ECOLOGICAL CHEMISTRY AND ENGINEERING A

Vol. 17, No. 8 2010

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# MOBILITY OF LEAD IN CONDITIONS OF ACID SOILS OF PODLASIE REGION

## MOBILNOŚĆ OŁOWIU W WARUNKACH KWAŚNYCH GLEB PODLASIA

**Abstract:** The researches were conducted in three districts of Podlasie Region. The research covered the determination of total content of lead and its two fractions: I (lead in soil solution, exchangeable) and II (lead bound with oxides and hydroxides of Fe and Mn). There was determined also pH of soils, the content of organic carbon in them, base exchange capacity and hydrolytic acidity.

It was found that the content of carbon in analyzed soils was low and typical for slightly contaminated soils. The content of both mobile fractions of lead was also low, but the percentage in total content was high and ranged between 12.8 and 36 %.

**Keywords:** acid soils, lead, mobility, fractions

The occurrence of lead in soils is in a direct relation with their mineralogical and glanurometrical composition, the origin of parent rock of soils, traffic and industrial emission and the use of industrial waste and municipal sewage sludge in liming [1–4].

Lead in soil environment is less mobile than cadmium and zinc, however it moves easily into food chain in a condition of soil contaminations. Acid reaction of soils, low content of humus and low sorptive capacity is in favour of excessive lead uptake by plants [5]. The conditions which limit the uptake of this element by plants is liming, organic and phosphorus fertilization [4, 6]. Dziadek and Waclawek [7] claim that phosphorus introduced into the soil contaminated by lead decreases slightly the amount of its easily soluble forms and forms bound with carbonates and oxides, while it causes the increase of organic fractions content and most of all share of fractions strongly bound with residual remains. After intake of lead into soils in the form of different inorganic compounds, it surrenders to absorption on organic and mineral colloids and it creates stable and insoluble in water chelation combinations with organic compounds. Sparingly soluble hydroxides $PbOH^+$, phosphates and carbonates of lead $Pb(CO_3)_2$

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precipitate in soils with slightly acid, neutral and alkaline reaction. A part of lead in acid soils occurs in forms of $Pb^{2+}$ and $PbHCO_3^+$ which are easily available for plants. Soils which are not under direct influence of contaminations do not show the tendency of lead accumulation. Lead content in geochemical background of soils in Poland amounts 20 $mg \cdot kg^{-1}$. In soils formed from sands it is even lower and amounts to 16 $mg \cdot kg^{-1}$ on average [4].

As far as the content of heavy metals is concerned, soils in Poland are assessed on the basis of their total content, however the main danger for plants is their content in easily available forms [8]. That is why the aim of presented researches was the assessment of chosen soils of Podlasie region, taking into account the content of mobile forms of lead, which is considered as one of the most dangerous element for people and animals.

## Material and methods

The samples for researches were taken from arable layer of soils in three districts of Podlasie province (105 samples) after plants crop in 2007. In soil samples there was determined the total content of lead after mineralisation in concentrated nitric(V) acid and two fractions modified by BCR method (Community Bureau of Reference, nowadays Standards Measurement and Testing Programme) [9]. It concerns fractions of metals: exchangeable, soluble in water and light acid bound with carbonates (1 stage), iron and manganese hydroxides (2 stage) and organic matter (3 stage). On the first stage of sequential analysis acetic acid is used (0.11 $mol \cdot dm^{-3}$), on the second one – hydroxylamine hydrochloride (0.5 $mol \cdot dm^{-3}$), but on the third one – hydrogen peroxide and ammonium acetate (1 $mol \cdot dm^{-3}$, pH = 2).

In the conducted researches there were determined two most mobile fractions: soluble fraction in 0.11 $mol \cdot dm^{-3}$ of acetic acid and reducible fraction (iron and manganese oxides), which was extracted by 0.5 $mol \cdot dm^{-3}$ of hydroxylamine hydrochloride solution. The fraction bound with organic matter was passed because of minimal content of carbon in analyzed soils. The determination of lead was done by atomic absorption spectrometry (Flame Atomic Absorption Spectrometry). There was counted the share of individual fractions and their sum in total content of lead. Moreover, there was determined agronomic category of soils, pH of soils in 1 $mol \cdot dm^{-3}$ of KCl solution, organic carbon measured by carbon analyzer – Total Organic Carbon 1200 as well as hydrolytic acidity and base exchange capacity by Kappen method.

## Results and discussion

Most of analyzed soils from three districts of Podlasie region (94 samples) were classified to very acid (pH < 4.5) and acid (pH 4.5–5.5) soils. Only 8 soils from Kolno district were slightly acid (pH 5.5–6.5) and 3 were neutral (pH > 6.5) (Table 1).

Table 1

Physicochemical properties of soils

| Range of pH and number of soils | Parameter | Organic carbon | Hydrolytic acidity | Base exchange capacity | Sorptive capacity |
|---|---|---|---|---|---|
| | | [g C · kg$^{-1}$] | [mmol H$^+$ · kg$^{-1}$] | [mmol(+) · kg$^{-1}$] | |
| Jasionowka | | | | | |
| < 4.5 n = 21 | range | 0.5–4.9 | 27–78 | 16–80 | 69–158 |
| | $\bar{x}$ | 2 | 61.4 | 42.5 | 104 |
| 4.5–5.5 n = 11 | range | 0.8–3.1 | 33–69 | 32–144 | 74–180 |
| | $\bar{x}$ | 1.8 | 45.3 | 60.7 | 106 |
| Korycin | | | | | |
| < 4.5 n = 23 | range | 0.7–4.3 | 39–72 | 20–116 | 62–164 |
| | $\bar{x}$ | 2.3 | 45.5 | 41.9 | 87.4 |
| 4.5–5.5 n = 10 | range | 0.6–4.3 | 24–60 | 32–88 | 59–112 |
| | $\bar{x}$ | 2.1 | 36.6 | 52 | 88.6 |
| Kolno | | | | | |
| < 4.5 n = 17 | range | 0.9–5.3 | 21–111 | 4–172 | 59–193 |
| | $\bar{x}$ | 2.5 | 60.3 | 38.8 | 99.2 |
| 4.5–5.5 n = 12 | range | 0.7–4.9 | 21–69 | 28–152 | 67–201 |
| | $\bar{x}$ | 2.7 | 51.5 | 74.3 | 125.8 |
| 5.5–6.5 n = 8 | range | 1.1–4.3 | 27–51 | 16–100 | 59–145 |
| | $\bar{x}$ | 2.9 | 33 | 5.3 | 95 |
| > 6.5 n = 3 | range | 1.7–5.5 | 15–21 | 132–260 | 153–281 |
| | $\bar{x}$ | 3.6 | 19 | 174.7 | 205.7 |

According to agronomical category over 90 % of soils was very light and light and the rest was medium-heavy. The content of organic carbon in most soils was low and amounted to 2 g C · kg$^{-1}$. Slightly more carbon was determined in soils of Kolno district and its content ranged from 0.7 to 5.6 g · kg$^{-1}$. Most of soils demands liming application which is proved by pH in 1 mol KCl and the level of hydrolytic acidity, which fluctuated from 27 to 78 mmol $H^+$ · kg$^{-1}$ in very acid and acid soils from Jasionowka district. Similar values of this parameter were found in soils from other districts. Smaller acidity was determined in soils of neutral reaction from Kolno district. Sorptive capacity of analyzed soils was low and only in some cases it exceeded 200 mmol · kg$^{-1}$.

The analyzed soils had very low content of total lead (Table 2) which amounted to 2.8 mg · kg$^{-1}$ on average in soils from Kolno district, 3.6 mg · kg$^{-1}$ in soils from Korycin district and in soils from Jasionowka district lead content was higher and equaled 5.7 mg · kg$^{-1}$. These values indicate that there is no contamination by lead in analyzed soils.

Table 2

The content of total lead and its mobile forms [mg · kg$^{-1}$] as well as share of mobile forms in total Pb amount [%]

| Range of pH and number of soils | Parameter | Total lead | Fraction I (soluble) | | Fraction II (reducible) | | Σ I and II fractions | |
|---|---|---|---|---|---|---|---|---|
| | | | content | share | content | share | content | share |
| Jasionowka | | | | | | | | |
| < 4.5 n = 21 | range | 0.5–12.5 | 0.0–0.3 | 0.3–58.3 | 0.1–0.5 | 0.2–58.0 | 0.2–0.7 | 2.1–106.0 |
| | $\bar{x}$ | 6.3 | 0.2 | 6.0 | 0.3 | 7.9 | 0.4 | 12.8 |
| 4.5–5.5 n = 11 | range | 1.0–11.5 | 0.0–0.3 | 0.5–29.7 | 0.1–0.3 | 1.6–28.3 | 0.2–0.6 | 2.1–58.0 |
| | $\bar{x}$ | 5.5 | 0.2 | 6.2 | 0.2 | 6.6 | 0.4 | 12.8 |
| Korycin | | | | | | | | |
| < 4.5 n = 23 | range | 1–6.5 | 0.3–0.5 | 5.9–41.6 | 0.2–0.5 | 4.4–48.0 | 0.6–0.9 | 12.3–89.5 |
| | $\bar{x}$ | 3.6 | 0.4 | 15.2 | 0.3 | 13.1 | 0.7 | 28.3 |
| 4.5–5.0 n = 10 | range | 1.0–5.0 | 0.3–0.5 | 8.2–36.3 | 0.3–0.4 | 6.2–26.2 | 0.6–0.8 | 14.5–62.5 |
| | $\bar{x}$ | 3.6 | 0.4 | 13.7 | 0.3 | 11.4 | 0.7 | 25.2 |
| Kolno | | | | | | | | |
| < 4.5 n = 17 | range | 1.0–7.5 | 0.0–2.5 | 0.0–50.2 | 0.2–0.7 | 3.4–38.9 | 0.5–3.0 | 10.5–89 |
| | $\bar{x}$ | 3.5 | 0.5 | 18.5 | 0.4 | 15.3 | 0.9 | 33.7 |
| 4.6–5.5 n = 12 | range | 1–5.0 | 0.0–1.2 | 0.0–47.4 | 0.3–0.7 | 5.83–49.7 | 0.5–1.6 | 15.6–62.6 |
| | $\bar{x}$ | 2.8 | 0.5 | 18.2 | 0.4 | 17.8 | 0.9 | 36.0 |
| 5.5–6.5 n = 8 | range | 0.5–2.5 | 0.5–0.6 | 10.3–96.7 | 0.05–0.4 | 5.2–21.4 | 0.5–1.0 | 15.5–49.7 |
| | $\bar{x}$ | 3.0 | 0.5 | 29.8 | 0.3 | 11.2 | 0.8 | 25.7 |
| > 6.5 n = 3 | range | 2.5–2.5 | 0.0–5.2 | 0.0–20.6 | 0.3–0.3 | 11.6–13.7 | 0.3–0.8 | 12.4–32.9 |
| | $\bar{x}$ | 2.5 | 0.3 | 13.3 | 0.3 | 12.5 | 0.6 | 25.4 |

The results of researches conducted by Terelak [4] in soils on arable land in Poland show that the average content of this element was 13.6 mg · kg$^{-1}$, with the range of 7.4 to 25 mg · kg$^{-1}$, however arable land of Podlasie province was characterised by the lowest content of lead throughout the country. While conducting the researches of soils on arable land of eastern Poland, Raczuk and Tkaczuk [10] found higher content of Pb, which ranged from 9.4 to 14.2 mg Pb · kg$^{-1}$. According to Bozko and Puchty [11] arable land of Poland is classified to uncontaminated by lead, which proves the results of Terelak et al [4]. The low content of this element in most soils of the country is caused by high content of light soils (60 %) which contain 20 % of floatable fractions. According to Kabata-Pendias and Pendias [3], the content of lead in soils formed from sands is generally lower in comparison with the content of this metal in soils made of more solid deposits. Similar relation found Czekala et al [12] while analysing arable soils of former Poznan province. The average content of lead in very light soils amounted to 15.8 mg · kg$^{-1}$, in light – 16.0 mg · kg$^{-1}$, in medium heavy – 18.3 mg · kg$^{-1}$

while in heavy ones – 18.8 mg · $kg^{-1}$. The influence of reaction on the content of this element in analyzed soil deposits was very weak.

The content of lead in first and second fraction in analyzed soils was at the similar level (Table 2). However, their share in total content of lead was slightly higher in case of the first fraction than in the second one in soils from Kolno district. The percentage of sum of two fractions containing easily soluble combinations of lead decreased in these soils together with the increase of pH and it reached: 33.7 % in very acid soils, 36.0 % in acid soils, 25.7 % and 25.4 % in lightly acid and neutral ones. In soils from the rest of districts, the content of lead in both fractions was similar but their share in total lead was different. In very acid and acid soils from Jasionówka first lead fraction constituted about 6 %, in acid soils from Korycin amounted 13.7 % and in very acid ones it equaled 15.2 %. Similar relations were found in soils from these districts in case of second fraction of lead. Karczewska [13], Keizer and Bruggenwert [14] prove strong influence of iron oxides in lead fixation especially in acid soils. The percentage of both fractions in total content of Pb indicates its highest mobility in soils from Kolno district, a little less in those from Korycin and the least from Jasionowka. Variation coefficient for individual fraction of lead was high and reached respectively for I and II fraction: 66.3 % and 34.7 % in Kolno district, 34.7 % and 52.0 % in Jasionowka, and 11.8 % and 16.0 % in Korycin district. There was not observed essential relation between active forms of lead, agronomical category and soil reaction. While conducting soil researches of arable land of Podlasie province Skorbilowicz et al [15] registered higher contents of active forms of lead that the ones presented in this paper, which fluctuated between 2.9 and 14.5 mg · $kg^{-1}$ with the share in total lead content ranging from 7.3 to 36.1 %. The contents of exchangeable form of Pb in arable soils of Malopolska province ranged from 0.63 to 37.5 mg · $kg^{-1}$, with the average of 8.44 mg · $kg^{-1}$ [16]. The mobility of lead was influenced mainly by acid reaction of soils and low content of organic matter. Terelak et al [4] found that excessive uptake of lead and other heavy metals is caused by acid reaction of soils, low content of humus and low sorptive capacity. Lead is very strongly bound by organic matter in soils with pH > 4.5. It is proved by the results obtained for lightly acid and neutral soils from Kolno district, where the percentage of mobile forms of lead was lower than in soils with higher pH values. Filipek-Mazur and Gondek [17] in their researches claimed that lead was bound mainly with organic matter within the range of 39–43 % in total content. The amount of lead bound with manganese and iron oxides reached 20 % of total content that is much more than in analyzed soils. Analyzed soils contained very little organic matter that is why a large part of lead stays in residual fraction. The researches of speciation of heavy metals in poor soil conducted by Pakula and Kalembasa [18] prove that the share of lead in this fraction fluctuated between 36.8 and 51.6 %.

## Conclusions

1. The analyzed soils were characterised by acid and very acid reaction, high hydrolytic acidity and low content of organic carbon.
2. The content of total lead in soils was low and classified to natural values.

3. The higher share of mobile fractions of lead in total its content (about 30 %) was found in very acid and acid soils from Kolno and Korycin district, and distinctly lower (about 13 %) in soils from Jasionowka district.

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## MOBILNOŚĆ OŁOWIU W WARUNKACH KWAŚNYCH GLEB PODLASIA

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**Abstrakt:** Przeprowadzono badania gleb w trzech gminach Podlasia. W glebach oznaczono ogólną zawartość ołowiu i dwie jego frakcje I (ołów w roztworze glebowym oraz wymienny) i II (ołów związany z tlenkami oraz wodorotlenkami Fe i Mn). Oznaczono także pH gleb, zawartość w nich węgla organicznego, sumę zasad wymiennych i kwasowość hydrolityczną.

Stwierdzono, że zawartość ołowiu w badanych glebach była bardzo mała, typowa dla gleb lekkich niezanieczyszczonych. Również zawartość obu mobilnych frakcji ołowiu była mała, ale ich udział w zawartości ogólnej był znaczny i wahał się od 12,8 do 36 %.

**Słowa kluczowe**: gleby kwaśne, ołów, mobilność, frakcje