CHAPTER 23
APPLICATION OF MATHEMATICAL AND CHEMOMETRICAL APPROACHES IN THE STUDY OF HEAVY METAL IONS – SOIL INTERACTIONS.

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ABSTRACT
This study presents an overview of soil-metal ions interactions, modelling of heavy metals binding to soil constituents and the application of column leaching experiments. The soil and its constituents are also fully characterized here. The conventional modelling approach employing dispersion-convection-sorption equalizations is compared to statistical modeling. This contribution also presents the experimental results of using the artificial neural networks approach to ion leaching experiments.
1 SOIL-HEAVY METAL IONS INTERACTIONS

The soil environment is one of the major reservoirs for many contaminants. Its constituents possess great ability to influence behavior, including sorption, transport, degradation and immobilization, of introduced chemicals [1]. A special group of soil contaminants are heavy metals. Substantial amounts of heavy metals (e.g. Ni, Co, Zn, Cu, Cr, V, Ti, Cd, Hg, Mo and other) may occur in soils due to industrial pollution, transportation as well as widespread use of fertilizers and organic soil amendments e.g. sewage sludges and composts of waste origin [2,3].

The soil-heavy metal interactions are generally due to the presence of highly dispersed colloidal fraction of the soil solid phase called “soil sorption complex”. The soil sorption complex is the main important soil structural unit. It influences the chemical and physicochemical properties of the soil including buffering capacity, cationic exchange capacity, water content, soil aggregate stability [4]. The crucial feature of the soil colloids is that their surface is negatively charged. Hence, the Electric Double Layer (EDL) is formed on the surface of the soil colloid particles in contact with soil solution.

The soil colloid particle is formed from three kinds of constituents: (i) mineral particles, (ii) organic matter and (iii) organic-mineral complexes [2].

The inorganic (mineral) colloidal fraction of the soil solid phase is the most responsible for sorption of metal ions by its mineral particles. It comprises of clay minerals, oxides, sesquioxides and hydrous oxides of minerals [4]. The clay minerals are hydrous aluminium, magnesium or iron silicates. There are two major types of clay minerals found in soils: 1:1 and 2:1. The 2:1 type is typical for clays montmorillonite and illite. The unit cell here is built from two silica tetrahedral layers, \( \text{Si}_2\text{O}_5 \), surrounding an aluminium octahedral layer, \( \text{Al}_2\text{O}_4(\text{OH})_2 \). 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 being often immobilised. This also causes the ability of expansion of montmorillonite or illite when it contacts with water. The water content in montmorillonite can vary so its chemical formula can be written \( \text{Al}_2(\text{OH})_2(\text{Si}_2\text{O}_5)_2\cdot n\text{H}_2\text{O} \). The 1:1 type is typical for clay kaolinite. A unit cell of a 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 \( \text{Al}_2(\text{OH})_4(\text{Si}_2\text{O}_5) \) [4-7].

**TABLE 1.** Characteristics of typical soil sorbents [4].

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Montmorillonite</th>
<th>Illite</th>
<th>Kaolinite</th>
<th>Hydrous oxides of Fe and Al</th>
<th>Humic acids</th>
<th>Fulvic acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of layering</td>
<td>2:1</td>
<td>2:1</td>
<td>1:1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Layer charge</td>
<td>0.25-0.6</td>
<td>0.6-0.9</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEC cmol (+) / kg</td>
<td>80-120</td>
<td>20-50</td>
<td>1-10</td>
<td>4</td>
<td>485-870</td>
<td>900-1400</td>
</tr>
<tr>
<td>Surface area ( \times 10^3 \text{m}^2 \text{kg}^{-1} )</td>
<td>600-800</td>
<td>70-120</td>
<td>10-20</td>
<td>800-900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH dependent charge</td>
<td>minor</td>
<td>medium</td>
<td>extensive</td>
<td>extensive</td>
<td>extensive</td>
<td>extensive</td>
</tr>
</tbody>
</table>
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 [4-7]. The expandable clay minerals have also much greater cationic exchange capacity (CEC) than the nonexpanding types and thus have much greater propensity for immobilizing chemicals such as metal ions. The basic characteristics of main soil sorbents are listed in the Table 1.

There are at least two major possibilities as how to surface negative charges are formed. The hydroxyl groups which exist on the edges and on the outer layers of minerals can dispose of hydrogen which is a pH dependent process (Figure 1a). The ability to split of the hydrogen atom decreases when the pH of the medium decreases. The negatively charged surface can easily interact with positively charged ions that exist in soil solution e.g. Ca^{2+}, Al^{3+}, Pb^{2+}, Cd^{2+}. The second process of creating negative charges is due to the isomorphous ion replacement in the minerals (Figure 1b). 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 is quite persistent. The ability of creating negative charges is the highest for 2:1 type of clays [4].

The oxides and hydrous oxides of iron and aluminium are commonly found in soils in several mineralogical forms including hematite, goethite and gibbsite, bohemite respectively [1]. 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:

\[-\text{AlO}^- + \text{H}^+ = -\text{AlOH} + \text{H}^+ = \text{Al(OH}_2)^+\]  \hspace{1cm} (1)

Figure 1. The mechanisms responsible for creation of negative charge on the soil colloid surface [4].
The Soil Organic Matter (SOM) may range in soils from 0.1% in desert soils to 90% in organic soils [8,9]. The organic fraction of soil colloids consists of undecayed plant and animal tissues, their partial decomposition products, and the soil biomass and includes: identifiable, high-molecular-weight organic compounds such as polysaccharides and proteins, simpler substances such as sugars, amino acids, etc. and humic substances. Humic substances (HS) are of major importance to the soil environment. They influence physicochemical properties including sorption, biochemistry, and biology of soil. Humic substances are structurally complex because of macromolecules which have a yellow to black appearance, are acidic and generally heterogenous and polydisperse [1,8,9]. They consist of carbon, oxygen, hydrogen and sometimes small amounts of nitrogen and occasionally phosphorous and sulfur. They are formed as a result of decay and transformation of plant residues (roots, twinges, leaves) and other unaltered material. Humic substances make up approximately 85-90% of the total organic carbon (TOC) in soils and influence sorption properties of soil to a great extent [10].

Humic substances are traditionally defined according to their solubility [4,8]. They are generally divided into three classes of materials on the basis of operational definitions. 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. This definition reflects only the traditional methods for separating fractions from soils.

Despite many decades of research the structure of humic substance is still under discussion although numerous tentative structures have been proposed (Figure 2.).

![Figure 2. Model structures of humic acids according to Stevenson (1982) (a) and Schulten, Plaige and Schnitzen (1991) (b) [1](a)](image)

![Figure 2. Model structures of humic acids according to Stevenson (1982) (a) and Schulten, Plaige and Schnitzen (1991) (b) [1](b)](image)
In the broadest terms the structures of humic acids can be described as assemblies of covalently linked aromatic and aliphatic residues carrying carboxyl, phenolic and alkoxy groups although sulphate esters, alanine moieties, semiquinone, phosphate ester and hydroquinone groups have been proposed to exist in some humic isolates [8]. The existence of humic material in soils strongly influences sorption of chemicals [11]. The Cationic Exchange Capacity (CEC) for humic and fulvic acids is very high in comparison to other soil constituents (see Table 1.). Humic and fulvic acids can exist in a dissociated form and thus negatively charged (Figure1c.). The main sources of these charges are carboxylic and phenolic groups in which hydrogen can be spitted off. 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.

Many studies have shown that humic substances interact with pollutants including heavy metals, radioactives, pesticides and hydrophobic organic compounds. It has been proved that the mobility of heavy metals in soils is increased by the presence of humic ligands, e.g. compost origin [12,13]. It is also thought that humic substances, particularly in the early stage of humification affect bioavailability of metals to plants. It has been shown that lower molecular weight fractions, do increase the uptake of cadmium by plants [14].

Both nonhumic and humic organic substances can bind to inorganic particles of soils like aluminium and iron oxides and clay minerals [4-9]. They 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 bindings, (iv) adsorption by association with hydrrous oxides [4].

There are many measurable parameters that control metal ions binding and hence transport or movement in soil media. They can be divided into two groups; related to soil parameter, e.g. Cationic Exchange Capacity (CEC), granulometric soil fractions (clay content), organic fraction, mineral composition, redox potential, pH and the second set of variables related to metal ion parameters, e.g. ion charge, ion radius, oxidation state, rank of hydration, complexation ability [1,4].

The CEC decreases with increasing particle size [1]. The biggest value is for fine clay 57.4-81.3 cmol (+)/kg. Other values are shown in the Table 2. The contribution of soil organic matter (SOM) to CEC is larger in sand and silt than in clay fraction.

**TABLE 2.**

<table>
<thead>
<tr>
<th>Fraction</th>
<th>CEC cmol (+)/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>20.9 – 110</td>
</tr>
<tr>
<td>Fine silt</td>
<td>6.8 – 41.4</td>
</tr>
<tr>
<td>Medium silt</td>
<td>6.3 – 34.5</td>
</tr>
<tr>
<td>Coarse silt</td>
<td>1.2 – 12.8</td>
</tr>
<tr>
<td>Sand</td>
<td>1.0 – 15.6</td>
</tr>
</tbody>
</table>
The content of heavy metals usually decreases from clay to coarse silt [1]. It is caused by the high surface area of clay minerals and weak pH dependence of CEC in clays. Hence, soils with high amounts of clay fraction and organic matter can be more contributed with heavy metals than others. The distribution of 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 affinity for binding heavy metals varies between different soil mineral constituencies and organic material [7]. Some examples are listed in Table 3.

**TABLE 3.**
Range of affinities of metal ions to soil sorbents [7].

<table>
<thead>
<tr>
<th>Soil adsorbent</th>
<th>Affinity of metal ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>$\text{Ca}^{2+} &gt; \text{Pb}^{2+} &gt; \text{Cu}^{2+} &gt; \text{Mg}^{2+} &gt; \text{Cd}^{2+} &gt; \text{Zn}^{2+} &gt; \text{Ni}^{2+}$</td>
</tr>
<tr>
<td>Illite</td>
<td>$\text{Pb}^{2+} &gt; \text{Cu}^{2+} &gt; \text{Zn}^{2+} &gt; \text{Ca}^{2+} &gt; \text{Cd}^{2+} &gt; \text{Ni}^{2+}$</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>$\text{Pb}^{2+} &gt; \text{Ca}^{2+} &gt; \text{Cu}^{2+} &gt; \text{Mg}^{2+} &gt; \text{Zn}^{2+} &gt; \text{Cd}^{2+} &gt; \text{Ni}^{2+}$</td>
</tr>
<tr>
<td>Hydrous oxides of Fe</td>
<td>$\text{Pb}^{2+} &gt; \text{Cu}^{2+} &gt; \text{Zn}^{2+} &gt; \text{Co}^{2+} &gt; \text{Ni}^{2+}$</td>
</tr>
<tr>
<td>Humic acids</td>
<td>$\text{Fe}^{3+} &gt; \text{Al}^{3+} &gt; \text{Cu}^{2+} &gt; \text{Ni}^{2+} &gt; \text{Co}^{2+} &gt; \text{Pb}^{2+} = \text{Ca}^{2+}, \text{Zn}^{2+} &gt; \text{Mn}^{2+}$</td>
</tr>
</tbody>
</table>

The binding forces of metal ions to soil constituents decrease with increasing pH of the environment. The ions with higher charge like $\text{Al}^{3+}$ are stronger bound to soil particles than lower charged such as $\text{Cu}^{2+}$. When considering the metal ions with the same charges the most important factors are ionic radius and rank of hydration [1,4]. The bigger ionic radius the smaller electric field the ion emits, consequently it is less hydrated than ions with smaller radius which emits a stronger electric field. This explains why the ions with the higher ionic radius are preferably sorbed from soil solution by soil particles (They are less hydrated)[1].

There are a few different kinds of sorption in soils [4]. Generally the most important is exchangeable sorption controlled by such soil parameters like CEC, pH, mineral composition and properties of soil colloids (mineral composition, organic matter, surface area, etc.), cation and accompanying anion, its concentration and ambient temperature. The exchangeable sorption is said to be generally reversible depending on variable soil parameters e.g. pH.

Additionally the exchangeable sorption the chemical physical and biological sorption are distinguished.

In chemical sorption the metal ions are immobilized by precipitation. The insoluble soils are formed due to special conditions in soils (high pH, high concentration of phosphates, sulphates). In the case of biological sorption the soil biota (living organisms, plants) act as sorbets. The metal ions may enter into the body of organism, may be assimilated, transported with moveable organisms or removed from soils with crops.

The physical sorption is related to the presence of weak van der Waals forces and hence has limited impact into transport or distribution of metal ions in soils.
Heavy metals may exist in soils in many chemical forms (e.g. due to oxidation states), bound to different soils constituents (organic or mineral fractions) or in various soils phases or environments (in: solution, solid phase or absorbed by biota). This multidimensional distribution of heavy metals in soil environment is called speciation [9]. Basically there are two types of speciation; chemical speciation and physical speciation [9,10]. It is possible to distinguish four main types of chemical speciation analytics. They are presented on the Figure 3.

For the understanding of sorption and transport phenomenon of heavy metals in soil systems physical speciation is very important [15]. Physical speciation takes place when different forms of the same chemical species have to be determined in a sample [15]. It also may be operationally defined as speciation procedure and mostly applied for 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.

2 CHEMOMETRICS AND MODELING OF BEHAVIOUR OF HEAVY METALS IN SOILS

Chemometrics is a new domain, which can improve the understanding of chemical information, characterize multidimensional data and create some model of described chemical phenomena by applying different mathematical, statistical, graphical or symbolic methods. Modelling and simulation is one of the most important parts of chemometrics. These two are very useful in describing the chemical problems in different environmental matrices [16,17].

A general algorithm of creation any model can be represent as shown on Figure 4.
Every model is created on the data received as a result of observation of a natural or (oftener) simplified ("pseudo-natural") system, which must be accurately defined and in controlled conditions. Obtained results are transformed into a general formula. On the grounds of this formula the scientist chooses a suitable model. The last step is checking the model in different physiochemical conditions to define where and when this model can be applied.

There are two types of approach to modelling the system, the predictive and the descriptive [18]. In predictive modelling the primary objective is to obtain the best possible fit to the available data, since in that way there will be the maximum possible confidence in the predictions made by the model in regions where there are no experimental data with which to compare it. In descriptive modelling, on the other hand, the object is to use the model to gain more information about the way in which the real system functions. In other words, the primary intent is not to obtain the best possible fit to experimental data, but rather to increase knowledge of the binding process. The descriptive model describes the mechanisms at the molecular level involved in a process. There has been a limited amount of descriptive modelling approach in the field of soil-metal binding, since the primary interest is predicting the behaviour of metals in the environment.

Although the Langmuir and Freundlich (typical predictive models) were first introduced about 70 years ago, they still remain the most common used in study of sorption phenomena [19]. Their success undoubtedly reflects their ability to fit a wide variety of adsorption data quite well, but it may also partly reflect the appealing simplicity of the isotherm equations and the ease with which their adjustable parameters can be estimated.
The Freundlich equation:

\[ q = K_f \cdot C^n, \quad n < 1 \quad (1) \]

where \( q \) is amount of sorbed chemical in equilibrium, \( C \) means concentration of chemical in solution, \( K \) and \( n \) are empirical constants, has an empirical origin and there is no strict adsorption theory according to it. The Langmuir model described by the equation:

\[ q = M \cdot \frac{k \cdot C}{1 + k \cdot C} \quad (2) \]

where: \( q \) – concentration of sorbent in solid state, \( C \) – concentration of solution in equilibrium, \( K \) – equilibrium constant, \( M \) – capacity of monolayer, assumes monolayer adsorption on uniform surface which cannot be always true when sorption of chemicals by such heterogeneity and complex medium as soil is considered.

There are many extensions to the Langmuir and Freundlich isotherm like multisite Langmuir, Toth and modified Dubinin-Radushkevich, Langmuir-Freundlich and Redlich-Petersen isotherm. They are particularly suitable for describing adsorption on heterogeneous surfaces [19,20].

To consider the sorption of heavy metals in a more descriptive way it must be remembered that there are two main sorption centres for metal ions of different origin in soils: the mineral surface and soil organic matter, hence the separate models for these two soil fractions had to be elaborated.

The sorption on oxides and clay mineral edges is very often described by the following models: The Constant Capacitance Model (CCM), The Diffuse Layer Model (DLM), The Triple Layer Model (TLM), The Basic Stern Model (BSM), and The Three Plane Model (TPM) [21]. The most commonly used are The CCM, DLM and TLM. They are incorporated into the MINTEQ2 speciation code.

The constant capacitance (CCM), diffuse-layer (DLM), and triple-layer (TLM) models all treat trace metal surface reactions as complexation reactions analogous to the formation of complexes in solution. Surface sites are represented as SOH groups where S's are metals associated with the solid structure and located at the solid-liquid interface. Some ions, such as H\(^+\), OH\(^-\), and a variety of trace metal ions are presumed to be specifically adsorbed at the surface via complexation with the surface sites [22]. In all three models, a charge (\( \sigma \)) associated with the surface is assumed to be balanced by a charge (\( \sigma_d \)) associated with a diffuse layer of counterions. These charges are such that:

\[ \sigma + \sigma_d = 0 \quad (3) \]

In the constant capacitance and diffuse-layer models, all specifically adsorbed ions contribute to the surface charge (\( \sigma \)). However, in the triple-layer model, the net charge due to adsorption is the sum of the charges associated with two adsorbing planes rather than one. The innermost of the two planes (the o-plane) specifically adsorbs H\(^+\) and OH\(^-\) and is characterized by charge \( \sigma_o \). The other plane (\( \beta \)-plane) has charge \( \sigma_B \) resulting from the adsorption of other ions (metal ions).
The net surface charge is given by:

\[ \sigma_o + \sigma_p = \sigma \]  

(4)

and is balanced by the charge in the diffuse layer such that:

\[ \sigma + \sigma_d = 0 \]  

(5)

Because the electrical potential gradients extending away from the surface are the direct result of the surface charge, the specifically adsorbed potential determining ions also govern distribution of counterions in the diffuse layer [22].

Activities of ions in solution and near the surface are influenced by the presence of electrostatic potentials arising from the surface charge. The activity difference between ions near the surface and those far away is the result of electrical work in moving the ions across the potential gradient between the charged surface and the bulk solution. The activity change between these zones is related to the ion charge (Z) and the electrical potential (ψ) near the surface and can be expressed using the exponential Boltzmann expression:

\[ \{X_s^z\} = \{X^z\} \cdot \exp\left(-\frac{\psi F}{RT}\right)^z \]  

(5)

where: Z – charge of ion, \( \{X_s^z\} \) - activity of an ion X of charge z near the surface, \( \{X^z\} \) - corresponding activity of X in bulk solution outside the influence of the charged surface, F - Faraday constant, R - ideal gas constant, T - absolute temperature.

The schematic presentation of constant capacitance, diffuse-layer and triple-layer models are presented on Fig 5.

Figure 5. Schematic representation of the surface charge/potential relationships used in the constant capacitance and diffuse-layer models (a) and triple-layer model (b) [22].
There are two main distinct families of humic models that describe the metal – soil organic matter interactions: (i) discrete site and (ii) continuous distribution [18]. The major difference between models of different families is the way that they deal with intrinsic heterogeneity. Discrete site models assume that the heterogeneous humic may be represented by a finite number of individual binding sites, each with their own single binding constant. Continuous distribution models implement distribution functions to imitate the behavior of humics.

The most important discrete site model is Model V which has been developed over the past few years by Tipping [18 and references within]. The model describes the humic as having a certain number of discrete binding sites, each of which has an associated quotient which is related to an equilibrium constant. It is assumed that there are eight different functional group types on the humic, four lower pH that correspond to carboxylates (pK_A) and four higher pH corresponding to phenolics (pK_B). The eight different equations are used to define the pKs of the sites (Figure 6).

Metal binding may occur either at any of the eight single functional group sites or at certain permitted combinations of two. Hence there are maximum 21 types of different binding sites on the surface of humics [18]. The model also allows for non-specific binding, by taking into account the metal ions present in the Donnan layer. However they are not bound to a specific site but they are removed from the bulk solution. The volume of the Donnan layer $V_D$ is calculated in the model as follows:

$$
V_D = \frac{10 \cdot N_A}{M_r} \cdot \frac{4\pi}{3} \left[ \left( r + \frac{1}{\kappa} \right)^3 - r^3 \right]
$$

(6)

where $M_r$ – is the molecular weight of the humic, $N_A$ – Avogadro’s constant, $r$ – is the humic radius and $\kappa$ is the ionic strength dependent Debye-Hückel parameter.
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The continuous distribution models use the probability distributions which describe the distribution of sites on the humic substance [18]. For a single distribution of sites, the probability of a humic site having a \( \log K \) value in the region \( a \) to \( b \), \( P(a, b) \) is given by:

\[
P(a, b) = \int_a^b f(\log K) d\log K
\]  

(7)

where \( f(\log K) \) is the site distribution function. The continuous distribution models generally differ in the definition of \( f(\log K) \). The second feature that differentiates the models is the local adsorption isotherm that describes the binding behaviour of a group of identical sites with a single binding constant \( K_i \).

The NICA-Donnan continuous distribution model developed by de Wit and Kinniburgh [23], uses quasi—Gaussian distribution of \( \log K \) [24] and Henderson-Hasselbalch/Rudziński [25] sorption isotherm. It also assumes that there are two types of site presents which are nominally classed as carboxylate (type 1) and phenol (type 2). The analytical solution of a total amount of component \( i \) (metal ion or proton) bound to humic acid is then given by:

\[
\Theta_{i,t} = Q_{\text{max}1}^{p_1} \left[ \sum_{j} \left( K_{i,j} \cdot c_j \right)^{p_{j,1}} \right] \frac{\left[ \sum_{j} \left( K_{i,j} \cdot c_j \right)^{p_{j,2}} \right]^{p_{2}}}{1 + \left[ \sum_{j} \left( K_{i,j} \cdot c_j \right)^{p_{j,1}} \right]} + Q_{\text{max}2}^{p_2} \left[ \sum_{j} \left( K_{i,j} \cdot c_j \right)^{p_{j,2}} \right]^{p_{2}} \frac{\left[ \sum_{j} \left( K_{i,j} \cdot c_j \right)^{p_{j,2}} \right]^{p_{2}}}{1 + \left[ \sum_{j} \left( K_{i,j} \cdot c_j \right)^{p_{j,2}} \right]} 
\]  

(8)

where \( \Theta \) is the total amount of component \( i \) bound to humic substance, \( Q_{\text{max}1} \) and \( Q_{\text{max}2} \) are the total site densities for site 1 and 2, the parameter \( n_i \) accounts for the non-ideal behaviour and \( p \) determines the width of the distribution due to the intrinsic chemical heterogeneity of the sorbent. The NICA model also uses the Donnan approach to calculate the non-specific metal-humic interactions [26].

3 ARTIFICIAL NEURAL NETWORKS AS A NEW TOOL FOR MODELING

The fundamental structure of digital computers is based on the principle of sequential (serial) processing. In contrast, this neurocomputing involves processing information by means of changing the states of networks formed by interconnecting extremely large numbers of simple processing elements, which interact with one another by exchanging signals. Networks such as the one just described are called artificial neural networks (ANNs), in the sense that they represent simplified models of natural nerve or natural neural networks. Figures 7a,b presents schemes of natural and artificial neurons. The similarity of these graphs shows that these two individuals work in the same way however the artificial neuron is only the model of its natural brother and its structure is much more simplified.
Since 1958, when psychologist Frank Rosenblatt [27] proposed the "Perceptron," a pattern recognition device with learning capabilities, the artificial neural networks has been widely studied. The most popular structure of ANNs is the hierarchical neural network. This is the one that links multiple neurons together hierarchically. The special characteristic of this type of network is its simple dynamics. That is, when a signal is input into the input layer, it is propagated to the next layer by the interconnections between the neurons (Figure 8). Simple processing is performed on this signal by the neurons of the receiving layer prior to its being propagated on to the next layer. This process is repeated until the signal reaches the output layer completing the processing process for that signal. The manner in which the various neurons in the intermediary (hidden) layers process the input signal will determine the kind of output signal it becomes (how it is transformed). If input signals can be transformed to the proper output signals by adjusting these values (parameters), then hierarchical networks can be used effectively to perform information processing. Since it is difficult to accurately determine multiple parameter values, a learning method is employed. This involves creating a network that randomly determines parameter values. This network is then used to carry out input-to-output transformations for actual problems.
The correct final parameters are obtained by properly modifying the parameters in accordance with the errors that the network makes in the process. Quite a few such learning methods have been proposed. All of these method minimize the error between predicted and observed output values. Probably the most representative of these is the error back-propagation learning method proposed by Rumelhart. This learning method has played a major role in the recent neurocomputing boom [28].

In working with the various applications, many have found that the back-propagation algorithm can be very slow. Without using advanced learning techniques to speed the process up such us Conjugate Gradient Descent, Linear Singular Value Decomposition, Quasi-Newton’s or Levenberg-Marquardt’s methods, it is hard to effectively apply backpropagation to real-world problems. Overfitting of a neural network model is another area which can cause beginners difficulty. Overfitting happens when an ANN model is trained on one set of data, and it learns that data too well. This may cause the model to have poor generalization abilities - the model may instead give quite poor results for other sets of data.

ANNs can be regarded, in one respect, as multivariate nonlinear analytical tools, and are known to be very good at recognizing patterns from noisy, complex data, and estimating their nonlinear relationships. Many studies have shown that ANNs have the capability to learn the underlying mechanics of the time series, or, in the case of trading applications, the system dynamics.

4. EX-SITU LEACHING COLUMN EXPERIMENTS AS A VALUABLE METHOD IN HEAVY METALS TRANSPORT RESEARCHES.

Due to the complexity of soil or sediment systems and the variability of numerous influencing factors, modelling of mobilization of metals from soils is highly complicated. Despite the large uncertainties involved, predictions of heavy metals mobility from laboratory leaching experiments may support in-situ researches.

Soil column experiments play an important role in research on the identification of physical and chemical properties of soils. Particularly column leaching experiments are the most useful to determine transport, sorption and transformations of different contaminants in this matrix. The majority of these experiments were performed in full water saturation conditions with the assumption that the transport of solution is characterized by convection and dispersion processes allowing sorption of contaminants on the soil constituents. Such experiments are comparatively cheap, fast and simple to control. Estimation of transport of contaminants is performed by the observation of breakthrough curves (BTCs). Its shape is used for the identification of specific interactions between the solution and solid phase. Commonly the BTCs were drawn as the dependency of ratio of the momentary contamination concentration and concentration of contaminant in solution \((C/C_0)\) to PV value. PV is the volume of water that fully fills all pores of soil column. The most well-known models of contaminant transportation were based on dispersion-convection-sorption equalizations (Bolt, 1979):
\[ \frac{\partial C}{\partial t} = D_d \frac{\partial^2 C}{\partial x^2} - \nu \frac{\partial C}{\partial x} - \frac{(\rho / \theta)}{\partial S / \partial t} \]

\[ [1 + (\rho / \theta)(\partial S / \partial C)](\partial C / \partial t) = D_d \frac{\partial^2 C}{\partial x^2} - \nu \frac{\partial C}{\partial x} \]

\[ S = \frac{m_a}{m_s} \]

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

The graphical interpretation of those equations is presented on Figure 9.

Figure 9. Elution curves in ADS model

This form of equalization is named “equalization of confusion”, because of misunderstandings, which it evokes in researchers and may be applied in a situation when in our system we have a constant moisture content in soil (\( \theta = \text{const.} \)) or when the soil is fully saturated with water. However there do exist some computer programs based on this equalization (e.g. MT3DMS program) [29].

The main advantage of these method is that both liquid/solid ratio and pH can be suitably adjusted to the required values [30]. The L/S ratio may be related to a time scale for estimating heavy metal release with time in actual field situation. The major disadvantage is that the leaching conditions may not be exactly the same for each column, even through we tried to keep conditions similar [31]. A typical leaching column design is presented on the Figure 10.
Totshe et al. [33] applied column leaching experiments in the closed flow design mode for the description of transport of dissolved organic matter (DOM) on silica sand. As a non reactive medium chlorides were used. Figure 11 presents the obtained curves. The experiment was performed in three steps: adsorption, desorption and resorption.

The chlorides appears in the eluent after PV = 4. In the case of DOM the breakthrough curve was delayed and appear in the solution after PV = 32. During next the 15 units of PV a desorption process was observed. Resorption of DOM was much faster and occurs during next 10 PV.

Yong and co-workers applied column leaching experiments for assessment of illic materials as linear barriers having the ability to immobilize heavy metals [34]. All experiments have performed in small plexiglas columns (115x125 mm). The contamination solution containing elevated concentrations of Pb, Zn and Cu has pH = 1,6 and was pumped to the column by the pressure of 68 kPa. The experiments were carried out until five PV was reached. After this, profiles were carefully removed and
were divided to 1 cm parts. In such prepared samples total concentration of heavy metals as well as concentration of different fractions (according to Tessier selective sequential extraction procedure) were analysed.

Tam i Wong [35] applied column experiments for assumption of mobility of selected heavy metals (Cu, Zn, Mn, Cd) in soil. Profiles were divided into two tallies. The first one was saturated by heavy metals solution three times a week during 150 days. The second one was saturated by marine water as the control material. After elution step 20 cm profiles were divided to 5 cm parts. Total and exchangeable concentrations of heavy metals were analysed. The most interesting aspect of this work was creation of correlation matrix between soil properties and concentrations of HMs (Table 4).

**TABLE 4.**
Correlation matrix between heavy metals concentrations and different soil properties [35]

|          | CEC | pH | Tot  | Tot Cu | Tot Zn | Tot Cd | Tot Mn | Ext7 Cu | Ext7 Zn | Ext7 Cd | Ext7 Mn | Ext4 Cu | Ext4 Zn | Ext4 Cd | Ext4 Mn |
|----------|-----|----|------|--------|--------|--------|--------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|          |     |    |      | -0.45**| -0.02 | 0.93** | 0.90** | -0.14  | 0.75**  | 0.73**  | 0.66**  | 0.66**  | -0.25   | 0.56**  | 0.92**  | -0.20   |
|          | 0.90**| 0.09 | 0.70 | -0.02 | -0.04 | 0.16   | 0.22   | 0.14    | 0.78**  | 0.84**  | 0.87**  | 0.90**  | 0.86**  | 0.90**  | 0.86**  |
| Tot Zn  | 0.05 | 0.01| 0.04 | 0.93** | 0.97** | 0.75** | 0.79** | 0.67**  | 0.73**  | 0.84**  | 0.87**  | 0.90**  | 0.90**  | 0.90**  | 0.90**  |
| Tot Cd  | -0.00| -0.00| -0.02| 0.92** | 0.97** | 0.79** | 0.79** | 0.67**  | 0.73**  | 0.84**  | 0.87**  | 0.90**  | 0.90**  | 0.90**  | 0.90**  |
| Tot Mn  | 0.97**| 0.97**| 0.36 | 0.24   | 0.22   | 0.14   | 0.14   | 0.14    | 0.14    | 0.14    | 0.14    | 0.14    | 0.14    | 0.14    | 0.14    |
| Ext7 Cu | -0.39| -0.39| 0.24 | -0.24  | 0.75** | 0.79** | 0.67** | 0.73**  | 0.84**  | 0.87**  | 0.90**  | 0.90**  | 0.90**  | 0.90**  | 0.90**  |
| Ext7 Zn | -0.36| -0.36| 0.14 | 0.78** | 0.84** | 0.73** | 0.84** | 0.67**  | 0.73**  | 0.84**  | 0.87**  | 0.90**  | 0.90**  | 0.90**  | 0.90**  |
| Ext7 Cd | -0.16| -0.16| 0.04 | 0.89** | 0.88** | 0.90** | 0.90** | 0.90**  | 0.86**  | 0.85**  | 0.86**  | 0.86**  | 0.86**  | 0.86**  | 0.86**  |
| Ext7 Mn | 0.91**| 0.92**| -0.42| 0.39   | 0.40   | 0.31   | 0.96** | 0.96**  | -0.05  | -0.01  | -0.01  | -0.01  | -0.01  | -0.01  | -0.01  |
| Ext4 Cu | -0.33| -0.36| 0.19 | 0.83** | 0.88** | 0.78** | 0.78** | 0.78**  | 0.78**  | 0.96**  | 0.96**  | 0.96**  | 0.96**  | 0.96**  | 0.96**  |
| Ext4 Zn | -0.00| -0.03| -0.02| 0.90** | 0.94** | 0.89** | 0.90** | 0.90**  | 0.90**  | 0.90**  | 0.90**  | 0.90**  | 0.90**  | 0.90**  | 0.90**  |
| Ext4 Cd | -0.05| -0.11| -0.08| 0.89** | 0.90** | 0.95** | 0.95** | 0.96**  | 0.96**  | 0.96**  | 0.96**  | 0.96**  | 0.96**  | 0.96**  | 0.96**  |
| Ext4 Mn | 0.96**| 0.96**| -0.36| 0.22   | 0.21   | 0.13   | 0.96** | 0.96**  | -0.26  | -0.21  | -0.21  | -0.21  | -0.21  | -0.21  | -0.21  |
| OM      |     |     |      |        |        |        |        |         |         |         |         |         |         |         |         |
| CEC     |     |     |      |        |        |        |        |         |         |         |         |         |         |         |         |
| pH      |     |     |      |        |        |        |        |         |         |         |         |         |         |         |         |
| Tot Cu  |     |     |      |        |        |        |        |         |         |         |         |         |         |         |         |
| Tot Zn  |     |     |      |        |        |        |        |         |         |         |         |         |         |         |         |
| Tot Cd  |     |     |      |        |        |        |        |         |         |         |         |         |         |         |         |
| Tot Mn  |     |     |      |        |        |        |        |         |         |         |         |         |         |         |         |
| Ext7 Cu |     |     |      |        |        |        |        |         |         |         |         |         |         |         |         |
| Ext7 Zn |     |     |      |        |        |        |        |         |         |         |         |         |         |         |         |
| Ext7 Cd |     |     |      |        |        |        |        |         |         |         |         |         |         |         |         |
| Ext7 Mn |     |     |      |        |        |        |        |         |         |         |         |         |         |         |         |
| Ext4 Cu |     |     |      |        |        |        |        |         |         |         |         |         |         |         |         |
| Ext4 Zn |     |     |      |        |        |        |        |         |         |         |         |         |         |         |         |
| Ext4 Cd |     |     |      |        |        |        |        |         |         |         |         |         |         |         |         |
| Ext4 Mn |     |     |      |        |        |        |        |         |         |         |         |         |         |         |         |

where: OM, Tot, Ext4, Ext7, CEC means respectively: organic matter content, total concentration, extractable concentration (NH₄OAc extraction with pH=7 or 4) and cation exchange capacity.

Simulation of elution was carried out in in-situ conditions by Munoz and coworkers [36]. In this research sulphuric acid was applied to elute copper ions. H₂SO₄ solution was injected in 16 points on the 1x1m experimental field. 9 different points were chosen for collection of eluents. The experimental data permit to create 2-dimensional model of copper transport which includes following processes: (i) horizontal and vertical transport of Cu ions and H₂SO₄ based on the ADE equation; (ii) neutralization of sulphuric acid based on a kinetic model with the first-rate character of this process; (iii) linear sorption of different ions; (iv) extraction of Cu by acidic solution. This model was verified on the base of agreeability of experimental data with prediction data set. Difference between these two data sets was in the range of 20-22%.

Kowalkowski and Buszewski [37, 38] applied the column leaching experiment to estimate HMs transport in three different types of soils. All samples were collected in the vicinity of the city of Torun. On the basis of these soil types, three soil columns were prepared. The soil profiles were 80 cm in length and 80 mm in diameter. All profiles were treated with a 300 cm-3 solution containing four metals: zinc (2500 mg/dm-3), lead (1000 mg/dm-3), cadmium (50 mg/dm-3) and nickel (500 mg/dm-3). After one week the soil profiles were treated with an acid solution. This “acid rain” was prepared on the base of HNO₃ with a pH range from 5.0 to 2.5. At this stage eluents were taken from the profiles. During column leaching experiments 13 parameters of the soil and solution were analyzed. Correlation matrices, cluster and principal component analysis were prepared.
analyses were applied to select the adequate parameters for modeling. The division between the input and output parameters is presented in Figure 12.

Statistica Neural Networks 4.0 was used for ANNs development. These cases permit the building of 425 different structures of ANNs. The selection of the best AAN was based on the minimization of the residual mean square error (RMSE) between the experimental and predicted values. Testing cases were used for sensitivity testing and final selection of the best structure. Generalized regression neural network (GRNN) architecture was chosen. This architecture can predict heavy metals concentrations with the highest precision. The linear correlation coefficients between the experimental and predicted values are listed in Table 5.

TABLE 5.
Linear correlation coefficients between the experimental and predicted values

<table>
<thead>
<tr>
<th>Profile</th>
<th>Element</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sideric soil</td>
<td>Nickel</td>
<td>0.9623</td>
</tr>
<tr>
<td></td>
<td>Cadmium</td>
<td>0.8798</td>
</tr>
<tr>
<td></td>
<td>Lead</td>
<td>0.9853</td>
</tr>
<tr>
<td>Albic soil</td>
<td>Nickel</td>
<td>0.9880</td>
</tr>
<tr>
<td></td>
<td>Cadmium</td>
<td>0.9793</td>
</tr>
<tr>
<td></td>
<td>Lead</td>
<td>0.9894</td>
</tr>
<tr>
<td>Sandy soil</td>
<td>Nickel</td>
<td>0.9421</td>
</tr>
<tr>
<td></td>
<td>Cadmium</td>
<td>0.8702</td>
</tr>
<tr>
<td></td>
<td>Lead</td>
<td>0.9522</td>
</tr>
</tbody>
</table>

Figure 13 presents comparison between experimental and modeled breakthrough curves for nickel and cadmium in albic soil profile.
5 CONCLUSIONS AND OUTLOOK FEATURES
In order to apply the newest analytical techniques, modern environmental laboratories must be equipped with mathematical and statistical computer software. Finding correlations or other dependencies between different variables is easier with multivariate chemometrical analyses. Heavy metal transport in soil and other solid matrices is a very complicated problem, taking into account e.g. the complexity of the matrix. Chemometrical methods must be employed to develop the required model. Application of an artificial neural network seems to be the new way in these researches.

Using column leaching experiments scientists can obtain the data given from outflow only, without the possibility of inspecting the transport process inside the profile. Although the soil profile may be softly forwarded from the column after the end of the leaching experiment. This operation gives an opportunity to analyze each depth of soil profile, but acquires only present heavy metals concentration decay without any data about the passing transportation phenomena. To improve this ex-situ measuring system Buszewski and Kowalkowski [39] propose a new version of leaching column (Figure 14). The column in this mode is partitioned on separate segments connected to each other by a glass frits. To provide collection of eluants from each profile depth, the segments have a lateral tap. Therefore the researcher may control the transportation process in all heights of the column - the collection of eluant has an multidimensional character. It is possible to observe elution head movement through the profile. The lateral taps allows measurement of other soil solution parameters e.g. pH, redox potential and carbon content.
On the other hand Kosson et al. [40] proposed developing a three-dimensional system for column experiments. The tiers of this system were defined as follows: (i) Tier 1 – screening based assessment (availability) – carried out in the narrow range of properties (pH, L/S ratio); (ii) Tier 2 – equilibrium based assessment (preformed over a range of pH and L/S conditions); (iii) Tier 3 – mass transfer based assessment. Tier 1 is a screening test that provides an assessment of maximum potential of release under limits of anticipated environmental conditions, without consideration of the time frame for release to occur. Tier 2 is based on defining liquid-soild equilibrium as a function of pH and L/S ratio (chemical retention in the matrix). Tier 3 testing uses information on liquid-solid equilibrium in conjunction with mass transfer rate information (physical retention of constituents in addition to chemical retention in the matrix). Processing from Tier 1 to 3 provides increasingly more realistic and tailored, and less conservative, estimates of release, but also requires more extensive testing.

REFERENCES


