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PROFILE DIFFERENCES OF ZINC, COPPER, AND NICKEL CONTENTS IN FOREST SOILS ON SOUTH-PODLASIE LOWLAND

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Keywords: Zinc, copper, nickel, forest soils, South-Podlasie Lowland.

Abstract: The profile differences of zinc, copper, and nickel contents in forest podzolic soils on South-Podlasie Lowland were studied. Their considerable differentiation was found. Contents and differentiation of analyzed heavy metals in studied soil horizons were determined by: parents rock and soil-forming processes (mainly podzolization) characteristic for those soils.

INTRODUCTION

Among all environmental elements, the soil is commonly considered as the most important medium for accumulating the heavy metals originating from natural (parents rocks) and anthropogenic sources (industry, energy production, transport, plant pesticides, fertilizers, municipal wastes) [3, 6, 8, 11]. Forest soils (namely those with low level of anthropopression) may be a reference (standard) for comparison in ecological, soil science, and screening studies upon the environment. Determination of zones (genetic horizons), where heavy metals are deposited, as well as conditions and opportunities of their transfer within soil profile, are very important question in an aspect of their bio-geochemistry and potential threats for natural environment.

The aim of present study was to determine zinc, copper, and nickel contents in forest podzolic soils on South-Podlasie Lowland as well as to evaluate the influence of lithogenic, pedogenic, and anthropogenic factors on the amount and distribution of these heavy metals within soil profiles.

MATERIAL AND METHODS

The soil study was carried out within three regions (Siedlce Upland, Łuków Plain, Podlasie Bug River Gorge) of South-Podlasie Lowland. Twelve soil outcrops were made in forests of Siedlce, Łuków, and Sarnaki Forest Inspectorates, within habitat types that dominated on those areas: fresh coniferous forest (FCF), fresh mixed coniferous forest (FMCF), and fresh mixed deciduous forest (FMDF). The outcrops were made in sites with possibly weak anthropogenic influences on pedogenic processes (nature reserves:

Gołobórz, Zabuże, and Jata, as well as old forests not covered by reserve protection). The studied soils were counted to Dystric Arenosols (4 profiles), Albic Podzols (5 profiles) and Haplic Podzols (3 profiles) developed from fluvioglacial and boulder sands, accumulatively associated with the Warta river stadial of middle-Polish glaciations. The collected soil samples were subjected to determinations of: granulometric composition – areometric method; bulk density – dryer-weight method; organic carbon content (C_{org}) – elemental analyzer CHN equipped in thermal conductivity detector (TCD) (in organic horizons), as well as oxidation-titrimetric method (in mineral horizons); pH – potentiometry in 1 M KCl; sorption capacity (CEC) – Kappen's method.

Heavy metals (Zn, Cu, Ni) contents, as well as iron and aluminum, were determined by applying atomic emission spectrometry combined with inductively coupled plasma (ICP–AES) after combustion (at 450°C) and preparing extracts in 20% HCl. It is accepted that hydrochloric acid dissolves mainly the weathered part of soil mineral matter, while constituents soluble in HCl can be gradually taken by plants for a longer time. Partial dissolving of the soil samples is applied in environmental studies, among others, to determine the level of soil contamination. Underestimated (for mineral material) or close (for plant material) levels of elements in reference to their total contents in studied material are then determined [4, 5]. Moreover, total concentrations of iron and aluminum were analyzed taking into account the pedogenesis of studied soils.

Studies were performed in three replications, and the obtained results were calculated in reference to absolute dry matter of soils. The paper presents mean values and ranges (for soil sub-types and genetic horizons with similar genesis). For particular genetic horizons, coefficients of enrichment (w.w.) in heavy metals (in reference to parents rock) were calculated on the basis of metals content (in $mg \cdot dm^{-3}$). The obtained results were statistically processed and expressed as simple correlation coefficients.

RESULTS AND DISCUSSION

Well developed organic horizons characteristic for forest soils of mor and moder types of humus were found in studied soils, which may indicate continuous soil-forming processes for a longer time. Morphology and basic properties of soils (Tab. 1) are typical for taxonomic units of Polish Lowlands [1, 9, 10]. The examined soils were characterized by acidic and very acidic reaction, considerable accumulation of organic matter in organic horizons as well as characteristic profile variability of iron and aluminum contents determined by soil-forming processes.

Parents rocks of studied Dystric Arenosols, Albic Podzols and Haplic Podzols had similar concentrations of determined heavy metals (mean values in $mg \cdot kg^{-1}$: Cu – 1.28; Zn – 6.89; Ni – 2.32). These contents were lower than average levels cited by Czarnowska [2] for geochemical background of different-genesis sands from northern and middle Poland.

In organic horizons (Tab. 2) the higher copper content (1.35–1.73 $mg \cdot dm^{-3}$, on the average) was found in $O_{fh.}$ O_f, O_h (with greater extent of processed organic matter) compared to O_l horizons (0.392–0.427 $mg \cdot dm^{-3}$, on the average).

In mineral horizons with continuous soil-forming processes (A, B, and E) copper content was recorded on the average from 1.01 to 2.18 $mg \cdot dm^{-3}$. In Haplic Podzols, profile copper distribution was modified by podzolization process, which was indicated by

Table 1. Some properties of investigated soils (ranges)

Soil, genetic horizon (thickness [cm])*	pH_{KCl}	Soil organic matter [%]**	CEC [cmol(+)·kg^{-1}]	Fe	Al	Bulk density [g·cm^{-3}]	Fraction Ø < 0.02 mm [%]
				[g·kg^{-1}]			
Dystric Arenosols							
O_l (2)	3.8–4.8	75.9–86.0	103–166	0.95–2.08	0.46–1.15	0.059–0.066	–
O_{fh} (3)	3.3–4.5	30.5–56.0	62.6–100	1.93–3.24	1.31–2.09	0.135–0.248	–
AB (15)	2.7–3.5	2.29–4.29	8.5–12.1	1.48–3.40	1.51–2.93	1.13–1.32	8–10
B_v (42)	3.9–4.5	0.09–0.76	2.59–3.90	1.19–3.18	1.95–3.43	1.43–1.55	3–7
C (74)	3.7–4.8	0.03–0.09	1.28–6.07	0.95–2.57	1.13–3.17	1.52–1.64	2–15
Albic Podzols							
O_l (2)	2.7–5.2	63.4–88.3	123–245	0.81–1.49	0.84–2.80	0.049–0.068	–
O_f, O_h, O_{fh} (7)	2.5–5.1	35.0–64.5	104–85	1.74–3.35	1.05–3.97	0.155–0.284	–
AE (11)	2.4–2.9	1.51–6.72	5.96–13.9	1.05–2.64	1.94–3.52	1.12–1.39	6–18
$B_{fe}B_v$ (38)	3.5–4.4	0.03–1.11	2.61–5.87	2.21–4.47	3.89–5.54	1.41–1.62	3–19
C (70)	3.6–4.9	0.04–0.15	1.32–6.62	0.42–1.80	0.96–1.96	1.59–1.68	2–11
Haplic Podzols							
O_l (2)	3.6–4.7	82.8–90.3	109–162	0.45–0.88	0.61–0.93	0.042–0.050	–
O_f, O_h, O_{fh} (8)	2.5–3.6	40.9–60.3	82–176	2.09–2.58	1.99–2.97	0.177–0.266	–
A (14)	2.3–3.1	2.90–5.74	9.64–14.8	0.63–1.07	0.85–1.29	1.20–1.35	7–9
E_{es}, AE (16)	2.3–4.3	0.30–3.47	3.22–11.6	0.17–0.38	0.40–0.60	1.35–1.56	4–11
B_{hfe}, B_h, B_{fe} (17)	3.5–3.9	0.55–1.86	4.35–9.96	1.49–2.81	2.01–3.72	1.54–1.67	6–10
C (70)	3.0–4.8	0.04–0.36	2.54–5.46	1.13–2.40	1.43–1.97	1.60–1.71	2–6

* – mean, ** – soil organic matter [%] = C_{org} [%]·1.724

low value of enrichment coefficient in eluvial horizons. Due to the fact that copper is bound by many soil components (organic matter, clay, Fe and Al hydroxides), this element is a metal with long duration in the soil and weakly migrates within the soil profile. In very acidic soils, lability of its cationic forms is potentially increased – as similar as in the case of copper binding with low-molecular organic compounds formed from soil organic matter decomposition [6].

Profile differentiated zinc content was found in studied soils. Less of that metal was recorded in organic horizons (namely O_l horizons) (4.63 mg·dm^{-3}, on the average) in relation to mineral horizons (10.4 mg·dm^{-3}, on the average). Podzolization process had a modifying effect on profile zinc amount differentiation. Zinc is an element with great lability in the soil, namely in acidic environment, where mobile mineral-organic complexes are formed. The metal is also strongly bound by soil organic matter and iron and manganese compounds [6].

The nickel concentration zones were found in illuvial horizons (B) and parents rocks (C) of all twelve studied soils. Considerable influence of podzolization process on profile nickel distribution was also recorded, namely in Podzols. Nickel bound to organic matter (including mobile chelates) dominated in the soil environment, while in mineral horizons, it was additionally sorbet by Fe and Mn hydroxides: its solubility and mobility increases along with the acidity increase [6].

Table 2. Content of heavy metals and value of enrichment coefficient in investigated soils

Genetic horizon	Cu			Zn			Ni		
	[mg·kg^{-1}]	[mg·dm^{-3}]	w.w.	[mg·kg^{-1}]	[mg·dm^{-3}]	w.w.	[mg·kg^{-1}]	[mg·dm^{-3}]	w.w.
Dystric Arenosols									
O_l	6.6*(3.77–9.06)**	0.392*	0.16	93.6 (31–123)	5.34	0.44	7.05 (3.24–12.0)	0.341	0.11
O_{fh}	10.5 (5.72–14.2)	1.73	0.70	39.6 (34.5–45.3)	6.95	0.57	8.60 (3.46–15.7)	1.41	0.38
AB	1.09 (0.94–1.35)	1.30	0.53	9.75 (8.81–12.4)	11.6	0.95	1.54 (0.90–2.50)	1.83	0.49
B_v	0.82 (0.6–1.13)	1.74	0.71	8.82 (4.33–13.5	12.6	1.03	2.20 (1.03–3.40)	3.14	0.84
C	1.51 (0.61–3.56)	2.45		7.43 (2.62–12.9)	12.2		2.27 (1.30–3.63)	3.70	
Albic Podzols									
O_l	7.5 (6.50–9.15)	0.427	0.24	52.7 (36.8–64.3)	3.04	0.29	12.5 (3.10–25.6)	0.714	0.19
O_f, O_h, O_{fh}	8.19 (5.23–10.4)	1.35	0.76	43.0 (28.3–67.0)	7.14	0.68	17.7 (3.24–37.9)	2.93	0.78
AE	1.06 (0.36–1.67)	1.27	0.71	7.97 (4.19–13.4)	10.3	0.98	2.89 (0.57–4.73)	3.46	0.92
$B_{fe}B_v$	1.53 (0.09–4.33)	2.18	1.23	10.8 (5.20–17.6)	15.5	1.47	3.50 (1.51–5.92)	5.00	1.33
C	1.08 (0.04–4.65)	1.78		6.38 (1.75–16.7)	10.5		2.28 (0.57–7.10)	3.76	
Haplic Podzols									
O_l	6.93 (1.59–9.79)	0.420	0.20	68.1 (15.8–117)	4.52	0.39	10.1 (2.09–17.1)	0.694	0.17
O_f, O_h, O_{fh}	9.61 (4.06–13.6)	1.64	0.78	45.5 (25.8–54.6)	8.00	0.69	15.5 (5.98–29.1)	2.77	0.68
A	1.15 (0.28–2.44)	1.41	0.67	5.74 (4.20–7.61)	7.08	0.61	0.57 (0.52–0.61)	0.694	0.17
E_{es}, AE	0.64 (0.38–0.94)	1.01	0.48	3.42 (2.13–5.54)	5.10	0.44	0.31 (0.14–0.57)	0.49	0.12
B_{hfe}, B_h, B_{fe}	1.25 (0.54–2.20)	1.83	0.87	8.56 (3.89–11.9)	12.6	1.09	2.06 (0.56–3.93)	3.01	0.74
C	1.24 (0.27–2.51)	2.10		6.85 (3.84–12.5)	11.6		2.40 (1.07–4.19)	4.08	

* – mean, ** – range, w.w. – enrichment coefficient calculated on the basis of metals content [mg·dm^{-3}]

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B_v	0.82 (0.6–1.13)	1.74	0.71	8.82 (4.33–13.5	12.6	1.03	2.20 (1.03–3.40)	3.14	0.84
C	1.51 (0.61–3.56)	2.45		7.43 (2.62–12.9)	12.2		2.27 (1.30–3.63)	3.70	
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E_{es}, AE	0.64 (0.38–0.94)	1.01	0.48	3.42 (2.13–5.54)	5.10	0.44	0.31 (0.14–0.57)	0.49	0.12
B_{hfe}, B_h, B_{fe}	1.25 (0.54–2.20)	1.83	0.87	8.56 (3.89–11.9)	12.6	1.09	2.06 (0.56–3.93)	3.01	0.74
C	1.24 (0.27–2.51)	2.10		6.85 (3.84–12.5)	11.6		2.40 (1.07–4.19)	4.08	

* – mean, ** – range, w.w. – enrichment coefficient calculated on the basis of metals content [mg·dm^{-3}]

In others papers the contents of heavy metals in forest soils are expressed in mg·kg^{-1} more often than in mg·dm^{-3}. Other authors also observed similar tendencies and similar contents of profile distribution of studied metals in podzolic soils [3, 9–11, 14]. In podzolic soils, there are factors that immobilize heavy metals (humus accumulation in organic and humus horizons, active Fe, Al, and Mn forms), and on the other hand, those increasing its migration (high acidity, permeability and slight content of soil mineral colloids).

The Polish norms, concerning heavy metals contents in soils, present permissible levels also expressed in mg·kg^{-1}. The comparison of the amounts of studied metals with their published permissible levels may be the measure of anthropogenization intensity. So far, no norms that would take into account the specificity of forest soils, were defined. Accepting values of contamination for arable soils given by Kabata-Pendias *et al.* [7], it can be concluded that mineral horizons of studied forest soils contained low "natural" levels of heavy metals. These authors also gave the limiting values of metals for organic soils, to which organic horizons of forest soils could be compared (to some extent). In reference to those limits, the studied soils did not show excessive values of heavy metals. Taking into account the norms included in the Decree of Environmental Ministry [12], heavy metals contents in the analyzed soils were within the range of permissible values for forest soils. Konecka-Betley *et al.* [10] suggested preliminary, limiting contents of some heavy metals in organic sub-horizons; when these limits would be exceeded, concentrations should be related to as "elevated", i.e. Cu – 30, Zn – 75, Ni – 35 mg·kg^{-1}. In reference to these values, their slight excess was recorded in particular organic horizons only for Zn (in litter organic horizons) and for Ni (in a single case).

Statistical analysis of the obtained results revealed many significant correlation dependencies (differing between organic and mineral genetic horizons) for Cu, Zn, Ni contents and selected soil properties (Tab. 3). Values of correlation coefficients suggest that the content of studied heavy metals in organic horizons is mainly a function of the organic matter amount, while in mineral horizons – the content of the finest granulometric fractions (statistically significant values of the coefficient). In mineral horizons, strong (positive) correlations were found between contents of studied heavy metals and iron and aluminum concentrations, which indirectly confirm the influence of soil-forming processes on distribution of studied metals in mineral genetic horizons of examined soils.

Table 3. Values of correlation coefficients between content of Cu, Zn, Ni and same soils properties

Parameter	Organic horizons n = 33			Mineral horizons n = 71		
	Cu	Zn	Ni	Cu	Zn	Ni
pH$_{KCl}$	0.05	0.29	0.46*	-0.03	0.08	0.26*
Soil organic matter	0.34*	0.45*	-0.45*	0.11	0.13	-0.34*
CEC	0.08	0.14	-0.11	0.32*	0.21	-0.25*
Fe	-0.01	-0.01	-0.59*	0.59*	0.42*	0.41*
Al	0.17	0.15	-0.63*	0.40*	0.39*	0.30*
Ø < 0.02 mm	–	–	–	0.68*	0.51*	0.29*
Cu	x	0.68*	-0.17	x	0.60*	0.49*
Zn	x	x	-0.38*	x	x	0.65*

* – significant at $\alpha = 0.05$

CONCLUSIONS

The copper, zinc, and nickel contents in the studied 12 forest podzolic soils localized on South-Podlasie Lowland were mostly determined by poor parents rock.

Profile distribution of the studied heavy metals was differentiated by pedological processes, namely forming the organic and humus horizons as well as podzolization process (impoverishment of eluvial vs. enrichment of illuvial horizons) as well as rusting (to a lesser extent).

In organic horizons of the studied soils, the strongest correlations were recorded between Cu, Zn, Ni contents and organic matter amount; in mineral horizons – between these metals contents vs. < 0.02 mm fraction, iron and aluminum contents.

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PROFILOWE ZRÓŻNICOWANE ZAWARTOŚCI CYNKU, MIEDZI I NIKLU W LEŚNYCH GLEBACH BIELICOZIEMNYCH NA NIZINIE POŁUDNIOWOPODLASKIEJ

Badano profilowe zróżnicowanie zawartości miedzi, cynku i niklu w leśnych glebach bielicoziemnych na Nizinie Południowopodlaskiej. Stwierdzono znaczne ich zróżnicowanie. Na zawartość i zróżnicowanie w profilu analizowanych metali ciężkich w badanych glebach największy wpływ miały: mało zasobna skała macierzysta oraz charakterystyczne dla tych gleb procesy glebotwórcze (głównie bielicowanie).