). Lower values of pressure drop are characteristic of biofilters made of organic materials (Kennes and Thalasso 1998).

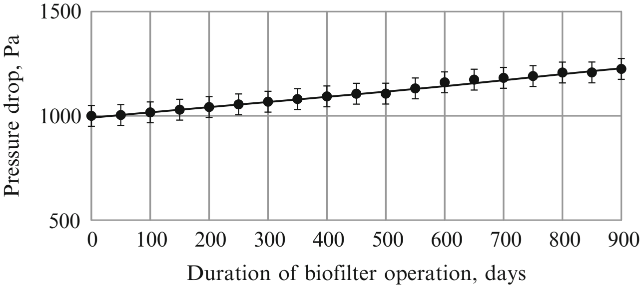


Fig. 7.5 Dependence of pressure drop in biofilter on performance of biofilter

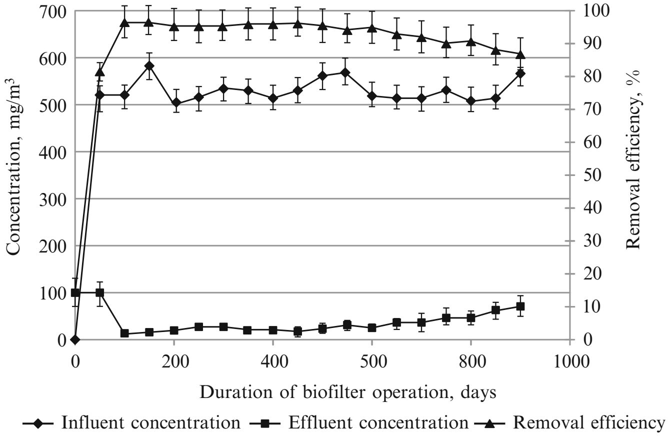


Fig. 7.6 Dependence of treatment efficiency of biofilter on performance of biofilter

Figure 7.6 shows the dependence of the treatment efficiency of the biofilter on the performance of the biofilter. The highest decrease in the concentration of acetone was recorded after 500 days, following which the treatment efficiency of the biofilter reduced from 98 to 95 %. After 900 days of the operating, the biofilter's efficiency decreased to 88 %. The conducted research has shown that the packing material made of natural zeolite pellets, foam cubes, and wood chips operated efficiently even after 900 days. The physical properties of the employed packing material did not change significantly, and the packing material maintained its operating properties.

Changes in the Temperature of the Packing Material and Their Impact on Biofilter Operation

The maintenance of an optimal temperature is important in terms of creating conditions favorable to the activity of microorganisms. Temperature has an impact on variations in the composition and structure of materials in the cells of microorganisms and, at the same time, changes the rate of reactions taking place in the course of biochemical processes. Baltrėnas et al. (2015a, b) focused primarily on the impact of different temperatures (7, 14, and 28 °C) on the efficiency of biofilters when the concentration of the supplied pollutant (butyl acetate, butanol, and xylene) was 30–100 mg/m^3.

Under low concentrations of pollutants (up to 30 mg/m^3), the efficiency of removing butanol and butyl acetate from the air reached 73–77 % (Fig. 7.7).

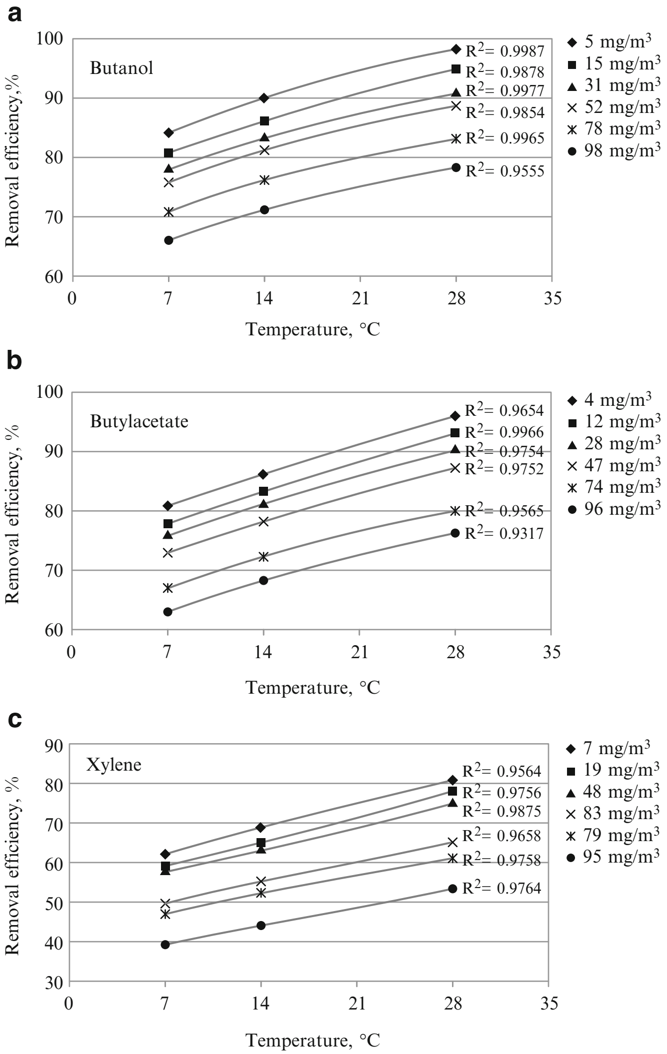


Fig. 7.7 Efficiency of removing butanol (**a**), butyl acetate (**b**), and xylene (**c**) from air under different temperatures

An increase in pollutant concentrations (up to 100 mg/m^3) resulted in a reduction in the efficiency of removing butanol and butyl acetate and reached 77 and 60 %, respectively. The decomposition of xylene was much slower. Under a xylene concentration of 21 mg/m^3, the efficiency of the operating biofilter was 59 % (Fig. 7.7). An increase in the initial xylene concentration of 95 mg/m^3 resulted in a reduction of air treatment efficiency of 39–41 % following five layers of packing materials. Thus, under the maintained temperature of 7 °C, the initial pollutant concentration of 100 mg/m^3, and slower microbiological decomposition, the efficiency of removing xylene decreased on average by 30 %.

A comparison of different temperatures (7 and 14 °C) maintained in the biofilter revealed that the efficiency of removal of all investigated pollutants (butanol, butyl acetate, and xylene), under a higher temperature (i.e. 14 °C), increased on average by 5 % (Fig. 7.7); for example, when temperature reached 7 °C and the initial concentration of butanol in the filter was 45 mg/m^3, the efficiency of removing the pollutant was 69 %. When the temperature increased up to 14 °C, the efficiency of removing butanol (under the initial concentration of 46 mg/m^3) from the air increased by up to 74 %. The increased temperature of the packing material of the filter (up to 28 °C) resulted in a higher efficiency of removal. For example, when pollutant concentrations in the filter reached 30 mg/m^3, air treatment efficiency increased on average by 18–19 %. When the initial concentrations of pollutants were increased up to 100 mg/m^3, air treatment efficiency rose on average by 13–14 %.

Considering the ability of microorganisms to oxidize the investigated pollutants, it can be stated that the highest efficiency of this process is achieved when a temperature of 28 °C is maintained in the biofilter. The analysis of separate pollutants and the biological decomposition of their concentrations revealed that microorganisms living in the filter more intensively oxidize compounds (butyl acetate and butanol) that are soluble in water; however, compounds that are less soluble in water and highly biologically dissoluble, such as xylene, are oxidized less intensively. The decomposition of pollutants whose initial concentrations are relatively low (up to 30 mg/m^3) is easier and more effective, i.e., the testing results of different initial concentrations differ only by several percentage points. A larger difference in efficiency results is observed when higher pollutant concentrations (from 30 to 100 mg/m^3) are emitted through the filter and a lower temperature (7 and 14 °C) is maintained in the biofilter. Thus, the packing material of a biofilter made of wood products efficiently removes butanol, butyl acetate, and xylene under different temperatures (7, 14, and 28 °C), but air treatment efficiency is better under a temperature of 28 °C. The performance of the packing material remains the same in all investigated cases.

Micromorphological Changes in Packing Material Under Different Temperatures and Removed Pollutants

A micromorphological analysis was made of the packing material of a biofilter made of packing material of mixed biochar and birch fiber (mixed at a ratio of 10–1) and used in the biofilter for removing different volatile compounds, including acetone, xylene, and ammonia, at different temperatures (24, 28, 32 °C). The pollutants were consistently supplied at a concentration of 300 mg/m^3, and the discharge of airflow polluted with them reached 100 m^3/h. For the packing material of the biofilter, the biochar was prepared at a temperature of 700 °C for 2 h and granulated up to fractions of 4–6 mm. Pictures of biochar specimens before and after testing the biofilter were taken employing the method of scanning electronic microscopy. Two types of granules were monitored in the selected specimens: a metallic black glossy surface and a matt black surface. The pores of the two types, with a large (40–45 μm) and a small (5–8 μm) diameter (Fig. 7.8a, b), were observed in the cross section of the birch biochar specimen. The observed small amounts of wood fiber on the surface of the tested biochar are shown in Fig. 7.8a. Membranes completely covering the cross section of the small-diameter pores are also observed in the cross section (Fig. 7.8b).

The analyzed data on the elemental composition of biochar surfaces were obtained using an Inca Energy 350 spectrometer measuring the energy dispersion of the X-ray waves of an electron microscope (Figs. 7.9 and 7.10). Elements C and O were found in the walls of the pores of birch biochar. The worked out method fails to identify H; therefore, it can be asserted that the used birch biochar was made of elemental carbon and the rest of a relatively insignificant amount of transitive organic compounds. Birch biochar consists (without taking into account H), on average, of 84.68 % C and 15.32 % O. The membranes completely covering the small pores of the biochar were observed for the first time. To determine their nature, elemental analysis was carried out. The obtained findings are displayed in Fig. 7.9. These membranes must identified as being part of the woody structure to

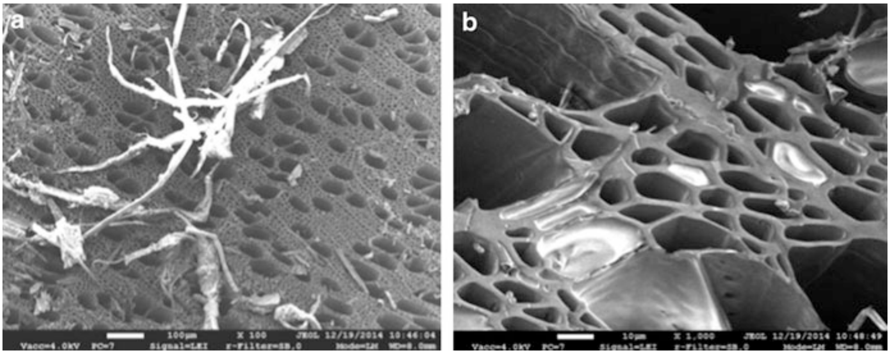
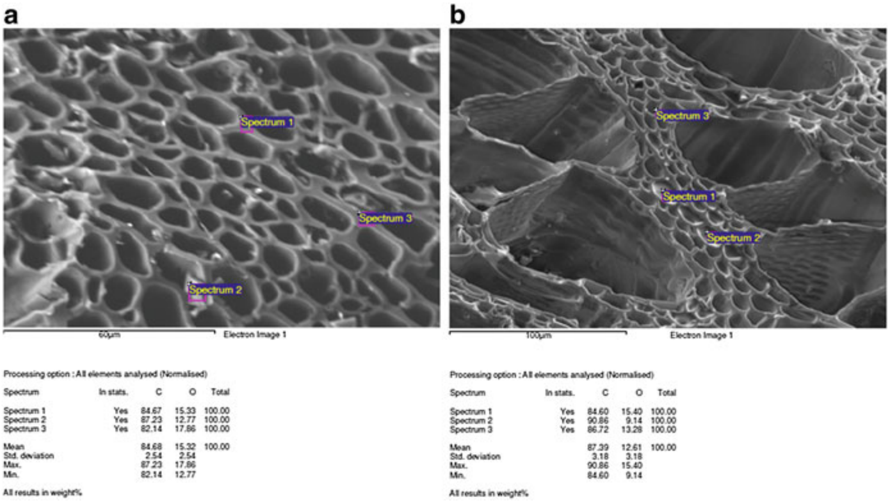


Fig. 7.8 Birch biochar before testing: (**a**) magnification 100×, (**b**) magnification 1000×



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Total
Spectrum 1	Yes	84.67	15.33	100.00
Spectrum 2	Yes	87.23	12.77	100.00
Spectrum 3	Yes	82.14	17.86	100.00
Mean		84.68	15.32	100.00
Std. deviation		2.54	2.54	
Max.		87.23	17.86	
Min.		82.14	12.77	

All results in weight%

Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Total
Spectrum 1	Yes	84.60	15.40	100.00
Spectrum 2	Yes	90.86	9.14	100.00
Spectrum 3	Yes	86.72	13.28	100.00
Mean		87.39	12.61	100.00
Std. deviation		3.18	3.18	
Max.		90.86	15.40	
Min.		84.60	9.14	

All results in weight%

Fig. 7.9 Data on elemental analysis of birch biochar pore walls

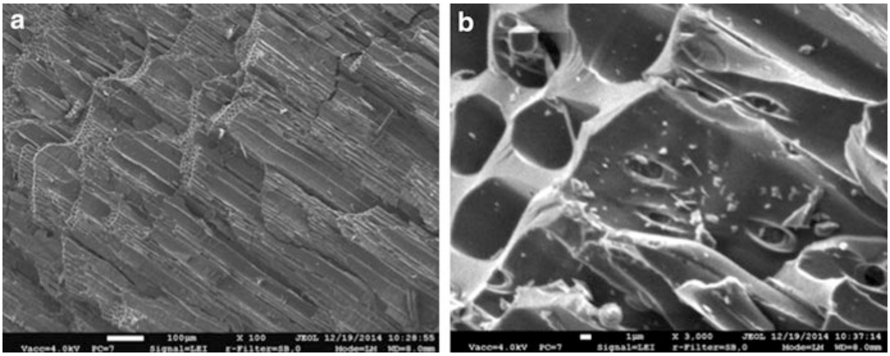


Fig. 7.10 Birch biochar treated with acetone: (**a**) magnification 100×, (**b**) magnification 3000×

the structure of wood. Their elemental composition only slightly differs from that of the walls of pores; however, the content of C is higher (87.39 %), and that of O is lower (12.61 %). Although these elements are of an extremely small thickness, the full transition of organic compounds of timber to C was not attained.

The images of the surface structure of birch biochar processed with acetone are presented in Fig. 7.10a, b.

No birch fiber on the surface and membranes covering the cross section of the pores in these specimens was noticed. The diameter of the large pores observed in the specimen is 50–60 μm and that of small onesis 6–7 μm. The new structures, absent in the specimen of biochar before processing, of the elongated shape (0.5–1 μm) on the lateral surfaces of the pores can be monitored (Fig. 7.10b).

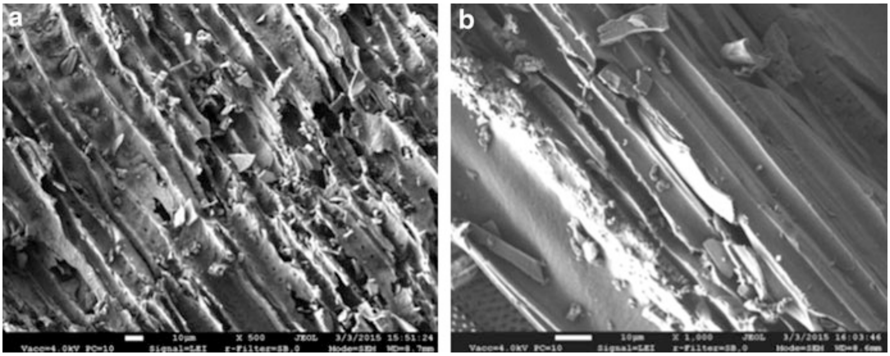


Fig. 7.11 Birch biochar: (**a**) magnification 500× (treated with xylene), (**b**) magnification 1000× (treated with ammonia)

Table 7.6 Micromorphological properties of birch biochar

No.	Specimen	Porosity (%)	Surface area of pores (m^2/g)	Specified volume of pores (cm^3/g)
1	Birch biochar (not treated)	62.89	6.15	1.08
2	Birch biochar treated with acetone	79.70	13.49	1.91
3	Birch biochar treated with xylene	73.29	20.39	1.71
4	Birch biochar treated with ammonia	75.95	12.84	1.91

Images of the porous structure of biochar specimens processed with xylene and ammonia in a tubular biofilter are presented in Fig. 7.11.

The presented images show damage to the outer layer of the biochar. Damaged tracheids, an uneven surface, and a number of small fragments 10–50 μm in length can be observed. Data on research into the porous structure of birch biochar were obtained using the mercury porosimetry technique and are shown in Table 7.6.

The obtained data display considerable differences in the porous structure of the investigated specimens. This may be due to difficulties in selecting the mean specimen from the tested samples. As mentioned earlier, the selected specimens of birch biochar varied in color as well as, obviously, in structure. However, the porosity (62.89 %) of the unprocessed specimen, and the surface area of pores in particular (6.15 m^2/g), is significantly lower than that of the processed specimens. The specified volume of pores is also lower. The impact of xylene is assumed to be exceptional, which dramatically increases the surface area of biochar pores. This can be explained by the impact of xylene on residual organic compounds melting them and thus forming a structure of additional micropores.

Biofiltration Affecting Processes in Biofilter Loading

Removal efficiency is an incomplete descriptor of biofilter performance because it varies with contaminant concentration, airflow, biofilter size, and design and only reflects the specific conditions under which it is measured. The elimination capacity allows for direct comparison of the results of several different biofilter systems because the volume and flow are normalized.

Elimination capacity can only be equal to or less than the mass loading rate. When the load is increased, a point will be reached where the overall mass loading rate will exceed the overall elimination capacity. This point is called the critical load or critical elimination capacity and can be visually detected in the elimination capacity vs. load curve. In Fig. 7.12a this point is 600 g/m^3/h for toluene removal in a biofilter operated with wood biochar mixed with glass beads as the biofilter medium. The curve favors the identification of two distict zones, which explains the two different mechanisms that control biofiltration (Fig. 7.12b).

Almost constant toluene removal efficiency is observed up to a loading rate of 600 g/m^3/h. This is because at a low loading rate, the diffusional flux of the contaminant (toluene) through the biofilm will also be low, causing mass-transfer limitations in the biofilm. In this case, the internal layer of the biofilm (at the surface of the biochar) will be deficient in toluene (source of carbon and energy); thus, the capability of biofilm is not being fully utilized for degrading toluene. As the loading rate is increased, the utilization rate of biofilm increases and becomes fully utilized at a loading rate of 600 g/m^3/h. Increasing the loading rate beyond 600 g/m^3/h results in changes in the biofiltration controlling mechanism from mass transfer to bioreaction, and hence the removal efficiency starts decreasing and the elimination capacity of toluene increases slowly compared to the mass-transfer controlling zone. Sometimes medium inhibition may also be responsible for a poor removal efficiency, particularly in the case of pollutants at higher concentrations that have good solubility in water (low Henry's constant). To obtain optimum results, the biofilter should be operated in a bioreaction controlling zone with a desired removal efficiency. For practical operations, the contaminant inlet loading rate at which the mechanism in the biofilter changes from a diffusion to a bioreaction controlled zone indicated by the point of intersection of removal efficiency versus elimination capacity curves (Fig 7.12c) may be taken as an approximate estimate of the operating range of the biofilter. In the present study the optimum operating range was found between 600 and 800 g/m^3/h (Singh et al. 2010a, b, c).

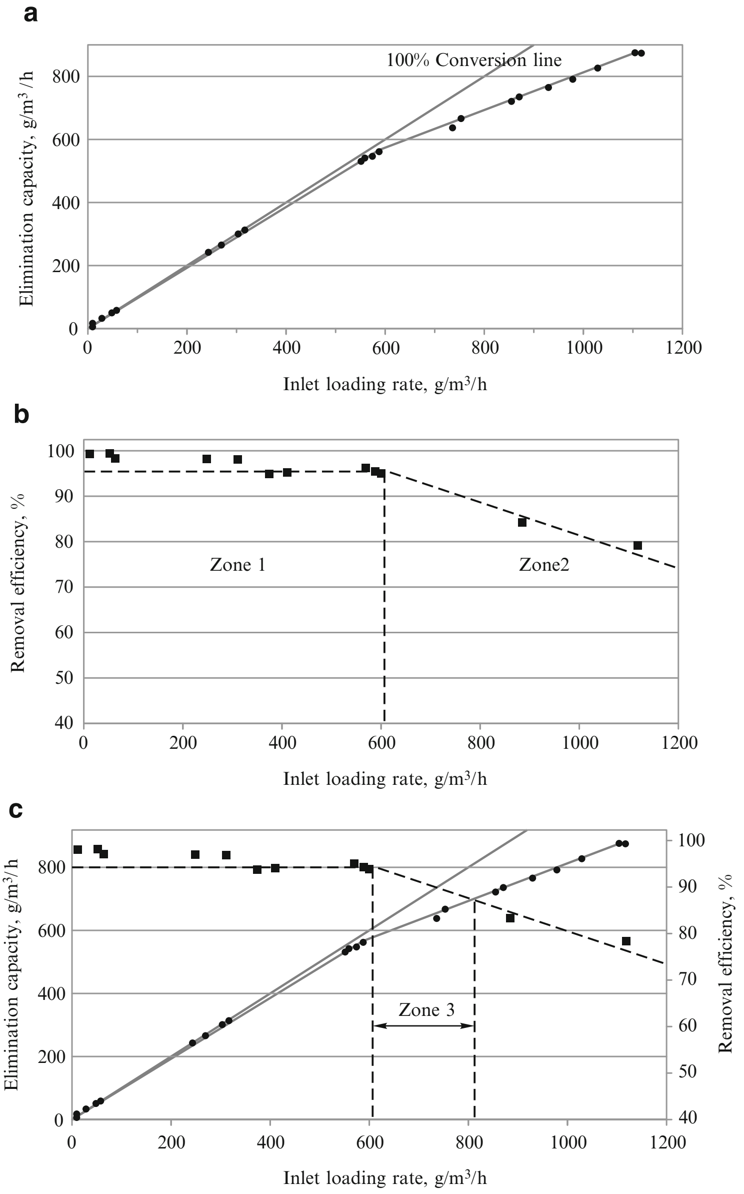


Fig. 7.12 Influence of inlet toluene load on removal efficiency and elimination capacity of biofilter with wood biochar as biofilter media and glass beads for improved air distribution (after Singh et al. 2010a, b, c): Zone 1: mass controlling zone; Zone 2: reaction controlling zone; Zone 3: proposed operating zone

7.3 Microbiological Characteristics of Wood Products Used in Systems for Biological Air Treatment

Most of the microorganisms found in biofilter packing materials are the bacteria *Pseudomonas* and *Bacillus* and the filamentous fungi belonging to the *Mortierella*, *Rhizopus*, *Penicillium*, *Aspergillus*, *Cladosporium*, *Fusarium*, *Trichoderma*, *Alternaria*, *Botrytis*, and others genera (van Groenestijn and Hesselink 1993).

The results of testing a biofiltration procedure for the removal of acetone, xylene, and ammonia from contaminated air and the application of indigenous microorganisms and the inoculum of various microorganisms on a biochar-based medium are further presented and discussed.

Two identically constructed biofilters, one with the other without inoculum, were tested. The biofilter consisted of 86 perforated tubes filled with a biochar and fiber mix (10:1). The total height of the substrate in the tubes was 30 cm, and the volume was 4600 cm^3 (4.6 l). Four tubes in different places of the biofilter were desinged to sample the substrate for analysis and for making aerodynamic measurements. Samples were taken from each of these tubes to monitor parameters at three different heights (2/3*h*, 1/2*h*, 1/3*h*, where *h* is the tube height). The ends of the tubes were submerged in a medium: K_2HPO_4: 1.0, KCl: 0.5, $MgSO_4{\cdot}7H_2O$: 0.5, $FeSO_4{\cdot}7H_2O$: 0.1, $NaNO_3$: 0.90 (g/l H_2O). The moisture content, temperature, and pH in the biofilter tubes, as well as the concentration of the inlet and outlet pollutants, were monitored constantly.

The whole biofiltration experiment lasted 55 days (15 days each with acetone, xylene, and ammonia plus 10 days for biofilter medium activation). The medium of the biofilter was activated after 10 days with each pollutant starting at 25 mg/m^3 and increased. For each pollutant-absorption test, the target influent concentrations every 3 days were 300 mg/m^3, 500 mg/m^3, and then 700 mg/m^3 for 4 days. The rate of volatile inlet was 0.47–0.61 m/s. The temperature in the biofilter varied between 19.3 and 21.2 °C.

The inoculum consisted of four strains of fungi (*Aspergillus versicolor* BF-4, *Cladosporium herbarum* 7KA, *Gliocladium virens* BF-81, and *Stachybotrys* spp. BF-90), three strains of yeast (*Aureobasidium pullulans* BTLAP1.2, *Exophiala* spp. BTLBF1, and *Sporobolomyces roseus* BTLBF23), and three strains of bacteria (*Bacillus subtilis* BTLBS1, *Burkholderia convexa* BTLBC4, and *Rhodococcus* spp. BTLRS 1.5). The inoculum was obtained from strains isolated from environments rich in volatile compounds such as acetone, xylene, and ammonia. The pure microorganism cultures were incubated at 26 °C for 5 days before preparation of the suspension. One liter of the suspension was sprayed over the biofilter tubes using a pump. Samples from biofilters with and without inoculum were collected every 5 days during the biofiltration process. The specimens were taken and placed in sterile glass dishes. A total of 22 samples of biofilters with and without inoculum medium were taken for microbiological analysis.

The procedure for isolating the microorganisms from the biofilters with and without inoculum was identical. Five grams wet weight of biofilter packing material was put in 95 mL of sterilized saline and shaken at 200 rpm for 10 min. Following serial dilution, 1.0 mL aliquots were prepared and poured onto plates to count the bacteria, fungi, and yeasts in the inoculum. Agar plates for counting bacteria – nutrient agar (Oxoid, UK) for fungi, malt extract agar amended with chloramphenicol (100 mg/mL) to inhibit bacterial growth for yeasts, Rose Bengal Agar (Liofilchem, Italy) with chloramphenicol (100 mg/mL) – were used. The pour plates were incubated at 26 °C for 5 days before counting the colony forming units (CFUs). The biochar-based medium from the biofilter tubes was dried at 105 °C and weighed to estimate the dry weight. Microbial concentration results are reported as CFUs per unit mass dry packing material. The dominant species of fungi were purified and identified by routine methods (Domsch et al. 2007). Yeasts were identified following Kurtzman et al. (2011) handbooks and employing api® 20 C AUX (Biomérieux, Marcy l'Etoile, France) diagnostic systems; bacterial genera were identified according to Garrity's (2005) manual. All microorganism groups were regularly isolated from the biofilter. The startup of the biofiltration process was intended as an acclimatization period for indigenous microorganisms.

Indigenous Microorganims in Biochar-Based Biofilter Medium

It was noticed that at the beginning of the acclimatization period the packing material was dry enough, and this condition was less favorable for fungi. However, after 10 days, the moisture of the packing material increased, and there was a higher number of microorganisms. At the end of the acclimatization period, the percentage of bacteria was higher in comparison with other groups of microorganisms (Fig. 7.13).

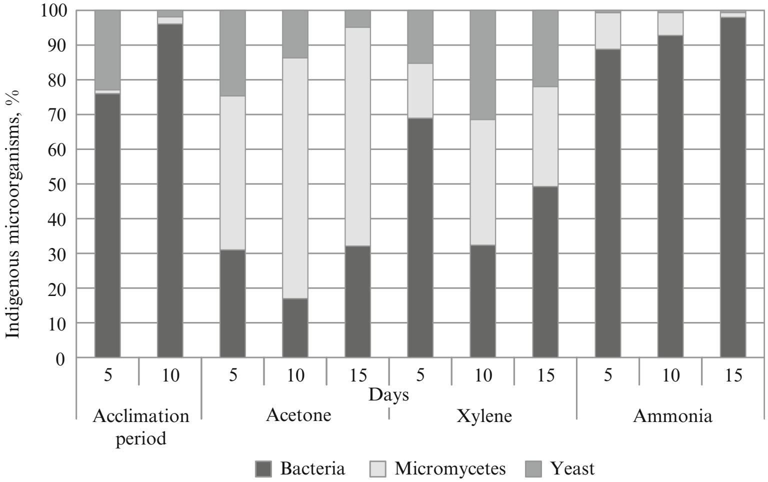


Fig. 7.13 Percentage of indigenous microorganisms in biofilters during removal of different pollutants

At the end of the removal of acetone in low concentration, the number of bacteria was 3.6×10^6 CFU/g DW, the number of yeasts was 4.3×10^4 CFU/g DW, and the number of fungi was 2.3×10^4 CFU/g DW. The difference in the density of microorganisms could be explained by the different growth rates of bacteria and fungi. After the acclimatization period the most resistant microbial consortium formed naturally and a microbial hierarchy was established in the colony. At this period the dominant microorganism species were *Aspergillus niger*, *Penicillium* spp., *Rhodotorula mucilaginosa*, *Bacillus subtilis*, *Pseudomonas putida*, and *Staphylococcus aureus*.

During the removal of acetone at a 300–700 mg/m^3 concentration, the number of bacteria significantly decreased, while the number of fungi increased. Fungi such as *Aspergillus fumigatus*, *Paecilomyces variotii*, and *Penicillium* spp. were shown to be the dominant species during the filtration of acetone. The amount of yeast was higher (4.2 times) in comparison with the number of yeasts at the end of the acclimatization period.

At the beginning of the removal of xylene the number of fungi decreased, while yeasts and bacteria increased. *Rhodotorula mucilaginosa* was the dominant yeast species during removal of acetone and xylene. The bacteria *Bacillus subtilis*, *Staphylococcus aureus*, and *Rhodococcus* spp. species were found at different inlet concentrations of xylene. The fungi of *Cladosporium* spp., *Geotrichum* spp., *Penicillium* spp. genera were isolated during removal of xylene in 300–700 mg/m^3 concentrations. Prachuabmorn and Panich (2010) showed that *Aspergillus flavus*, *A. terreus*, *A. niger*, and *Penicillium glabrum* were able to degrade xylene.

During the removal of ammonia the number of bacteria was at its highest (1.2×10^9 CFU/g DW) in comparison with other investigated pollutants. Ammonia has a negative effect on the number of yeasts: the lowest number was recorded (1.4×10^4 CFU/g DW) during the whole period of the experiment. Bacteria and fungi were the dominant microorganism groups present in the biofilter during removal of ammonia.

Microorganims Introduced in the Biochar-Based Biofilter Medium

Removal of different pollutants (acetone, xylene, and ammonia) using the biofilter with inoculum was carried out over a period of 55 days under various operating conditions. At the beginning of the acetone biofiltration, the number of fungi was 1.8×10^7 CFU/g DW, the number of yeasts was 3.1×10^6 CFU/g DW, and the number of bacteria was 4.2×10^8 CFU/g DW, and these numbers were higher than in biofilters with indigenous microorganisms after the acclimatization period. During the removal of acetone, the percentage of bacteria was higher in comparison with other groups of microorganisms (Fig. 7.14).

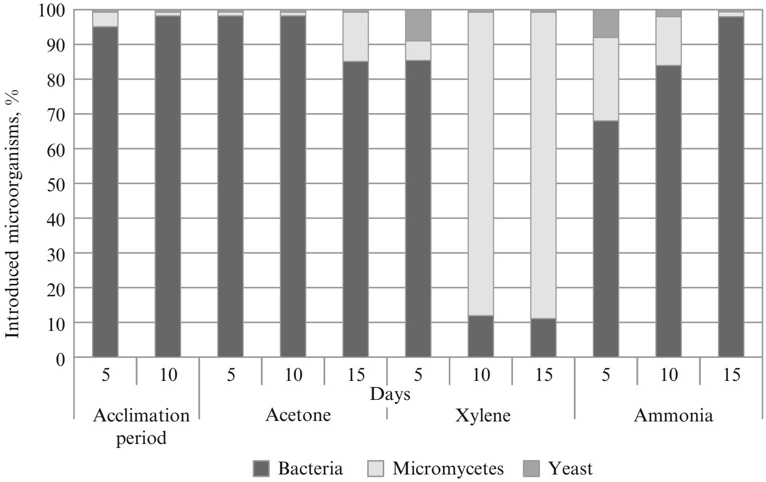


Fig. 7.14 Percentage of introduced microorganisms in biofilters during removal of different pollutants

Pseudomonas putida has been widely used for the biodegradation of acetone and toluene in various biofilters (Asadi et al. 2009). Other authors (Pielech-Przybylska et al. 2006) have observed that biofilters packed with different materials and mixed with *Burkholderia cepacia* and *Acinetobacter baumannii* were able to remove acetone from the air.

At the beginning of the biofiltration of xylene, the counts of fungi increased and dominated. Apart from the *Aspergillus versicolor* and *Cladosporium herbarum* strains used as inoculum, other fungi found were *Penicillium* spp. during the biofiltration of xylene. Fungi generally grow more slowly, and their large size gives them a smaller surface-to-volume ratio for substrate uptake. However, they can degrade a greater variety of contaminants and withstand harsher conditions (Prachuabmorn and Panich 2010).

During the removal of ammonia the percentage of bacteria increased. Besides the presence of the introduced bacteria strains, other dominant bacteria found were *Bacillus cereus* and *Pseudomonas aeruginosa*. After 5 days of ammonia removal the number of yeasts was 10^5 CFU/g DW and was higher throughout the experiment. During the removal of ammonia the number of fungi decreased (from 10^6 to 10^5 CFU/g DW).

The use of *Aspergillus versicolor*, *Cladosporium herbarum*, *Gliocladium virens*, *Stachybotrys* spp., *Exophiala* spp., and *Bacillus subtilis* in our case was found to be a very good choice because they all dwelt in the biofilter with the biochar and fiber mix.

These results demonstrate that the biochar and fiber mix (10:1) was an effective biofilter medium for the growth of the indigenous and introduced microorganisms. The experiment showed that ammonia was the most resistant to microbial degradation, while acetone and xylene presented differences, with a preference for acetone. Inoculation of the biofilter with special microorganism strains was more beneficial to biofiltration efficiency than indigenous microorganisms. Bacteria and fungi were the dominant microorganism groups present in the biofilter during biofiltration of all the investigated pollutants.

Microorganisms Introduced into Biochar-Based Medium at Different Temperatures

While filtering acetone under all examined temperatures – 24, 28, and 32 °C – the number of microscopic fungi remained almost unchanged and reached 10^8 CFU/1 g dry weight; the highest number was established in the last week of investigation: 1.8×10^9 CFU/1 g DW. During an adaptation period, it was lower, 10^6 CFU/1 g DW. In the meantime, the number of yeast gradually increased under a rise in temperature from 24 to 32 °C. The lowest amount of yeast was identified within the first, and the highest during the last week of research (1.1×10^7 and 4.1×10^9 CFU/1 g DW, respectively). In the course of the adaptation period, the secreted yeast was 2.6×10^8 CFU/1 g DW. The number of bacteria was highly dependent on temperature. An interesting point is that the highest number of bacteria was recorded under an injection of acetone at a temperature of 24 °C (2.4×10^{10} CFU/g DW); an increase in a temperature of up to 28 °C resulted in a reduction in bacteria of up to 10^9 and 10^8 CFU/1 g DW, while at an increase in a temperature of up to 32 °C, the number of bacteria started gradually growing and reached 1.3×10^{10} CFU/1 g DW. Thus, it is supposed that the growth of bacteria was not significantly affected by acetone.

Acetone filtering and changes in temperature from 24 to 32 °C revealed differences in the composition of the species of microorganisms. In the adaptation period and at a later stage, *Penicillium* was mainly predominating for acetone filtering. At temperatures of 24 and 28 °C, *Paecilomyces variotii* were still identified. *Geotrichum* spp. occurs when the temperature reaches 32 °C and subsequently starts to predominate. These are potential pathogenic micromycetes. Throughout adaptation to acetone, the introduced *Cladosporium herbarum* 7KA perfectly were preserved and developed prodigiously. Nevertheless, the other introduced fungus, *Aspergillus versicolor* BF-4, was identified in the course of filtering acetone and ammonia and did not disappear. As for yeast, the introduced *Exophiala jeanselmei* predominated and substantially identified at all investigated temperatures. Also, micromycetes were identified because the filter itself was covered with macroscopic fungi. Acetone filtering under different temperatures resulted in a generic and varietal composition of bacteria. In the course of the adaptation period and releasing acetone at a temperature of 28 °C, in the majority of cases, *Bacillus subtilis*, *Staphylococcus aureus*, *Pseudomonas putida*, and *P. fluorescens* were identified. At 24 °C, *Bacillus subtilis* and *Staphylococcus aureus* predominated. At 28 °C, a varietal composition of the identified bacteria coincided with the species of the bacteria of the adaptation period; also, *Bacillus cereus* was identified. At 32 °C, the number of bacteria grown for whose functioning a higher temperature is required – *Pseudomonas aeruginosa* and *Enterobacter* spp. – was at its highest. With the injection of acetone at 32 °C, *Pseudomonas fluorescens* remained.

With the injection of xylene at all investigated temperatures, 24, 28, and 32 °C, the number of micromycetes reached 10^8–10^9 (CFU)/1 g DW. The largest number of micromycetes, compared to yeast and fungi, was identified at 24 °C. Thus, it can be concluded that this temperature is the most favorable for the growth of micromycetes, whereas xylene has little impact on them. Meanwhile, at 28 and 32 °C, the number of the investigated yeast was at its highest during the entire experiment: it varied from 1.4×10^{10} to 2.9×10^{10} CFU/1 g DW (32 and 28 °C, respectively). The number of bacteria under the investigated temperatures did not exceed 10^9 CFU/1 g DW.

Variations in temperature from 24 to 32 °C resulted in minor changes in the varietal composition of microorganisms. As for micromycetes, *Penicillium* and the introduced *Cladosporium herbarum* predominated. Even at 32 °C, the varietal composition of the species of fungi remained the same. The introduced *Exophiala jeanselmei*, which significantly identified at all investigated temperatures, predominated among the yeast. A considerable amount of micromycetes was also identified because the filter itself was covered with these macroscopic fungi. At all investigated temperatures, *Bacillus subtilis* and *Staphylococcus aureus* predominated. At 28 °C, apart from the aforementioned bacteria, *Pseudomonas fluorescens* was identified. At 32 °C, the variety of bacteria was the greatest: *Bacillus subtilis*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *P. putida*, as well as a small number of *Rhodococcus* spp. and *Enterobacter* spp., were identified.

With an injection of ammonia at 24 and 28 °C, the number of bacteria gradually decreased from 10^9 to 10^{10} CFU/1 g DW; at 32 °C, the number of these microorganisms decreased again down to 10^9 CFU/1 g DW. Meanwhile, the highest number of micromycetes and yeast was established at 24 (5.8×10^9 I and 2.9×10^9 CFU/1 g DW, respectively). A further increase in temperature ended in a reduced number of the aforementioned microorganisms. Thus, it can be concluded that a higher temperature and ammonia inhibit the growth and development of fungi, yeast, and bacteria. Throughout the adaptation period, the number of micromycetes, yeast, and bacteria did not exceed 10^9 CFU/1 g DW. The process of filtering acetone at different temperatures revealed a different generic and varietal composition of bacteria. Acetone filtering within the adaptation period and at 24 and 28 °C demonstrated an increase in the number of *Paecilomyces variotii* and a decrease in the introduced fungi. However, a rise in the temperature up to 32 °C, besides the predominating *Penicillium*, points to the secretion of the introduced *Cladosporium herbarum*. Moreover, as usual, *Geotrichum* spp. abundantly developed at this temperature. Almost no *Exophiala jeanselmei* were observed in the course of ammonia adaptation. For ammonia filtering, a temperature of 24 °C was found to be the most suitable for the growth of *Exophiala jeanselmei*. Within the adaptation period at a temperature of 28 °C, with an injection of ammonia, *Bacillus subtilis*, *Staphylococcus aureusi,* and *Pseudomonas fluorescens* predominated. At 24 °C, the variety of species of bacteria significantly increased. Species of *Bacillus subtilis*, *B. cereus*, *Staphylococcus aureus*, *Pseudomonas fluorescens*, and *P. putida*, as well as the genus of *Micrococcus* spp., *Rhodococcus* spp., and *Methylobacterium* spp., were identified. Ammonia filtering at 28 °C demonstrated that the varietal composition of the identified bacteria coincided with the species of bacteria identified at 24 °C; however, no bacteria of *Rhodococcus* spp. grew.

Thus, the findings of the present research have revealed that bacteria, yeast, and micromycetes are able to function in tubular biofilters filled with packing material of carbon changing temperatures from 24 to 32 °C and injecting contaminants – acetone, xylene, and ammonia. For the growth and development of microscopic fungi, in the course of filtering volatile materials, including acetone, xylene, and ammonia, a temperature of 24–28 °C was found to be optimal, whereas that for yeast and bacteria was in the range 28–32 °C. The introduced microorganisms, such as yeast *Exophiala jeanselmei*, bacterium *Bacillus subtilis*, and fungus *Cladosporium herbarum*, as well as *Aspergillus versicolor*, were identified throughout the entire experiment at 24–32 °C while filtering the investigated volatile materials – acetone, xylene, and ammonia – found in the air.

Indigenous Microorganisms in Biofilter Medium Formed in Mixture of Wood Fiber and Inorganic Material

Research was conducted to estimate the number of and dominant indigenous microorganisms in plate-type biofilters with innovative packing material. This offers an original structure that enables the reduction of aerodynamic resistance and of energy costs. The main component of the biofilter is a cassette loaded with a packing material consisting of porous plates (900 × 200 × 10 mm). The counts of fungi, bacteria, and yeast are provided in Figs. 7.15, 7.16, and 7.17.

The indigenous microorganisms arrived on the packing material from the surrounding environment. To increase the number of microorganisms, the adaptation period was applied for 16 days with acetone (concentration increased from 15 to 199 mg/m^3 in this case). The whole biofiltration experiment lasted 46 days (16 days for adaptation and 10 days each for the removal of acetone, xylene, and ammonia). The moisture, temperature, pH in the biofilter, and concentration of inlet and outlet pollutants were monitored constantly. The rate of volatile inlet was 0.10–0.13 m/s.

The packing material samples were collected every 2–5 days during the biofiltration process. The specimens were cut from the bottom, middle, and top of the porous plates and placed in sterile glass vessels (in three replications). A total of 54 samples of the biofilter material were taken for microbiological analysis.

The serial dilution technique was used to count the cultivable microorganisms. One gram wet weight of biofilter packing material was added to 99 mL of sterilized

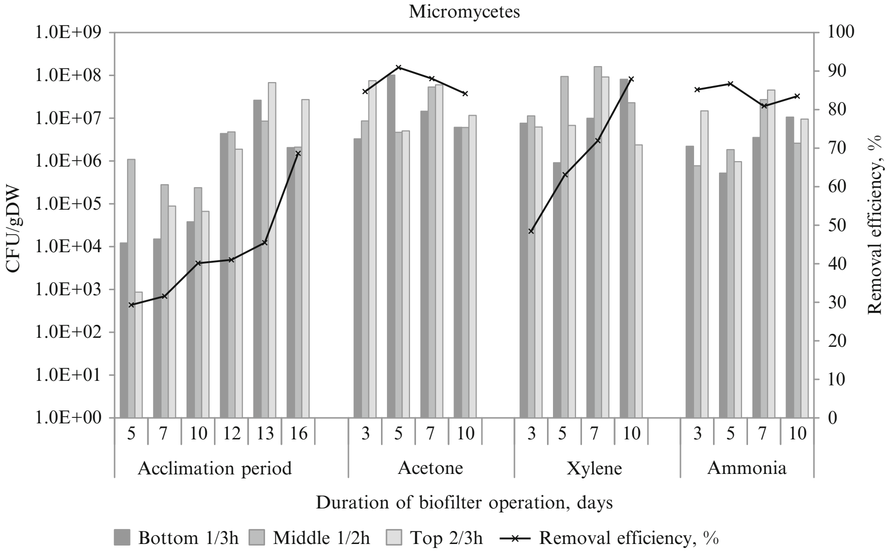


Fig. 7.15 Number of micromycetes on various parts of biofilter plates during removal of separate volatile pollutants and the effectiveness of their elimination

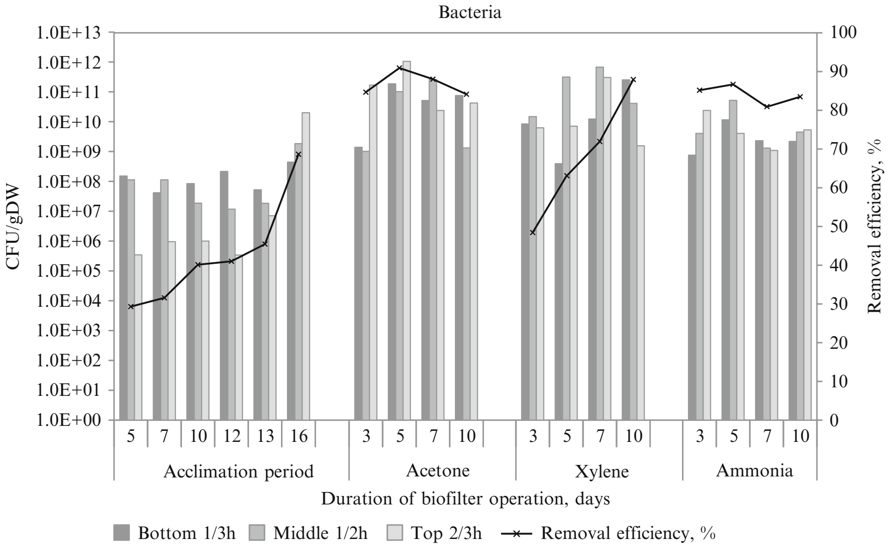


Fig. 7.16 Number of bacteria on various parts of biofilter plates during removal of separate volatile pollutants and the effectiveness of their elimination

saline and shaken at 200 rpm for 10 min, and then a dilution series was prepared. One milliliter of suitable suspension was plated in Petri dishes in three replicates and then filled with a certain medium: nutrient agar (Oxoid, UK) was used for

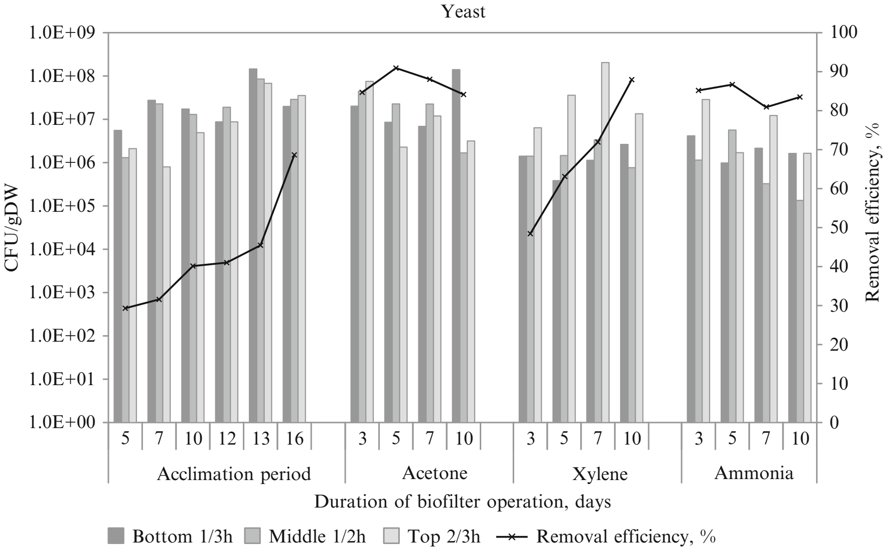


Fig. 7.17 Number of yeast on various parts of biofilter plates during removal of separate volatile pollutants and the effectiveness of their elimination

bacteria, Sabouraud CAF agar (Liofilchem, Italy) for yeasts, and malt agar with chloramphenicol (250 mg/L for bacteria growth inhibition) for fungi isolation. The cultures were incubated at 26–30 °C temperature for 2–7 days. After incubation, the microbial colonies were counted and CFUs per gram DW (CFU/g DW) of biofilter were calculated. The dominant species of fungi were purified and identified using routine methods (Domsch et al. 2007). Yeasts were identified following Kurtzman et al.'s(2011) handbooks and employing api® 20 C AUX (Biomérieux, France) diagnostic systems; bacterial genera were identified according to the Garrity (2005) manual.

The adaptation period and origin of packing materials are important for the formation of microbial communities in biofilters. According to the data of Pielech-Przybylska et al. (2006), at the end of the adaptive phase, the number of bacteria was 10^8–10^{10} CFU/g DW and the number of fungi 10^2–10^3 CFU/g DW (on coconut fiber and Plexiglass chip biofilters, respectively). In our case, the packing material consisted of birch fiber covered with needle-punched nonwoven fabric, which was more suitable for the development of fungi.

At the beginning of acetone removal, the number of fungi and yeasts was higher in the middle of the porous plates (owing to higher moisture content); however, from day 16, their number increased in the different parts of the biofilter: fungi on the top, yeasts in the middle and bottom (Figs. 7.15, 7.16, and 7.17).

The maximum yeast number (1.5×10^8 CFU/g DW) was estimated on day 27 of the experiment at the bottom of the biofilter plates. When the inlet of acetone exceeded 322 mg/m^3 (after 5 days), the number of bacteria gradually increased to the maximum rates: 1.1×10^{12} CFU/g DW. The most significant growth in bacterial numbers was determined in the middle and the top of the biofilter plates.

During removal of xylene, the prevailing trend was that the highest number of fungi was isolated from the middle and the lowest from the waterlogged bottom of the biofilter plates. Xylene was the most available solvent for fungal biodegradation – the maximum number of fungi (1.6×10^8 CFU/g DW) was recorded on day 7 of this pollutant's removal. Similar results were obtained in other studies: the number of fungi on a biofilter with xylene vapors was 9.0×10^7–8.2×10^8 and 8.5×10^6–8.0×10^7 CFU/g DW after 30 and 60 days of acclimatization, respectively. Other authors stated that the increase in microorganism cells in biofilters was 1.12×10^8/g of dry peat (Yoon and Park 2002).

The yeasts successfully developed on the top of the biofilter plates during the whole period of xylene removal. The maximum yeast number (2.0×10^8 CFU/g DW) was recorded on day 7 of this pollutant's removal. Some decrease in bacterial numbers was established after the first 5 days of xylene removal. At this time, the minimum amount (4.9×10^7 CFU/g DW) was recorded on the top of the plate during the experiment. Later, the bacteria consortium adapted to this pollutant and the number of bacteria reached previous values.

The inlet of ammonia significantly increased the moisture of the packing material. High moisture and pollutant origin have a negative influence on the number of fungi; the lowest amount (5.4×10^5 CFU/g DW) was estimated on day 5 of ammonia removal. The maximum yeast number (2.9×10^7 CFU/g DW) was recorded on day 3 at the beginning of ammonia filtration on the top of the plates. The yeast number during removal of ammonia decreased constantly, and at the end of the experiment, their lowest amount was recorded (1.4×10^5 CFU/g DW) in the middle of the plates.

The ammonia vapor did not have a significant effect on the number of bacteria: it fluctuated from 8.1×10^7 to 5.4×10^{10} CFU/g DW. It is interesting to note that the bottom and middle were more often suitable for bacteria growth in comparison with the top of the biofilter plates. The number of bacteria isolated in our experiment from the plate-type biofilter was similar to or lower than that reported by other authors. Commonly, their number reaches 10^8–10^{10} CFU/g of packing material (Krailas et al. 2000).

Application of nonparametric statistics (Spearman's rank correlation coefficient) revealed significant correlations among the numbers of all studied microorganism groups during removal of acetone (Table 7.7). Their numbers depended on the inlet concentration of this pollutant as well as pH. Maestre et al. (2007) showed that fungi progressively colonized biofilters and became the predominant degrading microorganisms when low pH values were reached in the biofilters. Meanwhile, the influence of pH on microorganisms during the removal of xylene and ammonia was not estimated. The inlet concentration of xylene was in strong correlation with bacteria number.

Some experimental data show strong dependence between the filter bed temperature and microbial activity (Jorio et al. 2009). During our experiment, the temperature fluctuated between 16.2 and 22.4 °C during the adaptation phase and was nearly 27 °C during the removal of different pollutants. Possibly, therefore, the

Table 7.7 Spearman's rank correlation coefficient (Spearman's ρ)

	Fungi	Yeasts	Bacteria
Acetone			
Yeasts	0.331**		
Bacteria	0.626**	0.152	
Inlet concentration	0.761**	0.234*	0.785**
Temperature	0.269*	−0.246*	0.688**
pH	0.601*	0.341**	0.745**
Biofilter moisture	−0.226*	0.175	0.124
Xylene			
Yeasts	0.313		
Bacteria	0.288	0.071	
Inlet concentration	0.359*	0.167	0.859**
Temperature	−0.359*	−0.167	−0.859**
pH	−0.230	−0.115	0.256
Biofilter moisture	−0.370*	−0.606**	−0.133
Ammonia			
Yeasts	0.131		
Bacteria	−0.402*	0.111	
Inlet concentration	0.409*	−0.505**	−0.139
Temperature	−0.431**	0.193	0.344*
pH	0.136	0.261	−0.297
Biofilter moisture	−0.785**	−0.169	0.150

*Correlation is significant at the 0.05 level**Correlation is significant at the 0.01 level

influence of temperature in the biofilter on the number of microorganisms was ambiguous and depended on pollutant origin. It produced a negative effect on the number of yeasts during acetone removal, on fungi and bacteria during xylene, and on fungi during ammonia removal.

A statistically significant negative correlation was estimated between numbers of fungi and bacteria during ammonia removal. The inlet concentration of this pollutant negatively influenced the number of yeasts. Nevertheless, as mentioned earlier, biodegradation of this pollutant was efficient.

Significant negative correlations among the number of fungi and the moisture of biofilter plates during removal of all tested pollutants were estimated, while this effect on yeast number was registered only during xylene removal. The water content in the biofilter is one of the most important parameters for efficient biodegradation and odor removal activity (Gutiérrez et al. 2014).

Some difficulties have been reported in defining the correlation between biodegradation activities and microbial community structure (Khammar et al. 2005). After just 5 days of activation with acetone, microorganisms of all tested groups were isolated from the packing material: fungi *Aspergillus flavus*, *Aspergillus niger*, species of *Penicillium*, *Aureobasidium*, and *Geotrichum* genera, yeasts *Rhodotorula mucilaginosa*, *Sporobolomyces* spp., and *Candida guilliermondii*, and bacteria from the genera *Bacillus*, *Pseudomonas*, *Staphyloccoccus*, and

Micrococcus. From day 7 to day 16 of activation, *Fusarium* spp. were isolated rather often, especially from the bottom part of the plates, but later these fungi were not found in the biofilter. Some Fusarium isolates are able to grow very well and to sporulate under acetone vapor (Dandge 2012).

The results obtained show that fungi, yeasts, and bacteria are able to adapt to a packing material consisting of birch fiber and needle-punched nonwoven fabric in a newly developed plate-type biofilter and take part in the degradation of acetone, xylene, and ammonia during their sequenced removal. Acetone was available for all tested groups of microorganisms, xylene for fungi and bacteria, while the inlet concentration of ammonia showed weak correlation with the number of fungi and negative with yeasts. The most favorable conditions for fungi and yeast growth were on the top and middle of the porous plates, whereas for bacteria they were on the bottom and middle. Indigenous microorganisms *P. variotii*, *R. mucilaginosa*, *Exophiala* spp., and *B. subtilis* dominated in the plate-type biofilter during the whole experiment independently of the inlet pollutant. Nevertheless, some differences in the complexes of microorganisms formed were observed in different parts of the porous plates and the origin of the pollutant. The original packing material was suitable for the development of *Myrothecium* spp., *Sporobolomyces* spp., and some other species not referred to in previous researches. The microorganism communities formed in the biofilter remained stable under rather prolonged biofiltration conditions and effectively metabolized organic and nonorganic volatiles. The results obtained provide useful information for optimizing the biological processes in biofilters and for their application in industry for the removal of certain types of volatile compounds from the environment.

Finally, changes in microbial number and community structure are useful for understanding the biodegradation process of various volatile compounds in a plate-type biofilter ecosystem. A wide distribution of various groups of microorganisms in the biofilter allows for a more effective elimination of pollutants from the air.

A high value of correlation coefficient r between variables A_i and $\mathrm{EC_i}$ and the narrow confidence intervals of both the regression line coefficients and regression equations significantly confirm that when the pollution inlet loading rate, A_i, is within the interval $0 \leq A_\mathrm{i} \leq 400$, the relationship between $\mathrm{EC_i}$ and A_i follows the distributions provided in Fig 7.18 and Table 7.8.

Moreover, in the case of introduced medium, the joining of acetone and xylene data sets yielded to the following regression Eq. (7.12):

$$\mathrm{EC} = 0.821A + 0.007. \tag{7.12}$$

The data set n of 47 values was highly sufficient to test the hypothesis of whether true conditional expectations disperse in a straight line. The hypothesis was tested using Eq. (7.13), which follows the Fisher criterion, with $k_1 = g - 2$, $k_2 = n - g$ representing the degrees of freedom:

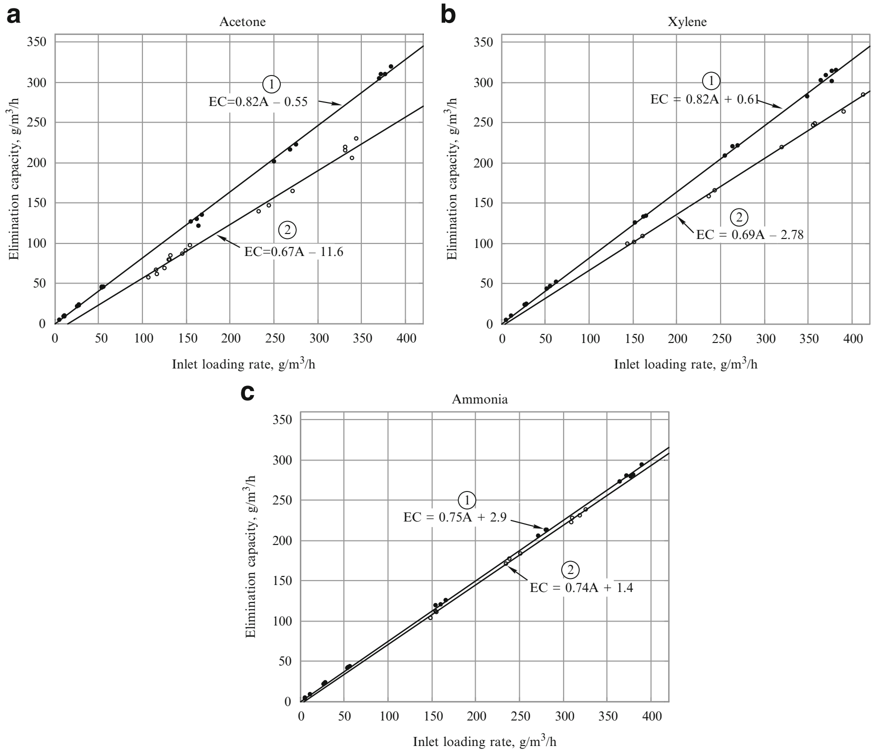


Fig. 7.18 Relationship between pollutant elimination capacity, EC_i, of biofilter with indigenous and introduced microorganism media and pollutant inlet loading rate A_i: (*1*) with introduced microorganisms; (*2*) with indigenous microorganisms

Table 7.8 Statistical dependencies of elimination capacity, EC_i, of gas pollutant on inlet loading rate A_i

Gas pollutant	Biofilter medium	Equation of regression line	Efficiency of biofilter EC/*A* 100 % (%)	Number of tests
Acetone	With inoculum	$EC = 0.820A - 0.55$	82 ± 2	23
	Without inoculum	$EC = 0.675A - 11.6$	68 ± 5	17
Xylene	With inoculum	$EC = 0.820A + 0.61$	82 ± 1	24
	Without inoculum	$EC = 0.695A - 2.78$	70 ± 3	10
Ammonia	With inoculum	$EC = 0.747A + 1.43$	75 ± 1	23
	Without inoculum	$EC = 0.739A - 2.88$	74 ± 3	10

$$F = \frac{n-g}{g-2} \frac{\sum_{j=1}^{g} m_{\mathrm{j}} \left(\overline{y_{x_{\mathrm{j}}}} - \bar{y} - r\frac{s_y}{s_x}\left(x_{\mathrm{j}} - \bar{x}\right) \right)^2}{\sum_{j=1}^{g} \left(m_{\mathrm{j}} - 1\right) s_y^2 \Big|_{x=x_{\mathrm{j}}}}, \tag{7.13}$$

where g is the number of groups of the whole data set, m_{j} is the number of data in a group, x_{j} is the mean of x values from a group j, ${s_y}^2$ is the dispersion of y values. When a data set was grouped into visible groups, the obtained F value was 0.506 (the critical value of a parameter was 2.85 below a confidence level of 0.05). This led to the conclusion that a biofilter efficiency of 82 % can be kept constant under an inlet loading rate up to the 430 g/m^3/h for acetone and xylene.

The statistical estimation of the correlation coefficient between a pollutant inlet loading rate and elimination capacity confirmed the stability of the biofilter operation. The linear dependence between the variables was determined to be statistically significant when a pollutant inlet loading is in range of 0 to 400 g/m^3/h. Moreover, the Fisher criterion enabled us to conclude that the biofilter yielded a stable 82 % removal of volatile organic compounds under their inlet loading rate of 430 g/m^3/h.

Establishing the Penetration Coefficient of the Packing Material

Assuming that the packing material of the tube creates a porous medium through which the polluted air gets through and with reference to Darcy's law, the basic vectorial relation of laminar filtration is obtained:

$$v = -\frac{k}{\mu} \operatorname{grad} p, \tag{7.14}$$

where $v = [u, v, w]$ is a vector of filtration rate, μ is the coefficient of the dynamic viscosity of the supplied air, p is the pressure, and k is the penetration coefficient of the porous medium. Since movement takes place in one direction only, i.e., along the tube, supposedly in the direction of the Ox-axis, Eq. (7.14) becomes scalar:

$$u = -\frac{k}{\mu} \frac{\partial p}{\partial x}. \tag{7.15}$$

Moreover, the rate must satisfy the equation of continuity:

$$\frac{\partial(m\rho)}{\partial t}+\frac{\partial(u\rho)}{\partial x}=0, \tag{7.16}$$

where m is the porosity of the packing material defined as the volume of the pores of the packing material in one unit of its volume. When the matter of the packing material is not deformed, the volume of the pores remains constant, so $m = \text{const}$; consequently, from Eq. (7.15) we obtain that

$$m=\frac{\partial\rho}{\partial t}=\frac{\partial}{\partial x}\left(\frac{k\rho}{\mu}\frac{\partial p}{\partial x}\right). \tag{7.17}$$

Unknown pressure p is usually replaced by the function *q(p)* in the gas filtration theory:

$$q(p)=\int\rho\mathrm{d}p,\quad q(0)=0. \tag{7.18}$$

Then

$$\rho\frac{\partial p}{\partial x}=\frac{\partial q}{\partial x},\quad \frac{\partial\rho}{\partial t}=\frac{\partial\rho}{\partial q}\frac{\partial q}{\partial t} \tag{7.19}$$

and Eq. (7.19) becomes a parabolic equation, and to find a solution to that equation, it is necessary to formulate appropriate boundary and initial conditions:

$$\left(\frac{m\mu}{\rho k}\right)\frac{\partial q}{\partial t}=\frac{\partial^2 q}{\partial x^2}. \tag{7.20}$$

In the case of a polytrophic process

$$p^{1/n}=RT\rho, \tag{7.21}$$

where n is polytrophic index, R a gas constant, and T the temperature. Because filtration takes place under a constant temperature (isothermal process $n = 1$),

$$q=\frac{1}{2RT}p^2,\quad p=RT\rho\,, \tag{7.22}$$

and so q equation is obtained:

$$\left(\frac{m\mu}{k\sqrt{2RT}}\right)\frac{1}{\sqrt{q}}\frac{\partial q}{\partial t}=\frac{\partial^2 q}{\partial x^2}. \tag{7.23}$$

Under a stationary regime (observed in the course of conducting experiments),

$$\frac{\partial q}{\partial t} = 0, \tag{7.24}$$

and function q becomes harmonic:

$$\frac{\partial^2 q}{\partial x^2} = 0, \tag{7.25}$$

i.e., $q(x)$ is a linear function $q(x) = c_1 + c_2 x$, and the constants c_1 and c_2 are established on the basis of the values of the pressure at the initial $x = 0$, $p(0) = p_1$, and final $x = L$, $p(L) = p_2$ points of the tube. With reference to Eq. (7.18) we obtain

$$q(x) = \frac{p^2(x)}{2RT}; \tag{7.26}$$

thus, the constants c_1 and c_2 can be calculated observing that a change in pressure will take place according to the parabolic law

$$p^2(x) = p_1^2 - \frac{p_1^2 - p_2^2}{L} x. \tag{7.27}$$

In addition, with reference to Eqs. (7.15), (7.19), and (7.27), the expressions of the filtration rate

$$\rho u = -\frac{k}{\mu}\frac{\partial q}{\partial x}, \quad \rho u = \frac{k}{2\mu RTL}\left(p_1^2 - p_2^2\right) \tag{7.28}$$

and the laws of variations in rate and density (along the tube) are obtained:

$$u(x) = \frac{k}{2\pi L}\frac{p_1^2 - p_2^2}{\sqrt{p_1^2 - \frac{p_1^2 - p_2^2}{L} x}}, \tag{7.29}$$

$$\rho(x) = \frac{1}{RT}\sqrt{p_1^2 - \frac{p_1^2 - p_2^2}{L} x}. \tag{7.30}$$

Referring to the specific structure that uses a biofilter made of a number of tubes, the penetration coefficient k of the employed packing material will be calculated. The conducted tests revealed that variations in the air pressure at the inlet (the tube is 42 mm in diameter, length $L_1 = 0.2$ m, airflow velocity $v_1 = 20$ m/s, $\mathrm{Re} = 84{,}000$) and outlet (tube is 96 mm in diameter, length $L_2 = 0.2$ m, air rate $v_2 = 3.8$ m/s, $\mathrm{Re} = 36{,}480$) of the biofilter between measurement points are approximately

450 Pa. To estimate the aerodynamic resistance of the packing material in the biofilter, falls in pressure from the gauges to the packing material must be rejected. This is a turbulent motion regime, and therefore the preceding equation is used:

$$\Delta p_{\mathrm{i}} = \lambda_{\mathrm{i}} \frac{L}{d_{\mathrm{i}}} \frac{\rho v_{\mathrm{i}}^2}{2}, \tag{7.31}$$

where the parameter is found from the following equation:

$$\frac{1}{\sqrt{\lambda}} = 21\mathrm{g}\sqrt{\lambda}\mathrm{Re} - 0.8. \tag{7.32}$$

Consequently, $\lambda_1 = 0.019$, $\lambda_2 = 0.022$ and $\Delta p_1 = 23$ Pa, $\Delta p_2 = 0.52$ Pa. Substantial resistance is caused by a bend of the inlet pipe equal to

$$\Delta p_3 = \varsigma \frac{\rho v_1^2}{2} = 52 \ \text{Pa}. \tag{7.33}$$

Therefore, the aerodynamic resistance of the packing material of a single tube is approximately 375 Pa. Next, with reference to Eq. (7.28), when $\rho = 1.29$ kg/m^3, $u = 0.13$ m/s, $\mu = 2 \times 10^5$ N·s/m^2, $R = 287$ J/(kg K$^{\circ}$), $T = 300$ °K, $L = 0.6$ m, $p_1 = 10^5$ Pa, and $p_2 = p_1 - 375$ Pa, the penetration coefficient of the packing material $k = 4.6 \times 10^{-9}$ m^2 is obtained.

7.4 Design and Performance of Systems with Wood Products for Biological Air Treatment

In biofiltration systems, the bioreactor design, reactor vessel, biofiltering medium material, air distribution system, waste gas pretreatment system, and moisture control system are important considerations before designing the biofilter. Original designs of biofilters aim to reduce aerodynamic resistance, minimize energy costs, and use innovative materials for the biofilter medium. Based on several combinations of the aforementioned considerations a few types of bioreactors and their performance are described in what follows.

Cartridge Biofilter

The structure of a cartridge biofilter is given in (Fig. 7.19). Five cartridges coherently installed in a casing and filled in the substances of the packing material constitute the main feature of the structure. To maintain the relative moisture (60–90 °C), nozzles are mounted above the cartridges. To regulate the temperature

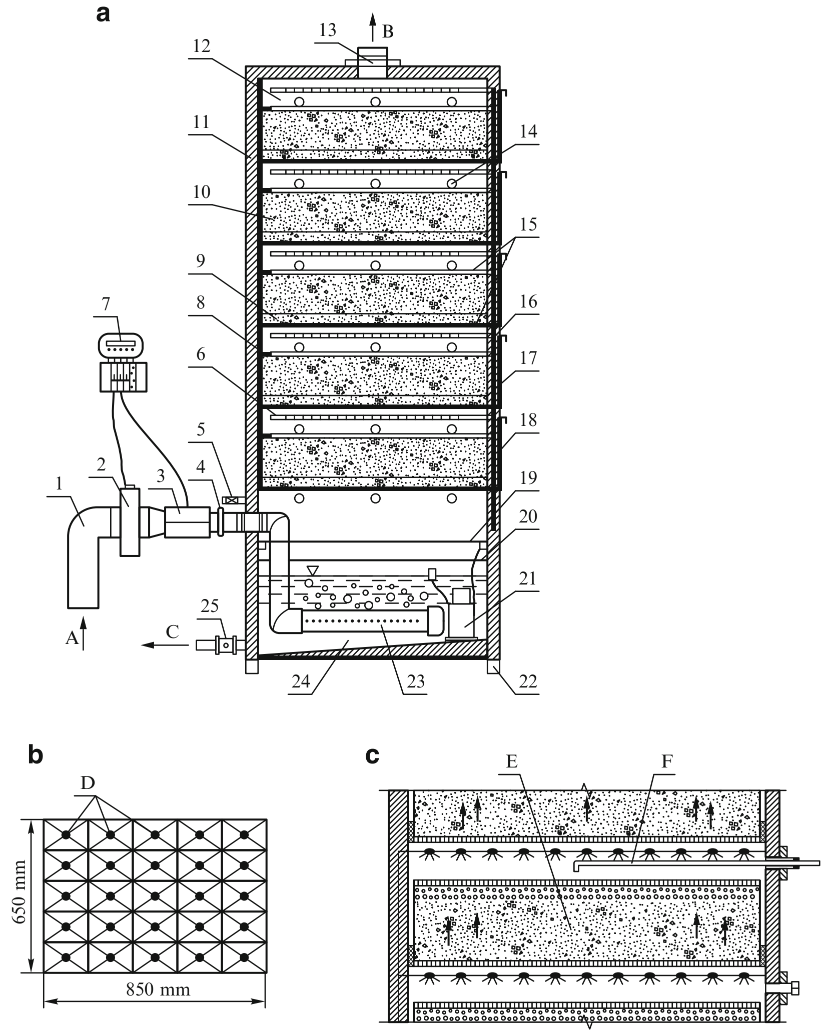
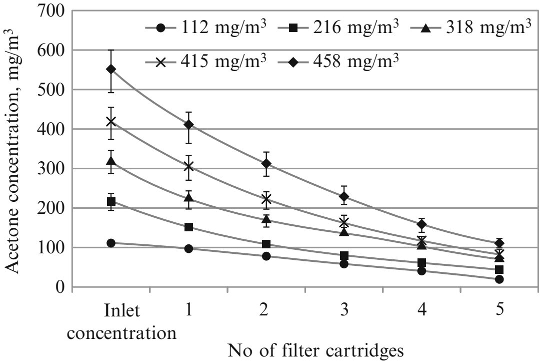


Fig. 7.19 Biofilter design (**a**): (*1*) polluted air supply duct; (*2*) ventilator with turbine; (*3*) channel air heater; (*4*) airflow control valve; (*5*) water supply branch with valve; (*6*) charge humidifying system; (*7*) control panel; (*8*) frame for mesh fastening; (*9*) angle bars; (*10*) biofilter charge; (*11*) biofilter wall; (*12*) charge humidifying tube holders; (*13*) treated air discharge duct; (*14*) branches for air sampling; (*15*) meshes; (*16*) rubber hose; (*17*) biofilter cassettes; (*19*) protective mesh; (*20*) water runoff tray; (*21*) water pump; (*22*) biofilter leg; (*23*) collector; (*24*) aeration chamber; (*25*) slag collection pipe with valve; (**b**) *D*: sampling points for airflow and temperature measurements; (**c**) *E*: biofilter bed, *F*: air sampling points for contaminant removal evaluation (Baltrėnas and Zagorskis 2009a, b, c)

(25–30 °C), heating elements are installed. Cartridge biofilters are designed such that polluted air enters the underneath part of the biofilter and moves at a rate of 0.05–1 m/s through the cartridges filled with the packing material.

Fig. 7.20 Change in concentration of acetone simultaneously using cartridges with different packing materials



A cartridge biofilter was tested by filling the cartridges with different wood products. The first and second cartridges (considering the movement directions of the polluted air) were filled with pine bark, the third and fourth with a mixture of pine bark and wood chips, and the fifth with pine wood chips. It has been established that the greatest decrease in the concentration of acetone was observed in the first two layers of the packing material (cartridge 1) made of activated spruce bark (Fig. 7.20).

It is assumed that, the higher porosity of spruce bark, compared with spruce wood chips, creates more favorable conditions for the development of microorganisms.

Following the first two layers of the packing material, the concentration of acetone in the cartridges reduced from 112.0 to 72.9 mg/m^3, i.e., 35 %. A rise to as much as 548 mg/m^3 in the concentration of acetone supplied to the device shows that, given two layers filled with spruce bark, the concentration decreased to 312 mg/m^3, or 43 %. It is assumed that such an increase in acetone concentration stimulated growth in the microorganisms and made the biofiltration more intensive. Depending on the initial concentration of the supplied acetone, the third and fourth layers of the activated packing material reduced the acetone concentration to 39–50 mg/m^3. The decreased pollutant treatment efficiency might have been impacted by the format of the packing material of the layer. The mixture of spruce bark and wood chips composing the packing material has a lower porosity and specific surface area. Following the fifth layer (cartridge 5) made of wood chips only, the concentration decreased by 25–26 %. An increase in the supplied airflow rate from 0.2 to 1.0 m/s resulted in a decrease in the efficiency of biofilter treatment (the initial acetone concentration reached 318 mg/m^3) (Fig. 7.21).

The contact time for the packing material and pollutant in the biofilter reached 2 s. A rise in the supplied airflow rate of 1.0 m/s shows that the contact time for the microorganisms living in the packing material and acetone was shortened twice, i.e., up to 1 s. To improve the treatment efficiency of the equipment, the airflow rate supplied to the device must be reduced. The highest decrease in acetone concentration was observed in the first four layers of the substrate (Fig. 7.21).

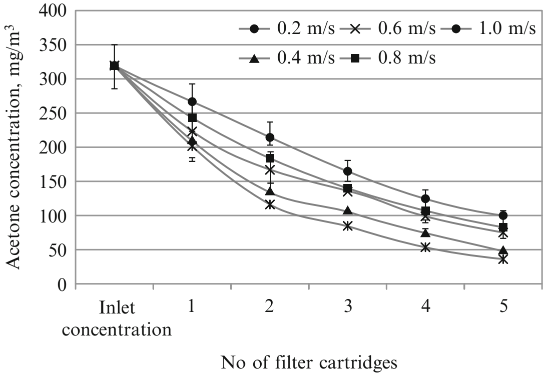


Fig. 7.21 Dependence of decreased concentration on number of layers of packing material under different airflow rates

Biofilter-Adsorber

The structure of the biofilter-adsorber is unique because it is made of a number of vertical tubes having porous or perforated partition walls filled with wood grains 2.0–6.0 mm in diameter. The grains are mixed with heat-treated wood fiber at a ratio of 10–1. The tubes are arranged in rows where the distances between them are around 1.0–2.0 mm. The rows are installed at an angle of 30–45° in the direction of the polluted air movement, and the distance between these rows does not exceed the radius of the tube. The tubes are immersed in activated solution at one-third their own height from the bottom, causing capillary humidification of the biofiltration part.

In a biofilter-adsorber, polluted air is supplied through an inlet of polluted air whose inner diameter is 42 mm. The duct has an installed blower that is used to control the airflow rate and pressure. The air passed through the blower is heated using an air-heating element. The polluted airflow passes through the valve, gets into the aqueous medium of the biofilter, and, through tubes filled with the packing material and during the ongoing process of treating the polluted airflow, moves toward the purified air duct. The heating element of the aqueous medium is required to heat the nutrient solution, causing the aqueous medium to form an appropriate medium for the survival of microorganisms. Water temperature is observed in the screen of the gauge measuring the temperature of the aqueous medium. When affected by the pressure created by the blower, the treated air moves upward toward the purified air duct 96 mm in diameter.

Wood biochar was chosen as the biofilter material. From a practical point of view, the decision was determined by its relatively low cost owing to local availability and the ease of preparation (avoiding the chemical or physical activation of the adsorbent), the possibility of regeneration owing to the prevalence of physical adsorption, a low probability that the adsorbent will cause chemical reactions, the convenience of filling large-volume biofiltration systems with biochar, thermal and chemical stability, the possibility of producing an adsorbent from biodegradable (wood) waste thus implementing requirements for the end-of-waste status following directive 2008/98/EC, promoting innovative environmental protection technologies, and anticipating an opportunity to utilize biochar as an ameliorant of soil with a minimal possibility of pollution (EBC 2012). Because of its hydrophobicity, biochar is suitable for adsorbing nonpolar and weakly polar pollutants that are adsorbed better than water (in particular, with regard to the structure examined in this paper when the packing material is additionally humidified because of the capillary effect). Biochar was mixed with birch fiber at a 10–1 ratio in the biofilter; the fiber was seen as a medium for providing nutrients for microorganisms. Biochar was prepared at 750 °C. This type of biochar has a large BET surface area determined by the developed microporous system, creating conditions for the adsorption of pollutants as well as for the survival of microorganisms, particularly bacteria, which, being resistant to environmental conditions, are extremely actively involved in the biodegradation processes of contaminants. The highest number of bacteria was also established in this type of biochar. In terms of other parameters, pine tree and birch wood were processed at 750 °C and showed only slight differences. Lower processing temperatures resulted in a biochar pH that induced a more acidic medium, which might end in anaerobic processes in the biofiltration system. Moreover, low microporosity is characteristic of processed wood at a lower temperature, which would mean a limited adsorption capacity of pollutants (Fig. 7.22).

Prior to the stage of experimental research on the packing material inside biofilters, introduced microorganisms are inserted. In the first week of research, the biofilter was supplied with concentrated acetone vapor of 300 ± 25 mg/m^3 under air traffic flow of 30 ± 1.5 m^3/h. In the second week, the concentration of xylene vapor was set. In the third week, the concentration of ammonia vapor and the maintained air temperature of 28 ± 1 °C were provided.

In 3 weeks' time, the output of the biofilter increased up to 100 ± 5 m^3/h, and for 6 weeks, experimental research on supplying biofilters with acetone vapor and maintaining temperatures of 24 ± 1, 28 ± 1, and 32 ± 1 °C of removed air was carried out (for 2 weeks, air polluted with acetone vapor was supplied and a temperature of 24 ± 1 °C of the removed air was maintained; for the next 2 weeks, air polluted with acetone vapor was supplied and a temperature of 28 ± 1 °C of the removed air was preserved; for the remaining 2 weeks, air polluted with acetone vapor was supplied and a temperature of 32 ± 1 °C of the removed air was maintained). Following a similar principle, investigation into two other pollutants, i.e., xylene and ammonia, was carried out. The vapor of pollutants entered the device every day of the experiment four times for 1 h each. Thus, a concentration of 300 ± 25 mg/m^3 of a pollutant (acetone, xylene, ammonia) was injected daily, which allowed us to monitor the efficiency of pilot biofilters for treatment. The concentration of the pollutant was measured before and after it passed through the treatment equipment at five points after the packing material.

The concentration of pollutants supplied to the biofilter remained constant and equalled 300 mg/m^3, the air pressure reached on average a level of 470 Pa in the air supply duct and 28 Pa in the air exhaust duct while the tubes maintained a pressure

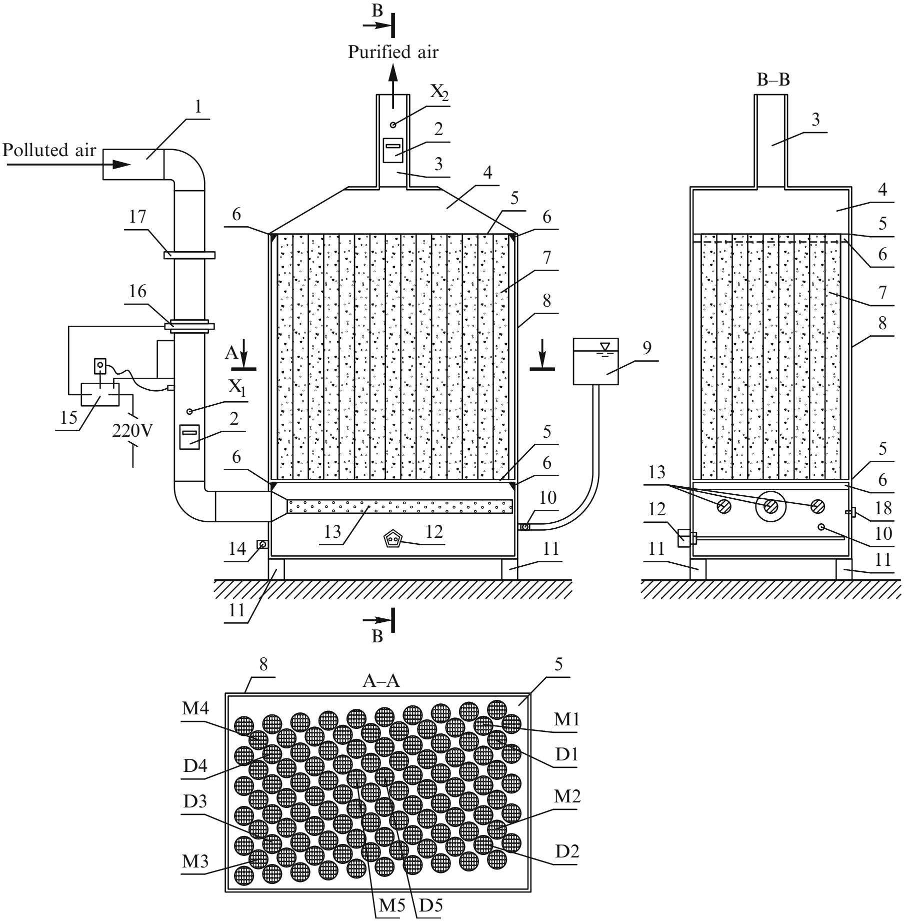


Fig. 7.22 Scheme for biofilter model: *1*: inlet of polluted air, *2*: gauge of airflow rate, temperature and humidity, *3*: outlet of purified air, *4*: biofilter lid, *5*: sealing plate, *6*: fastener of sealing plate, *7*: biofilter tubes filled with packing material, *8*: biofilter casing, *9*: aqueous medium refilling tank, *10*,*17*: valves, *11*: biofilter poles, *12*: heating element of aqueous medium, *13*: air distribution system, *14*: drain valve, *15*: control unit, *16*: blower and air heating element, X_1, X_2, *D1*, *D2*, *D3*, *D4*, *D5*: points for measuring biofilter parameters, *M1*, *M2*, *M3*, *M4*, *M5*: points for sampling the medium

of 8.2 Pa. The tendency toward variations in the efficiency of filtering acetone, xylene, and ammonia vapor through the packing material of biochar and wood fiber is presented in Figs. 7.23, 7.24, and 7.25.

Thus, the use of tubular biofilters and the removal of acetone and xylene vapor, independently of air temperature (i.e., in the course of the research), made it possible to observe an increase in efficiency, attaining a level of 0.25–0.30 % per day. This situation can be explained by a monitored ongoing increase in the population of microorganisms. Therefore, a higher efficiency in the biofilters of a similar structure can be achieved after a longer period of time.

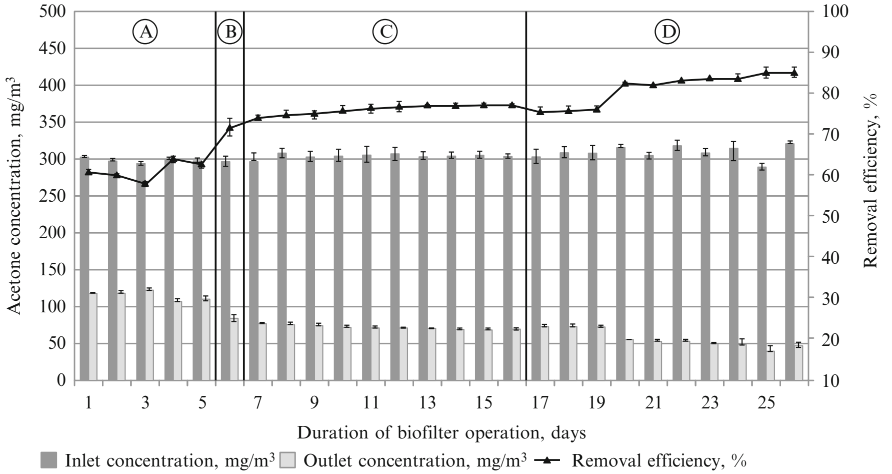


Fig. 7.23 Relationship between air treatment efficiency of biofilter and supplied air polluted with acetone vapor and maintained air temperature: *A*: 24 °C, *B*: 28 °C, *C*: 32 °C

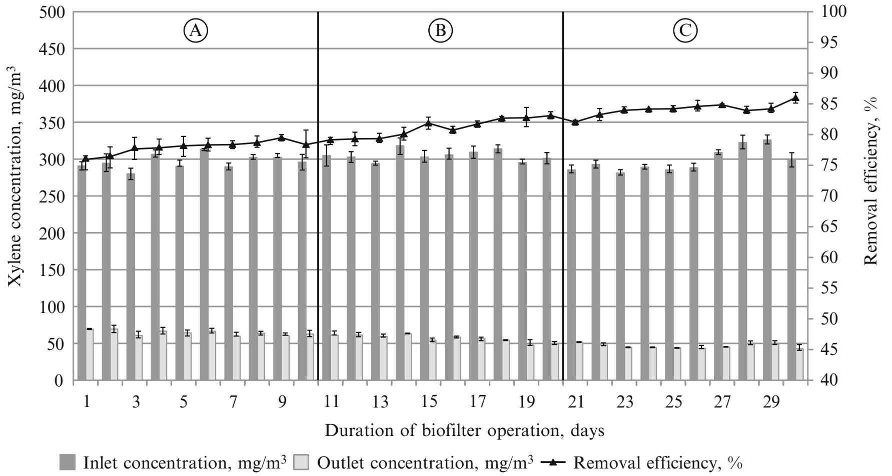


Fig. 7.24 Relationship between air treatment efficiency on biofilter and supplied air polluted with xylene vapor and maintained air temperature: *A*: 24 °C, *B*: 28 °C, *C*: 32 °C

Quite different tendencies toward variations in efficiency at separate temperature-controlled stages have been established examining the results of research on air polluted with the inorganic material of ammonia. Although a general tendency toward an increase in efficiency remains, it is much slower and attains on average a level of only 0.05–0.1 % per day, thus achieving its maximum value at the initial stage, i.e., 10 days; subsequently, the efficiency of the biofilter remains uniform, which is ≈80 %. This could be determined by the previously described steady number of microorganisms in the ammonia medium.

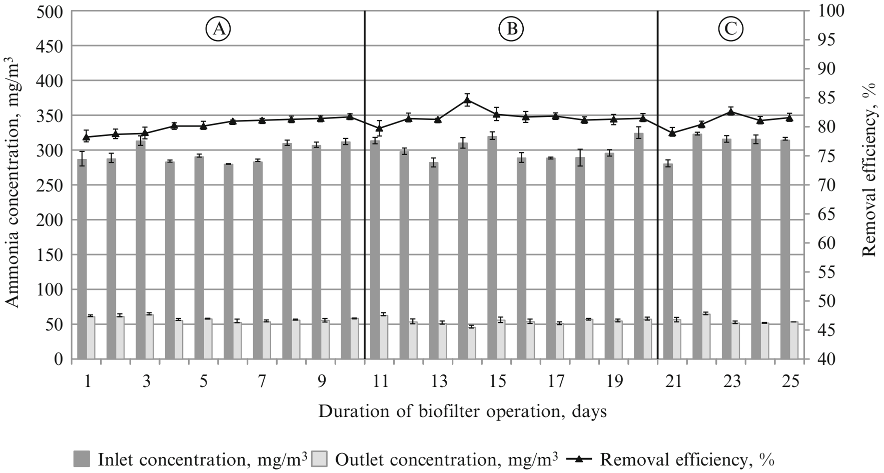


Fig. 7.25 Relationship between air treatment efficiency of biofilter and supplied air polluted with ammonia vapor and maintained air temperature: *A*: 24 °C, *B*: 28 °C, *C*: 32 °C

The examined model of biofilter is suitable for removing volatile organic and nonorganic compounds from polluted air, which can be demonstrated by the fact that the air treatment degree reaches up to 85 %, the aerodynamic resistance of the biofilter, which is 4050 Pa, and the penetration coefficient of the porous medium, 4.6×10^{-9} m^2. The packing materials employed in biofilters are appropriate for the development of microorganisms whose population reaches 10^7–10^9 CFU/g for micromycetes, 10^7–10^{10} CFU/g for yeast, and 10^8–10^{10} CFU/g for bacteria.

Having investigated various types of biochar, to test the biofilter, pine biochar made at a temperature of 750 °C was selected. The introduced biochar had a large BET surface area, which resulted in the development of a microporous system, creating conditions for the adsorption of pollutants and in a substratum for the survival of microorganisms, particularly bacteria, which, being resistant to environmental conditions, are very actively involved in the processes of pollutant degradation.

Plate-Type Biofilter

The structure of this type of biofilter has a distinctive feature – lamellar plates. These plates serve as a biofiltration material and are installed in the casing, thereby increasing the contact surface of the polluted air and the biofiltration material. This makes it possible to additionally increase the efficiency of the biofilter by 5–7 %.

A laboratory plate-type biofilter bench was used for study of acetone, xylene, and ammonia removal. It offers an original structure, which enables reduction of aerodynamic resistance and reduces energy costs. The main component of the

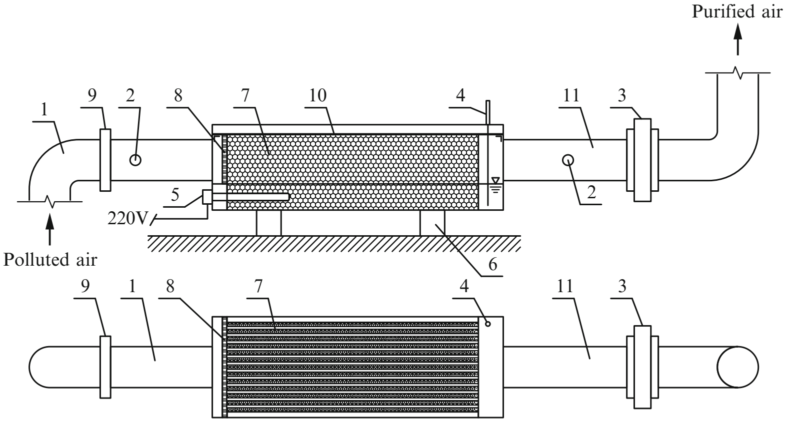


Fig. 7.26 Lamellar structure wavy air biofiltering system with capillary irrigation system boot scheme

biofilter is a cassette loaded with a packing material consisting of porous plates (900 × 200 × 10 mm) (Fig. 7.26). Polluted air is supplied to the biofilter through a 100 mm diameter duct for polluted air (1). An airflow that passes through the biofilter is created by a ventilator (3) fitted in the clean air duct. The valve (9) in the polluted air duct regulates the velocity of airflow and the yield of supplied air. Then the polluted air flows into the biofilter. The latter is fitted with a load made up of porous lamellas. The airflow is evenly distributed by a perforated lamella (8) throughout the entire volume of the load (7) via a perforated lamella. Polluted air flows between the porous lamellas (10), which are immersed in a liquid environment and arranged 4 mm apart from each other. After passing through the biofilter, purified air enters a 100 mm diameter duct for purified air (11) and is emitted into the environment. The biofilter is fitted onto the fastening elements (6). Sampling hollows (2) are installed within both polluted and purified air ducts. It is in these measurement points that airflow velocity, temperature, and concentrations of pollutants that are fed into and expelled from the biofilter are measured. Proper temperature of the air supply is ensured with a thermoregulator and a sensor (4). The temperature of the biomedium is maintained with a biomedium-heating element (5). Porous plates are arranged vertically next to each other (with 4 mm between them) to produce a capillary humidification effect. These plates consist of solid polymer board and thermally processed (to maintain durability) birch fiber fixed on both sides. To increase the plate capillarity, the birch fiber is covered with needle-punched nonwoven fabric. The ends of the plates (50 mm) are submerged in a mineral medium: K_2HPO_4, 1.0; KCl, 0.5; $MgSO_4 \cdot 7H_2O$, 0.5; $FeSO_4 \cdot 7H_2O$, 0.1; and $NaNO_3$, 0.90 (g L^{-1} H_2O).

Studies were carried out by running acetone-, xylene-, and ammonia-polluted air through the biofilter load. The average airflow velocity between the wavy lamellas was 0.08 m/s.

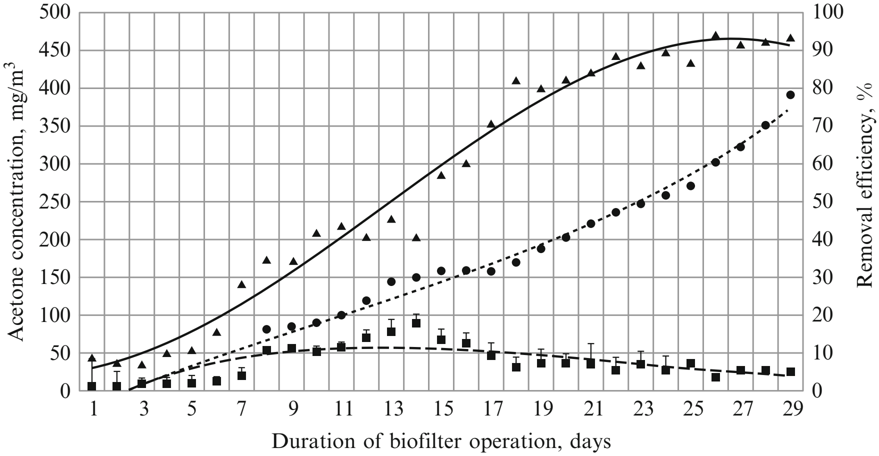


Fig. 7.27 Acetone concentrations before and after treatment (mg/m^3) and removal efficiency when using wavy plate and loading of wood fiber with nonwoven material caulked and without inoculum: (*filled circle*) acetone concentration before treatment, (*filled square*) acetone concentrations after treatment, (*filled triangle*) removal efficiency

The initial acetone concentration was 5.7 mg/m^3, and by the end of the experiment it had reached 390 mg/m^3. As we can see in Fig. 7.27, the efficiency of the biological breakdown process gradually increased throughout the experiment's period. The highest air purification efficiency, 94.2 %, was recorded on the 26th day of the experiment. The self-contained microorganism number reached 1.2×10^4 CFU/cm^2 for micromycetes and 11×10^6 CFU/cm^2 for bacteria at the beginning of the experiment, and 4.3×10^4 CFU/cm^2 for micromycetes and 1.38×10^{10} CFU/cm^2 for bacteria at the end of the experiment. *Penicillium* spp., *Aspergillus niger*, *Aureobasidium* spp., and *Geotrichum* spp. types of micromycetes dominated on the surface of porous lamellas.

Experimental research data, relating to the supply of xylene-contaminated air through a bioload, consisting of birch fiber and nonwoven caulked material, are provided in Fig. 7.28. The initial xylene fume concentration in the air supplied to the biofilter was 145.8 mg/m^3, reaching 712.5 mg/m^3 by the end of the experiment. As we can see in Fig. 7.28., the biofilter's air purification efficiency gradually increased until the fifth day of the experiment, reaching 89.7 %. Further increasing the pollutant concentration in the supplied air, the biofilter's air purification efficiency declined until the end of the experiment. The biofilter's air purification efficiency of 78 % was recorded when the supplied air had the highest pollutant concentration of 712.5 mg/m^3. The change in the microorganism growth was also measured during the experiment. The number of micromycetes changed from 5.6×10^4 to 2.2×10^5 CFU/cm^2, from 6.8×10^6 to 2.45×10^8 CFU/cm^2 in bacteria, and from 2.9×10^4 to 3.9×10^4 CFU/cm^2 in yeast. The types of micromycetes remained similar to those present when the acetone was filtered. Later on, *Paecilomyces variotii* fungi and *Aureobasidium* and *Geotrichum* yeast cultures dominated.

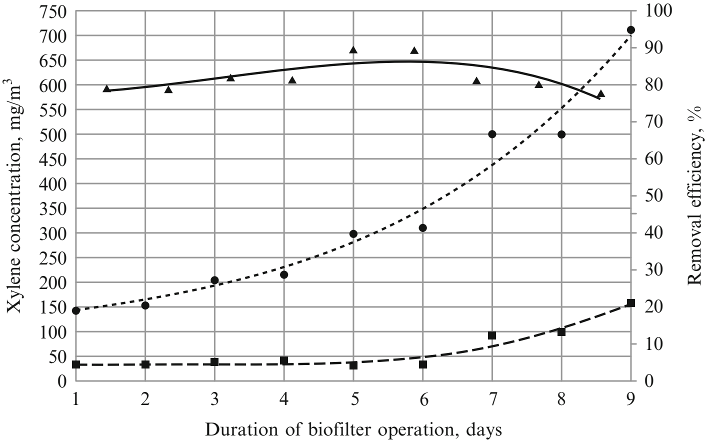


Fig. 7.28 Xylene concentrations before and after treatment (mg/m^3) and removal efficiency when using wavy plate and loading of wood fiber with nonwoven caulked material: (*filled circle*) xylene concentrations before treatment, (*filled square*) xylene concentrations after treatment, (*filled triangle*) removal efficiency

When air polluted with acetone fumes was being purified, the efficiency of the biological breakdown process was higher than when xylene fumes were supplied to the filter. This might have been determined by a lower gas solubility in the water coefficient. The dependence of gas solubility in a biomedium on pressure is determined by Henry's law, which states that the gas solubility in a medium is directly proportional to the gas pressure when the temperature is constant. Increasing the temperature decreases the gas's solubility in the medium; decreasing the temperature increases it (Miller and Allen 2004).

In Fig. 7.29 the ammonia concentration in the air supplied to the device and in the expelled air, as well as the air purification efficiency, depends on time, with the airflow velocity in the bioload being 0.08 m/s. Research was conducted with an airflow rate of 1.1 L/s. An increase in the biofilter's air purification was observed during the first 6 days of the experiment, reaching 88.2 % when the pollutant concentration in the air was 300 mg/m^3. Later on, when the pollutant concentration was increased to 500 mg/m^3, the efficiency dropped by approximately 6 %, and when the pollutant concentration was increased to 700 mg/m^3, the efficiency dropped by approximately 10 %. During the experiment, the change in the number of microorganisms was also measured. A change was recorded from 5.0×10^4 to 1.8×10^5 CFU/cm^2 for micromycetes, 2.4×10^6 to 6.4×10^6 CFU/cm^2 for bacteria, and 3.7×10^4 to 1.3×10^5 CFU/cm^2 for yeast cultures. Micromycete types also changed slightly. *Penicillium* spp. and not yet fully identified *Myrothecium* spp., which create white colonies, joined the previously dominant species. However, *Geotrichum* spp. and *Paecilomyces variotii* fungi remained the dominant species.

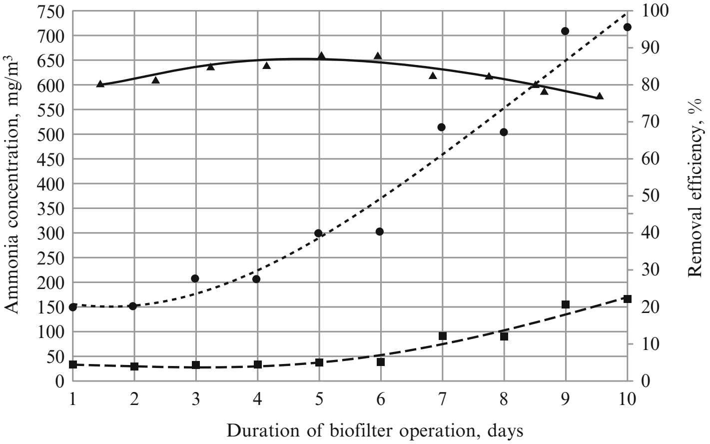


Fig. 7.29 Ammonia concentrations before and after treatment (mg/m^3) and removal efficiency when using wavy plate and loading of wood fiber with nonwoven caulked material: (*filled circle*) ammonia before treatment, (*filled square*) ammonia concentration after treatment, (*filled triangle*) removal efficiency

Removal Efficiency Under the Application of Wavy Lamellar Plates and Packing Material Made of Wood Fiber and Nonwoven Caulking Material (with Introduced Microorganisms)

Figure 7.30 shows that the air treatment efficiency of the biofilter increased up to the tenth day of the experiment. This is the exact time when the highest established treatment efficiency was reached, 94.7 %, which was caused by a growing amount of bacteria, up to $(1.0 \pm 0.2) \times 10^{10}$ CFU/cm^2. The initial acetone concentration before treatment was 25 mg/m^3, whereas at the end of the experiment it reached 700 mg/m^3. On the tenth day, 220 mg/m^3 acetone vapor concentration was supplied to the biofilter. Under a pollutant concentration of 300 mg/m^3, the air treatment efficiency of the biofilter was 93.4 %. Later, growth in the amount of pollutant concentration in air up to 500 mg/m^3 reduced the air treatment efficiency of the biofilter to 86 %. On the 16th day of the investigations, the concentration of acetone was increased to 700 mg/m^3, which resulted in a treatment efficiency of 84 %. The analysis of the following chart showing the treatment efficiency of acetone demonstrates that, under steady analysis (starting from the tenth day of the experiment), treatment efficiency was higher than 80 %. The average amount of bacteria after the tenth day of research was $(6.8 \pm 0.2) \times 10^8$ CFU/cm^2, the average amount of yeast was $(3.8 \pm 0.4) \times 10^6$ CFU/cm^2, and that of fungi was $(3.2 \pm 0.6) \times 10^7$ CFU/cm^2.

The study was carried out at an airflow velocity of 1.08 L/s. Time for contact between the packing material and the polluted air reached 11.39 s.

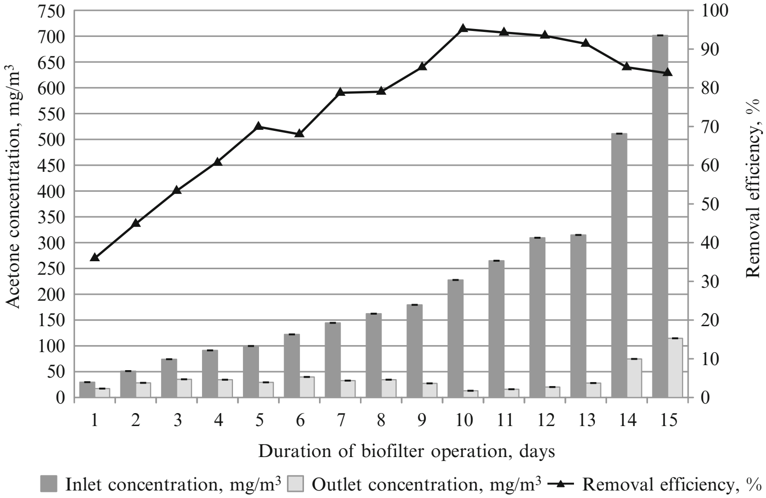


Fig. 7.30 Acetone concentration before and after treatment (mg/m^3) and removal efficiency with application of wavy lamellar plates and packing material made of wood fiber and nonwoven caulking material

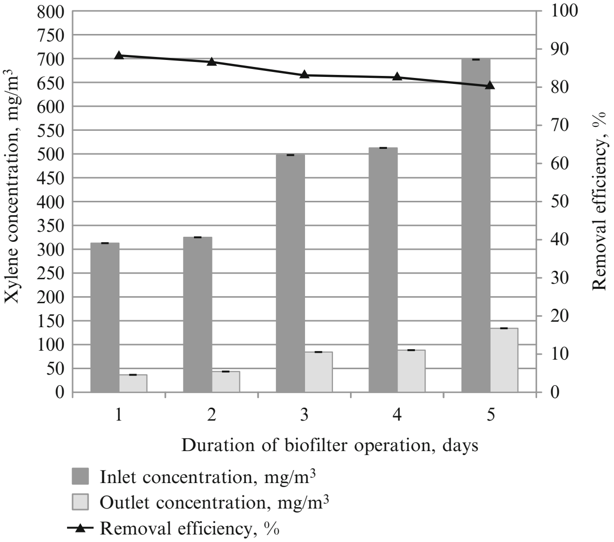


Fig. 7.31 Xylene concentration before and after treatment (mg/m^3) and removal efficiency with application of wavy lamellar plates and packing material made of wood fiber and nonwoven caulking material

Figure 7.31 shows that treatment efficiency within the biodestruction process of xylene on all days of the performed investigation reached more than 80 %. The initial pollutant concentration before treatment was 313 mg/m^3, whereas at the end of the experiment it was 699 mg/m^3. Figure 7.31 also demonstrates that the air treatment efficiency of the biofilter, under a pollutant concentration of 300 mg/m^3 (first day of research), reached 87.7 %, under a concentration of 500 mg/m^3 (third day of research) 83.1 %, and under a concentration of 700 mg/m^3 (fifth day of research) 80.6 %.

An increase in pollutant concentration in the supplied air resulted in a gradual decrease of 3–4 % in air treatment. A reduction of microorganisms in the packing material can also be attributed to this phenomenon. At the beginning of the research, the average amount of bacteria was $(1.8 \pm 0.3) \times 10^9$ CFU/cm^2, that of yeast was $(4.1 \pm 0.1) \times 10^6$ CFU/cm^2, and that of fungi was $(1.2 \pm 0.6) \times 10^5$ CFU/cm^2, whereas at the end (fifth day of research)these numbers were $(4.6 \pm 0.0) \times 10^8$ CFU/cm^2, $2.2 \pm 0.1) \times 10^5$ CFU/cm^2, and $(1.4 \pm 0.3) \times 10^6$ CFU/cm^2, respectively.

Japanese scientists Jeong et al. (2008) also investigated biofilters, supplying them with concentrations of xylene vapor. The obtained results indicate that, under a biofilter productivity of 50 g/m^3/h, the treatment efficiency reached a level of 80–85 %. Wu et al. (2006) studied biofilter treatment efficiency at a device productivity level of the same 50 g/m^3/h and obtained a biodestruction process efficiency of xylene of 70 %. As regards our research, under a similar biofilter productivity, the efficiency of the biodestruction process was 83 %.

Figure 7.32 displays ammonia concentration in the air supplied to and removed from the device and the dependence of air treatment efficiency on time considering the airflow rate in the packing material (0.079 m/s). The research was carried out

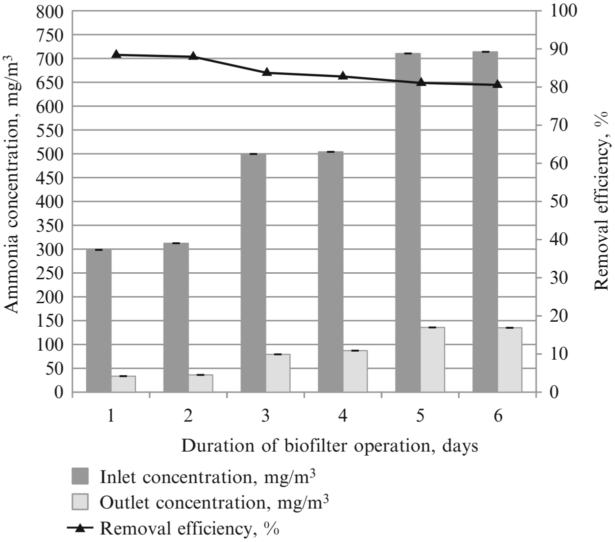


Fig. 7.32 Ammonia concentration before and after treatment (mg/m^3) and removal efficiency with application of wavy lamellar plates and packing material made of wood fiber and nonwoven caulking material

under treated airflow of 1.1 L/s. Time for contact between the biopacking material and polluted air was 11.42 s.

Figure 7.32 also shows that the treatment efficiency of the ammonia biodestruction process, on all days of the investigation, like xylene, was more than 80 %. The air treatment efficiency of the biofilter, at 300 mg/m^3 (first day of research), in the concentration of ammonia vapor reached 88.1 %, at 500 mg/m^3 (third day of research) it reached 83.3 %, and at 700 mg/m^3 (sixth day of research) it reached 80.9 %.

The tendency toward efficiency of ammonia removal from the air, like xylene, remained similar – an increase in the concentration of ammonia in the supplied air resulted in a gradual decrease of 4–5 % in the efficiency of removing the pollutant. This brought about a reduction in microorganisms in the packing material. At the beginning of the study, the average amount of bacteria was $(7.8 \pm 1.0) \times 10^8$ CFU/cm^2, that of yeast was $(2.6 \pm 0.1) \times 10^7$ CFU/cm^2, and that of fungi was $(5.6 \pm 0.9) \times 10^6$ CFU/cm^2, whereas at the end of the study (sixth day) those amounts were $(1.6 \pm 0.2) \times 10^8$ CFU/cm^2, $(6.1 \pm 0.2) \times 10^6$ CFU/cm^2, and $(2.4 \pm 0.2) \times 10^5$ CFU/cm^2, respectively. The biopacking material contained the largest established amount of bacteria and the smallest amount of fungi.

Figure 7.33 shows the use of indigenous microorganisms multiplied naturally on the biopacking material from ambient air, which is why a lower air treatment efficiency of the biofilter was achieved.

During the experimental investigations into wavy lamellar plates and based on the use of packing material made of nonwoven caulking material and wood fiber, both the indigenous and introduced microorganisms survived under the same maintained conditions: the average humidity ranged from 70 to 80 %, the moisture content of the packing material was 60–65 %, the air temperature was 26–28 °C, and the airflow rate was 0.08 m/s. The contact time for the biomedium remained the same, 11.25 s, the pH index varied between 7.2 and 7.3, and the temperature of the medium was 30 ± 1 °C. Thus, it can be asserted that the conditions for the development of the indigenous and introduced microorganisms were favorable enough, and therefore the findings of the research can be compared with each other.

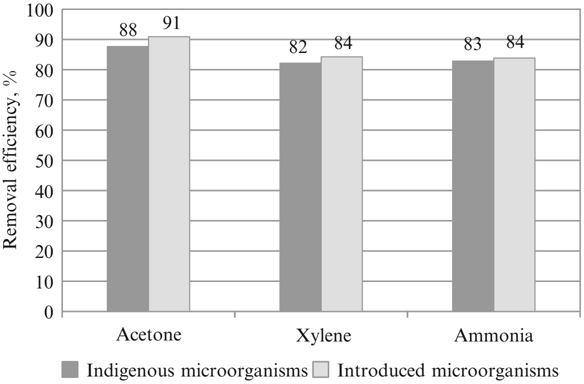


Fig. 7.33 Comparison of air treatment efficiency of biofilter using indigenous and introduced microorganisms

The research has shown that the use of a capillary system for the humidification of packing material made of porous polymer wavy lamellar plates with wood fiber and nonwoven caulking material results in a biofilter air treatment efficiency of more than 80 %. The performed investigation demonstrates that the highest air treatment efficiency was achieved using introduced microorganisms. When air contaminated with acetone vapor was treated, the air treatment efficiency reached 90.7 %, with air contaminated by xylene it was 84.4 %, and with air contaminated with ammonia it was 84.1 %. The average use of the introduced microorganisms points to an air treatment efficiency that is 2.4 % higher than with indigenous microorganisms.

Conclusions

Various kinds of trees make up about a quarter of more than 100,000 plant species, while their biomass accounts for 99 % of the biomass of terrestrial organisms. This amount is no smaller than the total biomass of living matter in the world because terrestrial organisms also make up 99 % of it. Thus, world forests have accumulated a relatively stable and long-lasting biomass, which composes the so-called biomass supplies. The role of trees, as discussed in the monograph, allows us to consider them from various perspectives. On the one hand, as a result of their specific properties, functions, and applications, trees demonstrate their sustainability at all stages of their life cycle. On the other hand, the application of trees follows the main principles of sustainability at any stage of their life cycle.

The ecosystems of forests have accumulated approximately 90 % of the carbon of terrestrial plants. Every year, about 60 Gt carbon from the atmosphere is involved in the process of synthesizing new biomass, and nearly the same amount of carbon is brought back to forest soil by tree litter. Long ago, the processes of climate warming intensified in periods of increased volcanic activity. At that time, O_2 was thrown out into the atmosphere from the bowels of the earth, and its higher content promoted the growth of biomass and the expansion of areas covered by forest. This in turn helped to recover the CO_2 equilibrium in the atmosphere. However, because of the Industrial Revolution, the burning of fossil fuels, and the intense cutting of forests, regulation of CO_2 content failed. In recent years, CO_2 concentration in the atmosphere has increased by 43 %, which also demonstrates a weakening of trees' function as regulators of CO_2 content in the atmosphere. Moreover, rising atmospheric and ambient air temperatures cause a weakening of forest ecosystems in their function as short-term reservoirs of global terrestrial carbon.[1]

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[1] In this book, the balance between the atmosphere and the ocean, as much larger CO_2 reservoirs, has not been discussed.

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Based on a monetary expression of the function of ecological trees, the usefulness of 1 ha of forest for the environment and humans is nearly two as great as the cost of cultivating a forest in the same area. Moreover, it should be noted that, in this case, only the removal of particulates from the air and CO_2 stabilization in wood are evaluated. This function of trees and its economic assessment have been widely discussed. The present monograph also discusses other effective applications of trees and their products and describes the increase in their profitability owing to this effect, for example, using wood products in various technologies, more precisely, the production of biochar from wood. This process is rather expensive because 1 t biochar costs about 200 EUR. However, when it is used for soil amendment and tp increase the production of grain crops, the profit might come to more than 150 % of expenses.

The consideration of trees in this work as sustainable objects that could be used in environment protection technologies is based on their three major functions: (1) to stabilize atmospheric CO_2 in tree biomass; (2) to stabilize atmospheric carbon accumulated in wood in biochar as a soil amendment for long-term sequestration, which is considered to be an additional way of transferring carbon removed by trees from the atmosphere to soil as a long-term terrestrial reservoir; (3) to enhance the capacity of trees and forests to improve the quality of life not only from the described perspective in reference to CO_2 flow to the technosphere but also from the perspectives of developing technologies for using wood products. These include the use of filters that retain inorganic pollutants whose basic element is made of wood or its products. In addition, the function of trees as “regulators” of environmental quality indicating changes taking place, supplement the earlier described tree functions, showing them to be sustainable elements of environmental protection systems that can not only observe and indicate but also perform the functions of an analytic matter, i.e., protect the environment during their (trees’) life cycle and maintain their capacity to protect the environment even after their “death,” i.e., at the phase when they become products (3).

The analysis of trees’ functions in environment protection technologies focused on aspects relating to environmental quality in association with the long-term accumulation of pollutants in both local and global trees’ environments.

Though pollutants are transferred to trees mainly via roots, pollutants of a technogenic nature also take part in this process. These pollutants settle on soil as a result of wet and dry deposition. They are brought from local sources or are transferred from remote countries, which often determines the specific character of the pollution. For example, soils in western Lithuania are characterized by an increased concentration of metals, particularly Ag, Pb, Zn, and Sn, which can be attributed to their long-distance transfer from countries burning large amounts of fossil fuels in industrial regions to the west of Lithuania. A comparison of soils of similar mechanical composition but different types of usage revealed that concentrations of siderophiles, such as Cr, Ni, Co, and V, higher than those found in cultivated and uncultivated meadow soils can be observed in sandy or sandy-loamy forest soils. In clay-loam soils, an opposite trend can be observed. In particular, the concentrations of chalcophiles, such as Zn and Cu, in these soils differ insignificantly, depending on the land use and the mechanical composition of the soil, while the Pb concentration more strongly depends on the mechanical soil composition rather than on the land use and is higher in heavier soils.

In regions with heavy local pollution, the bark of trees can serve as a reliable long-term biomonitor of pollution with metals, indicating quantitative changes in environmental quality. The zone experiencing the impact of the JSC Orlen Lietuva oil refinery, which is the largest in the Baltic States, is grouped among those territories that have low to average pollution levels with regard to pine-tree bark as an industrial pollutant deposition medium. With regard to other pollutants' deposition media (e.g., soil, moss, snow cover), the pollution in this territory was assessed as moderately or highly hazardous. Though the bark of a Scots pine can indicate that territory contaminated with the same pollutants can be grouped among territories having low pollution levels compared to other metal-depositing media, its consideration in the long-term context shows that trees retain pollutants for much longer periods of time than other media (e.g., mosses retain pollutants mainly with their 3-year shoots, while snow cover retains them for only 3 months).

The extent of environmental pollution is shown by the quantitative composition of a tree during the transformation of the substances taken up from the environment, when the tree's biomass is formed, or at the stage of formal evaluation of the life cycle known as "resource processing." In some areas of Lithuania, the concentration of heavy metals in the wood of pine trees and birches more than 30 years old, including zones polluted with aerogenic metal pollutants or areas contaminated by pollutants of edaphic origin, does not exceed the values determined in the literature for phytotoxins. However, the concentrations of metals in trees and metal-accumulating media, such as soils, differ depending on the dominant type of technogenic pollution (which may be aerogenic or edaphic), the source of pollution, the microclimatic conditions, and the relevant biotic factors. Concentrations of Zn, Ni, and Cu in wood exceeding natural concentrations by four, five, and three times, respectively, were found in pine trees growing near military training grounds. Thus, the concentration of Zn in soil was approximately three times higher than the natural value, while the concentrations of Ni and Cr in the pond exceeded the natural values by 19–22 times. It is possible to predict the aerogenic pollution in a territory based on the concentrations of Cu and Ni in the pine tree bark in the area, which are twice as high as the concentrations of these metals in its wood. The concentrations of metals in the soil under the crowns of trees depend on the wind direction: metal concentrations in soil at a depth of 0–40 cm, determined from the leeward direction with respect to the tree stem, were lower by 20 % (Zn) or around 2.5 times (Mn) than those found for the opposite case (windward direction). Soil amendments of technogenic origin (e.g., sludge) can increase the concentrations of metals in bioavailable forms by two times for Zn and by five times for Cu and Pb, compared to those in the control territory. Biotic factors (e.g., root rot) and abiotic factors (e.g., aerogenic pollution by metals) intensify the biophilicity and bioaccumulation of macroelements (K, Mg) or typomorphic microelements in pine tree wood, respectively. The metals accumulated in trees growing in the soil of a forest amended with technogenic sludge are distributed in a basipetal way, as observed in the control territory. However, later, the signs of this type of distribution were not as evident, which can be attributed to the increase in the total amount of metals concentrated in the soil. The most intense accumulation of metals in tree biomass was observed for Cd and Zn, while Pb rarely accumulated in large amounts. The order of frequency of metal accumulation in trees growing in the polluted territory was Cd > Zn > Cu > Pb and matched the relationship between the values of their mobile forms found in the soil of the polluted territory: Cd > Cu > Pb.

Though the conditions for trees growing in the territory polluted with the spread technogenic sludge, had to be better because of the better properties of its soil, the functional traits, which determine the growth and development of trees, had not confirmed it. A negative biomass increase and smaller root biomass indicated that, in general, the impact of this amendment on tree development was negative. To quantitatively assess the biogeochemical properties and functional traits of a plant, a number of ecotechnological methods, also functioning as tools for describing the life cycle of trees called the "use of product," have been developed.

The effect of the soil environment associated with nutrient factors on the functional traits of trees was evaluated based on the root length, the ratio of the tree's root length to its shoot length and the degree of branching. The assessment of changes in tree height, stem diameter, and biomass shows the impact of soil pollution on plants. To assess the biogeochemical properties of trees, original methods of two types, some of them developed by the authors, were used. They include a method based on the dynamic factors and simplified evaluation of the integral process of metal transfer in the soil–plant system and models using parameterization of the soil–tree system. The method based on dynamic factors aims to assess the changes taking place in the process of transferring chemical elements in the soil–plant system while the system itself is changing, for example, in the case of amending soil with sludge. The criteria describing the dynamic effect of bioaccumulation, biophilicity, translocation, and phytoremediation are used in the dynamic criteria method. The practical advantages of this method are as follows: (1) the integration of four types of data (the concentration of a chemical element in the control territory soil and plants and the concentration of this element in the components of a modified system) into a single value; (2) their nondimensional and easily compared expression; (3) the minimization of risk of the system error in chemical analysis and the reliability of evaluation. In the context of biogeochemical analysis, the proposed method allows for comparing changes in the process of transferring chemical elements to plants depending on the geochemical properties of the investigated area. It also makes it possible to appropriately compare the effect produced by soil modification on the participation of chemical elements in the metabolism of plants. More precisely, the dynamic phytoremediation factor accurately describes the phytoremediation effect.

Parameterization of the soil–plant system was performed using the adapted model of Hung and Muckay describing the transfer of pollutants from soil to plants and the model of soil self-cleaning, BALANS. The first model, validating the research results obtained under natural conditions, showed only 10 % error and, therefore, was recognized as fully satisfying its purpose. The BALANS model of soil self-cleaning considers the main flows of metals that make their way into soil and are removed from it in the atmosphere–plant–soil system. It takes into account the aerogenic uptake of metals, the amount of metals that get into the soil together with soil amendments, and natural physicochemical migration beyond the limits of the examined soil layer, expressed by annual metal migration coefficients and the assimilation of metals by the biomass of plants growing in the soil, as well as their removal from the system together with crops (a phytoremediation effect). The model makes it possible to analyze the effectiveness of soil self-cleaning with regard to various forms of the field microrelief (i.e., hills and depressions).

The Phyto-DSS model applied to the analysis of territory amended with technogenic sludge and planted with young pine trees and birches allowed us to compare the effectiveness of the phytoremediation method over the course of 9 years of use with the efficiency of other methods of soil rehabilitation. Phytoremediation of the 2 ha territory would cost around 16,700 EUR, while application of the alternative technologies based on stabilizing metals in soil would cost 167,700 EUR. The natural self-cleaning of soil, not supported by the application of any specific technologies, but taking into account limiting of the soil and forest functions, would cost around 1,673,000 EUR. Thus, the advantage of phytoremediation is quite evident not only from the perspective of sustainable development but from an economic perspective as well.

Those tree functions associated with a tree's life cycle stage of waste utilization can be considered realizable not only at the stage where trees are living plants but also when they are wood products. In this case, they can also be used in ecotechnologies and environmental protection engineering. Minimization technologies employed for reusing and recycling waste, as well as their recovery as new substances for profit and benefits in the field of environmental protection, can be mentioned as an example. Let us consider the latter two methods, which sit atop the hierarchy of waste processing priorities. Regarding the use of trees and their products, such as, for example, bark, wood fibers, and wood chips, in engineering technologies, for example, in biofiltering systems, this is categorized as waste recycling. Examples of the recovery of materials include the production of biochar and ashes and their use in environmental protection technologies.

Biochar obtained from wood can be effectively used as a substrate in filtering systems owing to its property of retaining moisture and nutrients, which are required for microorganisms. It also maintains the optimal pH value needed for the destruction of pollutants over a long period of time and has a much larger specific surface area (4 times larger than that obtained from bones and about 80 times larger than that obtained from sludge). In addition, the cost of biochar may be only one-fourth of the activated carbon cost. Considering the growth rate of microorganisms, it can be stated that, in biochar-based biofilters, biodegradation of acetone can be achieved in the shortest time, while that of xylene and ammonia requires a little more time. The optimal temperature for the growth of microorganisms in biochar-based biofilters, when the previously named pollutants are removed from the air, is 28–32 °C. Microorganisms inoculated in biochar in a biofilter can survive when the concentration of pollutants in it falls in a range of 25–500 mg/m^3.

After 30 days of biofiltration, the observed changes in the biochar surface structure become more evident when the biofiltration is continued. The impact of xylene on the process can be considered particularly strong because it increases the specific surface area of biochar pores. This may be attributed to the influence of xylene on residual organic compounds, which causes them to dissolve and causes the formation of new pores in the biochar microstructure. The considered mixtures of biochar as wood product and other substrates used in biofiltration (e.g., spruce tree bark, wood chips), as well as mixtures of wood products and mineral materials (e.g., zeolite), can be effectively used in biofiltering systems, which can achieve an efficiency of 80–90 %.

Biochar, achieving about 40 % efficiency in absorbing metals from water solution, has great potential for engineering modifications aimed at increasing the absorptive properties and selectivity of adsorbents. Biochar as a soil amendment is efficient owing to its relatively large specific surface area, high porosity, ability to increase the retention of soil water and nutrients, relatively high capacity cation exchange, surface sorption, and the potential for decreasing soil acidity. As determined by research, biochar of pine trees and birches is a particularly suitable substrate for various microorganisms. For example, biochar produced at a temperature of 750 °C demonstrated alkaline properties (pH 8–9) relevant for decreasing soil acidity and a relatively large specific surface area (380–425 m^2/g), which strongly influences the process of sorption.

The limited application of wood ash known from ancient times is considered in the present monograph in the context of risks of having metals as a component of ash. The concentrations of metals in wood ash, which sometimes exceed the maximum allowable concentration values, cause us to doubt whether it is worth using it as an amendment capable of optimizing acidic soil pH and enrich soil with valuable nutrients, such as Ca, K, Mg, and P. However, in practice, the concentration of dangerous metals in wood ash is usually much lower than the limits set by the maximum allowable concentration values. In cases where wood from polluted territories, including wood from forests affected by the Chernobyl accident, is used as fuel for boiler power plants, its usage should be strictly controlled in accordance with specification requirements.

The novelty of the present monograph stems from the consideration of the tree as an object of a biogeochemical system and the application of research results to modeling and predicting the transportation and accumulation of pollutants in the atmosphere–tree–soil system. The tree has been considered from the point of view of biochemists and environmental protection engineers who have both thorough knowledge of their field and extensive practical experience.

The topics considered in the monograph may serve as a basis for a wider practical use of the methods discussed, allowing for a more thorough comprehension and evaluation of the process of transferring pollutants from the soil to plants (trees) as well as for focusing more attention on the major paths of pollutant migration in biogeochemical systems, including the transfer of pollutants and their aerogenic accumulation in plants and soil, the uptake of pollutants by plants via their root systems and their migration within plants (translocation mechanism), and the removal of pollutants from soil as a result of natural physicochemical and biogeochemical migration.

Changes in the biosphere caused by the greenhouse effect are raising more and more questions that demand answers; the most important of these questions relate to the possibilities of using non-invasive methods of regulating the sequestration of atmospheric carbon with respect, including in addition the extension of areas of the world's forest ecosystems and carbon stabilization in biochar as a soil amendment. As a result of technogenesis and the use of imperfect technologies, a problem arose of stable accumulation in soil of metals found in the biosphere and the system of land water that could, at least partially, be solved by more effective utilization of industrial waste and by the use of the rather large potential of planting more trees in the world's forests to stabilize metals in wood. The problem of optimizing the life cycle of trees with regard to the increasing rate of carbon leakage from the atmosphere and the need for stabilizing metals awaits new solutions, which will be found only on the basis of systematic interdisciplinary research.

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