Abstract. The purpose of this study was to determine the effect of soil properties and Cd or Pb addition on the transformations of Pb in soils and its distribution between different fractions determined according to Tessier et al. The study was carried out in model pots filled with mineral or organic soils taken from the surface soil layer. The soils showed either acidic or neutral reactions. The mineral soil (Haplic Podzols) has the granulometric composition of light loamy sand. The soils were altered with the addition of: 0 mg kg\(^{-1}\) of Cd or Pb (control sample); 10 mg kg\(^{-1}\) of Cd in the form of Cd(NO\(_3\))\(_2\); 100 mg kg\(^{-1}\) of Pb in the form of Pb(NO\(_3\))\(_2\). Speciation data indicate that in non-adjusted mineral soil, lead was associated mainly with Fe-Mn oxide and residual fractions (near 80% of total Pb), and relatively small amounts of Pb with others forms. In non-adjusted organic neutral soil, the dominant fractions of Pb were Fe-Mn oxide bound (56%) and organic (24%), while in organic acidic soil: organic (42%), exchangeable (21%) and Fe-Mn oxide bound (19%) fractions. Introducing 100 mg kg\(^{-1}\) of Pb into the mineral soil changed the Pb distribution pattern among the particular fractions, while for organic soils it did not change the Pb distribution in comparison to that of uncontaminated soils. The addition of Pb to mineral and organic soils caused an increase in Pb bound to Fe-Mn oxides and in organic neutral soil also to the organic bound fraction. In the mineral soil, significant amounts of Pb were also present in the carbonate form. A significant amount of Pb associated with the non-residual fraction (> 65%) indicates that Pb in these soils may be easily available for plants.

The transformations of lead (Pb) and other heavy metals in contaminated soils, and their speciation are a common concern [2, 8, 9, 10]. Sequential extraction techniques are increasingly being developed to study the problem as sequential fractionation helps us to reassess metal bioavailability and mobility in terrestrial systems and is also used in environmental hazard assessment [9]. The mobility of metals, related to their geochemical forms, decreases in the order of the extraction sequence, i.e. exchangeable > carbonate > Fe-Mn oxide bound > organic > residual. The first two fractions are very easily mobilised and can release their
metal loads by a drop in pH. The risk to the environment by Pb in contaminated soils depends on the solubility of the metal, which is determined by its speciation or chemical form.

Lead accumulates in the soil as, for example, the result of diffuse contamination (industrial emissions) or from flooding by contaminated waters. In agriculture this metal can be also introduced into the soil with mineral fertilizers and organic substances [5]. The behaviour of lead in soil, its mobility and availability for plants are governed by soil properties such as pH, composition and organic matter content, cation exchange capacity (CEC), plant species and fertilization [3, 7, 10].

The aim of this study was to determine the effect of soil properties (pH, organic matter content) and addition of metals (Pb, Cd) on the distribution of Pb between different fractions, determined according to Tessier et al. [13].

MATERIAL AND METHODS

The study was based on the analysis of soil material gained from a two-year pot experiment. The study was carried out with organic soils and a mineral one with a differentiated reaction. Soil material was taken from the surface layer (0-20 cm). Organic peat-bog soil developed from short peat with a neutral reaction was taken from arable lands near the Hajdów municipal and industrial purification plant. Acidic soil developed from tall peat was taken from the surroundings of Łucze Lake in the Lublin region. The mineral soil (Haplic Podzols) with a granulometric composition of light loamy sand was taken from agricultural areas of the Lubelskie region. A neutral reaction was obtained by applying calcium carbonate by the method of double hydrolytic acidity.

The soil samples were collected and air-dried, then ground in a porcelain mortar and sieved through a 1 mm mesh. The following items were determined in such prepared samples: granulometric composition by means of the Casagrande areometric method with the Prószyński modifications, pH – potentiometrically in 1 M KCl, content of organic matter (C_{org.}) by the Tiurin method, content of available phosphorus and potassium using the Egner and Riehm method, and content of available magnesium using the Schachtschabel method. The total contents of cadmium and lead in the soils were analyzed after the digestion of soil samples in the mixture of concentrated acids HCl and HNO₃ in the ratio of 3:1 (aqua regia) according to PN-ISO 11466 [12]. The total metal concentrations in the solution were determined by flame atomic absorption spectrometry (AAS) with Hitachi Z – 8200 apparatus. The main properties of soils, determined before the study started, are listed in Table 1.

The soil material was placed in pots of 5 dm³ volume. The pots contained 4.8 kg of organic acidic soil, 5.5 kg of organic neutral soil and 6.4 kg of mineral soil.
The study, including 6 plots in four replicates on mineral soil and 6 plots in four replicates on organic soils, was set up using a randomised block method. The soils had the following added:

- 0 mg kg\(^{-1}\) of Cd or Pb (control sample, 0 soil),
- 10 mg kg\(^{-1}\) of Cd in the form of Cd(NO\(_3\))\(_2\) – Cd soil,
- 100 mg kg\(^{-1}\) of Pb in the form of Pb(NO\(_3\))\(_2\) – Pb soil.

Mineral fertilization in a form of mineral salts: NH\(_4\)NO\(_3\) – 0.10 g N kg\(^{-1}\) soil, CaHPO\(_4\) – 0.07 g P kg\(^{-1}\) soil and KCl – 0.15 g K kg\(^{-1}\) was applied in all pots both in the first and in the second year of study, dividing the ammonium nitrate dose into two equal parts – before and after shooting. Cadmium and lead in a form of Cd(NO\(_3\))\(_2\) and Pb(NO\(_3\))\(_2\) were applied once before sowing.

Spring rape (Brassica napus ssp. Oleifera Netzg., Sinsk) and buckwheat (Fagopyrum esculentum Moench) were sown in the first year of study, and orchard grass (Dactylis glomerata L.) in the second year. During the study, mineral soil humidity was adjusted to 60% maximum water capacity and 80% in the case of organic soils by adding water to maintain a constant weight.

After two years of the study the content of Pb was determined using mean soil samples from individual study plots using the Tessier et al. [13] sequential chemical extraction method. This procedure partitions trace metals into five operationally defined fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter and residual. A list of assayed fractions is shown in Table 2. Details are documented in Tessier et al. [13].

Samples for analyses were prepared as weighted means from four replications of each object. The percentage contribution of particular Pb fractions in the soil was calculated in relation to the sum of all fractions (sum of the amounts of metal extracted in the five steps) (Table 3).
The soils used in the study (both in mineral and organic) were characterized by a natural total content of Pb [7].

The partitioning of Pb in the mineral and organic soils from Lubelskie region was based upon the sequential extraction procedure of Tessier et al. [13] (Fig. 1). The sequential extraction used in this study is useful for indirectly assessing the potential mobility and bioavailability of Pb in natural and Pb adjusted soils. The

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<table>
<thead>
<tr>
<th>Stage and fraction</th>
<th>Reagents</th>
<th>Reaction procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Exchangeable</td>
<td>1 M MgCl₂, pH 7</td>
<td>The quantities indicated below refer to 1 g samples used for the initial extraction. The samples were extracted at room temperature for 1 h with continuous agitation.</td>
</tr>
<tr>
<td>2. 'Carbonate-bound'</td>
<td>1 M NaOAc, adjusted to pH 5 with HOAc</td>
<td>The suspension shaken for 5 h at 25 °C.</td>
</tr>
<tr>
<td>3. Fe-Mn oxide bound</td>
<td>0.04 M NH₄OH HCl in 25% v/v HOAc</td>
<td>The suspension was heated to 96 ± 3°C for 6 h, mixture was occasionally agitated.</td>
</tr>
<tr>
<td>4. Organic matter bound</td>
<td>2 ml of 0.02 M HNO₃ and 5 ml of 30% H₂O₂ adjusted to pH 2 with HNO₃ + 5 ml 3.2 M NH₄OAc in 20% v/v HNO₃</td>
<td>Mixture was heated at 85 ± 2°C for 2 h with occasional agitation. Mixture again heated at 85 ± 2°C for 3 h with intermittent agitation. After cooling NH₄OAc in 20% v/v HNO₃ was added.</td>
</tr>
<tr>
<td>5. Residual</td>
<td>HF-HClO₄</td>
<td>Residue from the organic fraction was digested with HF and HClO₄, then the mixture was evaporated to near dryness. The residue was dissolved in 12 N HCl and diluted with distilled, deionized water to 25.0 ml volume.</td>
</tr>
</tbody>
</table>

Following each extraction or wash, mixtures were centrifuged at 12 000x g for 30 min. Prior to the start of the next extraction steps, residues were shaken with 8 ml of ultra pure water for 30 min, centrifuged and the wash solutions discarded.
five chemical fractions are operationally defined by an extraction sequence based on the order of decreasing solubility: exchangeable > carbonate > Fe-Mn oxide > organic > residual.

In mineral soil in all objects, the highest proportion of total Pb content were found in the Fe-Mn oxides fraction and the residual fraction. At the same time, the sum of both forms was nearly 80% of the total Pb contents. The remaining part consisted of exchangeable, carbonate and organic forms. Introducing 100 mg kg\(^{-1}\) of Pb into the mineral soil changed the Pb distribution pattern among particular fractions compared to that of the uncontaminated soils: carbonate – more than a 3-fold increase and residual 4-5-fold decrease of its share in comparison to the control object. Also Martinez and Motto [10] noted that in metal adjusted calcareous soil, a significant fraction of the metals (Pb, Cu, Zn) reacts with carbonates, where a decreased pH resulted in a much higher metal dissolution. Additional amounts of Pb introduced into mineral soils caused an increase of Pb bound to organic and Fe-Mn oxides, and in neutral soil a slight increase of exchangeable Pb. Such dependencies were also shown by Chlopecka et al. [4]. Authors reported that, in polluted soils, a small proportion of the lead occurred in the exchangeable form. The majority of this metal was associated mainly with Fe-Mn oxides, and, released from this form or not bound into this form,

<table>
<thead>
<tr>
<th>Soil No.</th>
<th>Exchangeable</th>
<th>'Carbonate'</th>
<th>Oxide</th>
<th>Organic</th>
<th>Residual</th>
<th>Sum of forms</th>
<th>Non-residual</th>
<th>Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.1</td>
<td>1.6</td>
<td>7.2</td>
<td>1.0</td>
<td>5.0</td>
<td>15.9</td>
<td>68.5</td>
<td>31.5</td>
</tr>
<tr>
<td>II</td>
<td>1.8</td>
<td>1.6</td>
<td>7.2</td>
<td>1.0</td>
<td>5.0</td>
<td>16.5</td>
<td>69.7</td>
<td>30.3</td>
</tr>
<tr>
<td>III</td>
<td>2.7</td>
<td>33.6</td>
<td>52.0</td>
<td>9.6</td>
<td>5.0</td>
<td>102.9</td>
<td>95.1</td>
<td>4.9</td>
</tr>
<tr>
<td>IV</td>
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<td>1.3</td>
<td>7.2</td>
<td>0.6</td>
<td>5.0</td>
<td>15.6</td>
<td>67.9</td>
<td>32.1</td>
</tr>
<tr>
<td>V</td>
<td>1.4</td>
<td>1.1</td>
<td>6.0</td>
<td>0.6</td>
<td>5.0</td>
<td>14.2</td>
<td>64.8</td>
<td>35.2</td>
</tr>
<tr>
<td>VI</td>
<td>11.0</td>
<td>28.8</td>
<td>48.0</td>
<td>7.7</td>
<td>7.5</td>
<td>103.0</td>
<td>92.7</td>
<td>7.3</td>
</tr>
<tr>
<td>VII</td>
<td>9.1</td>
<td>3.2</td>
<td>8.4</td>
<td>18.6</td>
<td>5.0</td>
<td>44.3</td>
<td>88.7</td>
<td>11.3</td>
</tr>
<tr>
<td>VIII</td>
<td>7.5</td>
<td>3.0</td>
<td>8.4</td>
<td>16.0</td>
<td>5.0</td>
<td>40.0</td>
<td>87.5</td>
<td>12.5</td>
</tr>
<tr>
<td>IX</td>
<td>25.1</td>
<td>13.8</td>
<td>30.4</td>
<td>50.2</td>
<td>10.0</td>
<td>129.5</td>
<td>92.3</td>
<td>7.7</td>
</tr>
<tr>
<td>X</td>
<td>1.8</td>
<td>4.8</td>
<td>32.8</td>
<td>13.8</td>
<td>5.0</td>
<td>58.1</td>
<td>91.4</td>
<td>8.6</td>
</tr>
<tr>
<td>XI</td>
<td>1.1</td>
<td>5.1</td>
<td>33.6</td>
<td>14.7</td>
<td>5.0</td>
<td>59.6</td>
<td>91.6</td>
<td>8.4</td>
</tr>
<tr>
<td>XII</td>
<td>1.8</td>
<td>11.2</td>
<td>92.0</td>
<td>44.2</td>
<td>7.5</td>
<td>156.6</td>
<td>95.2</td>
<td>4.8</td>
</tr>
</tbody>
</table>

TABLE 3. LEAD (Pb) ASSOCIATED WITH EXTRACTABLE FORMS IN CONTAMINATED AND UNCONTAMINATED SOILS
precipitated as carbonates, absorbed on carbonate minerals, or complexed by organic substance and by humic acids [4]. In research into polluted soils, the highest amounts of Pb were found in the Fe-Mn oxide fraction [1, 11]. Ma and Uren [8] in their new sequential extraction procedure stated that most Pb added to alkaline soil was found in the specifically adsorbed and residual fractions, while a particularly high affinity of Pb to Mn oxides was also found [8]. The processes associated with the transformations of added Pb may be attributed to the diffusion of the surface species into the micropores and their entrapment in microporous solids [7].

Acidic and neutral mineral soil only slightly differed if considering the contents of particular forms of lead. In acidic soil, the shares of the exchangeable Pb form and the residual one were lower, but other forms were a little higher than those in the neutral soil. A higher share of the exchangeable form of Pb in the mineral soil,
with cadmium added, indicates the stimulating effect that Cd has when applied to
that soil on the mobility of Pb, especially at lower values of soil pH.

The distribution of Pb among particular fractions in organic soils varied from
the mineral one. In organic uncontaminated soils the share of Pb associated with
the organic fraction was higher, while the residual was lower in comparison to the
mineral soil. In organic soils the greatest amounts of lead (50-86%) were found in
the Fe-Mn oxides and the organic bound forms. Also Geiger et al. [6] reported a
strong affinity of Pb to soil humic acids and easing of complexation of Pb by humic
acid function groups and its immobilization in metal-organic complex forms.
Introducing 100 mg kg\(^{-1}\) of Pb into organic soils did not change the Pb distribution
pattern among particular fractions in comparison to natural organic soils. Organic
Pb adjusted soils, both acidic and neutral, differed from the share of lead form in
the total content. In general, acidic organic soil consisted of the highest proportions
of following forms: organic (39%), Fe-Mn oxides (23%) and exchangeable (19%).
Such a high share of lead in an exchangeable form shows that soil acidification has
a very large effect on the increase of Pb mobility in organic soils. The distribution
of Pb among fractions also highly depended on the organic matter content in the
organic soils, with Pb showing a significant association with this fraction. The
level of association for Pb in organic soils was almost proportional to the organic
matter content in those soils. The percentage values for the various forms in the
neutral organic soil samples were Fe-Mn oxides (59%), organic (28%), carbonate
(7%), residual (5%), and exchangeable (1%). Changing the lead in organic soils
did not cause considerable variations in concentrations of particular Pb forms as
compared to the control object, only a small increase in Pb bound to Fe-Mn oxides
and a decrease in exchangeable Pb form were observed.

The significant amount of Pb associated with the non-residual fractions in
natural uncontaminated soils (> 65% in mineral, > 87% in organic) and > 92% in
contaminated soils indicates that Pb may be easily available for plants, especially
in metal contaminated mineral soils.

CONCLUSIONS

1. All non-adjusted soils differed in the distribution of Pb among fractions. In
the mineral soil, lead was associated mainly with Fe-Mn oxide and residual
fractions, with the sum of both forms near 80% of total Pb, and relatively small
amounts of Pb in others forms. In the organic neutral soil, Pb had the following
order of association: Fe-Mn oxide bound > organic > residual > carbonate >
exchangeable, and in organic acidic soil: organic > exchangeable > Fe-Mn oxide
bound > residual > carbonate.

2. Altering mineral soil with Pb resulted in an increase of Pb bound to carbo-
nates (3-fold increase) and in slight increase in Fe-Mn oxides, while introducing
additional amount of Pb into the organic soils did not cause considerable variations
in the concentrations of particular Pb forms as compared to uncontaminated objects, only a small increase in Pb bound to Fe-Mn oxides and decrease in exchangeable Pb form was stated.

3. The significant amount of Pb associated with the non-residual fractions (> 65% in uncontaminated and > 92% in contaminated soils) indicates that Pb may be easily available for plants.

REFERENCES


SEKWENCYJNE FRAKCJONOWANIE PB W GLEBACH ZANIECZYSZCZONYCH I NIE ZANIECZYSZCZONYCH

Celem badań było określenie wpływu właściwości gleby oraz dodatku Cd lub Pb na przemiany związków Pb w glebach zanieczyszczonych. Wyodrębnione formy metali (wymienną, weglanową, tlenków Fe-Mn, organiczną, pozostałości) oznaczono metodą Tessier’a i in. Eksperyment obejmował modelowe badania wazonowe przeprowadzone na glebach organicznych (kwaśnej i obojędnej) i glebie mineralnej wytworzonej z piasku gliniastego o zróżnicowanym odczynie. W powyższych glebach wyróżniono obiekty, w których stosowano: 0 mg · kg⁻¹ Cd lub Pb (obiekt kontrolny); 10 mg Cd · kg⁻¹ gleby w postaci Cd(NO₃)₂; 100 mg Pb · kg⁻¹ gleby w postaci Pb(NO₃)₄. Na podstawie specjacji Pb w glebie mineralnej stwierdzono, że największą część stanowił Pb związany z tlenkami Fe-Mn, zaś mniejszą w formie pozostałości (obie formy prawie 80% jego ilości ogółem). W glebie organicznej obojętnie dominującymi frakcjami Pb były: Fe e Mn (56%) oraz organiczna (24%). Natomiast w glebie organicznej kwaśnej: organiczna (42%), wymienna (21%) oraz tlenków Fe-Mn (19%). Dodatkowa ilość Pb wprowadzona do gleby mineralnej powodowała zmiany w rozkładzie poszczególnych frakcji Pb w porównaniu z rozkładem stwierdzonym w glebach z naturalną zawartością Pb. Natomiast w glebach organicznych dodatkowa ilość Pb rozkładła się tak, jak w glebach nie zanieczyszczonych. Dodatek ołowiu do gleb spowodował wzrost udziału frakcji Pb związanego z tlenkami Fe e Mn, zaś w glebie mineralnej również formy weglanowej. Duży udział ołowiu związanego z frakcjami nierozdualnymi (> 65% w glebach nie zanieczyszczonych i > 92% w zanieczyszczonych) wskazuje, iż w badanych glebach metal ten może być łatwo przyswajalny dla roślin.