TRACE ELEMENTS IN SOILS OF UPPER ZONE OF SPRUCE FOREST ON SZRENICA MOUNT AND THE KOWARSKI GRZBIET RANGE IN THE KARKONOSZE MOUNTAINS

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Abstract

New regular examination of soil contamination with trace elements (Pb, Zn, Cu) in the upper zone of spruce forest in the western (Mount Szrenica) and eastern (Kowarski Grzbiet range) Karkonosze Mountains was carried out as part of the monitoring network of forest ecosystems in the Karkonosze Mountains National Park. Soil samples were taken at the following three depths: forest litter (the whole layer), 0-10 cm and 10-20 cm. Clearly raised concentrations of lead were found, particularly in forest litter (mean $83.2 \text{ mg} \cdot \text{kg}^{-1}$) and in horizons 0-10 cm (mean $73.3 \text{ mg} \cdot \text{kg}^{-1}$). Copper and zinc occurred in smaller amounts, in the ectohumus layer $47.5 \text{ mg} \text{ Zn} \cdot \text{kg}^{-1}$ and 23.8 mg Cu $\cdot \text{kg}^{-1}$ (mean concentrations), and in the layer 0-10 cm $- 33.7 \text{ mg} \text{ Zn} \cdot \text{kg}^{-1}$ and 19.9 mg Cu $\cdot \text{kg}^{-1}$. Zinc and copper concentrations in soils of the upper spruce forest zone did not increase with altitude above mean sea level, and were slightly higher in the eastern part of Karkonosze Mts. (the Kowarski Grzbiet). Concentrations of lead were apparently higher in the western part of the Karkosze Mts. and increased with altitude AMSL.

Key words: soils, trace elements, upper spruce-zone, the Karkonosze Mountains.

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ZAWARTOŚĆ PIERWIASTKÓW ŚLADOWYCH W GLEBACH REGLA GÓRNEGO SZRENICY I KOWARSKIEGO GRZBIETU W KARKONOSZACH

Abstrakt

W strefie regla górnego Karkonoszy zachodnich (Szrenica) i wschodnich (Kowarski Grzbiet) przeprowadzono analizę zanieczyszczenia gleb pierwiastkami śladowymi (Pb, Zn, Cu) opartą na monitoringu ekosystemów leśnych Karkonoskiego Parku Narodowego. W tym celu pobrano próbki z trzech głębokości: próchnicę nadkładową (w całej miąższości), 0-10 cm i 10-20 cm. Stwierdzono wyraźnie podwyższoną zawartość ołowiu, szczególnie w próchnicach nadkładowych (średnio 83,2 mg·kg⁻¹) i warstwie 0-10 cm (średnio 73,3 mg·kg⁻¹). Miedź i cynk występują w mniejszych ilościach, w ektohumusie średnio 47,5 mg Zn·kg⁻¹ i 23,8 mg Cu·kg⁻¹, a w warstwie 0-10 cm średnio 33,7 mg Zn·kg⁻¹ i 19,9 mg Cu·kg⁻¹. Zawartość cynku i miedzi w glebach regla górnego nie zwiększa się z wysokością n.p.m. i jest nieco wyższa we wschodniej części Karkonoszy (Kowarski Grzbiet) niż w zachodniej (Szrenica). Zawartość ołowiu jest wyraźnie wyższa w zachodniej części Karkonoszy i zwiększa się z wysokością n.p.m.

Słowa kluczowe: gleby, pierwiastki śladowe, regiel górny, Karkonosze.

INTRODUCTION

Concentration of trace elements in soils is often used as a universal indicator of degree of anthropogenic transformations in ecosystems. The ecological disaster that struck the entire Sudety Mountains in the1980s became an important impulse for undertaking extensive research on causes of that catastrophy and its effect on the soil environment (DOBROWOLSKA 1995, DROZD et al. 1998a,b, KABAŁA 1995, 1998). The rapid decay of dense spruce forests caused transformation of natural habitats and the expansion of grasses, which influenced the circulation of trace elements in transformed ecosystems (DROZD et al. 1998a).

One of the consequences of a large-scale decay of forests in the Karkonosze Mountains was an implementation of permanent monitoring of forest ecosystems. The main task of the monitoring system is (i) establishing the present state of mountain ecosystems and (ii) observation of the ongoing changes resulting from anthropogenic and natural influences (MoL et al. 1998,VAN DULIVENBOODEN 1998).

The aim of this work was to determine the gradients of spatial variability in concentrations of selected trace elements (Pb, Zn and Cu) in surface horizons of soils and forest litter in the upper zone of spruce forests in the Polish part of the Karkonosze Mountains. The analysis is based on data from the monitoring system of forest ecosystems collected in years 2006--2007. For comparison, two peripheral areas were selected: the Kowarski Grzbiet Range in the eastern periphery of the Karkonosze Mountains and Mount Szrenica in the western part of the Karkonosze Mountains (Figure 1).

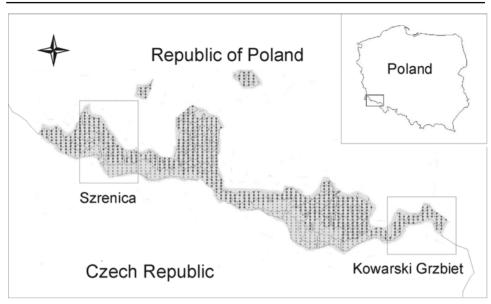


Fig. 1. Location of the investigated objects in Karkonosze Mountain National Park

METHODS

The system of forest environment monitoring in the Karkonosze Mountain National Park consists of 630 spherical areas located in forest zone and 230 areas in subalpine zone, arranged in a regular grid 200×300 m. Pedological field research was conducted in September 2006 on the Kowarski Grzbiet Range and in August 2007 on Mount Szrenica. The choice of these two mountain ranges situated on the eastern and western edges of the Karkonosze Mountains is supposed to enable the comparison of soil degradation degree as a function of the distance to the sources of atmospheric pollution, located mainly along the Czech – German – Polish border, west of the Karkonosze Mountains. Polluted air masses are moving to the Karkonosze area mainly with westerly and south-westerly winds.

Samples for analysis were generally taken in the upper zone of spruce forest in 40 monitoring areas located on the Kowarski Grzbiet Range, at the altitude of 1000-1270 m above mean sea level, and in 41 monitoring areas located on Szrenica Mount, at the altitude of 1000-1240 m AMSL. Predominating soils in these areas are Podzols, mostly with redoximorphic features (*stagnic*) and peat accumulation, locally extremely gravelly or stony (*hyperskeletic*). Podzols occurs in a mosaic with Histic Gleysols and Fibric Histosols, where the thickness of organic layer is up to 60 cm. All areas under investigation are covered with spruce mountain forests, degraded to some extent. The density of tree canopy runs up to 60-80% in the lower part of the upper zone of spruce forests, while above the altitude of 1000 m AMSL it is reduced to 40-50%. Above 1100 m AMSL, in the zone of a very strong decline of spruce stands, the density of tree canopy is generally less than 20%. Lower density of tree crowns enables the expansion of grasses and perennial plants, therefore as the altitude rises, the percentage of the surface covered with dense mossy and grassy undergrowth also increases. The entire area under investigation has very diversified microrelief resulting from numerous fallen trees with excavated roots, which strongly influences the spatial variability of the surface layers of soils and surface accumulation of organic matter.

The average field sample for analyses was prepared by mixing at least four primary soil samples taken with a pedological sampler in places randomly arranged over the monitored surface. Samples of forest litter and samples of soil taken at depths 0-10 cm and 10-20 cm were stored and analyzed separately (KARCZEWSKA et al. 2006). The ectohumus layer (forest litter) was not sampled in areas covered with grass communities, where spruce stands were extremely degraded and thinned out.

Soil and litter samples were prepared for analyses by drying, grinding and sieving through a 2 m mesh sieve. The following analyses were made on all samples: soil texture (in mineral samples taken at the depth 10-20 cm), pH in 1 mol·dm³ KCl – potentiometrically, organic carbon (in mineral and organic-mineral samples) – by Tiurin method, loss on ignition (in organic samples), as well as total content of trace elements (Pb, Cu and Zn) – with atomic absorption spectrometry after wet mineralization of soil samples in a mixture of nitric and hydrochloric acids in a ratio of 3:1. Mineralization was made in a microwave stove, in closed, high-pressure Teflon vessels.

Results of analyses were analyzed statistically with using Statistica 8 package (StatSoft Inc., Tulsa, USA). Statistical significance of differences between mean concentrations of trace elements was assessed using Duncan's test of multiple comparisons (at p < 0.05) with an appointment of homogeneous groups of means.

RESULTS AND DISCUSSION

Soils on the analyzed monitoring surfaces have a texture of loamy sand and sandy loam and acid or strongly acid reaction (Table 1). Values of pH apparently increase with depth into the soil profile: the lowest pH is in the ectohumus layer (average pH_{KCl}=2.92), in the layer 0-10 cm it averages pH_{KCl}=3.16, and in the layer 10-20 cm it achieves pH_{KCl}=3.40. No statistically significant differences were found between the reaction of analogous

Localization	Kowa	arski Grzbiet 1	ange	Mount Szrenica		
Soil layer	ectohumus	0-10 cm	0-20 cm	ectohumus	0-10 cm	0-20 cm
$\mathrm{pH}_{\mathrm{KCl}}$	2.92*a 2.6-3.4**	3.17^a 2.7-3.7	3.40^a 2.9-4.1	2.92^a 2.5-3.3	3.15^a 2.7-3.9	3.39^a 2.9-4.9
Organic carbon, %	-	15.3a 7.4-55.2	8.0^a 2.45-49.2	-	18.6 ^a 3.9-49.2	10.8^a 1.9-44.6
Loss on ignition, %	83.2 ^a 62.3-96.4	-	-	81.8 ^a 64.6-95.4	-	-
Zn, mg·kg ⁻¹	47.5 ^a 34.5-61.0	33.7 ^a 10.4-94.3	30.6 ^a 5.8-97.2	35.4^b 29.0-42.0	34.2 ^a 13.0-90.0	24.9 ^a 7.5-66.7
Cu, mg∙kg ⁻¹	23.8^a 12.5-31.7	19.9^a 4.8-40.3	15.0 ^a 1.9-38.4	16.9^b 11.3-24.0	14.6^a 3.7-29.8	8.8^b 2.0-23.0
Ph. mg.kg-1	83.2^{a}	73.3^{a}	36.7^{a}	110.7^{b}	97.4^{b}	46.2^{b}

Soil reaction, content of organic matter and total concentrations of trace elements in soils of the Kowarski Grzbiet and the Mount Szrenica

Pb, mg · kg⁻¹

62.3-96.4

Explanation: *arithmetic mean, **range (minimum – maximum), a, b – homogeneous groups of Duncan's multiple range test (compared mean values of particular properties in the same soil layer on the Kowarski Grzbiet range and the Mount Szrenica)

18.5-137.6

3.8-88.2

69.0-180.0

39.2-225.5

soil horizons on the Kowarski Grzbiet Range and on Mount Szrenica (Table 1). However, slightly higher pH of litter and surface layers of soils was noticed in the zone of the expansion of grass vegetation (above 1100 m AMSL) as compared to the zone of dense spruce forests (<1100 m AMSL). Even though these differences are not statistically significant, they confirm earlier reports indicating lower pH of soils under existing spruce stands than of analogous soils existing under strongly degraded forests (DROZD et al. 1998a, Kabała 1998).

Soils under investigation have in general a high content of organic matter in surface layers, averaging from 15.3 to 18.6% in 0-10 cm layers, and from 8.0 to 10.8% in 10-20 cm layers (Table 2). Such a high content of organic carbon in surface layers, above 12%, may qualify them as belonging to organic materials. The presented mean values may, however, be somewhat inflated as a result of including peat soils (Histosols) into calculation. Accumulation of organic matter in the layers 0-10 cm of soils under degraded forests can be also remnants of forest litter covered with dense grass vegetation. Somewhat higher accumulation of organic matter in ectohumus layers of soils was identified on the Kowarski Grzbiet, whereas soils of Mount Szrenica contained more organic matter in layers 0-10 and 10-20 cm (Table 1). However, these differences are not statistically significant at p < 0.05. Moreover, no essential and statistically significant differences in organic matter accumulation were found between altitude zones. The content of organic

Table 1

3.8 - 150.5

Table 2	Grzbiet and Mount Szrenica in altitude zones
	Soil reaction, content of organic matter and trace elements in soils of the Kowars] ≤1100 and >1000 m AMSL

Localization		K	Kowarski Grzbiet range	rzbiet rang	çe				Mount S	Mount Szrenica		
Soil layer	ectoh	ectohumus	0-10 cm) cm	0-20	0-20 cm	ectoh	ectohumus	0-10	0-10 cm	0-20 cm	cm
Altitude zone, m a.s.l.	≤1100	>1100	≤1100	>1100	≤1100	>1100	≤1100	>1100	≤1100	>1100	≤1100	>1100
pH _{KCl}	2.85^{a}	2.91^a	3.16^a	3.20^v	3.46^a	3.38^a	2.93^a	3.00^{a}	3.16^a	3.13^a	3.38^{a}	3.40^a
Organic carbon, $\%$	-		21.6^a	19.8^a	9.9^{a}	6.9^{a}	1		14.3^b	24.3^{c}	7.2^a	12.6^b
Loss on ignition, $\%$	80.2^{a}	89.1^{a}					81.0^{a}	79.8^{a}		-		
Zn, mg \cdot kg ⁻¹	48.6^a	46.6^a	33.8^a	33.7^{a}	32.7^a	29.5^{a}	35.8^{b}	34.4^b	33.5^a	34.7^a	26.8^a	23.1^a
Cu, mg·kg ⁻¹	21.5^a	24.5^a	19.6^a	20.0^{a}	16.9^{a}	14.1^a	16.6^b	15.7^b	13.5^b	15.7^b	8.2^b	9.4^b
Pb, $mg \cdot kg^{-1}$	71.6^{a}	83.4^a	73.3^a	73.4^a	45.4^a	32.5^b	117.3^{b}	109.0^b	83.2^{b}	109.8c	42.4^a	49.7^{a}
Explanation: a, b, c – homogeneous groups of Duncan's multiple range test (compared mean values of particular properties	- homogen	eous grout	os of Dunc	an's multic	le range te	est (compa	red mean	values of p	articular r	properties		

ž 5. 5 n D D Explanation. In the same soil layer on the Kowarski Grzbiet range and Mount Szrenica in altitude zones ≤1100 i >1000 m AMSL)

matter in the ectohumus layer increases with altitude on the Kowarski Grzbiet Range but decreases on Mount Szrenica (Table 2). And inversely, in the layers 0-10 and 10-20 cm of soils on Mount Szrenica the accumulation of organic matter was apparently larger in the altitude zone >1100 m AMSL than in the zone <1100 m AMSL (Table 2). These differences may not be a consequence of the stronger decline of tree stands in the zone > 1100 m AMSL, but of greater frequency of peat soils in soil cover at this high altitude zone.

In all the analyzed soils layers, lead was found to be exceeding the content of zinc, which is the first symptom of soil pollution and imbalance of natural proportions between trace elements. Anthropogenic accumulation of lead in the soil environment is confirmed by wide differences between the minimum and the average content (almost ten-fold in the layers 0-10 cm), as well as between the content in deeper mineral layers (10-20 cm) and in forest litter. The lead content was the highest in ectohumus layers (mean value 83.2 mg·kg⁻¹ of dry mass on the Kowarski Grzbiet Range, and 110.7 mg·kg⁻¹ d.m. on Mount Szrenica), and decreased with depth into the soil profile to the level of 36.7 mg \cdot kg⁻¹ (the Kowarski Grzbiet) and 46.2 mg·kg⁻¹ (Mount Szrenica) in the layer 10-20 cm (Table 1). In all the tested soil horizons, the concentration of lead was apparently larger on Mount Szrenica (differences between mean values are statistically significant), which agrees with some earlier reports documenting stronger pollution of soils in the western part of the Karkonosze Mountains (DROZD et al. 1998a) and confirms the permanence of soil contamination with heavy metals. Stability of lead content in soil environment rich in organic matter is related to high affinity of lead to humic substances. Correlation of total lead content and organic carbon was confirmed by good statistical significance of coefficients (Table 3). Concentration of lead in the zone >1100 m

Table 3

Localization	Kowarski Grzbiet range	Mount Szrenica				
Zn	0.34**	0.12				
Cu	0.26*	0.36**				
Pb	0.55**	0.48**				

Coefficients of correlation between organic matter and concentration of trace elements in soils of the Kowarski Grzbiet and Mount Szrenica

Explanation: * significant at *p*<0.05, **significant at *p*<0.01

AMSL was elevated in some soil layers as compared to the zone <1100 m AMSL. It was, however, simultaneously related to differences in the content of organic matter in the compared layers (Table 2). A new, important observation was made in the zone >1100 m AMSL on Mount Szrenica, where the Pb content in ectohumus and the layers 0-10 cm was levelling, which con-

tradicts the regularities described earlier by DROZD et al. in. (1998a), and confirms reduced immission of lead to the mountain environments during the last decade (KARCZEWSKA et al. 2006).

In contrast to lead, concentrations of zinc and copper did not vary so significantly, both among soil layers and in spatial arrangement. Even though zinc and copper theoretically have weak affinity to humic substances and did not correlate with organic matter (Table 3), their highest concentrations were found in the ectohumus layer: average zinc contents were, respectively, 47.5 and 35.4 mg kg⁻¹, and average copper contents – 23.8 and 16.9 mg kg⁻¹, respectively on the Kowarski Grzbiet and on Mount Szrenica. The lowest concentrations, as compared among analyzed soil layers, were found in the layer 10-20 cm, where mean zinc contents were 30.6 and 24.9 mg kg⁻¹, and copper contents – 15.0 and 8.8 mg kg⁻¹, respectively. Concentrations of zinc were somewhat higher in soils of the Kowarski Grzbiet than on Mount Szrenica, but statistically significant difference was calculated only in the case of ectohumus layers (Table 1). Copper concentrations were both apparently and statistically higher on the Kowarski Grzbiet, particularly in ectohumus and in the layer 10-20 cm (Table 1). It is probably related to the kind of parent material rather than to the pollution. The Kowarski Grzbiet consists of metamorphic schists, often enriched with trace elements, while Mount Szrenica is build of granite, weathering into regoliths poor in trace metals. Some differences were found between zinc and copper concentrations in compared analogous soil levels in two altitude zones (above and below 1100 m AMSL), but in all cases the differences are statistically insignificant (Table 2). It means that there is no relation between the altitude or the degree of forest decline and the contents of Zn and Cu in soils of the upper zone of spruce forests of the Karkonosze Mountains. We found as well that differences between maximal and minimal concentrations, or minimal and average contents were not so large as in the case of lead (Table 1). The concentrations of Zn and Cu in the layers 10-20 cm, particularly in soils containing small amounts of organic matter, were similar to the so-called geochemical background established for soils derived from "acid" igneous and metamorphic rocks (KABATA-PENDIAS, PENDIAS 1992). It was concluded that the content and distribution of zinc and copper in soils of the upper zone of spruce forest in the Karkonosze Mountains are not suffering from contamination with these elements.

CONCLUSIONS

1. Elevated contents of lead in forest litters (ectohumus) and surface layers of soils in the upper zone of spruce forest in the Karkonosze Mountains indicate contamination with lead, whereas contents of zinc and copper are recognised as close to the geochemical background. 2. Significantly higher concentrations of lead in soils of Mount Szrenica (as compared to the Kowarski Grzbiet) indicate stronger anthropogenic influence on the ecosystems in the western part of the Karkonosze Mountains. Somewhat higher concentrations of zinc and copper in soils of the Kowarski Grzbiet are probably related to a geochemical abundance of metamorphic gneisses and schists building of the eastern Karkonosze Mountains.

3. Comparison of the currently measured concentrations of lead and those reported in 1990s indicate a similar level of soil contamination with this metal and lack of any improvement in the quality of soil environment during this period.

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