*Polish Journal of Environmental Studies Vol. 10, No. 1 (2001) 1-10*

*Reviews*

# Adsorption and Migration of Heavy Metals in Soil

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*Received: July 24, 2000*
*Accepted: August 12, 2000*

## Abstract

Soil is a major reservoir for contaminants as it posseses an ability to bind various chemicals. These chemicals can exist in various forms in soil and different forces keep them bound to soil particles. It is essential to study these interactions because the toxicity of chemicals may strongly depend on the form in which they exist in the environment. Another thing is that soil variability and some environmental properties (e.g. climate factors) may change equilibrium found in soil and cause leaching of trace toxic elements like heavy metals tightly bound to soil particles.

Mathematical and computer modeling help us with understanding processes occurring in soils. A number of models are being developed now which can quantitatively predict movements and sorption of heavy metals in soil with good accuracy. However, investigations for determining chemical properties of soil, heavy metal interactions, should continue because a lot of questions about this strongly heterogenic matrix is still not answered.

**Keywords:** soil properties, heavy metals, sorption, speciation, modeling

## Introduction

Diverse amounts of heavy metals may by found everywhere; in soils, water, sediments, plants [1-5], even the Arctic [6]. The emission sources of these xenobiotics have been studied for several years in order to reduce pollution.

Chemicals like heavy metals once introduced to the environment by one particular method may spread to various environmental components, which may be caused by the nature of interactions occurring in this natural system. Heavy metals may chemically or physically interact with the natural compounds, which changes their forms of existence in the environment. In general they may react with particular species, change oxidation states and precipitate [7]. Heavy metals may be bound or sorbed by particular natural substances, which may increase or decrease mobility. Studying the dissipation of heavy metals is called speciation [8]. Literature study shows that the speciation may be understood in different ways and in various aspects, but in all cases when we generally talk about different forms of existence of studied compounds we talk about speciation [8-10]. In general two forms of speciation are distinguished by environmental scientists: chemical and physical [8, 10]. However chemical speciation may be distinguished further, it is said about group speciation, distribution speciation, individual speciation and many more [8, 10].

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Physical speciation is very important for the study of sorption and migration of chemicals in soils because it deals with various physicochemical forms of the same chemical: in solution, adsorbed, precipitated.

The transport mechanisms of heavy metals through soil has long presented great interest to both environmental and soil scientists because of the possibility of groundwater contamination through metal leaching [11]. In general many soils contain a wide range of heavy metals with varying concentration ranges depending on the surrounding geological environment and anthropogenic and natural activities occurring or once occurred. These metals can be Fe, Cr, Mn, Ni, Zn, Cu, Pb, Cd, Hg, ect. Metal transport is not only dependent on the physiochemical properties of the metals but mostly on the physical and chemical properties of the soil, like for example: soil organic matter content, clay fraction content, mineralogical composition, pH, and more, all of which collectively determine the binding ability of soil. The properties of the soil may change due to climate change but mostly due to anthropogenic impact. The influence of acid rains on soils and sorption properties of soil complex has been extensively studied by scientists from various disciplines [12-15]. In almost all cases they found that acid rains decrease the ability of binding heavy metals to soil particles. However, for naturally high acidic soils or very weak soils like rusty soils the effect of acid rains on soils is shown to be much smaller [15]. The complexity of the soil matrix makes it difficulty to selectively choose interactions, which mostly contribute to the adsorption of a specific metal. This problem contributes more difficulty in the process of formulating meaningful soil models for the prediction of metal transport. It is imperative to fully understand the metal binding properties of the soil, develop and validate procedures for metal speciation in soils and carefully choose appropriate models, to understand the adsorption and migration of heavy metals in the soil matrices. Therefore, the objectives of this review are:

(i) to describe soil properties that mostly influence the sorption of heavy metals in soils,
(ii) to present new concepts of environmental analytical studies called speciation,
(iii) to show some aspects of mathematical representation of the environment and processes governing the distribution of chemicals in soils.

The most utilised new models of sorption phenomena will be discussed here.

## Properties Influencing Sorption of Heavy Metals in Soil

Soil has the ability to immobilise introduced chemicals like heavy metal ions. The immobilisation of xenobiotics is mainly due to sorption properties which are determined by physicochemical properties of the soil such as: amount of clay and organic fraction, pH, water content, temperature of the soil and properties of the particular metal ion [16, 24].

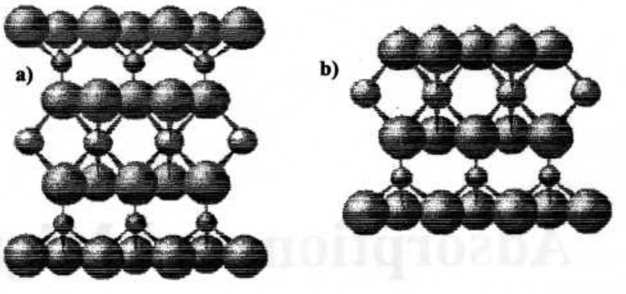

Fig. 1. The arrangement of silica tetrahedral layers and aluminium octahedral layers in montmorillonite (a) and kaolinite (b) according to [27].

The solid state of soils composes an average of 45% of soil bulk. It consists of mineral particles, organic matter and organic-mineral particles. They all play a very important role in giving the soil the ability to adsorb, exchange, oxidise, reduce, catalyse and precipitate chemicals and metal ions in particular [16].

The inorganic colloidal fraction of soil is the most responsible for sorption by its mineral particles. It is comprised of clay minerals, oxides, sesquioxides and hydrous oxides of minerals. The clay minerals are hydrous aluminium, magnesium or iron silicates [25]. They originated from other forms of silicates. There are two major types of clay minerals found in soils: 1:1 and 2:1 (Figure 1). The 2:1 type is typical for clays montmorillonite and illite. The unit cell here is built from two silica tetrahedral layers, ($Si_2O_5$), surrounding an aluminium octahedral layer, $Al_2O_4(OH)_2$. Only weak van der Waals forces exist between two units so that water, nutrients, chemicals can readily enter the interlayer regions and react with the inner surface, often being immobilised. This also causes the ability to expand montmorillonite or illite when in contact with water. The water content in montmorillonite can vary so that its chemical formula can be written $Al_2(OH)_2(Si_2O_5)_2 \bullet nH_2O$ [25]. The 1:1 type is typical for clay kaolinite. A unit cell of kaolinite is composed of one silica tetrahedral layer bonded to an aluminium octahedral sheet. The unit cells in 1:1 type are hydrogen bonded together providing no interlayer regions. Thus water and chemicals cannot enter between cells so the distance between them remains constant opposite to montmorillonite. The chemical formula of kaolinite is $Al_2(OH)_4(Si_2O_5)$.

The major difference between expandable, type 2:1, and nonexpanding clays is in the surface area. The 2:1 type of clays have much higher total surface area than the 1:1 type has because of the existence of the internal surface area [16, 24, 25]. The expandable clay minerals have also a much greater cation exchange capacity (C.E.C.) than the nonexpanding types and thus have a much greater propensity for immobilizing chemicals such as metal ions. The basic characteristics of some soil sorbents are listed in Table 1.

Clay particles are usually negatively charged. This is a very important factor influencing sorption properties of the soil. There are at least two major possibilities as to how these charges are formed [27]. Firstly the hydroxyl groups which exist on the edges and on the outer layers

Table 1. Characteristics of typical soil sorbents according to [24, 25].

| Characteristics | Montmorillonite | Illite | Kaolinite | Hydrous oxides of Fe and Al | Humic acids | Fulvic acids |
|---|---|---|---|---|---|---|
| Type of layering | 2:1 | 2:1 | 1:1 | | | |
| Layer charge | 0.25-0.6 | 0.6-0.9 | 1.0 | | | |
| C.E.C. cmol(+)/kg | 80-120 | 20-50 | 1-10 | 4 | 485 -870 | 900-400 |
| Surface area (x$10^3$ $m^2$ $kg^{-1}$) | 600-800 | 70-120 | 10-20 | | | |
| pH dependent charge | minor | medium | extensive | extensive | extensive | extensive |

of minerals can dispose of hydrogen which is bonded with oxygen probably covalently, not very tight. This is a pH-dependent process and the ability to split the hydrogen atom decreases when pH decreases. When pH is above 6 hydrogen may easily by replaced by other ions like $Ca^{2+}$, $Al^{3+}$, $Pb^{2+}$, $Cd^{2+}$. The second process of creating negative charges is connected to the isomorphous ion replacement in the minerals. In the silica tetrahedral $Al^{3+}$ can replace the silicon ion $Si^{4+}$ because these two have a similar ionic radius, whereas $Mg^{2+}$ $Fe^{2+}$ can exist in the octahedral layers instead of $Al^{3+}$. The negative charge, which appears as a result of isomorphous ion replacement, is pH-independent and therefore quite persistent. The ability to create negative charges is the highest for 2:1 type of clays [25, 26].

The total amount of clay minerals in soil bulk is very important, as they are the major inorganic component of soil sorption complex.

The oxides and hydrous oxides of iron and aluminum are commonly found in soils in several mineralogical forms including hematite, goethite and gibbsite, and bohemite [16]. Manganese oxides are also found in moderately high amounts in some soils. These minerals have a pH-dependent charge and thus may exist as positive, neutral or negatively charged particles, as depicted:

$$-MO'' + H^+ = -A1OH + H^+ = A1(OH_2)^+ \quad (1)$$

Soil organic matter (SOM) is the second main component of the soil solid fraction [24]. The term SOM is generally used to represent the organic constituents in soils including undecayed plant and animal tissues, their partial decomposition products, and soil biomass. Thus, this term includes: identifiable, high-molecular-weight organic materials such as polysaccharides and proteins, simpler substances such as sugars, amino acids, and other small molecules and humic substances [23, 24]. On the other hand SOM is frequently said to consist of humic substances and nonhumic substances. Nonhumic substances are all those materials that can be placed in one of the categories of discrete compounds such as sugars, amino acids, fats and so on. Humic substances are the other, unidentifiable components. This apparently simple distinction, however, is not as clear-cut as it might appear. From the point of view of sorption properties of soils humic substances have a major importance [24]. Soil Organic Matter may range in soils from 0.1% in desert soils to 90% in organic soils. Humic substances make up approximately 85-90% of the total organic carbon in soils [28, 29]. These substances are formed as a result of decay and transformation of plant residues (roots, twings, leaves) and other unaltered material. However, several pathways exist for the formation of humic substances during the decay of plant and animal remains in soil the origin of humic substances in the environment is still not proven [28]. It strongly depends on environmental conditions that influence soil proprieties such as local climate, temperature, humidity, insulation, topographic profile, landuse [29]. Humic substances consist of a heterogeneous mixture of compounds for which no single structural formula will suffice. However, there is no strict chemical formula for these materials, though substantial evidence exists that humic materials consist of a skeleton of alkyl/aromatic units cross-linked mainly by oxygen and nitrogen groups with the major functional groups being carboxylic acid, phenolic and alcoholic hydroxyls, ketone and quinone groups [23]. The formula depends on various factors like soil characteristics and origin pathways of humic substances. However, some researchers present models of humic material that can differ from each other a lot. Recent models of humic and fulvic acids are not as detailed as they were previously they present only some skeleton of these substances. A lot of studies show now quite large variability of the structure properties of the humic material found in the different soil environments. Two model examples of humic acid are presented below in Figure 2.

Humic substances are traditionally defined according to their solubilities. Fulvic acids are those organic materials that are soluble in water at all pH values. Humic acids are those materials that are insoluble at acidic pH values <2. Humin is the fraction of natural organic material that is insoluble in water at all pH values [28]. However, this definition reflects only the traditional methods for separating fractions from soils. Some important differences between these fractions can be seen. Humic acids have larger average molecular masses than fulvic acids and are not so movable in soils as fulvic ones. They are strongly sorbed by clay minerals. The percentage of carbon and oxygen is also higher in humic acids and hydrogen and nitrogen are in comparable amounts when compared to fulvic acids. Fulvic acids have more alkyl groups than humic ones and their aromatic core is not so matured [23, 29].

The existence of humic material in soils strongly influences sorption of chemicals [24]. Humic and fulvic acids can exist in a dissociated form and thus are negatively

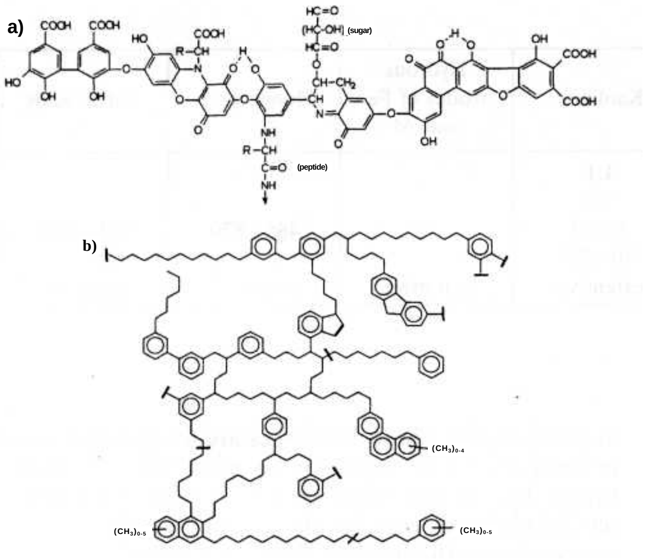

Fig. 2. Model structures of humic acids according to Stevenson (1982) (a) and Schulten, Plaige and Schnitzen (1991) (b) according to [23, 24].

charged. The main sources of these charges are carboxylic and phenolic groups in which hydrogen can be replaced by metal ions. This source of negative charges in soil colloids is strongly pH-dependent so the sorption of heavy metals in organic soils or in soils with relatively high organic content is mostly pH dependent. The Cation Exchange Capacity (C.E.C.) is also very high for soil organic matter, especially for fulvic acids according to clay minerals (see the Table 1) [24].

The inorganic part of soil and soil organic matter do not exist separately in soil. Both nonhumic and humic organic substances can bind to inorganic particles of soils like aluminium and iron oxides and clay minerals [16,17]. The ways in which organic material is combine with mineral portions of soil are as follows:

(i) as salts of low - molecular organic acids (acetate, oxalate, lactate and others),
(ii) as salts of humic substances with alkaline cations - humate, fulvate,
(iii) as chelate with metal ions,
(iv) as substances held on clay mineralsurfaces[9].

The complexing ability of humic and fulvic acids results largely from their content of oxygen-containing functional groups, such as carboxylic -COOH, phenolic -OH and carbonylic -C=O group. Chelate complexes are of especially major importance. The humic and fulvic functional groups play a role as ligands. Each group may occupy two or more coordinating positions about metal ions and form closed rings.

Organic substances can bind to silicate surface in clay minerals via several mechanisms:

(i) $Al^{3+}$, $Fe^{2+}$, $Ca^{2+}$ and $Mg^{2+}$ bridges,
(ii) van der Waals forces,
(iii) hydrogen bondings,
(iv) adsorption by association with hydrous oxides[23].

The intercalation of organic matter in clay minerals has only seldom been found under natural conditions. Probably macromolecules such as humic or fulvic acids are larger than the interlayer spaces in clays like montmorilonite. Hence, the properties of external surface are much more important for binding of organic matter than the inner-particle crystal structure of clays [30].

The organic-mineral particles have great influence on the physicochemical soil properties. They mostly determine the texture of soil. Important physical properties of the soil depend significantly on the $C_{ogr}$ and $N_t$ content of individual soil size fraction. The r-values decreased in the order of clay > fine silt = coarse silt > sand » medium silt [31]. The great aggregation potential of small-sized and charged particles explains the strong correlation between physical properties and organic carbon content of clay and fine silt. From these microaggregates macroaggregates can be formed by the action of soil organisms and binding forces of microbial metabolites or plant mucilages. This forms macrostructure of the soil. The three dimensional soil fabric contains many fine pores that give the soil molecule a sieve-like characteristic [16].

Organic-mineral particles can vary widely in their adsorption properties because of diverse specific surfaces, charge densities and widely different SOM content. The C.E.C. decreases with increasing particle size [17]. The biggest value is for fine clay 57.4-81.3 cmol(+)/kg. Other values are shown in the Table 2. The contribution of SOM to C.E.C. is larger in sand and silt than in clay fraction (it is worth remenbering that the negative charge of SOM is strongly pH-dependent). Hence in typical sandy soil C.E.C. is pH-dependent for the most part [31].

Table 2. Characteristic ranges for soil fraction according to [17].

| Fraction | C.E.C 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 |

The distribution of xenobiotics like, for instance, heavy metals between different size classes of organic-mineral particles is important because the physical movement of these particles leads to their re-distribution in the landscape. The content of heavy metals usually decreases from clay to coarse silt [17]. It is caused by the high surface area of clay minerals and weak pH dependence of C.E.C. Hence, soils with high amounts of clay fraction and organic matter can be more contributed with heavy metals than others.

The binding forces between heavy metals and soil fractions are dependent on pH and ion properties like charge, ionic radius [25].

The binding forces of metal ions to soils decrease with increasing pH of the environment. The ions with higher charge like $Al^{3+}$ are stronger bound to soil particles than smaller charges such as $Ca^{2+}$. When considering metal ions with the same charges the most important factors are ionic radius and rank of hydration [25]. The bigger ionic radius the smaller electric field the ion emits; consequently it is less hydrated than ions with smaller radius which emit stronger electrical fields. This explains why ions with higher ionic radius are preferably sorbed from soil solution by soil particles.

The other important thing is that affinity for binding heavy metals varies between different soil mineral constituencies and organic material [21]. Some examples are listed in Table 3.

Table 3. Range of affinities of metal ions to soil sorbents according to [20].

| Soil adsorbent | |
|---|---|
| Montmorillonite | $Ca^{2+}>Pb^{2+}>Cu^{2+}>Mg^{2+}>Cd^{2+}>Zn^{2+}>Ni^{2+}$ |
| Illite | $Pb^{2+}>Cu^{2+}>Zn^{2+}>Ca^{2+}>Cd^{2+}>Ni^{2+}$ |
| Kaoline | $Pb^{2+}>Ca^{2+}>Cu^{2+}>Mg^{2+}>Zn^{2+}>Cd^{2+}>Ni^{2+}$ |
| Hydrous oxides of Fe | $Pb^{2+}>Cu^{2+}>Zn^{2+}>Co^{2+}>Ni^{2+}$ |
| Humic | $Fe^{3+}>Al^{3+}>Cu^{2+}>Ni^{2+}>Co^{2+}>Pb^{2+} = Ca^{2+}, Zn^{2+}>Mn^{2+}$ |

This indicates that competitive sorption phenomena of various metals in soils are also dependent on strict mineralogical composition of soils.

## Speciation in the Investigation of Heavy Metals Transport in Soils

The concept of conservation of mass, around which the analysis of fate and transport of environmental chemicals can be organised and which can also serve as a check of completeness of know-how of chemicals' behaviour, is vital in the study of physiochemical properties of heavy metals in soils.

If at any time of the analysis the original mass of a chemical can not be fully accounted for, then there is incomplete understanding of how the transformation (speciation) and transportation processes of that chemical occur.

The IUPAC [32] definition of speciation narrowly views this term as the state of distribution of an element among its possible different chemical species in a sample. In practice, the term is widely used, specifying the transformation and/ or the distribution of species or the analytical activity of both identifying chemical species and measuring their distribution. Basically, there are two types of speciation: chemical speciation and physical speciation [23, 24]. It is possible to distinguish four main types of chemical speciation analytics (Fig. 3). One may find some other types of chemical speciation like individual speciation, whose task is to determine all species of an element in a sample. Chiral or cytological speciation are also mentioned in literature [25]. For the understanding of sorption and migration phenomenon of heavy metals in terrestrials systems (soil <=> water) physical speciation is very important. Physical speciation takes place when different forms of the same chemical species have to be determined in a sample [24]. It also may be operationally defined as speciation procedure and mostly applied to investigations of geo-biochemical cycling of different elements in the environment. For trace metals, it may involve soluble and suspended fractionation process, identification and quantification of different forms present in the soil after single, sequential or solvent extraction or derivatization.

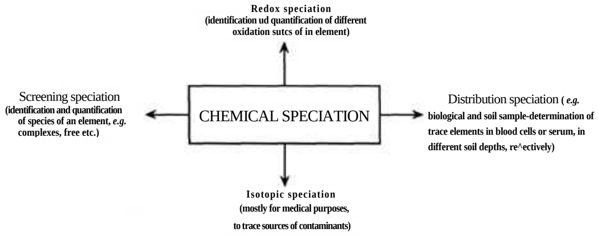

Fig. 3. Classes of chemical speciation.

Since the behaviour of the elements in soil <=> water systems depends largely on their existing forms therefore the determination of trace metals in soils is succeeded by the application of single or sequential extraction and or derivatization techniques. Extraction involves subjecting a solid matrix to successive attacks by reagents of different chemical properties (acidity, redox potential, complexing properties) with each extract representing a fraction of trace element associated with the sample [10]. There is a well-documented sequential extraction scheme [33] with five steps in which heavy metals are distributed amongst different forms, namely;

- exchangeable fraction (sorbed metal),
- carbonates fraction,
- reducible substrates (metals bound to Mn and Fe oxides),
- oxidisable substrates (metals bound to organic and sulphide compounds), and residual fraction (metals bound to mineral "lattice").

In general, there are currently many extractants in application but the choice largely depends on the nature of metal (e.g., "hard" metals are better extracted with solvents containing oxygen while "soft" metals are better extracted with solvents containing Sulphur or Phosphorus) [34]. A large number of different reagents, can extract almost all or part of the metals commonly found in soils, namely $H_2O$, $NaNO_3$, $NH_4NO_3$, $KNO_3$, $CaCl_2$, CH3COONH4, EDTA and CH3COOH have been reported [32, 33, 35-38].

Therefore, the use of sequential extraction in connection with physical speciation can be used to define bioavailable metal soluble metal fractions both of these metal fractions in soils can provide a good indication to the possible extent of groundwater contamination by metal leaching [39, 40].

For soil matrices, Solid Phase Extraction (SPE), has been reported for metal speciation studies [41-47], Tin [41-43], Selenium [44, 45] and Arsenic [46, 47] (the last two for redox speciation). The main parameter in the choice of the most suitable adsorption phase is the adsorption capacity but other parameters such as sample flowrate and breakthrough are also important [48].

The lack of Certified Reference Materials (CRMs) has continued to restrict application of single and se-

Table 4. MAT three-stage sequential extraction scheme according to [49]

| Extraction step | Trace metal fraction | Composition of aquatic extract solution (concentration in mol I$^1$) |
|---|---|---|
| 1 | Free metal, carbonates, exchangeable | $CH_3COOH$ (0.11) |
| 2 | Iron/ manganese oxyhydroxides | $NH_2OH.HCI$ (0.1 at pH 2) |
| 3 | Organic matter and sulphides | $H_2O_2$ (8.8), then $CH_3COONH_4$ (1.0 at pH 2) |

quential extraction procedures for metal speciation in soil matrices. This limitation is due to the lack of homogeneity in soil matrices and the difficulty in monitoring and standardising the parameters that control both efficiency and reproducibility in single and sequential extraction procedures [48], such as:

- chemical properties, selectivity and efficiency of the extractant chosen,
- sequence of individual steps
- operating conditions (extraction time, solid to solution ratio, etc) and
- specific matrix effect such as cross contamination and re-adsorption.

The process of procedural validation is very important for speciation results; therefore as an attempt to validate these extraction methods, the Measurement and Testing Programme (MAT, formerly BCR), under the auspices of the European Community (EC), has developed a single-step procedure using EDTA/acetic acid to characterise the bioavailable metal fraction in soil sample and a three-stage sequential extraction protocol in which metals are characterised as bound to exchangeable/carbonate, Mn and Fe oxides, and organics/sulphide substrates. The latter scheme [49] is presented in Table 4.

Soxhlet extraction and sonication are also the most widely used extraction techniques for metal speciation [48]. Organic solvents, acids and bases are used alone or in mixture, with or without the addition of complexing agents. A number of publications have described solvent extraction for the speciation of lead [50-52] and mercury [53, 54]. Supercritical Fluid Extraction (SFE) has also been proposed for metal speciation [55-58].

Derivatization techniques have not been used regularly for metal speciation in soil matrices in particular. Hydride generation after extraction has been applied for analysis of several hydride-forming elements such as Hg, Sn, Pb, Se, Ge and Bi [58-70]. The usefulness of this technique for metal speciation is severely restricted by either the thermodynamic inability of some to form hydrides or considerable limitations of hydride formation in some cases [71].

The main reactions of derivatization, hydride, ethylation and phenylation are for use with Gas Chromatography - Microwave Inducted Plasma (GC-MIP-AES), Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES), Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) or Atomic Absorption Spectrometry (AAS).

In general after isolation of a specific metal fraction from the soil matrix, a wide variety of analytical techniques for detection can be used, depending on the nature and concentration of the analyte and many other factors. Chromatographic, electromigration, spectroscopic and electrochemical techniques may be applied.

## Modeling and Simulation of Transport of Heavy Metals in Soils

Developing computer methods is one of the driving forces in modern environmental chemistry. In the 1970s the modern discipline of chemistry was born - chemometrics [62]. Chemometrics is the new domain, which can improve the understanding of chemical information, characterize multidimensional data and get some model of described chemical phenomena by applying different mathematical, statistical, graphical or symbolic methods. Modeling and simulation is one of the most important parts of chemometrics. These two mentioned methods are very useful in describing the chemical problems in different environmental matrices [63-67].

The general algorithm of creating every model can be represented as follows in Fig. 4.

Each model is created on the data received in result of observation of simplified ("pseudo-natural") system, which must be accurately defined and in controlled conditions. Obtained results are transformed into a general formula. On the ground of this formula a researcher chooses a suitable model. This model permits us to receive some parameters characterizing occurrences reaching the examined system. The last step is checking our model in different physicochemical conditions to define where and when this model can be applied.

On account of the role of soil in ecosystems, a lot of models of different heavy metals sorption and transportation in this matrix have arisen. The most of well-known sorption models are partitioned into two groups:

- models, which takes account of electrostatic forces and bonding
- models, which do not include this interaction.

In classical models adhered to second group sorption process was described by Langmuirs isotherm:

$$S_i = \frac{b \cdot K \cdot C}{1 + K \cdot C} \qquad (2)$$

where:

$Si$ - concentration of sorbent in solid state;
$C$ - concentration of solution in equilibrium;
$K$ - equilibrium constant;
$b$ - capacity of monolayer;

*or*

Freundlich isotherm:

$$Si = K \cdot C^{1/n} \tag{3}$$

where: $n$ - constant [68, 69].

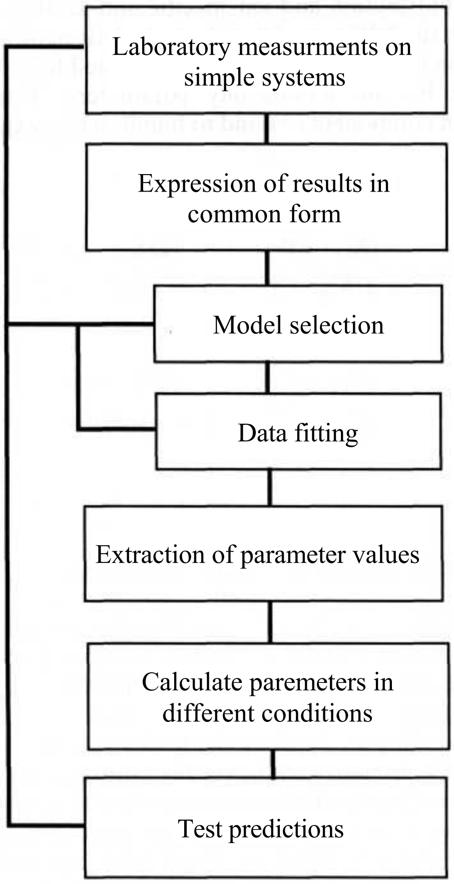

Fig. 4. The modeling cycle according to [68].

Application of models which are of modification of these isotherms, e.g. CFAM - Competitive Freundlich Adsorption Model or Modified CFAM (MCFAM), which are used in cases of extremely heterogeneous surfaces [65] and have proven practical purposes. Heavy metals sorption on soil was well described by a Langmuir equation at low concentrations, whereas a Freundlich isotherm was necessary at high concentrations [70].

There also exist some sorption models including electrostatic power as a model of constant capacity, model of diffusion layer and model of triple layer [71]. The adsorption of ionic matter on surface of small particles is in these models due to presence of charges. The electrostatic models are based on an equation which showed that the thermodynamic constant K can be represented as a product of $K_{inter}$ (specific, independent from charge influence among bonded ion and active place) and Kei$_{ec}$t (responding only for influences among ion and electrostatic potential in active place):

$$K = K_{elect} \cdot K_{inter} \tag{4}$$

The second basic element of these models is the establishment of a clean solid phase containing only one kind of active place. On its surface they should be groups such as the (SOH), which can stay in contact with liquid phase. The increase or decrease of protons on the surface is a result of change of the distribution of charges on the surface. For example for simplest equilibrium:

$$SOH + H^+ \Leftrightarrow SOH_2^+ \tag{5}$$

constant $K_{inter}$ is calculated according to the equation:

$$K_{inter} = \frac{[SOH_2^+]}{[SOH] \cdot [H^+]_s} \tag{6}$$

*where:* $[H_s]$ - concentration of protons on the the surface of bonding sites;
This value is calculated using Boltzmann delay:

$$[H^+]_s = [H+]_b \bullet exp(-F\Phi/RT) \tag{7}$$

where:
O is potential of surface, $[H^+]_b$ is total concentration of protons in solution.

In this case electrostatic constant $K_{elec}$, is described by Poisson - Boltzmann distribution:

$$K_{elec} = [H^+]_s / [H^+]_b \bullet exp(-F\Phi/RT) \tag{8}$$

The basic equalization in all electrostatic models relating surface potential Φ with surface charge δ by means of planar Gouy-Chapman's equalization:

$$\sigma = \{2 \bullet \varepsilon_0 \bullet \varepsilon \bullet RT \Sigma c_i \bullet [exp(-z_i \bullet F \bullet \Phi/RT) - 1]\}^{1/2}$$
$$= (8 \bullet \varepsilon_o \bullet \varepsilon \bullet RT)^{1/2} \bullet sinh(zF\Phi/2RT) \tag{9}$$

where:
$z_i$ - charge of ion "i",
$c_i$ - concentration of this ion,
$\varepsilon_o$ - permittivity in free space,
ε - relative permittivity.

At the limit of small potentials: sinh $(zf\Phi/2RT) \approx (zf\Phi/2RT)$ and eq. (9) gives the simple relationship:

$$\sigma = 2.5 \bullet \sqrt{I} \bullet \Phi = C \bullet \Phi \tag{10}$$

where:
*C* is capacitance of double layer and I is the ionic strength.

Davis and coworkers proposed [58] a more elaborate model, triple layer model, with two adsorption layers, one for protons and second for other (larger) dissolved ions.

In opposition of sorption models in soil modeling of transport of this type of inorganic pollutants is still "the clean card" in present days. In literature many mathematical or physical transport models of different chemical pollutants in soil matrix is described [73]. These models have some bugs: there are very complicated - it means, that they required many parameters at the beginning of modeling, or they are simply physical equalizations of transport inside soil profile without consideration of interaction between contamination and soil matrix. These models also contain some approximations and assumptions, which in a significant manner modify descriptions of transport phenomena. Obtained results on the basis of these models are not always compatible with real measurements in the natural environment [74]. One of the most well-known models were based on dispersion-convection-sorption equalisations [75]:

$$\partial C/\partial t = D_d \partial^2 C/\partial x^2 - v\partial C/\partial x - (\rho/\theta)\partial S/\partial t \tag{11}$$

$$[1 + (\rho/\theta)(\partial S/\partial C)](\partial C/\partial t) = D_d \partial^2 C/\partial x^2 - v\partial C/\partial x \tag{12}$$

$$S = \frac{m_a}{m_s} \tag{13}$$

where:
$\rho$ - concentration of pollutant in soil solution;
$C$ - total concentration of pollutant in soil
$\theta$ - volumetric moisture content
$D_d$ - dispersion coefficient
$m_a$ - mass of pollutant in unitary volume of soil
$m_s$ - mass of sorbent in unitary volume of soil

This form of equalization is named equalization of confusion", because of misunderstandings, which its evokes in researchers and may be applied in situations when in our system have constant moisture content in soil ($\theta$ = const.) or when the soil is saturated with water.

The modern approach to modeling sorption and transport of heavy metals in soil gives chemometrics. A researcher can simulate natural soil and behaviour of heavy metals in leaching column experiments and then try to use some chemometrics method to describe obtained results. Chemometrics give possibility to describe environmental phenomena without the necessity of looking inside to what mechanisms were responsible for these processes. Another possibility is the application of artificial neural networks to modeling sorption and migration in soil. In this case we have the same situation: neural network can predict reasonable data, but we don't know anything about physiochemical processes setting inside soil [76].

## Modeling Humic Substances Metal Ions Interactions

The study on understanding interactions and modeling of heavy metals with soil organic matter (SOM) has been one of the most important subjects of environmental and soil scientists as SOM influences soil sorption of heavy metals in the great part (see Table 1 for C.E.C.). Some models exist yet, which deal with these interactions phenomena [78, 79]. The Non-Ideal Competitive Adsorption model has been used to investigate metal binding to humic substances in the presence of competing ions (e.g. protons) [18, 77]. In this model humic substances are considered as heterogeneous ligands where carboxylic and phenolic groups are of particular importance. The NICA model assumes continuos distribution of heterogeneous ligands and non-ideality of local binding which is divided into an intrinsic (binding site) heterogeneity contribution and ion-specific non-ideality contribution. In the NICA model, polyelectrolytic nature of ion adsorption to humic substances is accounted for in a generic way by the non-ideality parameters. The total amount of component *i* bound to humic acid is expressed here:

$$\theta_{i,t} = Q_{\max 1} \frac{(K_{i,1} \cdot c_i)^{n_{i,1}}}{\sum_i (K_{i,1} \cdot c_i)^{n_{n,1}}} \; \frac{\{\sum_i (K_{i,1} \cdot c_i)^{n_{i,1}}\}^{p_1}}{1 + \{\sum_i (K_{i,1} \cdot c_i)^{n_{i,1}}\}^{p_1}} + $$

$$+ Q_{\max 2} \frac{(K_{i,2} \cdot c_i)^{n_{i,2}}}{\sum_i (K_{i,2} \cdot c_i)^{n_{n,2}}} \; \frac{\{\sum_i (K_{i,2} \cdot c_i)^{n_{i,2}}\}^{p_2}}{1 + \{\sum_i (K_{i,2} \cdot c_i)^{n_{i,2}}\}^{p_2}} \tag{14}$$

where:

$\theta$ is the total amount of component / bound to humic acid,
$Q_{max1}$ and $Q_{max2}$ are the total site densities for site 1 and 2, the parameter n, accounts for the non-ideal behaviour and/? determines the width of the distribution due to the intrinsic chemical heterogeneity of the sorbent.

Benedetti [4] used this model to describe the binding of H, Ca, Cu, Cd ions and the results confirmed all model assumptions. Veeken [80] developed the NICA model by considering electrostatic interactions more specifically. He employed a Donnan potential term and used his model to compute proton and Cu(II) binding to organic particles in organic municipal waste. The Poisson - Bolzmann equation also can be used to compute the electrostatic potential [81]. Tight metal binding by humic acids was studied by Davies et. al. [17]. They investigated $Cu^{2+}$, $Fe^{3+}$, and $Mn^{2+}$ binding by different humic acids using equilibrium study and fitting data to typical Langmuir isotherm. They found that humic acids have three specific binding sites A,B, and C. The A site consists of carboxylates, mixed ligands probably constitute site B and site C is tentatively assigned as the interior of the humic acid helix. In their study they used a new helical HA molecular model based on empirical formula $C_{36}H_{30}N_2O_{15} \cdot nH_2O$.

For better understanding possible contamination of ground water with heavy metals it is essential to investigate interactions the chemicals with dissolved organic matter (DOM) which is the part of soil organic matter. The exogenous DOM can also be introduced to soils as amendments like sewage sludge, compost. DOM influences sorption equilibra in soil by binding with heavy metals and leaching them as dissolved organics move through soil profile with soil water. This very important problem is widely discussed in literature, including modeling [83-88].

Table 5. Parameters required for surface complexation models.

| | Diffuse Layer model | Constant Capacitance model | Triple Layer model |
|---|---|---|---|
| Common parameters<br>$H^+$ parameters<br>metal parameters | 2 (surface area, total site concentration)<br>2 (pK values for proton gain and loss)<br>$pK_{int.}$ | 3 (surface area, total site, concentration, capacitance)<br>2 (pK values for proton gain and loss)<br>$pK_{int}$ | 4 (surface area, total site, concentration, 2 capacitances)<br>2 (pK values for proton gain and loss)<br>$pK_{int.}$ |
| total parameters | 5 | 6 | 7 |

## Conclusions

The description of some sorption and migration phenomena for heavy metals in soils was the primary objective of this work. The presence of heavy metals in soils represents a significant environmental hazard, and one of the most difficult contamination problems to solve. There are two main reasons: firstly, the chemical character of heavy metals - they are not subjected to biodegradation processes, and accumulate in the environment and, secondly, the complexity of the soil matrix. The unhomogeneity of soils is so high, that we can not provide all features of soil samples without employment of some approximations. Simplification of this matrix increases chances of recognition of basic soil processes. Another possibility, for understanding soil processes is computer simulation. However, it seems most effective to apply computer methods with the simulation of natural physicochemical processes in a simplified soil matrix

## Acknowledgement

Allen Dube thanks to WITS University for scholarschip. This work was supported within framework of the EuroCat Project No. EVK1-2000-00510.

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