

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.

2.1 Edaphic Contamination and Its Ecogeological Evaluation

According to contamination inheritance 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.

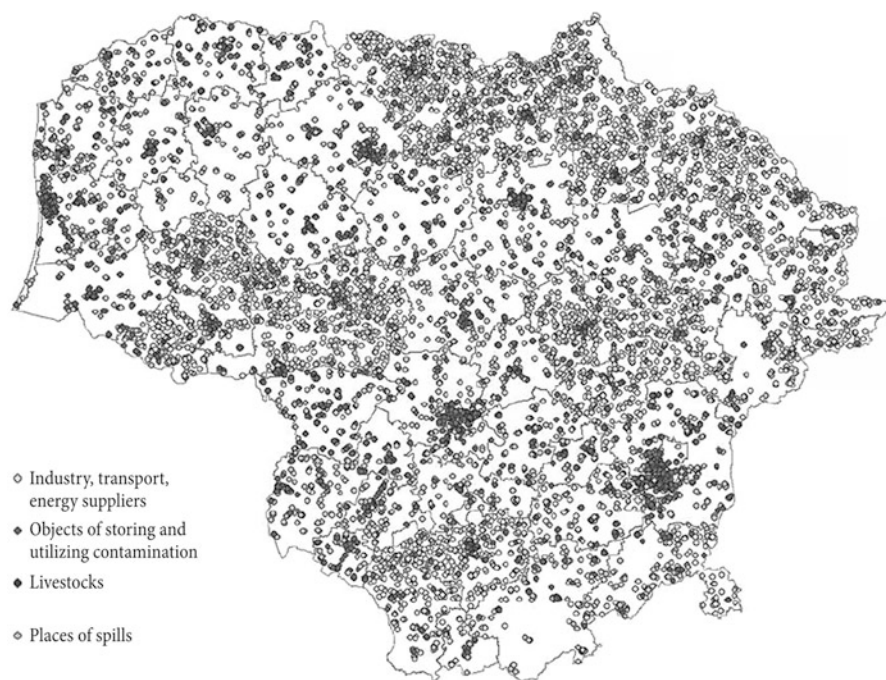


Fig. 2.1 Location scheme of potential sources of geological environmental contamination (LGS Annual Report 2006)

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

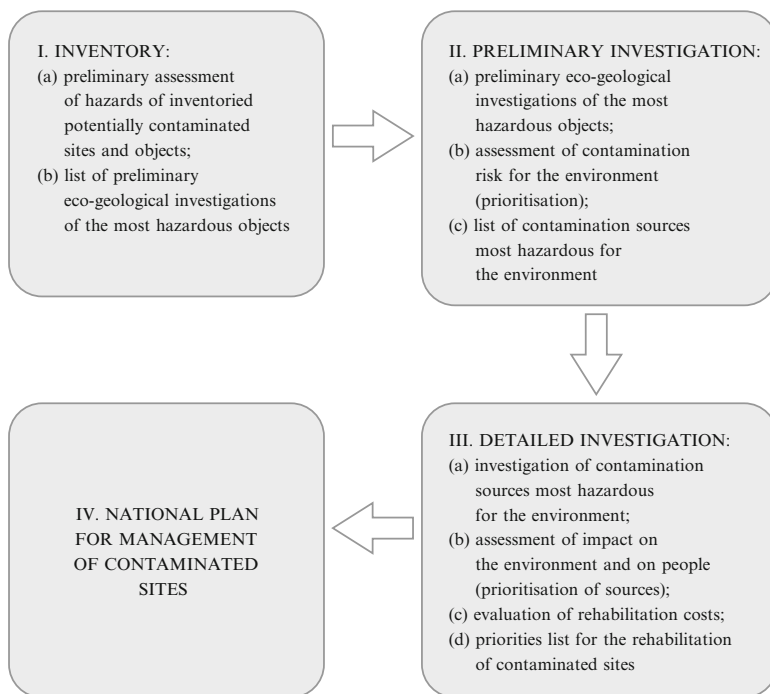


Fig. 2.2 Scheme of management of contaminated sites

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:

$$LVa = LV \times \frac{A + (B \times [CL_ \%]) + (C \times [OM_ \%])}{A + (10 \times B) + (3 \times C)}, \quad (2.1)$$

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

Indicator, mg/kg DW	Soil				Groundwater	
	Category of territory sensitivity to contamination					
	I	II	III	IV	I	II, III, IV
	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	<i>A</i>	<i>B</i>	<i>C</i>
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

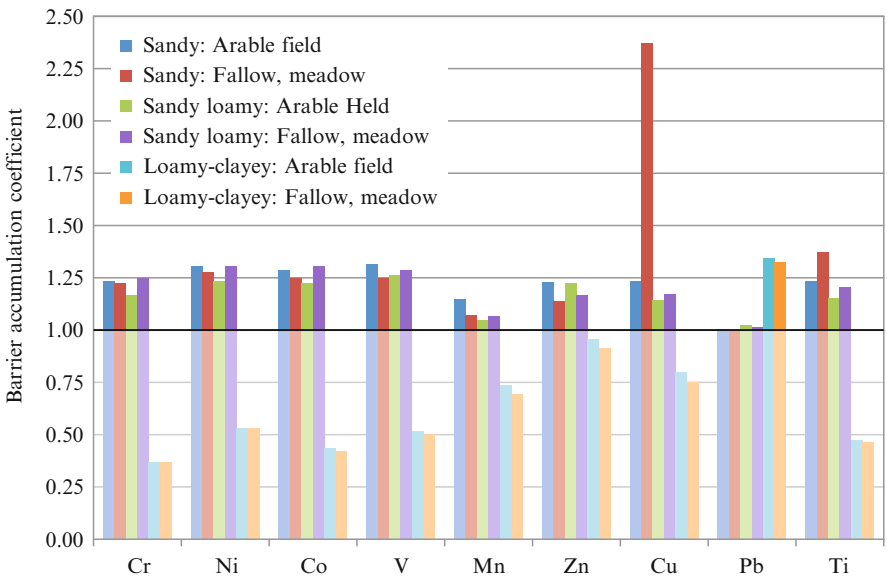


Fig. 2.3 Values of forest barrier accumulation coefficients K_{for} in Lithuanian soils

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

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 (IMs) 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)

Metal	Annual metal flux (range), $\mu\text{g}/\text{m}^2/\text{year}$	
	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; Milukaitè 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)
	–	1.5	20.0	33.0	27.0	–	430.0	270.0		–		Karvelas et al. (2003)
Wastewater from wastewater treatment plants												
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

^aMedian metal concentrations (no evidence of state of metal concentrations)
^bAverage value of previous studies (no evidence of state of metal concentrations)
^cNo 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 $K_{d,i}$ calculated according to the following Eq. (2.3) was used:

$$K_{d,i} = \frac{C_{i,s}}{C_{i,w}}, \quad (2.3)$$

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 ($\mu\text{g/L}$) identified in SRW samples from roads, roofs, and pathways, compared to maximum allowable concentrations of metals in environment ($\mu\text{g/L}$) 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 ($\mu\text{g/L}$)	Maximum allowable concentration (MAC) for acceptor water body ($\mu\text{g/L}$)	Sampling site		
			Road ($\mu\text{g/L}$)	Roof ($\mu\text{g/L}$)	Pathway ($\mu\text{g/L}$)
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 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

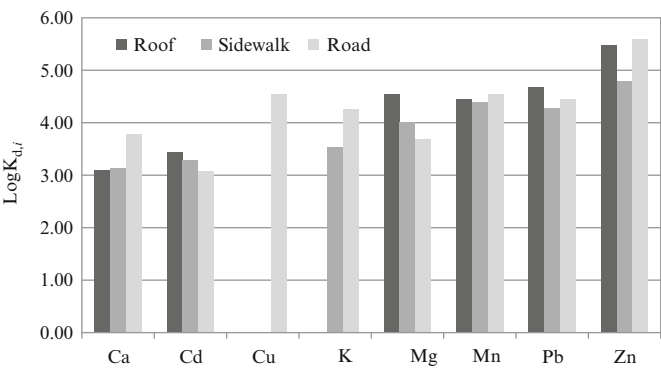


Fig. 2.4 Partition coefficients ($\log K_{d,i}$) calculated for macro elements (Ca, K, Mg) and metals (Cd, Cu, Mn, Pb, Zn) in urban stormwater runoff samples from road, roof, and pathway surfaces

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:

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

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:

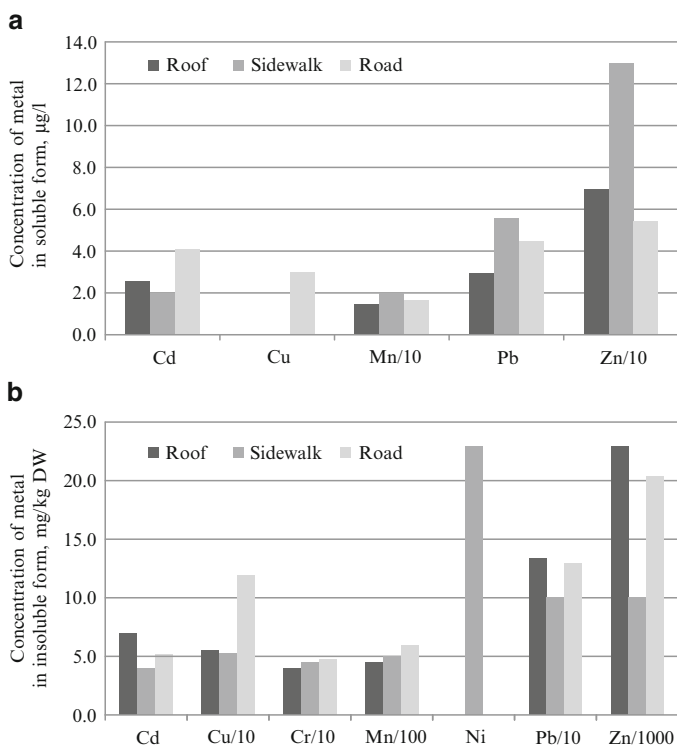


Fig. 2.5 Average concentration of metals detected in soluble (µg/L) (a) and insoluble (mg/kg of dry weight) (b) forms in urban stormwater runoff samples from road, roof, and pathway surfaces

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

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):

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

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 CO₂ 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 Pb²⁺ ion activity is negligible. In road SRW modeling, Cu-FA complexes were found to amount to around 99 % of the total dissolved Cu.

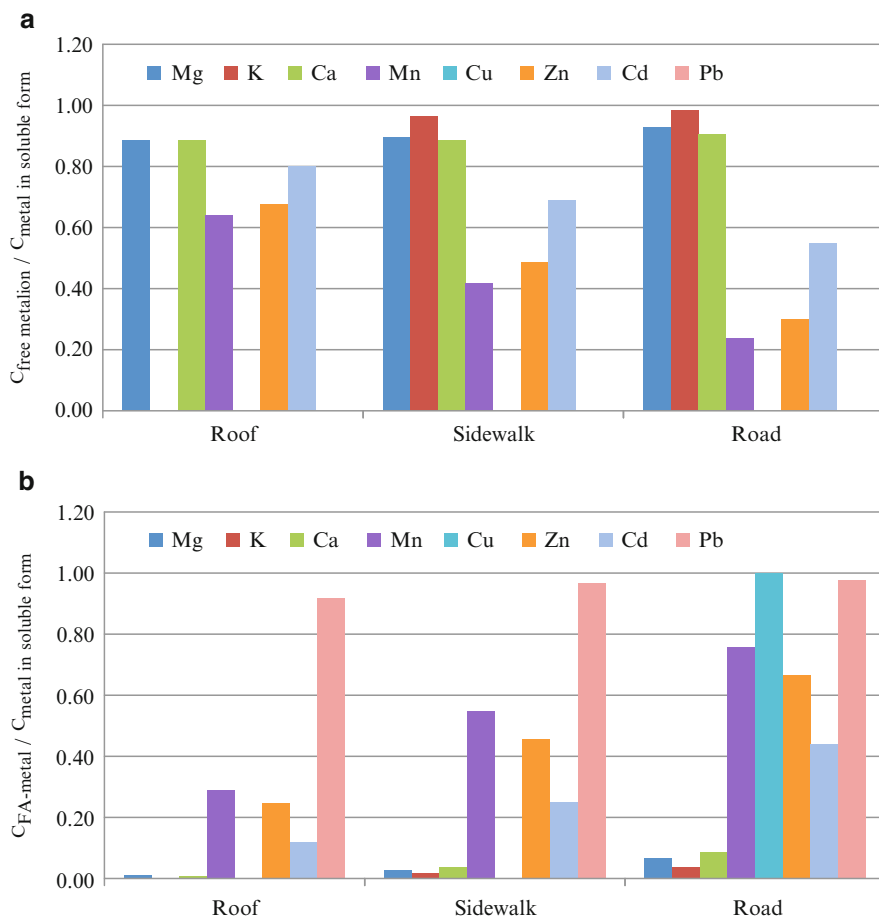


Fig. 2.6 Free ion activity and fraction bound to colloid (FA) of metals (Cd, Cu, Mn, Pb, Zn) and macro elements (Ca, K, Mg) in urban stormwater runoff (SRW) from different surfaces were calculated using WHAM7. *Roof*, *Road*, and *Pathway* refers to sites where the SRW samples were taken. [FA-M], the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

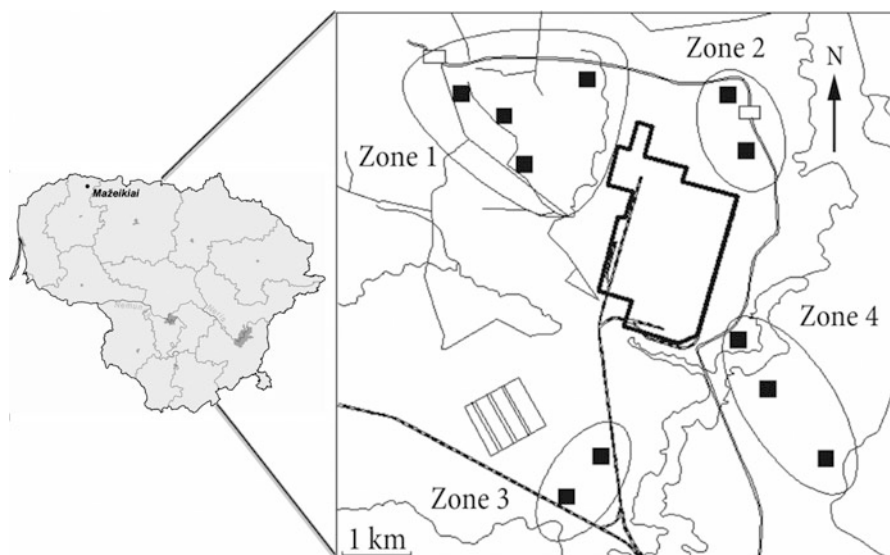
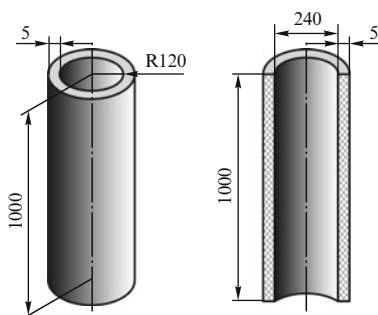


Fig. 2.7 Places in territory affected by AB ORLEN Lietuva where snow, soil, moss, and bark samples were taken. The control area was chosen 10 km to the west of the area affected by the company (not shown here)

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 bryophytes, 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-U110 (contaminated soil-trace elements)* and *ERM[®]-CD100 [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):

$$A_n = \frac{D}{S \cdot T}, \quad (2.4)$$

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:

$$K_{a-b} = \frac{A_a}{A_b}, \quad (2.5)$$

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

$$Z_d = \sum_{i=1}^n K_{k,i} - (n - 1), \quad (2.6)$$

$$K_{k,i} = \frac{C_i}{C_f}, \quad (2.7)$$

where Z_d is the total contamination factor calculated based on the considered metals with $K_{k,i} \geq 1$, $K_{k,i}$ is the concentration coefficient of metal i , n is the number of metals with $K_{k,i} \geq 1$, 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):

$$K_0 = \frac{C_i}{DLK_i}, \quad (2.8)$$

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* $I_{geo,dt}$ (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	$K_0 > 10$

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

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 $I_{\text{geo},dt}$ 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:

$$TCI_{dt} = (C_{f,1} \cdot C_{f,2} \cdot \dots \cdot C_{f,i})^{\frac{1}{n}}, \quad (2.10)$$

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 $I_{\text{geo},dt}$, pollution classes, and levels (Müller 1981)

Geoaccumulation index ($I_{\text{geo},dt}$)	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_{rd}^i shows the accumulation level of a metal in parent rock of the corresponding soil horizon (Lietuvninkas 2012) and is calculated using Eq. (2.11):

$$K_{\text{rd}}^i = \frac{C_{\text{dir},j}^i}{C_{\text{uol}}^i}, \quad (2.11)$$

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

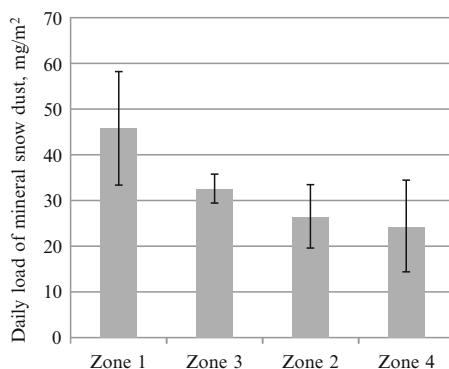
Use of Deposit Media for Evaluating Level of Ecosystem Contamination

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/m²/day. This load corresponds to a **lower than average hazard** level (average daily load of 250–450 mg/m²) of pollution according to the scale presented in Table 2.13. The largest snow dust load per day (45.8 mg/m²) was found in Zone 1, while the smallest (24.4 mg/m²) was found in Zone 4 (Fig 2.9). Comparing snow dust loads in the downwind (Zone 1) ($A_1 = 45.8$ mg/m²) and upwind (Zone 4) ($A_4 = 24.4$ mg/m²) 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-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: $K_{1-4} = 1.88$,

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 reached 160 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

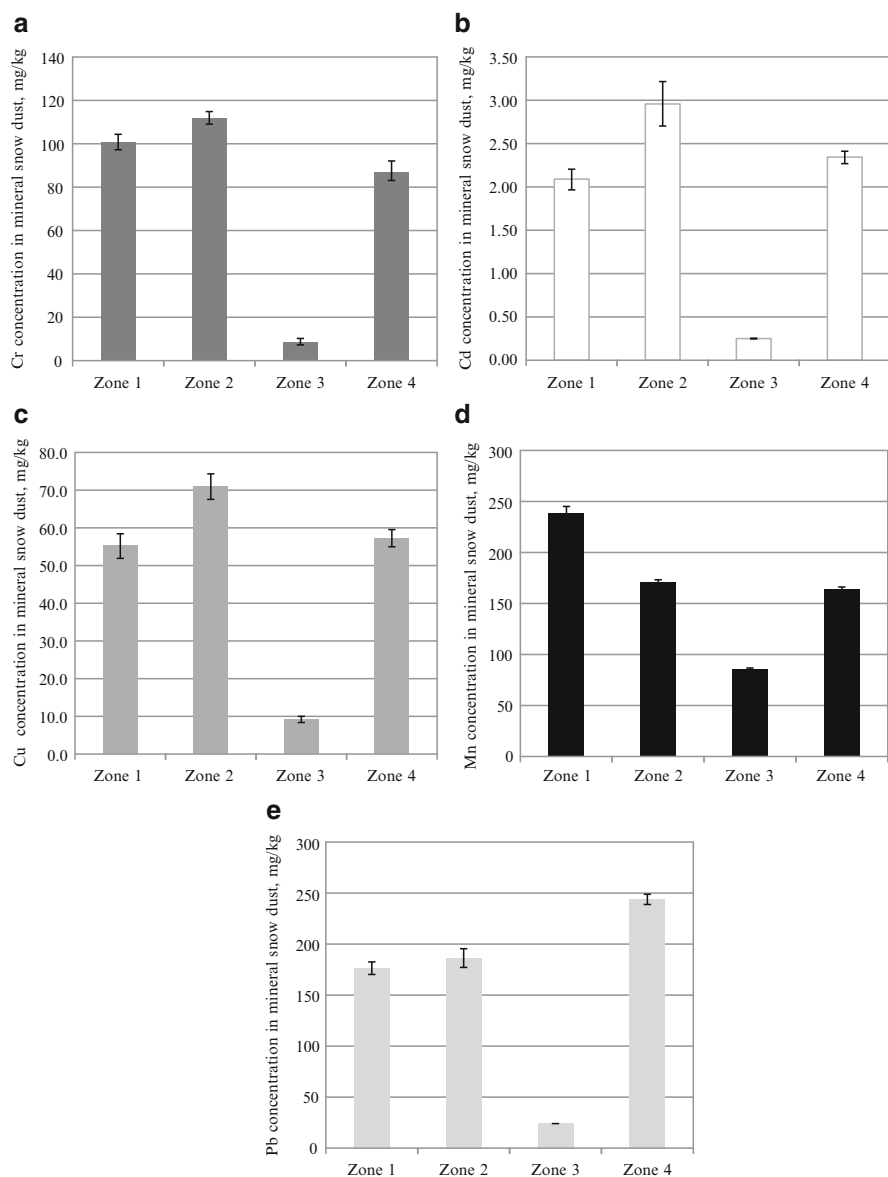


Fig. 2.10 Concentration of metals (mg/kg) in snow dust in zones of the territory affected by AB ORLEN Lietuva. Cd*10 means that Cd concentration was increased tenfold to show the obtained results more clearly. (a) Cr, (b) Cd, (c) Cu, (d) Mn, (e) Pb

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

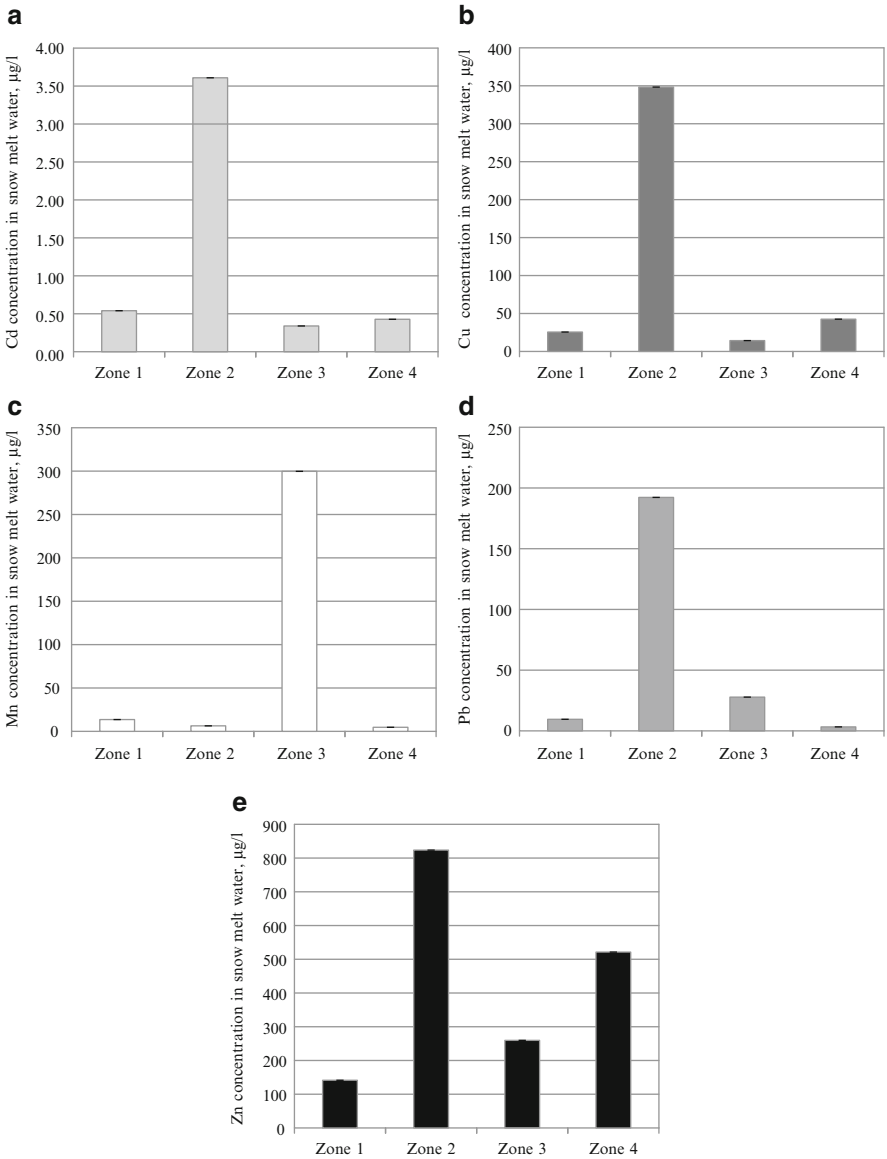


Fig. 2.11 Concentration of metals ($\mu\text{g/L}$) in snowmelt water in zones of the territory affected by AB ORLEN Lietuva. Cd*50 means that Cd concentration was increased 50-fold, while Zn/10 denotes that Zn concentration was decreased tenfold to show the obtained results more clearly. (a) Cd, (b) 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

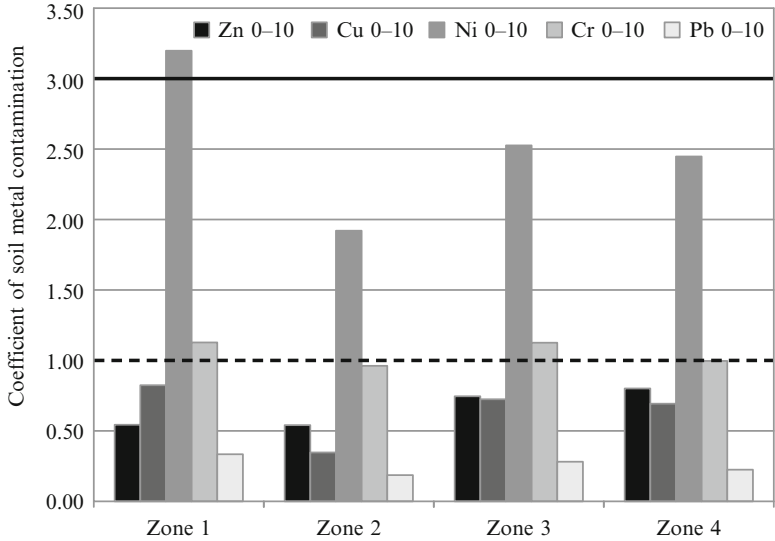
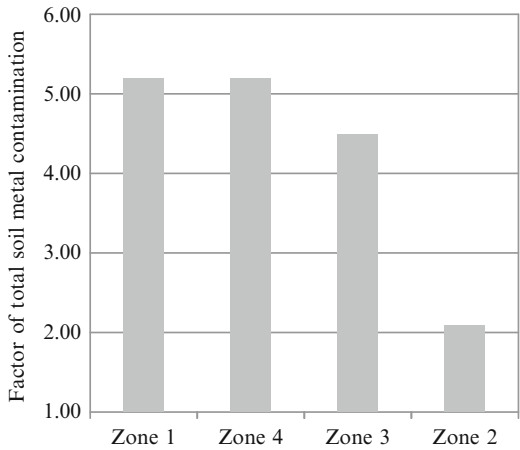


Fig. 2.12 The coefficient K_0 for topsoil (0–10 cm) metal contamination in various zones of territory affected by AB ORLEN Lietuva

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).

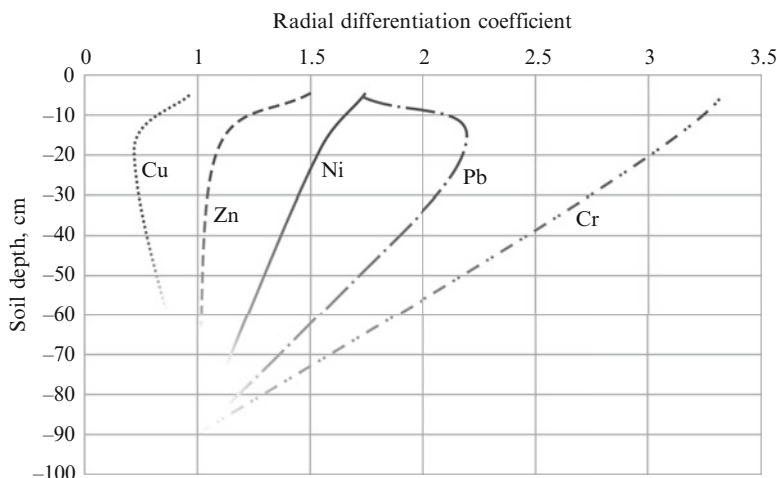


Fig. 2.14 Variation in radial differentiation coefficient (K^i_{rd}) values for metals in soil profile of area affected by AB ORLEN Lietuva

The values of the factor Z_d for total soil metal contamination are shown in Fig. 2.13. The maximum values of the factor ($Z_d = 5.2$) 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 $Z_d < 16$, 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 $K^i_{rd} > 1$, this signifies metal accumulation. Otherwise, when $K^i_{rd} < 1$, 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 $K_{k,i}$, 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

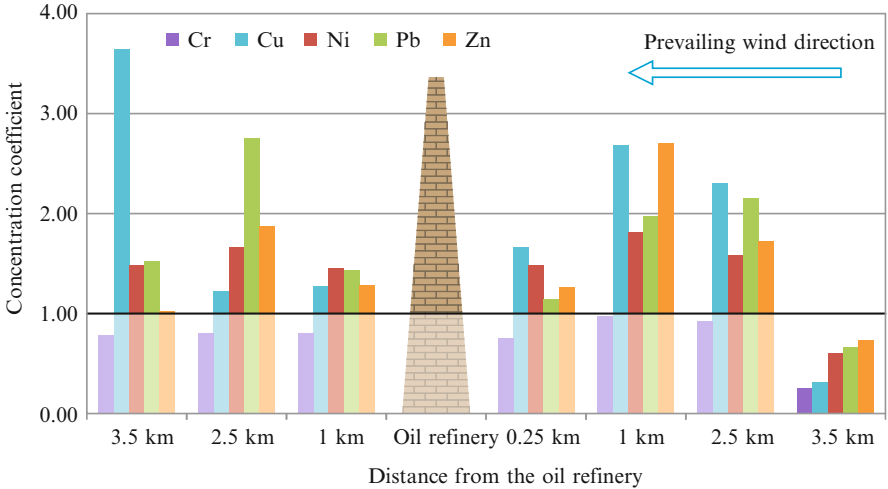


Fig. 2.15 Coefficient K_{k-i} for metal concentration in topsoil layer (0–10 cm) in prevailing wind direction (in areas downwind and upwind relative to company territory) based on distance to refinery

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 $I_{\text{geo},\text{dt}}$ (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 $0 < I_{\text{geo},\text{b}} < 1$ (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)
Hajavalta 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)

^aThe wood was infected by rotting caused by *H. annosum* fungus, nd no data available

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

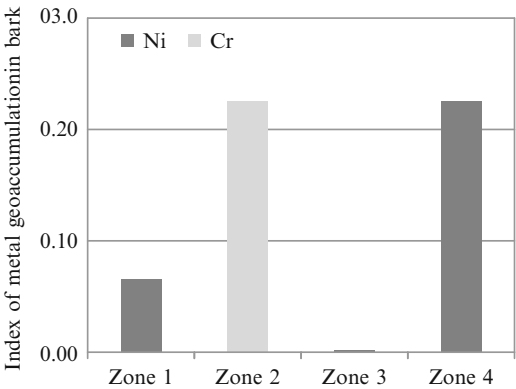


Fig. 2.17 Values of total metal contamination index TCI_b based on metal concentrations in pine bark from various zones of territory affected by AB ORLEN Lietuva

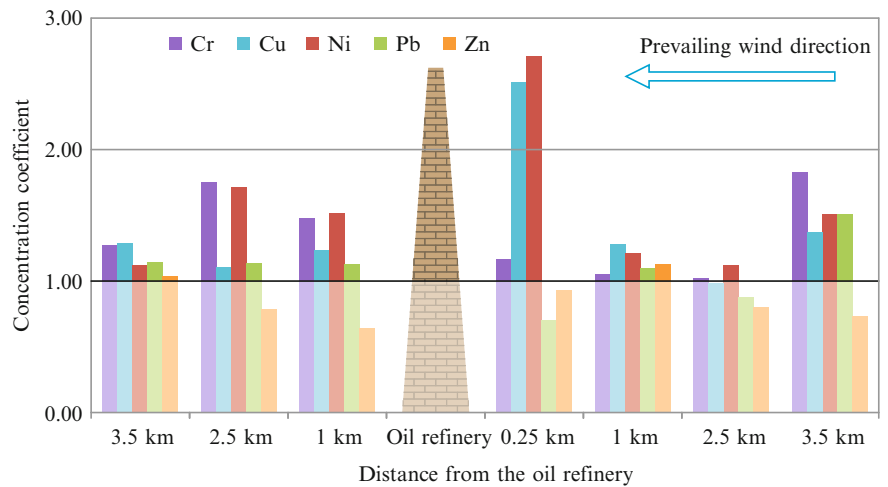
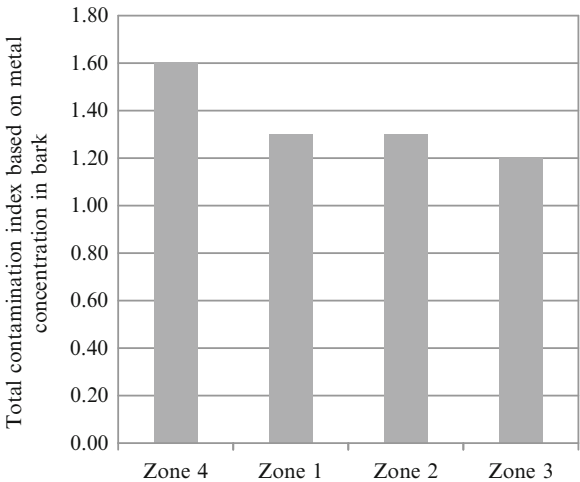


Fig. 2.18 Values of coefficient $K_{k,b}$ for metal concentration in pine bark determined at various distances from territory affected by the company in prevailing wind direction

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 $I_{geo,m}$ 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	Baltėnaitė et al. (2014a, b, c))	
Territory of Mažeikiai district	45.3	6.17	1.52	0.51	1.49	0.57	32	nd	Čeburnis et al. (2002)	
Zone in Mažeikiai district affected by a boiler	nd	nd	2.37–21.4	nd	nd	nd	nd	5.90–59.3		
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	Rüling (1994)	
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		

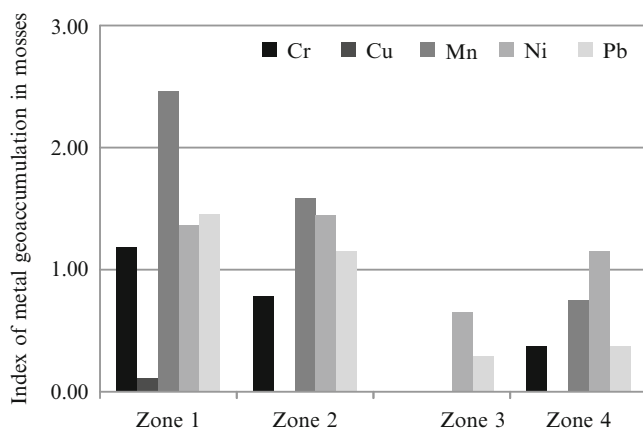


Fig. 2.19 Geoaccumulation index $I_{geo,m}$ for metals in epigeic mosses (*Hylocomium splendens*) from various zones of territory affected by ORLEN Lietuva

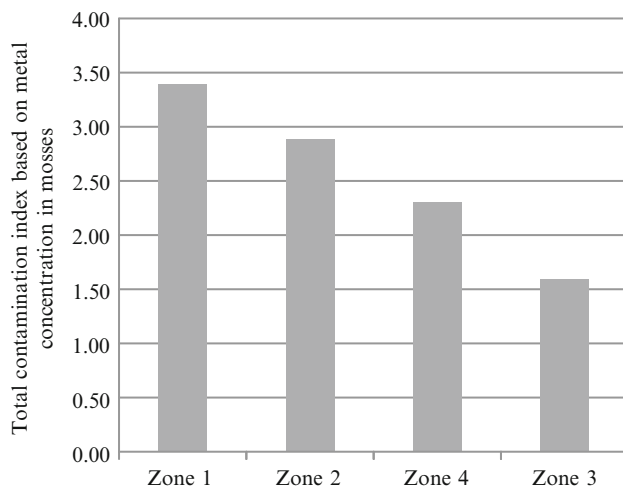


Fig. 2.20 Values of total metal contamination index TCI_m based on metal concentrations in epigeic mosses (*Hylocomium splendens*) from various zones of territory affected by AB ORLEN Lietuva

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

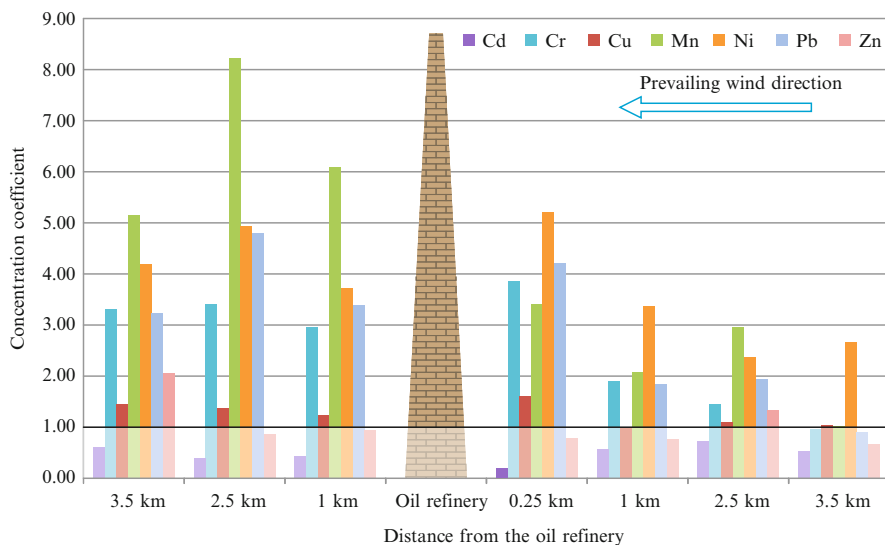


Fig. 2.21 Values of coefficient $K_{k,m}$ for metal concentration in epigeic mosses (*Hylocomium splendens*) determined at various distances from territory affected by the company in prevailing wind direction

determined for the territory of Mžeikiai 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 $250\text{--}450 \text{ mg/m}^2/\text{day}$, 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 ($0 < I_{\text{geo},m} < 1$). 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 ($0 < I_{\text{geo},b} < 1$). 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: $\text{Zn} > \text{Cu} \approx \text{Mn} \approx \text{Pb} > > \text{Cd}$.

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.

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