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PROFILE DISTRIBUTION AND MOBILITY OF LEAD IN SELECTED ARABLE SOILS FROM PRADOLINA GLOGOWSKA

PROFILOWA DYSTRYBUCJA I MOBILNOŚĆ OŁOWIU W WYBRANYCH GLEBACH UPRAWNYCH Z OBSZARU PRADOLINY GŁOGOWSKIEJ

Abstract: Analysis of the total content of microelements in soils and their speciation and mobility enables to asses the quality of the environment and identify the impact of anthropogenic factors on the functioning of various natural ecosystems.

The aim of the research was to determine the mobility and profile distribution of lead and sequentially isolated fractions of lead in arable Luvisols of various texture from Pradolina Glogowska.

The total content of metals was performed using AAS method, after the digestion of soils in mixture of HF and $HClO_4$ and the content of mobile forms of Pb using sequential analysis. In the soils studied the total content of lead was in the range 17.40–45.36 mg · kg^{-1}. These values do not exceed the geochemical background level, for this metal. The sequential analysis showed that the highest share in total lead content was fraction VII (residual) of approximately 40 % and the lowest in fractions I–III below 5 % of the total metal. The above results allow to classify the soils tested to uncontaminated. The results also indicate a relatively low mobility of lead in soils. These soils can be used for all agricultural and horticultural crops production, due to principles of rational use of agricultural production area.

Key words: soil, lead, sequential analysis

Most heavy metals, except Fe and Ti occurs in the Earth's crust in the amounts less than 0.1 %, so they are among the trace elements [1]. From the biogeochemical point of view, they are divided into two groups, namely: the elements necessary for normal metabolic processes, and toxic elements, like lead [2, 3]. One of the sources of heavy metals in soils is non-ferrous metallurgy, including metallurgy of copper. In the area of Pradolina Glogowska (Zukowice) in 1978 Copperworks Glogow II began the production, which causes emission of gaseous and solid particles that affect the surrounding soils and crop quality. The previous research undertaken on soils in the vicinity of

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copperworks, showed a dramatic increase of metal concentration in the surface layer of soils in the early years of operation of copperworks. These concentrations then decreased and stabilized at relatively low levels in agricultural areas, while in wooded areas there was a secondary increase of the content of heavy metals in the surface layers of soils. Study of soils and plant material from the vicinity of the copperworks in 2004 did not show any accumulation of metals in soils, while elevated concentrations of Pb in plant material from this area was detected. The source of lead in this case may be, the dust emissions associated with metallurgical processes, resulting in adsorption of lead oxides on the surface of leaves, which may lead to secondary contamination of soils.

The purpose of this study was to determine the mobility and profile distribution of lead in arable Luvisols in the area of Pradolina Glogowska, being under the copper industry impact.

Material and methods

The research was conducted in the agricultural area affected by the emission of gasses and dusts from the Copperworks Glogow. The research material consists of 4 soil profiles located in the distance of 3.0 to 6.8 km from the copperworks. In the soil samples from each genetic horizon the following soil analyses were made: texture using Cassagrande method with the modification by Pruszynski, pH in H_2O and in the KCl solution (1 mol/dm^3) using potentiometric method, C_{org} using Tiurin method, content of $CaCO_3$ by Scheibler volume method [4]. The total lead content was determined after mineralization of the soils in a mixture of HF and $HClO_4$ acid [5]. The mobile forms of lead was determined based on chemical sequential analysis by Miller et al [6] with modification [7]. To validate the accuracy of analysis and measurements, analysis of certified materials Till-3 and SV-M had been performed. Total and mobile forms of Pb were determined by *atomic absorption spectrometry* (AAS) using PU 9100X spectrometer. The analysis was performed in triplicates. The average values are shown in tables.

Results and discussion

The morphological characteristics of the examined soil profiles, allowed to classifiy them as typical Luvisols formed from loamy dust (Systematics of Polish Soils 1998) [8]. The bedrocks of analyzed soils show the granulation of loamy dust (Table 1), and in textural B horizon – clayey dust was determined, which is the result of lessive process. In terms of agricultural science (PTG 2008) they are classified as loamy soils (Wierzchowice – P1 and Modla – P2) and clayey soils (Kurowice – P3 and Nielubia – P4). The content of the coarse skeleton particles in the range from 5 % to 15 % is typical for low skeletal soils [9]. The pH of the investigated soils was in range of 7.33–8.55 pH_{H_2O} and pH_{KCl} of 5.81–7.75 and it was the lowest in illuvial horizon for the most of the sites (Table 1). Calcium carbonate was detected in all sites except profile P1. The richest in this component was C horizon of P3 and P4 profiles and illuvial

Table 1

Physicochemical properties of the soils

Profile genetic horizon	Depth [cm]	Percentage content of fraction [mm]				pH		$CaCO_3$ [%]	C_{org} [g · kg^{-1}]
		> 2	2–0.05	0.005––0.002	< 0.002	H_2O	KCl		
P1 Wierzchowice									
Ap	0–20	10.3	35	55	10	7.33	6.07	< 1	18.1
Eet	20–45	3.2	25	63	12	7.54	5.91	< 1	3.2
Bt	45–90	4.3	23	60	17	7.95	5.81	< 1	n.d.
C	90–100	1.2	85	9	6	8.16	6.62	< 1	n.d.
C1	> 100	9.7	34	57	9	8.14	6.58	< 1	n.d.
P2 Modla									
Ap	0–30	13.0	66	25	9	7.53	6.89	< 1	7.2
Eet	30–60	10.0	48	45	7	8.20	7.50	< 1	3.9
Bt	60–100	7.7	28	55	17	7.82	6.46	11.60	n.d.
C	> 100	5.7	23	66	11	8.48	7.65	< 1	n.d.
P3 Kurowice									
Ap	0–25	112.6	35	51	14	8.19	7.49	1.93	7.0
Eet	25–48	12.9	26	67	7	8.55	7.72	< 1	1.2
Bt	48–90	5.9	25	58	17	8.13	7.30	6.72	n.d.
C	> 90	7.1	27	63	10	8.38	7.75	8.58	n.d.
P4 Nielubia									
Ap	0–20	11.5	20	65	15	7.55	7.22	< 1	18.4
Eet	20–45	9.1	29	59	12	7.33	7.05	< 1	4.9
Bt	45–95	6.2	28	56	16	7.70	6.98	3.46	n.d.
C	> 95	8.0	27	61	12	8.10	7.30	5.82	n.d.

horizon of P2, P3 and P4 profiles. High content of $CaCO_3$ in the soils studied did not always correspond to the high value of pH.

A neutral pH of soil may be caused by the ions washed out to this horizon, such as Fe, Al, Mn [2]. In the samples from Eet and C horizons in P2 profile, alkaline pH is not accompanied by a high content of $CaCO_3$, which shows that high value of pH may be due to other forms of metals alkalizing soil environment, occurring in the form of salts or hydroxides. The content of C-organic in humus horizons of investigated soils was in the range of 7.0–18.1 g · kg^{1} (Table 1). These are the typical values for soils of this region [3, 10–12].

The total content of lead was in range of 17.40–45.36 mg · kg^{-1}. Significantly higher total content of Pb was found in the surface horizons of the investigated profiles (Table 2), which may indicate its anthropogenic origin. Lead is an element with low mobility and significant affinity to clay minerals and hydrated oxides [1, 13]. It also easily combines with soil organic matter. Elevated concentration of Pb in surface layers was also reported by other authors [14–16].

Table 2

The total content of lead and metal fractions in soils

Profile genetic horizon	Total Pb content [mg · kg^{-1}]	F I	F II	F III	F IV	F V	F VI	F VII*
		[mg · kg^{-1}]						
P1 Wierzchowice								
Ap	44.64	p.d	p.d	1.60	5.72	12.72	11.60	13.00
Eet	31.36	p.d	p.d	1.12	4.40	8.12	5.92	11.80
Bt	30.16	p.d	p.d	1.72	4.80	7.80	5.52	10.32
C	27.16	p.d	p.d	1.32	5.00	8.32	2.80	9.72
C1	27.36	p.d	p.d	0.20	4.92	8.32	4.52	9.40
P2 Modla								
Ap	31.44	0.16	p.d	0.52	3.60	9.12	6.52	11.52
Eet	23.84	p.d	p.d	0.40	2.80	6.92	3.32	10.40
Bt	24.48	p.d	p.d	0.76	3.00	6.60	2.20	11.92
C	21.96	p.d	p.d	0.44	2.60	7.32	1.40	10.20
P3 Kurowice								
Ap	34.68	p.d.	p.d	0.80	2.12	11.52	7.92	12.32
Eet	17.56	0.28	p.d	p.d	1.80	5.76	1.00	8.72
Bt	22.44	p.d	p.d	0.08	0.80	6.12	3.92	11.52
C	17.40	0.24	p.d	p.d	0.92	5.52	1.12	9.60
P4 Nielubia								
Ap	45.36	p.d	p.d	1.52	5.12	19.00	5.52	14.20
Eet	34.80	p.d	p.d	1.00	5.08	10.52	6.00	12.20
Bt	32.44	p.d	p.d	0.44	4.00	8.40	8.40	11.20
C	28.72	p.d	p.d	0.40	4.20	7.40	4.92	11.80

F I – exchangeable and soluble in water fraction, F II – forms soluble in acids, F III – forms occluded on manganese oxides, F IV – forms associated with organic matter, F V – lead bound to amorphous iron oxides, F VI – forms associated with crystalline iron oxides, F VII – residual forms, p.d. – below detection limit.

The values of the total Pb content lead to a conclusion that the investigated Luvisols are not polluted with this metal [2]. These soils may be used for all agricultural crops in accordance with the principles of rational use of agricultural production area [17]. Sequential extraction studies were carried out, in order to investigate the mobility of lead and its possible release into the environment [18]. In the conducted sequential analysis, seven fractions were separated: exchangeable and soluble in water fraction (F I), fraction soluble in acids (F II), forms occluded on manganese oxides (F III), associated with organic matter (F IV), bound to amorphous iron oxides (F V), associated with crystalline iron oxides (F VI) and residual fraction (F VII) (Table 2). In the investigated soils lead dominated in fraction VII – residual form (Table 2), which is hardly soluble and unavailable for plants, due to association with soil matrix. The content of lead in this fraction was in range of 8.72–14.20 mg · kg^{-1}, which was from 29 to 55 % of total lead content. A significant portion of this fraction was observed by others in the soils from unpolluted areas [19–21]. The highest content of this fraction was determined in surface horizon of the investigated soils. The five fractions in the sequential extraction procedure used, include solid phase lead species, that can be mobilised under natural conditions. Fractions I and II are below the detection limit for almost all soil samples (Table 2). Gerritse and van Driel [21] found that Pb in exchangeable fraction was as low as 1–5 % the total Pb. In environmental samples these forms are usually very low, less than 5 % of the total content [23–26]. The content of Pb associated with manganese oxides (F III) is relatively low (Figs. 1–4). Lead bound to soil organic matter (F IV) is significant [25, 26]. The high partition of Pb fraction associated with organic matter may lead to temporary metal release, as a result of

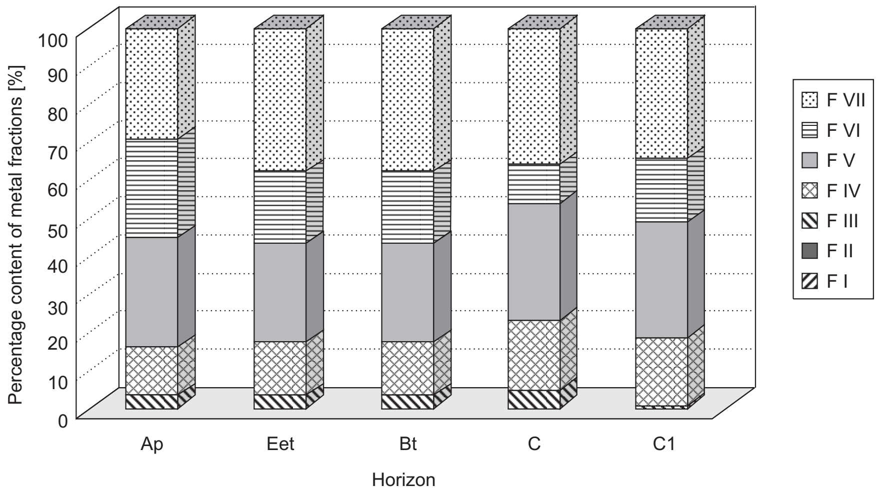

Fig. 1. Distribution of lead fractions in profile P1

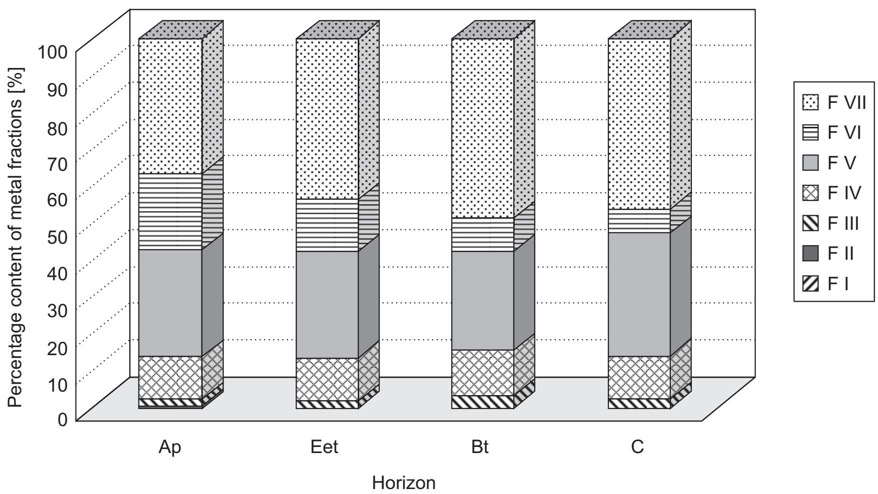

Fig. 2. Distribution of lead fractions in profile P2

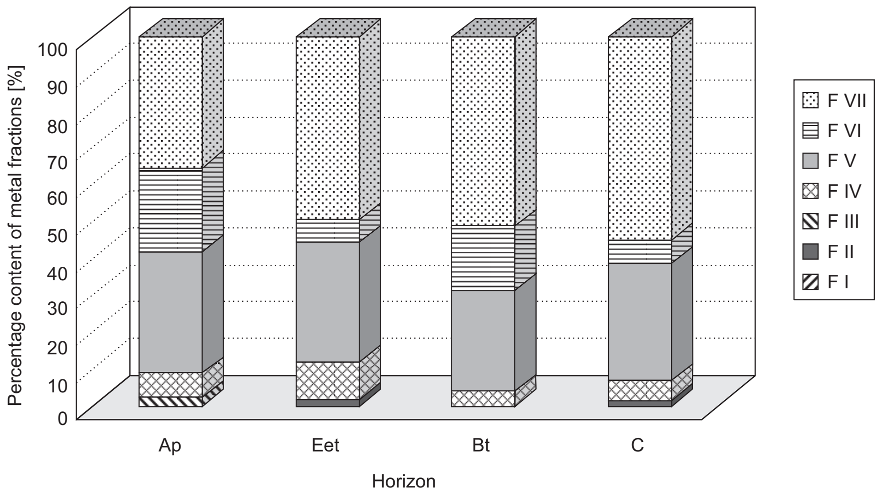

Fig. 3. Distribution of lead fractions in profile P3

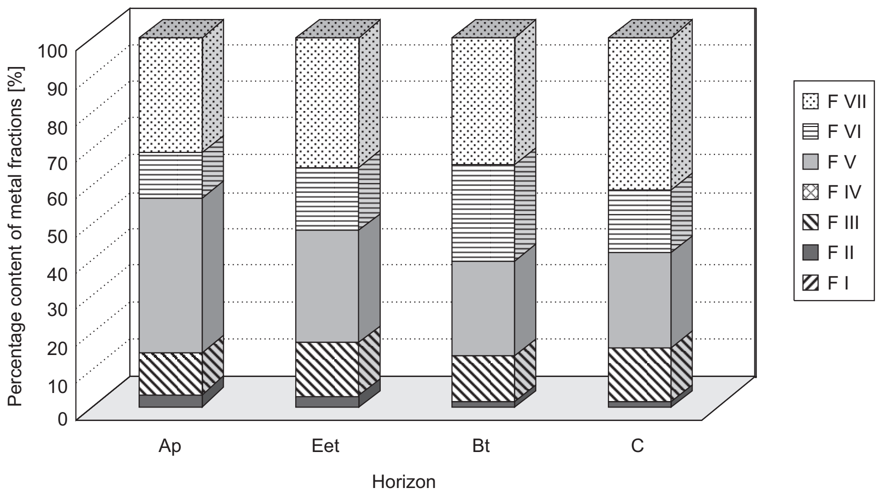

Fig. 4. Distribution of lead fractions in profile P4

naturally occurring processes of decomposition of organic material [27]. It has been shown that organic matter is the dominant constituent contributing to Pb retention in soils [27]. However, the highest contents of Pb was associated with amorphous (F V) and crystalline (F VI) iron oxides. Thus, pedogenic iron oxides are effective sink for lead. But in case of water status change in soils (water logging) iron oxides can be dissolved under the redox gradient effect and lead can be liberated from its associations.

The results of the sequential extraction shows, that lead has limited mobility in studied soils, unless changes such as mineralization of soil organic matter [26] or reduction of pH or redox potential will occur. The solubilisation of iron oxides will lead to release of Pb held by these compounds [28].

The results of the sequential extraction analysis indicate that for soils with sliglitly elevated level of Pb there is a need to monitor changes in soil pH and potential redox in order to predict lead liberation due to dissolution processes of a particular soil components.

Conclusions

Morphological and physicochemical properties allowed to classify the investigated soil profiles from Pradolina Glogowska as typical Luvisols formed from loamy dust and to category to loamy and clayey soils. Their pH was in range of pH_{KCl} 5.81–7.75 and in bedrock horizon they contained calcium carbonate (except P1 profile). The investigated soils are classify as soils with the natural total lead content, which was in range of 17.40–45.36 $mg \cdot kg^{-1}$. In the performed sequential analysis seven lead fractions were separated. In the investigated soils fraction VII – residual forms, which are hardly soluble and unavailable for plants dominated. The most mobile fractions of lead (F I and F II), readily and potentially bioavailable, were beneath the detection threshold in the investigated soils.

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PROFILOWA DYSTRYBUCJA I MOBILNOŚĆ OŁOWIU W WYBRANYCH GLEBACH UPRAWNYCH Z OBSZARU PRADOLINY GŁOGOWSKIEJ

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Abstrakt: Analiza całkowitych zawartości mikroelementów w glebach oraz ich mobilności umożliwia ocenę stanu środowiska na danym terenie oraz określenie wpływu czynników antropogennych na funkcjonowanie ekosystemów przyrodniczych.

Celem niniejszej pracy było określenie mobilności oraz profilowej dystrybucji ołowiu w uprawnych glebach płowych z obszaru Pradoliny Głogowskiej, będących pod wpływem oddziaływania Huty Miedzi Głogów.

Całkowitą zawartość ołowiu oznaczono metodą AAS po mineralizacji w mieszaninie kwasów HF i $HClO_4$, natomiast zawartość form mobilnych Pb, wg zmodyfikowanej przez Millera i in. (1986) [6] analizy sekwencyjnej.

Morfologia, uziarnienie i właściwości fizykochemiczne pozwoliły zakwalifikować badane gleby do podtypu gleb płowych typowych, wytworzonych z utworów pyłowych oraz do gleb o odczynie w zakresie od lekko kwaśnego do zasadowego. Całkowita zawartość ołowiu wynosiła 17,40–45,36 mg · kg^{-1}. Wartości te nie przekraczają poziomu tła geochemicznego, co pozwala uznać gleby tego regionu za niezanieczyszczone tym pierwiastkiem. W analizie sekwencyjnej największy udział w zawartości całkowitej ołowiu miała frakcja 7 (rezydualna) około 40 %, a najmniejszy frakcje 1–3, poniżej 5 % zawartości całkowitej badanego metalu. Uzyskane wyniki wskazują na stosunkowo małą mobilność ołowiu w badanych glebach. Gleby te mogą być przeznaczone pod wszystkie uprawy ogrodnicze i rolnicze, zgodnie z zasadami racjonalnego wykorzystania rolniczej przestrzeni produkcyjnej.

Słowa kluczowe: gleba, ołów, analiza sekwencyjna