Adsorption of Lead on Agricultural Land at Žitný Ostrov (Slovakia)

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Abstract. 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 ecological effects of heavy metals in soils are closely related to the content and speciation of the elements in the solid and liquid phases of soils. In connection with the possible binding mechanisms of heavy metals in soils, the concept of specific and non-specific adsorption was discussed. Recent results have indicated that the adsorption of heavy metals on the soil particles is not only restricted to the formation of surface complexes but can also take place in the interior of minerals. Heavy metal sorption by the organic residues at all concentrations was very high. A positive relationship between the rate of adsorption and dosage was obtained indicating that the adsorption process was influenced by increasing the dosage of the residue as well as the shaking period. The sorption data obtained were fitted Freundlich and Langmuir isotherms out of which the Freundlich adsorption model was found to have the best fit for Pb. Movement and attenuation of heavy metals in soils are 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 the Žitný ostrov area (Slovakia) has been studied in laboratory conditions. The aims were the estimation of adsorbed amount of lead S, determination of adsorption parameters for several soil types (L1, L2, L3, L4 loam soils, SL1, SL2, SL3, SL4 sandy-loam soils, CL5 clay-loam soil, C6 clay soil) and comparison of the obtained results with the results introduced in publishing works. Batch adsorption experiments were performed with a very wide range of lead concentrations (0.01-500 mg/l Pb2+) at a constant soil/solution ratio. The parameters KF, n of Freundlich isotherm and parameters Qmax, KL of Langmuir isotherm were determined experimentally.

1. 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 the environment. The increase in agricultural production efficiency causes using large quantities of chemical products in soils and water. Therefore, 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 a 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 [1-4].

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: \( \text{Pb}^{2+} \) and \( \text{PbCO}_3^{\text{aq}} \), which may be in wide pH-range the dominant form of occurrence. Lead solubility is limited mainly solubility of \( \text{PbCO}_3^{\text{s}} \). Only in alkaline conditions is coming up for \( \text{Pb}_3(\text{CO}_3)_2(\text{OH})_2^{\text{s}} \) and \( \text{Pb}(\text{OH})_2^{\text{s}} \) in dependence on \( \text{CO}_2 \) concentrations. In the presence of organic contamination, a considerable part of lead may be bind in organic complexes [5, 6, 7].

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 carboxylic and OH surface groups, that is, potential sorption sites for heavy metals [8].

Movement and attenuation of heavy metals in soils are 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 [9].

Soil represents a major sink for pollutants emitted by both natural sources and human activities. Interactions of pollutants, especially trace elements in the 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 behaviour 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. [10, 11]. In most soil sorption processes regulate the solubility of heavy metals. [12-15] 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 to 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 the soil solution. The persistence of these metal-organic complexes is attributed to the tendency of metals to form stable complexes with dissolved organic matter. Typically, Pb forms 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 [16-19]. 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 [20-22].

2. Materials and methods

An equation describing the transport of water and chemicals in porous media, including sorption and microbial transformation terms is [23, 24, 7]: 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:

\[ \frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \frac{\rho \partial S}{\partial t} \] (1)

where

- \( c \) – the solute mass per unit volume of solution (ML\(^{-3}\))
- \( D \) – the dispersion-diffusion coefficient (L\(^2\)T\(^{-1}\))
- \( v \) – average pore-water velocity (LT\(^{-1}\))
- \( \theta \) – the volumetric water content (L\(^3\)L\(^{-3}\))
- \( \rho \) – is the dry mass density (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 are valid:

\[ S = K_D \ c_e \] (2)

\[ S_F = K_F \ (c_e)^{1/n} \] (3)

\[ S_L = \frac{K_L \ Q_{max} \ c_e}{1 + K_L \ c_e} \] (4)

where

- \( S, S_F, S_L \), represent the adsorbed amount of ion per mass unit of soil complex (M/M\(^{-1}\))
- \( c_e \) – is the equilibrium concentration of ion in the liquid phase (ML\(^{-3}\))
- \( K_D, K_L, K_F \) - are distribution coefficients (ion ratio between liquid and solid state of the system) (L\(^3\)M\(^{-1}\))
- \( Q_{max} \) – is adsorption maximum (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:

\[ \log S_F = \log K_F + 1/n \log c_e \] (5)
Characteristics of investigated soil types

Sorption studies of Pb(II) have been conducted on soils of different physico-chemical properties. Table 1 lists the measured properties (sand, silt and clay contents, pH values, organic matter content, cation exchange capacity) of the soil horizons studied.

Table 1. Physico-chemical properties of investigated soil types

| Soil | Sand | Silt | Clay | Texture       | \(\rho_s\) (g.cm\(^{-3}\)) | \(\rho_d\) (g.cm\(^{-3}\)) | \(p_{H\text{KCl}}\) | \(\text{CaCO}_3\) (%) | OM (%) | CEC (mg/100g) |
|------|------|------|------|---------------|-----------------|-----------------|---------------|----------------|---------|-------------|
| 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, \(p_{H\text{KCl}}\) – potential soil reaction, \(\text{CaCO}_3\) – content of carbonates, OM – organic matter, CEC – cation exchange capacity, grain composition

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.

Ten soil horizons were obtained at locations in Žitný ostrov (Slovakia) – figure 1. 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).
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.

Each sorption experiment involved 10 g of soil sample and 50 ml of salt matrix (10^{-3} M CaCl_2) equilibrating in a 500-ml polyethylene bottle for 24 h before the metal was added from a standardized solution Pb(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 µm) and the solute was preserved with acid (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 analysed by Pb-ion selective electrode Crytur. The pH was preserve at the about equal value. At the higher pH-range precipitation of Pb as 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.

3. Results and discussions
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 figure 2, 3, 4.

Parameters of Freundlich and Langmuir isotherms were measured for lead (Pb) in laboratory batch experiments for 10 soils at environmentally relevant solute concentrations in approximately equal conditions (pH).

The sorption data of the ten soils studied could be fit satisfactorily using the Freundlich and Langmuir isotherm. The Freundlich and Langmuir equation have 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_{max} was shown to correlate significantly (P<0.001) with organic matter and sorption capacity of the soils. The K_F-values ranged from 298.10^{-3} to 1055.10^{-3} m^3.kg^{-1} and K_L-values ranged from 5 to 30.10^{-3} L.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 persistence of these metal-organic complexes is attributed to the tendency of metals to form stable complexes with dissolved organic matter. Typically, Pb forms 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. 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.

Figure 2. Pb(II) adsorption isotherms, described by the dependence of the 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
y = 0.5212x - 0.1225  
$R^2 = 0.875$

y = 0.5083x - 0.0748  
$R^2 = 0.8778$

y = 0.688x - 0.4534  
$R^2 = 0.7782$

y = 0.7076x - 0.5256  
$R^2 = 0.791$

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

y = 0.0539x + 8.372  
$R^2 = 0.99$

y = 0.0513x + 6.8498  
$R^2 = 0.9857$

y = 0.0454x + 6.0369  
$R^2 = 0.9973$

y = 0.037x + 5.89  
$R^2 = 0.9869$

Figure 4. Linearised Langmuir adsorption isotherms of lead for loamy soils L1, L2 and sandy-loamy soils SL1, SL2 - experimental data
The experimentally determined Freundlich and Langmuir isotherm’s parameters are listed in table 2.

Table 2. Freundlich and Langmuir parameters for Pb (II) sorption by different soil types

| Soil | Pb | Freundlich parameters | Pb | Langmuir parameters |
|------|----|------------------------|----|---------------------|
|      |    | K_F [m^3.kg^{-1}] | 1/n | R^2 | Q_max [mg.kg^{-1}] | K_L [l.kg^{-1}] | R^2 |
| L1   | 841,7.10^{-3} | 1,97 | 0,8778 | 740 | 8,372.10^{-3} | 0,99 |
| L2   | 754,2.10^{-3} | 1,92 | 0,875 | 690 | 6,849.10^{-3} | 0,985 |
| SL1  | 352,0.10^{-3} | 1,45 | 0,7782 | 550 | 6,036.10^{-3} | 0,997 |
| SL2  | 298,1.10^{-3} | 1,41 | 0,791 | 490 | 5,89.10^{-3} | 0,986 |
| L3   | 810,3.10^{-3} | 1,15 | 0,917 | 810,5 | 12,64.10^{-3} | 0,967 |
| L4   | 790,1.10^{-3} | 1,71 | 0,893 | 801,3 | 10,80.10^{-3} | 0,935 |
| SL3  | 365,7.10^{-3} | 1,08 | 0,799 | 590,5 | 7,35.10^{-3} | 0,895 |
| SL4  | 320,9.10^{-3} | 1,26 | 0,792 | 567,8 | 7,10.10^{-3} | 0,901 |
| CL5  | 830,2.10^{-3} | 1,54 | 0,859 | 830 | 24,50.10^{-3} | 0,937 |
| C6   | 1055,7.10^{-3} | 1,18 | 0,887 | 980 | 30,60.10^{-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)

4. Conclusions

The aims of this study were the 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 appear 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 are 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.

Table 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 the highest OM content (5,24 %) and CEC (36,8 mg/100g). The Freundlich parameters reach of values K_F = 1055,7.10^{-3} m^3.kg^{-1}, 1/n = 1,18 and the Langmuir parameters are Q_max = 980 mg.kg^{-1}, K_L = 30,6.10^{-3} l.kg^{-1}. Soil CL5 with OM content (2,18 %) and CEC (22,5 mg/100g) has the Freundlich parameters K_F = 830,2.10^{-3} m^3.kg^{-1}, 1/n = 1,54 and the Langmuir parameters Q_max = 830 mg.kg^{-1}, K_L = 24,5.10^{-3} l.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 forms very stable complexes with dissolved organic matter, only a very small fraction of these metals exist 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.
Acknowledgment(s)
This research was supported by project VEGA 2/0025/19 and project VEGA 1/0805/16.

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