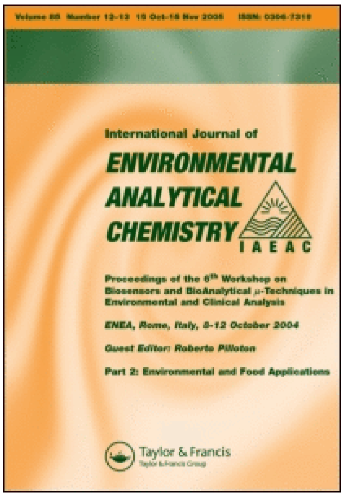
This article was downloaded by:
On: *17 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Assessment of mobility of heavy metals in two soil types by use of column leaching experiments and chemometric evaluation of elution curves

Tomasz Kowalkowski[a]; Hlanganani Tutu[b]; Leonard Mihaly Cozmuta[c]; Miroslav Sprynskyy[a]; Ewa M. Cukrowska[b]; Bogusław Buszewski[a]
[a] Department of Environmental Chemistry and Bioanalytics, Faculty of Chemistry, Nicolaus Copernicus University, 87-100 Toruń, Poland [b] Department of Environmental Analytical Chemistry, Faculty of Science, University of the Witwatersrand, Johannesburg, South Africa [c] Chemistry-Biology Department, North University of Baia Mare, Romania

Online publication date: 05 July 2010

To cite this Article Kowalkowski, Tomasz , Tutu, Hlanganani , Cozmuta, Leonard Mihaly , Sprynskyy, Miroslav , Cukrowska, Ewa M. and Buszewski, Bogusław(2010) 'Assessment of mobility of heavy metals in two soil types by use of column leaching experiments and chemometric evaluation of elution curves', International Journal of Environmental Analytical Chemistry, 90: 10, 797 — 811

To link to this Article: DOI: 10.1080/03067310903195003

URL: http://dx.doi.org/10.1080/03067310903195003

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Environ. Anal. Chem.
Vol. 90, No. 10, 20 August 2010, 797–811

Downloaded At: 13:02 17 January 2011

Assessment of mobility of heavy metals in two soil types by use of column leaching experiments and chemometric evaluation of elution curves

Tomasz Kowalkowski[a]*, Hlanganani Tutu[b], Leonard Mihaly Cozmuta[c], Miroslav Sprynskyy[a], Ewa M. Cukrowska[b] and Bogusław Buszewski[a]

[a]*Department of Environmental Chemistry and Bioanalytics, Faculty of Chemistry, Nicolaus Copernicus University, Gagarina 11, 87-100 Toruń, Poland;* [b]*Department of Environmental Analytical Chemistry, Faculty of Science, University of the Witwatersrand, Private Bag 3 WITS 2050 Johannesburg, South Africa;* [c]*Chemistry-Biology Department, North University of Baia Mare, Victoriei Str., No. 62A, Baia Mare, Romania*

(*Received 5 January 2009; final version received 22 June 2009*)

The objectives of this study were to evaluate the mobility of heavy metals (HMs) in two types of soils (acidic forest soil and neutral agricultural soil) by leaching with calcium chloride solution in column experiments. The screening properties of neutral agricultural soil towards pollution by heavy metals (Ni, Cu, Zn and Cd) are approximately 10 times higher than those of acid forest soil. The neutral agricultural soil, polluted artificially by one pore volume (PV) of an HMs solution of concentration $200\,\mathrm{mg\,L^{-1}}$, can screen the leaching of these metals over several hundreds of years. The higher apparent desorption rate and per cent desorption of HMs (especially Cd) in acid forest soil indicated a higher potential of intensive migration of the metals across the profile and indicated potential risk of Cd pollution for this type of soil. The latest approach of artificial neural networks to describe transport of HMs in soil has been also evaluated. Using a simple three-layer perceptron topology with three hidden neurons, the experimental data could be simulated. The results suggested that the pH of soil is a major factor controlling the retention of the heavy metals in the soils.

Keywords: heavy metals transport; soil pollution; column leaching experiments; artificial neural network

1. Introduction

Adsorption and precipitation are the most common processes regulating the concentration of contaminants between soil particles and soil solution. These processes are related to the type of soil, particularly the content of inorganic colloidal and organic fractions. The inorganic particles of soil play the most important role in sorption phenomena. Different types usually occur in the soil profile, namely: clay minerals, sesquioxides and hydrous oxides of minerals. The soil organic matter (SOM) is the second major component of the soil solid fraction. The term SOM is generally used to represent the organic constituents in soils including undecayed plant and animal tissues, their partial decomposition

---

*Corresponding author. Email: pinez@chem.uni.torun.pl

ISSN 0306–7319 print/ISSN 1029–0397 online
© 2010 Taylor & Francis
DOI: 10.1080/03067310903195003
http://www.informaworld.com

products, and the soil biomass [1]. 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. SOM consists of humic and non-humic substances. Non-humic 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 [2]. Humic substances are the other unidentifiable component. From the perspective of the sorption properties of soils, humic substances are of primary importance. The SOM may range from 0.1% in desert soils to 90% in organic soils. Humic substances make up approximately 85–90% of the total organic carbon (OC) in soils.

The transport mechanisms of HMs through soils and other environmental matrices has long presented great interest to both environmental and soil scientists because of the possibility of groundwater contamination through metal leaching [3]. A number of models have been developed to quantitatively predict transport and sorption of HMs in the soil. The models can be divided into three groups:

- models with electrostatic and bonding forces taken into account;
- simple models that do not include this interaction;
- statistical models that do not include any theoretical information on sorption phenomena.

In common classical models belonging to the second group, the sorption process is often described by the Langmuir or Freundlich isotherms or their modifications, e.g. Competitive Freundlich Adsorption Model (CFAM) or Modified CFAM (MCFAM) which are used in the case of extremely heterogeneous surfaces [4]. Heavy metals sorption in the soil is well described by the Langmuir equation at low concentrations, whereas the Freundlich isotherm is necessary at high concentrations of evaluated chemical component [5]. Other less popular models from this group are based on exponential equations. The equation proposed by Kowalkowski [6] is characterised by a constant and high value of metal concentration in the top layer and exponential decrease of this concentration with depth. It can easily fit the adsorption/elution data from the soil leaching tests. The free coefficient of this equation permits to observe transportation of metallic ions in the superficial layer of the soil.

The models described above enable the prediction of linear or linearised sorption curves. The sorption of contaminants by soil particles may have also non-linear character. Typical non-linear models are: model of constant capacity, model of diffusion layer and model of triple layers [7]. In these models, the adsorption of ionic matter onto the soil surface takes place due to the presence of charges. This assumption is based on the equation showing that the thermodynamic constant K can be represented as the product of $K_{\text{interaction}}$ (specific, independent of the charge influence between the bonded ion and active site) and $K_{\text{electrostatic}}$ (responsible for the interactions between the ion and electrostatic potential in active site). The second basic element of these models is the assumption that the clean solid phase contains only one kind of active sites.

In opposition to the sorption models, the modelling of transport of inorganic pollutants can still be considered as a research field that needs exploration. Many mathematical or physical transport models of different chemical pollutants in the soil matrix are described in literature [8]. They are usually very complicated and require many parameters for modelling, or they are just simple physical equations of transport inside the solids, ignoring the interaction between the chemical constituent and the soil matrix.

Downloaded At: 13:02 17 January 2011

These models also contain some approximations and assumptions which significantly modify the description of transport phenomena. The results obtained on the basis of these models are not always compatible with real measurements in the natural environment [9].

One group of the commonly used models is based on dispersion-convection-sorption equations [10]. This form of equations is called 'equations of confusion' because of misunderstandings it causes among researchers. The models may be applied in a situation where constant moisture content of the soil appears ($\theta = \text{constant}$) or where the soil is fully saturated with water. However, there are some computer programs based on this equation (e.g. MT3DMS program) [11].

The modern approach to modelling sorption and transport of heavy metals in the soil is based on kinetic research of transport phenomena [12–15] involving speciation of metals in porous media [16–19] and chemometric interpretation of obtained results [20] or geochemical modelling of the investigated system. Scientists can simulate natural soil conditions and behaviour of heavy metals *in-situ* or *ex-situ*, for example in leaching column experiments, and then try to use some chemometric methods to describe the results [21]. Chemometrics enables the description of environmental phenomena without determining what mechanisms were responsible for these processes or, in other words, without applying theoretical assumptions required in physiochemical models [22]. The possibility to analyse multi-dimensional data sets without information about spatial locations is one of the advantages of multivariate statistics. As stated by Einax [23], the complexity and the large variance of environmental sets limits the use of common statistical methods for the assessment of the state of pollution such that the application of geostatistical and multivariate statistical methods is highly recommended. Classification methods are most often used to interpret spatial distribution of pollutants. Facchinelli [24] used multivariate statistical methods such as PCA and CA to predict potential non-point heavy metal sources in the soil on a regional scale. GIS-supported software was used for data presentation. In contrast to this, Yao [25] utilised a geostatistical linear model of coregionalisation (LMC) to estimate the concentrations of selected heavy metals at unsampled points on the basis of a spatial correlation between their properties at different locations. In this study, 359 sampling points were used (259 were applied to constrain the model and the other 100 to cross-validate it). The most important feature of this data set was that several attributes were significantly cross-correlated, which allowed to test the purposed algorithm (LMC). A very interesting baseline regression model for a variety of components on Al was introduced by Hanson [26]. Based on covariation of elements at 15 estuaries remote from contaminant inputs, linear regressions of metals on Al were used to model the metal content of baseline sediments. A geochemical model of covariation was developed, verified and used. Some of the methods were also applied to sorption data. Covelo *et al.* [27,28] used classification and regression trees (CARTs) to explore the relationship between sorption phenomena and soil properties.

One of the newest approaches of transport modelling is based on the utilisation of artificial neural networks. This tool has proved to be very efficient for simulating the behaviour of HMs in soils [21,29] and other pollutants [30]. Since 1958, when the psychologist Frank Rosenblatt [31] developed the 'perceptron', a pattern-recognition device with learning capabilities, artificial neural networks (ANNs) have been widely used. They represent simplified models of natural nerves or natural neural networks. The correct final parameters are obtained as ANN output by proper modification of the original parameters in accordance with the errors that the network makes in the process. All these learning methods minimise the error between the predicted and observed output values.

Downloaded At: 13:02 17 January 2011

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

The objectives of our study were to assess the availability of HMs in two types of soils (acidic forest soil and neutral agricultural soil) by leaching with calcium chloride in column experiments. The study uses the latest approach to HMs transport modelling by artificial neural networks to enhance data interpretation.

2. Experimental

Two types of soil were utilised in the study. Both were taken from Piwnice in the vicinity of Torun (Poland). Only the top layer of soil (50 cm) was used. One of the profiles, identified as an albic soil, was taken from the Nature Reserve Park ('Piwnicki' area). This forest, with 400-year-old oaks and 200-year-old pines, is located far from any anthropogenic input. The second soil profile of sideric soil was collected at agricultural fields near the park. Two layers were identified within both profiles. This choice of soil was made to compare transport characteristics in soil intensively used by agriculture with uncontaminated and fragile forest soil. The samples were initially dried at room temperature and were sieved after 48 h to obtain a particle size smaller than 1 mm. Moisture, volumic density, pH and cationic exchange capacity (CEC) were evaluated in these soil samples. The mechanical analysis of the soil samples was carried out using the hydrometric method with isolation of clay, silt and sand fractions.

Two glass columns (50 mm × 800 mm) were used to perform leaching tests on both soils. The experiments were performed in parallel to minimise the differences between the columns. Research done before using these columns indicates good reproducibility of results [32] due to optimal diameter to height ratio. Both soil profiles consisted of two layers: 500 mL of each layer. Both profiles had the same height of 500 mm. The columns were filled with the solution from the bottom of the column to wet the soil to its surface. The pore volumes (PV) of both beds were measured volumetrically, defined as the maximum volume of a solution that fills all pores in the soil profile [22]. This parameter has been used as a time domain of the experiment and to secure the same scale even when the profiles differ in porosity. A volume of 412.5 mL of water filled the forest soil bed, while 337.5 mL was sufficient to saturate the agricultural soil bed. Such prepared beds were treated with a volume of 1 PV solution containing a mixture of heavy metal ions consisting of 200 $\mathrm{mg\,L^{-1}}$ of each metal. The HM solution and soil were allowed to contact for 24 h until equilibrium was reached and this was followed by leaching with a 0.01 M $CaCl_2$ solution adjusted to a pH of 5.76 using HNO_3. This solution can be considered as a model electrolyte solution for soil with natural pH [33]. The application of high concentrations of metals was adopted from calculations of sorption capacity obtained in previous static experiments. Five PVs of the model solution were percolated through each profile.

The nitrates of the selected HMs (Cu, Cd, Ni and Zn) used in experiments were supplied by POCH, Poland. Stock solutions of nitrate salts and all solutions used in the study were prepared with deionised water.

Downloaded At: 13:02 17 January 2011

Downloaded At: 13:02 17 January 2011

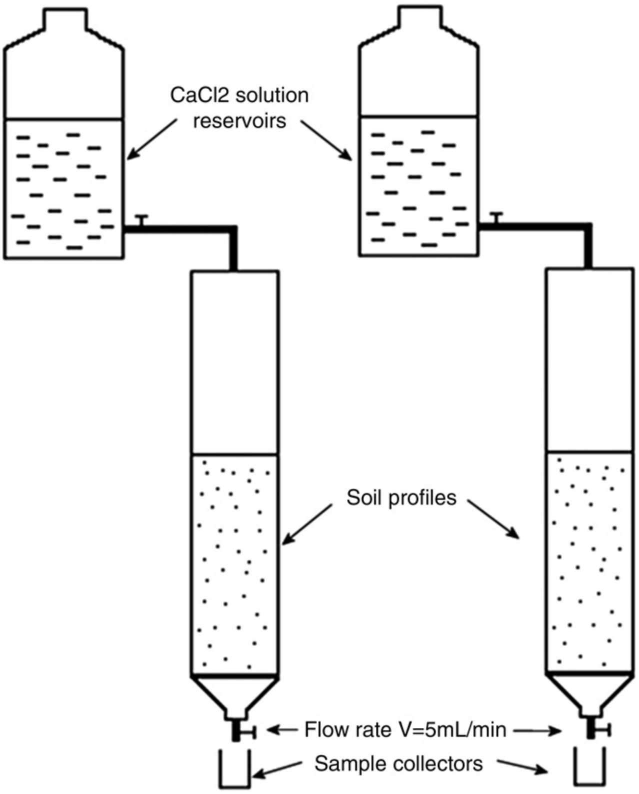


Figure 1. Set-up of column leaching experiment.

The exchange of solutions in columns was performed in a closed system as shown in Figure 1.

A fixed flow rate of $5\,\mathrm{mL\,min^{-1}}$ was maintained during the entire experiment. The leaching experiment was performed continuously to avoid any equilibrium states. The leachate samples were collected in 50 mL plastic containers and analysed by FAAS (AAnalyst 800, Perkin Elmer, Shelton, USA) and automatic total organic carbon analyser (TOC-5000, Shimadzu, Kyoto, Japan). The pH and conductivity of samples were also measured using the appropriate probes (Elmetron, Zabrze, Poland) connected with multimeter CX-732 (Elmetron, Zabrze, Polska).

A simple ANN has been utilised to predict the behaviour of HMs in both profiles under experimental conditions. One thousand different topologies of multi-layer perceptron networks have been tested using Statistica DataMiner 7 (Statsoft, Tulsa, USA). The back propagation algorithm was used as a training method. The selection of the best topology was based on two criteria: small testing error and simplicity of ANN structure. The selected topology was retrained using the conjugate gradients method. Four parameters were used as input values: organic carbon (OC), inorganic carbon (IC) concentration, pH, and electrical conductivity (EC) values. The concentration of four HMs was the output of the model. The selected ANN consists of only two hidden neurons responsible for the modelling with linear aggregation function and linear function with

Table 1. Topology of artificial neural network applied in the study.

No. of layer	No. of neurons	Aggregation function	Activation function
1	4	Linear	Linear
2	2	Linear	Linear with saturation
3	4	Linear	Logistic

Table 2. Characteristics of soil layers used in the study.

Acronym of layer	Moisture [%]	Volumic density [g cm^{-3}]	CEC [mmol (+)/ 100 g]	pH	Granulometric composition (%)* Clay	Silt	Sand
Forest top	1.38	1.063	8.24	4.89	9.1	3.0	87.9
Forest bottom	0.81	1.380	7.32	5.15	5.2	2.9	92.0
Agricultural top	1.24	1.376	9.35	6.18	7.4	27.2	63.4
Agricultural bottom	0.89	1.345	8.72	6.39	13.4	30.6	56.0

Note: *Particle-size: Clay – <0.002 mm; Silt – 0.063–0.002 mm; Sand – 1.02 –0.063 mm.

Downloaded At: 13:02 17 January 2011

saturation as an activation function. The characteristics of ANN topology used in the study are presented in Table 1.

3. Results and discussion

The physical-chemical characteristics of the studied soil layers are presented in Table 2. Some slight variations between the top and bottom layers of the agricultural soil can be observed, for instance the lower moisture content, CEC and pH values in the bottom layer compared to the top layer. This could be attributed to the fact that the top layers in both cases have higher organic content which can enhance CEC in this layer. However, forest soil is characterised by bigger differences in the analysed parameters. It could be related with no agricultural activity such as tillage.

Figure 2 shows pH, EC, IC and OC changes during leaching experiments for agricultural soil while the HM elution curves are presented in Figure 3. It can be observed from both figures that the concentration of HMs in the leachates is small (varying from 0.1 mg L^{-1} for cadmium to 0.6 mg L^{-1} for zinc). This relates to the slightly elevated pH of the soil. The pH remained buffered between 5.5 and 6.5 during the experiment. Moreover, no simple correlation between HMs content and carbon species or pH was observed. The observation of the elution curve in the PV range between 0 and 1 gives information about the non-sorbed fraction of metals during equilibrium states. Metal concentrations in PV1 show that almost 100% of all four metals were sorbed by the agricultural soil in the equilibrium state. Sorption efficiency was 99.96%, 99.98%, 99.88% and 99.99% for Ni, Cu, Zn, and Cd, respectively (see Table 3). During PV1 of the eluent, relatively higher concentrations of zinc were eluted compared to the other HMs. It was found that 20.1% of the total eluted amount of zinc was released during this step of the experiment, while the values for the rest of the metals was much smaller: 9.4%, 13.0% and

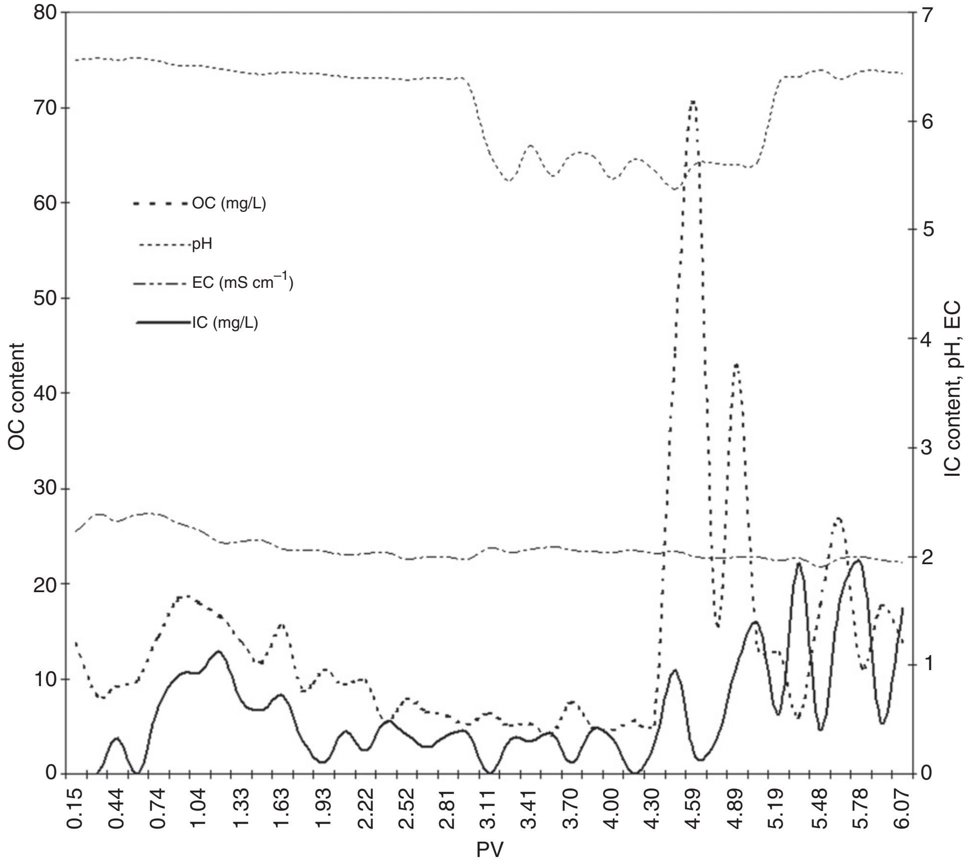


Figure 2. Elution curves of OC, IC, pH and EC in agricultural soil.

Downloaded At: 13:02 17 January 2011

14.2% for Cd, Cu and Ni, respectively. The rest of the elution curve (PV2–PV6) shows that metals are relatively strongly bonded to soil particles. The amount of metals desorbed by the $CaCl_2$ solution generally did not exceed 0.1% (0.04% for Ni, 0.02% for Cu, 0.06% for Zn and 0.01% for Cd). Those values are negligible because they are comparable with uncertainty of analytical procedure. If we suppose that leaching by the studied $CaCl_2$ solution is twice as strong as leaching by atmospheric precipitation (about 700 mm per year (70 mL cm^{-2}) for this region), it may be calculated that leaching of the corresponding amount of the HMs from this soil column (PV for agricultural soil –337.5 cm^2, diameter of column 5 cm with area of cut 19.6 cm^2) will occur for more than 4000 years. The calculations are based on assumptions that: mean yearly filtration is 1372 mL (equals to ~4 PV), desorption is stable and amount of HM desorbed by atmospheric precipitation will be the same as desorbed by 0.01 M $CaCl_2$ solution. Then the time needed to desorb 100% of HM from soil will be 10,000 years for Cd, 5000 years for Cu, 2500 years for Ni and 1600 years for Zn (on average higher then 4000 years). Such estimations are very rough and do not reflect reality fully because it assumes constant conditions of the natural system. The efficiency of metal desorption by the $CaCl_2$ solution may be considered as an evaluation criterion of the strength of metal-soil particle bonds and mobility of the metals

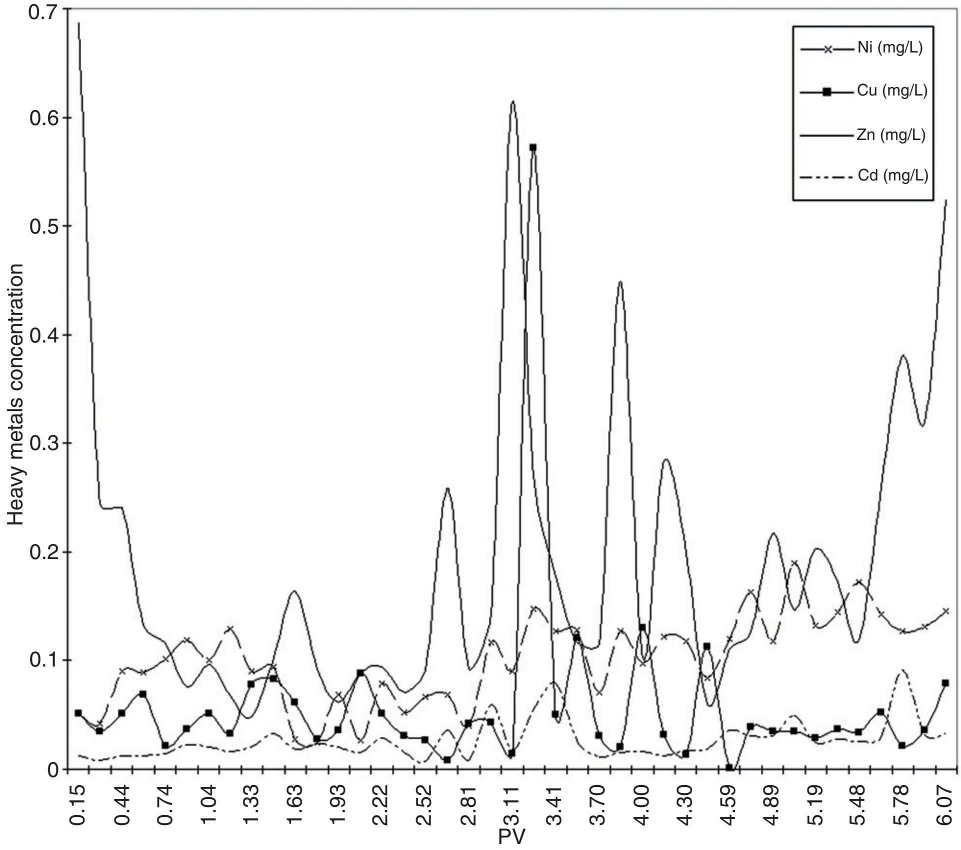


Figure 3. Elution curves of heavy metals in agricultural soil.

Downloaded At: 13:02 17 January 2011

Table 3. Gross amount of heavy metals eluted and adsorbed in soil column during the experiment.

	Amount of HM absorbed in soil column, mg				Amount of HM eluted in PV1, mg				Amount of HM eluted in PV2–PV5, mg			
	Ni	Cu	Zn	Cd	Ni	Cu	Zn	Cd	Ni	Cu	Zn	Cd
Agricultural	67.47	67.48	67.4	67.49	0.03	0.02	0.08	0.01	0.2	0.11	0.32	0.05
Forest	82.2	83.34	81.37	81.04	0.25	0.16	1.13	1.46	4.48	1.28	2.9	4.19

in polluted soils. HMs mobility in this type of soil (transition to solution) is in the following order: Zn > Ni > Cu > Cd. The highest estimated mobility of Zn is obviously caused by the fact that these ions occur mainly in the exchangeable form that may be relatively easily released by $CaCl_2$ [34].

The strong bonding of copper and cadmium in soil may be due to the formation of their stable complexes with humified organic matter. The possibility of such complexes forming has been investigated in several studies [e.g 35,36]. It is also known that metal complexes with humic acids are less mobile and have significantly low solubility especially in acidic media [37]. In this case, a buffer effect becomes apparent regarding HMs migration [38]. Sorption data reported by Lair *et al*. [39] also demonstrates the fact that Cu ions were mainly sorbed by organic compounds and bound as immobile organic forms. According to their paper, desorption of Cd ions is higher from the minerals than from the organic phase. These results may be extrapolated to similar results obtained in our experiment and related to the strong binding of Cu and Cd ions to humified organic matter of soils.

However, the importance of clay and silt particles in HMs binding phenomena should not be neglected. In particular, positive correlation between clay content, Ni and Cd amounts in soil was established by Papadopoulos. Evaluation of 750 samples of different soils also indicated positive correlation between the concentration of Zn and sand content [40]. Other results [39] show that desorption of Cd and Zn is higher from the mineral phase than from the organic matter. Cu ions are less sorbed onto the mineral phase than they are to the organic phase.

Figures 2 and 3 show that the contents of dissolved OC and IC were not changed much during the elution. However, in the range of the filtrate volumes PV 4–PV 6 a general increase of both carbon forms in leachate was observed. In this PV range, Ni and Zn concentrations are also increased. Statistics do not show a significant relation between OC, IC and the metals concentrations. Only a relation between IC and Ni is significant on a $p = 0.01$ level; however, linear correlation coefficient does not show simple correlation either ($r = 0.43$). It should be noted that these variations in OC and IC as well as the concentration peaks were asynchronous. This relation may be explained by the assumption that some part of the Ni is bound to the oxygen or hydroxyl functional groups of dissolved organic compounds while Zn is bound to the carboxylic functional groups of dissolved organic compounds.

The pH values of leachates from the agricultural soil profile ranged from 5.5 to 6.5 during the leaching process. Low pH values were observed between PV 3–PV 5 with a corresponding increase of metal concentrations (in particular Zn and Ni) in the eluent (see Figures 2 and 3). This may be attributed to the displacement of prior sorbed metals as well as H^+ ions from sorption positions in soil particles (most likely the organic ones) by Ca^{2+} ions from the $CaCl_2$ solution. The slight variations of electrical conductivity in this case may also indirectly point to the domination of the exchange role of Ca-ions in the filtration process.

A totally different situation was observed for the forest soil profile (Figures 4 and 5). The biggest fraction of metals was eluted with the first volume of solution. Transport of other fractions (at $PV > 1$) is related with the change of solution from water to $CaCl_2$ solution. Calcium ions dramatically change the sorption ability of HMs. This effect was not visible in the agricultural profile. The concentration of selected HMs in the leachates was higher compared to agricultural soil. The sorption ability of HMs on forest soil was also lower. According to the metal concentration at PV 1, the forest soil column sorbed 91.96% of Ni, 99.80% of Cu, 98.61% of Zn and 98.21% of Cd in equilibrium states. The part of leached metals in relation to their sorbed amount in equilibrium state were: Ni–4.28%; Cd–4.19%; Zn–2.91% and Cu–1.28%. After PV 4, the amount of leached metals was increased and one PV of the leakage contained the following amounts of metals: 0.36% Ni, 0.23% Cu, 0.37% Zn and 0.44 Cd. It may be concluded that mobility of HMs in forest soil is approximately a dozen times higher than in the agricultural profile. The order of migration ability for forest soil was also different: Ni > Cd > Zn > Cu.

Downloaded At: 13:02 17 January 2011

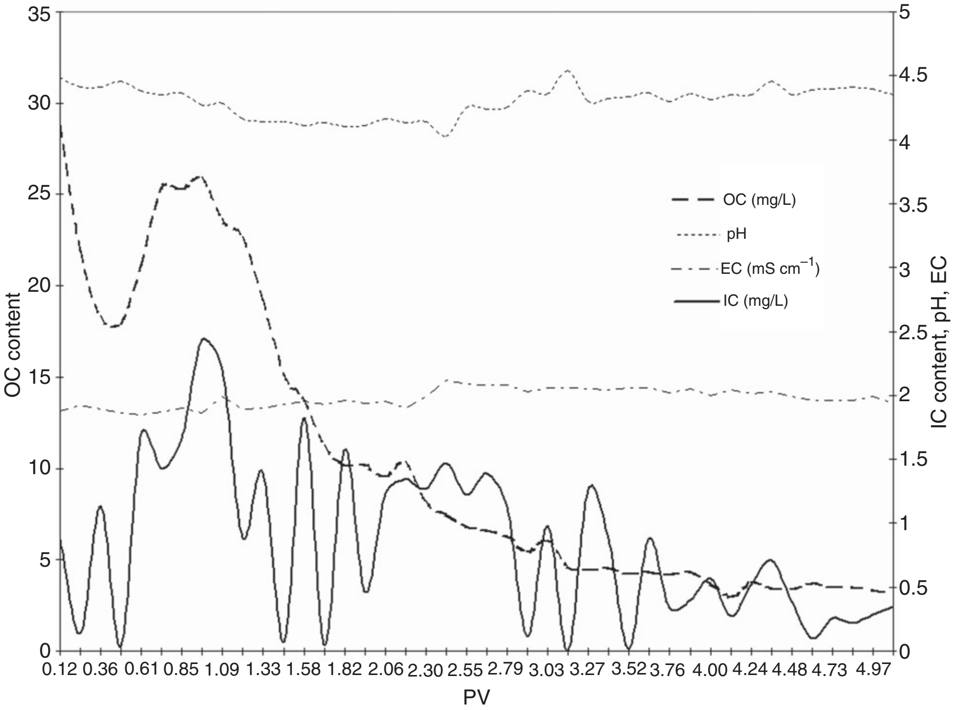


Figure 4. Elution curves of OC, IC, pH and EC in forest soil.

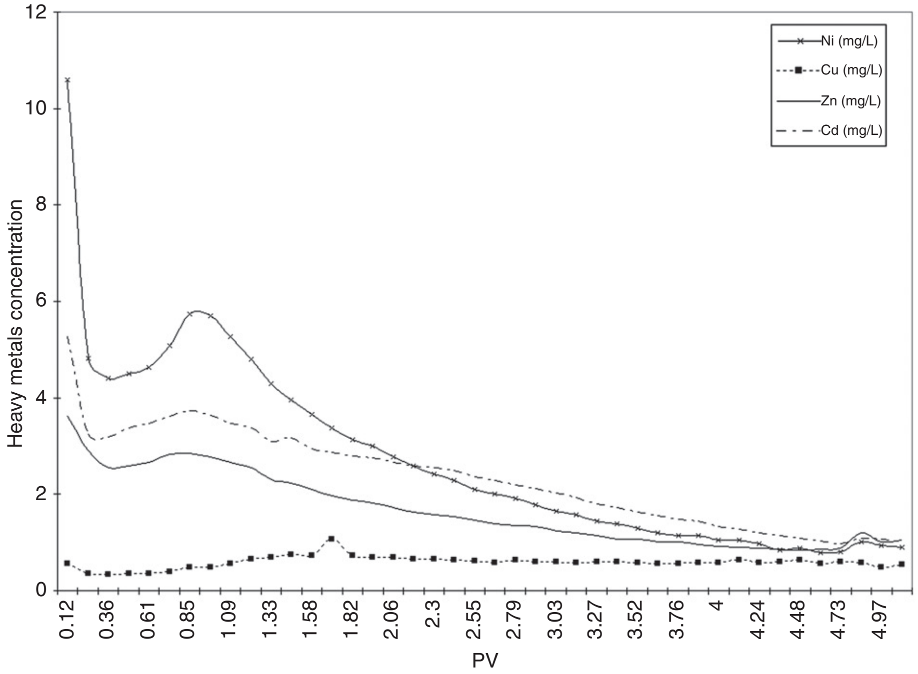


Figure 5. Elution curves of heavy metals in forest soil.

Downloaded At: 13:02 17 January 2011

Copper was the most strongly bound by soil while nickel and cadmium had the weakest bonding ability. The findings are in agreement with previous studies [e.g. 41,42].

One has to keep in mind that the conditions created during the experiment can be far from those occurring in a natural system. It is obvious that in leaching tests water saturation is kept at maximum which reflects heavy rain or flooding events in the environment. The periods of drought or dry weather are not simulated by the column tests. Structure of SOM and even inorganic fractions are changing during this period; this has an effect on sorption ability. This example clarifies the disadvantage of the simulation methods. Notwithstanding, there is no other possible simulation to assess the transport of pollutants in heterogeneous media. It has obviously a major share in variations between simulated and real concentrations of pollutants. Another, much faster option is usage of computer software, such as geochemical models, but this usually gives much higher error related to a simplified description of processes and heterogeneity of materials.

The high migration ability of Cd, Ni and Zn in forest soil points to the danger of utilisation of different fertilisers containing high amounts of these metals, such as phosphates or some sewage sludge for this type of soil.

The migration is related specifically to the relatively low pH of forest soil. The pH value of all samples was quite stable having a mean value of 4.3 with 3% variation. Moreover, the HMs transport was strongly related with OC content in leakage. It should be noted that contents of OC in leakage from the forest soil profile were in the range of 17–28 $\mathrm{mg\,L^{-1}}$ only for PV1 with a gradual decrease in the following volumes from 17 to 5 $\mathrm{mg\,L^{-1}}$ with only slight variations. Figure 4 shows a decrease in metal concentration in the leachates with decrease of total organic carbon (OC). This relation is expressed by a logarithmic equation:

$$\mathrm{C_{Me} = a + b * \ln OC} \tag{1}$$

where $\mathrm{C_{Me}}$ is the concentration of metals; a and b are constants; and OC is total organic carbon.

Correlation coefficients for the three metals (Ni, Zn and Cd) are presented in Table 4. High values of coefficients were obtained while Cu did not show any correlation.

The dependence of copper concentration on organic carbon was not so obvious, probably because of the relatively strong sorption of this metal in the soil profile. It is well known that metals which readily hydrolyse in water (e.g. $\mathrm{Cu^{2+}}$, $\mathrm{Pb^{2+}}$ and $\mathrm{Zn^{2+}}$) alter the surface charge properties of adsorbents such as silica so that they behave like the respective metal hydroxides [43]. This is chemisorption and is described by the equation:

$$\mathrm{Si-OH + Cu^{2+} \rightarrow Si-OCu^{+} + H^{+}}$$

Table 4. Coefficients of logarithmic equations ($\mathrm{C_{Me} = a + b * \ln OC}$) and correlation coefficients for selected metals in forest soil.

	a	*b*	*r*
Ni	−2.37	2.46	0.9164
Zn	−0.36	0.98	0.9751
Cd	−0.33	1.28	0.9607

Downloaded At: 13:02 17 January 2011

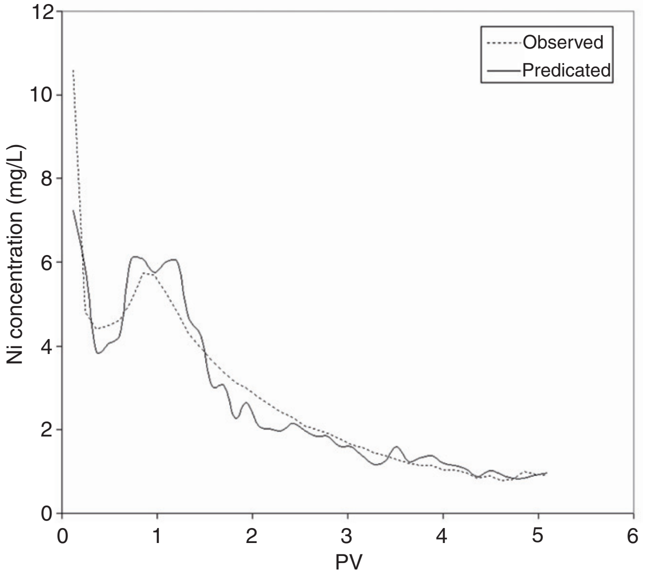


Figure 6. Predicted versus observed concentrations of nickel in the leakage from forest soil.

Downloaded At: 13:02 17 January 2011

This reaction occurs around pH 4–5. Metal affinity for the silanol groups of silica follows the order: $Pb^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Ni^{2+} = Cd^{2+} > Sr^{2+} > Mg^{2+}$ [44,45]. This sequence is consistent with the tendency of the metals to hydrolyse [46].

The established difference of sorption capacity and mobility of HMs for the two soil types is obviously related to the difference in their granulometric composition. The part of silt and clay particles is higher in agricultural soil (see Table 2). Forest soil contains a higher amount of well soluble organic compounds (see Figure 4). HM correlation with OC followed the order: $Ni \geq Cd > Zn \gg Cu$.

For the forest soil, the total amount of metals eluted during the entire experiment (five exchanges of solution in the soil profiles) is small (Table 3).

An adequate ANN model was developed to simulate HMs transport from both soil profiles. The model has simple topology, due to a strong relation between OC and HM concentration in forest soil. Slightly higher differences were observed for the agricultural profile; however, obtained correlation coefficients between observed concentrations versus predicted ones for the entire dataset were as follows: 0.9375; 0.9181; 0.9640 and 0.9561 for nickel, copper, zinc and cadmium, respectively. It indicates good efficiency of simulation. Figure 6 presents an example of predicted concentrations of nickel in leakage from the forest profile compared to the experimental data. Some slight variations were related with small resolution of experimental results, application of analytical technique that enhance resolution of experimental data like online coupling AAS with the soil column may reduce variance between experimental and estimated results.

With ANN, the data were additionally classified according to the type of soil profile. This classification is based on sign of weight of hidden neurons. The opposite signs for hidden neurons were observed for data representing the forest profile and the agricultural profile, respectively. It seems that neurons responsible for modelling are recognising data from particular profiles. This indicates different characteristics of transport mechanisms

Table 5. Sensitivity analysis of ANN input parameters.

	pH	EC ($mS * cm^{-1}$)	IC ($mg\,L^{-1}$)	OC ($mg\,L^{-1}$)
Ratio	5.0	1.1	1.1	2.8
Rank	1	3	4	2

within the studied profiles. Moreover, the sensitivity analysis of the input parameters (see Table 5) indicates the order of importance of input parameters. The primary factor limiting the mobility of HMs in examined soil profiles is pH while release of organic carbon is related to the transport of investigated metals.

4. Conclusions

The transport ability of investigated heavy metal ions was rather small under experimental conditions. The agricultural use of soil, especially fertilisation with organic and inorganic compounds, boosts the sorption capacity of soil. Migration of HMs across the agricultural profile is very slow and quite insignificant under investigated conditions. In contrast to this, forest soil had a smaller sorption ability and the concentrations of HMs in leachates were relatively higher. This type of soil is also sensitive to changes in solution composition. Addition of Ca^{2+} ions reduces the binding ability of HMs as Ca^{2+} tends to displace the HMs. The problem of contamination of natural soil is more important due to the leaching ability of HMs in this type of profile. The screening properties of neutral agricultural soil towards pollution by HMs (Ni, Cu, Zn and Cd) are higher than those for acid forest soil.

The higher apparent desorption rate and per cent desorption of HMs (especially Cd) in acid forest soil indicated a higher potential of intensive transport of HMs across the profile of this soil and indicated potential danger of Cd pollution for this type of soil.

The application of statistics helps to identify relations between investigated parameters. Regression analysis points out a strong correlation between organic carbon and HM concentrations while the ANN model estimates amounts of metals in leachate and classifies soil profiles with respect to pH, EC, IC and OC. The results of sensitivity analysis suggest that the pH of soil is a major factor controlling the mobility and retention of the HMs in the soils.

Downloaded At: 13:02 17 January 2011

Acknowledgements

This work was supported by Ministry of Science and Higher Education Grant No. N N523 1054 33, Polish-South African bilateral programme, and CEEPUS II Project No. CII-PL-0004-04-0809 PL-130-05/06.

References

[1] M.M. Kononova, *Soil Organic Matter* (Pergamon, Oxford, 1966).
[2] J.E. Giesking, *Soil Components, Organic Compounds* (Springer-Verlag, New York, 1975), Vol. 1.
[3] A. Dube, R. Zbytniewski, T. Kowalkowski, E. Cukrowska, and B. Buszewski, Pol. J. Environ. Stud. **10**, 5 (2001).

[4] F. Bayracharya, S. Vinneswaran, and A. Das Gupta, Wat. Qual. Hydrol. **10**, 19 (1996).
[5] H. Kun-Huan and H.L. Dar-Yaun, Soil Sci. **2**, 115 (1998).
[6] T. Kowalkowski, A. Jastrzębska, J. Mierzwa, and B. Buszewski, Toxic. Environ. Chem. **78**, 199 (2001).
[7] D.G. Strawn, A.M. Scheidegger, and D.L. Sparks, Environ. Sci. Technol. **32**, 2596 (1998).
[8] L. Hinz and H.M. Selim, Soil Sci. Soc. America J. **58**, 1316 (1994).
[9] M.E. Hodson and S.J. Langan, Environ. Pollut. **104**, 11 (1999).
[10] G.H. Bolt, *Soil Chemistry* (Elsevier Scientific, New York, 1979).
[11] C. Zheng and P.P. Wang, *MT3DMS: A Modular Three-dimensional Multi species Transport Model for Simulation of Advection, Dispersion and Chemical Reactions of Contaminants in Groundwater Systems* (Department of Geology and Mathematics, University of Alabama, Tuscaloosa, 1998).
[12] P. Quevauviller, G. Rauret, J.F. Lopez-Sanchez, A. Ure, and H. Muntau, *Three-step Sequential Extraction Procedure for the Determination of the Extractable Contents of Trace Metals in Sediment*. Report of the European Commission's Standards, Measurements and Testing Programme (BCR) of DG XII (Luglio, 1999).
[13] P. Quevauviller, A. Ure, H. Muntau, and B. Griepink, Intern. J. Environ. Anal. Chem. **51**, 129 (1999).
[14] P. Quevauviller, H.A. Van der Sloot, A. Ure, H. Muntau, A. Gomez, and G. Rauret, Sci. Tot. Environ. **178**, 133 (1996).
[15] G. Rauret, J.F. Lopez-Sanchez, A. Sahuquillo, R. Rubio, C. Davidson, A. Ure, and P. Quevauviller, J. Environ. Monit. **1**, 57 (1998).
[16] A. Bermond, I. Yousfi, and J.P. Ghestem, The Analyst **123**, 785 (1998).
[17] C. Brunori, C. Cremisini, L. D'Annibale, P. Massanisso, and V. Pinto, Anal. Bioanal Chem. **381**, 1347 (2005).
[18] Q.J. Song and G.M. Greenway, J. Environ. Monit. **6**, 31 (2003).
[19] Q.J. Song and G.M. Greenway, Intern. J. Environ. Anal. Chem. **88**, 359 (2006).
[20] M. Otto, *Chemometrics* (Wiley-VCH, New York, 1998).
[21] B. Buszewski and T. Kowalkowski, Environ. Eng. Sci. **23**, 589 (2006).
[22] J. Einax, *Chemometrics in Environmental Chemistry – Statistical Models* (Springer, Berlin, 1995).
[23] J.W. Einax, H. Zwanziger, and S. Gneiss, *Chemometrics in environmental analysis* (VCH, Weinheim, 1997).
[24] A. Facchinelli, E. Sacchi, and L. Mallen, Environ. Pollut. **114**, 313 (2001).
[25] T. Yao, Geoderma **88**, 13 (1999).
[26] P.J. Hanson, D.W. Evans, and D.R. Colby, Mar. Environ. Res. **36**, 237 (1993).
[27] E.F. Covelo, J.M. Matías, F.A. Vega, M.J. Reigosa, and M.L. Andrade, Geoderma **147**, 75 (2008).
[28] F.A. Vega, J.M. Matías, M.L. Andrade, M.J. Reigosa, and E.F. Covelo, J. Hazard. Mater. **167**, 615 (2009).
[29] F. Amegashie, J.Q. Shang, E.K. Yanful, W. Ding, and S. Al-Martini, Can. Geotech. J. **43**, 100 (2006).
[30] J. Langman, Inzynieria Rolnicza. **1**, 153 (1999).
[31] F. Rosenblatt, *Principles of Neurodynamics: Perceptrons and the Theory of Brain Mechanisms* (Wiley, New York, 1962).
[32] T. Kowalkowski and B. Buszewski, J. Environ. Sci. Health A **44**, 522 (2009).
[33] K. Michel, M. Roose, and B. Ludwig, Geoderma **140**, 207 (2007).
[34] Z. Li and L.M. Shuman, Environ. Pollut. **95**, 219 (1997).
[35] H.B. Bradl, J. Colloid Interf. Sci. **277**, 1 (2004).
[36] E.F. Covelo, F.A. Vega, and M.L. Andrad, J. Hazard. Mater. **140**, 308 (2007).
[37] G.H. Bolt, M.F. de Boodt, M.H.B. Hayes, and M.B. McBride, *Interactions at the Soil Colloid-soil Solution Interface* (Kluwer Academic, The Netherlands, 1991).

Downloaded At: 13:02 17 January 2011

[38] D.V. Ladonin and S.E. Margolina, Zeszyty Problemowe Postepow Nauk Rolniczych **448b**, 169 (2007).

[39] G.J. Lair, M.H. Gerzabek, and G. Haberhauer, Environ. Chem. Lett. **5**, 23 (2007).

[40] A. Papadopoulos, C. Prochaska, F. Papadopoulos, N. Gantidis, and E. Metaxa, Environ. Manage. **40**, 719 (2007).

[41] G. Kandpal, P.C. Srivastava, and B. Ram, Water Air Soil Pollut. **161**, 353 (2005).

[42] A. Voegelin, K. Barmettler, and R. Kretzschmar, J. Environ. Qual. **32**, 865 (2003).

[43] R.O. James and N.J. Barrow, in *Copper in Soils and Plants*, edited by J.F. Loeragan, A.D. Robson, and R.D. Graham (Academic Press, New York, 1981), p. 47.

[44] D.L. Dugger, J.H. Stanton, B.N. Irvy, W.W. Cummings, and R.W. Maatman, J. Phys. Chem. **68**, 757 (1964).

[45] P.W. Schindler, B. Furst, B.R. Dick, and P.U. Wolf, J. Colloid Interface Sci. **55**, 469 (1976).

[46] J. Gerth and G. Brummer, Fresenius J. Anal. Chem. **316**, 616 (1983).

Downloaded At: 13:02 17 January 2011