Theoretical Evaluation of Heavy Metals Migration and Sorption in Soil

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Abstract. Heavy metals are one of the group of toxic pollutants in the soil. Over the past years, many researches have been conducted on the migration of heavy metals in soils and various models were developed in order to study the mobility of toxic heavy metals. The convection-dispersion equation is the most commonly used equation for describing the migration of toxic pollutants in the soil. Various properties of the soil influence the mobility of heavy metals: soil pH, texture, sorption characteristics. Heavy metals not only migrate in the soil, but also interact with mineral and organic soil particles. The mobility of heavy metals in soils is determined by their partitioning between solid and aqueous phases of the soil. The partitioning of heavy metals between these two phases are described by sorption/desorption, precipitation/dissolution, and redox processes. Natural mineral and organic sorbents present in soils have a strong influence on heavy metals sorption. As these sorbents are usually negatively charged, they attract heavy metals cations through electrostatic force.

Keywords: convection, diffusion, sorption, precipitation, two-site sorption model.

Conference topic: Environmental protection.

Introduction

Soil is a complex heterogeneous medium consisting of solid phases containing minerals (clay, sand, sediments) and organic matter and fluid phases (soil solution and air), which can interact with ions entering the soil (Bradl 2004). Due to human activities the soil is constantly contaminated by various chemical substances. The widespread soil contamination with heavy metals is an important environmental problem (Komárek *et al.* 2013). Heavy metals are toxic inorganic chemical elements (Zvilnaitė, Tričys 2009). The soils are contaminated with heavy metals from various anthropogenic emission sources: the rapidly expanding industrial areas, power plants, transport, disposal of waste which contain heavy metals, fertilizers, sewage sludge, atmospheric deposition (Jankaité 2009). In the contaminated sites the most commonly found heavy metals are lead (Pb), chrome (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg) and nickel (Ni) (Wuana, Okieimen 2011).

Heavy metals do not degrade, but only move from one area to another, posing the risk to environmental components and human health (Jankaitė, Vasarevičius 2005; Vilniaus aplinka 2016). The mechanisms of heavy metals migration in soil is very important due to the possibility to contaminant the groundwater by leaching from soil (Dube *et al.* 2001). The constituents of soils, solution pH are one of the most important parameters influencing the behaviour of heavy metals, including mobility and sorption (Yahya, Abdulfatai 2007). Concept of mobility is often used in soil science in order to evaluate the risk of contamination of places far from sources of pollution (Domergue, Vedy 1992). The dissolved organic matter in soil solution can increase the mobility of heavy metals in soils (Weng *et al.* 2002). In low pH soils, retention and migration of metals are mainly controlled by adsorption/desorption reactions. Heavy metals such as Cd, Cr, and Zn are mobile under low pH conditions (Michel *et al.* 2007). The neutral and slightly alkaline pH of soil solution reduces the mobility of many heavy metals (Cd, Cr, Pb, Ni) (Sherene 2010).

The most well-known model of contaminant transportation in the soil is based on convection-dispersion-sorption equalization (Zbytniewski *et al.* 2003). The convection and dispersion of heavy metals occur in soil solution, whereas sorption can be defined as pollutant removal from soil solution by binding it on the surface of the soil particles. Mathematical models describing the migration of heavy metals must include the description of the retention processes in the soil matrix (Selim, Zhang 2013). Adsorption is the process of accumulation of an adsorbate at the interface between a solid surface and a solution. In this case two-dimensional structure is formed (Smith 1999). Specific and non-specific adsorption, and precipitation of insoluble heavy metals forms are the main processes responsible for heavy metal retention (Michel *et al.* 2007). The most important components of soil involved in heavy metal adsorption are inorganic colloids such as clays, metal oxides and hydroxides, metal carbonates and phosphates (Bradl 2004).

The objectives of the review: 1) to describe transport and retention of heavy metals in soils using mathematical equations and sorption models, 2) to characterize processes in soil resulting the distribution of heavy metals between mobile and immobile forms, 3) to characterize naturally occurring soil sorbents contributing to heavy metals retention in soil matrix.

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Migration of heavy metals

In the soil migration of heavy metals takes place due to mass transfer, which involves water carrier, diffusion. Migration of metals in soils depends on various properties of soil: texture, clay fraction, organic matter content, the amount of iron, aluminium, manganese oxides, soil pH (Januševičiūtė *et al.* 2015).

In continuous water flow conditions, the transport of dissolved heavy metals in soils can be described in one of the most used equations based on terms of dispersion, convection, and sorption (Dube *et al.* 2001; Selim, Zhang 2013; Yahya, Abdulfatai 2007):

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \frac{\rho}{\Theta} \frac{\partial s}{\partial t}, \qquad (1)$$

where: c – concentration of dissolved pollutant in soil pollution; t – time, h; D – the diffusion coefficient, cm² h⁻¹; x – the distance, cm; v – the advective velocity of dissolved pollutant, cm h⁻¹; ρ – Darcy's water flux density, cm h⁻¹; Θ – the soil volumetric water content, cm³ cm⁻³; s – the amount of sorbed dissolved pollutant, mg kg⁻¹.

Equation (1) contains advection, diffusion and sorption terms. $-v \frac{\partial C}{\partial x}$ and $D \frac{\partial^2 C}{\partial x^2}$ are advection and diffusion

terms, respectively, $\frac{\partial s}{\partial t}$ term describes reversible solute (dissolved heavy metal) removal from the soil solution

(Selim, Zhang 2013; Yahya, Abdulfatai 2007).

Advection term. In case of a conservative solute, the dissolved heavy metal transport equation can be written using only the advection:

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x}, \qquad (2)$$

Diffusion term. Diffusion describes the spread of particles through random motion usually from regions of higher concentration to regions of lower concentration. For diffusion in porous media (soil), the change of contaminant concentration over time in volume can be calculated by Fick's second law (Baltrenas *et al.* 2015):

$$\frac{\partial C}{\partial t} = \mathbf{D} \frac{\partial^2 C}{\partial x^2},\tag{3}$$

Sorption term. Describing heavy metals transport in soils requires sorption models. Empirical adsorption models are based on mathematical relationships between concentration of the heavy metal in the soil solution and the solid phase at equilibrium. These relationships are called sorption isotherms (Bradl 2004).

Equilibrium type models for heavy metals retention in soils. Linear, Freundlich and Langmuir sorption models are the most commonly used types of equilibrium models for description of dissolved chemical substances retention in soil. Linear and Freundlich models use solute distribution coefficient (K_d), that distinguishes solute which is present in the soil solution and adsorbed amount of solute by soil matrix. In contrast, the linear and Freundlich models do not include the adsorption maxima term (s_{max}). This is a disadvantage, because the capacity of the soil to remove pollutant from soil solution (adsorb solute), i.e. adsorption sites have finite number and should be important limiting factor (Selim, Zhang 2013).

The simplest model is a linear sorption model:

$$s = K_d C , (4)$$

where: s – the amount of the considered element adsorbed per unit mass of the soil, mg kg⁻¹; K_d – the distribution coefficient, L kg⁻¹; C – concentration of the element in the equilibrium solution, mg L⁻¹.

The distribution coefficient describes distribution of the metal between solid and liquid phases over the concentration range of interest and it is analogous to a chemical reaction equilibrium constant (Selim, Zhang 2013).

Kd values depends on:

- the adsorbing part of the soil (mineral particles or organic material);
- physical properties of adsorbent;
- chemical characteristics of adsorbent;
- temperature;
- ionic strength.

The Freundlich equation (non-linear):

$$s = K_d C^n, (5)$$

where: K_d – Freundlich sorption coefficient, L/kg; n – constant, usually ≤ 1 .

K and *n* parameters are adjustable.

Langmuir model is probably the most used equilibrium model describing solutes such as heavy metals fate in the soils (Selim, Zhang 2013). General expression of Langmuir isotherm:

$$s = \frac{s_{max}K_L c_{eq}}{1 + K_L c_{eq}},$$
(6)

where: C_{eq} – equilibrium concentration in solution (mol/L); K_L – binding constant (L mol⁻¹); s_{max} – adsorption maxima (mol/g).

Kinetic type models for heavy metals retention in soils. Other types of heavy metals retention models are kinetic models. The amount of heavy metals sorbed and released from the soil solution can be time-dependent (Selim, Zhang 2013). A linear first-order kinetic type sorption reaction is expressed by the following formula:

$$\frac{\partial s}{\partial t} = k_1 \left(\frac{\Theta}{\rho}\right) C - k_2 s , \qquad (7)$$

where: k_1 and k_2 – are the sorption (forward) and desorption (backward) reaction rates, h^{-1} , t – reaction time, h. *n*th order kinetic type reaction is expressed by the following formula:

$$\frac{\partial s}{\partial t} = k_1 \left(\frac{\Theta}{\rho}\right) C^n - k_2 s , \qquad (8)$$

where: n – the reaction order.

The two-site heavy metals transport model. A main feature of the two-site model is the assumption that two types of retention sites exist on soil matrix surfaces: the equilibrium sites (S) and the time dependent sites (S_k) (Li *et al.* 2006; Liu *et al.* 1991). Figure 1 shows the schematic diagram of the two-site retention (multireaction) model for sorption of heavy metals in soils.



Fig. 1. Schematic diagram of the two-site sorption model. C is the concentration in the solution, S_1 is the amount of solute sorbed on equilibrium sites, S_2 is the amount of solute sorbed on kinetic sites, k_1 and k_2 are the rates of reactions (Zhang and Selim 2005)

The multireaction model assumes that a part of the total sorption sites can interact rapidly with solutes (equilibrium sites) in the soil solution and the remaining part of sites is kinetic in nature (Zhang, Selim 2005).

Under above mentioned conditions, the heavy metal convection-dispersion equation for a combined model of equilibrium and kinetic retentions can be expressed by the following formula (Li *et al.* 2006):

$$R\frac{\partial C}{\partial t} + \frac{\rho}{\Theta} \left(\frac{\partial S_1}{\partial t} + \frac{\partial S_2}{\partial t} \right) = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x},$$
(9)

$$R = 1 + \frac{\rho}{\Theta} K_d \,, \tag{10}$$

$$\frac{\partial S_1}{\partial t} = f K_d \, \frac{\partial C}{\partial t},\tag{11}$$

$$\frac{\partial S_2}{\partial t} = \alpha \Big[(1 - f) K_d C - S_2 \Big], \tag{12}$$

where: R – the dimensionless retardation coefficient, f – the fraction of the equilibrium sites; α – the rate coefficient, h⁻¹; S_I – sorbed amount of the heavy metal on equilibrium sites, mg kg⁻¹; S_2 – sorbed amount of the heavy metal on the time dependent sites, mg kg⁻¹.

Processes resulting the mobility of heavy metals in soil

Two basic forms of heavy metals exist in soil:

1) Mobile form of heavy metals (it consists of metal compounds dissolved in the soil solution);

2) Potentially mobile form of heavy metals (it consists of heavy metals associated with other elements in the soil solid phase).

When heavy metals are present in the solid phase of the soil they are immobile, while heavy metals present in aqueous phase are mobile. In the solid phase, heavy metals are immobilised through adsorption on inorganic and organic components of the soil, surface complexation or may be precipitated as solids (Ogundiran, Osibanjo 2009) Heavy metals ions in the solid phase may become mobile if there is change in oxidation–reduction potential, due to the metals exchange processes, the changing soil composition, pH. The mobile form of heavy metals is important as they can migrate in the soil and access the sensitive receptors (plants, groundwater) (Januševičiūtė *et al.* 2015).

Metal ions can be retained in the soils by sorption, precipitation and complexation or removed by leaching into the groundwater, entering plants or volatilization (e.g., Hg or Se can form gaseous compounds) (Bolan *et al.* 2014).

Heavy metal sorption processes. The adsorption of heavy metals on the surface of the soil components can be classified into specific (more selective and less reversible) and non-specific (or ion exchange) adsorption. Non-specific adsorption is a process, in which metal cations balance the charge on soil particles through electrostatic force, whereas specific adsorption occurs when chemical bond is formed between cations present in soil solution and ions present in the surface of the soil particles (Bolan *et al.* 2014; Bradl 2004). Both soil properties and the composition of soil solution influence dynamic equilibrium between heavy metals in soil solution and the solid phase (Bolan *et al.* 2014). In general, heavy metals sorption increases and mobility reduces with increasing pH (Li *et al.* 2006; Sherene 2010). This is associated with an increased cation exchange capacity of the soil (Bolan *et al.* 2014).

Precipitation. The term "precipitation" is used when there is a three-dimensional accumulation of adsorbed heavy metals at the solid surface phase (Smith 1999). Precipitation is the predominant process in high pH soils and in the present of anions such as $SO_4^{2^-}$, $CO_3^{2^-}$, OH^- and others. Surface precipitation is dependent on the pH and the quantity of previously mentioned anions. Heavy metals can precipitate as carbonates, oxides, hydroxides, phosphates onto soils. The precipitation of metals phosphates/carbonates is considered one of the mechanisms for heavy metals such as Cu and Pb immobilization in soils (Bolan *et al.* 2014; Bradl 2004).

Oxidation/reduction. Many metals can change their oxidation state in the oxidation/reduction reactions depending on the redox conditions. The examples of the most active redox couples can be As (III) – As (V), Cr (III) - Cr (VI), Se (IV) – Se (VI), U (IV) –U (VI). Heavy metals having different oxidation states may show very different properties of solubility/mobility and toxicity (O'Carroll *et al.* 2013). For example, As (III), Cr (VI), Se (VI), U(VI) are considered more mobile than corresponding ions (Liu *et al.* 2015). Metals including As, Cr and Se often participate in microbial oxidation/reduction reactions and these reactions influence their form and mobility. For example, heavy metals such as Cu and Hg are less soluble in their higher oxidation state, and As solubility and mobility depend on both oxidation state, and ionic form. Arsenic in soils can be oxidized by bacteria to As (V). Since As (V) can be strongly bound to the inorganic soil components, microbial oxidation leads to the immobilization of arsenic in soil. Under the reduction conditions As (III) would be predominant in soils, and a small amount of arsenic [As (0)] also would be present. Cr (VI) can be reduced to Cr (III) in such soil environment, where the source of electrons is present (Fe(II)) (Bolan *et al.* 2014). Cr⁶⁺ is very soluble and mobile in soils, whereas Cr³⁺ oxides and hydroxides are relatively insoluble compounds. Cr (III) can easily precipitate as Cr(OH)₃ under alkaline or even slightly acidic conditions (O'Carroll *et al.* 2013; Singh *et al.* 2011).

Natural sorbents existing in soils

There are a number of parameters, which control sorption of heavy metals ions and thereby migration and mobility of soil. The parameters can be divided into two groups (Zbytniewski *et al.* 2003):

- 1. Related with parameters of soil: soil texture (the amount of clay and sand fractions in soil), organic fraction, cation exchange capacity of soil sorbents, pH;
- 2. Related with parameters of heavy metals ions: charge, oxidation state, capability to form complexes.

Most heavy metals exist mainly as cations in the soil solution (Alloway 1995) and their adsorption depends on cation exchange capacities of natural occurring soil sorbents. The cation exchange capacities of typical soil minerals are shown in Table 1.

Table 1. Cation exchange capacities of typical soil mineral sorbents (Zbytniewski et al. 2003)

Soil adsorbent	Cation exchange capacity, cmol (+)/kg			
Clay	20.9–110			
Fine silt	6.8–41.4			
Medium silt	6.3–34.5			
Coarse silt	1.2–12.8			
Sand	1.0–15.6			

Cation exchange capacity decreases with increasing particle size. The amount of sorbed heavy metals usually decrease from clay (clay particles are the smallest) to sand. The biggest cation exchange capacity has clay particles – 20.9-110 cmol (+)/kg, the smallest cation exchange capacity has sand particles – 1.0-15.6. The contribution of the soil organic matter to the carbon exchange capacity is higher in sand and silt than in clay fraction.

Hence, the migration of heavy metals in soils containing a large amount of clay and organic matter particles can be significantly reduced (Zbytniewski *et al.* 2003). The clay fraction in soils retains higher amount of heavy metals when compared to sandy soil (Sherene 2010).

The other important parameter related to heavy metals sorption is their affinity to natural soil sorbent (Zbytniewski *et al.* 2003). Table 2 shows sorption selectivity sequences for divalent metal cations on some of inorganic minerals and organic matter.

Soil adsorbent	Selectivity sequences for divalent metal cations			
Humic acids	$Cu^{2+} > Ni^{2+} > Co^{2+} > Pb^{2+} = Zn^{2+}$			
Fulvic acids	$Cu^{2+} > Pb^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$			
Hydrous oxides of Fe	$Pb^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$			
Illite	$Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+}$			
Kaolinite	$Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+}$			
Montmorillonite	$Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+}$			

Table 2. Sorption selectivity sequences for divalent metal cations (Zbytniewski et al. 2003)

The competitive sorption phenomena of various heavy metals depends on mineralogical composition of the soil. A very important feature of soil colloids is that their surface is negatively charged (Zbytniewski *et al.* 2003). Heavy metals cations are retained in the soils by these negatively charged clay and organic particles through electrostatic forces (negatively charged soil particles attract positively charged metal cations) (Cornell University Cooperative Extension 2007).

Table 3. Characteristics of typical soil sorbents (Zbytniewski et al. 2003)

Characteristics	Montmorillonite (2:1)	Illite (2:1)	Kaolinite (1:1)	Fe and Al hy- drated oxides	Humic acids	Fulvic acids
Cation ex- change capacity cmol (+) / kg	80–120	20–50	1–10	4	485–870	900–1400
Surface area (x10 ³ m ² /kg)	600–800	70–120	10–20	_	800–900	800–900

2:1 type clay particles have much greater total surface area than 1:1 type, because of the presence of the internal surface area. 2:1 type clay minerals also have much greater cation exchange capacity and thus greater ability to immobilize than 1:1 type clay particles (Zbytniewski *et al.* 2003).

Iron and aluminium oxides and hydroxides are most commonly found in soils in such mineralogical forms as hematite (Fe₂O₃), goethite (FeO(OH)), gibbsite (Al(OH)₃). These minerals have pH dependent charge and can exist as neutral, positively or negatively charged particles (Zbytniewski *et al.* 2003). For example, surface adsorption of Feoxides in soil operates through Fe–OH group. This group attains negative or positive charge by dissociation (FeOH \rightarrow FeO⁻ + H⁺) or association (FeOH + H⁺ \rightarrow Fe OH⁺₂) of protons (Schwertmann 2008).

The presence of humic materials in the soils has strong influence on chemical materials sorption. Cation exchange capacity of humic and fulvic acids is very high compared to other soil components (Table 3). Humic and fulvic acids can exist in dissociated form and be negatively charged. The main cause of these charges is the separation of hydrogen in carboxylic and phenolic groups. The hydrogen separation is strongly dependent on pH, hence the heavy metal sorption in soil, containing relatively large amounts of organic matter, mainly depends on the pH.

Other chemical interactions between heavy metals and soil colloidal particles, which have influence on metal retention include complexation between metals and inorganic or organic ligand ions (Bolan *et al.* 2014).

Complexation reactions have the following effects:

1) inhibit precipitation of heavy metals;

2) complexes can act as carriers in the soil solution (Violante et al. 2010).

However, due to the complexation of heavy metals by soluble organic matter, the addition of organic matter can result in release of heavy metals from solid phase to the soil solution. Sherene (2010) reported that the increase in the

solubility of the heavy metals Cu and Pb is related to the dissolution of the humic acids in soil solution at increased pH.

The organic components of soil have a strong affinity to heavy metals cations such as Cu, Cd and Pb, due to the presence of ligands or groups, which can form chelates with metals. When pH of the soil is increasing, carboxyl, phenol, alcohol and the carbonyl functional groups present in organic material dissociate, and the affinity of ligands ions to heavy metals ions increases (Bolan *et al.* 2014).

Conclusions

- 1. The study deals with transport and sorption processes of heavy metals in soils. Heavy metals are not subjected to degradation in soil, but only migrates from one area to another or accumulate. One of the negative effects of mobility is the contamination of groundwater. The transport of heavy metals in the soil and soil solution occurs under convection, diffusion and is described by widely used convection-dispersion equation.
- 2. The main retention processes of heavy metal cations at soil surfaces are adsorption and surface precipitation. Sorption models are useful for understanding and predicting the mobility of heavy metals in soils. Retention of heavy metals models can be divided into equilibrium and time-dependent (kinetic) sorption models. The two-site sorption model is the combination of these two different types of sorption models.
- 3. The transport of heavy metals is aggravated by physical and chemical processes. The important physical factor, which controls the transport of heavy metals are the presence of organic and mineral sorbents in the soil. Clay particles, soil organic matter, metal oxides and hydroxides have large surface area and are often electrically negatively charged which leads to the attraction and adsorption of heavy metals cations.
- 4. Sorption-desorption processes in soils and respectively immobility and mobility of heavy metals are controlled by such parameters as pH, sorption selectivity sequences and cation exchange capacities of typical soil sorbents, oxidation-reduction reactions, presence of organic ligands and anions.

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