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Content diversity of Zn, Pb and Cd in *Lithic Leptosols* of the Tatra National Park (Poland)

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Abstract. In Lithic Leptosols of the Tatra National Park total contents of zinc, lead and cadmium were determined. Studied soils were most often characterized by high or very high content of these metals and elevated values of accumulation coefficients (AC) resulting from soil pollution by dust containing heavy metals. A large concentration of heavy metals most frequently occurred in soils derived from carbonate rocks, which were richest in organic matter and had higher pH and a higher degree of sorption complex base saturation than soils developed from igneous and metamorphic rocks. The content of heavy metals in parent rocks hardly influenced their amount in studied soils. In all soils derived from carbonate rocks, heavy metal content increased with increasing altitude, whereas in soils developed from igneous and metamorphic rocks it dacreased.

Key words: lead, zinc, cadmium, the Tatra National Park, Lithic Leptosols

Introduction

Lithic Leptosols are shallow soils, having continuous hard rock within 10 cm of the soil surface (Word reference base for soil resources 1998). In the Tatra Mountains they occur mainly in the subnival vegetation zone, but they also cover a considerable area in the alpine and subalpine zone and form soil cover of montane zone rocks (Komornicki and Skiba 1996). They developed from various parent rocks vastly differing in their zinc, lead and cadmium content, high content of these metals is characteristic of Tatra amphybolites, biotitic granodiorites, Cretaceous marls and Triassic shales as well as for myllonites and graphitoidal slates. Considerable quantities of lead and cadmium often occur in limestones and dolomites, while granodiorites have great amounts of zinc. Among Tatra, rocks white granites and granito-gneisses reveal the smallest amounts of heavy metals. Very low contents of zinc and lead have been also registered in Triassic quartzites (Miechówka and Niemyska-Łukaszuk 2002).

Beside parent rocks, sources of heavy metals in Tatra soils include atmospheric pollution, primarily of anthropogenic origin (Schejbal-Chwastek and Tarkowski 1988, Niemyska-Łukaszuk and Miechówka 1999), which finds its way into soils mainly in rainfall. Heavy metal content in Tatra soils also depends on soil properties (Niemyska-Łukaszuk *et al*. 1998, Niemyska-Łukaszuk *et al*. 1999, Niemyska-Łukaszuk and Miechówka 1999), influenced by various soil forming factors, among which climatic factors are considered the most important in higher zones (Skiba 1985).

The present work aimed to determine the effect of lithopedogenetic factors and soil location on the content of zinc, lead and cadmium in *Lithic Leptosols* of the Tatra National Park. The causes of heavy metal content diversification in these soils may be easier to interpret than those in better developed soils because, the soil profiles most frequently consist of a single weakly developed AC horizon whose depth does not exceed 10 cm.

Material and Methods

Material sampled from AC 73 horizons of 73 *Lithic Leptosols* profiles was used in the work. Of these, 32 derived from igneous and metamorphic rocks and 41 from carbonate rocks. Depending on the substratum these occurred under various non-forest plant communities. Calcareous grasslands of *Seslerietalia varie* order occurred on carbonate rocks and myllonites, whereas on acidic igneous and metamorphic rocks there were acidophilic swards of *Caricetalia curvulae* order (Matuszkiewicz 2001). Studied soils were situated at various altitudes above sea level, in different climatic zones and on slopes of different inclination and aspect (Fig. 1, Table 1).

In earth parts (<2 mm) of the studied soils pH was determined in 1 mol · dm^{-3} KCl solution using the electrometric method, carbonate CO_2 concentration using Scheibler's volumetric method, organic carbon content by oxidation with potassium bi-chromate (VI) by modified Tiurin's method, total nitrogen was essayed by Kjeldahl's method, degree of sorption complex base saturation by determining individual cations (Ca^{+2}, Mg^{+2}, K^{+}, Na^{+}) extracted with 0.5 mol · dm^{-3} ammonium chloride, hydrolytic acidity was assessed in 1 mol · dm^{-3} calcium acetate by Kappen's method and total contents of zinc, lead and cadmium in air-dried samples after soil digestion in a mixture of concentrated nitric and perchloric acids, using ASA method in PU 910 Phillips spectrophotometer with acetylene and air flame used for atomization.

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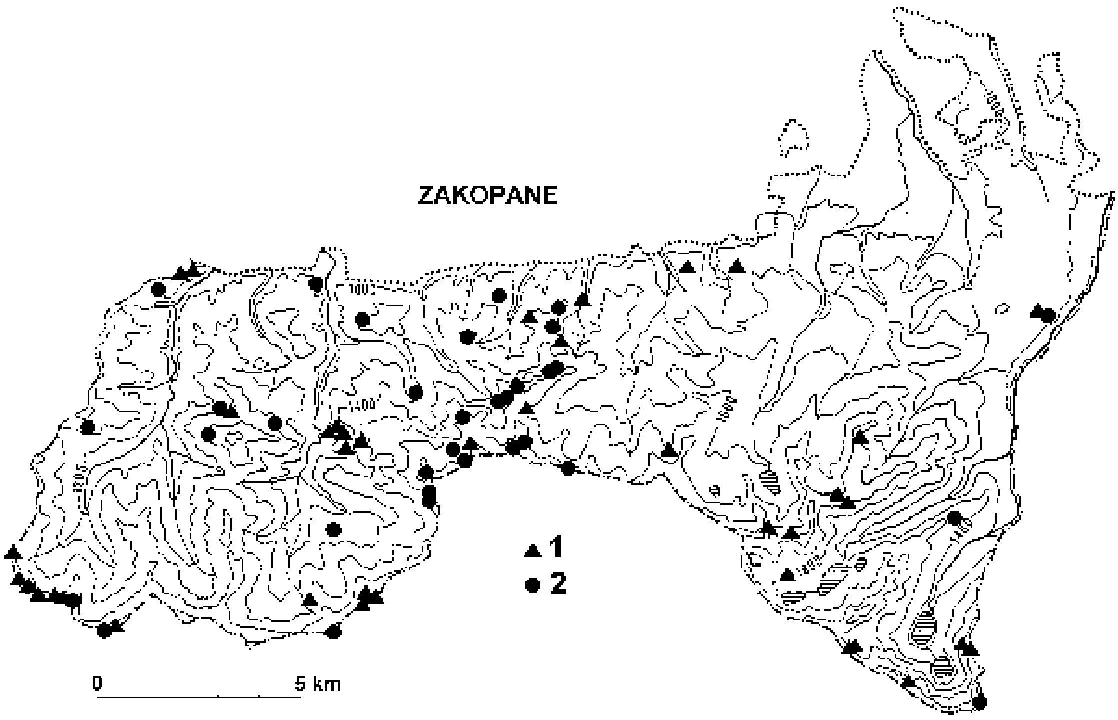

Fig. 1. Location of investigated soil profiles in the area of the Tatra National Park: 1 – soils with low or medium Zn, Pb or Cd contents, 2 - soils with high or very high Zn, Pb or Cd contents.

Climatic belts (m a.s.l.)	Mean annual temperature and precipitation	Parent rocks
Temperate cool (700-1,100)	4 - 6 ˚C 1,000-1,400 mm	quartzites (1), dolomites and limestones (5), marls (1)
Cool (1,100-1,550)	2 - 4 ˚C 1,400-1,800 mm	dolomites and limestones (15), marl shales and marls (3)
Very cool (1,550-1,850)	0 - 2 ˚C 1,600-1,800 mm	granodiorites (4), pegmatite granites (1), aplite granites (1), quartzites (1), dolomites and limestones (10), marl shales (1)
Temperate cold (1,850-2,200)	0 - 2 ˚C 1,800-1,750 mm	granodiorites (9), aplite granites (4), andesine-biotite (4) and biotite (4), gneisses, mylonites (4), limestones (6)
Cold (2,200-2,663)	-2 - -4 ˚C 1,750-1,625 mm	granodiorites (1)

Table 1. Climatic zones from which samples were collected.

Content estimation	Zn	Pb mg.kg^{-1}	Cd
Low (I)	<100	<50	<1.0
Medium (II)	101-300	51-100	1.1-3.0
High (III)	301-600	101-200	3.1-6.0
Very high (IV)	>600	>200	>6.0

Table 2. Concentration scale of metals in soils (modified after Gorlach 1991).

Total content of zinc, lead and cadmium was also assessed in parent rock fragments. A scale of metal concentrations in surface horizons after Gorlach (1991) and modified by the authors was used (Table 2).

Results and Discussion

Total heavy metal content in AC *Lithic Leptosols* horizons of the Tatra National Park was highly diversified (Table 3). Among soils derived from igneous and metamorphic rocks the most numerous group consisted of soils with low zinc and cadmium content and with medium concentration of lead,

Soil propeties	Soils derived from igneous and methamorphic rocks		Soils derived from carbonate rocks	
	Range	Arithmetic mean (coefficient of variation)	Range	Arithmetic mean (coefficient of variation)
pH H_2O	3.4 - 6.2	4.5 (15)	5.5 - 7.9	6.7 (10)
pH KCl	2.4 - 5.5	3.7 (19)	5.0 - 7.6	6.4 (12)
$g.kg^{-1}$				
Carbonate CO_2	0.0	0.0	0.00 - 343.1	58.5 (148)
Organic C	13.2 - 340.9	90.5 (72)	14.4 - 461.2	151.4 (77)
Total N	2.0 - 11.8	5.6 (51)	1.3 - 27.1	10.4 (69)
C : N	9.4 - 3.5	14.1 (33)	10.0 - 23.5	14.8 (26)
$mmol(+).kg^{-1}$		**Sorption properties**		
Ca^{2+}	0.1 - 117.0	13.5 (179)	15.7 - 619.1	167.1 (96)
Mg^{2+}	1.4 - 29.2	8.6 (83)	1.8 - 390.0	70.3 (133)
Na^+	0.2 - 7.0	0.9 (132)	0.3 - 10.6	1.5 (156)
K^+	0.6 - 8.9	3.5 (55)	0.2 - 21.7	3.4 (106)
Base cation capacity	4.0 - 141.3	26.5 (109)	24.9 - 881.0	242.3 (82)
Hydrolytic acidity	25.1 - 1,005.4	237.7 (78)	3.8 - 466.2	51.5 (180)
Cation exchange capacity	59.5 - 1,067.0	264.2 (72)	36.9 - 895.3	293.7 (71)
Base cation saturation (%)	1.7 - 41.7	11.0 (114)	20.8 - 98.9	79.72 (26)
$mg.kg^{-1}$		**Total level**		
Zn	19.9 - 256.5	93.2 (67)	87.5 - 744.5	251.8 (55)
Pb	31.1 - 296.8	89.5 (58)	37.8 - 410.7	133.6 (54)
Cd	0.01 - 4.9	1.0 (94)	0.4 - 17.4	4.0 (81)

Table 3. Selected properties of investigated *Lithic Leptosols*.

while soils with high zinc and cadmium but medium lead concentrations prevailed among soils developed from carbonate rocks (Fig. 2).

Soils that revealed high or very high content of at least one of the studied metals were considered contaminated with heavy metals of anthropogenic origin. This category comprised 62% of tested soils developed from carbonate rocks, among which over half contained high or very high quantities of all three studied metals, and 25% of soils derived from igneous and metamorphic rocks, having high or very high lead concentrations.

Pollution of studied soils was also shown by high coefficients of zinc, lead and cadmium accumulation, whose values exceeded 2 in over 80% of soils. High metal accumulation coefficients more often characterized soils developed from carbonate rocks than those derived from igneous and metamorphic rocks (Fig. 3).

In studied *Lithic Leptosols*, as in Tatra *Umbric* and *Rendzic Leptosols* (Niemyska-Łukaszuk and Miechówka 1999, Niemyska-Łukaszuk *et al.* 1998, Niemyska-Łukaszuk *et al.* 1999), heavy metal accumulation was primarily affected by soil chemical properties. Heavy metal content in parent rocks hardly influenced their concentrations in studied soils. Only a low correlation (r = 0.290*) was found between lead content in tested rocks and that in soils. On the other hand, parent rocks indirectly influenced heavy metal concentrations through forming soil properties. Soils developed from carbonate rocks were characterized by higher pH values, much greater humus content and higher degree of sorption complex base saturation than

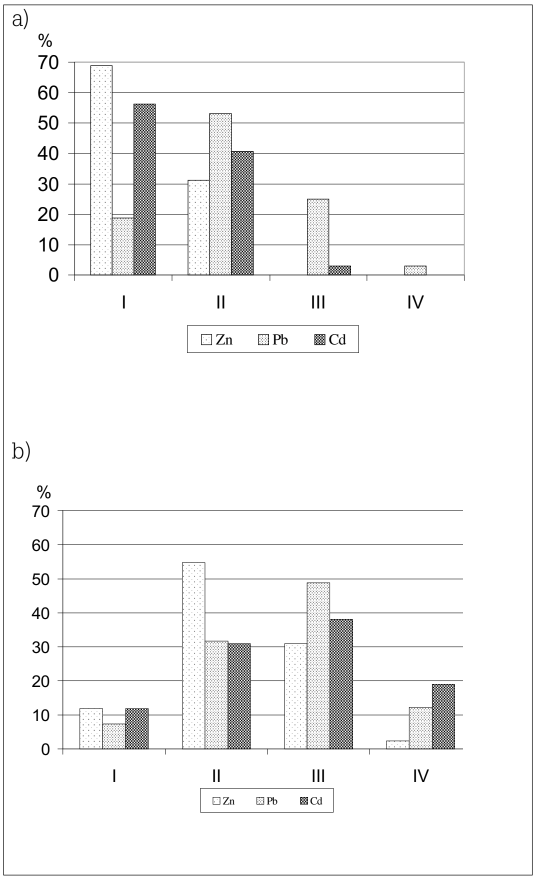

Fig. 2. Proportional fraction of lithosols (a) and initial rendzinas (b) with low (I), medium (II), high (III) and very high (IV) Zn, Pb and Cd contents.

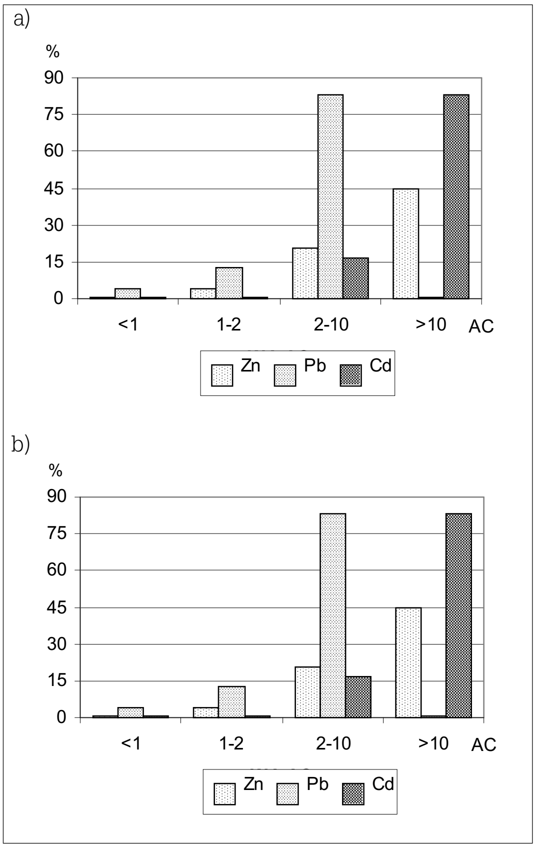

Fig. 3. Proportional fraction of lithosols (a) and initial rendzinas (b) with different values of Zn, Pb and Cd accumulation coefficients (AC).

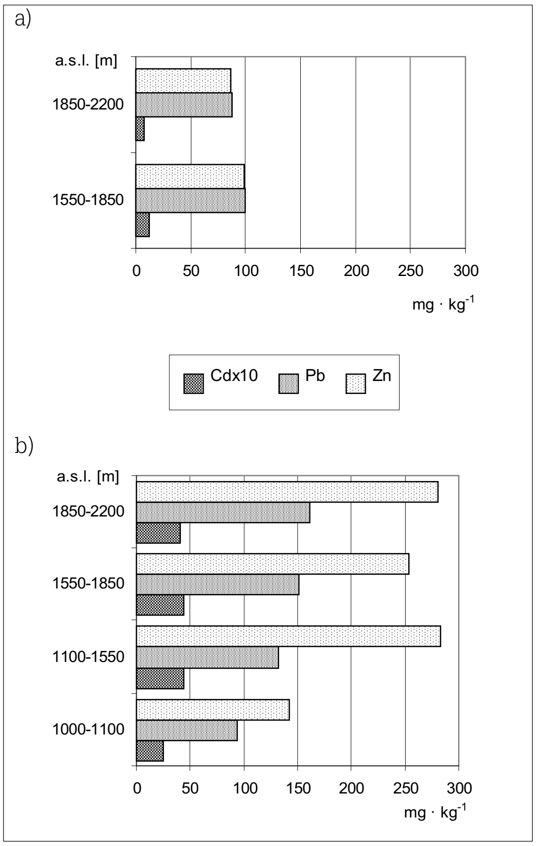

Fig. 4. Mean Zn, Pb and Cd contents in lithosols (a) and initial rendzinas (b) situated at different altitudes above sea level.

soils derived from non-carbonate rocks. These properties, mainly determining soil heavy metal accumulation ability (Herms and Brűmer 1980) affected high total heavy metal content in tested soils developed from carbonate rocks. Their mean cadmium concentrations were four times higher, zinc almost three times and lead 1.5 times higher than in soils derived from rocks without carbonates (Table 3). Similarly as in Tatra *Leptosols* with greater depth (Niemyska-Łukaszuk and Miechówka 1999, Niemyska-Łukaszuk *et al.* 1998, Niemyska-Łukaszuk *et al*. 1999) organic substance content had the greatest effect on heavy metal content in *Lithic Leptosols.* Relationships between zinc, lead and cadmium content and organic carbon concentrations in studied soils were characterized by simple correlation coefficients, respectively 0.295***, 0.410*** and 0.419***. Significant relationships (although with low correlation coefficients) were also registered between zinc content and pH values (r = 0.197***) and degree of sorption complex base saturation (0.236***).

Variation in altitude above sea level and associated climatic conditions, particularly rainfall, that bring atmospheric pollution to soils, also affected heavy metal concentrations in studied soils the content of all tested metals in soils developed from carbonate rocks increased with increasing altitude above sea level, whereas in soils derived from rocks without carbonates it decreased this (Fig. 4). This phenomenon may be due to increasing quantities of metal supplied to soils in rainfall, which accumulate in soils with higher pH, but it is leach from acid soils. Similar relationships have been found in *Umbric* and *Rendzic Leptosols* (Niemyska-Łukaszuk and Miechówka 2002).

Conclusions: High and very high contents of zinc, lead and cadmium and high values of accumulation coefficients (AC) in a major part of Tatra National Park *Lithic Leptosols* (particularly developed from carbonate rocks), evidence their pollution with anthropogenic dust containing heavy metals. Heavy metal content in parent rocks has very slight effect on their content in AC horizons of *Lithic Leptosols*.

Zinc, lead and cadmium concentrations in AC horizons of *Lithic Leptosols* are primarily determined by their chemical properties conditioned by parent rock.

Along with altitude above sea level contents of all studied metals increase in soils developed from carbonate rocks, whereas they decrease in soils derived from igneous and metamorphic rocks.

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