

**INFLUENCE OF SOIL TYPE, ORGANIC MATTER AND TOTAL Pb  
CONTENT ON LEAD ADSORPTION FROM THE SOIL SOLUTION**

Viera Kováčová

Movement and attenuation of heavy metals in soils is among other processes controlled by sorption onto the surfaces of soil particles. Processes like precipitation/coprecipitation, complexation and competitive effects of other cations may also influence the attenuation, but in all cases sorption will be involved, and at natural and slightly polluted concentration levels sorption may be the predominating attenuation process. The Pb sorption on ten investigated soils from Žitný ostrov area (Slovakia) has been studied in laboratory conditions. Batch adsorption experiments were performed with a very wide range of lead concentrations (0,01-500 mg/l Pb<sup>2+</sup>) at a constant soil/solution ratio. The aim was estimation adsorbed amount of lead S, determination of adsorption parameters for several soil types and comparison obtained results with results introduced in publishing works. Previous experiments showed, that sorption of lead is well-described by Freundlich and Langmuir isotherm. Experimentally were determined parameters  $K_F$ ,  $n$  of Freundlich isotherm and parameters  $Q_{max}$ ,  $K_L$  of Langmuir isotherm. The influence of soil type, organic matter and total Pb content on adsorption were estimated. The results are introduced in this contribution.

KLÚČOVÉ SLOVÁ: sorption, heavy metals, lead, soil solution

**VPLYV TYPU PÔDY, ORGANICKEJ HMOTY A CELKOVÉHO OBSAHU OLOVA NA ADSORPCIU OLOVA Z PÔDNEHO ROZTOKU** Pohyb a zoslabenie vplyvu ťažkých kovov v pôde je jedným z procesov ovládaných sorpciou na povrchu pôdnych častíc. Môžu ich ovplyvňovať procesy ako zrážanie, komplexácia, výmenné reakcie s inými kationmi, vo všetkých prípadoch je však prítomná sorpcia, a v prirodzených podmienkach s nízkymi koncentraciami môže byť sorpcia prevládajúcim procesom. V predkladanom príspevku sú uvedené výsledky sorpčných experimentov Pb na vzorkách desiatich skúmaných pôd z lokality Žitného ostrova (Slovensko) v širokom rozsahu počiatočných koncentrácií olova (0,01-500 mg/l Pb<sup>2+</sup>). Cieľom bolo stanovenie adsorbovaného množstva olova S, určenie adsorpčných parametrov pre daný typ pôdy a porovnanie výsledkov s výsledkami dostupnými v literatúre. Predchádzajúcimi experimentami bolo zistené, že priebeh sorpcie olova dobre popisuje Freundlichova a Langmuirova izoterma, ktorých parametre  $K_F$ ,  $n$  (Freundlichova) a  $Q_{max}$ ,  $K_L$  (Langmuirova) boli stanovené pre dané pôdy. Bol vyhodnotený vplyv pôdneho typu, organickej hmoty a celkového množstva rozpusteného Pb na adsorpciu. Výsledky sú prezentované v tomto príspevku.

KEY WORDS: sorpcia, ťažké kovy, olovo, pôdny roztok

### Introduction

Heavy metals like cadmium, lead, chromium, mercury and arsenic are the major toxic metals posing a threat to human health. Industrialization, urbanization and agricultural production have become permanent resources of extraneous chemicals in environment. The increase in agricultural production efficiency causes using of large quantities of chemical products in soils

and water. Therefore, an attention should be paid to understanding the problems of detention of contaminants in soils and their penetration to water. The toxicities induced by excessive levels of some of these elements, such as cadmium (Cd), lead (Pb) chromium (Cr) and mercury (Hg) are well known. Pollution of the environment with metals, such as lead, is a world-wide problem. Lead alkyl additives into petrol are combusted and emitted into the atmosphere and can be responsible

for high concentration of lead in some vegetation, roadside, soil, air, water and plants. Lead has been added to petrol (gasoline) as an antiknocking agent since the 1920s in order to improve fuel performance and reduce wear on vehicle engines. Since this time, leaded petrol has been reported to cause more lead exposures than any other source worldwide. During the 1970s, health impacts associated with lead emissions from vehicles became a widely discussed issue. Many studies have reported that environmental lead emissions have resulted in significant health effects (Salomons et al., 1995, Tong et al., 2000, Tunegová et al., 2016).

Lead naturally in the soil in concentrations ranging from 10 to 50 mg/kg (ppm). Enhanced levels lead contamination is common in urban areas because of the widespread use of lead in man-made products and industrial processes. In natural conditions predominate dissolved forms of lead :  $Pb^{2+}$  and  $PbCO_3(aq)$ , which may be in wide pH-range the dominant form of occurrence. Lead solubility is limited mainly solubility of  $PbCO_3(s)$ . Only in alkaline conditions is coming up for  $Pb_3(CO_3)_2(OH)_2(s)$  and  $Pb(OH)_2(s)$  in dependence on  $CO_2$  concentrations. In the presence of organic contamination may be considerable part of lead bind in organic complexes (Pitter et al., 1990, Richter et al., 1993, Yong et al., 1992).

Heavy metals are important environmental pollutants threatening the health of human populations and natural ecosystems. Like other inorganic and organic contaminants, the fate of heavy metals in the environment is largely controlled by sorption reaction with soil colloids. The three main active soil colloidal constituents, clay minerals, metal oxides and organic matter are important sorbents of heavy metals owing primarily to their cation-exchange capacity (CEC) and their ability to form inner-sphere complexes through surface reactive groups, such as carboxylic and hydroxyl groups. Mutual interactions between clay minerals, Fe oxides, and organic matter can greatly alter the sorptive properties of these soil constituents for heavy metals, because such interactions usually involve cation exchange sites and carboxyl and OH surface groups, that is, potential sorption sites for heavy metals (Crus-Guzmán et al., 2003).

Movement and attenuation of heavy metals in soils is among other processes controlled by sorption onto the surfaces of soil particles. Processes like precipitation/coprecipitation, complexation and competitive effects of other cations may also influence the attenuation, but in all cases sorption will be involved, and at natural and slightly polluted concentration levels sorption may be the predominating attenuation process. (Christensen et al., 1996).

Soil represents a major sink for pollutants emitted by both natural sources and human activities. Interactions of pollutants, especially trace elements in cationic form, with soil components, particularly Fe- and Mn-oxides, clay minerals and humic substances, affect their mobility and therefore their potential to penetrate towards

deeper soil horizons and groundwater reservoirs. Accordingly, the studies of pollutants behavior in relation to soil type are of crucial importance for the prediction of the fate of contaminants and the selection of appropriate methods for soil rehabilitation. (Krishnamurti et al, 1999, 2003). In most soil sorption processes regulate the solubility of heavy metals. Anderson et al, 1988, Basta et al, 1992, Pokrovsky et al., 2012, Urmínská et al., 2015 studied sorption of heavy metals by equilibrating soils with solutions of various heavy metals concentrations and subsequently removing a proportion of the sorbed ions with salt solutions. These experiments indicated that most soils have a high capacity to sorb heavy metals. A large portion is apparently sorbed in an exchangeable form, adsorption in a non-exchangeable form tended be more important in the low concentration range. The adsorption of non-exchangeable form is attributed to specific sites such as hydroxyl and carboxyl groups on inorganic and organic components of the soil.

Soil organic matter is one of the most important components for the retention of trace metal ions. Trace metal complexation by organics is particularly important for metals such as Pb, Cu, Ni and Hg, but the interaction with organic complexes is also significant for the other metal ions. The presence of organic matter increases the cation exchange capacity (CEC) of soils, and , thus, negative correlations between CEC and the solubility of trace metals are observed because the added organic matter immobilizes the metals. At higher soil pH, soluble organic matter (fulvic acid) can suppress the trace metal adsorption on silicates and oxides and promote dissolution of trace metals from adsorption sites on clay minerals. Several investigations have revealed that the soluble organics are able to raise the trace metal carrying capacity of soil solution. The persistency of these metal-organic complexes is attributed to the tendency of metals to form stable complexes with dissolved organic matter. Typically Pb form very stable complexes with dissolved organic matter, thus, only a very small fraction of these metals exists as free hydrated metal ions when pH is not strongly acid. On the other hand, metals such as Cd and Zn are less prone to form such stable metal-organic complexes, hence, a larger fraction of these metals is recovered as free hydrated metal ions (Almas et al., 2000, Čelková, 2016, Dulovičová et al., 2016, McBride et al., 1997). For soils of the same total Pb content, Pb was more soluble and more plant available in sand soil than in clay soil. In the soils, the more soluble fractions of Pb increased as the pH was lowered (Eriksson et al., 1988, 1990, Vega et al., 2008).

## **Materials and methods**

Equation describing transport of water and chemicals in porous media, including sorption and microbial transformation terms is (Bolt, 1979, de Smedt, 1978, Yong et al., 1992) - the governing differential equation

in the one-dimensional form used for consideration of advective-dispersive transport assume isothermal conditions, absence of significant density difference, no-volume change conditions, without transformations for ions :

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \frac{\rho}{\theta} \frac{\partial S}{\partial t} \quad (1)$$

where

$c$  – the solute mass per unit volume of solution ( $\text{ML}^{-3}$ ),

$D$  – the dispersion-diffusion coefficient ( $\text{L}^2\text{T}^{-1}$ ),

$v$  – average pore-water velocity ( $\text{LT}^{-1}$ ),

$\theta$  – the volumetric water content ( $\text{L}^3\text{L}^{-3}$ ),

$\rho$  – is the dry mass density ( $\text{ML}^{-3}$ ),

$t$  – the time (T),

$x$  – the distance (L),

$\partial S / \partial t$  represent sorption term.

Adsorption processes we can quantify by adsorption isotherms. The most frequent are used linear and nonlinear (Freundlich and Langmuir) isotherms. In steady state conditions is valid:

$$S = K_D c_e \quad (2)$$

$$S_F = K_F (c_e)^{1/n} \quad (3)$$

$$S_L = \frac{K_L Q_{\max} c_e}{1 + K_L c_e} \quad (4)$$

where

$S$ ,  $S_F$ ,  $S_L$ , represent adsorbed amount of ion per mass unit of soil complex ( $\text{M/M}^{-1}$ ),

$c_e$  – is equilibrium concentration of ion in the liquid phase ( $\text{ML}^{-3}$ ),

$K_D$ ,  $K_L$ ,  $K_F$  – are distribution coefficients (ion ratio between liquid and solid state of system) ( $\text{L}^3\text{M}^{-1}$ )

$Q_{\max}$  – is adsorption maximum ( $\text{M/M}^{-1}$ ),

$1/n$  – nondimensional empirical factor,  $0 < n \leq 1$ . If  $n = 1$ , Freundlich non-linear isotherm transform to linear form.

In linearized form the equations (3) and (4) are:

$$\log S_F = \log K_F + 1/n \log c_e \quad (5)$$

$$\frac{c_e}{S} = \frac{1}{Q_{\max} K_L} + \frac{c_e}{Q_{\max}} \quad (6)$$

### Characteristics of investigated soil types

Sorption studies of Pb(II) have been conducted on soils of different physico-chemical properties.

Table 1 list the measured properties (sand, silt and clay contents, pH values, organic matter content, cation exchange capacity) of the soil horizons studied.

The purpose of this research project was to measure Freundlich and Langmuir isotherm's parameters of lead (Pb) for a range of soils and investigate any correlation between these parameters and characteristic parameters of the soils.

The use of Freundlich and Langmuir isotherm's parameters to quantify heavy metal sorption onto soil horizons as determined by laboratory batch experiments assumes that: (1) equilibrium distribution is obtained in the batch experiments, (2) sorption is the governing process (equilibrium conditions involving precipitation of the metal studied cannot be described adequately by a distribution coefficients), (3) the distribution is reversible.

Ten soil horizons were obtained at locations in Žitný ostrov (Slovakia). The locations cover a variety of soils with extensive agricultural activity. The soils were sampled, and air dried until the experiments were performed. The physico-chemical characteristics were measured (the texture, organic matter, content of organic carbon, pH).

**Table 1. Physico-chemical properties of investigated soil types**

**Tabuľka 1. Fyzikálne a chemické vlastnosti pôd.**

Soil	Sand	Silt	Clay	Texture	$\rho_s$	$\rho_d$	$\text{pH}_{\text{KCl}}$	$\text{CaCO}_3$	OM	CEC
	%	%	%		( $\text{g.cm}^{-3}$ )	( $\text{g.cm}^{-3}$ )		(%)	(%)	( $\text{mg}/100\text{g}$ )
L1	40,2	43,7	16,1	loam	2,66	1,16	5,0	17,0	5,0	18,4
L2	33,4	55,5	11,1	loam	2,81	1,79	5,92	15,6	0,5	12,7
SL1	23,1	67	9,9	sandy-loam	2,72	1,53	5,86	2,9	0,8	11,7
SL2	17,2	74,4	8,4	sandy-loam	2,76	1,39	5,07	1,8	0,4	12,8
L3	38,7	38,6	22,7	loam	2,5	1,47	5,3	11,7	4,7	35,0
L4	37,4	36,8	25,8	loam	2,46	1,36	5,26	10,5	3,9	28,1
SL3	48,8	12,2	39,0	sandy-loam	2,8	1,35	5,7	5,7	0,82	14,5
SL4	45,5	16	38,5	sandy-loam	2,85	1,44	5,4	3,5	0,76	13,5
CL5	26,1	43,8	30,1	clay-loam	2,3	1,12	5,6	11,1	2,18	22,5
C6	25,4	31,2	43,4	clay	2,5	1,1	5,1	0,41	5,24	36,8

where:  $\rho_s$  – particle density,  $\rho_d$  – bulk density,  $\text{pH}_{\text{KCl}}$  – potential soil reaction,  $\text{CaCO}_3$  – content of carbonates, OM – organic matter, CEC – cation exchange capacity, grain composition

kde:  $\rho_s$  – merná hmotnosť,  $\rho_d$  – objemová hmotnosť,  $\text{pH}_{\text{KCl}}$  – výmenná pôdna reakcia,  $\text{CaCO}_3$  – obsah karbonátov, OM – obsah organickej hmoty, CEC – výmenná kapacita, zrnitostné zloženie

Each sorption experiment involved 10 g of soil sample and 50 ml of salt matrix ( $10^{-3}$  M  $\text{CaCl}_2$ ) equilibrating in a 500-ml polyethylene bottle for 24 h before the metal was added from a standardized solution  $\text{Pb}(\text{NO}_3)_2$ . The metal distribution between solid and solute equilibrated for 12 h. Solids and solute were separated by centrifugation (equivalent particle separation diameter:  $0,2 \mu\text{m}$ ) and the solute was preserved with acid ( $\text{HNO}_3$ ) and analysed. The concentration of the metal on the soil material was calculated from the mass balance as the difference between metal added and metal in the solute after equilibrium. The samples were analyzed by Pb-ion selective electrode Crytur. The pH was preserved at the about equally value. At the higher pH-range precipitation of Pb as  $\text{PbCO}_3$  may take place during the experiment and violate the assumption that metal bound to the solids was controlled by sorption. Pb-carbonate complexes may form and increase the solute concentration.

### Results and discussion

Sorption of Pb is well described by Freundlich and Langmuir isotherms (concentration of metal on the solid vs. concentration of metal in the solute) as shown in Fig. 1, 2, 3.

Parameters of Freundlich and Langmuir isotherms were measured for lead (Pb) in laboratory batch experiments for 10 soils at environmentally relevant solute concen-

trations in approximately equal conditions (pH).

The experimentally determined Freundlich and Langmuir isotherm's parameters are listed in Table 2.

The sorption data of the ten soils studied could be fit satisfactorily using the Freundlich and Langmuir isotherm. The Freundlich and Langmuir equation gave an excellent fit to the isotherm data for investigated soils, with correlation coefficients  $> 0,89$  for Langmuir and  $> 0,79$  for Freundlich isotherm. The parameters  $K_F$ ,  $n$ ,  $K_L$ ,  $Q_{\text{max}}$  was shown to correlate significantly ( $P < 0,001$ ) with organic matter and sorption capacity of the soils. The  $K_F$ -values ranged from  $298 \cdot 10^{-3}$  to  $1055 \cdot 10^{-3} \text{ m}^3 \cdot \text{kg}^{-1}$  and  $K_L$ -values ranged from 5 to  $30 \cdot 10^{-3} \text{ l} \cdot \text{kg}^{-1}$  for Pb.

The presence of organic matter increases the cation exchange capacity (CEC) of soils, and negative correlations between CEC and the solubility of trace metals are observed because the added organic matter immobilizes the metals. At higher soil pH, soluble organic matter can suppress the trace metal adsorption on silicates and oxides and promote dissolution of trace metals from adsorption sites on clay minerals. The persistency of these metal-organic complexes is attributed to the tendency of metals to form stable complexes with dissolved organic matter. Typically Pb form very stable complexes with dissolved organic matter, thus, only a very small fraction of these metal exists as free hydrated metal ions when pH is not strongly acid.

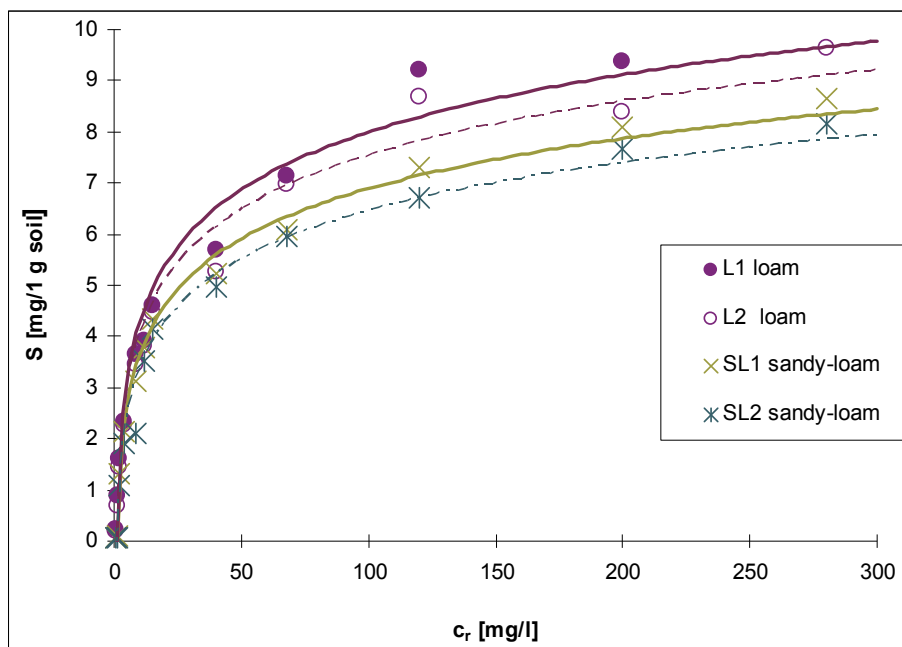


Fig. 1. Pb(II) adsorption isotherms, described by dependence of amount of adsorbed lead  $S$  on equilibrium concentration of lead in solution  $c_r$  for loamy soils L1, L2 and sandy-loamy soils SL1, SL2 - experimental data.

Obr. 1. Adsorpčné izotermy olova, popisujúce závislosť adsorbovaného množstva  $S$  na rovnovážnej koncentrácii olova v roztoku  $c_r$  pre hlinitú pôdu L1, L2 a piesočnato-hlinitú pôdu SL1, SL2 - experimentálne údaje.

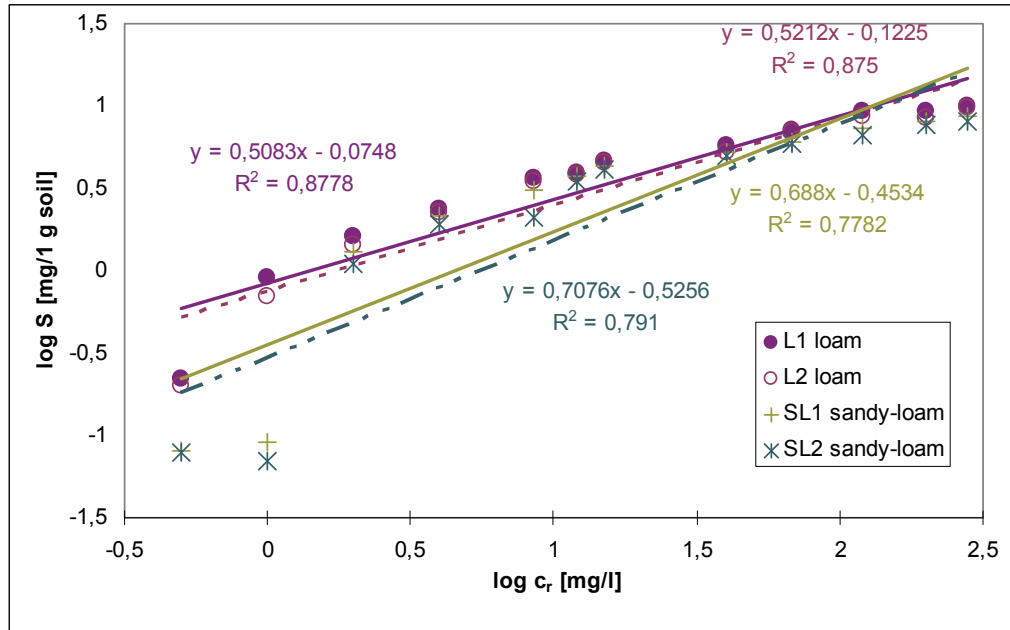


Fig. 2. Linearised Freundlich adsorption isotherms of lead for loamy soils L1, L2 and sandy-loamy soils SL1, SL2 - experimental data.

Obr. 2. Linearizovaná Freundlichova adsorpčná izoterma olova pre hlinité L1, L2 a piesočnato-hlinité pôdy SL1, SL2.

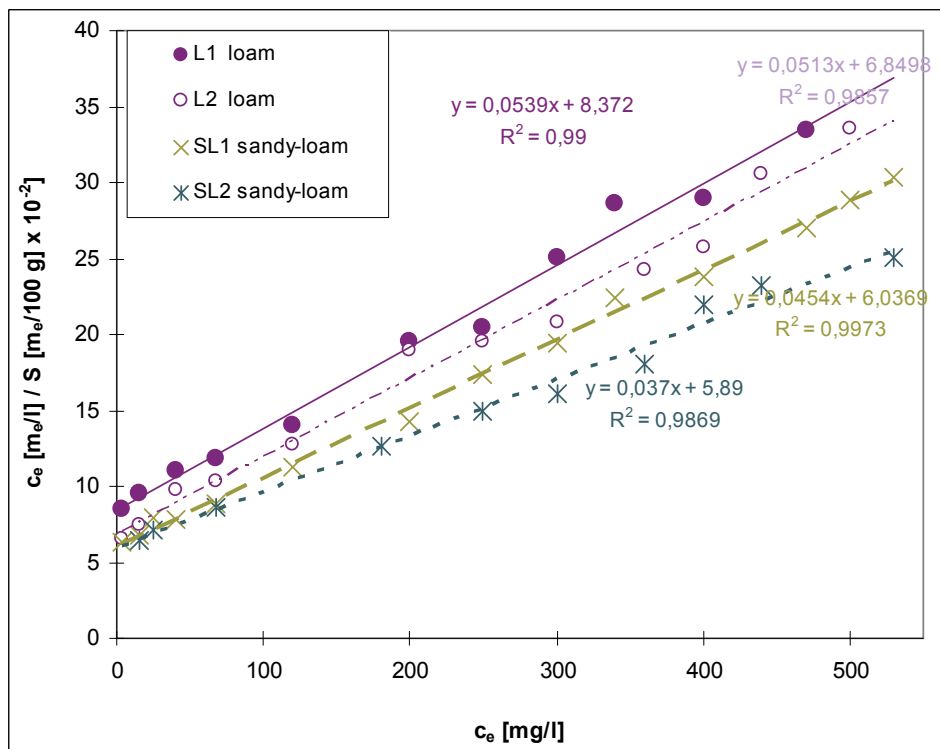


Fig. 3. Linearised Langmuir adsorption isotherms of lead for loamy soils L1, L2 and sandy-loamy soils SL1, SL2 - experimental data.

Obr. 3. Linearizovaná Langmuirova adsorpčná izoterma olova pre hlinité L1, L2 a piesočnato-hlinité pôdy SL1, SL2.

**Table 2. Freundlich and Langmuir parameters for Pb (II) sorption by different soil types**  
**Tabuľka 2. Parametre Freundlichovej a Langmuirovej izotermy sorpcie olova pre rôzne typy pôd**

soil	Pb			Pb		
	Freundlich parameters			Langmuir parameters		
	$K_F$	$1/n$	$R^2$	$Q_{max}$	$K_L$	$R^2$
	$m^3 \cdot kg^{-1}$	-		$mg \cdot kg^{-1}$	$l \cdot kg^{-1}$	
L1	$841,7 \cdot 10^{-3}$	1,97	0,8778	740	$8,372 \cdot 10^{-3}$	0,99
L2	$754,2 \cdot 10^{-3}$	1,92	0,875	690	$6,849 \cdot 10^{-3}$	0,985
SL1	$352,0 \cdot 10^{-3}$	1,45	0,7782	550	$6,036 \cdot 10^{-3}$	0,997
SL2	$298,1 \cdot 10^{-3}$	1,41	0,791	490	$5,89 \cdot 10^{-3}$	0,986
L3	$810,3 \cdot 10^{-3}$	1,15	0,917	810,5	$12,64 \cdot 10^{-3}$	0,967
L4	$790,1 \cdot 10^{-3}$	1,71	0,893	801,3	$10,80 \cdot 10^{-3}$	0,935
SL3	$365,7 \cdot 10^{-3}$	1,08	0,799	590,5	$7,35 \cdot 10^{-3}$	0,895
SL4	$320,9 \cdot 10^{-3}$	1,26	0,792	567,8	$7,10 \cdot 10^{-3}$	0,901
CL5	$830,2 \cdot 10^{-3}$	1,54	0,859	830	$24,50 \cdot 10^{-3}$	0,937
C6	$1055,7 \cdot 10^{-3}$	1,18	0,887	980	$30,60 \cdot 10^{-3}$	0,915

where  $K_F$ ,  $1/n$  – the parameters of Freundlich isotherm,  $Q_{max}$  – the adsorption maximum (me Pb/100 g of soil,  $K_L$  – the bonding energy coefficient (l/me)

kde  $K_F$ ,  $1/n$  – sú parametre linearizovanej Freundlichovej izotermy,  $Q_{max}$  – je adsorpčné maximum olova (me Pb/100 g pôdy,  $K_L$  – afinitný člen Langmuirovej izotermy (l/me)

For soils of the same total Pb content, Pb was more soluble and more plant available in sand soil than in clay soil. The observation of low distribution coefficients in sandy soils is consistent with a low content of sorption sites as supposedly related to the low clay and organic matter contents in these materials. Only at very low pH (<5), may the mobility of Pb in soils become substantial.

## Conclusions

The aims of this study was comprehensive evaluation and comparison of the capacities of soil horizons withstand pollution lead and determination of the parameters of Freundlich and Langmuir isotherms mentioned above for ten relevant soil horizons which appears to be a useful indicator of capacity for sorption in single-metal pollution situations. Sorption by soil colloids largely determines the bioavailability of heavy metals and their movement in soil and aquatic environments.

In the present work the sorption Pb ions in the individual model sorbents is reported and compared soil properties effect of various types of soils. Experiments were conducted at high metal ion concentrations and low pH to simulate a worst-case scenario of contamination by heavy metals.

Tab.2 shows that from the ten investigated soils CL5 (clay-loam) and C6 (clay) have the best sorption properties (sorption capacity) for Pb in context of their physico-chemical properties. Investigated soil C6 has highest OM content (5,24%) and CEC (36,8 mg/100g). The Freundlich parameters reach of values  $K_F = 1055,7 \cdot 10^{-3} m^3 \cdot kg^{-1}$ ,  $1/n = 1,18$  and the Langmuir parameters are  $Q_{max} = 980 mg \cdot kg^{-1}$ ,  $K_L = 30,6 \cdot 10^{-3} l \cdot kg^{-1}$ . Soil CL5 with OM content (2,18%) and CEC

(22,5 mg/100g) has the Freundlich parameters  $K_F = 830,2 \cdot 10^{-3} m^3 \cdot kg^{-1}$ ,  $1/n = 1,54$  and the Langmuir parameters  $Q_{max} = 830 mg \cdot kg^{-1}$ ,  $K_L = 24,5 \cdot 10^{-3} l \cdot kg^{-1}$ .

The presence of organic matter increases the cation exchange capacity (CEC) of soils, and negative correlations between CEC and the solubility of trace metals are observed because the added organic matter immobilizes the metals. Typically Pb form very stable complexes with dissolved organic matter, only a very small fraction of these metal exists as free hydrated metal ions when pH is not strongly acid. For soils of the same total Pb content, Pb was more soluble and more plant available in sand soil than in clay soil. In the soils, the more soluble fractions of Pb increased as the pH was lowered.

The information provided in this work may be helpful for a better understanding of the role of the main factors (except pH) in Pb(II) sorption when associated in naturally occurring soil aggregates, and for soil remediation and water protect studies as well.

## Acknowledgments

*This research was supported by project VEGA 2/0058/15, project APVV-14-0735 and the project ITMS 26240120004 Centre of excellence for integrated flood protection of land supported by the Research & Development Operational Programme funded by the ERDF*

## References

- Almas, A.R., McBride, M.B., Singh, B.R. (2000): Solubility and lability od cadmium and zinc in two soils treated with organic matter. *Soil Sci.*, Vol. 165, No. 3, 250 – 259.

- Anderson, P.R., Christensen, T.H. (1988) : Distribution coefficients of Cd, Co, Ni and Zn in soils. *J. of Soil Science*, 1988, 39, 15-22.
- Basta, N.T., Tabatabai, M.A. (1992): Metal Adsorption by Soils. Effect of cropping systems on adsorption of metals by soils : I. Single-metal adsorption, *Soil Sci.*, Vol. 158, no.2, 108-114.
- Crus-Guzmán, M., Celis, R., Hermosín, M.C., Leone, P., Negre, M., Cornejo, J. (2003): Sorption-Desorption of Lead (II) and Mercury (II) by Model Associations of Soil Colloids. *Soil Sci. Soc. Am. J.*, 67, 1378-1387.
- Čelková, A. (2016): Individual and competitive adsorption of lead and cadmium on soil and its impact on their transport [Adsorpcia a jej vplyv na transport iónov olova a kadmia v pôde v nekonkurenčných a konkurenčných podmienkach]. *Acta Hydrologica Slovaca*, Vol. 17, 2, p. 182-189. ISSN 1335-6291.
- Dulovičová, R., Velísková, Y., Schügerl, R. (2016): Modification of Silts Hydraulic Conductivity along the Lowland Channel Gabčíkovo-Topoľníky (Slovakia). In 16th International Multidisciplinary Scientific GeoConference SGEM 2016: conference proceedings. Book 3, vol. 1. Hydrology and Water Resources. - Sofia p. 521-528. ISBN 978-619-7105-61-2.
- Eriksson, J.E. (1990): Factors Influencing Adsorption and Plant Uptake of Cadmium from Agricultural Soils. Swedish University of Agricultural Sciences, Department of Soil Sciences.
- Eriksson, J.E. (1988): The effects of clay, organic matter and time on adsorption and plant uptake of cadmium added to the soil. *Water, Air and Soil pollution*, 40, 359 – 373.
- Eriksson, J.E. (1989): The influence of pH, soil type and time on adsorption and plant uptake by plants of Cd added to the soil. *Water, Air and Soil pollution*, 48, 317 – 335.
- Christensen, T.H., Lehmann, N., Jackson, T., Holm, P.E. (1996): Cadmium and nickel distribution coefficients for sandy aquifer materials. *J. of Contaminant Hydrol.*, 24, 75 – 84.
- Krishnamurti, G.S.R., Huang, P.M., Kozak, L.M. (1999): Sorption and desorption kinetics of cadmium from soils: Influence of phosphate. *Soil Sci.*, Vol 164, No. 12, 888 – 898.
- Krishnamurti, G.S.R., Naidu, R. (2003): Solid-solution equilibria of cadmium in soils. *Geoderma*, 113, 17 – 30.
- Pitter, P. (1990): *Hydrochemie*. SNTL Praha, 1990, 565 s.
- Pokrovsky, O.S., Probst, A., Leviel, E., Liao, B. (2012): Interactions between cadmium and lead with acidic soil: Experimental evidence of similar adsorption patterns for a wide range of metal concentrations and the implications of metal migration. *J. of Hazardous Materials*, Vol. 199-200, 2012, 358-366.
- Richter, B.C., Kreitler, C.H.W. (1993): Geochemical techniques for identifying sources of ground-water salinization. EPA, USA, 225 p.
- Salomons, W., Stigliani, W.M. (1995): Biogeodynamics of pollutants in soils and sediments. Springer, Berlin, 1995, 352 p.
- McBride M., Sauve, S., Hendershot, W., (1997): Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *European Journal of Soil Science*, Vol. 48, Issue 2, 337-346.
- Vega, F.A., Covelo, E.F., Andrade, M.L. (2008): A versatile parameter for comparing the capacities of soils for sorption and retention of heavy metals dumped individually or together: Results for cadmium, copper and lead in twenty soil horizons. *J. of Colloid and Interface Sci.*, 327, 275-286.
- Tong, S., von Schirring, Y.E., Prapamontol, T. (2000): Environmental lead exposure: a public health problem of global dimensions. *Bulletin of World Health Organization*, vol. 78, 2000, p. 1068–1077.
- Tunegová, M., Toman, R., Tančin, V. (2016): Heavy metals-environmental contaminants and their occurrence in different types of milk. *Slovak J. Anim. Sci.*, 49, 2016 (3): 122–131
- Urminská, J., Václav, B., Ondříšek, P. (2015): Evaluation of exchange reaction in soil and sediments of a region affected by anthropogenic activity in relation to the time and to the selected potentially toxic elements. *Acta Horticulturae et Regiotechnicae*, 2, 2015, 30-34.
- Yong, R.N., Mohamed, A.M.O., Warkentin, B.P. (1992): Principles of contaminant transport in soils. Elsevier Science Publishers B.V., Amsterdam, 1992, 327p.

## VPLYV TYPY PŮDY, ORGANICKEJ HMOTY A CELKOVÉHO OBSAHU OLOVA NA ADSORPCIU OLOVA Z PŮDNEHO ROZTOKU

Kontaminácia pôd je integrálnou súčasťou životného prostredia, je súčasne aj zdrojom pre znečistenie ostatných zložiek životného prostredia a potravinového reťazca. Z hľadiska záťaže patria k najproblematickejším z anorganických kontaminantov ťažké kovy (olovo, kadmium, ortuť). V pôdach sa nachádzajú v rôznych koncentráciách, oxidačných stupňoch i väzbách. Ich riziká spočívajú v ekotoxicite i v kumulácii v abiotických a biotických zložkách prostredia. Je všeobecne známe, že biopristupnosť ťažkých kovov a ich prienik do povrchových a podzemných vôd ovplyvňuje celý rad

variabilných pôdných vlastností a ich sorpcia na pôdny sorpčný komplex.

V prírodných podmienkach vo vode prevládajú rozpustené formy olova:  $Pb^{2+}$  a  $PbCO_3(aq)$ , ktoré môžu byť v širokom rozsahu pH prevládajúcou formou. Rozpustnosť olova vo vodách je v závislosti na hodnote pH a koncentracii celkového  $CO_2$  limitovaná rozpustnosťou uhličitanu olovnatého  $PbCO_3(s)$  a hydroxidu olovnatého  $Pb(OH)_2(s)$ . Okrem jednoduchého iónu a anorganických iónových asociátov sa vyskytuje vo forme organických komplexov s rôznymi organickými ligandami (najviac

je viazané v komplexoch s humínovými látkami). Mobilita olova v pôdach je ovplyvňovaná radom faktorov, z ktorých najvýznamnejšie sú pôdna reakcia, typ pôdy, obsah a kvalita organickej hmoty, CEC, zrnitosťné zloženie pôd, ale tiež pôdna genéza, pôdna štruktúra, spôsob poľnohospodárskeho využívania. Správanie sa olova v pôde je ovplyvnené aj jeho fyzikálno-chemickými formami výskytu, ako výsledok interakcie s pôdnymi zložkami a pôdnym roztokom. Znalosti o chemických formách a ich väzbách na pôdne častice alebo koloidy sú dôležité kvôli stanoveniu ich chemickej reaktivity, pohyblivosti a biologickej prístupnosti. Hodnota celkového obsahu olova v pôde, zahŕňajúca údaje o jeho mobilnej a imobilnej frakcii nie je vhodným ukazovateľom bioprístupnosti. Niektoré práce venované mobilite olova v pôdnom prostredí berú do úvahy hlavne rozpustnosť olova za daných podmienok a prenos v rozpustenej forme. V reálnych podmienkach však rastie význam sorpcie olova na jemné častice pôd < 0,01 mm. Toxicita olova teda nezávisí len na jeho celkovej koncentrácii vo vode, ale predovšetkým na koncentrácii voľného jednoduchého iónu. Komplexné formy sú menej toxické v závislosti na hodnotách konštant stability. Čím je komplex stabilnejší, tým pôsobí menej toxicky. Riziko prieniku ťažkých kovov cez pôdny profil do podzemných vôd je možné stanoviť matematickou simuláciou prenosu vody a chemikálií. Na kvantifikáciu ich migrácie je potrebné poznať okrem hydrofyzikál-

nych charakteristík aj disperzno-difúzne a adsorpčné parametre.

V predkladanom príspevku sú uvedené výsledky sorpčných experimentov na vzorkách desiatich skúmaných pôd z lokality Žitného ostrova. Cieľom bolo stanovenie adsorbovaného množstva olova S, určenie adsorpčných parametrov pre daný typ pôdy a porovnanie výsledkov s výsledkami dostupnými v literatúre. Predchádzajúcimi experimentami bolo zistené, že priebeh sorpcie olova dobre popisuje Freundlichova a Langmuirova izoterma, ktorých parametre  $K_F$ ,  $n$  (Freundlichova) a  $Q_{max}$ ,  $K_L$  (Langmuirova) boli stanovené pre dané pôdy. Bol vyhodnotený vplyv pôdneho typu, organickej hmoty a celkového množstva rozpusteného Pb na adsorpciu.

Experimenty boli vykonané v širokom rozsahu počiatočných koncentrácií olova (0,01-500 mg/l  $Pb^{2+}$ ) a pri nízkom pH tak, aby sa simuloval najhorší možný scenár kontaminácie. Obsah organickej hmoty zvyšuje kationovú výmennú kapacitu pôdy (CEC). Existuje negatívna korelácia medzi CEC a rozpustnosťou, pretože olovo vytvára stabilné komplexy s organickou hmotou, iba veľmi malá frakcia existuje vo forme voľného hydratovaného iónu, ak pH nie je veľmi vysoké.

Pri pôdach s rovnakým celkovým obsahom Pb je olovo viac rozpustné, viac prístupné pre rastliny a existuje väčšie riziko prieniku do povrchových a podzemných vôd pre piesočnaté pôdy, ako pre piesočnato-hlinité a hlinité pôdy.

Ing. Viera Kováčová  
Institute of Hydrology SAS  
Dúbravská cesta 9  
841 04 Bratislava  
Slovak Republic  
Tel.: +4212 32 293 510  
E-mail: kovacova@uh.savba.sk