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POROSITY OF LEACHED FOREST-MEADOW CHERNOZEM POLLUTED WITH LEAD AND CADMIUM

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Abstract. The porosity of leached forest-meadow chernozem polluted by Cd and Pb was studied by mercury porosimetry. The samples were taken from the research field of the Lviv State Agrarian University, from layers of 0-10 cm and 10-20 cm deep. The pore volume of polluted soils ranged from 370 $mm^{-3}g^{-1}$ to 515 $mm^{-3}g^{-1}$ and was higher for Cd- than Pb-polluted polluted soil. The soil samples containing Cd were also characterized by higher total porosities and average pore radii. The pore size distributions for the investigated soils exhibited one or two peaks of different height. The distributions for Cd-polluted soils were shifted towards larger pore radii compared with those for Pb-polluted soils. Different influence of lead and cadmium on porosity of leached chernozem was connected with the chemical properties of both heavy metals and with the properties of the soil.

Keywords: soil pollution, lead, cadmium, mercury porosimetry method

INTRODUCTION

Contamination of soils with heavy metals is the subject of great concern because of their toxicity and threat to human life and environment. Numerous studies have been conducted on soils contaminated with heavy metals coming from various anthropogenic sources such as industrial wastes, traffic emissions, mining activity and agricultural practice. Soils are the receptors of large quantities of these pollutants, being therefore a key of several environmental chemical cycles. Among heavy metals lead and cadmium are among the most important contaminants present in natural wastes, which has a deleterious effect on various animals.

Many physicochemical processes in soils, such as water and ions adsorption, acid-base equilibria and transport phenomena are governed, among others, by the surface properties of soil solid phase. This phase may be highly porous due to its complex geometry resulting from chemical and physical composition. The basic characteristic of porous solids is provided by the micropore size distribution function that yields information about the fraction of pores of a given size in addition to the overall amount of the pores. The latter is characterised by the total pore volume of the material (Roquerol *et al.*, 1994).

The aim of this study was to investigate the porosity of leached forest-meadow chernozem polluted with lead and cadmium, using the mercury intrusion porosimetry.

MATERIALS AND METHODS

Our investigations were carried out on a soil taken from the research field of the Lviv State Agrarian University. The experiment was established on leached forest-meadow chernozem developed from loess. The experimental area of 300 m^2 was divided into 35 plots of 2 m^2 each. The phytotoxic effect of lead and cadmium on the growth of spring barley was investigated at the contamination levels of 1, 5 and 10 of the Threshold Limit Value. Heavy metals were applied into the top layer of the soil as water salt solutions of $Pb(CH_3COO)_2$ in the case of lead and $CdCl_2$ in the case of cadmium, at different doses, namely 0, 32, 160 and 320 mg kg^{-1} of soil in the case of Pb, and 0, 3, 15, and 30 mg kg^{-1} for Cd. Soil samples were taken from layers of the soil profile of 0-10 cm and 10-20 cm in depth. The results presented below were obtained for the doses of 320 mg kg^{-1} of Pb, and for the dose of 30 mg kg^{-1} in the case of Cd.

Basic chemical and physical properties of the studied soil were evaluated via routine laboratory analyses. Soil reaction was measured with a potentiometer with a combined glass/calomel electrode in 1 M dcm^{-3} KCl and in H_2O at 1 to 2.5 soil to solution ratio. Organic carbon was determined oxidometrically with potassium dichromate in hot sulphuric acid (i.e. according to modified Tiurin method) and the granulometric composition – with the areometric Cassagrande method, modified by Prószyński. The basic properties of the soil are given in Table 1.

Table 1. Basic properties of leached forest-meadow chernozem

No	Object/Dose of heavy metal/Depth (c)m	Granulometric composition (%)			Organic carbon (%)	pH	
		Sand 1-0.1	Silt 0.1-0.02	Clay <0.02		H_2O	1M KCl
			Soil + Pb 320 mg kg^{-1}				
1	0-10	13	65	22	1.55	7.9	7.4
2	10-20	17	59	24	1.49	8.0	7.5
			Soil + Cd 30 mg kg^{-1}				
3	0-10	20	60	20	1.57	7.9	7.4
4	10-20	20	47	33	1.47	8.1	7.5

Porosity of the soil was measured using a Micrometrics Mercury Porosimeter Autopore IV 9510 Model and applying pressures from the range of 0.0036 to 413 MPa. This range allowed determination of pores with equivalent radii ranging from 0.003 μm to 360 μm. Before performing analyses of porosity, the samples were oven-dried at 105°C and then outgassed up to 10^{-3} Pa to remove physically adsorbed water from their surface. The pore radii were calculated from the Washburn equation (Hajnos 1998). The surface tension and the contact angle of mercury were assumed to be 480 dynes cm^{-2} and 141.3°, respectively. All the calculations (pore size distribution, bulk density, surface area, average pore radius and total porosity) were carried out using cylindrical pore model by computer program Autopore IV 9500 Version 1.06.

RESULTS AND DISSCUSION

The ability of mercury to intrude into samples is inversely proportional to pressure, so filling of the smallest pores occurs at the highest pressures. The cumulative pore volume (CPV) curve gives the total mercury volume intruded into the pores versus the pore size. Figure 1 shows the CPV curves for soil polluted by lead (Fig. 1A) and cadmium (Fig. 1B). Overall shape of the obtained CPV curves is similar, except for the curves for the Cd-polluted soil. However, the detailed run of the curves and, in particular, the total amount of mercury introduced into pores, vary from sample to sample.

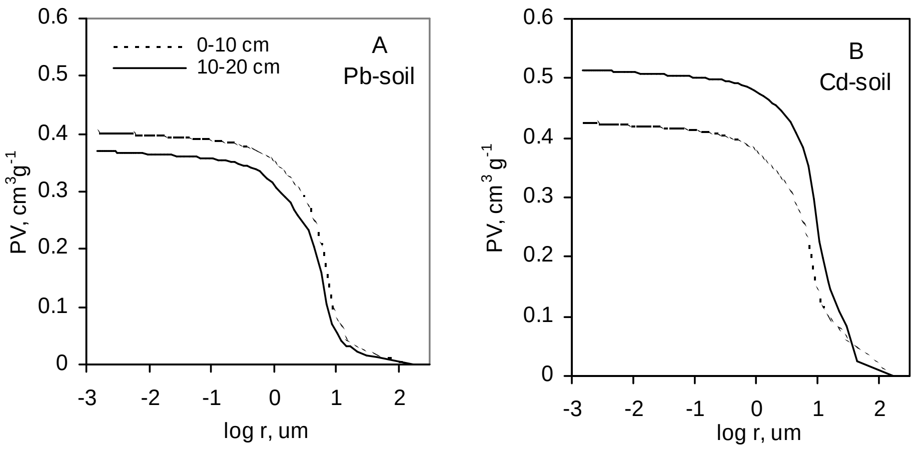

Fig 1. Cumulative pore volume curve of leached forest-meadow chernozem polluted with lead (A) and cadmium (B). Explanations: PV – pore volume, r – pore radius

The results of the mercury porosimetry measurements are collected in Table 2. The total intrusion volume (pore volume, PV) is the direct result of porosimetry measurement, and the total pore area (TPA), average pore diameter ($R_{aver.}$) and bulk density are obtained using the cylindrical pore model.

Table 2. Parameters of the pore structure of leached chernozem degraded by lead and cadmium

No.	Object/Dose of heavy metal/Depth (cm)	Total intrusion volume (mL g^{-1})	Total pore area (m^2g^{-1})	Average pore diameter (nm)	Bulk density (g mL^{-1})
		Soil + Pb 320 mg kg^{-1}			
1	0-10	0.404	3.60	448.3	1.259
2	10-20	0.370	3.72	398.2	1.300
		Soil + Cd 30 mg kg^{-1}			
3	0-10	0.426	3.44	495.3	1.211
4	10-20	0.515	3.73	552.2	1.100

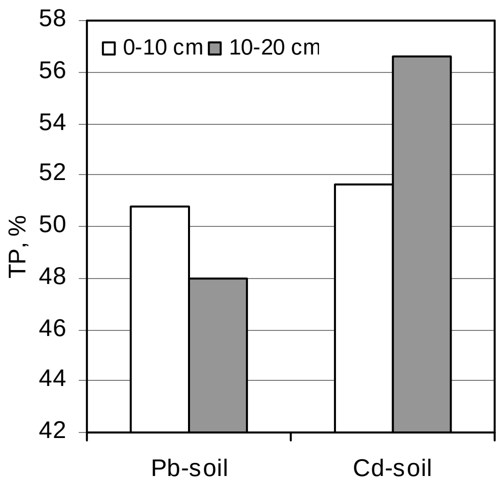

Fig. 2. Total porosity of leached forest-meadow chernozem polluted by lead and cadmium

The pore volume (PV) of the investigated polluted soils ranges from 370 mm^{-3} g^{-1} to 515 mm^{-3} g^{-1} and is higher for cadmium-polluted soil than for the soil polluted with lead. Both polluted soils exhibit also different values of PV for the upper and lower horizons. While PV decreases with depth for the Pb-polluted soil, it increases for the soil containing Cd (Tab. 2). The influence of Cd and Pb ions on the total porosity (TP) of chernozem is visualised in Figure 2. The porosity of Cd-soil is higher than Pb-soil, and the changes in TP with depth are similar to those already observed in the case of PV. In general, the values of PV, TP and average pore radii are found to be lower for Pb-soils compared with Cd-soils. Higher values of TP and lower average pore radius characterise soils with more pronounced porous structure. However, a decrease of the bulk density for Cd-soil can be also attributed to increasing pore volume, as well as to decreasing particle density of the soil.

Differential pore size distribution (PSD) can be regarded as a function reflecting the main aspect of soil porosity. This function, i.e. the dependence of dV/dlog R versus log R, permits comparisons of samples with variable pore volume. Pore size distributions for investigated polluted soils are displayed in Figure 3. For Pb-polluted soil the PSD functions obtained for the samples taken from two depths are quite similar and exhibit two peaks. The PSD function evaluated for the deeper soil layer is slightly shifted towards lower values of r, compared with that for the upper layer which possesses its maximum at about 6.97 μm. The differences between the PSDs obtained for the two depths are more pronounced for Cd- than for Pb-polluted soil (Fig. 3B). The PSD function for Cd-polluted soil exhibits one peak for the upper layer and two peaks for the lower layer. The shape of the latter function is similar to the functions evaluated for Pb-polluted soil (Fig. 3A). However, the main maximum of the PSD function is now at about 10.66 μm, while its secondary (i.e. lower) maximum is at about 45.32 μm. Moreover, the entire PSD function and its main maximum in particular are higher for Cd- than for Pb-polluted soil. This indicates the existence of a more pronounced porous structure of the former. The PSD function possesses only one maximum at about 8,63 μm for Cd-soil from the upper layer. Comparing the PSD curves for soils polluted by Pb and Cd we can state that the porosity and pore size are greater in Cd- than in Pb-polluted soil. This conclusion is also confirmed by the values of average pore diameter and pore area (see Table 2).

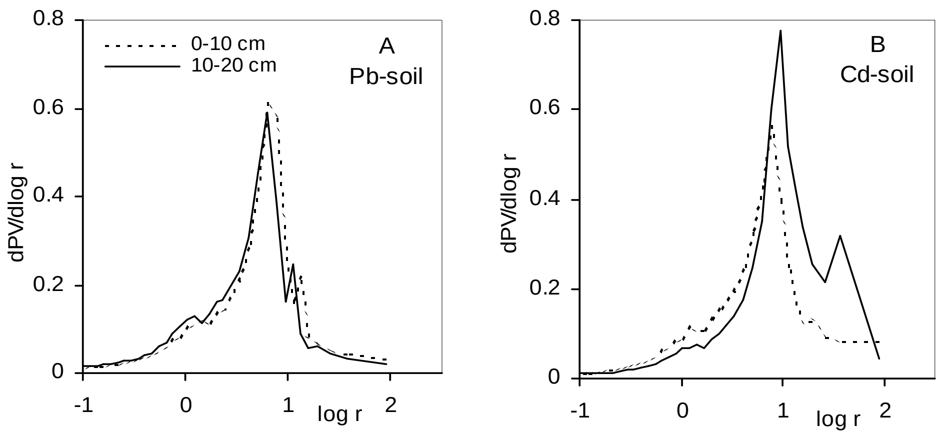

Fig. 3. Pore size distributions of leached forest-meadow chernozem polluted with lead (A) and cadmium (B)

The total porosity reveals nothing about the sizes or shapes of various pores in soil. Greenland (1979) proposed the classification of pores in terms of their agronomic function in soil. According to his classification, pores in the range of 0.5 to 50 μm, called the storage pores, hold water necessary for growth of plants. Pores ranging from 50 to 500 μm, called the transmission pores, are important because they regulate transmission of water and gases, and pores of sizes lower than 0.5 μm are the residual pores. However, the classification recommended by IUPAC (Sing 1982) (based on microscopic modelling and on the range of interactions of pore walls with confined molecules) divides pores into micropores (with dimensions <2.0 nm), mesopores (in the range of 2.0-50 nm) and macropores (with dimensions greater than 50 nm). Therefore, the Pb-soil contains mainly the storage pores (approx. 91-93% of its PV) and a small amount of residual pores (about 7-9% of its PV) or macropores (about 97-98%) and mesopores (about 2-3%). For the Cd-soil those values are about 93-95% of the storage pores and 5-8% of residual pores or 98% of macropores and 2% of micropores. The above numbers point to a somewhat more developed porous structure of the Cd-soil.

Generally, the samples of the Cd-soil are characterised by higher values of all investigated parameters, i.e. the total volume of intruded mercury, the pore volume, the total porosity, the average pore radius and the amounts of storage and residual pores. Also, the PSD curves for the Pb- and Cd-polluted soils are different. The above noted differences can be connected with the behaviour of Cd in environment. In their studies of adsorption of Cd in soils O'Connor *et al*. (1984) stressed that two mechanisms are responsible for metal retention by soil. The first mechanism, active at low concentration (0.01-10 mg L^{-1}) of added Cd, was attributed to specific sorption. At higher concentrations (100-1000 mg L^{-1}) of added Cd, the adsorption was attributed to exchange reactions. Desorption studies showed that Cd added at low concentration was not removed by 0.05 M $CaCl_2$ solution. At higher loading rates, the calcium salt removed significant amounts of adsorbed Cd. On the basis of stability diagrams Santillan-Medrano and Jurinak (1975) demonstrated that the solution activity of Cd is consistently higher than that of Pb, indicating that Cd is more mobile in the environment.

Different influence of lead and cadmium on porosity of leached chernozem is connected with the nature of both heavy metals and with the properties of a soil. It is well-known that the behaviour of both these cations in soils is different (Santillan-Medrano and Jurinak 1975, Puls *et al*. 1991, Japony and Young 1994, Hooda and Allowey 1998). The accumulation and mobility of heavy metals are determined largely by the extent of their adsorption by soil particles (McLean and Bledsoe 1992). In particular, soil organic and mineral particles can bind toxic elements through the formation of complexes. The retention of metals by soils and, consequently, their availability to plants, are also influenced by pH and ionic composition of the soil solution. The relationship between the amount of metal adsorbed and composition of the soil is quite complex, due to solid phase heterogeneity and influence of soil solution chemistry (Harter 1979, Zhou De-Zhi *et al*. 1991, Appel and Ma 2002, Diatta *et al*. 2003).

One should remember that mercury porosimetry measures pores ranging in their size from 3.5 to 7500 nm, and thus the pore volume is evaluated taking into account pores from this interval. Consequently, the total porosity does not include all macropores and micropores, as well as closed and bottle pores. A better description of porosity and pore size distribution across a wide range of pore sizes is not possible using one method. The full characteristics of the porous system of a porous material may be obtained by comparison of the results obtained using several methods simultaneously (Hajnos 1998). Hajnos *et al*. (2006) showed that the approach employing four methods, i.e. pF curve, mercury porosimetry, adsorption of water vapour and adsorption of nitrogen, is the most suitable tool for characterising a wide range of pore radii, from 0.001 to >50 μm, influenced by soil management practices.

CONCLUSION

Different influence of lead and cadmium on porosity of leached forest-meadow chernozem is connected with the nature of both heavy metals. The behaviour of lead and cadmium in soil are different. Pore volume (PV) of investigated polluted soils ranged from 370 $mm^{-3}\,g^{-1}$ to 515 $mm^{-3}\,g^{-1}$. The Cd-soil has higher values of all investigated parameters, i.e. total intrusion volume of mercury, pore volume, total porosity, average pore radii and amounts of storage and residual pores. Also the difference in PSD curves are visible. Also, both soils exhibit differences of investigated parameters between the upper and sub layers.

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POROWATOŚĆ WYŁUGOWANEGO CZARNOZIEMU LEŚNO-STEPOWEGO ZANIECZYSZCZONEGO OŁOWIEM I KADMEM

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S t r e s z c z e n i e. Metodą porozymetrii rteciowej badano porowatość wyługowanego leśno-stepowego czarnoziemu, zanieczyszczonego ołowiem i kadmem. Gleby pochodziły z poletek doświadczalnych stacji badawczej Uniwersytetu Rolniczego we Lwowie. Próbki glebowe pobrano z głębokości 0-10 i 10-20 cm. Maksymalne stężenie ołowiu w glebie wynosiło 320 $mg \cdot kg^{-1}$, a kadmu 30 $mg \cdot kg^{-1}$. Dla badanych gleb wyznaczono krzywe kumulatywne i krzywe rozkładu porów w funkcji promienia.

Objętość porów w badanych glebach zmieniała się od 370 $mm^3 \cdot g^{-1}$ do 515 $mm^3 \cdot g^{-1}$ i była wyższa dla gleb zanieczyszczonych Cd niż ołowiem. Dla obu gleb, tj. Pb-gleby i Cd-gleby, stwierdzono różną objętość porów w warstwie powierzchniowej i głębszej. Objętość porów, porowatość całkowita i średni promień porów były niższe dla Pb-gleby niż Cd-gleby. Dla czarnoziemu zanieczyszczonego Pb na krzywych różniczkowych objętości porów (PSD) występował jeden pik (przy promieniu porów ok. 6.97 μm), a krzywe miały podobny przebieg. W porównaniu do gleby zanieczyszczonej Pb, krzywe PSD dla gleby zanieczyszczonej Cd były bardziej zróżnicowane, szczególnie dla próbki pobranej z głębokości 10-20 cm. Dla tej próbki funkcja PSD charakteryzowała się dwoma pikami: wysokim pikiem występującym dla porów o promieniu ok. 10.66 μm oraz drugim mniejszym, dla porów o promieniu ok. 45.32 μm. Gleba zanieczyszczona Cd charakteryzowała się większą porowatością i obecnością porów o większym promieniu. Badane próbki czarnoziemu zanieczyszczonego Pb i Cd posiadały głównie pory magazynujące wodę. Zróżnicowany wpływ ołowiu i kadmu na porowatość czarnoziemu leśno-stepowego związany był z chemiczną naturą tych pierwiastków oraz właściwościami gleby.

Słowa kluczowe: zanieczyszczenie gleby, ołów, kadm, porozymetria rteciowa