

Vertical distribution of Cu, Ni and Zn in Brunic Arenosols and Gleyic Podzols of the supra-flood terrace of the Słupia River as affected by litho-pedogenic factors

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Abstract: The aim of the study was to assess the influence of lithological and pedogenic factors in the shaping of Cu, Ni and Zn distribution patterns in the profiles of Brunic Arenosols and Gleyic Podzols of the lower supra-flood terrace of the Słupia River, which is located outside the range of significant anthropogenic sources of pollution with these metals.

The contents of the investigated metals were analysed in aqua regia extracts of samples collected from three profiles of Brunic Arenosols, formed from river sands, and three profiles of Gleyic Podzols, formed from river sands transformed by eolian processes.

In general, river sands contained higher amounts of Ni and Zn ($2.6 - 6.9 \text{ mg} \cdot \text{kg}^{-1}$ Ni; $10.3 - 16.2 \text{ mg} \cdot \text{kg}^{-1}$ Zn) compared to eolian sands ($1.2 - 2.4 \text{ mg} \cdot \text{kg}^{-1}$ Ni; $3.3 - 17.3 \text{ mg} \cdot \text{kg}^{-1}$ Zn), while the content of copper tended to be higher in eolian sands ($1.3 - 1.9 \text{ mg} \cdot \text{kg}^{-1}$) than river sands ($0.1 - 1.5 \text{ mg} \cdot \text{kg}^{-1}$). The observed differences between the two types of sand are due to the loss of fine granulometric fractions and various minerals during eolian processes. Higher concentrations of the investigated metals in soil solum as compared to parent material are due to their uptake from deeper parts of the soil by roots and subsequent return to the soil surface as a component of litterfall. Therefore, the highest concentrations of Cu, Ni and Zn were observed in ectohumus. In the mineral component of the soil, the highest concentrations were observed in organic matter-rich A and B horizons, which indicate close interactions between heavy metals, humic substances and iron oxides.

The vertical distribution of the investigated metals in the profiles of Gleyic Podzols indicates their leaching during podzolization. The observed contents of Cu, Ni and Zn, both in Brunic Arenosols and Gleyic Podzols, were lower than the geochemical background, which confirms that anthropogenic contamination of the studied area with these metals is marginal.

Key words: copper, nickel, zinc, Brunic Arenosols, Gleyic Podzols

1. Introduction

Parent rocks are the primary, spatially varying source of heavy metals in soils. However, dry and wet atmospheric depositions, throughfall and stemflow (Linberg and Turner, 1988; Saur end Juste, 1994; Skřivan et al., 1995), plant litterfall (Silva et al., 1998), as well as surface and ground waters (Logan et al., 1997; Paulson, 1997) are their most important secondary sources. In re-

cent centuries, anthropogenic emissions have become an important source of soil contamination with heavy metals, having a relatively broad range of impact. Increasing environmental pollution caused by these substances in the 20th century is reflected in their elevated concentrations in the modern alluvial sediments and slope deposits (e.g. Taylor, 1996; Martin, 2000; Pasieczna, 2003; Zgłobicki, 2008). In river valleys, concentrations of heavy metals in the sediments accumulated in floodplain terraces being

under the anthropogenic impact are generally higher than those in the sediments of higher-located terraces accumulated during periods of lack of significant human activity (Brewer and Taylor, 1997).

Heavy metals present in the soil occur in various forms associated, in various ways, with other soil components. The use of suitable extraction procedures allows to isolate water-soluble forms, exchangeable forms and forms bounded to carbonates, iron and manganese oxides, organic and residual forms (Tessier et al. 1979; Sauvé et al. 2000, Singh et Kabała 2001; Konradi et al., 2005; Degryse et al. 2009). Each form differs in availability for plants and mobility. Both the forms and bioavailability of heavy metals are largely affected by a complex of physical and chemical properties of the soils, especially by their reaction (Martinez et Motto 2000; Strobel et al., 2005; McAlister et al., 2006; Fijałkowski et al., 2012).

Studies on concentrations of heavy metals in soils and their sequestration are conducted mainly in anthropogenically polluted areas. Relatively rare are studies on natural, lithopedogenic factors affecting the patterns of distribution of heavy metals in different types of soil in unpolluted areas (e.g. Ukonmaanaho et al., 2001).

This study aims to evaluate the role of lithological and pedogenic factors in shaping the vertical distribution of Cu, Ni and Zn in the profiles of forest Brunic Arenosols and Gleyic Podzols in the lower supra-flood terrace of the Słupia River, located beyond the area of significant impact of anthropogenic emission sources of these pollutants.

2. Materials and methods

2.1. Site characteristics

The investigated fragment of the lower supra-flood terrace of the river Słupia is built of loose-, fine- and medium-grained river sands, with thickness of nearly 4 meters (Florek 1989). Thermoluminescent age (TL) of the sediments is about 9000 years BP (Jonczak et al. 2013). The soils formed from these sands 5100–4200 years ago were locally dispersed by wind. As a result, usually in the local depressions formed eolian covers thick to about 2 meters. The texture of aeolian sands does not differ significantly from river sands, which confirms their origin from local sources and transport over a short distance (Florek 1989). Reactivation of the aeolian processes that evolved about 400–500 years ago was related to the local deforestations (Jonczak et

al. 2013). These processes have led, in some places, to accumulation of 20–30 cm thick aeolian layers on the surface of the existing soils (profiles G-1, G-2).

Brunic Arenosols arose from river sands, while Gleyic Podzols arose from aeolian sands, in conditions of shallow groundwater level. Gleyic Podzols characterised with humus rich and relatively poor in free iron oxides B-horizon (Jonczak et al. 2013). At the beginning of the 20th century, the central part of the studied terrace was drained, which has led to reduction in the local groundwater level and gradual transformation of peat-like horizons of these soils into murshic horizons. Undoubtedly, the local deforestations and anthropogenic changes in species composition of forests in the past centuries were other important factors influencing soil development in this area. Today, the entire study area is covered with pine, with admixtures of spruce, oak, beech and birch. The area is located beyond the range of significant anthropogenic sources of Cu, Ni and Zn emissions. This is reflected in the low concentration of these metals even in the urban soils of Słupsk where a slight increase of the geochemical background is rarely observed (Pasiczna 2003; Parzych et Jonczak 2014).

2.2. Methods

Field studies were conducted in 2010. Fifteen soil pits were dug, soil profiles were described and sampled. The samples were collected from each genetic horizon, dried and analysed. The soils were described after the 5th edition of the Classification of Polish Soils (Marcinek et al. 2011). The content of heavy metals was determined in three profiles of Haplic Brunic Arenosols and three profiles of Gleyic Podzols (Orsteinic and Murschic), whose morphology was not modified by human activity (Fig. 1). Some features were observed only in profile R-1, which indicates the post-agricultural nature of the soil. The following soil properties were analysed:

- bulk density – by gravimetric method in 100 cm³ volumetric samples,
- particle-size distribution – a combined sieve and pipette method. Division into granulometric fractions and granulometric groups was done after classification of Polish Soil Science Society (PTG 2008),
- pH – by potentiometric method in a suspension with water and 1 mol·dm⁻³ KCl solution in 1:2.5 proportion of soil:water/KCl,
- soil organic carbon (C_{org}) content – in mineral samples by the Tiurin's method, and in organic samples by the Alten's method,

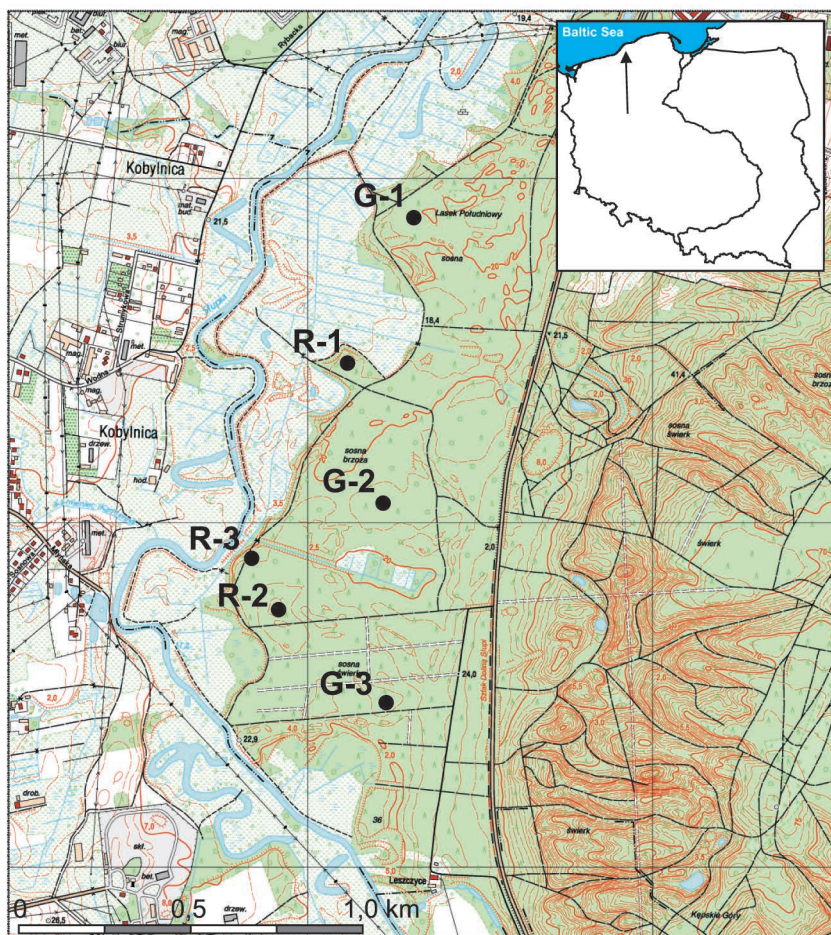


Figure 1. Location of soil profiles in the area of lower supra-flood terrace of the Słupia River: G – Gleyic Podzols; R – Brunic Arenosols

– the content of Cu, Ni and Zn – in aqua regia extracts (open system with reverse coolers) with microwave plasma atomic emission spectrometry (Agilent 4100 MP-AES). Two soil reference samples were simultaneously analysed to control quality of analysis.

2.3. Soil characteristics

All the investigated soils have occurred in the forest communities, with Scots pine as a dominant species for over more than a century (Table 1). These are light-textured soils of the texture of sand. The sum of silt and clay fraction does not exceed 6.9% in Brunic Arenosols (Table 2) and 4.3% in Gleyic Podzols (Table 3). The soils are characterised by acidic and very acidic reaction. The $\text{pH}_{\text{H}_2\text{O}}$ in organic horizon ranges from 3.53 to 4.78 for Brunic Arenosols and from 3.62 to 4.66 for Gleyic Podzols. The pH of mineral part of the soils is generally the lowest in humus horizons and ranges from 3.81 to 4.56 in Brunic Arenosols and from 3.80 to

3.97 in Gleyic Podzols. In all profiles, the observed increase of pH with depth may be due to the impact of the groundwater (Tables 2, 3). Brunic Arenosols are moderately rich in organic carbon whose content in humic horizons ranges from 9.9 to 48.6 $\text{g}\cdot\text{kg}^{-1}$ (Table 2). Gleyic Podzols are characterised by a much higher content of this component. Humic horizon (excluding the initial humic horizon formed in young Aeolian horizons) contains 32.3–77.0 $\text{g}\cdot\text{kg}^{-1}$ of organic carbon, and orsteinic horizon contains 13.0–35.6 $\text{g}\cdot\text{kg}^{-1}$ (Table 3).

4. Results and discussion

The chemical and physical properties of the parent material, water regime and vegetation cover are among the main natural factors affecting vertical distribution of heavy metals during soil development (Silva et al., 1998; Rusek et al., 2005; Kabała et al. 2008). The percolative type of water regime in the temperate climate zone favours the leaching of various soil components, including heavy

Table 1. Groundwater level and tree-species composition of the stand in the surrounding of soil profiles (order of species according to their declining share in the stand)

Profile number	Groundwater level [m]	Components of tree-stand
R-1	2.0	Scots pine, silver birch, European beech, pedunculate oak
R-2	3.0	Scots pine, pedunculate oak
R-3	3.0	Scots pine, pedunculate oak
G-1	1.2	Scots pine, Norway spruce, pedunculate oak
G-2	2.0	Scots pine, pedunculate oak
G-3	2.0	Scots pine, Norway spruce, European beech

Table 2. Selected properties of Brunic Arenosols

Soil horizon	Depth [cm]	Bulk density [g·cm ⁻³]	Textural group	Percentage of fraction <0.05 mm [%]	pH _{H2O}	pH _{KCl}	C _{org.} [g·kg ⁻¹]
Profile R-1							
Ol	5–3				4.63	4.13	442.4
Ofh	3–0				4.70	4.08	433.6
A	0–6	1.04	sand	0.8	3.81	2.98	48.6
A(p)	6–25	1.49	sand	6.9	4.20	3.54	9.9
Bv	25–49	1.37	sand	5.0	4.67	4.20	6.1
BvC	49–68	1.48	sand	1.6	4.67	4.38	2.3
Cg	68–105	1.52	sand	2.4	4.79	4.46	0.0
Cg2	105–140	1.46	sand	0.5	4.94	4.52	0.0
Profile R-2							
Ol	10–7				4.25	3.51	461.5
Of	7–4				3.84	2.78	403.8
Oh	4–0				3.53	2.40	391.9
AEs	0–7	1.04	sand	1.7	4.03	2.97	10.3
Bvhs	7–40	1.39	sand	0.1	4.55	4.07	6.1
BvC	40–65	1.53	sand	1.9	4.05	3.33	11.0
C	65–150	1.53	sand	1.5	4.84	4.63	0.0
Profile R-3							
Ol	9–6				4.78	4.32	502.5
Of	6–4				4.65	3.97	362.8
Oh	4–0				3.99	2.99	309.3
A1	0–19	1.40	sand	6.7	4.29	3.67	10.3
A2	19–31	1.36	sand	4.2	4.56	4.10	7.3
ABv	31–45	1.37	sand	3.7	4.69	4.19	5.1
Bv	45–70	1.45	sand	2.6	4.54	4.30	3.2
Cg1	70–110	1.56	sand	0.0	4.81	4.43	0.0
Cg2	110–150	1.53	sand	0.5	5.02	4.53	0.0

Table 3. Selected properties of Gleyic Podzols

Soil horizon	Depth [cm]	Bulk density [g·cm ⁻³]	Textural group	Percentage of fraction <0.05 mm [%]	pH _{H2O}	pH _{KCl}	C _{org.} [g·kg ⁻¹]
Profile G-1							
Ol	6–4				4.33	3.65	477.6
Of	4–3				4.38	3.68	415.7
Oh	3–0				3.80	2.79	274.4
AEs	0–6	1.26	sand	0.4	3.80	2.96	23.5
Bhs	6–18	1.47	sand	1.1	4.26	3.69	7.2
2AEs	18–31	1.37	sand	1.0	4.11	3.49	35.1
2Es	31–40	1.39	sand	1.0	4.30	3.56	5.4
2Brg	40–58	1.48	sand	4.3	4.35	3.75	35.6
2Bhsg/C	58–92	1.51	sand	0.8	4.95	4.53	3.3
3Cg	92–130	1.55	sand	0.7	4.85	4.62	-
Profile G-2							
Ol	12–10				4.55	3.97	463.7
Of	10–3				3.92	2.91	348.2
Oh	3–0				3.62	2.59	302.9
Es	0–7	1.39	sand	1.7	3.99	3.06	16.5
Bhs/C	7–13	1.45	sand	0.0	4.90	4.34	1.7
2A	13–20	1.19	sand	3.1	3.95	3.27	77.0
2Es	20–32	1.42	sand	1.8	4.35	3.60	5.4
2Brg	32–51	1.54	sand	4.1	4.38	3.77	20.9
2Bhsg	51–76	1.44	sand	1.3	4.66	4.48	3.7
2Cg	76–123	1.56	sand	0.6	4.82	4.41	-
3Cg	123–150	1.57	sand	1.5	4.94	4.55	-
Profile G-3							
Ol	3–0				4.66	4.15	489.7
Au	0–31	1.21	sand	1.9	3.97	3.21	32.3
Es	31–42	1.32	sand	1.5	4.76	3.61	5.2
Brg	42–73	1.52	sand	3.1	5.17	4.03	13.0
Br/Cg	73–140	1.50	sand	0.6	5.48	4.26	4.6
Cg	140–200	1.52	sand	1.8	5.77	4.48	-

metals. The intensity of this process is conditioned by the physical and physicochemical soil properties (such as texture, bulk density, porosity, sorption capacity and pH) and forms of metals. The light-textured river and aeolian sands that build up the soil of the investigated fragment of the Słupia supra-flood terrace are not a limitation for the percolating water. Also the acidic and strongly acidic soil pH is conducive to the mobility of metals. Differences in the

groundwater level may differentiate the vertical distribution patterns of metals in the investigated Brunic Arenosols and Gleyic Podzols. Today, the groundwater level is beyond the range of the solum of Brunic Arenosols and within the range of the solum of Gleyic Podzols.

Cu, Ni and Zn, which are important micronutrients for plants, are uptaken by their root systems to be partially returned to the soil surface as a component of plant lit-

terfall. Their concentration in litterfall depends primarily on the species composition of plant communities and the complex of environmental factors determining their bio-availability. There may be a limiting factor in litterfall decomposition when their concentration is too high (Strojan 1978, Berg et al., 1991; Cotrufo et al., 1995). The critical values of concentrations, however, are relatively high and are exceeded only in areas that are heavily contaminated anthropogenically (Tyler 1992).

The maximum concentrations of heavy metals in forest soils usually occur in the organic horizon. It is the cu-

mulative effect of the dry and wet atmospheric deposition of these metals on the surface area, influx with litterfall and their bounding by humic substances (Tyler 1973 Bergbäck et Carlsson, 1995; Saur et Juste 1994). In addition, in the studied soils, the maximum concentrations of Cu, Ni and Zn were noticed in general in the ecohumus (Tables 4, 5). The content of Cu in the OI horizon was not much variable, despite the differences in the species composition of forest stands (Table 1), and ranged from 9.5 to 11.4 mg·kg⁻¹ (Tables 4, 5). A slight increase in the concentration of Cu was observed in the Of, Oh and Ofh

Table 4. Vertical distribution of heavy metals in the profiles of Brunic Arenosols

Soil horizon	Depth [cm]	Cu [mg·kg ⁻¹]	Ni [mg·kg ⁻¹]	Zn [mg·kg ⁻¹]
Profile R-1				
Ol	5–3	10.2	8.0	60.8
Ofh	3–0	12.4	10.9	87.5
A	0–6	3.9	3.4	18.2
A(p)	6–25	3.3	3.3	24.4
Bv	25–49	2.5	3.5	25.0
BvC	49–68	2.1	3.9	19.7
Cg	68–105	1.5	3.9	16.2
Cg2	105–140	1.1	2.6	11.8
Profile R-2				
Ol	10–7	9.8	7.7	79.5
Of	7–4	9.5	9.5	62.5
Oh	4–0	11.2	12.5	73.2
AEs	0–7	1.5	2.3	12.7
Bvhs	7–40	1.8	2.7	20.1
BvC	40–65	1.3	2.5	15.8
C	65–150	1.0	2.7	15.5
Profile R-3				
Ol	9–6	11.4	12.6	47.6
Of	6–4	12.3	16.1	55.0
Oh	4–0	9.3	15.6	34.5
A1	0–19	1.8	6.7	13.6
A2	19–31	2.3	6.2	11.0
ABv	31–45	2.6	4.4	13.7
Bv	45–70	0.5	6.2	12.1
Cg1	70–110	0.3	5.9	10.9
Cg2	110–150	0.1	6.9	10.3

Table 5. Vertical distribution of heavy metals in the profiles of Gleyic Podzols

Soil horizon	Depth [cm]	Cu [mg·kg ⁻¹]	Ni [mg·kg ⁻¹]	Zn [mg·kg ⁻¹]
Profile G-1				
Ol	6–4	9.5	6.6	52.9
Of	4–3	10.0	7.0	49.2
Oh	3–0	8.2	7.5	26.6
AEs	0–6	1.9	1.4	6.6
Bhs	6–18	2.2	2.4	9.5
2AEs	18–31	2.4	2.4	4.1
2Es	31–40	1.2	1.3	3.9
2Brg	40–58	1.6	2.4	7.4
2Bhsg/C	58–92	1.5	2.8	7.5
3Cg	92–130	1.6	3.1	8.8
Profile G-2				
Ol	12–10	9.7	8.1	75.1
Of	10–3	9.6	9.6	66.7
Oh	3–0	8.4	14.0	54.3
Es	0–7	3.8	2.8	19.1
Bhs/C	7–13	1.8	3.0	21.3
2A	13–20	2.6	2.9	14.7
2Es	20–32	0.9	1.6	12.0
2Brg	32–51	1.2	2.2	14.4
2Bhsg	51–76	1.2	2.8	17.2
2Cg	76–123	1.3	2.4	17.3
3Cg	123–150	1.3	2.2	13.2
Profile G-3				
Ol	3–0	9.6	13.7	94.7
Au	0–31	2.0	5.4	6.6
Es	31–42	0.2	3.5	4.4
Brg	42–73	0.3	6.0	8.3
Br/Cg	73–140	1.3	0.4	6.3
Cg	140–200	1.9	1.2	3.3

horizons, generally to a maximum level of $12.4 \text{ mg}\cdot\text{kg}^{-1}$. The recorded concentrations of Cu were usually several times lesser than in the organic horizon in the profiles of Brunic Arenosols and Gleyic Podzols in the area of northern Poland, according to the Atlas of Polish Forest Soils (Brożek, Zwydak 2003: profiles 81, 109 (Tuchola), 91 (Gryfino), 94 (Osie), 95, 103, 111 (Kliniska), 98 (Gdańsk), 101 (Dobrocin), 112, 120 (Wejherowo).

Much higher differences were noticed in the content of Ni and Zn. In the O1 horizon the content of Ni ranged from $6.6 \text{ mg}\cdot\text{kg}^{-1}$ in profile G-1 to 13.7 in profile G-3, and in remaining sub-horizons of ectohumus from 7.0 to $16.1 \text{ mg}\cdot\text{kg}^{-1}$ (Tables 4, 5). In turn, the Zn content ranged from 47.6 to $94.7 \text{ mg}\cdot\text{kg}^{-1}$ in the O1 horizon and from 26.6 to $87.5 \text{ mg}\cdot\text{kg}^{-1}$ in the remaining organic horizons. The observed concentrations of Ni and Zn did not differ from the values for this type of forest soils in northern Poland presented in the Atlas of Polish Forest Soils (Brożek, Zwydak: 2003 Ni from $5.1 \text{ mg}\cdot\text{kg}^{-1}$ in profile No. 91 to $13.6 \text{ mg}\cdot\text{kg}^{-1}$ in profile No. 94, and Zn from $36.0 \text{ mg}\cdot\text{kg}^{-1}$ in profile No. 81 to 82.0 in profile No.103).

Released during decomposition of plant litterfall, heavy metals are adsorbed by mineral and organic components of soil, uptaken by plant roots and microorganisms and leached into the deeper parts of the soil. The proportions between these processes vary in space and time. The contents of Cu, Ni and Zn in mineral horizons of the investigated soils were several times lower than in the ectohumus. Concentrations lower than the geochemical background values ($5.4 \text{ mg}\cdot\text{kg}^{-1}$ for Cu, $4.9 \text{ mg}\cdot\text{kg}^{-1}$ for Ni and $27.0 \text{ mg}\cdot\text{kg}^{-1}$ for Zn) confirm the lack of a significant impact of anthropogenic emission sources of these elements and very low contamination of environment. The low concentration of heavy metals is also conditioned by the light texture of soils. Numerous studies have shown that the concentration of Cu, Ni and Zn, as well as of many other metals, is closely, positively related to the degree of disintegration of the mineral part of the soil, especially to the content of clay fraction (e.g. Kabala et al. 2008). The concentrations of Cu ranged from 0.1 to $3.9 \text{ mg}\cdot\text{kg}^{-1}$ in Brunic Arenosols, and from 0.2 to $3.8 \text{ mg}\cdot\text{kg}^{-1}$ in Gleyic Podzols. The minimum concentration of Cu occurred in the parent material and the maximum in the A and B horizons. Nickel in the mineral horizons of Brunic Arenosols amounted to 2.3 – $6.9 \text{ mg}\cdot\text{kg}^{-1}$, showing a slight vertical variability. The concentration of this element in Gleyic Podzols was slightly higher and amounted to 0.4 – $6.0 \text{ mg}\cdot\text{kg}^{-1}$. The observed maximum concentrations of Cu in A and B horizons of these soils indicate close association of the element with soil organic mat-

ter, which is one of the most effective sorbents of metals (Leenaers et al., 1988; Logan et al., 1997; Charriau et al. 2011). Free iron oxides are also important sorbents of metals in soils (Dąbkowska-Naskręt 2013). In the investigated soils, the components were concentrated mainly in B horizons. The observed concentrations of Cu and Ni were within the range of values recorded by Brożek and Zwydak (2003) in the profiles of forest Brunic Arenosols and Gleyic Podzols in northern Poland.

The concentration of Zn in the mineral horizons of Brunic Arenosols ranged from 10.3 to $25.0 \text{ mg}\cdot\text{kg}^{-1}$ and of Gleyic Podzols from 3.3 to $21.3 \text{ mg}\cdot\text{kg}^{-1}$. Degryse and Smolders (2006) recorded a lower content of this element in anthropogenically uncontaminated Gleyic Podzols in Belgium ranging from 4.5 to $13.3 \text{ mg}\cdot\text{kg}^{-1}$. Lower values were also recorded by Brożek and Zwydak (2003) in Brunic Arenosols and Gleyic Podzols in Poland. The maximum concentrations of Zn in the profiles of Brunic Arenosol were noted in enrichment and humic horizons, and minimal concentrations in the parent material. The distribution patterns of Zn in individual Gleyic Podzol profiles varied. The maxima in G-1 profile occurred in the initial Bhs horizon and 3Cg horizon, in G-2 profile – in the initial Es and Bhs/C horizons, while in G-3 profile in the Brg horizon. The distribution of Zn in profiles of these soils indicates vertical transport of Zn during podsolization, with labile fractions of organic matter. Degryse and Smolders (2006) observed a similar distribution pattern of Zn in the uncontaminated profiles of Gleyic Podzols. In turn, in areas contaminated with Zn, the authors recorded the maximum concentrations of the metal in humic horizons. The distribution pattern of both Zn and other heavy metals in the profiles of Gleyic Podzols may therefore be an indicator of the environmental pollution by these substances.

4. Summary

Results of the studies conducted in the area of the lower supra-flood terrace of the Słupia River highlight the role of lithogenic and pedogenic factors in the spatial and vertical variability of Cu, Ni and Zn concentrations in forest soils in the areas uncontaminated anthropogenically. Accumulated in the early Holocene, poorly sorted river sands, which are the parent material of Brunic Arenosols, contained 0.1 – $1.5 \text{ mg}\cdot\text{kg}^{-1}$ of Cu, 2.6 – $6.9 \text{ mg}\cdot\text{kg}^{-1}$ of Ni and 10.3 – $16.2 \text{ mg}\cdot\text{kg}^{-1}$ of Zn. During 5100–4200 BP in some places, the process of their aeolization occurred. As a result, in local land depressions formed small aeolian covers built of the partially sorted

and depleted in silt, clay and heavy minerals as compared to the initial material. Aeolian sands, being the parent material of Gleyic Podzols, contained slightly higher concentrations of Cu ($1.3\text{--}1.9\text{ mg}\cdot\text{kg}^{-1}$) and generally lower concentrations of Ni ($1.2\text{--}2.4\text{ mg}\cdot\text{kg}^{-1}$) and Zn ($3.3\text{--}17.3\text{ mg}\cdot\text{kg}^{-1}$).

During pedogenesis, Cu, Ni and Zn were translocated by vegetation, from the deeper soil layers upwards to its surface, causing their concentration in the solum. Currently, the maximum concentrations of the investigated metals occur in ectohumus. This is a typical pattern found in forest soils. There were no significant differences between the ectohumus of Brunic Arenosols and Gleyic Podzols in terms of metal concentration despite the spatial variation of the species composition of forest stands. Differences were observed in the distribution patterns of Cu, Ni and Zn in the soil solum. In Gleyic Podzols, the minimum concentrations were noticed in eluvial horizons, while the maximum in orsteinic and humic horizons, which indicates metals translocation with percolating water, and close relationship of their distribution patterns with the podsolization process. Such relationships confirm the results of the studies of other authors. The maximum concentrations of the investigated metals in Brunic Arenosols occurred in humic and brunic horizons. Their distribution patterns indicate a close relationship between the metals and humic substances as well as iron oxides, as carriers and sorbents of ions.

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References

- Berg B., Ekbohm G., Söderström B., Staaf H. 1991. Reduction of decomposition rates of Scots pine needle litter due to heavy metal contamination, *Water, Air & Soil Contamination*, 59, 165–177.
- Bergbäck B., Carlsson M. 1995. Heritage of cadmium and lead. A case study of a Swedish accumulator factory. *Science of The Total Environment*, 166: 35–42.
- Brewer P.A., Taylor M.P. 1997. The spatial distribution of heavy metal contaminated sediment across terraced floodplains, *Catena*, 30: 229–249.
- Brożek S., Zwyczaj M. Atlas gleb leśnych Polski. Warszawa, Centrum Informacyjne Lasów Państwowych, pp. 467. ISBN 978-83-932256-0.
- Charriau A., Lesven L., Gao Y., Leermakers M., Baeyens W., Ouddane B., Billon G. 2011. Trace metal behaviour in riverine sediments: Role of organic matter and sulfides. *Applied Geochemistry*, 26: 80–90.
- Cotrufo M.F., De Santo A.V., Alfani A., Bartoli G., De Cristofaro A. 1995. Effects of urban heavy metal contamination on organic matter decomposition in *Quercus ilex* L. woods. *Environmental Contamination*, 89, 81–87.
- Dąbkowska-Naskręt H. 2013. Nanocząsteczki – naturalne i syntetyczne tlenki żelaza w glebach. In: Jonczak J., Florek W. (eds.) Środowisko glebotwórcze i gleby dolin rzecznych. Poznań-Słupsk, Wydawnictwo Naukowe Bogucki: 7–11.
- Degryse F., Smolders E., Parker D.R. 2009. Partitioning of metals (Cd, Co, Cu, Ni, Pb, Zn) in soils: concepts, methodologies, prediction and applications – a review. *European Journal of Soil Science*, 60: 590–612.
- Degryse F., Smolders E. 2006. Mobility of Cd and Zn in polluted and unpolluted Spodosols. *European Journal of Soil Science*, 57: 122–133.
- Fijałkowski K., Kacprzak M., Grobelak A., Placek A. 2012. The influence of selected soil parameters on the mobility of heavy metals in soils. *Inżynieria i Ochrona Środowiska*, 15(1): 81–92.
- Florek W. 1989. Osady dna doliny Słupi i ich wiek radiowęglowy. *Zeszyty Naukowe AGH. Geologia*, 15(1–2): 73–102.
- Huang J.H., Ilgen G., Matzner E. 2011. Fluxes and budgets of Cd, Zn, Cu, Cr and Ni in a remote forested catchment in Germany. *Biogeochemistry*, 103: 59–70.
- Jonczak J., Olszak I., Łazarczyk A. 2013. Geneza, ewolucja i właściwości gleb niższej terasy nadzalewowej Słupi w południowej części Słupska, in: Jonczak J., Florek W. (eds.) Środowisko glebotwórcze i gleby dolin rzecznych, Poznań-Słupsk, Wydawnictwo Naukowe Bogucki: 33–40.
- Kabała C., Singh B.R. 2001. Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter. *Journal of Environmental Quality*, 30: 485–492.
- Kabała C., Gałka B., Karczewska A., Chodak T. 2008. Zróżnicowanie zawartości pierwiastków śladowych w glebach różnych zbiorowisk leśnych w dolinie rzeki Dobra. *Roczniki Gleboznawcze*, 49(3/4): 72–80.
- Kalbitz K., Wennrich R. 1998. Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter. *The Science of the Total Environment*, 209: 27–39.
- Konradi E.A., Frentiu T., Ponta M., Cordos E. 2005. Use of Sequential Extraction to Assess Metal Fractionation in Soils from Bozanta Mare, Romania. *Acta Universitatis Cibiniensis Seria F Chemia*, 8(2): 5–12.
- Leenaers H., Schouten C.J., Rang M.C. 1988. Variability of the metal content of flood deposits. *Environmental Geology and Water Sciences*, 11: 95–106.
- Lindberg S.E., Turner R.R. 1988. Factors influencing atmospheric deposition, stream export, and landscape accumulation of trace metals in forested watersheds. *Water, Air and Soil Pollution*, 39: 123–156.

- Logan E.M., Pulford I.D., Cook G.T., Mackenzie A.B. 1997. Complexation of Cu^{2+} and Pb^{2+} by peat and humic acid. *European Journal of Soil Science*, 48: 685–696.
- Marcinek J., Komisarek J., Bednarek R., Mocek A., Skiba S., Wiatrowska K. 2011. Systematyka Gleb Polski, wydanie V. *Roczniki Gleboznawcze* 62(3): pp. 193.
- Martin C.W. 2000. Heavy metal trends in floodplain sediments and valley fill, River Lahn, Germany. *Catena*, 39: 53–68.
- Martinez C.E., Motto H.L. 2000. Solubility of lead, zinc and copper added to mineral soils, *Environmental Pollution*, 170: 153–158.
- McAlister J.J., Smith B.J., Török A. 2006. Element partitioning and potential mobility within surface dusts on buildings in a polluted urban environment, Budapest. *Atmospheric Environment*, 40: 6780–6790.
- Parzych A., Jonczak J. 2014. Pine needles (*Pinus sylvestris* L.) as bioindicators in the assessment of urban environmental contamination with heavy metals. *Journal of Ecological Engineering*, 15(3): 29–38.
- Pasieczna A. 2003. Atlas zanieczyszczenia gleb miejskich Polski. Warszawa, PIG, pp 105.
- Paulson A.J. 1997. The transport and fate of Fe, Mn, Cu, Zn, Cd, Pb and SO_4 in a groundwater plume and in downstream surface waters in the Coeur d'Alene Mining District, Idaho, U.S.A. *Applied Geochemistry*, 12: 447–464.
- PTG. 2009. Klasyfikacja uziarnienia gleb i utworów mineralnych – PTG 2008. *Roczniki Gleboznawcze* 60(2): 5–17.
- Rusek A., Kabała C., Drozdowska J. 2005. Zawartość ołowiu, cynku i miedzi w wybranych typach próchnic leśnych Dolnego Śląska. *Roczniki Gleboznawcze*, 56(1/2): 137–146.
- Saur E., Juste C. 1994. Enrichment of trace elements from long-range aerosol transport in sandy podzolic soils of southwest France. *Water, Air, and Soil Pollut.*, 73: 235–246.
- 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.
- Silva C.A.R., Lacerda L.D., Ovalle A.R., Rezende C.E. 1998. The dynamics of heavy metals through litterfall and decomposition in a red mangrove forest. *Mangroves and Salt Marshes*, 2: 149–157.
- Skřivan P., Rusek J., Fottová D., Burian M., Minařík L. 1995. Factors affecting the content of heavy metals in bulk atmospheric precipitation, throughfall and stemflow in central Bohemia, Czech Republic. *Water, Air, and Soil Pollution*, 85: 841–846.
- Strobel B.W., Borggaard O.K., Hansen H.C.B., Andersen M.K., Raulund-Rasmussen K. 2005. Dissolved organic carbon and decreasing pH mobilize cadmium and copper in soil. *European Journal of Soil Science*, 56: 189–196.
- Strojan C.L. 1978. Forest leaf litter decomposition in the vicinity of a zinc smelter. *Oecologia*, 32: 203–12.
- Taylor M.P. 1996. The variability of heavy metals in floodplain sediments: a case study from mid Wales. *Catena*, 28: 71–87.
- Tessier A., Campbell P.G.C., Bisson M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 51(7): 844–850.
- Tyler G. 1973. Heavy metal pollution and decomposition of spruce needle litter. *Oikos*, 24: 402–416.
- Tyler G. 1992. Critical concentrations of heavy metals in the mor horizon of Swedish forests. Solna, Swedish Environmental Protection Agency, Report 4078, pp. 38.
- Ukonmaanaho L, Starr M, Mannio J, Ruocho-Airola T. 2001. Heavy metal budgets in two headwater forested catchments in background area of Finland. *Environmental Pollution*, 114: 63–75.
- Zgłobicki W. 2008. Geochemiczny zapis działalności człowieka w osadach stokowych i rzecznych, Lublin, UMCS s. 240. ISBN: 978-83-227-2866-6.