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THE EFFECT OF HAPLIC PHAEOZEM AND LEPTIC PODZOL PROPERTIES ON SORPTION OF LEAD AND CADMIUM IN SOIL

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Abstract. The effect of soil acidity, organic matter, ortho-phosphate and clay content on sorption of lead and cadmium was studied for Haplic Phaeozem and Leptic Podzol. Adsorption isotherms of lead exhibited relatively low differences between the soils whereas higher differences were noted for cadmium, especially at high concentrations. Stronger immobilization of both heavy metals occurred in Haplic Phaeozem.

Keywords: soil pollution, lead, cadmium, adsorption isotherm

INTRODUCTION

Cadmium and lead are the most widely spread and extremely hazardous heavy metals from the environmental point of view (Hooda and Alloway, 1998). The uptake of lead and cadmium by plants is affected by their amount and availability in soils, which in turn depends on soil sorption properties, mineral and organic composition, pH, Ca^{2+} content, redox potential, microbial activity, as well as on solution flow (including gravity mass flow) and diffusion with concentration gradient (Siedlecka *et al*. 2001).

One of the important sources of arable soil pollution by cadmium are phosphorus fertilizers (Satarug *et al*, 2003). Cadmium concentration in arable and forest soils around 4 mg kg^{-1} is the rational average, however in heavily degraded soils over 250 mg kg^{-1} is common (Ostrowska *et al*. 1991). Cadmium usually occurs as highly mobile sulphide in neutral soils, and in calcareous soils it is fixed by carbonates. Sorption of cadmium occurs mainly on clays and organic matter and generally increases with increasing pH (Salama and Helmke 1998). Methods used to decrease toxicity of other heavy metals in soils are usually not sufficiently efficient with relation to cadmium. Because of its high mobility cadmium can be easily accumulated in plant tissues, thus entering the food chain.

Lead is significantly less mobile than cadmium. In soils of pH>6.5 it is immobilized by carbonates and phosphates. Iron and manganese oxides, clay minerals and soil organic matter also easily fixate lead (Siposa *et al.* 2005). Concentration of lead in arable and forest soils is usually lower than 150 mg kg^{-1} and may be much higher in heavily polluted soils where Pb contents up to 18 000 mg kg^{-1} are noted (Ostrowska *et al.* 1991).

The mobility of heavy metals and their concentration in soil solution determine the impact of toxic metals on the environment (Li and Shuman 1997). Processes of sorption-desorption affect their toxicity by influencing their concentration in soil solution (Swift and McLaren 1991).

The aim of this study was to compare sorption of lead and cadmium in two soils in relation to their properties.

MATERIAL AND METHODS

Two agricultural soils, Haplic Phaeozem developed from loess and Leptic Podzol developed from glacial sand, were studied. The soils were collected from 0-20 cm depth, air dried and passed through a 2 mm screen.

Basic properties of the studied soils are presented in Table 1. The pH was measured potentiometrically in $CaCl_2$, organic carbon by Tyurin method, soil granulometric composition by areometric Casagrande method modified by Prószyński, and orthophosphate content in saturated soil solution by flow spectrophotometry using FIA-Star 5010.

Samples of air dry soils were amended with $CdCl_2$ or $Pb(NO_3)_2$ solutions at solid/liquid phase ratio equal to 1:2.5. The concentrations of Cd^{2+} in the solutions were equal to: 0 (distilled water), 4.7, 9.3, 18.8, 37.5, 75, 150, and 300 mg dm^{-3} while the Pb^{2+} concentrations were: 0, 25.7, 51.4, 103, 205, 411, 822, 1645, 32901 and 65802 mg dm^{-3}. These concentrations were chosen to plot the adsorption isotherms and to obtain Cd and Pb content in soils close to that observed in soil from polluted areas. The ionic strength of the reaction medium was adjusted to ~ 0.1 mol dm^{-3} using 5 mol dm^{-3} solutions of NaCl and $NaNO_3$,

Table 1. Selected properties of the soils

Description	Haplic Phaeozem	Leptic Podzol
Sand (1-0.1 mm), %	19	29
Silt (0.1-0.02 mm), %	56	51
Clay (<0.02 mm), %	25	20
pH ($CaCl_2$)	7.4	6.9
Corg (%)	0.77	0.19
$P\text{-}PO_4$ (mg dm^{-3})	0.70	2.14

respectively. Concentrations of Pb^{2+} and Cd^{2+} in the supernatants were measured potentiometrically after 3 days of equilibration using Cole-Palmer Lead and Cadmium Ion Selective Electrodes. Calibration of the electrodes was made in $Pb(NO_3)_2$ and $CdCl_2$ solutions with concentrations of the analysed ions ranging from 10^{-6} to 10^{-1} mol dm^{-3} at the same ionic strength.

Freundlich equation was used to describe sorption of both heavy metals:

$$\log S = \log K_f + n^{-1} \operatorname{Log} C_e \qquad (1)$$

S – amount of Cd or Pb sorbed (mg kg^{-1});
K_f – sorption constant,
n^{-1} – coefficient connected with sorbent heterogeneity,
C_e – concentration of Cd or Pb in equilibrium solution (mg dm^{-3}).

RESULTS AND DISCUSSION

The measured sorption isotherms for the studied soils are presented in Figure 1 and Figure 2 whereas the calculated adsorption parameters are listed in Table 2.

The isotherms show higher sorption of cadmium and lead in the Haplic Phaeozem in the whole range of both heavy metals concentrations, which is in agreement with results of other studies (Hooda and Alloway 1998, Buchter *et al*. 1989, Elliott *et al.* 1986). The Freundlich adsorption constant K_f used to be considered as a measure of the binding force of a heavy metal by soil (Tab. 2) and this is lower for cadmium than for lead for both soils. On the other hand the K_f constants for both cadmium as lead are lower for Leptic Podzol than for Haplic Phaeozem. At the highest heavy metals concentrations, small differences between the amount of sorbed lead are found for both soils (0.1 to 3.6 %), and in the case of cadmium these differences are larger (from 22 up to 223%). Low differences between lead sorption by different kinds of soil are also noted by other authors (Hooda and Alloway 1997).

Two highest cadmium concentrations occurring in Leptic Podzol have very similar values, which may indicate Cd saturation of the exchange complex of this soil. This indicates that the sorption capacity of this soil for cadmium is very low, and equals around 200 mg Cd per kilogram of soil. Constant increase of adsorbed Pb in both soils was observed in the whole experimental window, which suggests that both soils can potentially accumulate more lead.

Eq 1 describes well the experimental data, which is seen from the calculated values of determination coefficients of the respective linear dependence (Tab. 2). Regression lines fitted into lead adsorption isotherms have similar slope (n^{-1}): 0.57 for Leptic Podzol and 0.61 for Haplic Phaeozem, respectively. These coefficients for cadmium adsorption isotherms differ more and are 0.51 for Haplic

Phaeozem and 0.57 for Leptic Podzol (this coefficient calculated excluding cadmium saturation point equals 0.69) showing faster increase of sorption in the former soil with increasing concentration of cadmium in solution.

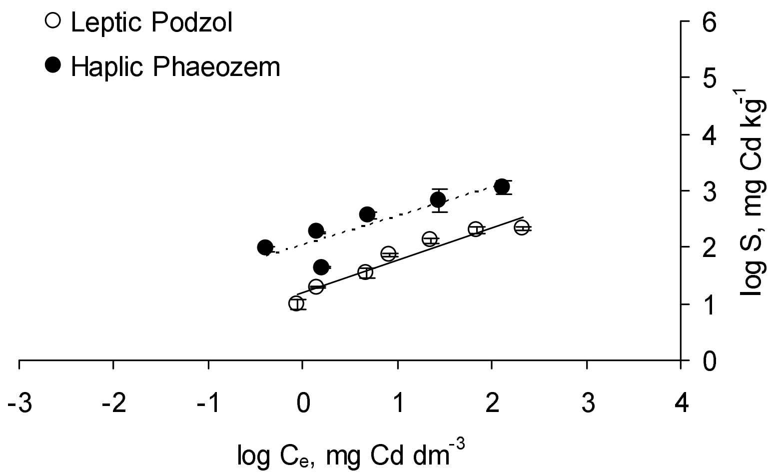

Fig. 1. Cadmium adsorption isotherms, bars represent standard error

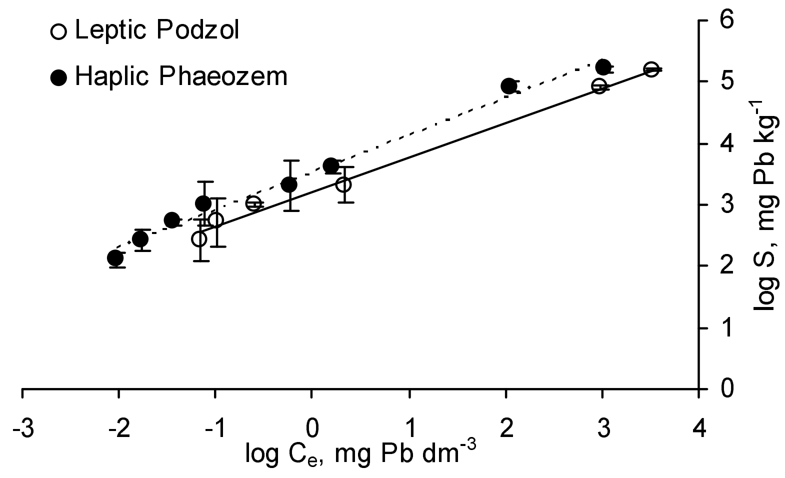

Fig. 2. Lead adsorption isotherms, bars represent standard error

Table. 2. Freundlich sorption parameters for studied soils

Soil	Cadmium			Lead		
	Log K_f	n^{-1}	R^2	Log K_f	n^{-1}	R^2
Haplic Phaeozem	2.03	0.51	0.77	3.51	0.61	0.99
Leptic Podzol	1.18	0.57	0.93	3.20	0.57	0.99

Reported strongly positive correlation between clay content and heavy metals sorption (Hooda and Alloway, 1998) is in an agreement with soil texture (Tab. 1) and values of logarithm of intercept of Freundlich isotherm K_f (Tab. 2).

Very close sorption isotherm parameters for lead were determined for the studied soils and brown earths (Hooda and Alloway 1997), which may indicate that these parameters cannot be directly linked to soil properties (texture, pH, organic carbon), at least for soils of different origin.

Haplic Phaeozem has higher content of clay and organic carbon, and higher pH than Leptic Podzol (Tab. 1), therefore a stronger effect of immobilization of heavy metals in the former soil should occur (Gerriste and van Driel 1984, Martinez and Motto 2000). However, similar sorption of lead in both soils may be due to Leptic Podzol having a higher ortho-phosphate content (resulting most probably from its cultivation and easier decomposition of organic matter), which may cause increased precipitation of lead.

CONCLUSION

Analyses of soil properties related to cadmium and lead fixation showed greater potential of Haplic Phaeozem than Leptic Podzol to adsorb cadmium and lead due to higher pH and clay and organic matter content. The adsorption of lead is higher than that of cadmium for both soils over the whole range of concentrations. Low differences between both soils in lead sorption may be due to high phosphate content in Leptic Podzol.

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WPŁYW WŁAŚCIWOŚCI GLEBY NA SORPCJĘ OŁOWIU I KADMU W GLEBIE

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Streszczenie. Badano wpływ wybranych właściwości gleb Haplic Phaeozem and Leptic Podzol na zdolności tych gleb do immobilizacji ołowiu i kadmu. Porównano kwasowość, zawartość materii organicznej, fosforanów, frakcji iłu mających wpływ na zdolność gleb do wiązania kadmu i ołowiu. Porównanie izoterm adsorpcji kadmu i ołowiu na glebach potwierdziły znacznie silniejszy efekt immobilizacji obu metali ciężkich w glebie Haplic Phaeozem niz Leptic Podzol.

Słowa kluczowe: zanieczyszczenie gleby, ołów, kadm, izotermy adsorpcji