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EFFECTS OF LEAD SOIL POLLUTION ON PHYSICAL AND CHEMICAL PROPERTIES OF LEACHED FOREST-MEADOW CHERNOZEM (BLACK SOIL) IN THE CONDITIONS OF WESTERN FOREST-STEPPE OF UKRAINE

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Contamination with heavy metals is a major concern because of their toxicity and threat to human life and environment. The object of the study was leached forest-meadow chernozem (black soil), polluted by lead. The samples were taken from the research field of Lviv National Environmental University, from the layer of 0–60 cm deep. Lead ($Pb(CH_3COO)_2$) was applied to the top layer of soil as water-salt solutions in different doses, namely 0; 32; 160; 320 mg kg^{-1}. Basic chemical and physical properties, such as soil reaction, organic carbon content, grain size composition, total surface area, porosity, and hydrolytic acidity of the samples were analyzed using routine laboratory procedures. The soluble forms of Pb were also investigated. The soil reaction ranged between 6.8 and 7.5 in 1M KCl and 7.3–8.1 in H_2O, whereas the content of organic C ranged between 0.66 and 1.56 %. For Pb-treated samples, the content of sand fraction changed from 8 to 25 %; silt fraction – from 48 to 65 %, and colloidal clay fraction – from 20 to 35 %. The pore volume of polluted soils ranged from 370 mm^3 g^{-1} to 420 mm^3 g^{-1}. The total surface area of the soils varied from 26.8 m^2 g^{-1} to 37.7 m^2 g^{-1}. The content of available forms of lead was the highest in the top layers of soils. The presence of those elements was similar to that in the control sample at the depth of 30 cm only for small initial doses of Pb. The content of Pb for the highest dose and at the deepest soil level was higher than for the control sample. The behaviour of lead in soil and influence of lead on the basic characteristics of leached chernozem (black soil) can be connected with the chemical properties of this metal and the properties of the soil. The rate of migration of lead forms in soils can be evidence and index of soil self-purification.

Key words: soil pollution, heavy metals, lead, forest-meadow chernozem (black soil), physical and chemical properties, soluble forms of heavy metals.

Качмар Н., Дацко Т., Іванків М., Дидів А. Вплив забруднення ґрунтів свинцем на фізико-хімічні властивості чорнозему вилуженого лісо-лучного в умовах Західного Лісостепу України

Забруднення важкими металами викликає серйозне занепокоєння через їх токсичність і загрозу життю людини та навколишньому середовищу. Досліджували забруднений свинцем чорнозем лісо-лучний вилужений. Зразки ґрунту відбирали із глибини 0-60 см на дослідному полі Львівського національного університету природокористування. Плюмбум (Pb(CH3COO)2) був внесений у верхній шар ґрунту у вигляді водно-сольових розчинів у різних дозах: 0; 32; 160; 320 мг/кг ґрунту. Основні хімічні та фізичні властивості, такі як реакція ґрунту, вміст органічного вуглецю, гранулометричний склад, загальна площа поверхні, пористість, гідролітична кислотність зразків, були проаналізовані за допомогою стандартних лабораторних методів. Досліджено також вміст розчинних форм свинцю. Реакція ґрунту коливалася від 6,8 до 7,5 в 1M KCl і 7,3–8,1 в H2O, тоді як вміст органічного вуглецю був у межах від 0,66 до 1,56 %. Для досліджуваних зразків вміст фракції піску змінювався від 8 до 25 %; фракції мулу – від 48 до 65 %, і фракції колоїдної глини – від 20 до 35 %. Об'єм пор забруднених зразків ґрунту становив від 370 мм^3 г-1 до 420 мм^3 г-1. Загальна площа поверхні ґрунтових зразків змінювалася в межах від 26,8 м^2 г-1 до 37,7 м^2 г-1. Найвищий вміст рухомих форм свинцю виявився у верхніх шарах ґрунту. Вміст забруднювача був на одному рівні з контрольними зразками на глибині 30 см за умови низького рівня забруднення. Вміст свинцю за високого рівня забруднення на найбільшій глибині ґрунту був значно вищим, ніж у контрольному варіанті. Особливості поведінки свинцю в ґрунті та вплив досліджуваного полютанта на основні характеристики чорнозему вилуженого можна пов'язати з хімічними властивостями цього металу та властивостями, притаманними досліджуваному ґрунту. Швидкість міграції рухомих форм свинцю у ґрунті може бути свідченням і показником його самоочищення.

Ключові слова: забруднення ґрунту, важкі метали, свинець, чорнозем лісо-лучний, фізико-хімічні властивості, розчинні форми важких металів.

Formulation of the problem. One of the elements of chemical degradation of soils is related with heavy metals content and they rank among the main pollutants in the environment. More than 85 %

of the total heavy metal content in soils originates from anthropogenic pollution. Contamination with heavy metals is a major concern because of their toxicity and threat to human life and environment.

Soils are receptors of large quantities of heavy metals. Their accumulation and mobility in soils are largely determined by the extent of their adsorption by soil particles. In particular, soil organic and mineral particles can bind toxic elements by the formation of complexes.

Analysis of recent research and publications. Three principal stages of technogenic heavy metals transformation in soil are 1) the formation of complexes; 2) heavy metals' highly intensive migration; 3) high humus horizon intrusion [1; 2]. Some of agricultural soils are contaminated with lead (Pb). Lead belongs to 10 chemical elements that are the basic contaminants of the environment and they can be found in the solid as well as in the liquid phase. The parent rock, which has formed the soils, is the natural source of heavy metals in those soils. Soils exhibit a high absorbing capacity to lead. Several soil properties, such as the pH value, organic carbon content, grain size composition, specific surface area, porosity, hydrolytic acidity, can influence the availability of exchangeable and water-soluble Pb determined as available for plants [7; 8]. On the other hand, several physic-chemical processes occurring in soils, such as water and ions adsorption, acid-base equilibrium, and transport phenomena, are related to or governed by the surface properties of the soil solid phase. The main factor influencing the mobility of heavy metals in the soil environment is its reaction (pH) which affects the stability of humus complexes with metals. In soil with a pH level considerably above 7 (alkaline and carbonate soils of high sorption capacity), the transfer of heavy metals into non-soluble forms takes place without any additional agrotechnical treatments [10]. The relationship between the amount of metal adsorbed and the composition of the soil is quite complex, due to solid phase heterogeneity and the influence of soil solution chemistry [3; 9]. In soils dominated by permanent charge surface, heavy metals are not mobile, but in variable charge soils, the low surface charge density creates conditions conductive to increased mobility. Consequently, the adsorption of heavy metals by strongly weathered soils concerning the effects of inorganic and organic ligands and the implications for metal transport were reviewed [11].

Setting objectives. This study aimed to investigate the basic properties of leached forest-meadow chernozem (black soil) polluted with lead. Basic chemical and physical properties, such as soil reaction, hydrolytic acidity, organic carbon, grain size composition, total surface area, soil porosity, and content of water-soluble forms of Pb were measured.

Presenting main material. The soil samples were taken from the research field of Lviv National Environmental University. The experimental area of 100 m^2 was divided into 20 plots of 2 m^2 each. The effects of lead on the physical-chemical properties of leached forest-meadow chernozem (black soil) were investigated at the contamination levels of 1,5 and 10 of the Threshold Limit Value. Heavy metals were applied onto top layer of soil as water salt solutions of $Pb(CH_3COO)_2$ at different doses, namely 0; 32; 160; 320 mg kg^{-1} of soil. The soil samples were taken from every successive 10 cm layer of the soil profile (of 0–60 cm depth). Soil reaction, organic carbon, grain size composition, specific surface area, porosity, and hydrolytic acidity of the studied soil were measured using routine laboratory analyses based on Institute of Agrophysics, Polish Academy of Sciences in Lublin. Soil reaction was measured by a potentiometer with a combined glass/calomel electrode in 1M KCl and in H_2O at 1:2.5 soil-to-solution ratio. Organic carbon was determined oxidometrically with potassium dichromate in hot sulphuric acid, according to the modified Tiurin method. The grain size composition was evaluated by the areometric Cassagrande method modified by Prószyński. The specific surface area of the investigated soil samples was obtained according to the Polish Standard PN-Z-19010-1. Before adsorption measurements, the soil samples were dried at 105 ^oC in a vacuum chamber with concentrated sulphuric acid until the weight of the samples reached constant values. The amount of adsorbed water vapour at $T = 20\ ^oC$ was computed as the difference between the weight of the sample with water and the dry sample. The relative water pressures were obtained from the density of sulphuric acid solutions. The adsorption measurements were replicated three times. Soil porosity was measured using a Micrometrics Mercury Porosimeter Autopore IV 9510 Model and applying the pressures from the range from 0.0036 to 413 MPa. This range allowed for the determination of pores with equivalent radii ranging from 0.003 μm to 360 μm. Before porosity measurements, the samples were oven-dried at 105 ^oC and then degassed up 10^{-3} Pa to remove physically adsorbed water from their surface. The pore radii were calculated by the Washburn equation [5]. The surface tension and the contact angle of mercury were assumed to be 480 dynes cm^{-2} and 141.3 ^oC, respectively. All calculations from obtained porosimetric data, i.e. the bulk density, pore surface area, average pore radius, and total porosity, were carried out using the cylindrical pore model by computer program Autopore IV Version 1.06. The content of available forms of lead in soils was investigated by atomic absorption spectrometry (AAS) using a Perkin Elmer 3300 apparatus. Soil was stressed with lead ($CH_3(COO)_2Pb$) with concentrations of 0; 32; 160 and 320 mg Pb per kg of soil. Soil samples for those studies were collected in the second year of the experiment from three depths – 10, 20, and 30 cm. Afterwards, equal-weight amounts of dried soils were extracted for 24 hours by the mixture of 1 M hydrochloric (HCl) and 1 M nitric acid (HNO_3) at the ratio of 1:1. Received extracts of available Pb forms were filtrated. The content of lead was analyzed in clear solutions [4]. Received data were statistically calculated using the t-student test for equal expectation value.

The study findings show that the reaction of polluted soil samples was 6.8–7.6 in 1M KCl and 7.3–8.1 in H_2O, while the pH of the control soil sample was 6.9–7.4 in 1M KCl and 7.5–7.9 in H_2O (see Table 1). The reaction of the soil was neutral. Significant differences ($P > 0.05$) between average values of pH in H_2O evaluated for the control plot and the plots contaminated with Pb were detected for the samples taken from 0–20 cm layers and contaminated at the doses of 160 and 320 mg Pb kg^{-1} of soil. In contrast, such differences were not observed for any other samples polluted with Pb. The fraction of organic carbon in all investigated samples was rather low. Indeed, the organic carbon content in the samples polluted with Pb ranged from 0.66 % to 1.56 %, whereas in the control soil, it changed from 0.71 % to 1.59 %. Statistically significant differences ($P > 0.05$) between average carbon content values in the whole soil profile (0–60 cm) of contaminated samples and the control soil occurred only in the case of soils contaminated with Pb in the doses of 160 and 320 mg Pb kg^{-1} of soil. However, within the layers of 0–20 cm (they exhibited the highest organic carbon content), significant differences in organic carbon content between contaminated and control samples were observed for all soils treated with Pb

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Table 1

Basic properties of the samples contaminated with lead and cadmium

No	Depth (cm)	Grain size composition (%)			C_{org} (%)	pH		TSA (m^2g^{-1})
		sand	silt	clay		H_2O	1M KCl	
Soil + Pb 32 (mg kg^{-1})								
1	0–10	22	58	20	1.56	8.0	7.5	29.9
2	10–20	23	56	21	1.47	8.0	7.5	30.1
3	20–30	11	54	35	1.45	8.1	7.5	27.7
4	30–40	19	55	26	1.20	7.9	7.2	27.9
5	40–50	24	45	31	0.88	7.6	7.1	37.3
6	50–60	25	51	24	0.66	7.4	6.8	37.7
Soil + Pb 160 (mg kg^{-1})								
1	0–10	19	60	21	1.53	7.9	7.4	29.1
2	10–20	21	56	23	1.46	8.0	7.4	29.0
3	20–30	22	50	28	1.41	8.1	7.6	28.5
4	30–40	8	54	38	1.19	7.7	7.2	29.4
5	40–50	8	57	35	0.95	7.5	6.9	356
6	50–60	12	55	33	0.70	7.5	7.0	37.4
Soil + Pb 320 (mg kg^{-1})								
1	0–10	13	65	22	1.55	7.9	7.4	28.9
2	10–20	17	59	24	1.48	8.0	7.5	29.8
3	20–30	17	61	22	1.44	8.0	7.4	29.8
4	30–40	17	54	29	1.16	7.6	7.1	31.2
5	40–50	17	48	35	0.91	7.3	6.9	33.0
6	50–60	9	58	33	0.67	7.5	7.0	37.2

Continuation of Table 1

Control								
1	0–10	20	54	26	1.59	7.7	7.2	30.1
2	10–20	18	59	23	1.50	7.9	7.4	30.4
3	20–30	13	57	30	1.46	7.9	7.3	26.8
4	30–40	9	56	35	1.23	7.6	7.2	30.4
5	40–50	15	55	30	0.94	7.7	7.1	33.9
6	50–60	13	54	33	0.71	7.5	6.9	38.7

Abbreviation: sand fraction 1–0.1 mm, silt 0.1–0.02 mm, clay < 0.02 mm, C_{org} – Organic carbon, TSA – Total surface area.

The transport and deposition of pollutants in soil profiles strongly depend on pH and the amount of organic matter. Several researchers have shown that heavy metals get bound to dissolved humic substances and this phenomenon significantly decreases the negative impact of heavy metals on plants and soil organisms [6; 7; 10].

For all contaminated soil samples their grain size composition was determined. For Pb-treated samples the content of sand fraction changed from 8 to 25 %; silt fraction – from 48 to 65 % and colloidal clay fraction – from 20 to 35 %. The grain size composition of the control soil was as follows: sand – 9–20 %, silt – 54–59 %, and clay – 23–35 %. The grain size composition depends on the soil horizon (Table 1). However, one can state that the grain size compositions of the polluted soil samples were not significantly different from the composition of the control soil. For all studied samples the TSA evaluated from the adsorption isotherms ranged from 27.7 to 37.7 m^2g^{-1} for soils polluted by Pb. The BET-specific surface area for control soil ranged from 26.8 to 38.7 m^2g^{-1} (Table 1) and there were no essential differences between the polluted soil samples and the control soil. The average values of specific surface area were 31.6 m^2g^{-1} and 31.7 m^2g^{-1} for soil-Pb and control soil, respectively. The highest values of specific surface area were observed for the samples taken from 40–60 deep layers and contaminated with lead. The differences between the surface area of the control sample and soil polluted by heavy metals were rather low. That may be connected with different factors, such as low concentration of metals in soil and heterogeneity of samples that were taken from the experimental plots.

The results of the mercury porosimetry measurements are given in Table 2. The samples were taken from the layers of 0–10 cm and 10–20 cm deep. The total intrusion volume (TV) was directly measured quantitatively, whereas the total pore area (TPA), average pore diameter (PD_{av}), and bulk density were calculated using the cylindrical pore model. The total intrusion volume (TV) of investigated soil samples ranged from 370 mm^3g^{-1} to 420 mm^3g^{-1}. Polluted soils exhibited also different values of TV for the upper and lower horizons. TV decreases with depth for the Pb-polluted soil (Table 2). The changes in TP (total porosity) with depth were similar to those already observed for TV.

Table 2

Parameters of pore structure of leached chernozem (black soil) degraded by lead

No	Depth (cm)	TV (mm^3 g^{-1})	TPA (m^2 g^{-1})	PD_{av} (nm)	D (g mL)	TP (%)
Soil + Pb 320 (mg kg^{-1})						
1	0–10	404	3.60	448.3	1.259	50.83
2	10–20	370	3.72	398.2	1.300	48.13
Control						
1	0–10	420	3.50	481.1	1.223	51.42
2	10–20	411	3.74	438.8	1.244	51.09

Abbreviations: TV – total intrusion volume, TPA – total pore area, PD_{av} – average pore diameter, D – bulk density, TP – total porosity.

The influence of lead on the porosity of leached chernozem (black soil) can be related to the chemical nature of this metal and the properties of the lbsoil [6]. The results of mercury porosimetry of samples from the experimental plot were compared to those for samples prepared in the laboratory. In Figure 1 the cumulative curves for laboratory and plot samples are shown.

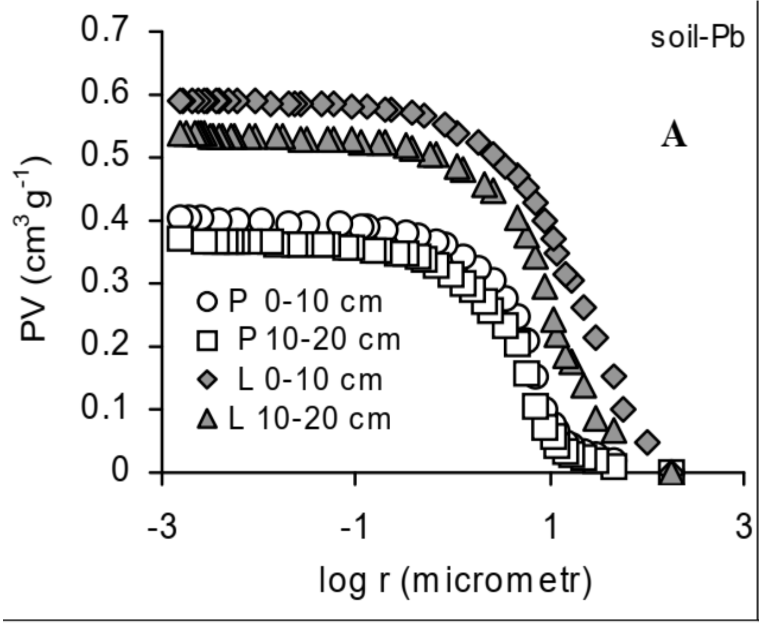

Fig. 1. Cumulative curves for chernozem (black soil) polluted by lead (320 mg kg-1). Abbreviations: r – pore radius, PV – pore volume, L – samples prepared in the laboratory, P – samples taken from the experimental plot, 0–10 cm and 10–20 cm – depth

The difference between the PV of polluted soil samples prepared in the laboratory and those from the experimental plot is rather connected with the heterogeneity of the samples. The results of the studies of lead content in selected levels of investigated soil are presented in Table 3.

Table 3

Lead content at the selected depths of soil and for different initial doses of metals

Depth (cm)	Metal content (mg dm^{-3})			
	Control soil	Soil + dose of Pb (mg kg^{-1})		
		32	160	320
10	0.61	2.93	5.17	9.81
20	0.51	1.01	3.95	7.46
30	0.56	0.74	3.52	6.07

The results show that after two years of the experiment, the highest concentration of lead remained constantly in the shallowest soil layer, irrespective of the initial dose of cation (Figure 2). In the soil samples polluted with lead, the highest dose (320 mg Pb per kg of soil) was illuviated faster than smaller doses of lead (32 and 160 mg Pb per kg of soil). The control sample contained also a small amount of lead, but it was definitely smaller in all layer levels than for the soils with metal. Generally, the content of lead decreased with an increase in soil depth, with the provision that in the case of the smallest dose of lead (32 mg Pb per kg of soil) and at the depth of 30 cm the content of Pb was similar to the content of Pb in the control sample. The decrease of heavy metals content along with depth is connected with the process of gradual migration and illuviation to the soil profile. Similar contents of lead as for the control samples can be evidence of a weak rate of migration of small amounts of lead (32 mg kg^{-1}). The highest doses of heavy metals migrate to the soil faster, and after the second year, a slightly higher content of lead can be observed at the depth of 30 cm. That fact can be connected with the possibility of the creation of less mobile and more sparingly soluble organomineral forms of lead in shallower layers of soil. In that way, small doses of Pb can remain longer in the layer of 0–20 cm. Application of big doses of heavy metals causes a part of them can be chemically bound and the rest will be illuviate to the soil.

Therefore, a higher presence of Pb can be observed at the depth of 30 cm.

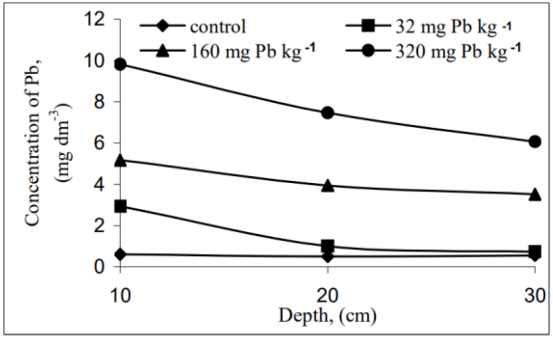

Fig. 2. Concentration of Pb at selected depths of soil for different initial doses of Pb

Conclusions. The behaviour of lead in soil and the influence of lead on the basic characteristics of leached chernozem (black soil) can be connected with the chemical properties of this metal and the properties of the soil. Pore volume of investigated polluted soils ranged from 370 mm^3 g^{-1} to 420 mm^3 g^{-1}. The reaction of the soil samples was neutral. Within 0–20 cm layers significant differences between average values of pH (in H_2O) for polluted and control soils were detected only in the case of the samples contaminated with 160 mg and 320 mg doses Pb (per 1 kg of soil). The soil samples were characterized by a low content of organic carbon fraction. Statistically significant differences ($P > 0{,}05$) between the average fraction of organic carbon in the whole soil profile (0-60 cm) occurred only for the samples contaminated with 160 and 320 mg of Pb per 1 kg of soil. In the case of results obtained from mercury intrusion experiments, the total intrusion volume of mercury, pore volume, total porosity, average pore radii and amounts of storage and residual pores varied with the soil horizon. The highest content of lead was observed at the depth of 0–20 cm for all doses of Pb. Presence of this element at the depth of 30 cm was significantly smaller for the smallest doses of lead because of the possibility the of creation of less mobile and more sparingly soluble organomineral forms of lead in shallower lyers of soil. The rate of migration of lead forms in soils can be evidence and index of soil self-purification.

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