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CONTENTS OF FORMS OF LEAD IN THE SOILS OF THE PROTECTED ZONE IN THE ROZTOCZE NATIONAL PARK AND ADJACENT PRODUCTION AREAS

ZAWARTOŚĆ FORM OŁOWIU W GLEBACH OTULINY ROZTOCZAŃSKIEGO PARKU NARODOWEGO I TERENÓW PRODUKCYJNYCH DO NIEJ PRZYLEGŁYCH

Abstract: The aim of the study was to determine the total contents of acid soluble and water soluble Pb in light soil profiles that belong to rusty soils in the protected zone in the Roztocze National Park and adjacent industrial areas. The investigated soils had a natural content of total Pb. In spite of that, the results revealed accumulation of the analysed metals in surface levels (Ap), as compared with parent rock levels (C). Higher concentration [%] of lead, zinc and copper in Ap levels was found in the soils of the production areas than in the soils of the protected zone. It was observed that the contents of total forms of Pb, acid soluble forms of Pb and water soluble forms of Pb in the analysed soils were significantly correlated with chemical properties, soil reaction, contents of organic carbon, and soil absorbing capacity.

Keywords: forms of Pb, light soils, protected zone, industrial areas, Roztocze National Park

National Parks are created in order to protect the areas with extraordinary natural values and unique landscapes. The parks allow the nature to preserve its original, undisturbed cycle [1]. The network of existing national parks in Poland covers, although not evenly, the whole territory of the country [2]. The Roztocze National Park is one of these parks. It was founded in 1974 in the Middle Roztocze and includes within its boundaries the most precious natural values of the region. The protected zone is situated in the areas adjacent to the park. Its aim is to counteract any harmful effects of external factors. The protected zone is a buffer zone between the pristine ecosystems and production areas with intensive agricultural activity.

The area of the Middle Roztocze where the Roztocze National Park is located has different types of soils; however, the majority of soils belong to light soils [3]. Light

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soils are usually acidic and not resistant to chemical degradation, including excessive accumulation of heavy metals [4].

The aim of the study was to determine the total contents of Pb and its forms soluble in hydrochloric acid and water, in light soils in the protected zone of the Roztocze National Park and its adjacent production areas.

Material and methods

The study was carried out on rusty soils deriving from loose sands and slightly loamy sands situated in southern and south-western parts of the protected zone of the Roztocze National Park (which is located in south-eastern part of Poland) and its adjacent production areas. The samples for the analysis were taken from whole soil profiles (from levels Ap, Bv, and C) – five samples from the arable fields situated in the protected zone and five from the areas adjacent to the protected zone. Field studies were carried out on arable lands where potatoes were cultivated.

The soil samples were analysed with methods commonly used in soil science.

The following were marked: granulometrical composition with Cassagrande's method in Proszynski's modification, contents of C organic with Tiurin's method in Simakow's modification, pH in H_2O and in 1 mol · dm^{-3} KCl potentiometrically, total absorptive capacity of soil (T) according to the formuls T = Hh + S, total contents of Pb with the atomic absorptive spectrometry method (AAS), Pb soluble in 1 mol · dm^{-3} HCl and water-soluble with Hornburg and Brummer's method, after Niemyska-Lukaszuk [5], which determines the percentage of forms of metals that can be absorbed, as compared with the total contents of these metals.

Results and discussion

The investigated soils in the protected zone of the Roztocze National Park had strongly acidic or acidic pH in the whole soil profile (Table 1). The values of pH_{KCl} varied: in Ap levels from 4.2 to 5.4, in Bv levels from 4.6 to 5.0, and in C levels from 4.4 to 5.0. Generally, Ap soil levels in the protected zone had lower values of pH_{KCl} than the soils situated in the production areas. Genetic levels of these soils had slightly acidic or acidic pH (Table 1). Ap levels of the soils in the production areas were about 56 % richer in C organic than the soils in the protected zone (Table 1). Ap levels of the soils in the production areas had about 40 % higher absorptive capacity than the soils in the protected zone (Table 1). Values of absorptive capacity of all the investigated soils decreased alongside with the increase in depth of the analysed soil profiles.

Contents of heavy metals in soil depends on chemical composition of soil and pollution emitted into the atmosphere by industry, cars, and agriculture. Trace elements (such as: Pb, Cr, Cd, Hg, Ni, Cu, Zn and other) that accumulate in soil in excessive amounts constitute the source of the most troublesome and long-enduring soil pollution. This is mainly due to slow migration of heavy metals.

Table 1

Basic chemical properties of investigated soils – range and mean values

Horizon	pH_{H_2O}	pH_{KCl}	Organic C [%]	Soil absorbing capacity (T) [cmol(+) · kg^{-1}]
Soils in the protected zone				
Ap	5.5[a] 4.4–5.8[c]	5.2[a] 4.2–5.4[c]	1.45[b] 0.85–1.52[c]	5.38[b] 4.25–5.85[c]
Bv	5.2[a] 4.9–5.7[c]	4.9[a] 4.6–5.0[c]	0.15[b] 0.12–0.16[c]	3.55[b] 3.47–3.76[c]
C	5.0[a] 4.8–5.4[c]	4.8[a] 4.4–5.0[c]		2.15[b] 2.02–2.18[c]
Soils in the production areas				
Ap	6.1[a] 5.9 –6.4[c]	5.8[a] 5.6–6.1[c]	2.26[b] 1.97–2.35[c]	7.48[b] 6.92–7.75[c]
Bv	5.7[a] 5.2–5.9[c]	5.2[a] 5.0–5.7[c]	0.21[b] 0.16–0.27[c]	3.92[b] 3.65–4.10[c]
C	5.2[a] 5.0–5.4[c]	4.8[a] 4.6–5.2[c]		2.66[b] 2.45–3.21[c]

[a] – value with logarithm; [b] – mean values; [c] – range of changes.

Heavy metals, including lead, are accumulated in the surface level of soil, also referred to as the humus level. It is due to chemical relation of heavy metals with organic matter present in the humus level [6, 7]. Lead is a low-mobility element because it undergoes strong absorption not only by organic matter but also by clay minerals, iron hydroxides and aluminium hydroxides [8]. Because of low migration of Pb, its natural distribution in a soil profile reflects its contents in the mother rock, and is treated as an indicator for geochemical prospection [9].

From vertical distribution of Pb in the investigated soil profiles located in the area of the protected zone in the Park and beyond the boundaries of the protected zone, it can be observed that Pb is accumulated in the surface levels. In the case of the soils located in the closest vicinity of the Park, enrichment of the Ap levels in Pb when compared with C levels was 553.8 %, and in the case of the soils from production areas – 600 % (Table 2). In spite of such a large enrichment of the humus levels in total lead, as compared with the mother rock levels, the investigated soils did not have the content of total lead that would exceed the norms, which means that the content of lead was natural. The results obtained by other authors confirm this. The natural content of lead in the surface levels of different arable soils in Poland ranges from 20 to 60 mg · kg^{-1} [10, 11]. Other authors suggest that when natural content of heavy metals in soil is estimated, type of soil and chemical properties of soil should be taken into account [12]. Natural content of lead in light soils with acidic pH and strongly acidic pH are 30 mg · kg^{-1}, and in the soils with neutral pH natural contents of Pb is 50 mg · kg^{-1}. On the basis of this criterion, it can be presumed that the investigated soils in the protected area of the Park and its adjacent production areas have natural content of lead. According to

Kabata-Pendias and Pendias [9], concentration of lead in given levels of soil is, to a large extent, connected with the influence of anthropogenic factors, and is usually higher than the natural content. Even soils situated beyond the reach of industrial emission and car fumes show higher content of lead in surface levels.

Table 2

Forms of Pb in investigated soils – mean values

Genetic level	Total Pb in soils [$mg \cdot kg^{-1}$]	Enrichment of genetic levels as compared to mother rock [%]	Acid-soluble forms of Pb [$mg \cdot kg^{-1}$]	Mobility index [%]	Water-soluble forms of Pb [$mg \cdot kg^{-1}$]	Mobility index [%]
Soils in protected zone of RPN						
Ap	28.8	553.8	18.9	65.6	2.3	8.0
Bv	18.4	353.8	12.7	69.0	1.5	8.2
C	5.2	100.0	4.1	78.8	0.4	7.7
Soils in production areas						
Ap	26.4	600.0	15.7	59.5	1.9	7.2
Bv	15.8	359.1	10.0	63.3	1.2	7.6
C	4.4	100.0	3.6	81.8	0.4	9.1

The statistical analysis that was carried out revealed many significant, positive correlations between the amount of total lead and pH, content of $C_{org.}$, and absorptive capacity, no matter where the soils were situated (Table 3).

Table 3

Correlation coefficients between Pb and basic chemical properties of soils
(correlation significant at p = 0.01)

Listing	pH_{H_2O}	pH_{KCl}	$C_{org.}$	T
pH_{KCl}	**1.** 0.999 **2.** 0.998	—		
Organic C	**1.** 0.994 **2.** 0.928	**1.** 0.994 **2.** 0.946	—	
T	**1.** 0.911 **2.** 0.966	**1.** 0.911 **2.** 0.978	**1.** 0.951 **2.** 0.993	—
Total content of Pb	**1.** 0.830 **2.** 0.998	**1.** 0.830 **2.** 0.993	**1.** 0.886 **2.** 0.902	**1.** 0.986 **2.** 0.947
Acid-soluble forms of Pb	**1.** 0.816 **2.** 0.997	**1.** 0.816 **2.** 0.992	**1.** 0.874 **2.** 0.896	**1.** 0.982 **2.** 0.943
Water-soluble forms of Pb	**1.** 0.817 **2.** 0.997	**1.** 0.817 **2.** 0.991	**1.** 0.875 **2.** 0.894	**1.** 0.982 **2.** 0.941

1. – soils in the protected zone; **2.** – soils in the production areas.

Ap levels of the soils in the protected zone of the Park had higher content of lead soluble in hydrochloric acid than Ap levels of the soils in the production areas (Table 2). The mean content of lead in the surface levels of the soils in the protected zone of RPN was 18.9 mg $\cdot$ kg^{-1}, and 15.7 mg $\cdot$ kg^{-1} in the soils in the production areas (Table 2). The mean mobility index [5] for the surface levels of the soils in the protected zone was 65.6 % of the total content of lead, and 59.5 % in the soils situated beyond the boundaries of the protected zone. The value of the mobility index increased systematically with the depth of soil profiles. Soil acidity helps in creation of phytosociological components because heavy metals, such as lead, occur in their soluble forms, which is more accessible for plants [7]. Badora [13] observed that when soil pH is acidic, solubility of most toxic elements for plants (including lead) increases, and solubility of main nutrients decreases. Mobile forms of lead in acidic soils occur mainly as cations Pb^{2+} and $PbHCO_3^+$, and organic complexes. Alkaline soils are dominated by PbOH and $Pb(CO_3)_2^{2-}$ [9].

The statistical analysis that was carried out revealed that forms of lead soluble in 1 mol $\cdot$ dm^{-3} HCl in the investigated soils positively correlated with pH (Table 3). The correlation coefficient for the soils in the protected zone of the park was r = +0.816, and for the soils in the production areas r = +0.997. Moreover, significant, positive correlations were observed between the amount of lead soluble in 1 mol $\cdot$ dm^{-3} HCl and the contents of total C and absorptive capacity of the investigated soils, no matter where these soils were situated.

Many authors emphasize the fact that the majority of lead compounds does not dissolve in water easily [14]. Compared with other metals, the mobility of lead is as follows: $Cd^{2+} > Zn^{2+} > Pb^{2+} > Cu^{2+}$ [8]. In the humus levels in the protected zone slightly higher content of water-soluble forms of lead was observed than in the same levels of the soils in the production areas (Table 2). For Ap levels of the soils situated in the protected zone, the mean value of water-soluble form of copper was 2.3 mg $\cdot$ kg^{-1}, with the mobility index 8.0 %, and for Ap levels of the production areas – 1.9 mg $\cdot$ kg^{-1}, with the mobility index 7.2 %. Regardless of where the soils were situated, the content of the investigated form of lead tended to decrease. The statistical analysis that was carried out revealed significant, positive correlations between the content of water-soluble forms of lead and pH of the soils in the protected zone of the park (r = +0.817), and the soils in the production areas (r = +0.991) (Table 3). Significant, positive correlations were obtained between the content of water-soluble forms of lead and the content of $C_{org.}$, and the absorptive capacity (Table 3).

A significant influence of the content of C organic on total content of lead and its soluble forms was observed in this study. This was proved by high, positive correlation coefficients (Table 3). Badora [13] noted that organic matter and mineral matter in soil largely contribute to changes in amounts of given forms of elements in soil, because they undergo various processes on surfaces. Moreover, a correlation between the negative value of the absorptive capacity and the content of the investigated forms of lead was observed.

Conclusions

1. The distribution of the content of total forms of lead throughout the soil profiles in the protected zone of the Roztocze National Park, and the production areas situated beyond its boundaries, is within the common norms for rusty soils.

2. Total forms of lead accumulated in the humus levels of the investigated soils in the amounts found in unpolluted soils.

3. Ap levels of the protected zone had higher content of acid-soluble and water-soluble forms than the corresponding levels of soils in the production areas.

4. The content of the investigated form of copper tended to decrease alongside with the increase in depth of the soil profiles; at the same time the mobility index increased.

5. Higher content of total forms of copper in Ap levels of the investigated soils points to their anthropogenic origin.

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ZAWARTOŚĆ FORM OŁOWIU W GLEBACH OTULINY ROZTOCZAŃSKIEGO PARKU NARODOWEGO I TERENÓW PRODUKCYJNYCH DO NIEJ PRZYLEGŁYCH

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Abstrakt: Celem pracy było określenie zawartości ogólnej Pb i jego form rozpuszczalnych w kwasie solnym i w wodzie w profilach gleb lekkich należących do klasy gleb rdzawych położonych na terenie otuliny Roztoczańskiego Parku Narodowego i terenów produkcyjnych do niej przyległych. Badane gleby charakteryzowały się naturalną zawartością Pb ogólnego. Pomimo tego otrzymane wyniki badań świadczą o nagromadzeniu analizowanych metali w poziomach wierzchnich (Ap) w odniesieniu do poziomów skał macierzystych (C). Większą względną koncentracją [%] ołowiu w poziomach Ap charakteryzowały się gleby terenów produkcyjnych w porównaniu do gleb otuliny. Stwierdzono, iż zawartość ogólnych form ołowiu i jego form rozpuszczalnych w kwasie solnym i wodzie w analizowanych glebach była istotnie skorelowana z właściwościami chemicznymi, w tym odczynem, zawartością węgla organicznego i pojemnością sorpcyjną.

Słowa kluczowe: formy ołowiu, gleby lekkie, otulina parku, tereny produkcyjne, Roztoczański Park Narodowy