Geoderma 192 (2013) 259–268

Contents lists available at SciVerse ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Spatial distribution of lead in the surface layers of mountain forest soils, an example from the Karkonosze National Park, Poland

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ARTICLE INFO

Article history:
Received 4 August 2011
Received in revised form 9 July 2012
Accepted 19 August 2012
Available online 17 November 2012

Keywords:
Soil
Lead
Pools
Mountains
Organic matter
Altitude

ABSTRACT

Total concentrations and pools of Pb in the surface layers of mountain soils in the Karkonosze National Park are presented and discussed in relation to site altitudes and soil properties. Soil samples were collected from a forest floor and from the depths of 0–10 cm and 10–20 cm in 372 monitoring sites situated in a forested zone of the Park. Particularly high concentrations of Pb (24–200 mg·kg^{-1}, most often over 100 mg·kg^{-1}), potentially hazardous for soil biota, were found in forest litter. The concentrations of Pb in soil layers 0–10 cm and 10–20 cm were in the ranges 19–248 and 4–196 mg·kg^{-1}, respectively. Pb distribution indicated very high spatial variability, confirmed by geostatistical analysis. Calculated pools of Pb varied in a broad range: 0.16–26.6 g·m^{-2} (mean: 6.20 g·m^{-2}), and correlated strongly with the stocks of organic matter, both being significantly higher in the lowest altitudinal zone (500–750 m a.s.l.) compared to the highest zone (1250–1380 m a.s.l.). Nevertheless, there was no simple correlation of Pb pools vs. altitude. The largest pools of Pb are stored in the layer 0–10 cm. The pools of accumulated Pb determined in this study are much higher than those assessed on the basis of available data on former and present Pb deposition rates. These findings may be assigned to a seeder–feeder effect and horizontal transport of pollutants. The highest amounts of Pb were identified in three distinct areas (hot spots), in particular in the vicinities of mountain passes, which may be explained by meteorological factors as well as by the influence of local pollution.

1. Introduction

Lead belongs to the most widespread trace metals in the environment, abundant not only in urban and industrial regions, but also in the remote areas (Johansson et al., 2001; Kabata-Pendias, 2009; Nowack et al., 2001; Van der Gon and Appelman, 2009; Wang et al., 2009). On a global scale, the anthropogenic emissions of Pb in 20th century exceeded its natural emissions by several orders of magnitude (FOREGS, 2005; Nriagu and Pacyna, 1988; Pacyna and Pacyna, 2001; Steinnes et al., 1997). Long range atmospheric transport has resulted in Pb deposition to forest ecosystems, as the forest canopy acts as receptor for various air-borne pollutants (Hernandez et al., 2003; Kaste et al., 2005; Nowack et al., 2001; Steinnes and Friedland, 2006). This effect is particularly well expressed in the mountain forests, because mountain ranges play the role of orographic barriers against coming air masses (Błaś et al., 2008; Dore et al., 1999; Likuku, 2006; Zimmermann et al., 2006). Pb absorption by the forest canopy, followed by litterfall and its decomposition, lead to inhomogeneous Pb-enrichment of forest floor and humus (Gandois et al., 2010; Klaminder et al., 2005, 2008a,b; Takamatsu et al., 2010). Pb that accumulates in surface organic layers of soils may consequently affect their biological activity. High concentrations of toxic metals, including Pb, in soils has been considered as an important factor of European forest decline in the 1980s (Akselsson et al., 2004; Lamersdorf et al., 1991; Manion, 1981; Zöttl and Hüttl, 1986). That phenomenon affected seriously the mountain ranges along a Polish–Czech border, in particular the Izerskie Mts. and Karkonosze Mts., that for several decades received air-borne pollutants of both local and distant origin, including those from "Black Triangle" (Dąbrowska-Prot, 1999; Dore et al., 1999; Mazurski, 1986; Suchara and Sucharová, 2004). Although the emissions have already been significantly reduced (Bindler, 2011; Matschullat et al., 2000; Miller and Friedland, 1994; UNEP, 2010; Von Storch et al., 2003), and Pb concentrations in forest floor tend to decrease (Friedland et al., 1992; Huang et al., 2008; Watmough et al., 2005), the content of Pb in soils is not likely to change significantly within the following 200–300 years (Klaminder et al., 2008a,b). Moreover, it has been proved that at present concentrations in soils, Pb occurring in soil solution, particularly in the case of acidic soils rich in organic carbon, may be toxic to plants (Lamersdorf et al., 1991). Several authors reported unfavorable ecotoxicological effects caused by Pb present in soils in the concentrations 200 mg·kg^{-1} (Bååth, 1989; Johansson et al., 2001; Tyler et al., 1989) or even much lower (de Vries et al., 2007). Soil microorganisms and

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http://dx.doi.org/10.1016/j.geoderma.2012.08.022

mesofauna are assumed to be much more sensitive indicators of Pb toxicity than are plants, and major research groups have estimated the maximum Pb level tolerable for soil biota at 70–150 mg·kg^{-1} (Rademacher, 2003). The lowest critical values for chronic exposure of various terrestrial organisms are in the range of 50–60 mg·kg^{-1}, a value that has been suggested by the EU's scientific committee on environmental toxicology, CSTEE, as the Predicted No-Effect Concentration (UNEP, 2010).

It should be stressed that Pb solubility in acidic organic soil horizons is usually much higher relative to the overall mineral soils. Soil–liquid partitioning coefficients (Kd) predicted by Sauvé et al. (2000, 2003), who compiled numerous data from the literature, when normalized to pH 4.4, are in the case of Pb by over fifty-fold higher in mineral soils than in organic horizons of forest soils (mean Kd: 171214 vs. 3357). Furthermore, the values of Kd tend to decrease significantly with increasing DOM, which indicates that the risk of Pb mobilization, and therefore the overall environmental risk, should be considered as much higher in the case of organic horizons relative to mineral soils with comparable total Pb concentrations.

In order to control environmental conditions in the most precious and fragile ecosystems, the authorities of the Karkonosze National Park established a system of environmental monitoring (Danielewicz et al., 2002; Karczewska et al., 2006a). Several previous studies, carried out in Karkonosze Mts., confirmed that the soils in this mountain range contained enhanced concentrations of heavy metals (Dradrach, 2002; Drozd et al., 1996; Grodzińska et al., 1990; Kocowicz, 2002). Several studies proved that Pb concentrations in those soils locally exceeded 200 mg kg^{-1} (Dradrach, 2002; Kocowicz, 2002), whereas the average Pb concentrations in European soils, according to FOREGS (2005), are at the levels: 40.7 mg kg^{-1} in humus (forest floor or peat soils), 22.6 mg kg^{-1} in top soil layers, and 17.2 mg kg^{-1} in mineral subsoil.

The data reported from Karkonosze Mountains by various authors were in fact highly inconsistent, most likely because of high spatial variability typical for mountain soils. Therefore, the data based on existing literature could not be used to construct a general model of Pb concentrations in soils of the Karkonosze nor to identify the factors governing Pb concentrations or indicate the zones with the highest pollution. Total concentrations and distribution of heavy metals in mountain soils depend not only on natural factors: parent rock, bioaccumulation and the effects of soil forming processes, and external factors, such as input of air-borne pollutants and changing chemistry of dry and wet precipitation, but are also strongly modified by site-specific factors like forest canopy, forest edge effect, and microrelief, including tree logs, rocks and local depressions (Bergkvist et al., 1989; Chawla et al., 2010; Friedland et al., 1984; Karczewska et al., 2006b; Liptzin and Seastedt, 2010; Moyse and Fernandez, 1987; Weathers et al., 2000). Although the geology of soil parent rock is almost homogeneous in the whole area, as the mountain range is built mainly of granite, with the exception of its very eastern part, where metamorphic shists are predominating rocks, and that of local mineralization in the contact zone in some valleys (Mazur, 2002), the other factors that determine trace metals accumulation in soils vary significantly. Site altitude has been indicated by various authors as an important factor that influences absorption of air-borne pollutants and their concentrations in mountain soils. Increasing concentrations of trace metals, particularly of Pb, at higher elevations were described by Friedland et al. (1984) in Vermont Green Mts., Bogle et al. (1987) in Great Smoky Mts., Lovett and Kinsman (1990) in Appalachian Mts., Ragsdale and Berish (1988) at Coweeta, as well as by Smidt and Herman (2004) and Zechmeister (1995) in the Alps. Other authors, however, found the highest depositions and accumulation of metallic pollutants at low altitudes (the case of Central Pyrenees, reported by Bacardit and Camarero, 2010), or at medium elevations (Gerdol and Bragazza, 2006). Several other reports proved that there was no evident relationship between the altitude and Pb accumulation (Liptzin and Seastedt, 2010; McNulty et al., 1991; Petty and Lindberg, 1990).

The main objective of this study was to provide actual information on the concentrations and pools of Pb accumulated in the surface layers of soils in the Karkonosze Mts., in order to identify the most contaminated areas and assess a potential ecological risk caused by Pb presence in the soil environment. Another important purpose of the work was to recognize the main factors that affect Pb spatial distribution in mountain soils, in relation to contradicting conclusions from the literature.

2. Materials and methods

2.1. Site description and soil sampling

The study was carried out in the Karkonosze Mts, a range in the western Sudetes, SW Poland (Fig. 1). Soil samples for analysis of trace elements were collected from the depths of 0–10 cm and 10–20 cm, as well as from the forest litter (O), in 372 of 630 monitoring sites situated in a forested zone of the Karkonosze Mts., that covers an area of 4,400 ha. Sampling localities were situated possibly uniformly within the whole area of the Park, represented the broad spectrum of altitudes in the range 500–1350 m a.s.l. (Fig. 1), and were considered as representative for the whole array of monitoring sites. The samples of forest litter (ectohumus) were collected if only that layer was present on the surface of mineral soil. The depth of forest litter was measured and reported. The types of forest litter depended on local conditions and the kind of forest stands (mainly spruce and beech stands), and in most sites represented either a mor or moder type. The depth of forest litter varied in a broad range 0.3–13 cm. Soil coverage with rocks and large stones was assessed in each sampling site. Detailed description of sampling procedure was presented elsewhere (Karczewska et al., 2006a).

2.2. Laboratory analyses

All the samples were air dried and homogenized prior to laboratory analyses. The basic soil properties, including grain size distribution, soil pH (in 1 mol·dm^{-3} KCl) and organic matter (OM) content, were determined according to the methods described by Tan (2005). Oxidometric method was used for organic carbon determination in mineral samples, whereas in organic samples OM was determined by loss on ignition. Total concentrations of Pb were determined by FAAS after microwave digestion with “diverse” aqua regia. Three certified reference materials: WEPAL RSM 2709 (San Joaquin Soil), RSM 2711 (Montana Soil) and CMI 7004, as well as internal standards, were used for validation of analytical methods.

On the basis of Pb and OM concentrations, the pools of Pb accumulated in the surface soil layers, down to the depth of 20 cm, were calculated for each sampling site. Soil bulk density was assessed basing on the model by Prevost (2004), worked out on the basis the Canadian boreal forest, that predicts soil density from organic matter content. The suitability of this model for the conditions of forest soils in the Karkonosze Mts. was checked for a series of samples and the prediction error was assessed as lower than 20%. Soil bulk density in the forest litter and in the layers 0–10 cm and 10–20 cm varied in the ranges: 0.16–0.42, 0.17–1.05, and 0.17–1.56 g·cm^{-3}, respectively Soil coverage with rocks and large stones, evaluated in the field, was taken into account in calculations of Pb and OM pools.

2.3. Data analysis and statistics

Analysed were both the concentrations of Pb in soil layers: ectohumus (O), 0–10 cm and 10–20 cm, and pools of Pb accumulated in soils down to 20 cm. In order to check a dependence of Pb concentrations and pools in soils on the altitude, all the sites were divided into four operationally defined altitudinal zones: <750, 750–1000, 1000–1250, and >1250 m a.s.l. The data were analyzed using basic

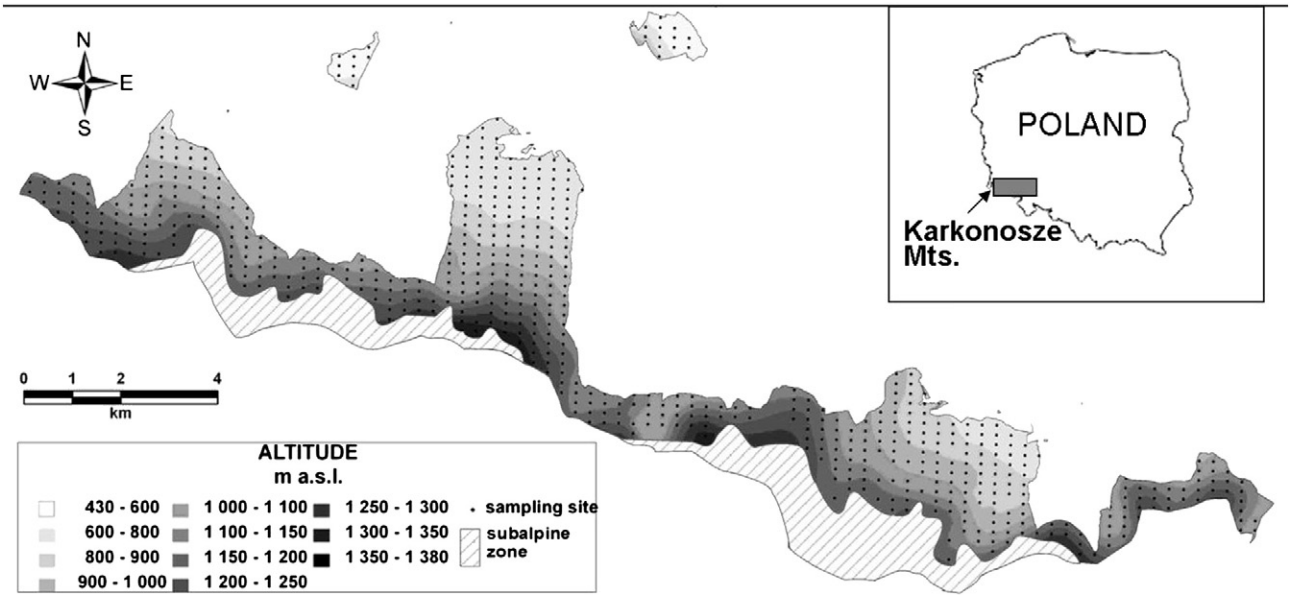

Fig. 1. Location of sampling sites in the Karkonosze National Park.

statistical methods: a one-way factorial analysis of variance (ANOVA) with Tukey's post hoc test, $P = 0.05$, as well as by linear regression. For each group of sites, the mean values and confidence ranges were calculated at the 0.05 probability level. Statistical analysis was performed using Statistica 9.0 (StatSoft Inc.) software package.

Additionally, an approach has been made to use geostatistical methods to analyze the spatial distribution of the data and to estimate the Pb concentrations and pools at unsampled locations. The statistical theory behind this analysis is the theory of regionalized variables, which means that the variance between two realizations of the random function depends only on the step width between those locations and not on the absolute location in space (Nielsen and Wendroth, 2003; Schaefer et al., 2010). Geostatistical analysis was carried out using the application Geostatistical Analyst in the software ESRI Arc Editor 10.0. Raster maps of Pb concentrations in separate layers (O, 0–10 cm, and 10–20 cm) and Pb pools in soils were created by data processing with the method of ordinary kriging, after their logarithmic transformation performed to obtain lognormal distribution. Empirical semivariograms were calculated at different lags and fitted with theoretical models by approximation with spherical models.

3. Results and discussion

3.1. Pb concentrations — general assessment

Particularly high concentrations of Pb were found in forest litter, where they varied in the range: 24–200 mg·kg^{-1} (mean value: 112 mg·kg^{-1}), and only rarely remained below 100 mg·kg^{-1}. The ranges of Pb concentrations in the layers 0–10 cm and 10–20 cm were 18.5–248 mg·kg^{-1} (mean: 82.8 mg·kg^{-1}), and 3.8–196 mg·kg^{-1} (mean: 46.3 mg·kg^{-1}), respectively (Table 1). Those data refer to both mineral soils and organic ones, i.e. those developed from peat, considered together as a common set. When excluding the organic soils (those containing over 30% organic matter), Pb concentrations in the mineral layers 0–10 and 10–20 cm appeared lower, in the ranges of: 26.3–149 mg·kg^{-1} (mean: 72.5 mg·kg^{-1}), and 4.0–119 mg·kg^{-1} (mean: 43.0 mg·kg^{-1}), respectively. High values of standard deviation (SD) and variability coefficient (Table 1) proved a high diversity of Pb concentrations, particularly in the deeper soil layers, i.e. 0–10 cm and 10–20 cm.

Pb concentrations in most samples of forest litter, and in the layer 0–10 cm, considerably exceeded a value of Polish soil quality standard for protected areas, established at the level of 50 mg·kg^{-1} (Decree by Ministry, 2002). Similar, i.e. 50–60 mg·kg^{-1}, are the values proposed by CSTEE as critical for chronic exposure of terrestrial organisms (UNEP, 2010). According to the current legislation, the cases of excessive pollutant concentrations in soils within protected areas, such as national parks, may be acceptable under the condition that they do not pose any detrimental effects on biological processes and do not cause any risk on ecosystem. Such a requirement, however, imposes a need of further research to be carried out, firstly in identified sites with the highest Pb concentrations in soils. The value of 50 mg·kg^{-1} was exceeded in 98% samples of forest litter, as well as in 77% and 29% samples collected from 0–10 cm and 10–20 cm. The concentration of 150 mg·kg^{-1}, defined as maximum Pb level torelable for soil biota (de Vries et al.,

Table 1
Statistical parameters characterizing variability of Pb concentrations in soils and their dependence on site altitude and organic matter concentrations. The cases of significant correlations at $P = 0.05$ are marked with asterisks.

Analysis	Parameter	Pb concentrations, mg·kg^{-1}			Pb pools, g·m^{-2}			
		O	0–10 cm	10–20 cm	O	0–10 cm	10–20 cm	Total
Descriptive statistics	Minimum	24	18.5	3.8	0.06	0.10	0.02	0.16
	Maximum	200	248	196	4.29	14.6	14.7	26.6
	Mean	112	82.8	46.3	0.91	3.13	2.70	6.20
	Median	105	68	41.8	0.88	2.81	2.47	5.92
	Standard deviation	35.3	42.1	26.1	0.51	2.43	2.08	4.32
	Variability coeff., %	31.6	50.8	56.4	56.1	77.6	77.0	69.7
Correlation coefficients	Altitude, m a.s.l.	0.11	0.12	0.00	−0.37	−0.06	−0.12	−0.16
	Organic matter, %	0.02	0.30*	0.40*	not determined			0.89*

2007; Rademacher, 2003), was exceeded in 14%, 9%, and 1% of the samples collected from forest litter, 0–10 cm, and 10–20 cm layers, respectively. Those high concentrations of Pb, combined with acidic soil reaction (mean pH values in the layers: 2.93, 3.15, and 3.41), described in another paper (Szopka et al., 2010), as well as high content of organic matter, may indicate enhanced risk of Pb mobilization and ecotoxicity, as elucidated by Sauvé et al. (2000, 2003). On the other hand, however, similar Pb concentrations in forest litter and surface soil layers were reported by other authors in other mountain ranges (FOREGS, 2005; Friedland et al., 1984, 1992; Reimann et al., 2009).

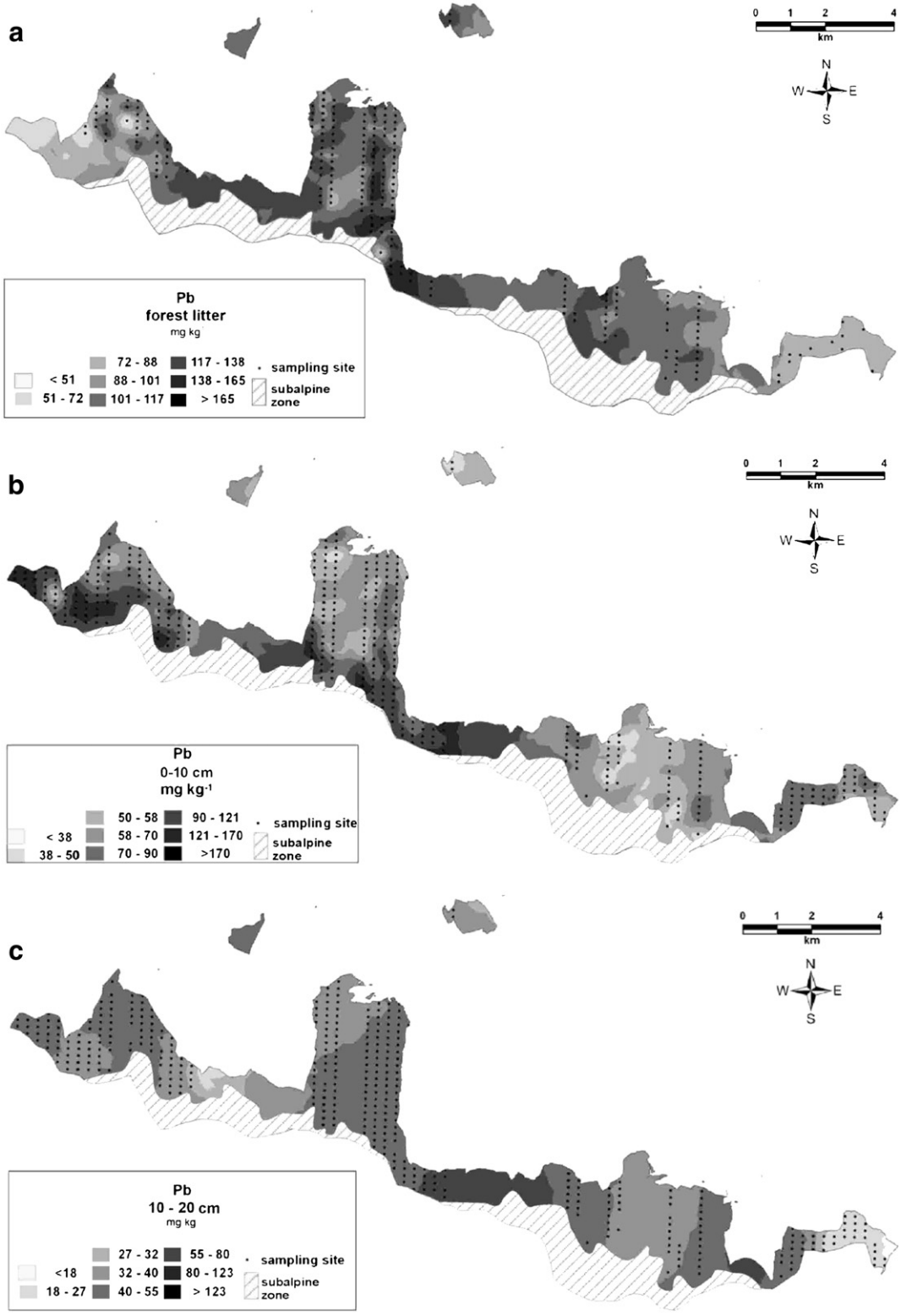

Fig. 2. Kriging maps of Pb concentrations (mg·kg^{-1}) in 3 soil layers: a) ectohumus (O), b) 0–10 cm and c) 10–20 cm.

3.2. Spatial distribution of Pb concentrations

The analysis of maps illustrating Pb concentrations in soil layers: ectohumus, 0–10 cm and 10–20 cm (Fig. 2a, b, c) indicated several areas where soils are particularly enriched in Pb. Those areas are very distinct in the case of ectohumus and 0–10 cm, however, similar patterns of spatial differentiation can also be recognized for the layer 10–20 cm. Closer examination of the matter let us identify those areas as situated in the vicinities of mountain passes, with relatively gentle slopes, preferential for the inflow of air masses. Higher concentrations of pollutants in bottom parts of the clouds, as well as high contribution of fog and rime to total deposition of pollutants (Błaś et al., 2008; Dore, et al., 1999) should be considered as important factors governing such a spatial distribution of Pb concentrations. Additionally, soils situated in such localities are usually very rich in organic matter, classified as Histic Leptosols or Skeleti-Histic Regosols. The layers 0–10 cm and 10–20 cm in those soils are often built of ombrothrophic peat material that strongly accumulates Pb. It should be stressed, however, that soil properties in those areas show extremely high local variability, caused mainly by rough microrelief and different coverage with rocks. Soil enrichment in Pb (particularly in the layers 0–10 cm and 10–20 cm), in the most eastern locality, may additionally be attributed to the kind of parent rock and possible local mineralization of rocks in that part of the mountain range (Mazur, 2002).

The results of statistical analysis did not indicate any simple relationships between the site altitude and Pb concentrations in any of the layers examined (Table 1). The concentrations of Pb in the 0–10 cm soil layer were in the highest altitudinal zone significantly higher than those in lower zones (Fig. 3a), but in the case of forest litter (O) and the layer 10–20 cm, a similar trend has not been found. Such an increase of Pb concentrations in the 0–10 cm layer with increasing altitude may be explained by an abundance of organic soils at the highest elevations, confirmed by the highest concentrations of organic matter in the 0–10 cm layer in the altitudinal zone >1250 m a.s.l. (Fig. 3b). Higher Pb concentrations in the layer 0–10 cm compared to forest litter result partly from natural processes of leaf and needle decomposition and transformation, in which organic matter-Pb compounds are usually stabilized via complexing, humification and adsorption to minerals, such as clay minerals and iron oxides (Laskowski et al., 1995; Lomander and Johansson, 2001; Sauvé et al., 2000, 2003; Scheid et al., 2009). In effect, the concentrations of Pb in the soil layer 0–10 cm, that contains well humified organic matter, are higher compared to freshly deposited forest litter. This effect is additionally strengthened by the facts that 1) atmospheric deposition gives a major input of Pb to forest litter compared with internal circulation through root uptake, translocation and litterfall (Hovmand et al., 2009), and 2) the amounts of Pb deposited onto the land in this part of Europe, decreased substantially in recent decades, both in a regional and in the local scale (Liana, 2010; RIEP, 2011; Twarowski et al., 2007; UNEP, 2010; von Storch et al., 2003).

3.3. Pb pools — general assessment

The values of Pb pools in the Karkonosze Mountains remain in a broad range of 0.16–26.6 $g \cdot m^{-2}$ and with the mean of 6.20 $g \cdot m^{-2}$ (Table 1) and should be considered as relatively high compared with the values reported by other authors (Table 2). It should be stressed, however, that the attempts to compare our findings with the data from the literature face some difficulties, because the other authors either reported the amounts of Pb accumulated in various horizons without supplying the details on their thickness (Klaminder et al., 2006), or calculated Pb pools accumulated within soil profiles of various depths. The depth of analyzed soil layer is in fact of crucial importance for data interpretation, as it has been proved that the pools of lithogenic Pb present in deeper soil horizons may be considerably high or even higher than those of air-borne origin (Table 2).

The pools of accumulated Pb determined in this study are by several-fold higher than those assessed on the basis of available meteorological data on former and present Pb deposition rates. Assuming that a significant part of Pb accumulated in the surface soil layers has derived from airborne deposition from the period 1950–2000, we estimated total amount of Pb deposited in those years, basing on the data from the literature and from meteorological stations situated at the foothills of the Karkonosze Mountains and on their highest peak, Śnieżka (IMGW, 2011; RIEP, 2011; Schulte-Rentrop et al., 2005; Twarowski et al., 2007; UNEP, 2010; von Storch et al., 2003). Reported annual Pb depositions varied in this period in the range of 5–50 $mg \cdot m^{-2}$, reaching the highest values in the 1960s, 1970s and 1980s, while they presently remain at the level of 0.2–1.5 $mg \cdot m^{-2}$. The data from the western part of the mountain range are by 30–50% higher than those from its central part. Total amount of Pb deposited in the years 1950–2000, calculated on the basis of meteorological data, has been assessed as 0.9–1.5 $g \cdot m^{-2}$. The results of our study yielded much higher values, with the mean pool of Pb accumulated in the layer down to 20 cm estimated as 6.2 $g \cdot m^{-2}$. Such a discrepancy may have resulted from a seeder–feeder effect (Dore et al., 1999) that makes the concentrations of pollutants in rime and fog much higher than those in rain and snow water, as well as

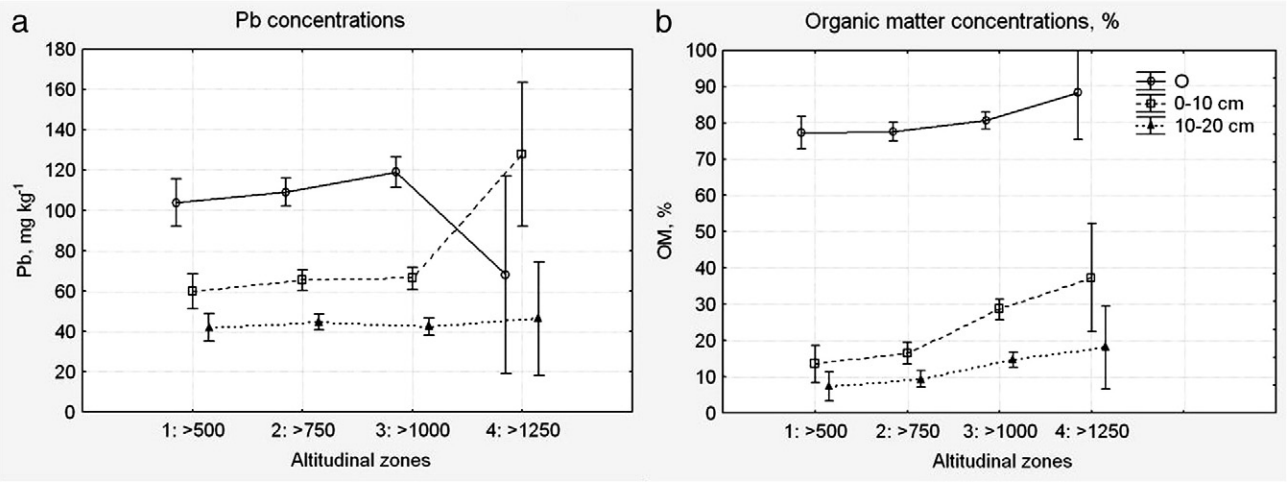

Fig. 3. Lead concentrations (a) and organic matter concentrations (b) in four altitudinal zones: <750, 750–1000, 1000–1250, and >1250 m a.s.l. Whiskers stand for the confidence ranges, $P = 0.95$ (determined by Tukey's post-hoc test).

Table 2
The pools of anthropogenic and lithogenic Pb in the surface layers of mountain forest soils, according to various authors.

Site localities	N	Depth, cm Horizon	Mean Pb pools, $g \cdot m^{-2}$	Comments	Source
Northeastern US	No data	Anthropogenic Pb accumulated in soil	1.7 > 3.0	At lower elevation At higher el. (> 1200 m)	Miller and Friedland (1994)
		Down to 90 cm	0.7–3.1 1.9–7.9	From pollution Natural	Brännvall et al. (2001)*
Sweden, Boreal forests	11	in that amount: Ectohumus (O) Eh + Bs (to 15–35 cm)	0.1–1.0 1.13–3.92	(100% from pollution) (45–90% from pollution)	
Germany, Fichtelgebirge, Lehstenbach	3	Ectohumus (O) Mineral soil 0–60 cm	1.75 22.2	Mean, wetland and upland granitic soils, elevation 700–700 m	Huang and Matzner (2004)
Germany, Fichtelgebirge, Coulissenhieb	1	Ectohumus (O) Mineral soil 0–30 cm	2.39 11.34	Elevation: 800 m	Huang et al. (2008)
North Sweden	1	Down to 35 cm	0.67 3.54	From pollution Geogenic	Klaminder et al. (2005)
North Sweden: Kulbäcksliden	11	Ectohumus (O) Ah E Bs	0.28 ± 0.07 0.14 ± 0.03 0.36 ± 0.20 0.55 ± 0.32	O and E layers – of different thickness. Bs = upper 4 cm of B-horizon	Klaminder et al. (2006) *
Japan, Kanto	17	Down to 14 cm	0.98 ± 0.40 − 1.49 ± 0.62	Anthropogenic Pb	Takamatsu et al. (2010)
Northern England	~40	Peat: 10 / 20 cm (wetter & drier sites)	0.96–22.8	0.1 M HNO_3-soluble Pb (geochemically active)	Tipping et al. (2010)

* Approximate data read from the figures.

from horizontal precipitation that may be by several-fold higher than wet deposition (Błaś et al., 2008; Dore et al., 1999).

3.4. Effect of altitude on Pb pools

The tendency of increasing Pb concentrations in soils with growing altitudes, described above, was not reflected by the increase of Pb pools accumulated in all layers down to the depth of 20 cm, which, in fact, decreased with increasing elevations (Fig. 4a). The mean values of Pb pools were: 8.02, 6.75, 5.80, and 4.04 $g \cdot m^{-2}$, respectively, in the zones ordered according to increasing altitudes. The significance of differences between the mean Pb pools in the highest and lowest altitudinal zones has been confirmed statistically at the probability level of $P = 0.05$.

A similar relationship referred also to the stocks of organic matter which were in the highest altitudinal zone significantly lower than those in the lowest zone (Fig. 4b). Such dependence was different from our first expectations, as severe environmental conditions at higher altitudes were supposed to suppress organic matter decomposition and favour its accumulation in the form of thick mor layers, typical for subalpine soils (Kirschbaum, 1995; Reichstein et al., 2000). However, several authors pointed out that large stocks of humified organic matter may accumulate also in mineral horizons of forest soils situated in lower altitudinal zones, where biomass production is usually much more intensive (Garten and Hanson, 2006; Kammer et al., 2009; Sheikh et al., 2009; Zhang et al., 2011; Zhu et al., 2010). Therefore, the net balance of organic matter accumulation / decomposition in subalpine environments depends on site specific conditions and cannot be simply predicted (Davidson and Janssens, 2006; Drewnik, 2006; Garcia-Pausas et al., 2007). The stocks of soil organic matter accumulated in the highest part of the forested Karkonosze zone, turned out to be lower compared to its lower parts.

3.5. Pb pools as related to organic matter

Our results confirm that the amounts of Pb accumulated in the very upper layers, i.e. in a forest litter (O) and in 0–10 cm layer, undoubtedly of predominant air-borne origin (Brännvall et al., 2001;

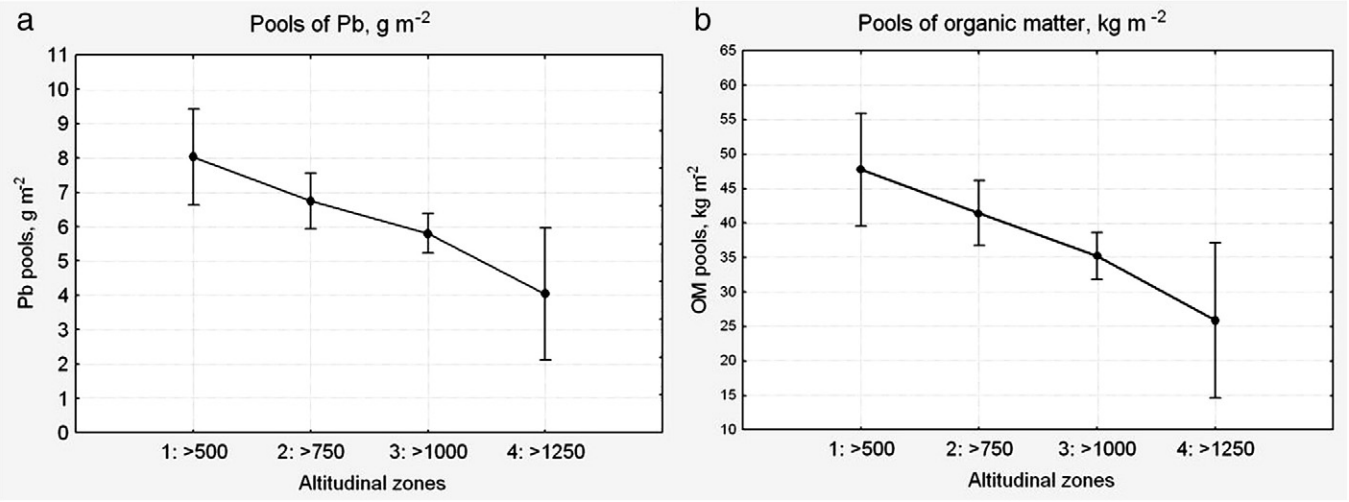

Fig. 4. Lead (a) and organic matter (b) pools accumulated in soils (down to 20 cm) in four altitudinal zones: <750, 750–1000, 1000–1250, and > 1250 m a.s.l. Whiskers stand for the confidence ranges, $P = 0.95$ (determined by Tukey's post-hoc test).

Hovmand et al., 2009), depend strongly on organic matter storage. Regression analysis based on Pearson correlation coefficient, indicated that the concentrations of Pb in the layers 0–10 cm and 10–20 cm were linearly dependent on the content of organic matter in soil (Table 1), similarly as reported by several authors from other mountain ranges (Donisa et al., 2000; Kaste et al., 2005; Wang et al., 2009), although the correlation coefficients were relatively low: $R = 0.30$ and 0.40, respectively. Particularly strong was, however, the dependence of Pb and organic matter pools in soils ($R = 0.89$; $R^2 = 0.791$), illustrated in the scatter-plot (Fig. 5a). It turns out that the pool of stored organic matter is a key factor governing the amounts of Pb accumulated in soils of the Karkonosze Mts. A 3D-chart illustrating the variability of Pb pools depending on the amount of OM and altitude (Fig. 5b), confirms that the importance of altitude was in fact negligible, whereas the pools of Pb depended strongly on the stocks of organic matter. Calculated ratio of Pb to OM pools varied in a relatively broad range 29–401 mg Pb g^{-1} OM, with an average value of 148 g Pb g^{-1} OM, and was considerably higher than the values reported by Liptzin and Seastedt (2010) for the Rocky Mts, assessed at the level 23.6–43.6 mg Pb g^{-1} OM. This difference should probably be attributed to the higher amounts of anthropogenic depositions in industrialized regions of central Europe, compared to central United States (Bindler, 2011; Huang et al., 2008; UNEP, 2010).

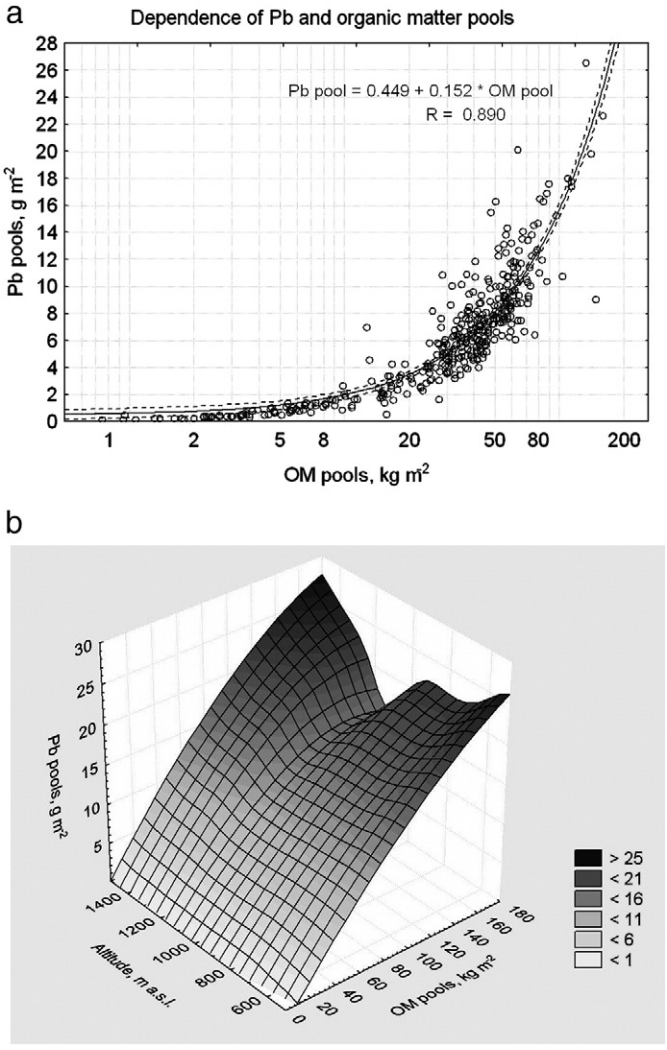

Fig. 5. Dependence of Pb pools accumulated in soils on OM pools in soils. a) scatterplot based on all sampling sites, b) 3D graph considering OM and altitude as the factors governing Pb spatial distribution in soils.

3.6. Pb accumulation in soil layers

We have found that the largest amounts of Pb were present in the layer 0–10 cm (19–92% of the total pool down to 20 cm), with its mean share of 51%. The contributions of Pb present in forest litter were much lower, in the range 1.2–38% (the mean 15%). Those contributions corresponded to the amounts of 0.06–4.29 $g \cdot m^{-2}$ (mean 0.91 $g \cdot m^{-2}$) Pb accumulated in forest litter, and considerably higher Pb pools stored in the layers 0–10, and 10–20 cm: 3.13, and 2.70 $g \cdot m^{-2}$, , respectively. The question should be asked now whether, and to which extent, Pb deposited to the soil surface has been translocated or leached from soils. Some authors reported high mobility of Pb in acidic forest soils, attributed to the strong affinity of Pb to dissolved or colloidal organic matter (Luster et al., 2006; Sauvé et al., 2003). On the basis of general knowledge on Pb biogeochemistry and its strong binding with humified organic matter (Adriano, 2001; Huang and Matzner, 2004; Kabata-Pendias, 2009; Scheid et al., 2009), we can suppose that the low pools of Pb accumulated in O layer reflect a reduced Pb deposition from the atmosphere, in comparison with previous periods, rather than the effects of Pb leaching. This will, however, remain only an assumption, as this study did not involve direct examination of Pb solubility and mobility.

3.7. Spatial distribution of Pb pools

The map illustrating a spatial distribution of Pb pools in the Karkonosze Mts. (Fig. 6) confirms great local variability of this parameter. Since the amounts of organic matter accumulated in the forest soils, particularly in the mountains, indicate a strong local variability, caused by well developed microrelief, various conditions of water stagnation and snow melting, and other factors governing litter accumulation or decomposition (Bruckner et al., 1999; Conen et al., 2005; Liski, 1995; Schulze et al., 2009; Spielvogel et al., 2009), therefore, consequently, a spatial distribution of Pb pools shows similar, strongly heterogeneous patterns. The attempts to apply simple geostatistical methods to examine Pb distribution in the soils of Karkonosze Mts. were in fact unsuccessful, because of documented extremely high local variability of the parameters examined. Semivariograms of Pb concentrations and pools proved their high differentiations and lack of clear spatial relationships. Assessed local influences were lower than 10 m, i.e. by manifold smaller than the spans between the neighbouring sampling sites in the monitoring network. Similar effects of high variability in Pb distribution in the mountain or forest soils were also reported by other authors (Bacardit and Camarero, 2010; Schaefer et al., 2010; Schöning et al., 2006; Spielvogel et al., 2009). Many authors have pointed out the importance of microrelief, soil type, diversity of snowpack properties, the effects of the canopy, filtering effect of forest edge and upper treeline, as well as several other local factors, that may considerably affect the annual deposition of Pb from the atmosphere, particularly at higher elevations (Chawla et al., 2010; Gandois et al., 2010; Hernandez et al., 2003; Kobler et al., 2010; Likuku, 2006; Liptzin and Seastedt, 2010; Weathers et al., 2000). In spite of high local variability, we have distinguished some areas with the highest amounts of Pb accumulated in soils. Such areas were identified as wide and relatively flat mountain passes (in the central and western parts of the mountain range), as well as northern, low-lying areas of the Park, subject to local emissions of air-borne Pb. Any comprehensive model for the transport of air masses has not been worked out for the Karkonosze Mts. yet, but several available meteorological data confirm that south-western winds bring round 50% of air borne pollutants (Liana, 2010), and the mountain range acts as an orographic barrier that makes contaminant depositions much larger in the south-western, wind-exposed, part of the mountains than in the other parts. Several papers confirmed that the greatest amounts of pollutants were deposited in the western part of the Karkonosze range (Błaś et al., 2008; Hůnová et al., 2004; Suchara and Sucharová, 2004). The mechanisms of seeder–feeder effect

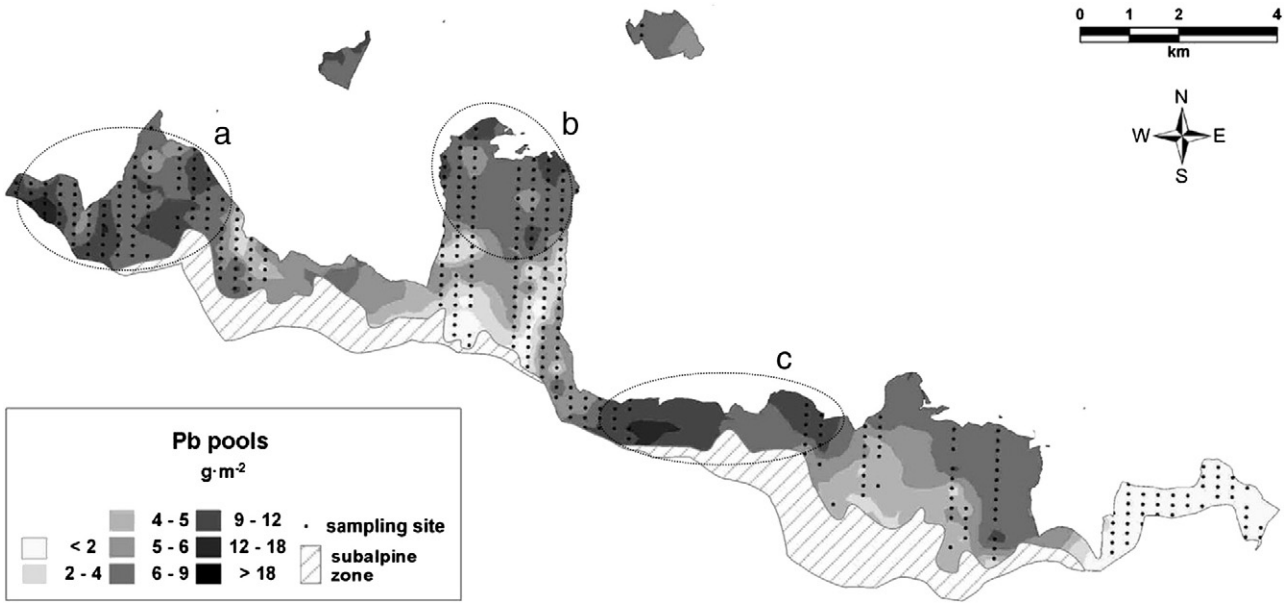

Fig. 6. The pools of Pb ($g \cdot m^{-2}$) accumulated in forest litter and soil layers down to 20 cm (a kriging map). The areas indicated with dotted lines as (a), (b) and (c) are the hot spots with the highest Pb pools. Related discussion — in the text.

and horizontal precipitation (Błaś et al., 2008; Dore et al., 1999) may be responsible for particularly high Pb deposition in the areas of vast mountain passes compared to wind-protected slopes, situated at the same altitude and hidden behind the mountain tops.

Our study confirms a well established knowledge about strong heterogeneity and high local variability of Pb distribution in the mountain forest soils, caused both by the large heterogeneity of organic matter accumulation, and most likely also by local differences in deposition of air-borne Pb. Such a high variability should be always taken into account when conducting research on biogeochemistry of trace metals, in particular Pb, in other forested mountainous areas.

4. Conclusions

Lead concentrations in surface soil horizons, both in the ectohumus (forest litter) and in the 0–10 cm layer of soils in the Karkonosze Mts., exceed considerably the value of 50 $mg \cdot kg^{-1}$ set up as a soil quality standard for the areas of protected nature, and therefore more detailed examination of those soils will be needed, particularly in the areas with identified high Pb accumulation. Pb concentration of 150 $mg \cdot kg^{-1}$, often referred to as maximum tolerable for soil biota, is exceeded in 14% of sites examined, and this fact, together with acidic soil reaction and high content of soil organic matter, indicates enhanced risk of Pb ecotoxicity. The highest pools of Pb are accumulated in the layer 0–10 cm. The total Pb pools down to 20 cm are several times higher than those assessed on the basis of available metheorological data.

Lead concentrations and pools in soils depend significantly on soil organic matter content, and both indicate high variability and mosaic patterns. Therefore, their spatial distributions cannot be described and predicted by simple geostatistical models. The study indicated, however, some areas with particularly high pools of accumulated Pb, namely the wide mountain passes, as well as several low locations situated close to residential areas. In such areas, a further study is needed to determine Pb speciation in soils and to more precisely assess the risk of Pb mobilization and potential harmful effects on ecosystems.

Acknowledgements

The authors express their gratitude to the authorities of the Karkonosze National Park for granting the opportunity to carry out this study. The study was supported by Ministry of Science and Higher Education in the frames of the project NN305 037334.

References

Adriano, D.C., 2001. Trace elements in the terrestrial environments: biogeochemistry, bioavailability and risks of metals, 2nd ed. Springer, New York.
Akselsson, C., Ardö, J., Sverdrup, H., 2004. Critical loads of acidity for forest soils and relationship to forest decline in the Northern Czech Republic. Environmental Monitoring and Assessment 98, 363–379.
Bååth, E., 1989. Effects of heavy metals in soil on microbial processes and populations (a review). Water, Air, & Soil Pollution 47, 335–379.
Bacardit, M., Camarero, L., 2010. Atmospherically deposited major and trace elements in the winter snowpack along a gradient of altitude in the Central Pyrenees: the seasonal record of long-range fluxes over SW Europe. Atmospheric Environment 44, 582–595.
Bergkvist, B., Folkeson, L., Berggren, D., 1989. Fluxes of Cu, Zn, Pb, Cd, Cr, and Ni in temperate forest ecosystems. A literature review. Water, Air, & Soil Pollution 47 (33), 217–286.
Bindler, R., 2011. Contaminated lead environments of man: reviewing the lead isotopic evidence in sediments, peat, and soils for the temporal and spatial patterns of atmospheric lead pollution in Sweden. Environmental Geochemistry and Health 33, 311–329.
Błaś, M., Sobik, M., Twarowski, R., 2008. Changes of cloud water chemical composition in the Western Sudety Mountains. Atmospheric Research 87 (2008), 224–231.
Bogle, M.A., Turner, R.R., Baes III, C.F., 1987. Lead in vegetation, forest floor, and soils of the Great Smoky Mountains National Park. Environment International 13 (3), 235–246.
Brännvall, M.L., Bindler, R., Emteryd, O., Renberg, I., 2001. Vertical distribution of atmospheric pollution lead in Swedish boreal forest soils. Water, Air, & Soil Pollution: Focus 1, 357–370.
Bruckner, A., Kandeler, E., Kampichler, C., 1999. Plot-scale spatial patterns of soil water content, pH, substrate-induced respiration and N mineralization in a temperate coniferous forest. Geoderma 93, 207–223.
Chawla, F., Steinmann, Ph., Pfeifer, H.R., Froidevaux, P., 2010. Atmospheric deposition and migration of artificial radionuclides in Alpine soils (Val Piora, Switzerland) compared to the distribution of selected major and trace elements. Science of the Total Environment 408, 3292–3302.
Conen, F., Zerva, A., Arrouays, D., Jolivet, C., Jarvis, P.G., Grace, J., Mencuccini, M., 2005. The carbon balance of forest soils: detectability of changes in soil carbon stocks in temperate and boreal forests. In: Griffiths, H., Jarvis, P.J. (Eds.), The carbon balance of forest biomes. Garland Science/BIOS Scientific Publ, pp. 233–247. Chapter 11.
Dąbrowska-Prot, E., 1999. Environmental characteristics of the Karkonosze Mts. region and the problems of spruce forest decline. Polish Journal of Ecology 47, 365–371.
Danielewicz, W., Raj, A., Zientarski, J., 2002. Forest Ecosystems of the Karkonosze National Park. Karkonoski Park Narodowy, Jelenia Góra.
Davidson, E.A., Janssens, I.A., 2006. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. Review. Nature 440, 165–173.
de Vries, W., Lofts, S., Tipping, E., Meili, M., Groenenberg, J.E., Schütze, G., 2007. Impact of soil properties on critical concentrations of cadmium, lead, copper, zinc and

mercury in soil and soil solution in view of ecotoxicological effects. Reviews of Environmental Contamination and Toxicology 191, 47–89.
Decree by Ministry, 2002. Decree by Ministry of Environment on Soil and Land Quality Standards, Poland. Official Journal of Laws 176 (Item 1453, Dated 9 Sept., 2002).
Donisa, C., Mocanu, R., Steinnes, E., Vasu, A., 2000. Heavy metal pollution by atmospheric transport in natural soils from the northern part of Eastern Carpatians. Water, Air, & Soil Pollution 120, 347–358.
Dore, A.J., Sobik, M., Migała, K., 1999. Patterns of precipitation and pollutant deposition in the western Sudete mountains, Poland. Atmospheric Environment 33, 3301–3312.
Dradrach, A., 2002. Concentrations and forms of heavy metals in soil of subalpine zone of Karkonosze Mountains in the region of ecological disaster. Part. 1. Trace elements in soils in the subalpine zone of the Karkonosze Mountains (Poland). Zeszyty Naukowe Akademii Rolniczej we Wrocławiu 445 (84), 47–63 (in Polish, with English abstract).
Drewnik, M., 2006. The effect of environmental conditions on the decomposition rate of cellulose in mountain soils. Geoderma 132, 116–130.
Drozd, J., Licznar, M., Weber, J., 1996. The content of heavy metals in the ectohumus horizons of soils of degraded forest ecosystem in the Karkonosze Mountains. Polish Journal of Soil Science 29, 33–38.
FOREGS, 2005. Geochemical Atlas of Europe. In: Salminen, R. (Ed.), Part 1 — Background information, methodology and maps. EuroGeoSurveys. Geological Survey of Finland, Espoo.
Friedland, A.J., Johnson, A.H., Siccama, T.G., 1984. Trace metal content of the forest floor in the Green Mountains of Vermont: spatial and temporal patterns. Water, Air, & Soil Pollution 21, 161–170.
Friedland, A.J., Craig, B.W., Miller, E.K., Herrick, G.T., Siccama, T.G., Johnson, A.H., 1992. Decreasing lead levels in the forest floor of the Northeastern USA. Ambio 21, 400–403.
Gandois, L., Tipping, E., Dumat, C., Probst, A., 2010. Canopy influence on trace metal atmospheric inputs on forest ecosystems: speciation in throughfall. Atmospheric Environment 44, 824–833.
Garcia-Pausas, J., Casals, P., Camarero, L., Huguet, C., Sebastià, M.T., Thompson, R., Romanyà, J., 2007. Soil organic carbon storage in mountain grasslands of the Pyrenees: effects of climate and topography. Biogeochemistry 82, 279–289.
Garten Jr., C.T., Hanson, P.J., 2006. Measured forest soil C stocks and estimated turnover times along an elevation gradient. Geoderma 136, 342–352.
Gerdol, R., Bragazza, L., 2006. Effects of altitude on element accumulation in alpine moss. Chemosphere 64 (5), 810–816.
Grodzińska, K., Szarek, G., Godzik, B., 1990. Heavy metal deposition in Polish national parks — changes during ten years. Water, Air, and Soil Pollution 49, 409–419.
Hernandez, L., Probst, A., Probst, J.L., Ulrich, E., 2003. Heavy metals in some French forest soils: evidence of distribution, origin and controlling factors. Science of the Total Environment 312, 195–219.
Hovmand, M.F., Nielsen, S.P., Johnsen, I., 2009. Root uptake of lead by Norway spruce grown on ^{210}Pb spiked soils. Environmental Pollution 157, 404–409.
Huang, J.H., Matzner, E., 2004. Biogeochemistry of trimethyllead and lead in a forested ecosystem in Germany. Biogeochemistry 71, 125–139.
Huang, J.H., Kalbitz, K., Matzner, E., 2008. Mobility of trimethyllead and total lead in the forest floor. Soil Science Society of America Journal 72, 978–984.
Hůnová, I., Prošková, J., Hesoun, R., Kurfürst, P., Ostatnická, J., 2004. 3. Atmosférická depozice na území České republiky. 3. Atmospheric Deposition in the Area of Czech Republic 2003. In: Šantroch, J. (Ed.), Znečištění ovzduší na území České Republiky v roce 2003. ČHMÚ, Praha.
IMGW 2011 – Database of air pollution in Poland (1963–2011). Institute of Meteorology and Water Management - National Research Institute. Unpublished data.
Johansson, K., Bergback, B., Tyler, G., 2001. Impact of atmospheric long range transport of lead, mercury and cadmium on the Swedish forest environment. Water, Air, & Soil Pollution 3–4, 279–297.
Kabata-Pendias, A., 2009. Trace elements in soils and plants, 4th ed. CRC Press.
Kammer, A., Hagedorn, F.H., Shevchenko, I., Leifeld, J., Guggenberger, G., Goryacheva, T., Rigling, A., Moiseev, P., 2009. Treeline shifts in the Ural mountains affect soil organic matter dynamics. Global Change Biology 15 (6), 1570–1583.
Karczewska, A., Bogacz, A., Kabała, C., Szopka, K., Duszyńska, D., 2006a. Methodology of soil monitoring for a forested zone of the Karkonosze National Park — with reference to the diversity of soil properties. Polish Journal of Soil Science 39 (2), 131–142.
Karczewska, A., Szopka, K., Kabała, C., Bogacz, A., 2006b. Zinc and lead in forest soils of Karkonosze National Park. Polish Journal of Environmental Studies 15 (2a), 336–342.
Kaste, J.M., Friedland, A.J., Miller, E.K., 2005. Potentially mobile lead fractions in montane organic-rich soil horizons. Water, Air, & Soil Pollution 167 (1–4), 139–154.
Kirschbaum, M.F., 1995. The temperature dependence of soil organic matter decomposition, and the effect of global warming on soil organic C storage. Soil Biology and Biochemistry 27, 753–760.
Klaminder, J., Bindler, R., Emteryd, O., Renberg, I., 2005. Uptake and recycling of lead by boreal forest plants: quantitative estimates from a site in northern Sweden. Geochimica et Cosmochimica Acta 69 (10), 2485–2496.
Klaminder, J., Bindler, R., Emteryd, O., Appleby, P., Grip, H., 2006. Estimating the mean residence time of lead in the organic horizon of boreal forest soils using 210-lead, stable lead and a soil chronosequence. Biogeochemistry 78, 31–49.
Klaminder, J., Bindler, R., Renberg, I., 2008a. The biogeochemistry of atmospherically derived Pb in the boreal forest of Sweden. Applied Geochemistry 23, 2922–2931.
Klaminder, J., Bindler, R., Rydberg, J., Renberg, I., 2008b. Is there a chronological record of atmospheric mercury and lead deposition preserved in the mor layer (O-horizon) of boreal forest soils? Geochimica et Cosmochimica Acta 72 (3), 703–712.
Kobler, J., Fitz, W.J., Dirnböck, T., Mirtl, M., 2010. Soil type affects migration pattern of airborne Pb and Cd under a spruce-beech forest of the UN-ECE integrated monitoring site Zöbelboden, Austria. Environmental Pollution 158, 849–854.
Kocowicz, A., 2002. Soil reaction and acidity versus content and distribution of selected heavy metals. Zeszyty Problemowe Postepow Nauk Rolniczych 482, 282–286 (in Polish, with English abstract).
Lamersdorf, N.P., Godbold, D.L., Knoche, D., 1991. Risk assessment of some heavy metals for the growth of Norway spruce. Water, Air, & Soil Pollution 57–58 (1), 535–543.
Laskowski, R., Niklinska, M., Maryanski, M., 1995. The dynamics of chemical-elements in forest litter. Ecology 76, 1393–1406.
Liana, E., 2010. Pollutant deposition as a function of atmospheric circulation in the Karkonosze Mts. Opera Concortica 47 (Suppl. 1), 9–22 (in Polish).
Likuku, A.S., 2006. Wet deposition of ^{210}Pb aerosols over two areas of contrasting topography. Environmental Research Letters 1, 1–6.
Liptzin, D., Seastedt, T.R., 2010. Regional and local patterns of soil nutrients at Rocky Mountain treelines. Geoderma 160, 208–217.
Liski, J., 1995. Variation in soil organic carbon and thickness of soil horizons within a boreal forest stand — effect of trees and implications for sampling. Silva Fennica 29 (4), 255–266.
Lomander, A., Johansson, M.B., 2001. Changes in concentrations of Cd, Zn, Mn, Cu and Pb in spruce (*Picea abies*) needle litter during decomposition. Water, Air, & Soil Pollution 132, 165–184.
Lovett, G.M., Kinsman, J.D., 1990. Atmospheric pollutant deposition to high-elevation ecosystems. Atmospheric Environment, Part A 24 (11), 2767–2786.
Luster, J., Zimmermann, S., Zwicky, C.N., Lienemann, P., Blaser, P., 2006. Heavy metals in Swiss forest soils: modification of lithogenic and anthropogenic contents by pedogenetic processes, and implications for ecological risk assessment. Geological Society, London, Special Publications 266, 63–78.
Manion, P.D., 1981. Tree disease concepts. Prentice Hall Inc., New Jersey.
Matschullat, J., Maenhaut, W., Zimmermann, F., Fiebig, J., 2000. Aerosol and bulk deposition trends in the 1990's, Eastern Erzgebirge, Central Europe. Atmospheric Environment 34, 3213–3221.
Mazur, S., 2002. Geology of the Karkonosze-Izera Massif: an overview. Mineralogical Society of Poland, Special Papers 20, 22–34.
Mazurski, K.R., 1986. The destruction of forests in the Polish Sudetes Mountains by industrial emissions. Forest Ecology and Management 17, 303–315.
McNulty, S.G., Aber, J.D., Boone, R.D., 1991. Spatial changes in forest floor and foliar chemistry of spruce-fir forests across New England. Biogeochemistry 14 (1), 13–29.
Miller, E.K., Friedland, A.J., 1994. Lead migration in forest soils: response to changing atmospheric inputs. Environmental Science and Technology 28, 662–669.
Moyse, D.W., Fernandez, I.J., 1987. Trace metals in the forest floor at Saddleback mountain, Maine, in relation to aspect, elevation, and cover type. Water, Air, & Soil Pollution 34 (4), 385–397.
Nielsen, D.R., Wendroth, O., 2003. Spatial and temporal statistics — sampling field soils and their vegetation. Geoecology Textbook. Catena Verlag, Reiskirchen.
Nowack, B., Obrecht, J.M., Schluep, M., Schulin, R., Hansmann, W., Köppel, V., 2001. Elevated lead and zinc contents in remote alpine soils of the Swiss National Park. Journal of Environmental Quality 30, 919–926.
Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace-metals. Nature 333, 134–139.
Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environmental Reviews 44 (9), 269–298.
Petty, W.H., Lindberg, S.E., 1990. An intensive 1-month investigation of trace metal deposition and throughfall at a mountain spruce forest. Water, Air, & Soil Pollution 53, 213–226.
Prevost, M., 2004. Predicting soil properties from organic matter content following mechanical site preparation of forest soils. Soil Science Society of America Journal 68, 943–949.
Rademacher, P., 2003. Atmospheric heavy metals and forest ecosystems — Current Implementation of ICP Monitoring Systems and Contribution to Risk Assessment. Report commissioned by: ICP Forests — Programme Coordinating Centre.Institute for World Forestry. Federal Research Centre for Forestry and Forest Products, Hamburg, Germany.
Ragsdale, H.L., Berish, C.W., 1988. Trace metals in the atmosphere, forest floor, soil, and vegetation. Forest hydrology and ecology at Coweeta. : Ecological Studies, Volume 66. Springer-Verlag, New York, pp. 367–380.
Reichstein, M., Bednorz, F., Broll, G., Kätterer, T., 2000. Temperature dependence of carbon mineralization: conclusions from a long-term incubation of subalpine soil samples. Soil Biology and Biochemistry 32, 947–958.
Reimann, C., Englmaier, P., Flem, B., Gough, L., Lamothe, P., Nordgulen, Ř., Smith, D., 2009. Geochemical gradients in soil O-horizon samples from southern Norway: natural or anthropogenic? Applied Geochemistry 24, 62–76.
RIEP, 2011. Regional Inspectorate for Environment Protection (RIEP) in Wrocław. Report on State of Environment in Lower Silesia in 2010 (in Polish).
Sauvé, S., Hendershot, W., Allen, H.E., 2000. Solid-solution partitioning of metals in contaminated soils: dependence on pH, total metal burden, and organic matter. Environmental Science & Technology 34, 1125–1131.
Sauvé, S., Manna, S., Turmel, M.C., Roy, A.G., Courchesne, F., 2003. Solid-solution partitioning of Cd, Cu, Ni, Pb, and Zn in the organic horizons of a forest soil. Environmental Science & Technology 37, 5191–5196.
Schaefer, K., Einax, J.W., Simeonov, V., Tsakovski, S., 2010. Geostatistical and multivariate statistical analysis of heavily and manifoldly contaminated soil samples. Analytical and Bioanalytical Chemistry 396, 2675–2683.
Scheid, S., Günthardt-Goerg, M.S., Schulin, R., Nowack, B., 2009. Accumulation and solubility of metals during leaf litter decomposition in non-polluted and polluted soil. European Journal of Soil Science 60, 613–621.

Schöning, I., Totsche, K.U., Kögel-Knabner, I., 2006. Small scale spatial variability of organic carbon stocks in litter and solum of a forested Luvisol. Geoderma 136, 631–642.
Schulte-Rentrop, A., Costa-Cabral, M., Vink, R., 2005. Modelling the overland transport of lead deposited from the atmosphere in the Elbe catchment over four decades (1958–1995). Water, Air, & Soil Pollution 160, 271–291.
Schulze, K., Borken, W., Muhr, J., Matzner, E., 2009. Stock, turnover time and accumulation of organic matter in bulk and density fractions of a Podzol soil. European Journal of Soil Science 60, 567–577.
Sheikh, M.A., Kumar, M., Bussmann, R.W., 2009. Altitudinal variation in soil organic carbon stock in coniferous subtropical and broadleaf temperate forests in Garhwal Himalaya. Carbon Balance and Management 4, 6.
Smidt, S., Herman, F., 2004. Evaluation of air pollution-related risks for Austrian mountain forests. Environmental Pollution 130, 99–112.
Spielvogel, S., Prietzel, J., Auerswald, K., Kögel-Knabner, I., 2009. Site-specific spatial patterns of soil organic carbon stocks in different landscape units of a high-elevation forest including a site with forest dieback. Geoderma 152, 218–230.
Steinnes, E., Friedland, A.J., 2006. Metal contamination of natural surface soils from long-range atmospheric transport: existing and missing knowledge. Environmental Reviews 14 (3), 169–186.
Steinnes, E., Allen, R.O., Petersen, H.M., Rambaek, J.P., Varskog, P., 1997. Evidence of large scale heavy-metal contamination of natural surface soils in Norway from long-range atmospheric transport. Science of the Total Environment 205, 255–266.
Suchara, I., Sucharová, J., 2004. Current atmospheric deposition loads and their trends in the Czech Republic determined by mapping the distribution of moss element contents. Journal of Atmospheric Chemistry 49, 503–519.
Szopka, K., Kabała, C., Karczewska, A., Bogacz, A., Jezierski, P., 2010. Pools of available nutrients in soils from different altitudinal forest zones located in a monitoring system of the Karkonosze Mountains National Park (Poland). Polish Journal of Soil Science 43, 173–188.
Takamatsu, T., Watanabe, M., Koshikawa, M.K., Murata, T., Yamamura, Sh., Hayashi, S., 2010. Pollution of montane soil with Cu, Zn, As, Sb, Pb, and nitrate in Kanto, Japan. Science of the Total Environment 408, 1932–1942.
Tan, K.H., 2005. Soil sampling, preparation, and analysis, 2nd ed. CRC Press.
Tipping, E., Rothwell, J.J., Shotbolt, L., Lawlor, A.J., 2010. Dynamic modelling of atmospherically-deposited Ni, Cu, Zn, Cd and Pb in Pennine catchments (northern England). Environmental Pollution 158, 1521–1529.
Twarowski, R., Gondola, T., Liana, E., Wostek-Zagraba, K., 2007. Deposition of pollutants from atmosphere with precipitation in the Giant Mountains in the years 1994–2004. In: Šturza, J., Knapik, R. (Eds.), Geoekologické problémy Krkonoš. Sborn. Mez. Věd. Konf., říjen 2006, Svoboda n. Úpou: Opera Corcontica, 44/1, pp. 213–225 (in Polish).
Tyler, G., Balsberg-Pahlsson, A.M., Bengtsson, G., Bååth, E., Tranvik, L., 1989. Heavy-metal ecology of terrestrial plants, microorganisms and invertebrates. A review. Water, Air, & Soil Pollution 47, 189–215.
UNEP, 2010. United Nations Environment Programme, Chemicals Branch, DTIE. Final review of scientific information on lead. Version of December 2010.
Van der Gon, H.D., Appelman, W., 2009. Lead emissions from road transport in Europe: a revision of current estimates using various estimation methodologies. Science of the Total Environment 407 (20), 5367–5372.
Von Storch, H., Costa-Cabral, M., Hagner, C., Feser, F., Pacyna, J., Pacyna, E., Kolb, S., 2003. Four decades of gasoline lead emissions and control policies in Europe: a retrospective assessment. Science of the Total Environment 311, 151–176.
Wang, X., Cheng, G., Zhong, X., Li, M., 2009. Trace elements in sub-alpine forest soils on the eastern edge of the Tibetan Plateau, China. Environmental Geology 58, 635–643.
Watmough, S.A., Dillon, P.J., Epova, E.N., 2005. Metal partitioning and uptake in central Ontario forests. Environmental Pollution 134, 493–502.
Weathers, K.C., Lovett, G.M., Likens, G.E., Lathrop, R., 2000. The effect of landscape features on deposition to Hunter Mountain, Catskill Mountains, New York. Ecological Applications 10, 528–540.
Zechmeister, H.G., 1995. Correlation between altitude and heavy metal deposition in the Alps. Environmental Pollution 89 (1), 73–80.
Zhang, Y., Duan, B., Xian, J.R., Korpelainen, H., Li, C., 2011. Links between plant diversity, carbon stocks and environmental factors along a successional gradient in a subalpine coniferous forest in Southwest China. Forest Ecology and Management 262, 361–369.
Zhu, B., Wang, X., Fang, J., Piao, S., Shen, H., Zhao, S., Peng, C., 2010. Altitudinal changes in carbon storage of temperate forests on Mt Changbai, Northeast China. Journal of Plant Research 4, 439–452.
Zimmermann, F., Matschullat, J., Brüggemann, E., Plessow, K., Wienhaus, O., 2006. Temporal and elevation-related variability in precipitation chemistry from 1993 to 2002, Eastern Erzgebirge, Germany. Water, Air, & Soil Pollution 170, 123–141.
Zöttl, H.W., Hüttl, R.F., 1986. Nutrient supply and forest decline in south-west Germany. Water, Air, & Soil Pollution 31, 449–462.