

Interactions between Metal Ions and Biogeo-Surfaces in Soil and Water

Basis for Quantitative Risk Assessment

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Propositions

1. Soil acidification will not only lead to increased concentration of heavy metals in the soil solution, but also to a shift towards more nonspecific cation-exchange type binding, especially for the metals of Cd, Zn and Ni.
(This thesis)
2. The characterization of humic acid transport in the acid sandy soil could be explained by the coagulation of humic acid, while for fulvic acid the adsorption to soil matrix was more likely the process that controls its solubility and mobility.
(This thesis)
3. The contribution of individual sorbents to the control of heavy metal speciation may be difficult or impossible to experimentally identify.
Mattigod S.V. & Zachara J. M. In *Methods of Soil Analysis. Part 3-Chemical Methods*" p1309-1358. SSSA, Madison.
4. In fact, it is often believed that modelers fail to recognize the difference between the real world and the models they make of it. Model users should realize that it is impossible to make perfect predictions of real world behavior.
Van Leeuwen C.J. & Hermens J.L.M. *Risk Assessment of Chemicals: An Introduction*. Dordrecht, Kluwer, 1995.
5. The beginning of wisdom is to call things by their right names.
6. Being in a small country does not necessarily mean that you realize the existence of the national boundaries more easily than in a big country.

Propositions belonging to the Doctoral Thesis entitled:
"Interactions between Metal Ions and Biogeo-Surfaces in Soil and
Water. Basis for Quantitative Risk Assessment"
By Liping Weng.

常記溪亭日暮，

沉醉不知歸路。

興盡晚回舟，

誤入藕花深處。

爭渡，爭渡，

驚起一灘鷗鷺。

Abstract

Weng, L. P. 2002. **Interactions between Metal Ions and Biogeo-Surfaces in Soil and Water. Basis for Quantitative Risk Assessment.**

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To provide the basis for an improved quantitative risk assessment of heavy metals in the environment, the interactions between the metal ions and the biogeo-surfaces in soil and water were studied using both experimental and modelling approaches.

The Donnan membrane technique was developed and optimised for the measurement of metal speciation in soil solutions, in which a soil column was connected to the Donnan cell to provide buffering capacities. In acid natural waters and soils, aluminium is potentially a relatively strong competitor for the heavy metals to the binding on colloidal particles such as organic matter. Using the Donnan membrane technique, aluminium binding to purified humic acid and to dissolved organic matter in soil solutions was measured. The ability of the NICA-Donnan model for the prediction of Al binding to humic substances was tested.

A multi-surface model was developed for the prediction of metal speciation in soil and water. This model can also be used to estimate the relative contribution of the individual sorbents to the control of metal distribution. This multi-surface model considers soil as a set of independent sorption surfaces. Metal binding to soil organic matter (solid and dissolved), to clay mineral and to iron hydroxides was modelled using the NICA-Donnan, Donnan, DDL and CD-MUSIC models. This model approach was validated against the concentrations of total dissolved metals and the activities of free metals in sandy soil samples measured using the Donnan membrane technique.

The interactions between the metal ions and the natural organic matter are not only important for the metal distribution, but also for the solubility and mobility of organic matter. Using the NICA-Donnan model, the effects of the binding of protons and metal ions on the physico-chemical behaviour of humic acid was studied. It was found that the coagulation of humic acid started when the calculated electrostatic potential was less negative. The electrostatic potential of the dissolved organic matter in the soil solution of six forest soil profiles was calculated using the same model. The measured concentration of the dissolved

organic matter also decreased in a soil profile, as the calculated potential became less negative. Humic and fulvic acids are the major components in the dissolved organic matter. The mobility and transport of humic and fulvic acids were studied in a column experiment. By comparing the breakthrough curves and the modelled physico-chemical behaviour, it was found that coagulation might be important in the control of the solubility and mobility of humic acid, while adsorption was more likely the mechanism that could explain the immobilisation of fulvic acid in this soil.

The experimental and the modelling approaches developed are helpful in improving the quantitative risk assessment of the heavy metals. Pot experiments using three different soils and a solution culture experiment have been conducted to study the effects of pH and soil characteristics on the phytotoxicity of nickel. Using the model predictions the differences in the bioavailability of Ni in the three different soils could be explained. By comparing the toxicity of free Ni^{2+} ion in the nutrient solution and in the soil solution, the toxicity of Ni in the soils could be predicted reasonably using the quantitative approach.

The developed Donnan membrane technique is proved to be a useful analytical technique for the determination of metal speciation in soil and water samples. Further research is needed to improve the method to make it capable to measure lower concentrations. The multi-surface model approach proposed in this research is validated against the measurements of samples from several different soils. Further validation and improvement of this model approach can be achieved by comparing the prediction with the measurement for more different soils, and by better understanding of the interactions between metal ions and the biogeo-surfaces.

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Chapter 1

General Introduction

Research project

The problem of contaminated land is an important issue for the European Union and through its various funding mechanisms under the Environmental and Sustainable Development program has stimulated a considerable amount of research and technology development. However, there is still a need for improved and cost-effective ways of carrying out quantitative risk assessments (QRA) for heavy metals, both generic and site-specific.

A European Commission framework 4 project entitled: "Fundamental aspects of metal speciation and transport in metal-contaminated soils and aquifers" was launched in 1997 and accomplished in 2000. The overall objectives of the project were to apply and extend recent developments in the speciation and transport of metals in soils and aquifers in order to verify predictive models for the long term fate and transport of metal-contaminated soils and aquifers. This was achieved through the four objectives (Kinniburgh, 2001):

Objective A (Speciation): To develop new field and laboratory methods for measuring heavy metal speciation in pore waters from metal-contaminated soils and aquifers.

Objective B (Characterisation): To characterise the physico-chemical properties of metal-contaminated soils and aquifer materials that control metal solubility.

Objective C (Modelling): To develop methods and modelling methodologies for predicting the solubility (partitioning), speciation and transport of metals and dissolved organic matter in metal-contaminated soils and aquifers.

Objective D (Transport): To use laboratory column studies to verify transport models in contaminated soils and aquifers and to explore the influence of soil and aquifer treatments on metal mobility.

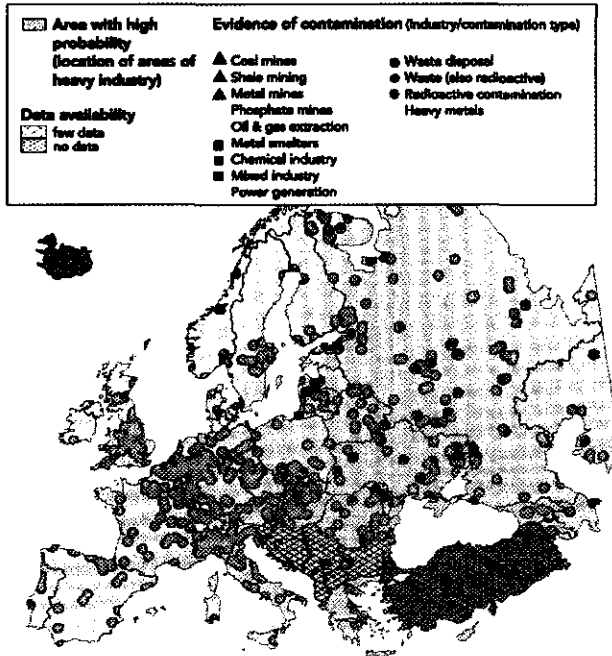
The four participating countries: the UK, France, The Netherlands and Switzerland, co-operatively accomplished this project. Most of the research in this thesis was carried out as part of this project and contributed to the achievement of the objectives stated above.

Soil quality and heavy metals

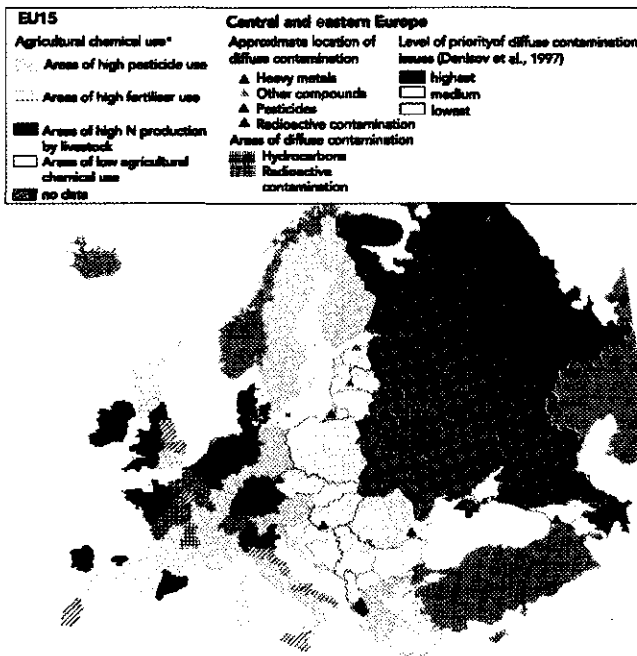
Soil is a finite natural resource that is essential for production of food and fibre and for ecosystem functioning. The soil ecosystem is vulnerable due to pollution. Herris *et al.* (1996) defined soil quality and health as the fitness of a soil body, within site-specific (*i.e.* specified land use, landscape and climate) boundaries, to protect water and air quality, to sustain plant and animal productivity and quality, and to promote human health. Changes in soil quality may impact the land use possibilities, the quality of groundwater and surface water. The contamination of soil with various pollutants together with the erosion, acidification and surface sealing are the major causes that lead to soil degradation in Europe (Gentile, 2000).

Map 1 shows the location of zones with high probability of soil contamination (through heavy industry) and zones where actual soil contamination has been reported in Europe (Gentile, 2000). Data used does not cover all countries and may not be complete in the area under study. Since there is no harmonised monitoring of local soil contamination in Europe and many countries do not yet have national inventories, the map shown here uses as a proxy data set of the location of areas of heavy industry. Map 2 shows areas with high probability of diffuse soil contamination and areas where actual contamination has been reported (Gentile, 2000). For the EU member states data on chemical use in agriculture has been used as a proxy for diffuse contamination in agricultural areas. In central and eastern European countries an assessment of priority levels for soil contamination has been made. It is likely that not all relevant "hot spots" have been identified. A substantial number of the contaminated sites may be related to pollution with heavy metals.

Heavy metals are metals with a density over 6000 kg/m^3 (Alloway, 1995). Except iron, they belong to the group of trace elements, which means that the average concentration in the



Map 1. *Probable problem areas of local contamination in Europe (Gentile, 2000)*



Map 2. *Probable problem areas of diffuse contamination in Europe (Gentile, 2000)*

earth's crust does not exceed 1 g/kg. Heavy metals are naturally circulated by biogeochemical cycling through the biosphere, lithosphere, hydrosphere and the atmosphere. The indigenous content of the heavy metals in the soils is generally low. The average concentrations of copper (Cu), cadmium (Cd), zinc (Zn), nickel (Ni) and lead (Pb) in soils are 30, 0.1, 50, 20 and 10 mg/kg (Lindsay, 1979; Uren, 1992). Human activities introduce heavy metals into the environment. Heavy metal pollution of soil varies from being due to obvious point sources such as around metal mines and a variety of industrial sites to more diffuse sources arising from sewage sludge disposal, the use of inorganic fertilisers, urban development and deposition from the air (Kinniburgh, 2001).

The heavy metals Cu, Zn and Ni are essential elements for the proper functioning of organisms, however no beneficial effects on organisms have been found for Cd and Pb. For both the essential and non-essential metals, negative effects on soil quality will occur once the content of the metals exceeds a critical level. The detrimental effects of heavy metals on the ecosystem functioning can arise due to toxicity to soil organisms. High content of heavy metals in soils may reduce the productivity of the soil and leads to economic cost. Through harvested crop and animal products, the heavy metals may enter the food chain and affect the human health. By leaching and runoff, heavy metals in soils and sediments may enter the groundwater that is the source of drinking water and the surface water.

Environmental problems related to heavy metals have a long history. Recent legislation has led to a marked and measurable decline of the emission over the past decades in many countries in Europe. However, there is still a large legacy of contaminated land throughout Europe and other parts in the world, and the inflow of freshly mined metals into the world economy has remained at a high level (Kinniburgh, 2001). In order to tackle these problems, it is necessary to understand the fate of the heavy metals in the environment for improved and cost-effective ways of carrying out quantitative risk assessments (QRA).

Interactions between heavy metal and biogeo-surfaces

The fate of the heavy metals in and their impact on the environment is closely related to the speciation of the metals. By speciation of a metal, the total content of the metal is divided into different physical and chemical forms (species) (Ure and Davidson, 1995). Metals occur in both the solid phase and the solution phase. In aquatic environment, the metals exist as free metal ions, inorganic and organic complexes, and associated with colloids. In the

solid phase, metals exist as precipitates, adsorbed on reactive soil surfaces, and occluded or bound by soil minerals. Soils and sediments usually contain mixtures of several adsorptive surfaces. Heavy metal adsorption to these surfaces is recognised as being important in controlling heavy metal speciation. Colloidal particles of soil organic matter (SOM), clay silicates and metal hydroxides, which have large surface area and are often electrically charged, are considered important adsorptive surfaces for the binding of heavy metals.

In the past two decades, it has been established that under most circumstances, free metal ion activity (or concentration) is the key factor in determining metal bioavailability and toxicity (Parker and Pedler, 1997). The dissolved metal pool reflects the soil metal fraction that could potentially be leached from the soil and contaminate groundwater and surface water (Sauvé et al., 2000b). Heavy metal speciation in soils, sediments and aquifers is important because of its relevance to the interpretation of toxicity and mobility control.

Generally there are two different approaches for the study of metal speciation in soils and aquifers: experimental determination and model calculation. The commonly used analytical methods for the studying of heavy metal solubility are the sequential extraction procedure and the pore water analysis. With sequential extraction procedure, metals can be fractionated into categories such as soluble, exchangeable, organic bond, oxides bond, occluded and residual (*e.g.* Tessier et al., 1979). In the pore water analysis, soil solution is extracted from field soils by centrifugation or filtration, and then metal concentration in the extracted pore water is measured (*e.g.* Castilho et al., 1993; Goody et al., 1995). The problem associated with pore water analysis is that the result is quite dependent on short-term fluctuations. The distribution coefficient that describes the partitioning of metals over the solid and solution phase is not constant but depends on the physicochemical situation (Castilho et al., 1993). For both the sequential extraction procedure and pore water analysis, the physical separation can, and usually does, disturb the chemical state of the sample so that every technique results in an “operational definition” for the dissolved, colloidal, or complexed metal (Nordstrom, 1996).

Besides the determination of the solid-solution distribution of heavy metals, there are several approaches that have been widely used to determine the solution speciation of metals. The most commonly used methods are the electrochemical method of ion selective electrode (ISE) potentiometry, voltammetric electrochemical methods such as anodic stripping

voltammetry (ASV) and adsorptive cathodic stripping voltammetry (ACSV), the competitive chelation method and the cation exchange resin method. Each method has its advantages and limitations (Apte and Batley, 1995; Mota and Correia dos Santos, 1995). An alternative method proposed by Lampert (1982) uses a semi-permeable cation exchange membrane, which separates the solution to be analysed and an acceptor solution, to measure free ion concentrations in soil solutions. This method has been used to measure free metal concentrations of Cu^{2+} and Cd^{2+} (Fitch and Helmke, 1989; Minnich and McBride, 1987; Salam and Helmke, 1998). Improvements were made by Temminghoff *et al.* (2000), and the resulting technique was named (Wageningen) Donnan membrane technique (WDMT). Before the research described in this thesis, the Donnan membrane technique has been used only with artificial solutions or soil extracts separated from the solid phase (Fitch and Helmke, 1989; Minnich and McBride, 1987; Salam and Helmke, 1998; Temminghoff *et al.*, 2000). The main problem of using a separated solution is the limited buffering capacity of the solution for trace metals, which can lead to changes of the chemical equilibrium as a result of the analysis.

Some problems limit the applicability of the analytical methods of heavy metal speciation for the assessment of heavy metal activity and solubility in the field. Analytical speciation techniques often have poor sensitivity at the low concentrations of most heavy metals. The analytical techniques can disturb the equilibrium speciation. In addition, numerous interference limit the applicability of analytical speciation techniques to natural samples (Nordstrom, 1996). The limitations of the analytical methods can be compensated by the computational approach. The effects of changes in environmental conditions on the fate of heavy metals can only be predicted quantitatively using modelling methods.

Geochemical models are often used to predict the speciation and transport of heavy metals. Examples of popular geochemical codes that compute heavy metal speciation are MINTEQA2 (Allison *et al.*, 1991), WATEQ4F (Ball and Nordstrom, 1992), GEOCHEM (Mattigod and Sposito, 1979), PHREEQC (Parkhurst *et al.*, 1990), SOILCHEM (Sposito and Coves, 1988), WHAM (Tipping, 1994) and ECOSAT (Keizer and Van Riemsdijk, 1994). Chemical models that calculate heavy metal speciation can only give meaningful results when all significant complexes are accounted for and the thermodynamic constants and the input analytical data are reliable. These criteria are often easier to meet for the modelling of the complexation between the inorganic ions, than for the prediction of the interactions

between the metal ions and the biogeo-surfaces. The reactive soil surfaces such as organic matter, clay and oxides are colloidal particles that are electrically charged. Metal binding to these surfaces is generally influenced by both specific chemical and non-specific electrostatical contributions. The magnitude of the binding depends on the type of metal and surface, the ionic strength and the competition of other components for the binding sites. The interactions between the soil surfaces, like organic matter and oxides, may influence the metal binding as well and make it more complicated for the modelling. For these reasons, in the chemical speciation calculations for heavy metals using the geochemical codes stated above, the interactions between heavy metals and the biogeo-surfaces are mostly treated in a fairly simple way.

Recent developments in the modelling of metal binding to the soil surfaces have made it possible to improve the predictions. For the description of metal binding to the organic matter, two advanced models, humic ion-binding Model V and VI (Tipping and Hurley, 1992; Tipping, 1998) and NICA-Donnan (NICA=Non Ideal Consistent Competitive Adsorption) (Koopal et al., 1994; Benedetti et al., 1995; Kinniburgh et al., 1996; Kinniburgh et al., 1999), have been developed and integrated in the computer code WHAM and ECOSAT respectively. Both models account for the site heterogeneity, electrostatic effects and include the competition between protons and metal ions. The default parameters of the NICA-Donnan and Model VI have been derived by fitting using extensive sets of published data (Milne, 2000; Milne et al., 2001; Tipping, 1998) (see Table 1 and 2, Appendix).

The CD-MUSIC model (Charge Distribution Multi-Site Complexation) is a recently developed advanced model for the description of the adsorption of ions on the oxide surfaces (Hiemstra and Van Riemsdijk, 1996; 1999). The difference in the reactivity of the various oxygen groups present on the goethite surface is taken into account in the model. The CD-MUSIC model has been shown to be able to scale from the microscopic as can be assessed by spectroscopy, to the macroscopic thermodynamic scale of the measured adsorption from solution. The CD-MUSIC model provides the possibility to model metal binding to oxides in soils but it has not yet been tested in that respect in practice.

Another challenge for the geochemical models in prediction of the heavy metal behavior in soils and aquifers arises when the solubility of natural organic matter is taken into account. Soil solutions and aquifers contain varying amount of dissolved organic matter (DOM),

which originates from plant litter, humus, and microbial biomass or from root exudates (Kalbitz et al., 2000). Only small proportions of DOM, mostly low molecular substances such as organic acids, sugars, amino acids, can be chemically identified (Herbert and Bertsch, 1995). Most of what is collectively termed "dissolved organic matter" in soils are complex molecules of relatively high molecular weight, namely humic substances (Kalbitz et al., 2000).

The partitioning and mobility of organic matter plays an important role in the speciation of heavy metals in the natural environment. Organic matter can enhance (when dissolved) or retard (when in the solid matrix) the transport of the heavy metals through the soil. The solubility of DOM in soil is governed by both the chemistry of the bulk solution and the composition of the soil solid phase, where the former determines DOM dissolution properties, and the latter controls the extent of DOM adsorption (Weigand and Totsche, 1998). Model V and VI and NICA-Donnan, which describe ion binding on humic substances, can predict the physico-chemical behaviour of organic matter that may be important in the control of the solubility of organic matter. Tipping and Woof (1990, 1991) proposed a model for the release of humic substances in acid organic soils based on the electrical charge calculated using Model V. Despite intensive research in the last decade, our knowledge of the formation and fate of DOM in soils and its response to changing environmental conditions is still fragmented and often inconsistent (Kalbitz et al., 2000).

Another issue that needs to be considered when conducting the quantitative risk assessment of heavy metals involving the effects on organisms is the interaction of the metals with the biota. Not only the distribution (speciation) of heavy metals over the abiotic phases depends on environmental factors, but also the metal binding or uptake by biota is influenced by factors such as pH and Ca concentration (Campbell, 1995; Nederlof and Van Riemsdijk, 1995; Plette et al., 1999). Metal interactions with organisms can be understood by considering an organism as an assemblage of reactive ligands (Morel, 1983). Metal uptake by the biota from the soils and aquifers may be predicted by the combination of the speciation models with the uptake models (Nederlof and Van Riemsdijk, 1995; Plette et al., 1999).

Model predictions can provide much insight in the control of metal speciation and availability in the soils and aquifers. However, the modelling approaches have to be

validated before being applied in the quantitative risk assessment. The comparison of heavy metal speciation by analytical determination with computations via a chemical model appears to be a useful approach to evaluate and improve our knowledge of speciation (Nordstrom, 1996).

Outline of the thesis

As part of the EU project "Fundamental aspects of metal speciation and transport in metal-contaminated soils and aquifers", the objectives of this thesis comply with the overall objectives of the project stated above: to apply and extend recent developments in the speciation and transport of metals in soils and aquifers in order to verify predictive models for the long term fate and transport of metal-contaminated soils and aquifers. One of the aims of this thesis is to develop sound experimental techniques for the determination of metal speciation in natural samples. The modelling part of this thesis focuses on the interactions of heavy metals with the important soil surfaces including soil organic matter (particulate and dissolved), clay minerals and iron hydroxides, and on the effects of these interactions on the speciation of heavy metals and the physico-chemical characteristics of the dissolved organic matter. In the end of this thesis, the experimental and modelling approaches that have been developed were applied for the interpretation and understanding of the bioavailability and toxicity of heavy metals in soil and solution.

Following the introduction chapter (Chapter 1), Chapter 2 and 3 focus on the development of the analytical techniques for the measurement of metal speciation. Chapter 2 is about the development and optimisation of the soil column Donnan membrane technique for the measurement of free metal ion activity or concentration in soils. The major development is the connection of a soil column with the Donnan cell. The operational aspects of the method, including equilibrium time, buffering capacity and correction for differences in ionic strength were investigated and optimised. The method was applied to determine concentrations of free Cu^{2+} , Cd^{2+} , Pb^{2+} and Zn^{2+} in the soil solution of 15 soil samples.

In Chapter 3, the applicability of the Donnan membrane technique for the measuring of free aluminium (Al^{3+}) concentration was tested. The study of Al speciation is of interest for the assessment of soil and water quality, not only because of its toxic effects at elevated concentrations, but also due to its influence on many related environmental processes.

Aluminium binding to purified humic acid (HA) and to DOM in soil solutions was measured and the results were compared with those predicted with the NICA-Donnan model.

The following two chapters, Chapter 4 and 5, focus on the development of speciation modelling of heavy metals. In **Chapter 4**, a multi-surface model was proposed and used to evaluate the contribution of various sorption surfaces in soil to the control of heavy metal activities. This multi-surface model considers soil as a set of independent sorption surfaces, *i.e.* organic matter, clay silicate and iron hydroxides. The predicted activities of Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} and Pb^{2+} in the soil solutions were compared to those measured using the Donnan membrane technique developed in Chapter 2.

Chapter 5 deals with the complexation of heavy metals with the dissolved organic matter (DOM) in soil solution. The complexation of Cu, Cd, Zn, Ni and Pb with DOM in the soil solution was measured using the Donnan membrane technique. The ability of two advanced models for ion binding to humic substances, *e.g.* Model VI and NICA-Donnan, to simulate metal binding to natural DOM was assessed by comparing the model predictions with the measurements. Furthermore, the solid-solution partitioning of the metals was simulated using the multi-surface model developed in Chapter 4, extended by including metal binding to DOM.

Chapter 6 and 7 focus on the factors that control the solubility and mobility of humic substances. In **Chapter 6**, the physico-chemical behaviour of purified humic acid from a forest soil coagulated with various cations at different pH was modelled with the NICA-Donnan model. Based on these results, an empirical relation between the Donnan potential of humic acid and its concentration in solution was derived. In addition, the Donnan potential of dissolved organic matter in the soil solution of six soil profiles under forest was calculated using the same model. The results were compared to those predicted by the empirical relation based on the humic acid coagulation experiment.

Chapter 7 deals with the transport of a humic acid (HA) and a fulvic acid (FA) in an acid sandy soil using a column experiment, which was conducted at two different calcium concentrations in the influent solution. Model calculations were carried out to predict the physico-chemical behaviour of the humic and fulvic acids in the experiment. With the observed breakthrough curves and the calculated physico-chemical behaviour, the possible

mechanisms that controlled the immobilisation of the humic and fulvic acids were studied. In addition, the mobility of Al and Cu in the soil column and the change in the Ca concentration was investigated and its relation to the solubility of humic and fulvic acids were studied.

Chapter 8 and 9 use the analytical and the modelling approaches developed in the previous chapters for the quantitative assessment and understanding of nickel bioavailability and toxicity to plants. In **Chapter 8**, pot experiments with three different soils were conducted to study the phytotoxicity of Ni to oats and the effects of pH and soil characteristics. After the pot experiment, batch desorption experiments were conducted and the differences in toxicity of Ni in the three soils were compared to Ni retention by the soils. Using the multi-surface model developed in Chapter 4 and 5, the effects of pH and soil composition on Ni speciation were studied.

In **Chapter 9**, the effects of pH on the bioavailability and toxicity of Ni to oats were studied with a solution culture experiment, and the results were compared with those of the pot experiments in Chapter 8. Using the Donnan membrane technique, the Ni speciation in 0.01 M CaCl₂ solution of soil samples, for which pot experiments have been conducted, was analysed. Toxicity of free Ni²⁺ in the soil solution were estimated and compared to those in the solution culture. With the data from the solution culture experiment, the pot experiment and the desorption experiment, the applicability of a quantitative model for the prediction of metal bioavailability and toxicity in a complexed system was validated.

Chapter 2

Determination of Free Ion Concentration of Trace Metals in Soil Solution Using a Soil Column Donnan Membrane Technique

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Co-authors: Erwin J. M. Temminghoff; Willem H. Van Riemsdijk

Abstract

Accurate measurement of the free metal ion is difficult, especially for trace metals present in very small concentrations (less than micro-molar) in natural systems. The recently developed Donnan membrane technique can measure the concentrations in solution in the presence of inorganic and organic complexing agents. We have developed this method further to make it applicable for analysing soil samples. The major development is the linkage of a soil column with the Donnan cell. The operational aspects of the method, including equilibrium time, buffering capacity and correction for differences in ionic strength were investigated and optimized. The method was applied to determine concentrations of free Cu^{2+} , Cd^{2+} , Pb^{2+} and Zn^{2+} in the soil solution of 15 soil samples (pH 2.9-7.1, organic C<2.9-137.4 g/kg, clay 0.2-51.6%). Compared with other speciation methods, the Donnan membrane technique has the advantage of allowing the measurement of several elements simultaneously and it minimizes the disturbance of substrate. The detection limit of the Donnan membrane technique is about 10^{-9} M. This method can be applied to study the biogeochemical behaviour of metals in soils, sediments and other solid materials.

Introduction

Trace metals in soils may have toxic effects on soil biota. It has been established that in most circumstances, the free metal ion concentration (or activity) is the key factor in determining metal bioavailability and toxicity (Parker and Pedler, 1997). The ion activity of trace metals can also be used in thermodynamics to describe the direction and impetus of chemical reactions such as precipitation, complexation and adsorption. To determine the concentrations of free metal ion both analytical and computational approaches can be followed. However, all models of speciation have to be validated before they can be applied to a speciation calculation. Therefore a reliable direct measurement method is indispensable.

There are several approaches that have been widely used to determine the free ion concentration (activity). Each method has its advantages and limitations (Apte and Batley, 1995; Florence, 1986; Mota and Correia dos Santos, 1995). The electrochemical method of ion selective electrode (ISE) potentiometry is one of the most powerful methods in speciation studies because the free metal ion activity is measured directly (Mota and Correia dos Santos, 1995). However, there are only five solid-state electrodes that can be used to measure free ion activities for trace metals: Ag, Pb, Cu, Cd and Hg (Buck, 1979). The applicability of such electrodes to measure free ion activity in natural samples can also be restricted by their selectivity. The interfering ions can be an important source of error, leading in general to overestimation of the ion concentration (Mota and Correia dos Santos, 1995).

The voltammetric electrochemical methods such as anodic stripping voltammetry (ASV) and adsorptive cathodic stripping voltammetry (ACSV) provide the most direct methods for the study of trace metal speciation at small concentrations (10^{-8} - 10^{-11} M) (Mota and Correia dos Santos, 1995). The fundamental problem of this technique, namely the solution equilibrium is disturbed by the application of a current, is nearly always present (Nordstrom, 1996). Further, the adsorption of organic matter on the electrode can depress the signal (Florence, 1986). To interpret the voltammetric signal into free ion concentration, assumptions have to be made as to which metal species are 'labile'.

The competitive chelation method (Norvell and Lindsay, 1982; Workman and Lindsay, 1990) has good sensitivity and provides estimates of ion activities (Amacher, 1984). However, chelates attain equilibrium with soils very slowly (Norvell and Lindsay, 1969;

1972). The accuracy of the competitive chelation method depends on the reliable estimation of chelated metal contents and reference ion concentration. The method can be successful only if the metal of interest and the selected competing metal are the principal chelated metals (Workman and Lindsay, 1990).

The cation exchange resin method can also be used to measure free metal activity in soil (Apte and Batley, 1995). It provides the possibility of simultaneous multi-metal measurement. However, using such a method requires detailed characterisation of the adsorption properties of the resin. Also, the soil solution composition must be considered during the speciation analysis (Fotovat and Naidu, 1997). An alternative method proposed by Lampert (1982) uses a semi-permeable cation exchange membrane, which separates the solution to be analysed and an acceptor solution, to measure free ion concentrations in soil solutions. This method has been used to measure free metal concentrations of Cu^{2+} and Cd^{2+} (Fitch and Helmke, 1989; Minnich and McBride, 1987; Salam and Helmke, 1998). Improvements were made by Temminghoff *et al.* (2000), and the technique was named Wageningen Donnan membrane technique (WDMT).

The Donnan membrane method is based on the theory of Donnan membrane equilibrium. During the analysis, the cationic metal species are separated from the substrate solution (donor solution) via a negatively charged cation exchange membrane. When the Donnan membrane equilibrium is attained, the activity ratios (corrected for charge) of the ions in the donor solution and in the acceptor solution are equal:

$$(a_{id}/a_{ia})^{1/Z_i} = (a_{jd}/a_{ja})^{1/Z_j}, \quad (1)$$

where a_{id} and a_{ia} are the activity of the i th cation in donor and acceptor solution and Z_i is its charge, and a_{jd} , a_{ja} and Z_j are the analogous quantities for the j th cation.

To date, the Donnan membrane technique has been used only with artificial solutions or soil extracts separated from the solid phase (Fitch and Helmke, 1989; Minnich and McBride, 1987; Salam and Helmke, 1998; Temminghoff *et al.*, 2000). The main problem of using a separated solution is the limited buffering capacity of the solution for trace metals, which can lead to changes of the chemical equilibrium as a result of the analysis. To overcome this disadvantage, in our study, we linked a soil column to the Donnan cell, and the soil solution

remained in contact with the soil during the determination of the concentration of free metal ion. The experimental conditions were optimised, and the concentrations of free Cu^{2+} , Cd^{2+} , Pb^{2+} and Zn^{2+} were measured in 15 soil samples.

Materials and methods

Soils

To develop and optimise the Donnan membrane method, we used two soil samples. The samples were taken from a field near Wageningen, The Netherlands. The soil is a Spodosol, sandy soil (3.4% clay, 4.0% organic matter). The field site was established as a randomised block design of four copper concentrations and four pH adjustments approximately 20 years ago. For details see Lexmond (1980). Samples from the topsoil (0-20 cm) from treatments of 4A (pH 4, 1.7 mmol Cu/kg) and 4D (pH 5, 2.2 mmol Cu/kg) were collected in June 1998 and used in this research. The samples were air-dried, sieved (<2 mm) and stored at 5°C.

After the optimisation, the concentrations of free Cu^{2+} , Cd^{2+} , Pb^{2+} and Zn^{2+} in 15 different soil samples were measured. The sampling sites cover both places with known sources of metal pollution and places considered to contain metals at natural background concentrations. The soils were sampled in 1997 from the top layer (0-20 cm) at sites in the Netherlands, except for Soil 15, which was sampled in Belgium. Aggregates were broken by hand or by machine, and the samples were sieved (<4 mm) and stored at 5°C as moist soil. Sub-samples were dried in air and sieved (<2 mm) prior to analysis. The moisture content of the soil was measured as the mass loss after air-drying. The organic carbon (C-org) content was determined with an Element Analyser (EA 1108, Fisons Instruments). Reactive iron and aluminium oxides (Fe-ox, Al-ox) were determined with the ammonium oxalate - oxalic acid extraction method. Soil properties and total metal contents measured after *aqua regia* digestion are given in Table 1.

Soil column Donnan membrane method

We chose to do the experiments with 0.002 M $\text{Ca}(\text{NO}_3)_2$ as the salt solution to obtain the soil solution. The only exception was in the experiment to optimise the equilibrium time, in which $\text{Ca}(\text{NO}_3)_2$ solution at both 0.002 M and 0.01 M concentrations were used. The solid solution ratio was 1: 2. The nitrate salt was chosen to limit complex formation.

Table 1. Soil properties and total metal content

Soil	Location	Source of pollution	Moisture by weight (%)	C-org (g/kg)	Clay (%)	Fe-ox (mmol/kg)	Al-ox (mmol/kg)	Metal content (<i>aqua regia</i>) ($\mu\text{mol/kg}$)			
								Cu	Cd	Pb	Zn
1	Woerden	Motorway	27.7	88.0	39.1	136.2	70.1	426.3	2.98	176.9	1522.7
2	Houthem	Lead and zinc mining	17.2	27.9	11.0	41.8	18.3	196.3	14.16	520.8	7072.8
3	Valkenswaard	River bank	2.8	15.1	1.3	8.3	20.7	69.9	8.58	106.8	844.7
4	Callantsoog	Shooting range	1.4	<2.9	0.2	2.0	1.1	10.0	-	265.1	112.4
5	Heurnen	Power line pylon	6.7	11.1	3.0	27.0	22.1	89.3	0.40	66.5	286.3
6	Boxtel	River bank	18.9	27.6	5.8	134.2	18.2	306.4	53.52	119.5	2282.3
7	Stuifzand	*	8.6	22.3	1.7	22.1	22.0	496.4	1.42	160.1	791.5
8	Veenoord	Galvanizing factory	11.0	30.5	1.7	16.6	40.5	280.7	2.31	183.4	6092.5
9	Lheebroekersand	*	37.3	54.5	1.4	24.1	80.0	33.8	2.15	113.3	159.5
10	Westerbork	*	11.8	31.4	1.1	14.8	28.6	40.4	0.71	42.5	119.4
11	Norgerholt	*	23.5	33.9	2.3	19.0	11.0	21.0	-	71.9	97.5
12	Genemuiden	*	36.7	137.4	29.3	389.2	51.6	427.0	6.47	245.4	1472.8
13	Eendenkooi	Natural rich in zinc	30.3	37.5	51.6	111.1	64.0	458.9	4.26	179.3	1679.3
14	Zandelei	*	23.3	40.1	3.8	60.9	28.1	94.1	0.73	130.7	204.5
15	Maatheide	Zinc smelter	6.5	8.0	0.7	2.5	9.2	109.7	5.28	209.5	677.4

* without known source of contamination - less than detection limit

One hundred gram air-dried soil was moistened with 2 ml ultra pure water, and transferred into a Perspex column (length 25cm, diameter 4cm) with two pieces of filter paper at the bottom. Salt solution was pumped (peristaltic pump, Gilson Miniplus III) from the polyethylene bottle initially containing 200 ml into the soil column from the bottom, and then sucked out from the top and circulated through the donor side of the cation exchange cell and back to the bottle again. The acceptor side of the cell was connected with a test tube initially containing 18 ml of the same salt solution. The acceptor solution was also circulated constantly by pumping. The concentrations of $\text{Ca}(\text{NO}_3)_2$ solution used in the donor and acceptor sides were the same unless otherwise indicated. The design of the cation exchange cell is described by Temminghoff *et al.* (2000). Figure 1 shows the system of the soil column Donnan membrane method.

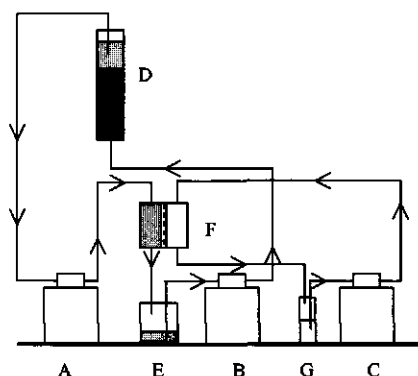


Figure 1. Scheme of the soil column Donnan membrane system

(A: pump I; B: pump II; C: pump III; D: soil column; E: stock bottle; F: Donnan exchange cell, left donor, right acceptor; G: test tube)

In the cell, a cation exchange membrane (BDH Laboratory Supplies, England) was used to separate the donor and the acceptor solutions. The membrane has a matrix of polystyrene and divinylbenzene with sulphonic acid groups, which are fully deprotonated at $\text{pH} > 2$. The thickness of the membrane is 0.15-0.17 mm and the cation exchange capacity (CEC) of the membrane is 0.8 mmol/g. The surface area of each membrane in one cell is 5.3 cm^2 with a weight of approximately 0.09 g. Before analysis, the membrane was prepared by shaking with 0.1 M HNO_3 , 1 M $\text{Ca}(\text{NO}_3)_2$, and 0.002 M or 0.01 M $\text{Ca}(\text{NO}_3)_2$ (depending on the concentration used to prepare the soil solution) successively.

All columns, cells, bottles and test tubes were washed with 0.1 M HNO_3 and ultra pure water. The ultra pure water was produced with the Elgastat Maxima-HPLC unit (Elga Ltd., England). Teflon tubes were first washed with a mixture of ethanol, ammonia and ultra pure water (1:0.1:1), and then with 0.1 M HNO_3 and ultra pure water successively.

Sampling and measurement

10 ml of the donor and 6 ml of the acceptor solution were sampled. The pH was measured with a meter in all the samples. The donor solution was filtered using a $0.45\mu\text{m}$ nitrate-cellulose membrane filter (Schleicher & Schuell, NC45). The concentration of dissolved organic C in the donor solution was measured with a fully automated analyzer (SK12, Skalar, Netherlands) by persulphate and tetraborate oxidation under ultra violet light using a nickel catalyst at 400°C . The carbon leached from the filter was measured, and the concentration of dissolved organic C in the filtered solution was corrected. Sub-samples of the donor and the acceptor solution were acidified with HNO_3 to a final HNO_3 concentration of 0.1 M. These acidified solutions were used to analyze metal concentrations. The concentrations of macro-elements were measured by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry, Eppendorf Elex 6361), and concentrations of other elements were measured by ICP-MS (Inductively Coupled Plasma Mass Spectrometry, Perkin-Elmer, Elan 6000). The quality of measurements in the laboratory is controlled regularly with standard solutions and with an inter-laboratory exchange programme.

Results and discussion

Equilibrium time

The effects of the percolation rate through the soil column on the equilibrium time of the divalent Cu^{2+} ion between the donor solution and the solid phase was investigated first. Experiments were done with soil samples 4A and 4D in 0.002 M and 0.01 M $\text{Ca}(\text{NO}_3)_2$ solution. Column percolation rates of >2.0 ml/minute, 2.0 ml/minute, 1.3 ml/minute and 0.3 ml/minute were tested.

The experiment showed that at the column percolation rate > 2.0 ml/minute, pressure was built up in the soil column and the soil column was damaged. At the rates of 2.0, 1.3 and 0.3 ml/minute, chemical equilibrium of Cu^{2+} between the donor solution and the soil solid phase was reached within 12 hours (29 pore volumes), 12 hours (19 pore volumes) and 48 hours (17 pore volumes) respectively. Both contact time and percolation rate are important in

determining the equilibrium time. We chose a column percolation rate of 2.0 ml/minute as standard in the other experiments, and pumped the donor and acceptor solution over the Donnan membrane cell at a rate of 2.5 ml/minute.

The change of Cu concentration in the acceptor solution showed that the Donnan membrane equilibrium was reached within 24 hours in 0.002 M $\text{Ca}(\text{NO}_3)_2$ soil solution and 48 hours in 0.01 M $\text{Ca}(\text{NO}_3)_2$ soil solution. The salt concentration of the initial salt solution influences the Donnan membrane equilibrium time in two opposing ways. First, at a smaller salt concentration, the absolute value of the Donnan potential of the cation exchange membrane is greater, and a larger Donnan potential favours faster cation flux (Temminghoff et al., 2000). Second, at smaller salt concentrations, the retardation in the membrane of cations of interest is intensified due to the large Donnan potential and reduced competition from the cations in the solution. The increased accumulation of cations in the membrane will diminish the cation flux. The overall effect of the salt concentration on the Donnan equilibrium time is the combination of the influence on the Donnan potential and on the cation accumulation in the membrane.

Buffering capacity

To avoid disturbing the chemical equilibrium in the soil solution, an analytical method should have negligible influence on the mass balance of the substrate system. In the soil column Donnan membrane analysis, the total metal mass balance can be written as:

$$\begin{aligned} M(\text{total}) = & \quad M(\text{soil solid}) + M(\text{donor solution}) + M(\text{cation exchange membrane}) \\ & + M(\text{acceptor solution}), \end{aligned} \quad (2)$$

where M represents a certain metal, terms in the brackets indicate the phases where the metal exists. In this equation, metal adsorption on to tubing and containers was assumed to be negligible. Based on this equation, the buffering capacity of the metal mass balance in the analysis can be evaluated by the fraction of the metal mass reduced due to the analysis method, *i. e.* $M(\text{acceptor solution}) + M(\text{cation exchange membrane})$, to the total metal content, *i. e.* $M(\text{total})$. The smaller the fraction is, the larger is the buffering capacity.

In principle, the amount of metal accumulated in the cation exchange membrane can be calculated if we know the Donnan potential and the Donnan volume of the cation exchange membrane. However, the Donnan potential and the Donnan volume are not known and

difficult to measure. Alternatively, metal accumulated in the membrane was measured directly after the analysis with soil 4A and 4D by shaking the membrane in 15 ml 0.1 M HNO_3 for 24 hours. We found that the amount of divalent metals (Cu^{2+} , Cd^{2+} , Ca^{2+} and Mg^{2+}) accumulated in the cation exchange membrane could be described reasonably well by a log-linear relationship ($R^2=0.99$, Figure 2), which relates the amount of metal accumulated in the membrane to the metal ion concentration in the acceptor solution. This accords with the Boltzmann equation.

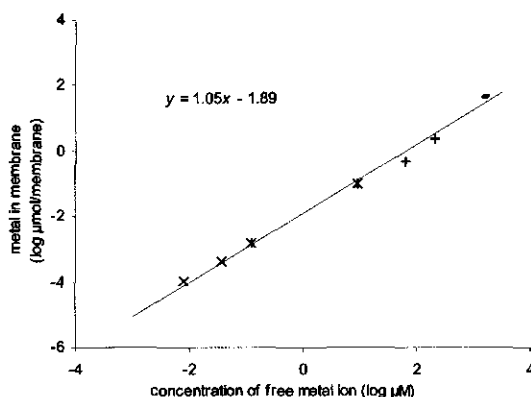


Figure 2. Divalent cation accumulation in the cation exchange membrane in 0.002 M $\text{Ca}(\text{NO}_3)_2$ solution. (The fitted line is that of the regression of the logarithm of y , i. e. cation accumulated in the membrane, over the logarithm of concentration of free metal ion, x . - Ca; + Mg; x Cd; * Cu)

Table 2. Mass balance of Cu in the Donnan membrane analysis (0.002 M $\text{Ca}(\text{NO}_3)_2$)

	Soil 4A			Soil 4D		
	Cu Conc.	Sample weight or volume	Amount of Cu	Cu Conc.	Sample weight or volume	Amount of Cu
Acceptor	9.57 μM	18 ml	0.17 μmol	0.15 μM	18 ml	0.0027 μmol
Membrane			0.10 μmol			0.0016 μmol
Soil (2 M HNO_3)	1.70 mmol/kg	100 g	170 μmol	2.22 mmol/kg	100 g	222 μmol
Mass reduction			0.16%			0.002%

In Table 2, the mass balance of the soil column Donnan membrane system for Cu in soil 4A and 4D was calculated. The 2 M HNO₃ extractable Cu was used as Cu (total). The calculation shows that the mass reduction due to the measurement was 0.16% and 0.002% of the total acid extractable Cu content in soil 4A and 4D respectively. We consider the loss and the effect on the chemical equilibrium to be negligible.

Correction of ionic strength difference

It is difficult to maintain exactly the same ionic strength in the donor and the acceptor solution. In the work of Fitch & Helmke (1989), small differences in ionic strength were corrected with radioactive ²²Na⁺ according to Equation (1). In the soil column Donnan membrane analysis, we propose to use the ratio of the potassium concentration in the donor to that in the acceptor solutions instead of the radioactive ²²Na⁺. Potassium occurs naturally in soils, and like Na it has a very small potential to form complex. We assume that all K in the donor solution is in the form of the free ion. The concentration of K in the donor and the acceptor solutions can be measured simultaneously with the analysis of the other macro-elements using ICP-AES.

An experiment was carried out to evaluate the correction for differences in ionic strength. In this experiment, soil column Donnan membrane analysis was done using the soil samples 4A and 4D. In all the treatments, 0.002 M Ca(NO₃)₂ was used as the initial salt solution in the donor side. The concentrations of Ca(NO₃)₂ in the acceptor side were chosen to be 0.001 M, 0.002 M, 0.003 M and 0.004 M.

The ionic strengths in the donor and acceptor solutions were calculated from the measured concentrations of the major cations (Ca²⁺, Mg²⁺, K⁺, Na⁺) and equivalent concentrations of the mono-valent anion. The activity coefficient (*f*) was calculated using the Davies equation. The combination of the Davies equation with Equation (1) results in:

$$[M^{2+}]_d = [M^{2+}]_a ([K^+]_d/[K^+]_a)^2 (f_a/f_d)^2, \quad (3)$$

where $[M^{2+}]$ represents the concentration of free divalent ion, $[K^+]$ is the potassium concentration, *f* is the activity coefficient of a mono-valent ion, and the subscripts d and a indicate the donor and acceptor solution respectively. This equation enables us to calculate the concentration of the free divalent cations in the donor.

The results of the experiment for the correction of the differences in ionic strength are listed in Table 3. The activity ratio of potassium in the donor and the acceptor solutions was compared with that of calcium corrected for charge, and the two were found to be similar. This indicates that in these soil solution samples most of the calcium is present as free ion.

Table 3 gives the Cu concentrations measured in the acceptor solution and the free Cu^{2+} concentrations in the donor solution calculated using Equation (3). Note that the effect of the ratio of the activity coefficient, *i. e.* $(f_a/f_d)^2$ in Equation (3), on the calculated free Cu^{2+} concentrations in the donor solution is very small. The main effect is the ratio of the potassium concentration. The measured concentration of free Cu^{2+} in the acceptor varied considerably with the salt concentration in the acceptor, whereas that calculated in the donor was fairly constant, as it should be. The remaining differences of concentration of free Cu^{2+} in the donor solution after the correction can be due partly to the small differences in the pH of the donor solution caused by the difference in ionic strength.

Table 3. Activity ratio of K, Ca and free Cu^{2+} concentration measured in the acceptor and calculated in the donor solution using Equation (3) (Data are the average of the measurements after 24 and 48 hours with the standard errors in the brackets).

Soil	Ca(NO ₃) ₂ acceptor (M)	pH donor	Activity ratio		Cu ²⁺ concentration (μM)	
			$(\text{K}^+)_d/(\text{K}^+)_a$	$\{(\text{Ca}^{2+})_d / (\text{Ca}^{2+})_a\}^{1/2}$	acceptor	donor
4A	0.001	3.78 (0.01)	1.67 (0.03)	1.61 (0.02)	4.24 (0.01)	13.28 (0.56)
	0.002	3.84 (0.01)	1.14 (0.05)	1.12 (0.01)	8.64 (0.25)	11.64 (0.70)
	0.003	3.85 (0.01)	0.95 (0.02)	0.92 (0.02)	12.47 (0.72)	11.03 (0.20)
	0.004	3.84 (0.04)	0.89 (0.04)	0.80 (0.01)	14.76 (1.33)	10.66 (0.06)
4D	0.001	5.25 (0.04)	1.63 (0.01)	1.63 (0.01)	0.11 (0.02)	0.34 (0.06)
	0.002	5.39 (0.13)	1.20 (0.04)	1.18 (0.01)	0.14 (0.04)	0.22 (0.04)
	0.003	5.40 (0.12)	1.00 (0.03)	0.98 (0.00)	0.15 (0.05)	0.15 (0.04)
	0.004	5.47 (0.06)	0.91 (0.03)	0.87 (0.01)	0.23 (0.07)	0.18 (0.05)

d: donor solution, a: acceptor solution

Mixing soil with quartz sand

It is problematic to apply the soil column method to scarcely permeable soils, such as heavy clays. If the percolation through the soil column is too slow, then it takes a long time to reach chemical equilibrium in the donor solution. Quartz sand is much less reactive than other soil constituents such as organic matter, clay and metal oxides, and has been used in many batch and column experiments to modify the texture of the matrix or to alter the permeability of porous media. We studied the possibility of mixing quartz sand with soil samples for the Donnan membrane analysis. In the experiment, 100 g clean quartz sand was mixed with 100 g soil samples (soil 4A and 4D). The quartz sand was cleaned by the magnetic removal of iron particles and washing with acid and purified water to eliminate other impurities. Considering the relative inertness of quartz sand, we estimated that the mixing would not significantly affect the chemical equilibrium in the soil and the soil solution. From the results, no significant influence of mixing quartz sand on the concentrations of dissolved organic carbon and metals was observed. The effect of mixing quartz on the Cu concentration in both the donor and acceptor solutions is shown in Table 4.

Table 4. *Effect of mixing quartz sand on measured Cu concentration in the donor (filtered) and acceptor solution (Data are the average of the measurements after 24 and 48 hours with the standard errors in the brackets).*

Soil 4A				Soil 4D			
Cu (μM)				Cu (μM)			
without quartz		with quartz		without quartz		with quartz	
donor	acceptor	donor	acceptor	donor	acceptor	donor	acceptor
17.65	9.57	17.05	9.42	5.41	0.15	5.30	0.13
(0.49)	(0.35)	(0.78)	(0.78)	(0.18)	(0.03)	(0.18)	(0.05)

Measuring concentrations of free Cu^{2+} , Cd^{2+} , Pb^{2+} and Zn^{2+} with the soil column Donnan membrane method

The concentrations of free Cu^{2+} , Cd^{2+} , Pb^{2+} and Zn^{2+} in the 0.002 M $\text{Ca}(\text{NO}_3)_2$ soil solution were measured for 15 different soil samples in the field moist state. The moisture content in the samples was taken into account to keep the soil sample equivalent to 100 g air-dried weight and the total volume of the solution (soil pore water and salt solution) at 200 ml. For the samples containing more than 35% clay, 100 g clean quartz sand was mixed with the soil samples. Solution samples were taken after 24, 36 and 48 hours.

The pH of the soil solution ranged from 2.9-7.1. The pH of acceptor solution could differ from that of the donor solution because of the difference in ionic strength and the dissolution of CO_2 from the atmosphere especially at high pH. The soil solutions have concentrations of dissolved organic C between 3.9-32.0 mg/l. From the calculation of chemical speciation with the chemical equilibrium program ECOSAT (Keizer and Van Riemsdijk, 1994), under the conditions in the acceptor solution, the nitrate, hydrolyzed and carbonate species take less than 1% of total dissolved Cd, less than 3% of dissolved Cu and Zn, and less than 6% of dissolved Pb in the acceptor. The metal reaction constants with NO_3^- , OH^- and CO_3^{2-} are taken from Lindsay (Lindsay, 1979) or MINTEQA2 (Allison et al., 1991). The complexed species of these metals are regarded as negligible in the acceptor, and we assume that concentrations of the measured metal in the acceptor were free metal ions. The concentrations of free metal in the soil solution were calculated with Equation (3).

In these soil solutions, the concentrations of free Cu^{2+} , Cd^{2+} , Pb^{2+} and Zn^{2+} range from less than the detection limit (about 6×10^{-9} M) to 3.6×10^{-5} M (Table 5). The concentrations of free Cd^{2+} and Pb^{2+} in five of the 15 soil samples were too small to be measured by the Donnan membrane method at this stage. Further study is necessary to make this technique applicable for measurements at much smaller concentrations.

The results show that the concentration of free ion of these metals depends not only on the pH. This implies that the adsorption/desorption process, rather than the precipitation/dissolution process, could control the concentrations of free ions in these soils. This is in agreement of the findings with statistical regression by McBride *et al.* (McBride et al., 1997). In the soil solution, the free Cu^{2+} , Cd^{2+} , Pb^{2+} and Zn^{2+} comprise 4-73%, 44-91%, 21-75% and 47-99% of the respective total dissolved metal. Even though there are big variations among the samples, the results in general confirm the previous observation that dissolved Cu and Pb are largely in the form of organo-metal complexes, whereas Cd and Zn occur substantially in the free cation form (McBride et al., 1997). Besides the type of metal, factors such as pH, concentrations of dissolved organic C and dissolved metals are important in metal speciation in soil solutions. For example, the comparisons of Soil 2 with Soil 11 shows that even though the two samples have similar total dissolved Cu, the free Cu^{2+} is approximately 7% in Soil 2 and 43% in Soil 11. The difference can be explained by the higher pH in Soil 2 (pH 7.1) than in Soil 11 (pH 2.9). Complexation of Cu with dissolved organic matter depends strongly on pH (Benedetti et al., 1996; Kinniburgh et al., 1999).

Table 5. Concentration of total dissolved and free Cu^{2+} , Cd^{2+} , Pb^{2+} and Zn^{2+} and dissolved organic C in soil solution measured with the Donnan membrane method (Data are the average of the measurements after 24, 36 and 48 hours with the standard errors in the brackets. -: less than detection limit)

Soil	pH		DOC	Cu (μM)	
	donor	acceptor	(mg/l)	dissolved	free
1	5.38 (0.04)	5.10 (0.01)	24.9 (1.0)	0.131 (0.021)	0.079 (0.038)
2	7.10 (0.28)	5.30 (0.01)	6.3 (0.3)	0.087 (0.006)	0.006 (0.006)
3	4.50 (0.06)	4.57 (0.06)	9.5 (1.5)	0.057 (0.027)	0.012 (0.005)
4	4.38 (0.02)	4.47 (0.00)	3.9 (0.5)	0.023 (0.005)	-
5	3.70 (0.06)	3.72 (0.06)	11.2 (1.2)	0.261 (0.054)	0.113 (0.007)
6	6.09 (0.11)	5.82 (0.13)	22.9 (4.8)	1.031 (0.142)	0.044 (0.014)
7	5.14 (0.05)	5.19 (0.10)	20.8 (1.8)	0.165 (0.013)	0.018 (0.001)
8	6.10 (0.07)	5.82 (0.31)	8.2 (1.6)	0.133 (0.006)	0.027 (0.015)
9	3.50 (0.02)	3.51 (0.04)	16.6 (0.6)	0.059 (0.037)	0.035 (0.022)
10	3.63 (0.02)	3.67 (0.03)	16.1 (0.6)	0.140 (0.135)	0.035 (0.032)
11	2.92 (0.06)	2.95 (0.05)	30.8 (4.8)	0.074 (0.028)	0.032 (0.018)
12	4.37 (0.75)	5.03 (0.12)	32.0 (0.8)	0.156 (0.014)	0.029 (0.006)
13	5.69 (0.18)	5.40 (0.00)	14.9 (1.0)	0.116 (0.004)	0.014 (0.012)
14	3.09 (0.05)	3.14 (0.03)	24.5 (0.5)	0.143 (0.026)	0.105 (0.068)
15	3.58 (0.02)	3.60 (0.03)	15.5 (3.3)	0.273 (0.042)	0.092 (0.024)

Soil	Cd (μM)		Pb (μM)		Zn (μM)	
	dissolved	free	dissolved	free	dissolved	free
1	-	-	-	-	0.466 (0.028)	0.448 (0.165)
2	-	-	-	-	0.412 (0.036)	0.350 (0.162)
3	0.243 (0.003)	0.210 (0.022)	0.067 (0.046)	0.014 (0.002)	41.991 (0.612)	36.357 (3.638)
4	-	-	5.172 (0.238)	2.451 (0.061)	1.154 (0.101)	0.882 (0.270)
5	0.035 (0.001)	0.029 (0.001)	0.102 (0.003)	0.077 (0.011)	6.670 (0.355)	5.894 (0.330)
6	0.484 (0.087)	0.214 (0.025)	0.031 (0.006)	0.017 (0.006)	23.881 (4.325)	11.303 (1.652)
7	-	-	0.017 (0.001)	0.011 (0.015)	6.332 (2.427)	4.092 (0.152)
8	0.009 (0.001)	0.007 (0.000)	0.011 (0.003)	-	43.123 (0.996)	36.151 (1.064)
9	0.167 (0.001)	0.097 (0.003)	0.274 (0.004)	0.152 (0.022)	7.946 (0.044)	4.720 (0.072)
10	0.034 (0.007)	0.020 (0.005)	0.041 (0.005)	0.020 (0.007)	6.706 (0.935)	4.628 (1.155)
11	0.011 (0.001)	0.010 (0.000)	0.167 (0.003)	0.096 (0.013)	2.540 (0.192)	2.513 (0.096)
12	0.010 (0.001)	0.006 (0.000)	0.008 (0.004)	-	2.686 (0.179)	1.756 (0.072)
13	-	-	0.005 (0.006)	-	0.338 (0.281)	0.184 (0.162)
14	0.025 (0.001)	0.021 (0.001)	0.195 (0.002)	0.143 (0.019)	5.485 (0.060)	4.384 (0.432)
15	0.580 (0.025)	0.442 (0.010)	1.124 (0.073)	0.693 (0.178)	38.914 (1.847)	28.833 (6.616)

Another comparison can be made for Zn in Soil 6 and 8, which have similar pHs in the soil solution. Free Zn^{2+} is about 47% of total dissolved Zn in Soil 6 and 84% in Soil 8. It seems that more Zn is in the complexed form in Soil 6, probably due to its containing more dissolved organic C and less total dissolved Zn than in Soil 8.

Conclusions

The Donnan membrane method has been developed for the measurement of the concentration of free metal ion in soil solutions. It is promising because concentrations of free ion of several trace metals can be measured simultaneously, which is impossible with the other methods such as ion selective electrode and competitive chelation. The linking of the soil column to the cation exchange cell provides buffering capacity, and the disturbance of chemical equilibrium is minimized. The method also has the advantage that there is negligible interference from other constituents of the measurement. In the analysis with Donnan membrane method, 24 - 48 hours are necessary for divalent metals to reach the Donnan membrane equilibrium. The smallest measurable ion concentration in this method is determined by the detection limit of ICP-MS. Further study is needed to make the technique applicable to measure ion concentrations less than 10^{-9} M. For this purpose, possible choices include introducing chelating ligands or using larger salt concentrations in the acceptor solution. The Donnan membrane method can be applied to study the biogeochemical behaviour of metals in soils, sediments and other solid materials.

Chapter 3

Aluminum Speciation in Natural Waters: Measurement Using Donnan Membrane Technique and Modeling Using NICA-Donnan

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Abstract

The study of Al speciation is of interest for the assessment of soil and water quality. For the measurement of “free” aluminum (Al^{3+}), a recently developed Donnan membrane technique was tested by measuring Al^{3+} in aluminum-fluoride solutions and gibbsite suspensions. It shows that the Donnan membrane technique can measure free Al^{3+} reliably up to 10^{-9} M and the equilibration takes 3-4 days. Next, Al binding to humic acid (HA) purified from a forest soil was measured using either the Donnan membrane technique or gibbsite suspension. Results were compared with those predicted with the NICA-Donnan model. The predictions using the generic parameters without fitting were in reasonable agreement with the measured data. Finally, the Donnan membrane technique was used to determine Al binding to dissolved organic matter (DOM) in the solutions of 24 soil samples at pH interval of 3-7. Measurements agree well with the predictions using the NICA-Donnan model assuming 30% of DOM is humic acid and 30% is fulvic acid. With this model, the effects of pH and DOM changes on the concentration of Al in 81 soil solutions were predicted reasonably without adjustment of model parameters. The comparison between the results of analysis and the modeling provides a mutual validation for the two methods.

Introduction

Aluminum is one of the most abundant elements in soils and it occurs in soil solution as well as in aquatic systems. The study of Al speciation is of interest for the assessment of soil and water quality, not only because of its toxic effects at elevated concentrations (e.g. Alva et al., 1986; Cronan and Schofield, 1979), but also due to its influence on many related environmental processes.

The soluble Al, as defined by filtration through 0.45 or 0.1 μm membrane filter (Bloom and Erich, 1989), includes free Al^{3+} [$\text{Al}(\text{H}_2\text{O})_6^{3+}$] ion, monomeric inorganic complexes (mainly with OH^- and F^-), fine colloidal mineral Al and Al associated with dissolved organic matter (DOM). Organically complexed Al can be the predominant form of Al in water (Driscoll, 1989). The organic complexes of Al are less toxic than free Al^{3+} ion and the monomeric complexes (Bloom and Erich, 1989). Binding of Al to dissolved organic matter can induce coagulation of DOM in natural waters (Ong and Bisque, 1968; Ares and Ziechman, 1988; Temminghoff et al., 1998; Masion et al., 2000), which in turn will affect the solubility and mobility of many environmentally relevant components, such as heavy metals and organic pollutants that are strongly bound to DOM. Aluminum can also compete with heavy metals for the binding sites on organic matter and thus influence the toxicity and mobility of these metals (Kinniburgh et al., 1999; Pinheiro et al., 2000).

Humic and fulvic acids represent up to 70% of DOM (Clark, 1995). There are only a few data sets available for Al binding to humic substances using different methods like equilibrium dialysis, ferron reaction kinetics, morin fluorescence technique, cation exchange, fluoride electrode and competitive binding methods (Tipping et al., 1988a, b; Browne and Driscoll, 1993; Sutheimer and Cabaniss, 1997; Kinniburgh et al., 1999; Pinheiro et al., 2000). The difficulty in the determination of Al species is the main reason for the few available data sets of Al binding.

The chemical behavior of Al severely limits choices among available analytical methods, and it is usually necessary to combine two or more techniques to describe adequately Al chemistry in a particular system (Nordstrom and May, 1989). Fluoride potentiometry is the central technique in the investigations of aqueous Al chemistry, through application of readily available ion-selective electrodes (ISE) for measuring F^- ion activities (Lindsay, 1979). The Al^{3+} concentration is then calculated with the known reaction constants of Al-F

complexes. For the measurement, fluoride is normally added to Al solution and Al speciation can be disturbed. The other important method to separate polymeric and monomeric Al species is based on the rates of reaction of Al with complexing ligands such as ferron. This method is the most rapid but least satisfactory, because these ligands are generally too aggressive and can sequester Al from organic complexes and other colloidal forms (Bloom and Erich, 1989). A review of the analytical methodology of Al speciation can be found in Clarke *et al.* (1996).

Recently, a Donnan membrane technique has been developed and used for the measurement of free ion activity (concentration) of the bivalent cations such as Cd^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+} (Temminghoff *et al.*, 2000; Weng *et al.*, 2001b; Osté *et al.*, 2002). Its applicability for the measurement of Al speciation has not previously been studied. Compared with other speciation methods, the Donnan membrane technique has the advantages of allowing the measurement of several elements simultaneously and minimizing the disturbance of the substrate.

Researchers often rely on models to calculate the speciation when measurements are not available. Calculations of inorganic Al are relatively straightforward because of the availability of good thermodynamic data. However, difficulty arises in estimating organically complexed Al. Backes and Tipping (1987) and Tipping *et al.* (1988b) proposed an empirical logarithmic linear expression to calculate Al bound to humic substances using known pH and Al^{3+} activity. Schecher and Driscoll (1988) coupled a chemical equilibrium model for the speciation of inorganic Al (ALCHEMI), with a binding model of Al to organic matter by regarding organic ligands as a triprotic acid. Sutherland and Cabaniss (1997) formulated a one-site model with a conditional Al binding constant to fulvic acid. These models are simple to use but are valid for limited conditions and can not be extended easily to a coupled model, in which metal binding competition, effects of salt level on the binding and change of the charge and potential of DOM due to Al binding are accounted for.

Tipping *et al.* (1995) used a chemical equilibrium model (WHAM) to calculate the solid-solution distribution of Al. The center of WHAM is the Humic Ion-Binding Model V (Tipping and Hurley, 1992), which has been upgraded to Model VI (Tipping, 1998). Model V is a discrete-site adsorption model and includes electrostatic and competitive effects. Another advanced model for ion binding to humic substances is the NICA-Donnan model

(NICA: Non Ideal Consistent Competitive Adsorption) (Kinniburgh et al., 1999). The NICA-Donnan model treats the sites as having a continuous affinity distribution. The model accounts for proton and multi-metal binding, binding site heterogeneity, ion specific non-ideality, variable stoichiometry and electrostatic effects (Kinniburgh et al., 1999). This type of model has been used to describe metal binding to natural organic matter in soil and solution (Benedetti et al., 1995; Benedetti et al., 1996a; Gooddy et al., 1995; Temminghoff et al., 1997). It has recently been parameterized for a range of metal ions including Al using the most extensive data set presently available (Milne, 2000; Milne et al., 2001) (Table 1, Appendix). The intrinsic equilibrium constants of Model V and NICA-Donnan allow comparison from results of different humic substances, under different conditions and with different techniques (Tipping et al., 1988a).

The objective of this paper is to develop sound measurement and modeling methods for the determination and prediction of Al binding to natural organic matter by applying the Donnan (cation exchange) membrane technique and the NICA-Donnan model. The Donnan membrane technique was tested for the determination of Al^{3+} by measuring Al^{3+} in aluminum-fluoride solutions and gibbsite suspensions. The binding of Al to purified humic acid and to DOM in the soil solution was measured and compared to those calculated with the NICA-Donnan using the generic parameters (Milne, 2000; Milne et al., 2001), in order to mutual validate the two methods. Using the model, the effects of pH and DOM content on the concentration and speciation of Al were assessed.

Materials and methods

Donnan membrane technique

Temminghoff *et al.* (2000) and Weng *et al.* (2001b) have described the method of the (soil column) Donnan membrane technique. The design of the cation exchange cell was described by Temminghoff *et al.* (2000). In the cell, a cation exchange membrane (BDH Laboratory Supplies, England) is used to separate the substrate solution (donor) and a blank salt solution (acceptor). The membrane has a matrix of polystyrene and divinylbenzene with sulphonic acid groups, which are fully deprotonated at $\text{pH} > 2$. Before analysis, the membrane is prepared by shaking with 0.1M HNO_3 and the same solution that will be used as the acceptor solution successively.

Both the donor and the acceptor solution are circulated continuously by pumping. When the Donnan membrane equilibrium is reached, samples from both sides are taken and concentrations of the target and reference cations are measured. The concentration of the free target cation is calculated based on the theory of Donnan membrane equilibrium that the charge corrected ratios of the cation activity in both sides of the membrane are equal (Fitch and Helmke, 1989):

$$(a_{td}/a_{ta})^{1/Z_t} = (a_{rd}/a_{ra})^{1/Z_r}, \quad (1)$$

where a_{td} and a_{ta} are the activity of the target cation in donor and acceptor solution and Z_t is its charge, and a_{rd} , a_{ra} and Z_r are the analogous quantities for the reference cation.

To keep the ionic strength in the two sides as close as possible, a salt solution is needed to prepare the donor and the acceptor solution. It is ideal that the composition of the salt solution does not disturb the chemical equilibrium of the target cation. And it is essential to have a multi-valent cation present in the background solution to compete with the target cation for the binding to the membrane, to ensure sufficient transport of the target cation cross the membrane (Osté et al., 2002). Calcium salt was chosen to provide a competing cation (Ca^{2+}) for the binding to the membrane. Ca^{2+} can be used as the reference cation in Equation (1) for the correction of the ionic strength difference, if Ca present in both sides is in the free ion form:

$$(\text{Al}^{3+}_d/\text{Al}^{3+}_a)^{1/3} = (\text{Ca}^{2+}_d/\text{Ca}^{2+}_a)^{1/2}, \quad (2)$$

However, when a ligand such as DOM is present in the substrate solution, Ca in the donor solution can be partly in the complexed form and can not be used for the purpose of correction. In this case, the salt solution can be prepared as a mixture of Ca and a mono-valent cation such as potassium. Potassium forms weak complexes with DOM and can be regarded as free ion and used in the correction:

$$(\text{Al}^{3+}_d/\text{Al}^{3+}_a)^{1/3} = (\text{K}^+_d/\text{K}^+_a)^{1/1}, \quad (3)$$

In soil solutions, potassium is always present and it is not necessary to introduce potassium in the salt solution.

After the analysis, the activity of the reference cation, Ca^{2+} or K^+ , in the donor and acceptor solution was calculated using their measured concentrations and the activity coefficients (Davies equation). Activity of Al^{3+} in the acceptor solution was calculated from the concentration of Al, pH and F^- activity measured, using the known Al hydrolysis constants and Al-F reaction constants. The chemical speciation calculations were done with the computer program ECOSAT (Keizer and Van Riemsdijk, 1994).

In all of the experiments, pH was measured with a pH-meter. Dissolved organic carbon (DOC) content was measured with a fully automated TOC/DOC analyzer (SK12, Skalar, The Netherlands) by persulphate and tetraborate oxidation. Concentration of DOC in the filtered solution was corrected for DOC leaching from the filter. The concentrations of the macro-elements (Ca, Mg, K and Na) were measured by ICP-AES (Eppendorf Elex 6361), and concentrations of Al were measured by ICP-MS (Perkin-Elmer, Elan 6000). Activity of F^- was measured using a fluoride ion selective electrode (ORION 9409).

Testing the Donnan membrane technique for the determination of Al speciation

The applicability of the Donnan membrane technique for the determination of Al speciation was tested by measuring Al^{3+} activity in Al-F solutions and in gibbsite suspensions. In the first experiment, the aluminum-fluoride solutions were prepared from the stock solution of 80 μM $\text{Al}(\text{NO}_3)_3$ and 0.1 M NaF in a background of 2 mM $\text{Ca}(\text{NO}_3)_2$. The total Al concentration was 0.4 mM and the pH was adjusted to 4.0 with NaOH and HNO_3 . The total F concentration varied from 0.2 to 1 mM. The experiment was designed in such a way that CaF_2 precipitation would not occur. The solutions were shaken for 2 days at 20°C before the Donnan membrane analysis was started. The aluminum-fluoride solution (200 ml) was used as donor solution in the Donnan membrane analysis. And as the acceptor solution, 18 ml of 2 mM $\text{Ca}(\text{NO}_3)_2$ was used. Samples were taken after 1, 2, 4, 6, 8, 10 and 13 days. Concentrations of Al and Ca, pH and F^- activity in both the donor and acceptor solutions were measured.

In the experiment with gibbsite suspension, the synthetic crystallized gibbsite particles were prepared as described by Hiemstra *et al.* (1987). A suspension of 0.5 g/l gibbsite in 2 mM $\text{Ca}(\text{NO}_3)_2$ solution was adjusted several times to reach pH 4-7 with NaOH and HNO_3 . No precautions were made to avoid CO_2 absorption. After shaking at 20°C for 5 days, the suspension was analyzed with the Donnan membrane technique for Al^{3+} activity. In the

analysis, the gibbsite suspensions (200 ml) were used as the donor solutions, and the 2 mM $\text{Ca}(\text{NO}_3)_2$ (18 ml) was used as the acceptor solution. Samples from both sides were taken after 4 and 5 days as replicates. The donor solution was filtered using a 0.45 μm nitrate-cellulose membrane filter (Schleicher & Schuell, NC45). The pH and the concentration of Al and Ca were measured in the donor and acceptor solution.

Measurement and modeling of Al binding to humic acid (HA)

The purified humic acid (HA) was extracted from the forest floor material taken from the Tongbersven forest in the Netherlands. The method used to purify the humic acid was described by Temminghoff *et al.* (1997). This humic acid material has been used in other studies (Temminghoff *et al.*, 1998; 1997). Its C content is 54% (Temminghoff *et al.*, 1997). Aluminum binding to HA at pH 3-5 was measured using the Donnan membrane technique. Solutions were prepared containing 500 mg/l HA, 50 mM KNO_3 , 1 mM $\text{Ca}(\text{NO}_3)_2$, and 10^{-1} - 10^{-5} M $\text{Al}(\text{NO}_3)_3$ and were adjusted to pH 3-5 with NaOH and HNO_3 . The Al-HA solutions (200 ml) were used as donor solutions in the Donnan membrane analysis, while a solution of 50 mM KNO_3 and 1 mM $\text{Ca}(\text{NO}_3)_2$ (18 ml) was used in the acceptor. After 4 and 5 days, samples of the donor and acceptor solutions were taken. Concentration of DOC in the donor solution and pH, concentrations of Al, Ca and K in both the donor and acceptor solutions were measured.

At pH above 6, Al^{3+} concentration is too low to be measured using the Donnan membrane technique. Therefore Al binding to HA at pH 6-7 was measured in the presence of gibbsite instead of using the Donnan membrane technique, assuming that gibbsite controls the Al^{3+} activity. Suspensions containing 2 g/l gibbsite and 100 mg/l HA in 50 mM KNO_3 and 1 mM $\text{Ca}(\text{NO}_3)_2$ were prepared. The pH was adjusted with NaOH and HNO_3 . The solutions were shaken at 20°C. Samples of the solution were taken after 1, 3, 7, and 10 days. After filtering the solution (0.45 μm), DOC, pH, and concentrations of Al, K and Ca were measured.

Measurement and modeling of Al binding to DOM in soil solution

Two sets of soil samples were used. The first sample set includes 32 soil samples collected in June 1998 from a field in The Netherlands (Wildekamp site) (Weng *et al.*, 2001a). In 1982, the field site was established as a randomized block design of four pH adjustments [nominal pH: 4.0, 4.7, 5.4 and 6.1] and four copper concentrations (0, 250, 500, and 750 kg $\text{CuSO}_4/\text{hectare}$). pH levels were established using calcium carbonate or sulfur. pH and Cu

levels were adjusted in the plough layer. In 1988, pH levels were readjusted to their nominal values (Korthals et al., 1996; Lexmond, 1980). From this site, soil samples at the lowest and highest pH were taken from 0-100 cm. The field samples were air-dried, sieved (<2 mm) and stored at 5°C.

Another soil set includes 49 topsoil (0-20cm) samples collected in 1997 from The Netherlands, Germany and Belgium (De Groot et al., 1998). The sampling sites cover both places with known sources of metal pollution and places considered to contain metals at natural background concentrations. The pH ranges from 2.9-7.8. Aggregates were broken by hand or by machine, and the samples were sieved (<4 mm) and stored at 5°C as moist soil. For all the soil samples in both data sets, the data on the Al concentration, pH and DOC content in the filtrated soil solution prepared with 2 mM $\text{Ca}(\text{NO}_3)_2$ (soil solution ratio 1: 2), which has been equilibrated with the soil for 2 days, are available.

Eight samples of soil set 1 and 16 samples of soil set 2 were selected for the measurement of Al^{3+} activity using the Donnan membrane technique linked with a soil column (Weng et al., 2001b). The soil material in the soil column provides the buffering capacity during the analysis. 100 g soil sample based on air-dried weight was used in the analysis. 200 ml and 18 ml of 2 mM $\text{Ca}(\text{NO}_3)_2$ solution were used as the salt solution in the donor and acceptor side respectively. The composition of the donor solution will after some time be determined by the buffering behavior of the soil, since the amount of ions added to the system is small compared to the ions bound to the solid phase matrix. The column percolation speed was 2 ml/minute. After 4 and 5 days, the donor and acceptor solutions were sampled. The donor solution was filtered over a 0.45 μm filter. DOC in the donor solution, pH, F^- activity, and the concentrations of Al, Ca, Mg, K, Na in the donor and acceptor solutions were measured.

Results and discussion

Using the Donnan membrane technique for the determination of Al speciation

A preliminary experiment using solution containing only $\text{Al}(\text{NO}_3)_3$ in a 2 mM $\text{Ca}(\text{NO}_3)_2$ background at pH 4 shows that it takes 3-4 days for the free Al^{3+} ion to reach the Donnan membrane equilibrium (data not shown). The equilibrium time for the free Al^{3+} ion (3-4 days) is longer than that for the bivalent cations such as Cd^{2+} and Cu^{2+} (1-2 days) (Temminghoff et al., 2000; Weng et al., 2001b). The larger charge of Al^{3+} than the bivalent cations leads to stronger binding of Al^{3+} in the membrane and slower release to the acceptor

solution. The set up of the Al-F experiment was chosen to give rise to a range of 0.06-99.9% of total Al being complexed by fluoride. Although the Donnan membrane equilibrium should have been reached for free Al^{3+} ion in 3-4 days as stated above, the total concentration of Al in the acceptor solution shows a very slow gradual increase with time in the Al-F experiment (Figure 1).

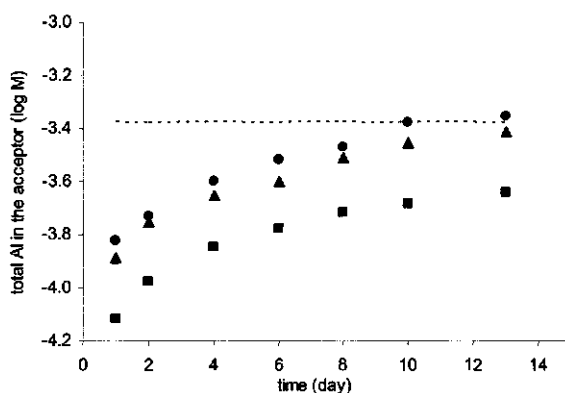


Figure 1. *Change of the total concentration of Al in the acceptor solution over time in the Al-F experiment (■ Al in acceptor, F^- activity in the donor is $10^{-4.1} M$, ▲ Al in acceptor, F^- activity in the donor is $10^{-5.3} M$, ● Al in acceptor, F^- activity in the donor is $10^{-6.3} M$, --- total Al concentration in the donor solution)*

Aluminum is easily hydrolyzed and most of the aqueous Al can be in its hydroxo species at natural pH. Because of the positive charge, the Al hydroxo species, such as $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}(\text{OH})_2^{2+}$ and $\text{Al}(\text{OH})_2^+$, will be also transported, together with the free Al^{3+} ion, through the cation exchange membrane in the Donnan membrane analysis. The distribution of total Al over its various hydrolysis products in the acceptor solution will be determined by the pH of the acceptor solution. Another fact that complicates the application of the Donnan membrane technique to Al measurement is the possible importance of Al fluoro complexes. The activity of F^- in soil solutions normally ranges from 10^{-10} to $10^{-4} M$ (Lindsay, 1979), and the degree of Al-F complexation can be very high (Lindsay, 1979). Similarly, the positively charged Al fluoro species, AlF^{2+} and AlF_2^+ , will be transported to the acceptor solution. The transported Al hydroxo and fluoro species will equilibrate with the OH^- or F^- activity in the acceptor. It is possible that the pH in the acceptor is different from the pH in the donor due to different ionic strength or due to the dissolution of CO_2 . In this case, the Donnan membrane equilibrium will not be reached for the hydroxo species. Once transported into the acceptor

solution, the Al-F species will dissociate because of the very low F^- activity in the acceptor solution originally. The F^- concentration in the acceptor solution will slowly increase due to the transport of Al-F species. Because of this slow increase in F^- concentration, a full equilibrium for all positively charged species of Al is not easily reached as shown in Figure 1. The figure shows that in the Al-F experiment the full equilibrium was slower when the F^- activity was larger. However, for the measuring of free Al^{3+} activity, it is not necessary to wait until the full equilibrium is reached, since the partial equilibrium for the free Al^{3+} ion can be obtained in 3-4 days, as we show below.

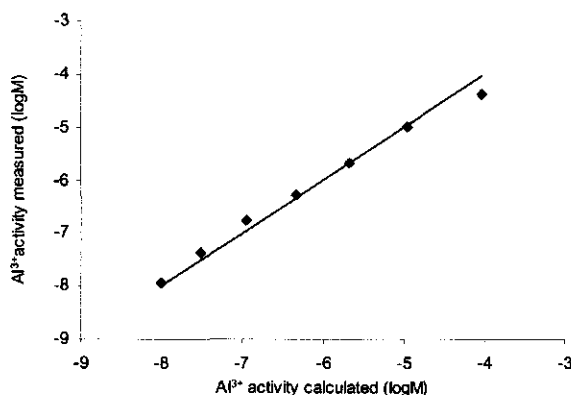


Figure 2. Comparison of the measured and calculated Al^{3+} activity in the Al-F experiment (measured using the Donnan membrane technique after 13 days of equilibration; calculated using the complexation constants of the fluoro specieses of Al. ■ Al^{3+} activity measured, — 1 to 1 line).

Figure 2 compares the “measured” Al^{3+} activity derived from the chemical analysis of the acceptor solution (pH, Al concentration and F^- activity), with the calculated Al^{3+} activity based on the composition of the donor solution. The results show that there is excellent agreement between the two approaches, which validates the Donnan membrane technique as a means to determine the Al^{3+} activity in solution containing fluoride. It also shows that although the full equilibrium was not reached yet at the end of the experiment (13 days), the free Al^{3+} activity can still be measured as long as there is equilibrium for this Al species.

The gibbsite material used in the experiment with gibbsite suspension is well-crystallized (Hiemstra et al., 1987). It is essentially possible to measure its solubility by filtrating the

solution and do speciation calculation of monomeric Al. In this experiment, we used the Donnan membrane technique to measure the solubility of gibbsite, in order to examine further the reliability of the technique in measuring Al^{3+} activity. The dissolution equilibrium of gibbsite can be written as:



The solubility product reported for gibbsite in the literatures varies. The Al^{3+} activity calculated based on the measurements of pH and Al concentration in the acceptor solution is compared in Figure 3 with the calculated activity using the solubility products of $\log K^0 = -33.96$ from Lindsay (1979) and $\log K^0 = -34.3$ from Palmer and Wesolowski (1992). The Al^{3+} activity can be calculated according to the following equations:

$$\log(\text{Al}^{3+}) = 8.04 - 3\text{pH} \quad (\text{Lindsay, 1979}) \quad (5)$$

$$\log(\text{Al}^{3+}) = 7.7 - 3\text{pH} \quad (\text{Palmer and Wesolowski, 1992}) \quad (6)$$

Results show that when the Al^{3+} activity is above 10^{-9} M, the Al^{3+} activity in the gibbsite suspension derived from the measurement of the acceptor solution is in good agreement with that calculated using the solubility product of Palmer and Wesolowski (Figure 3). The

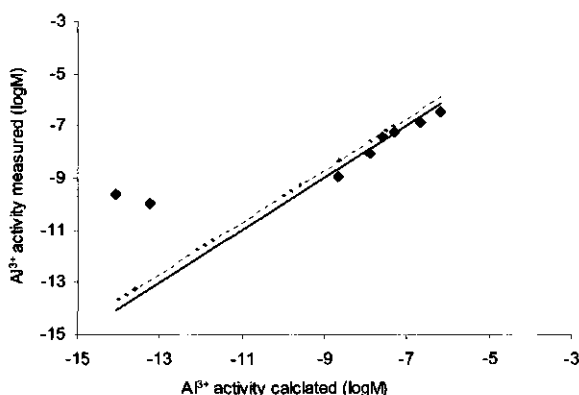


Figure 3. Comparison of Al^{3+} activity in the gibbsite solution measured and calculated using the solubility products of Lindsay (1979) and Palmer & Wesolowski (1992) (■ Al^{3+} activity measured, — 1 to 1 line of Al^{3+} activity calculated using the gibbsite solubility of Palmer & Wesolowski (1992), --- Al^{3+} activity calculated using the gibbsite solubility of Lindsay (1979)).

change of the gibbsite solubility with pH was very well reproduced with the Donnan membrane technique. The detection limit of the ICP-MS for the total Al concentration is about 10^{-8} M, which limits the detectable Al^{3+} activity to about 10^{-8} – 10^{-9} M depending on the pH in the acceptor solution. The Donnan membrane equilibrium with respect to pH is easily obtained at low pH. At a near neutral or basic pH of the donor solution, we observed a lower pH in the acceptor. The maximum pH measured in the acceptor was around 6, whereas in the donor pH can be as high as 7.8.

Measurement and modeling of Al binding to HA

Aluminum binding to HA was measured using the Donnan membrane technique at pH 3.05 ± 0.05 , 3.55 ± 0.05 , 4.05 ± 0.05 , 4.40 ± 0.10 and 4.85 ± 0.05 . For each pH level, Al binding was measured at different Al concentrations. The experiment was designed to avoid over-saturation with respect to gibbsite. The results are shown in Table 1.

The amount of Al bound to HA was calculated as the difference between the total Al and monomeric inorganic Al in the donor solution. The concentration of monomeric inorganic Al was calculated from pH and the Al^{3+} activity obtained using the Donnan membrane technique. The results show that Al bound to HA depends on the Al^{3+} activity and pH. The pH dependency is more pronounced at smaller Al^{3+} activity.

Aluminum binding to HA at pH 6.3, 6.5 and 7.0 was measured in a system where both gibbsite and HA were present and assuming that gibbsite controls the Al^{3+} activity in the solution. Figure 4 shows the change of pH, concentration of DOC and Al in the solution in one of the treatments during the 10 days reaction time. The DOC concentration decreased quickly at the beginning of the experiment due to the adsorption on gibbsite. The pH increased by 0.27 units due to the release of OH^- from the gibbsite surface upon humic acid adsorption. The Al concentration in the solution is almost stable after 7 days. The results of Al binding to HA obtained are given in Table 1 together with those measured using the Donnan membrane method. The gibbsite solubility product of $\log K^0 = -34.3$ from Palmer and Wesolowski (1992) was used to calculate the free Al^{3+} activity in the solution. The difference between the total Al in solution and the monomeric inorganic Al calculated from pH and Al^{3+} activity was considered as Al bound to HA.

Table 1. *Al binding to HA measured using the Donnan membrane technique (pH<5) after 4 and 5 days of equilibration or measured in the presence of gibbsite (pH>5) after 10 days of equilibration*

pH	Al in solution (M)	HA (mg/l)	Al ³⁺ activity (M)	Al bound to HA (mol/kg)	pH	Al in solution (M)	HA (mg/l)	Al ³⁺ activity (M)	Al bound to HA (mol/kg)
3.1	2.09 x10 ⁻⁵	432	1.42 x10 ⁻⁷	0.047	4.0	5.02 x10 ⁻⁴	474	4.99 x10 ⁻⁵	0.660
3.1	2.17 x10 ⁻⁵	432	1.12 x10 ⁻⁷	0.048	4.5	2.06 x10 ⁻⁵	460	7.84 x10 ⁻⁸	0.045
3.1	2.04 x10 ⁻⁵	432	2.37 x10 ⁻⁷	0.045	4.5	7.15 x10 ⁻⁵	460	1.78 x10 ⁻⁷	0.155
3.1	6.01 x10 ⁻⁵	432	2.71 x10 ⁻⁶	0.108	4.5	1.15 x10 ⁻⁴	460	1.43 x10 ⁻⁷	0.249
3.0	1.11 x10 ⁻⁴	432	7.70 x10 ⁻⁶	0.147	4.4	1.34 x10 ⁻⁴	460	2.04 x10 ⁻⁶	0.289
3.1	4.83 x10 ⁻⁴	432	7.82 x10 ⁻⁵	0.290	4.4	2.33 x10 ⁻⁴	460	1.40 x10 ⁻⁵	0.482
3.1	8.19 x10 ⁻³	432	6.66 x10 ⁻⁴	0.536	4.3	1.90 x10 ⁻⁴	460	3.06 x10 ⁻⁵	1.078
3.1	9.49 x10 ⁻²	432	3.60 x10 ⁻³	0.745	4.8	4.60 x10 ⁻⁵	474	4.92 x10 ⁻⁸	0.097
3.6	1.79 x10 ⁻⁵	460	1.14 x10 ⁻⁷	0.039	4.9	4.61 x10 ⁻⁵	474	3.51 x10 ⁻⁸	0.097
3.6	4.84 x10 ⁻⁵	460	3.58 x10 ⁻⁷	0.102	4.9	4.85 x10 ⁻⁵	474	5.35 x10 ⁻⁸	0.102
3.5	1.14 x10 ⁻⁴	460	2.63 x10 ⁻⁶	0.205	4.9	5.82 x10 ⁻⁵	474	3.99 x10 ⁻⁸	0.123
3.5	1.95 x10 ⁻⁴	460	2.33 x10 ⁻⁵	0.284	4.9	5.23 x10 ⁻⁵	474	4.39 x10 ⁻⁸	0.110
3.5	5.20 x10 ⁻⁴	460	7.38 x10 ⁻⁵	0.443	4.9	5.28 x10 ⁻⁵	474	2.19 x10 ⁻⁸	0.111
3.5	7.39 x10 ⁻⁴	460	1.25 x10 ⁻⁴	0.479	4.9	7.93 x10 ⁻⁵	474	5.20 x10 ⁻⁸	0.167
4.1	1.19 x10 ⁻⁴	432	3.67 x10 ⁻⁷	0.268	4.8	1.10 x10 ⁻⁴	474	4.24 x10 ⁻⁸	0.232
4.1	2.79 x10 ⁻⁵	432	4.88 x10 ⁻⁸	0.065	6.3	1.59 x10 ⁻⁶	11	7.76 x10 ⁻¹²	0.132
4.1	4.55 x10 ⁻⁵	432	1.59 x10 ⁻⁷	0.105	6.3	1.87 x10 ⁻⁶	15	5.50 x10 ⁻¹²	0.113
4.1	5.64 x10 ⁻⁵	432	1.06 x10 ⁻⁷	0.130	6.5	3.87 x10 ⁻⁷	12	1.29 x10 ⁻¹²	0.021
4.0	9.46 x10 ⁻⁵	474	2.47 x10 ⁻⁷	0.196	6.5	5.67 x10 ⁻⁷	16	1.48 x10 ⁻¹²	0.026
4.0	1.72 x10 ⁻⁴	474	4.61 x10 ⁻⁶	0.333	7.0	1.03 x10 ⁻⁶	21	4.68 x10 ⁻¹⁴	0.044
4.0	2.18 x10 ⁻⁴	474	7.78 x10 ⁻⁶	0.414	7.0	7.44 x10 ⁻⁷	16	6.17 x10 ⁻¹⁴	0.039

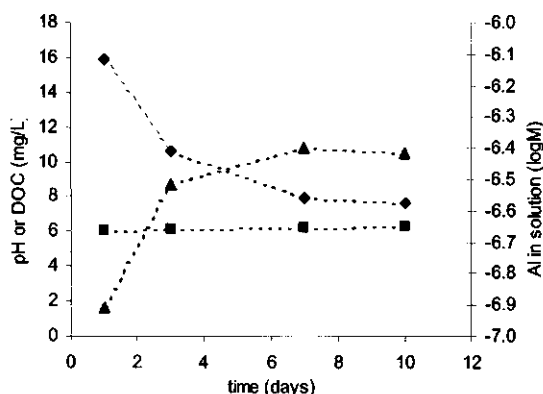


Figure 4. Changes of concentration of DOC, pH and concentration of Al in solution in one of the gibbsite-HA solutions (◆ DOC mg/l, ■ pH, ▲ Al in solution).

The results in Table 1 show that high loading of Al on humic acid can in practice only be obtained at low pH, although the binding in principle increases with increasing pH at constant Al^{3+} activity. However, as soon as gibbsite starts to control the Al^{3+} activity, one will observe a decrease of the Al binding with increasing pH, because the rate at which the Al^{3+} activity decreases with pH is stronger than the increasing effect of pH on the binding to humic acid. Table 1 shows that the decrease in Al binding becomes very fast above pH 6.3.

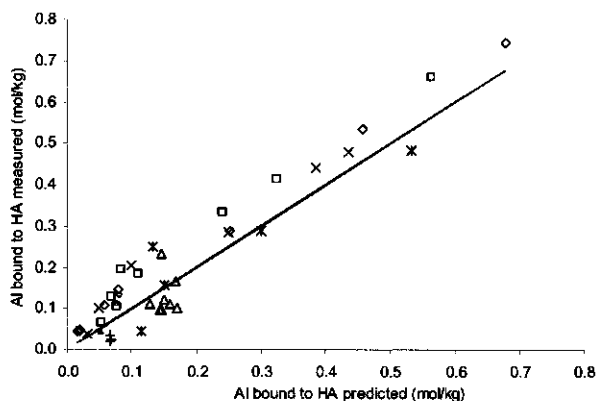


Figure 5. Comparison of Al bound to HA measured and modeled (\diamond pH 3.05 ± 0.05 , \times pH 3.55 ± 0.05 , \square pH 4.05 ± 0.05 , \triangle pH 4.85 ± 0.05 , $*$ pH 4.40 ± 0.10 , \circ pH 6.30 ± 0.03 , $+$ pH 6.50 ± 0.03 , $-$ pH 7.00 ± 0.03 , — 1 to 1 line of the model calculation).

Using the pH, Al^{3+} activity, concentrations of Ca and K, and DOC content measured in the Al-HA solutions, the Al bound to HA was calculated with the NICA-Donnan model using the generic parameters of humic acid (Milne, 2000; Milne et al., 2001) (Table 1, Appendix). The generic parameters were used because there were no parameters of Al binding available for the specific HA in this test. And it is desirable to validate the applicability of the generic parameters in the prediction of metal binding to individual humic acids. The calculation was done by the computer program ECOSAT (Keizer and Van Riemsdijk, 1994). In the calculation of Al binding, only the free Al^{3+} ion species was considered to bind specifically. The other charged Al species were treated as electrostatically bound as any other ions present. The competition of H^+ and Ca^{2+} for the specific binding and the ionic strength effects were accounted for. Figure 5 compares the Al bound to HA measured and calculated without changing the generic humic acid parameters. The agreement is reasonable. The mean residual (Al bound predicted – Al bound measured) is -0.04 mol/kg and the root mean square residual is 0.09 mol/kg.

Measurement and modeling of Al binding to DOM

With the soil column Donnan membrane method, the Al^{3+} activity in soil solutions of the 24 chosen soil samples was measured. The initial composition of the salt solution that was circulated through the column was 2 mM $\text{Ca}(\text{NO}_3)_2$. The pH of the soil solutions ranges from 3.0 to 7.4. The highest pH at which the free Al^{3+} activity could be reliably measured with the Donnan membrane technique was 6.0. DOC was between 4.8 and 93.7 mg/l, and F⁻ activity varied between 10^{-8} and 10^{-5} M.

The measured Al^{3+} activity in the soil solution was compared with gibbsite solubility (Palmer and Wesolowski, 1992). The results are shown in Figure 6. At low pH (<4.0), the measured Al^{3+} activity in the soil solution was mostly smaller than the gibbsite solubility and was around 10^{-5} M. At pH>4.0, the Al^{3+} activity was close to the gibbsite solubility. This observation is in agreement with other reports about the Al solubility control in soils (Adams et al., 2000; Cronan et al., 1986; David and Driscoll, 1984; De Wit et al., 1999; Walker et al., 1990). Berggren and Mulder (1995) have concluded that at pH<4.1 Al solubility was under-saturated with respect to gibbsite.

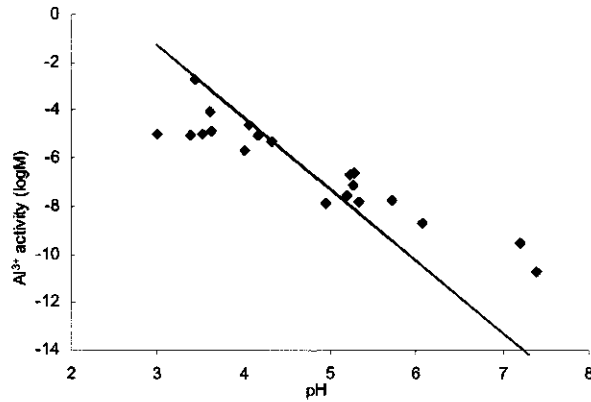


Figure 6. Comparison of Al^{3+} activity measured in the soil solution with that predicted by the solubility of gibbsite (◆ Al^{3+} activity measured, — 1 to 1 line of Al^{3+} activity calculated using gibbsite solubility of Palmer & Wesolowski, 1992).

Aluminum binding to DOM in the soil solution was calculated using the NICA-Donnan model. In this calculation, it was assumed that 30% of DOM behaves as humic acid, 30% as fulvic acid, and 40% is inert in metal adsorption. This assumption is based on the finding that a major fraction of DOM, but not all of it, is humic substances (Clark, 1995). The distribution between the humic and fulvic fractions varies from sample to sample and the assumption made here (equal amount of humic and fulvic acid) is for the best simultaneous prediction for the speciation of several metals (Cu, Cd, Pb, Ni, Zn), which we will discuss in a separate paper. When the Al^{3+} activity in soil solution was not measurable with the Donnan membrane technique, it was assumed that gibbsite controls the Al^{3+} activity in the solution. In Figure 7, the Al concentration measured in the soil solutions for which the Donnan membrane analysis was conducted is compared with that calculated with the NICA-Donnan model from the known Al^{3+} activity, pH and DOC concentration. As the figure shows the agreement is quite reasonable.

Using this modeling approach for Al binding to DOM, the range of Al concentration in solution was predicted for a salt solution of 2 mM $Ca(NO_3)_2$ containing either 0 or 100 mg/l DOC. For the calculation it was assumed that gibbsite controls Al^{3+} activity (solid line in Figure 8). Because it was found that at $pH < 4.0$, Al^{3+} activity in the soil solutions was mostly smaller than that predicted from the gibbsite solubility and was around 10^{-5} M, calculations were also done at fixed Al^{3+} activity of 10^{-5} M for pH 3-4 (dotted line in Figure 8). Total F was 10^{-5} M. In Figure 8, the model predictions for the range of Al concentration in solution

at pH 3.0-9.5 are shown, together with the Al concentration measured in the soil solution in the two data sets. The results show that most of the measured concentrations in the soil solutions, which except one sample all contain DOC between 0 to 100 mg/l, fall within this range.

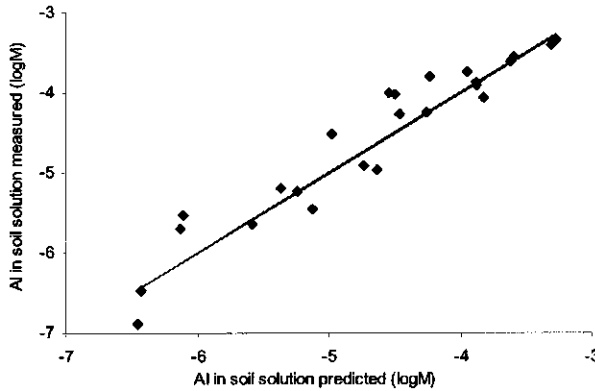


Figure 7. Comparison of concentration of Al in soil solution measured and modeled (♦ Al in soil solution measured, — 1 to 1 line of the Al in solution modeled).

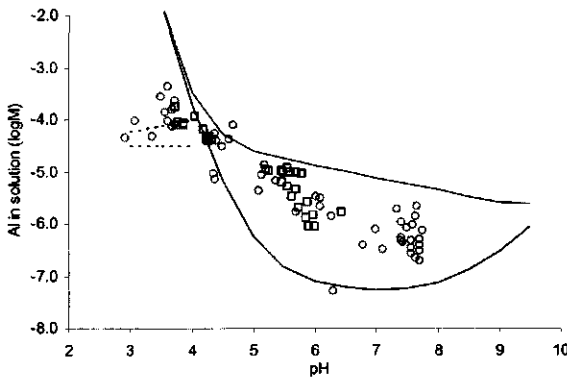


Figure 8. Model calculation of effects of pH and DOM on Al concentration in the solution ($I=0.006\text{ M}$) and comparison with the Al concentration measured in the soil solutions (soil set 1 and 2) (—Al in solution modeled when gibbsite controls Al^{3+} activity, upper line: 100 mg/l DOC; lower line: 0 mg/l DOC; --- Al in solution modeled when Al^{3+} activity is 10^{-5} M , upper line: 100 mg/l DOC; lower line: 0 mg/l DOC; □ Al in soil solution measured in soil set 1; ○ Al in soil solution measured in soil set 2)

It can be seen from Figure 8 that when DOM is absent, the concentration of dissolved Al controlled by gibbsite decreases with increasing pH until a minimum is reached at pH 6.5-7.5, then increases with pH due to the increase of $\text{Al}(\text{OH})_4^-$. However, when 100mg/l DOC is present, the concentration of Al in solution decreases continuously with increasing pH. As we have discussed if Al^{3+} activity is controlled by gibbsite, Al bound to DOM decreases with increasing pH. Therefore, with 100mg/l DOC in the solution, the concentration of Al in solution decreases with increasing pH, even at pH above 7.5 when the concentration of monomeric inorganic Al starts to increase (Figure 8).

Figure 8 also shows that when Al^{3+} activity is controlled by gibbsite, at $\text{pH} < 4.0$, the monomeric inorganic Al are the dominant Al species in solution, even when 100 mg/l of DOC is present. In this case, the change of DOM concentration will therefore not influence the concentration of Al in solution significantly, as demonstrated by the small difference in the Al concentrations in the solutions containing 0 or 100 mg/l DOC at low pH (Figure 8). As pH increases, the DOM-bound Al becomes more important. Although Al bound on each milligram of DOM decreases with increasing pH, the fraction of DOM-bound Al in the solution increases with pH at the same DOM concentration due to the stronger decreases of the concentration of monomeric inorganic Al. The model predicts that at 100 mg/l DOC, the DOM-bound Al becomes more and more important with increasing pH till pH 6.0-6.5. At pH above 6.5, the importance of DOM-bound Al becomes less due to the increase of $\text{Al}(\text{OH})_4^-$ concentration, but the DOM-bound Al still dominates in the solution. The change of DOM content will under this condition significantly influence the concentration of Al in solution. Note that at low pH ($\text{pH} < 4.0$), Al^{3+} activity in soils can be controlled by the binding to the solid organic matter leading to a Al^{3+} activity smaller than that due to gibbsite solubility (Berggren and Mulder, 1995). Binding of Al to the solid organic matter of the soil will be the most important at low pH as can be seen from the loading of HA with Al as a function of pH (Table 1), which has been discussed earlier.

Conclusions

In this paper we presented the results of measurement and modeling of Al binding to humic acid (HA) and to dissolved organic matter (DOM). Firstly, the reliability of the Donnan membrane technique in the determination of Al speciation was tested by measuring the change of Al^{3+} activity when F^- activity changes in the aluminum-fluoride solutions and when pH changes in gibbsite suspensions. The results show that the Donnan membrane

technique gives good measurements of Al speciation when Al^{3+} activity is above 10^{-8} - 10^{-9} M. Although it takes 3-4 days to reach the Donnan membrane equilibrium for Al^{3+} and it is relatively time consuming, the advantages of minimal disturbance of the chemical equilibrium, minimum interference from other components, and the possibility of simultaneous measurement of other cation speciation, makes the Donnan membrane technique a useful method. For the applications where the long equilibration time should be a problem, the volume of the acceptor solution, which is 18 ml in this work, can be reduced to obtain faster equilibrium.

The results of Al binding to the humic acid and to the dissolved organic matter show that Al binds strongly to humic acid and DOM, and that the binding is pH dependent. Compared with the measurements, the NICA-Donnan model gives reasonable predictions of Al binding over a very wide range of conditions without adjusting the model parameters. In soil solutions, Al^{3+} activity was close to the values predicted by gibbsite solubility when pH is higher than 4.0. At $\text{pH} < 4.0$, the Al^{3+} activity was mostly smaller than it would be if controlled by gibbsite. According to the experimental results and the model, when Al^{3+} is controlled by gibbsite, the load of Al on humic acid and DOM decreases with increasing pH. However, the fraction of organically bound Al in solution normally increases with increasing pH. The results are useful in the understanding and prediction of the effects of the changes of environmental factors on the solubility and toxicity of Al. The results can also be applied in the understanding and prediction of the effects of Al binding on the coagulation and concentration of DOM in waters. The model approach used here is applicable under various conditions, because the effects of ionic strength, pH, and competition are all taken into account.

Chapter 4

Contribution of Individual Sorbents to the Control of Heavy Metal Activity in Sandy Soil

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Co-authors: Erwin J. M. Temminghoff; Willem H. Van Riemsdijk

Abstract

A multi-surface model is used to evaluate the contribution of various sorption surfaces to the control of heavy metal activity in sandy soil samples at pH 3.7-6.1 with different sorbent contents. This multi-surface model considers soil as a set of independent sorption surfaces, *i.e.* organic matter (NICA-Donnan), clay silicate (Donnan) and iron hydroxides (DDL, CD-MUSIC). The activities of Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} and Pb^{2+} in equilibrium with the soil have been measured using a Donnan membrane technique. The metal activities predicted by the model agree with those measured reasonably well over a wide concentration range for all the metals of interest except for Pb. The modeling results suggest that soil organic matter is the most important sorbent that controls the activity of Cu^{2+} , Cd^{2+} , Zn^{2+} and Ni^{2+} in these sandy soils. When metal loading is high in comparison with soil organic matter content, the contribution of clay silicates to metal binding becomes more important. Adsorption to iron hydroxides is found not significant in these samples for Cu, Cd, Zn and Ni. However, for Pb the model estimates strong adsorption on iron hydroxides. The model predicts that acidification will not only lead to increased solution concentrations, but also to a shift towards more nonspecific cation-exchange type binding especially for the metals Cd, Zn and Ni. Lowering the pH has led to a loss of 56% of Cd, 69% of Zn and 66% of Ni during 16 years due to increased leaching.

Introduction

In the decision making process concerning the protection of soil quality, it is necessary to make accurate assessments of heavy metal speciation. This is important for formulating heavy metal standards and choosing appropriate soil remediation techniques. Land use change from agricultural production to nature conservation will lead to gradual acidification of especially sandy soils. It is therefore of interest to be able to predict effects of natural acidification on metal ion behavior, especially since long-term agricultural use may have increased the metal content of these soils. It has been established that under most circumstances, free metal ion activity (or concentration) is the key factor in determining metal bioavailability and toxicity (Parker and Pedler, 1997). The dissolved metal pool reflects the soil metal fraction that could potentially be leached from the soil to ground waters and surface waters (Sauvé et al., 2000a).

Soils and sediments usually contain mixtures of several adsorptive surfaces. Heavy metal adsorption to these surfaces is recognized as being important in controlling heavy metal activity. Colloidal particles of soil organic matter (SOM), clay silicates and metal hydroxides, which have large surface area and are often electrically charged, are considered important adsorptive surfaces to bind heavy metals. Zachara *et al.* (1992) reviewed the techniques that have been used to quantify the contribution of different sorbent phases to metal sorption in soils. These techniques include: (i) application of sequential extractions (Tessier et al., 1979; Tack and Verloo, 1995). (ii) development of statistical relationships between the sorption and soil properties (McLaren and Crawford, 1973; King, 1988a; Castilho et al., 1993; McBride et al., 1997; Gray et al., 1999; Sauvé et al., 2000b). (iii) observation of similarities in sorption on single sorbents and whole soils (Tiller et al., 1963; Korte et al., 1976). (iv) comparison of sorption on natural and treated soils (Zachara et al., 1992). As pointed out by Zachara *et al.* (1992), all these methods have limitations. The contribution of individual sorbents may be difficult or impossible to experimentally identify (Mattigod and Zachara, 1996).

Another approach is to try to predict the free metal activity in the soil solution using adsorption and ion-exchange models for the various soil constituents and compare these predictions with measurements. In this approach, one has to make a choice with respect to the types of adsorption models being used. One has to estimate the amount of reactive surface of each type sorbent, and one has to estimate the amount of metal in the solid phase,

which is active in the competitive binding to these surfaces for each relevant metal. One also has to deal with competition of ions other than the heavy metal ions of interest. Some multi-surface calculations have been done using various model approaches (Cowan et al., 1992; Tipping, 1994; Vermeer et al., 1999; Voegelin et al., 2001), but pure predictions of free metal activity using such an approach and comparing the results with measurements have so far not been published. The test of such an approach becomes more useful if a series of metals are included in the study. Since pH plays such an important role in metal adsorption and since the pH effect on metal ion binding is quite different for the different sorbents and for different metals, it is also important to use field soil samples that differ in pH.

In this paper, we propose and apply a multi-surface model to predict the Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} and Pb^{2+} activities in the soil solution of sandy soil samples at pH 3.7-6.1. The predicted metal activities were compared with those measured using a soil column Donnan membrane equilibrium method (Temminghoff et al., 2000; Weng et al., 2001b). The model approach also results in a calculated solid phase speciation of the metals bound to the soil. The relative importance of soil sorbents, *i.e.* SOM, clay and iron hydroxides, for the binding of heavy metals in sandy soils was studied.

Model description

The multi-surface model considers soil as a set of independent sorption surfaces, *i.e.* organic matter, clay silicate and iron hydroxides (amorphous and crystallized). The metal speciation was predicted using models of adsorption and ion-exchange for each sorbent in combination with models of inorganic solution chemistry, precipitation of aluminum hydroxides $[\text{Al}(\text{OH})_3]$ and chloropyromorphite $[\text{Pb}_5(\text{PO}_4)_3\text{Cl}]$. In the following, the models of adsorption and ion-exchange used in the multi-surface model will be discussed.

Binding to soil organic matter

Humic acid was used as an analogue for the reactive soil organic matter (SOM). The consistent Non Ideal Competitive Adsorption Donnan model (Kinniburgh et al., 1999), referred to as NICA-Donnan model, was chosen for metal binding to soil organic matter since it is one of the most advanced models for competitive metal ion binding to humic substances. It has recently been parameterized for the most extensive data set available (Milne, 2000; Milne et al., 2001). The model accounts for proton and multi-metal binding, binding site heterogeneity, ion specific non-ideality, variable stoichiometry, cation-exchange

and electrostatic effect (Kinniburgh et al., 1999). This type of model has been used previously to describe metal binding to natural organic matter in soil and solution (Benedetti et al., 1995, 1996a; Gooddy et al., 1995; Temminghoff et al., 1997, 1998). In the multi-surface model, the NICA-Donnan parameters of generic humic acid (Milne, 2000; Milne et al., 2001) were used in the model calculations (see Table 1, Appendix).

Binding to clay silicates

In the model, illite was taken as a representative of clay silicate, because it is an important aluminum silicate mineral in most soils of the Netherlands (Kuipers, 1984). The adsorption of metals to clay silicates can be attributed to two kinds of processes. At lower pH, nonspecific cation-exchange type binding based on the electrostatic interaction of the metal ions with the negatively charged clay particles is the dominant process. At higher pH, the adsorption of heavy metals seems to be more specific, which may be related to the chemical binding to the edge phases of the clay (Schindler et al., 1987). Because of the relatively low pH (<6.1) of the samples, it was assumed that electrostatic interaction is the main process for binding of cations to the clay silicates. The cation-exchange process of clay domains can be described using a Donnan approach (Tipping, 1994). The advantage of such a model is that there is no need to select ion-exchange coefficients from literature, since they are implicit in the model. Metal concentration in the Donnan phase is related to the concentration in the solution according to the Boltzmann accumulation factor.

Binding to iron hydroxides

In the multi-surface model, metal binding to two types of iron hydroxides, *i.e.* amorphous and crystalline, was considered. Hydrous ferric oxide (HFO) and goethite were assumed as the model substances of the soil amorphous and crystalline iron hydroxides respectively. Goethite is in general the most dominant crystalline iron hydroxide in many soils. Metal binding on HFO was described by a two site surface complexation diffuse double layer (DDL) model (Dzombak and Morel, 1990). Metal binding to goethite was calculated with the Charge Distribution Multi-Site Complexation (CD-MUSIC) model (Hiemstra and Van Riemsdijk, 1996; 1999). The model parameters of DDL and CD-MUSIC were taken from Dzombak & Morel (1990) and Hiemstra & Van Riemsdijk (1996, 1999, 2001) respectively (see Tables 3 and 4, Appendix). The influence of phosphate on metal binding on goethite was taken into account.

The calculation was done with the computer program ECOSAT (Equilibrium Calculation Of Speciation And Transport) (Keizer and Van Riemsdijk, 1994), since it has the possibility to use all the models relevant in this study. HNO_3 (2M) extractable metal was used as the total metal content that is assumed to be active in adsorption processes. The other chemical conditions, such as pH, ionic strength, soil solution ratio are the same as in the soil column Donnan membrane analysis (see Experimental Section). The competition between Al^{3+} , Ca^{2+} and the metal ions of interest for binding to SOM was considered. The effect of competition by Fe^{3+} was not taken into account explicitly, but is implicitly accounted for in the CEC determination since iron bound to SOM is not easily exchangeable. Iron may be one of the reasons for the lower site density of SOM compared to humic acid, as will be discussed in the Results and Discussion section. The PO_4^{3-} activity was calculated using the measured total P in the soil solutions and pH. The Cl^- activity was estimated from the total soil solution Cl measured.

Experimental section

Soil samples

The soil samples were collected in June 1998 from a field near Wageningen in the Netherlands (Wildekamp site). This area was used as permanent pasture for at least 30 years till 1978. From 1978, the soil has been used for crop production. During 1978-1981, liquid cattle manure and mineral fertilizers were applied. There after, only mineral fertilizers have been used. In 1982, the field site was established as a randomized block design of four pH adjustments (coded A, B, C and D for nominal pH of 4.0, 4.7, 5.4 and 6.1 respectively) and four copper concentrations (coded 1, 2, 3, and 4 for copper treatments of 0, 250, 500, and 750 kg CuSO_4 /hectare respectively). pH levels were established using calcium carbonate or sulfur. pH and Cu levels were adjusted in the plough layer. In 1988, pH levels were readjusted to their nominal values (Lexmond, 1980; Korthals et al., 1996).

Samples from the lowest and highest pH (treatments A and D) were taken from different soil layers in the range of 0-100 cm. The field soil samples were air-dried and sieved (<2 mm) before analysis. Soil organic matter (SOM) content was measured by loss-on-ignition at 550°C. Clay content (<2 μm) was measured by sieve and pipette method. Cation exchange capacity (CEC) was determined by unbuffered 0.01 M BaCl_2 method (Houba et al., 1997). Fe fraction in DCB (dithionite-citrate-bicarbonate) and ammonium oxalate – oxalic acid

extractions and metal content in 2 M HNO_3 (SSR=1:10) extractions were measured with ICP-AES (Eppendorf Elex 6361).

Donnan membrane method

The Donnan membrane method is based on a Donnan membrane equilibrium using a cation exchange membrane to separate the substrate solution (donor) and a blank salt solution (acceptor) (Fitch and Helmke, 1989; Temminghoff et al., 2000; Weng et al., 2001b). The charge corrected activity ratios of the cations on both sides of the membrane are equal at the Donnan membrane equilibrium. In one measurement the free metal ion activity of all cations can be determined simultaneously.

100 g air-dried soil sample was used in the soil column Donnan membrane analysis. 200 ml of 0.002 M $\text{Ca}(\text{NO}_3)_2$ solution was used as the salt solution in the donor side and 18 ml in the acceptor side. The composition of the donor solution will be determined by the buffering behavior of the soil that is stored in the soil column and linked to the donor side of the membrane, since the amount of ions added to the system is small compared to the ions bound to the solid phase matrix. The column percolation speed was 2 ml/minute. After 24 and 48 hours, the donor and acceptor solutions were sampled. pH was measured with a pH-meter in all the samples. The donor solution was filtered over a 0.45 μm nitrate-cellulose membrane filter (Schleicher & Schuell, NC45). The concentrations of macro-elements were measured by ICP-AES, and concentrations of micro-elements were measured by ICP-MS (Perkin-Elmer, Elan 6000).

Results and discussion

Analytical results

The analytical data show that there is a wide variation in most soil characteristics (Table 1). The organic matter content and the clay fraction ($<2 \mu\text{m}$) are between 0.4%-4.2% and 2.1%-4.9% respectively. The soil CEC is in the range of 9.0-42.1 mmol/kg. Down a soil profile, the organic matter content, the clay content and the CEC decrease with depth. The decrease of the organic matter content is stronger than the decrease of the clay content. Therefore the contribution of clay to soil CEC is more significant at the bottom of the profile.

The total Cu in the 2M HNO_3 extraction is between 6-2247 $\mu\text{mol/kg}$, which reflects the treatments of Cu levels. The 2M HNO_3 extractable Cd, Zn, Ni and Pb are 0.06-2.45, 4-183,

4-36, 5-124 $\mu\text{mol/kg}$ respectively (Table 1). When comparing the total Cu content in the surface layer (0-20 cm) at the same level of Cu treatment for the low pH soils (soils A) and the high pH soils (soil D), it follows that the amount in the low pH soils is 8-24% lower, indicating an enhanced Cu leaching by acidification during the 16 year period. If we assume that the original content and later input of the other metals is the same for all the treatments in the field, the data shows an even stronger leaching of Cd, Zn and Ni at lower pH. The average total Cd, Zn and Ni content in the surface layer (0-20 cm) for the low pH (soils A) is only 44%, 31% and 34% respectively of that at high pH (soils D). It means that acidification has led to an excess removal of Cd, Zn and Ni of approximately 56%, 69% and 66% of the "initial" amount over a period of 16 years. As for Pb, there is little difference observed in the average total Pb content in the surface layer at the low and high pH, suggesting that there is hardly leaching of this metal. It can be shown that these leaching data are roughly expected based on the amount of water available for leaching in this area (about 1 mm/day) and the measured metal concentrations in the solid and solution phases. We intend to analyze these data in more detail in a forthcoming paper.

The Cu^{2+} activity measured varies from $<10^{-8.2}$ to $10^{-4.9}$ M. Cd^{2+} activity varies from $<10^{-9.2}$ to $10^{-7.2}$ M. Zn^{2+} activity is between $10^{-7.2}$ - $10^{-4.8}$ M. Ni^{2+} activity ranges from $<10^{-8.2}$ to $10^{-5.9}$ M. And Pb^{2+} activity varies from $<10^{-10}$ to $10^{-7.4}$ M. For some soil samples, the metal activity was below the detection limit of the ICP-MS (Table 1). In general, the metal activity decreases with increasing pH. Among these metals, Pb has the lowest free ion concentration in comparison with total Pb. Less than 0.04% of the total 2M HNO_3 extractable Pb exists as free Pb^{2+} , whereas for Cu, this was less than 2.4%. Compared to Pb and Cu, the soil has much lower affinity for Cd, Zn and Ni. This is in agreement with the observation that more Cu and Pb are retarded in the upper layer of the soil profile than the other metals (Table 1). Lower solubility of Pb and Cu in soil has been observed previously (Gerritse and Driel, 1984; Gao et al., 1997; Sauvé et al., 1997).

Site density of soil sorbents

Before being able to do the model calculations, it is essential to make a reasonable estimation of the amount and the site density of soil sorbents. In our model, the clay content ($<2 \mu\text{m}$) measured in the samples was used as the estimation of the clay silicate content in the soil samples. The charge of clay was assumed to be the same as the CEC of illite, which

Table 1. Soil characteristics, total metal contents and metal activities

Soil	Depth (cm)	pH- 0.002M Ca(NO ₃) ₂	CEC- BaCl ₂ (mmol/kg)	Clay (<2 μm) (%)	O.M (%)	Fe- oxalate (g Fe/kg)	Fe- DCB (g Fe/kg)	Metal content (2MHNO ₃ extraction) (μmol/kg)						Metal activity (Donnan membrane analysis) (-log M)					
								Cu	Cd	Zn	Ni	Pb	Cu	Cd	Zn	Ni	Pb		
1A	0-20	3.78	18.7	4.2	3.7	2.08	2.34*	461.2	1.13	55.7	9.1	116.8	6.13	7.37	5.55	6.50	7.53		
2A	0-20	3.86	21.0	4.1	3.9	1.96	2.34*	958.7	1.22	56.5	10.0	115.7	5.69	7.32	5.49	6.42	7.66		
3A	0-20	3.88	20.7	4.2	3.9	2.03	2.34*	1331.6	0.98	50.7	8.8	115.9	5.36	7.45	5.53	6.49	7.60		
4A	0-20	3.76	20.5	4.2	3.9	2.02	2.34	1713.6	0.68	39.4	6.7	115.4	5.10	7.58	5.63	6.70	7.49		
1D	0-20	5.54	42.1	4.2	4.0	2.23	2.28*	519.0	2.20	155.2	19.2	111.4	7.93	8.37	6.25	7.65	>10		
2D	0-20	5.75	41.2	4.8	4.1	2.21	2.28*	1042.7	2.45	175.9	25.1	124.3	7.49	8.29	6.14	7.24	9.11		
3D	0-20	5.59	40.6	4.3	4.1	2.10	2.28	1685.9	2.18	143.5	26.2	107.1	7.15	8.31	6.12	7.01	9.32		
4D	0-20	5.47	40.1	4.5	4.0	2.08	2.29	2247.0	2.33	170.1	31.4	123.4	6.92	8.19	5.94	6.81	8.98		
4A	20-30	3.73	19.4	4.5	3.8	1.80	2.36	1625.6	0.84	51.0	7.5	97.0	4.92	7.21	5.43	6.52	7.43		
4A	30-40	4.07	21.7	4.1	2.4	1.19	4.11	744.5	1.35	46.2	14.0	31.5	5.45	7.19	5.62	6.00	8.13		
4A	40-50	4.19	11.6	3.2	1.0	0.57	1.84	235.6	0.99	42.0	11.2	12.6	6.11	7.25	5.61	6.15	8.88		
4A	50-60	4.25	9.0	2.6	0.4	0.29	1.38	80.9	0.61	25.5	8.4	5.6	6.47	7.35	5.48	6.24	8.87		
4A	60-70	4.26	16.0	2.5	0.4	0.30	1.57	115.5	0.58	52.8	11.2	8.9	6.32	7.44	5.35	6.14	8.62		
4A	70-80	4.25	10.1	2.1	0.4	0.16	1.34	52.5	0.50	51.8	12.2	5.7	6.45	7.42	5.35	6.04	8.79		
4A	80-90	4.29	12.6	2.1*	0.5	0.19	1.34*	102.3	0.59	155.4	16.7	8.5	6.14	7.33	4.78	5.91	8.62		
4A	90-100	4.33	13.3	2.1*	0.4	0.15	1.34*	45.1	0.49	81.3	17.8	6.5	6.79	7.50	5.22	5.99	8.76		
3D	20-30	5.61	39.8	4.9	4.1	2.18	2.13	1369.6	1.96	135.4	24.7	95.0	7.10	8.34	5.91	6.93	9.22		
3D	30-40	5.80	33.1	4.5	3.1	1.51	4.14	307.2	1.01	83.2	16.5	46.4	7.94	9.14	6.22	7.92	9.77		
3D	40-50	5.70	20.0	4.0	1.2	0.74	1.39	36.8	0.24	21.5	6.4	11.6	>8.2	9.05	6.85	>8.2	>10		
3D	50-60	5.64	13.4	2.8	0.6	0.30	0.88	5.7	0.09	4.0	4.3	5.7	>8.2	9.15	6.94	>8.2	>10		
3D	60-70	5.88	12.2	2.6	0.6	0.27	0.83	24.9	0.11	11.7	4.5	6.2	>8.2	9.04	7.07	>8.2	>10		
3D	70-80	5.87	13.4	2.8	0.5	0.15	0.53	8.8	0.06	14.0	4.5	4.8	>8.2	>9.2	6.96	>8.2	>10		
3D	80-90	5.98	13.5	2.8*	0.5	0.19	0.53*	51.4	0.11	48.2	7.8	6.5	>8.2	9.04	6.29	7.85	>10		
3D	90-100	5.92	19.4	2.8*	0.5	0.14	0.53*	17.0	0.07	20.6	8.0	6.0	>8.2	>9.2	7.15	>8.2	>10		
4D	20-30	5.49	41.7	4.9	4.2	2.09	2.36	2192.9	2.30	183.3	35.5	116.5	6.91	8.46	5.90	7.24	8.85		
4D	30-40	5.48	30.2	4.9	2.9	1.32	2.14	360.0	1.02	108.6	21.1	50.1	7.57	8.97	6.22	8.19	9.34		
4D	40-50	5.46	19.8	3.4	1.4	0.63	1.60	72.8	0.30	26.9	8.3	14.9	>8.2	8.85	6.85	8.01	>10		
4D	50-60	5.55	12.1	2.5	0.7	0.21	0.81	8.5	0.08	19.2	4.5	6.0	>8.2	>9.2	6.94	>8.2	>10		
4D	60-70	5.70	12.8	2.5	0.7	0.22	0.70	39.4	0.11	19.9	5.1	7.4	>8.2	>9.2	6.96	>8.2	>10		
4D	70-80	5.75	14.1	2.6	0.4	0.14	0.54	7.2	0.07	11.8	5.3	5.5	>8.2	>9.2	6.96	>8.2	>10		
4D	80-90	6.10	13.2	2.6*	0.6	0.21	0.54*	67.9	0.11	67.3	7.7	7.6	>8.2	>9.2	6.29	7.70	>10		
4D	90-100	6.00	16.6	2.6*	0.5	0.15	0.54*	23.0	0.06	28.7	10.4	6.7	>8.2	>9.2	7.15	7.97	>10		

* values that are missing and estimated as the same as in the similar samples

is normally in the range of 0.1-0.4 mol/kg (McBride, 1994). The charge of clay was assumed in the model to have a constant value independent of pH. In the calculation, we used the average and the extreme values of 0.1, 0.25 and 0.4 mol/kg for the charge of clay resulting in a range of the predictions. The Donnan volume of illite was estimated as 1 l/kg using the inter lattice distance (10 Å) and the surface area (80-150 m²/g) of illite (McBride, 1994).

The content of SOM was measured using loss-on-ignition. In the modeling, all the NICA-Donnan parameters for the generic humic acid were used and kept constant except for the site density (Milne, 2000; Milne et al., 2001). The site density needs to be estimated in a reasonable way because besides humic substances, SOM contains other subcomponents such as plant residual and microorganism biomass, which may have a metal binding reactivity differing from the humic substances. In addition, the interaction of SOM with soil minerals will also result in changes in site density for metal binding compared to the purified humic acid. The site density of SOM in comparison with generic humic acid was estimated in the following way: (i) calculate the contribution of clay to soil-CEC by multiplying the chosen clay charge (0.1, 0.25 or 0.4 mol/kg) with the clay content in each soil sample. (ii) calculate the CEC of SOM by subtracting clay-CEC from the measured soil-CEC. (iii) calculate the ratio of SOM-CEC to that of the generic humic acid under the same conditions. (iv) The thus estimated relative site density of SOM has a high uncertainty in case the SOM contributes little to the CEC (mainly samples at larger depth), we therefore take the average of the ratio as the relative site density of SOM in comparison with the generic humic acid. The results of this calculation show that at the clay charge of 0.1-0.4 mol/kg, the site density of SOM varies between 46%-16% of that of the generic humic acid. At the average value of clay charge of 0.25 mol/kg, the site density of SOM was 31% of that of the generic humic acid.

The amount of amorphous iron hydroxides was estimated from the oxalate extractable Fe, after subtracting the Fe that is calculated to be bound to SOM. The organically bound Fe was calculated with the NICA-Donnan model assuming that amorphous iron hydroxide controls Fe³⁺ activity. The solubility product of amorphous iron hydroxide used was 10^{-42.02} (Lindsay, 1979). The organically bound Fe was calculated to be 10-29% of the oxalate extractable Fe. The surface area of amorphous iron hydroxides was assumed to be the same as that of HFO, *i.e.* 600 m²/g (Dzombak and Morel, 1990). The amount of crystalline iron hydroxides was estimated as the difference between DCB and oxalate extractable Fe. The surface area of

crystalline iron hydroxides was assumed to be 100 m²/g. Ni adsorption on crystalline iron hydroxides was not considered due to the lack of the CD-MUSIC parameters for Ni.

Comparison between free metal activity predicted and measured

In Figure 1, the predicted Cu²⁺, Cd²⁺, Zn²⁺, Ni²⁺ and Pb²⁺ activities using the multi-surface model are compared to those measured. By taking the clay charge of 0.1, 0.25 and 0.4 mol/kg and the corresponding site density of SOM, i.e. 46%, 31% and 16% of the generic humic acid, the model gives three predicted metal activities for one soil sample. At 0.1 mol/kg clay charge and 46% site density of the generic humic acid for SOM, the model predicts lower metal activities than using higher clay charge and lower site density of SOM. This is due to the higher affinity of SOM for the metals than that of the clay.

The bandwidth of Cu²⁺ activity predicted by the model at the extreme clay charges and SOM site density is 1-1.2 log-unit. All the measured Cu²⁺ activities fall within this interval. The agreement between the model predicted and the measured Cu²⁺ activity is good (Figure 1-a). For Cd²⁺, Zn²⁺ and Ni²⁺, the bandwidth of predictions is narrower and it is about 0.1-1 log-unit. The interval is much smaller at higher metal activity than at lower metal activity (Figure 1-b, 1-c, 1-d). Cd, Zn and Ni form less strong complexes with SOM than Cu. At high metal activity, the adsorption to SOM is relatively more determined by the nonspecific Donnan ion-exchange part of the NICA-Donnan model and the model assumptions concerning CEC distribution between clay and SOM have therefore much less effect on the prediction of metal activity than at low metal activity. The predicted Cd²⁺ activity agrees with the measured well and all the measured Cd²⁺ activities are within the range of model predictions (Figure 1-b). For Zn²⁺ and Ni²⁺, the measured activities agree with the predictions reasonably well for most of the samples, except for some samples of high pH (soil 3D and 4D) at larger depth (Figure 1-c, 1-d). For these samples, the model predicts higher Zn²⁺ and Ni²⁺ activity than measured. A possible reason for the discrepancy for these samples could be the formation of Zn-Al, Ni-Al layered double hydroxide (LDH) which are more stable at near neutral pH values (Ford and Sparks, 2000; Roberts et al., 1999).

The bandwidth of the model predictions for Pb²⁺ activity is less than 0.3 log-unit (Figure 1-e). According to the model, Pb adsorption onto iron hydroxides is very important, therefore the change of the site density of clay and SOM has little influence on the predicted Pb²⁺

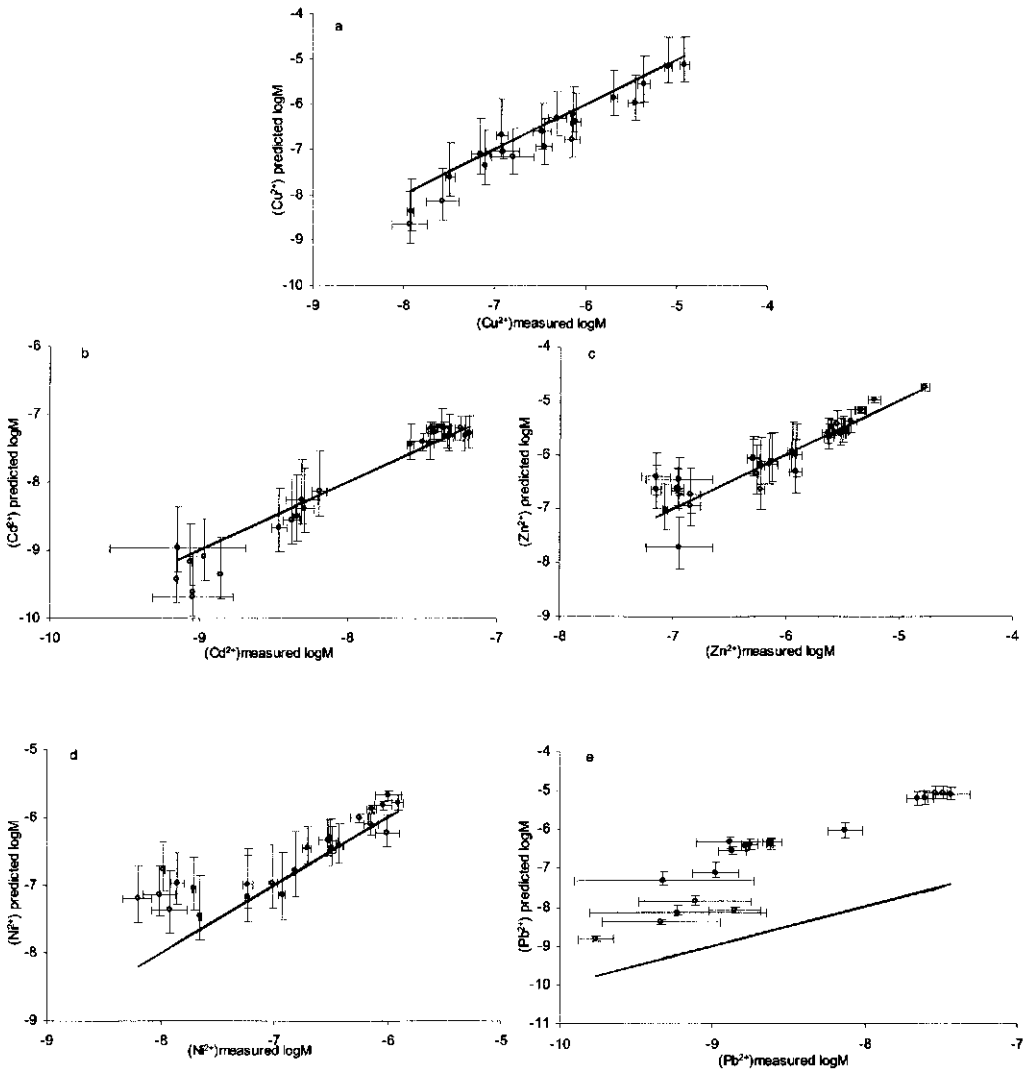


Figure 1. Comparison of predicted and measured metal activities (\circ model predictions at the mean clay charge of 0.25 mol/kg and site density of SOM equals to 31% of the generic humic acid. The vertical error bars are model predictions with extreme clay charge and site density of SOM. The horizontal error bars are the standard deviations of the metal activity measured; — 1 to 1 line).

activities. The predicted Pb^{2+} activities are about 0.5-2.5 log-unit higher than measured. The discrepancy can not be explained by the hypothesis that Pb^{2+} activity is controlled by Pb

phosphate minerals (Lindsay, 1979). The possibility of the existence of Pb phosphate minerals is excluded by comparing the ion activity product of Pb^{2+} , PO_4^{3-} and Cl^- to the solubility of the most insoluble Pb phosphate mineral, chloropyromorphite $[\text{Pb}_5(\text{PO}_4)_3\text{Cl}]$ (Lindsay, 1979). The measured Pb^{2+} activity was lower than those calculated using the solubility product. In addition to the uncertainties involved in the adsorption models and model parameters, there are other possible causes for the failure of the model for Pb^{2+} activity prediction. The irreversibility of Pb adsorption can be one of the explanations. Another possible reason can be the adsorption on other soil surfaces, for example manganese oxides, which we did not consider in the model (Hettiarachchi et al., 2000).

The failure of the model in predicting reasonable Pb^{2+} activities shows that the model approach is not necessarily adequate. Considering the fact that the predictions are fully based on models developed in the laboratory for individual sorbents and that no fitting has been involved in the calculations, the quite reasonable prediction for Cu^{2+} , Cd^{2+} , Zn^{2+} and Ni^{2+} are therefore rather encouraging.

Individual sorbents contribution to metal binding

Besides the prediction of the free metal ion activity, the multi-surface model gives an estimation of each sorbent contribution to metal adsorption in soils. In Figure 2, the model predictions of the sorbents contribution to Zn binding in the soil samples at low pH (4A) and high pH (4D) are shown as an example. Extensive results are available in Table 2. In Figure 2, Table 2 and in the following discussions, we refer to the model predictions using the average charge of clay (0.25 mol/kg) and accordingly estimated SOM site density (31% of the generic humic acid). At the end of Table 2, the uncertainty ranges of the predictions under the extreme cases of clay charge and SOM site density are given. This uncertainty range is smaller for Cu than for other metals, due to the very strong affinity of SOM to Cu. The prediction is in general more sensitive to assumptions of CEC distribution between the SOM and clay when the SOM is more or less saturated with the metal in respect to its binding capacity.

The model calculation confirmed the common recognition that soil organic matter is an important sorbent for heavy metals in soils, especially for Cu. For all the soil samples, the modeling results show that the organically bound Cu is more than 98% of the total adsorbed Cu. Only less than 2% of adsorbed Cu is attributed to clay and iron hydroxides. The

predominant role of organic matter for Cu adsorption in soils has been observed previously using different methods (McLaren et al., 1983; Sposito et al., 1982). The model predicted that the Cd bound to organic matter accounts for about 70-99% of the total adsorbed Cd. The organically bound Zn and Ni accounts for about 60-99% of the total adsorbed Zn and Ni. The intrinsic affinity of organic matter for these metals is not as strong as for Cu. However, the soil organic matter is still the most important surface that adsorbs Cd, Zn and Ni in these soils.

Table 2. Model estimation of individual sorbents contribution to metal adsorption in the soils (% of total sorbed)

Soil	Depth (cm)	Cu				Cd				Zn			
		SOM		clay	iron oxide	SOM		clay	iron oxide	SOM		clay	iron oxide
		specific	gel			specific	gel			specific	gel		
1A	0-20	99.6	0.22	0.13	0.05	82.1	11.3	6.59	0.00	77.1	14.4	8.42	0.02
2A	0-20	99.4	0.37	0.20	0.07	82.5	11.4	6.09	0.00	77.8	14.5	7.71	0.02
3A	0-20	99.1	0.54	0.30	0.11	82.7	11.1	6.22	0.00	77.1	14.7	8.22	0.02
4A	0-20	98.7	0.72	0.41	0.14	84.1	10.2	5.72	0.00	78.8	13.6	7.63	0.02
1D	0-20	99.5	0.01	0.00	0.48	97.7	1.60	0.56	0.17	93.8	3.48	1.22	1.46
2D	0-20	99.4	0.03	0.01	0.61	97.1	2.06	0.74	0.10	92.9	4.55	1.65	0.88
3D	0-20	99.4	0.09	0.04	0.50	95.1	3.48	1.43	0.05	90.3	6.62	2.70	0.38
4D	0-20	99.1	0.11	0.05	0.71	95.0	3.52	1.43	0.03	89.5	7.25	2.94	0.36
4A	20-30	98.7	0.70	0.37	0.23	83.6	10.7	5.70	0.00	77.0	15.0	7.99	0.04
	30-40	98.4	0.43	0.33	0.87	76.7	13.2	10.1	0.02	72.6	15.3	11.7	0.44
	40-50	98.6	0.30	0.42	0.67	69.4	12.7	17.9	0.02	62.1	15.6	21.8	0.57
	50-60	98.1	0.23	0.65	1.06	59.2	10.7	30.1	0.05	51.7	12.4	34.8	1.20
	60-70	98.6	0.32	0.89	0.24	59.2	10.9	29.9	0.02	44.8	14.8	40.4	0.07
	70-80	99.4	0.17	0.37	0.09	63.4	11.3	25.4	0.01	48.0	16.0	36.0	0.05
	80-90	98.9	0.20	0.30	0.56	70.3	11.8	17.8	0.04	45.5	21.2	32.0	1.30
	90-100	98.9	0.13	0.28	0.72	66.8	10.3	22.9	0.04	45.0	16.6	37.0	1.38
3D	20-30	98.9	0.03	0.01	1.06	97.6	1.62	0.60	0.13	94.0	3.58	1.34	1.05
	30-40	98.8	0.01	0.00	1.16	98.4	0.95	0.41	0.28	93.0	2.25	0.97	3.79
	40-50	99.8	0.00	0.00	0.24	97.9	0.93	0.90	0.25	93.8	1.92	1.86	2.44
	50-60	99.9	0.00	0.00	0.05	97.9	0.84	1.14	0.13	96.9	0.94	1.28	0.93
	60-70	99.6	0.00	0.00	0.45	98.5	0.59	0.71	0.20	92.9	1.70	2.08	3.28
	70-80	99.8	0.00	0.00	0.17	97.6	0.76	1.49	0.18	88.8	2.46	4.86	3.93
	80-90	99.3	0.00	0.01	0.71	98.7	0.53	0.69	0.12	85.5	4.04	5.28	5.18
	90-100	99.9	0.00	0.00	0.13	98.6	0.59	0.77	0.08	91.6	2.62	3.43	2.36
4D	20-30	98.7	0.06	0.02	1.20	97.1	2.05	0.77	0.08	92.4	4.91	1.83	0.83
	30-40	99.6	0.01	0.01	0.44	97.6	1.52	0.81	0.09	92.6	4.01	2.14	1.25
	40-50	99.7	0.01	0.00	0.28	97.6	1.31	0.97	0.09	93.5	2.94	2.18	1.43
	50-60	99.9	0.00	0.00	0.07	97.7	0.98	1.20	0.08	89.7	3.54	4.36	2.46
	60-70	99.9	0.00	0.00	0.10	97.6	0.95	1.41	0.08	91.2	3.15	4.59	1.10
	70-80	99.9	0.00	0.00	0.07	97.2	0.94	1.75	0.08	91.6	2.71	5.06	0.60
	80-90	97.7	0.00	0.00	2.27	99.2	0.29	0.35	0.18	83.5	3.39	4.03	9.03
	90-100	99.8	0.00	0.00	0.17	98.9	0.49	0.59	0.06	92.4	2.96	3.58	1.07
range	Min. \pm	0.14		0.01	0.10	1.34		1.12	0.00	5.42		2.60	0.01
	Max. \pm	4.64		2.82	4.63	26.2		26.2	0.45	27.9		27.8	5.36

Table 2-continued. *Model estimation of individual sorbents contribution to metal adsorption in the soils (% of total sorbed)*

Soil	Depth (cm)	Ni				Pb			
		SOM		clay	iron oxides	SOM		clay	iron oxides
		specific	gel			specific	gel		
1A	0-20	91.8	1.88	6.35	0.00	61.3	16.4	9.56	12.7
2A	0-20	92.1	1.98	5.90	0.00	62.3	16.4	8.70	12.6
3A	0-20	91.6	2.03	6.34	0.00	59.3	16.5	9.23	15.0
4A	0-20	92.3	1.87	5.88	0.00	60.4	17.2	9.65	12.7
1D	0-20	98.7	0.28	0.82	0.25	10.8	0.09	0.03	89.1
2D	0-20	98.2	0.46	1.16	0.14	12.9	0.15	0.06	86.9
3D	0-20	96.9	0.94	2.11	0.07	27.1	1.34	0.58	71.0
4D	0-20	96.6	1.04	2.30	0.04	24.7	0.79	0.32	74.2
4A	20-30	92.5	1.70	5.81	0.00	62.4	16.4	8.73	12.5
	30-40	84.4	4.42	11.2	0.00	59.8	9.72	7.40	23.1
	40-50	75.6	3.91	20.5	0.00	53.5	6.88	9.65	30.0
	50-60	60.8	4.13	35.1	0.01	43.3	4.55	12.8	39.4
	60-70	60.0	2.95	37.1	0.01	36.4	4.69	12.9	46.1
	70-80	62.9	3.58	33.5	0.00	52.2	6.19	14.0	27.7
	80-90	72.4	1.94	25.7	0.00	56.9	7.15	10.8	25.1
	90-100	61.9	3.45	34.7	0.00	55.8	6.74	15.0	22.5
3D	20-30	98.1	0.54	1.11	0.21	10.4	0.08	0.03	89.5
	30-40	98.2	0.43	0.95	0.46	7.80	0.03	0.01	92.2
	40-50	96.5	0.71	2.32	0.50	8.55	0.03	0.03	91.4
	50-60	92.4	3.24	4.06	0.31	11.5	0.05	0.07	88.4
	60-70	95.3	0.95	3.14	0.60	8.05	0.02	0.03	91.9
	70-80	92.6	0.95	6.02	0.48	10.1	0.04	0.08	89.8
	80-90	94.6	0.52	4.39	0.54	10.1	0.03	0.04	89.9
	90-100	93.6	1.40	4.70	0.30	14.7	0.06	0.08	85.1
4D	20-30	97.5	0.79	1.53	0.15	14.5	0.19	0.07	85.3
	30-40	97.4	0.65	1.78	0.15	14.0	0.11	0.06	85.9
	40-50	96.4	0.98	2.41	0.18	17.7	0.17	0.13	82.0
	50-60	95.1	0.73	4.07	0.14	17.6	0.12	0.15	82.2
	60-70	93.3	1.20	5.36	0.12	17.9	0.12	0.20	81.8
	70-80	91.5	1.53	6.77	0.16	18.0	0.13	0.25	81.7
	80-90	94.3	0.32	3.22	2.21	7.58	0.02	0.03	92.4
	90-100	94.0	1.29	4.46	0.29	15.8	0.07	0.08	84.0
range	Min. \pm	2.69		2.54	0.00	3.70		0.01	3.67
	Max. \pm	27.57		27.56	1.43	21.79		14.28	11.44

Although the model shows for Cd, Zn and Ni that SOM is a dominant sorbent, it is still possible that under certain conditions a considerable fraction of metal is adsorbed to the clay minerals. In these soil samples, the Cd bound to clay can be as high as 30% of total adsorbed Cd. The clay bound Zn and Ni can be as high as about 40% of total adsorbed Zn and Ni. The highest contribution of clay to Cd, Zn and Ni adsorption was found in the soil sample 4A (low pH) at larger depth. It suggests that metal adsorption to clay minerals is more important under the conditions of low pH and low organic matter content, when the soil organic matter is relatively saturated for metal adsorption.

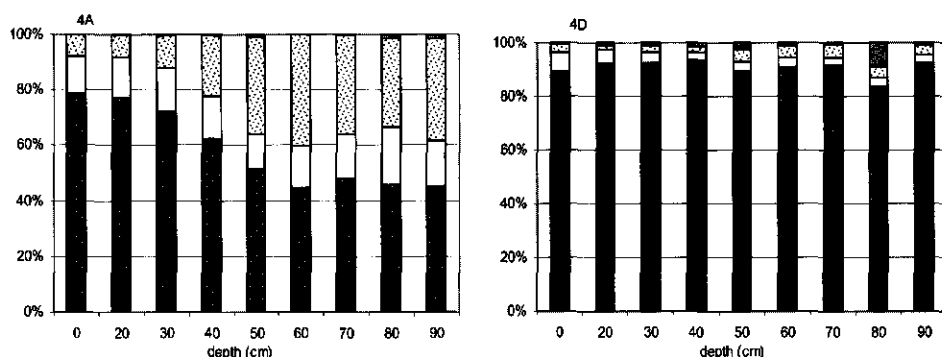


Figure 2. *Contribution of soil sorbents to Zn adsorption in soil 4A and 4D (0-100cm) (model predictions at the mean clay charge of 0.25 mol/kg and site density of SOM equals to 31% of the generic humic acid. Bars with black background and white dots: specifically bound to SOM; White bars: bound in the Donnan gel of SOM; Bars with white background and black dots: bound in the Donnan gel of clay; Grey bars: bound to iron hydroxides).*

From Figure 2 it can be seen that Zn bound to clay and to the Donnan part of SOM is more important in soil with low pH (4A) than in soil with high pH (4D). This also holds for other metals (Table 2). The specific binding of metals to SOM increases with increasing pH. Acidification thus leads to a shift in the binding of metal from specific binding to a more nonspecific ion-exchange binding. The effect of acidification on the shift in the type of binding is quite significant for Cd, Zn and Ni, and not significant for Cu.

In the literature, there is normally a lack of correlation between the soil cation exchange capacity (CEC) and the heavy metal binding. The importance of clay silicates as heavy metal adsorbents is uncertain (Zachara et al., 1992). The multi-surface model can be used to explain the contradictory findings in some previous work. Gray *et al.* (1999) concluded that pH and organic matter at high soil Cd content (*i. e.* 1.3 mg/kg) had little effect on the concentration of Cd in solution, with total soil Cd being the dominant controlling factor. However, at smaller Cd concentrations (*i. e.* 0.3 mg/kg), pH and organic matter play a much greater role in the controlling of the concentration of Cd in solution. According to our model calculation, Cd binding on organic matter is dominant at lower metal loading. When the metal loading is high, the binding to clay minerals becomes more important, therefore little effect of pH and organic matter is expected for such conditions. Because the relative importance of clay on metal binding is conditional, it is understandable that no correlation

can be found between metal binding and soil CEC or soil clay content in studies like the one with Cd by Gray *et al.* (1999).

According to the model, Cu, Cd, Zn and Ni adsorbed on iron hydroxides is less than 6% of their total amount bound in these samples. The model estimates that iron hydroxides are not important sorbents for Cu, Cd, Zn and Ni in these soils, which have relatively low pH, low content of the iron hydroxides compared to SOM and clay silicates. However, for soils with low organic matter content and high pH, metal binding to metal hydroxides can still be important, as was found by Zachara *et al.* (1992).

The model failed to give a reasonable prediction of free Pb^{2+} activity. However, the model prediction of individual sorbents contribution to Pb adsorption can still be an indication of the relative importance of various soil surfaces. The model results show that 8-79% of the total sorbed Pb is in association with SOM. The adsorption to organic matter is more important in soil samples A, which all have a relatively low pH. In soil samples D, which have a relatively high pH, the adsorption of Pb to iron hydroxides is calculated to be more significant. Pb adsorbed to iron hydroxides can be as high as 92% of the total adsorbed Pb. Pb adsorbed on clay can amount to 15% and it is only important in soil samples A, where the pH is low. Iron oxides and organic matter have a high capacity to adsorb Pb and concomitantly maintain a low Pb^{2+} activity in solution (Sauvé *et al.*, 2000b).

The model predicts that the acidification of sandy soils will not only result in a decreased binding affinity for metals in general, but will also lead to a shift of specific binding towards more nonspecific binding. The change will not only lead to higher solution activities, but will also make the metal activity more susceptible to the change of salt level. The model gives good results for Cu, Cd, Zn and Ni of the effect of acidification on the resulting metal activity.

Chapter 5

Complexation with DOM and Solubility Control of Heavy Metals in an Sandy Soil

(Submitted)

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Abstract

The complexation of heavy metals with dissolved organic matter (DOM) in the environment influences the solubility and mobility of these metals. In this paper, we measured the complexation of Cu, Cd, Zn, Ni and Pb with DOM in the soil solution at pH 3.7-6.1 using a Donnan membrane technique. The results show that the DOM-complexed species is generally more significant for Cu and Pb than for Cd, Zn and Ni. The ability of two advanced models for ion binding to humic substances, *e.g.* Model VI and NICA-Donnan, in the simulation of metal binding to natural DOM was assessed by comparing the model predictions with the measurements. Using the default parameters of fulvic and humic acid, the predicted concentrations of free metal ions from the solution speciation calculation using the two models are mostly within one order of magnitude difference from the measured concentrations except for Ni^{2+} and Pb^{2+} in a few samples. Furthermore, the solid-solution partitioning of the metals was simulated using a multi-surface model, in which metal binding to soil organic matter, dissolved organic matter, clay, and iron hydroxides were accounted for using adsorption and cation exchange models (NICA-Donnan, Donnan, DDL, CD-MUSIC). The model gave a reasonable estimation of the dissolved concentration of all the metals of interest except for Pb. The solubility of the metals depends mainly on the metal loading over soil sorbents, pH and the concentration of inorganic ligands and DOM in the soil solution. The strong increase in leaching after acidification is in reasonable agreement with the observed pH dependency of the solubility.

Introduction

To protect the environmental quality of soil, sediment, groundwater and surface water, it is necessary to make accurate assessment of the toxicity and mobility of the heavy metals. It is known that the processes of precipitation, adsorption, and complexation are important in controlling heavy metal speciation in soils. In soil solution, heavy metals can form hydrolysis species and complexes with inorganic ligands such as Cl^- and SO_4^{2-} . The importance of the hydrolysis species and inorganic complexes depends on pH and the concentration of metal and ligands. Heavy metals ions also form complexes with dissolved organic matter (DOM) in soils, sediments and aquatic systems. It has been shown that DOM can strongly bind heavy metals such as Cu, Pb, Cd, Zn, and Ni (Sauvé et al., 1997; Temminghoff et al., 1997; Christensen and Christensen, 1999a; Xue et al., 2001). It is therefore important to include the effect of DOM on the mobilization and transport of heavy metals and in the risk assessment of sites contaminated with heavy metals (Christensen and Christensen, 1999a).

Efforts have been made to develop models to describe heavy metal speciation in soil and soil solution. Mostly, these models are of empirical nature (Workman and Lindsay, 1990; Castilho et al., 1993; Christensen et al., 1996; McBride et al., 1997; Sauvé et al., 1997, 2000b; Celardin, 1999; Gray et al., 1999). The power of these models is limited in discriminating the importance of speciation processes and in the applicability to predict metal speciation in different soil samples. Recently, a multi-surface model was proposed by Weng et al. (2001a), which employs advanced adsorption and cation exchange models and default binding parameters. This type of process oriented model is necessary to adequately describe the interaction of metals with the particulate and dissolved surfaces over a wide range of conditions. This multi-surface model has been used to predict the free ion activity of Cu^{2+} , Cd^{2+} , Zn^{2+} and Ni^{2+} in a sandy soil over the pH range of 3.7-6.1 with reasonable success (Weng et al., 2001a). Because metal complexation with DOM is not important in the control of the free ion activity, it was not considered for their purpose. However, if we want to apply this model for the estimation of metal solubility, the metal binding to DOM has to be accounted for. Moreover, one can also predict the metal activity in solution based on the total dissolved metal concentration, the concentration of various ligands and pH.

Dissolved organic matter is a complex mixture of many molecules and is usually operationally defined as the organic matter that passes a 0.45 μm filter. Humic and fulvic

acid are major components and represent up to 70% of DOM (Masion et al., 2000). Model VI (Tipping, 1998) and NICA-Donnan (Kinniburgh et al., 1999) are two advanced models available for the description of the binding of proton and metal ions to humic substances. Both models consider the site heterogeneity, binding competition and electrostatic effects. However, the strength of a model depends on its ability to deal with humic substances of different origin and structure and with varying solution chemistry (Christensen et al., 1998). At present, there are few studies to evaluate how well these models with default parameters of purified humic and fulvic acid can predict the complexation of heavy metals with natural DOM (Benedetti et al., 1996a; Temminghoff et al., 1997; Christensen and Christensen, 1999a). Until now there is no study on the comparison of these two models using the same data set of metal complexation with DOM.

The aim of this paper is 3-fold: (i) To evaluate the ability of Model VI and NICA-Donnan in the prediction of metal binding to DOM by comparing the predictions with the measurements using a Donnan membrane technique. (ii) To include the NICA-Donnan model for the description of metal binding to DOM in the existing multi-surface model (Weng et al., 2001a) and to evaluate the ability of this model in the estimation of the metal solubility in soil. And (iii) To study the effects of metal complexation with DOM on the enhanced metal leaching by acidification.

Model description

Simulating solution speciation

The solution speciation of heavy metals is simulated with two advanced models for ion binding to humic substances, *e.g.* Model VI (Tipping, 1998) and NICA-Donnan (Kinniburgh et al., 1999), along with inorganic solution chemistry. Model VI has been described in detail by Tipping (1998). In this model, fulvic and humic acids are pictured as rigid spheres of uniform size with ion-binding groups positioned on the surface. The model is a discrete binding site model including two types of sites (types A and B), each having four different types of sites present in equal amount. Besides the site heterogeneity, Model VI also includes the electrostatic effects via a Donnan expression and the competition among protons and metal ions. The default parameters of the Model VI have been derived by fitting using extensive sets of published data (Tipping, 1998) (see Table 2, Appendix).

The NICA-Donnan model (NICA=Non Ideal Consistent Competitive Adsorption) (Kinniburgh et al., 1999) accounts for the site heterogeneity by including two types of sites (type 1 and 2) each having a continuous distribution. Similar to Model VI, the electrostatic effects are described with the Donnan approach. The NICA-Donnan model includes the competition between protons and metal ions, the ion specific non-ideality and variable stoichiometry. The default parameters for generic humic and fulvic acids have been derived against extensive published data (Milne, 2000; Milne et al., 2001) (see Table 1, Appendix).

The model calculation was carried out at two separate assumptions as to the composition of DOM: (i) 30% of DOM is humic acid, 30% is fulvic acid and 40% is inert; (ii) 65% of DOM is fulvic acid and 35% is inert. The calculations were executed with the computer program WHAM (Tipping, 1994) and ECOSAT (Keizer and Van Riemsdijk, 1994) for Model VI and NICA-Donnan respectively.

Simulating solid-solution distribution

As mentioned in the Introduction, we have developed a multi-surface model to predict metal activities in soil considering soil as a set of independent sorption surfaces in the solid phase (Weng et al., 2001a). In this model, metal binding to the soil organic matter, to clay and to the amorphous and crystalline iron hydroxides are calculated using respectively the NICA-Donnan model, a Donnan cation exchange model, a two site surface complexation diffuse double layer model (Dzombak and Morel, 1990) and the Charge Distribution Multi-Site Complexation (CD-MUSIC) model (Hiemstra and Van Riemsdijk, 1996, 1999). In this paper we included the NICA-Donnan for the description of metal binding to DOM into the multi-surface model. As to the composition of DOM, we used the first assumption discussed above, e.g. 30% of DOM is humic acid, 30% is fulvic acid and the rest is inert. Figure 1 depicts the important components considered and models used in the multi-surface model.

The calculation was done with the computer program ECOSAT (Keizer and Van Riemsdijk, 1994). The HNO_3 (2M) extractable metal is assumed to be the amount of metal in soil that is active in adsorption/desorption processes (Weng et al., 2001a). The other chemical conditions, such as pH, ionic strength, soil solution ratio are the same as in the Donnan membrane analysis (see the Experimental Section). The calculation was done in two steps. First the concentrations of free metal ions were calculated considering metal binding to the

solid surfaces. Thereafter, using the free metal concentrations as input, the concentrations of the dissolved metal was predicted taking metal binding to DOM into account.

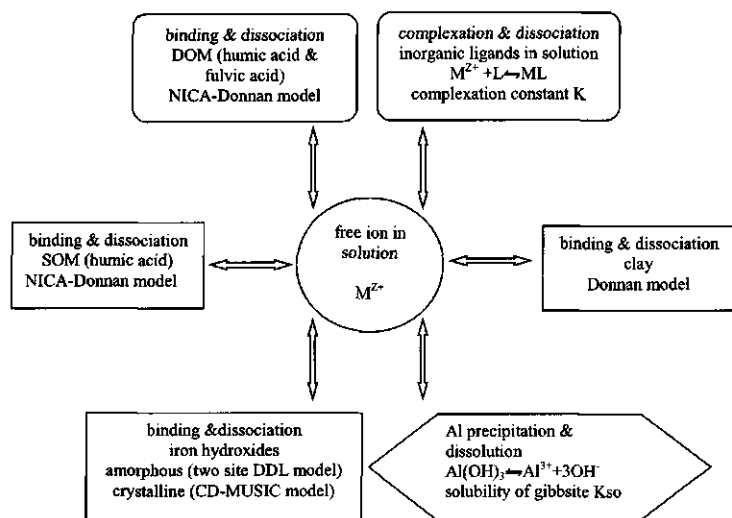


Figure 1. *Conceptual structure of the reactions and models used in the multi-surface model*

Experimental section

The data set used in this paper is the same as in the paper in which the free metal activities were predicted using the multi-surface model (Weng et al., 2001a). In this paper, we will provide the concentration of the total dissolved metal in addition to the concentrations of the total (including solid phase) and free metal that have been published before. The soil samples were collected in June 1998 from a field near Wageningen in the Netherlands (Wildekamp site). In 1982, the field site was established as a randomized block design of four pH adjustments [nominal pH (KCl): A: 4.0, B: 4.7, C: 5.4 and D: 6.1] and four copper concentrations (1: 0, 2: 250, 3: 500, and 4: 750 kg CuSO₄ /hectare). Samples from the lowest pH (soil A) and highest pH (soil D) were taken for different soil layers in the range of 0-100 cm. The field soil samples were air-dried and sieved (<2 mm) before analysis. The major soil characteristics have been measured and reported in the previous paper (see Table 1 in Weng et al., 2001a).

The concentrations of the free metal ion in these soils were measured using the Donnan membrane technique (Fitch and Helmke, 1989; Temminghoff et al., 2000; Weng et al., 2001b; Osté et al., 2002). 100 g air-dried soil sample was used in the soil column Donnan membrane analysis. 200 ml of 0.002 M $\text{Ca}(\text{NO}_3)_2$ solution was used as the salt solution in the donor side and 18 ml in the acceptor side. After 24 and 48 hours, the donor and acceptor solutions were sampled. pH was measured with a pH-meter in all the samples. The donor solution was filtered over a 0.45 μm nitrate-cellulose membrane filter (Schleicher & Schuell, NC45). Dissolved organic carbon (DOC) content in the donor solution was measured with a fully automated TOC/DOC analyzer (SK12, Skalar, Netherlands). The carbon leached from the filter was measured and the DOC concentration in the filtered solution was corrected. The DOM concentration in the soil solution was calculated as two times the DOC concentration. The concentrations of macro-elements in the donor and acceptor solution were measured by ICP-OES (Spectros, Spectro Flame), and concentrations of micro-elements were measured by ICP-MS (Perkin-Elmer, Elan 6000).

Results and discussion

Complexation with DOM

In the soil solutions, the concentration of the dissolved organic carbon (DOC) is between 7-34 mg/l (Table 1). The total dissolved concentrations of Cu, Cd, Zn, Ni and Pb in the soil solution are in the range of $10^{-7.3}$ - $10^{-4.6}$ M, $<10^{-9.0}$ - $10^{-6.9}$ M, $10^{-6.8}$ - $10^{-4.6}$ M, $10^{-7.9}$ - $10^{-5.7}$ M, and $10^{-9.6}$ - $10^{-7.1}$ M respectively (Table 1). The free Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} and Pb^{2+} was measured to be <2-76%, <18-92%, 30-100%, <3-98% and <10-70% of the total dissolved metal. Because of the small concentration of the anions such as SO_4^{2-} and Cl^- in these samples (SO_4^{2-} < 10^{-4} M, Cl^- < 10^{-3} M), and the low pH (<6.1), the inorganically complexed metals including hydrolyzed and carbonate species can be neglected. After subtracting the free metal ion from the total in soil solution, the metal left in the solution can be regarded as DOM-complexed. The DOM-complexed metals comprise from almost 0% to more than 98% of the dissolved metal. The complexation with DOM is found to be more significant for Cu and Pb than for Cd, Zn and Ni. Similar results have been observed in other studies (Gerritse and Driel, 1984; McBride et al., 1997; Salam and Helmke, 1998).

Metal complexation with DOM in the soil solutions, for which the concentrations of the free ions are measurable (see Table 1), is simulated using the Model VI and NICA-Donnan under two assumptions about DOM composition (see Model Descriptions). Figure 2 compares the

Table 1. Concentration of total dissolved and free ion of the metals

Soil	Depth (cm)	pH- 0.002M Ca(NO ₃) ₂	DOC (mg/l)	Metal concentration in soil solution (0.002 M Ca(NO ₃) ₂) (-log M)					Free ion concentration (Donnan membrane analysis) (-log M)				
				Cu	Cd	Zn	Ni	Pb	Cu	Cd	Zn	Ni	Pb
1A	0-20	3.78	24.5	5.63	7.10	5.34	6.29	7.15	5.96	7.20	5.38	6.33	7.36
2A	0-20	3.86	22.5	5.23	7.08	5.28	6.18	7.27	5.52	7.15	5.32	6.25	7.49
3A	0-20	3.88	23.4	4.99	7.18	5.32	6.26	7.24	5.20	7.29	5.37	6.33	7.44
4A	0-20	3.76	22.5	4.77	7.33	5.47	6.48	7.14	4.94	7.42	5.47	6.54	7.33
1D	0-20	5.54	19.0	5.95	8.06	5.96	6.96	8.04	7.73	8.17	6.05	7.45	>9.8
2D	0-20	5.75	19.3	5.69	7.95	5.88	6.73	7.92	7.29	8.09	5.94	7.04	8.91
3D	0-20	5.59	18.6	5.52	7.98	5.93	6.64	8.16	6.96	8.12	5.93	6.82	9.13
4D	0-20	5.47	22.1	5.36	7.87	5.76	6.45	7.99	6.72	7.99	5.74	6.61	8.78
4A	20-30	3.73	33.9	4.60	7.06	5.19	6.25	7.09	4.76	7.05	5.27	6.36	7.27
4A	30-40	4.07	26.3	5.17	6.93	5.29	5.83	7.82	5.29	7.03	5.46	5.84	7.97
4A	40-50	4.19	17.1	5.70	7.02	5.33	5.93	8.00	5.96	7.10	5.46	6.00	8.73
4A	50-60	4.25	15.0	6.00	7.15	5.30	6.02	8.41	6.32	7.20	5.33	6.09	8.72
4A	60-70	4.26	14.2	5.91	7.21	5.22	5.92	8.26	6.17	7.29	5.20	5.99	8.47
4A	70-80	4.25	12.6	6.06	7.21	5.22	5.82	8.44	6.30	7.27	5.20	5.89	8.64
4A	80-90	4.29	13.3	5.80	7.14	4.62	5.69	8.20	5.99	7.18	4.63	5.76	8.47
4A	90-100	4.33	13.1	6.26	7.26	4.92	5.74	7.86	6.64	7.35	5.07	5.84	8.61
3D	20-30	5.61	26.6	5.59	7.94	5.72	6.61	8.39	6.90	8.14	5.71	6.73	9.02
3D	30-40	5.80	23.8	6.08	8.28	6.02	6.97	8.77	7.75	8.95	6.03	7.73	9.58
3D	40-50	5.70	12.4	6.75	9.06	6.41	7.56	8.92	>8	8.88	6.68	>8	>9.8
3D	50-60	5.64	10.0	7.19	9.06	6.70	7.37	9.62	>8	8.98	6.77	>8	>9.8
3D	60-70	5.88	8.4	6.74	9.06	6.74	7.65	9.62	>8	8.88	6.91	>8	>9.8
3D	70-80	5.87	6.9	7.27	>9.1	6.58	7.89	8.10	>8	>9	6.80	>8	>9.8
3D	80-90	5.98	6.7	6.46	>9.1	6.15	7.33	8.54	>8	8.89	6.14	7.70	>9.8
3D	90-100	5.92	8.7	6.92	>9.1	6.47	7.28	9.62	>8	>9	7.00	>8	>9.8
4D	20-30	5.49	28.4	5.45	7.81	5.70	6.39	8.44	6.70	8.25	5.69	7.03	8.64
4D	30-40	5.48	25.3	5.85	8.02	5.96	6.40	8.39	7.37	8.77	6.02	7.99	9.14
4D	40-50	5.46	14.1	6.45	8.88	6.49	7.24	8.50	>8	8.68	6.68	7.84	>9.8
4D	50-60	5.55	10.4	7.01	8.88	6.70	7.65	8.58	>8	>9	6.78	>8	>9.8
4D	60-70	5.70	8.5	6.81	9.06	6.74	7.62	8.66	>8	>9	6.96	>8	>9.8
4D	70-80	5.75	7.6	7.10	>9.1	6.79	7.71	8.34	>8	>9	6.80	>8	>9.8
4D	80-90	6.10	8.8	6.27	8.88	6.04	7.11	8.58	>8	>9	6.13	7.54	>9.8
4D	90-100	6.00	9.4	6.74	>9.1	6.50	7.23	8.58	>8	>9	6.99	7.81	>9.8

percentage of the free ion over the total dissolved metal predicted and measured. The ability of the two models to predict metal complexation with DOM differs with respect to metals, models and assumptions regarding the composition of DOM.

The two assumptions for the DOM composition have generally minor effects on the predictions by Model VI, whereas the effects are larger for the NICA-Donnan model. Generally, the NICA-Donnan model predicts more complexation of Cu, Zn, Ni and Pb with DOM (smaller free ion concentration) under the first assumption, *e.g.* 30% of DOM is humic acid, 30% is fulvic acid and 40% is inert, than under the second assumption, *e.g.* 65% DOM is fulvic and the rest is inert. However, for Cd the NICA-Donnan predicts less binding and larger free Cd^{2+} concentration under the first assumption. By assuming that DOM is a mixture of humic and fulvic acid (the first assumption), the predictions by the NICA-Donnan model are generally closer to the measurements for the metals of Zn and Ni than assuming only fulvic acid presents (the second assumption). But it is the opposite for Cu and Pb, *e.g.* the second assumption leads to better prediction. For Cd, the difference between the two assumptions is small.

Compared with the measurements, both Model VI and NICA-Donnan captured the main trend in the big changes in the extent of Cu complexation with DOM (free Cu^{2+} is 2-76% of the total dissolved Cu). However, the Cu complexation with DOM is generally underestimated by Model VI and overestimated by NICA-Donnan. For Cd, according to the measurements, 18-92% of Cd in the soil solution is in the form of free ion. This range of complexation is well predicted by the NICA-Donnan model. Model VI tends to underestimate Cd binding to DOM. For Zn, 30-100% in the soil solution was measured as free ion. The lowest fraction of free Zn^{2+} was measured in the bottom layer of the soils with higher pH (3D and 4D). However, both models predict a range of about 60-100% of free Zn^{2+} . Both models underestimate the binding of Zn to DOM in the soils mentioned above. The free Ni^{2+} was measured to be 3-98% in the soil solution. Both Model VI and NICA-Donnan underestimated Ni binding to DOM, although the predictions by NICA-Donnan are closer to the measurements. As to Pb, 10-70% in the soil solution was measured as free ion, whereas the model prediction by assuming 65% of DOM is fulvic acid is about 1-95% for Model VI and 0.4-66% for NICA-Donnan. Model VI generally underestimates the binding of Pb and the NICA-Donnan model does the opposite.

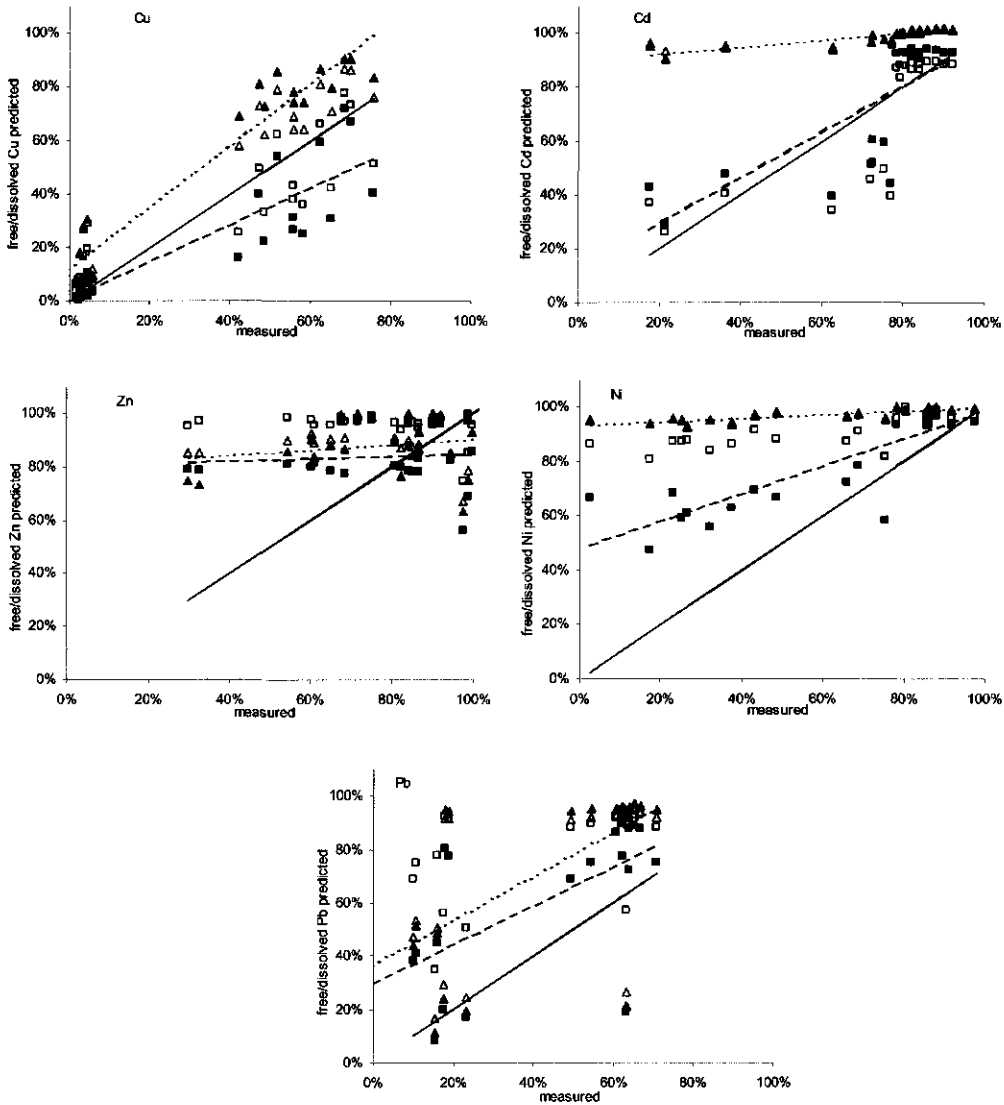


Figure 2. Comparison of the fraction of free ion concentration in the soil solutions measured and predicted by Model VI and NICA-Donnan (▲ prediction by Model VI, 30% humic acid, 30% fulvic acid; △ prediction by Model VI, 65% fulvic acid; ■ prediction by NICA-Donnan, 30% humic acid, 30% fulvic acid; □ prediction by NICA-Donnan, 65% fulvic acid; — 1 to 1 line; ---- regression line of prediction by Model VI, 30% humic acid, 30% fulvic acid; — regression line of prediction by NICA-Donnan, 30% humic acid, 30% fulvic acid).

Considering the range of the degree of metal complexation with DOM and the degree of variation between the prediction and measurement, the predictions with Model VI for Cu and with the NICA-Donnan model for Cu and Cd are quite reasonable. The predictions for the other metal ions are less good. It is a challenge for the thermodynamic models to simulate simultaneously the binding of several competing metals to DOM, each with its own affinity and pH dependence. The variation in the composition of DOM from sample to sample makes it essentially impossible with the approach followed for the models to produce exact predictions using the default parameters of purified humic and fulvic acid. The model description might however still be improved by updating the model parameters once more extensive data for their adsorption to humic substances become available. The model constants are presently often based on very few data sets, of which the quality varies (Milne, 2000; Milne et al., 2001; Tipping, 1998). Using the default parameters of fulvic and humic acid, the predicted concentrations of free metal ions from the solution speciation calculation using the two models are mostly within one order of magnitude difference from the measured concentrations except for Ni^{2+} and Pb^{2+} in a few samples (see Figure 1, Appendix).

Solid-solution partitioning

The solid-solution partitioning coefficient (K_d), which has been often used to describe the solid-solution distribution of metals, is the ratio of the total metal in the solid phase relative to that found in the solution phase. The K_d values found in the soil samples varied widely between the metals and for the same metal. The K_d values are in the range of 58-616 l/kg for Cu, 6-274 l/kg for Cd, 3-140 l/kg for Zn, 6-347 l/kg for Ni, and 469-32085 l/kg for Pb. Larger K_d value indicates smaller solubility. However, the partitioning coefficient is conditional and depends on the physicochemical situation.

In Figure 3, the predicted concentrations of dissolved Cu, Cd, Zn, Ni and Pb using the multi-surface model are compared to those measured. The model gives dissolved metal concentrations between a low and a high boundary by taking the clay charge of 0.1, 0.25 and 0.4 mol/kg and corresponding site density of SOM (46%, 31%, 16% of generic humic acid) (see Weng et al., 2001a). At 0.1 mol/kg clay charge and 46% site density of the generic humic acid for SOM, the model predicts smaller concentration of dissolved metal than using higher clay charge and lower site density of SOM. This is due to the stronger affinity of SOM for the metals than that of the clay.

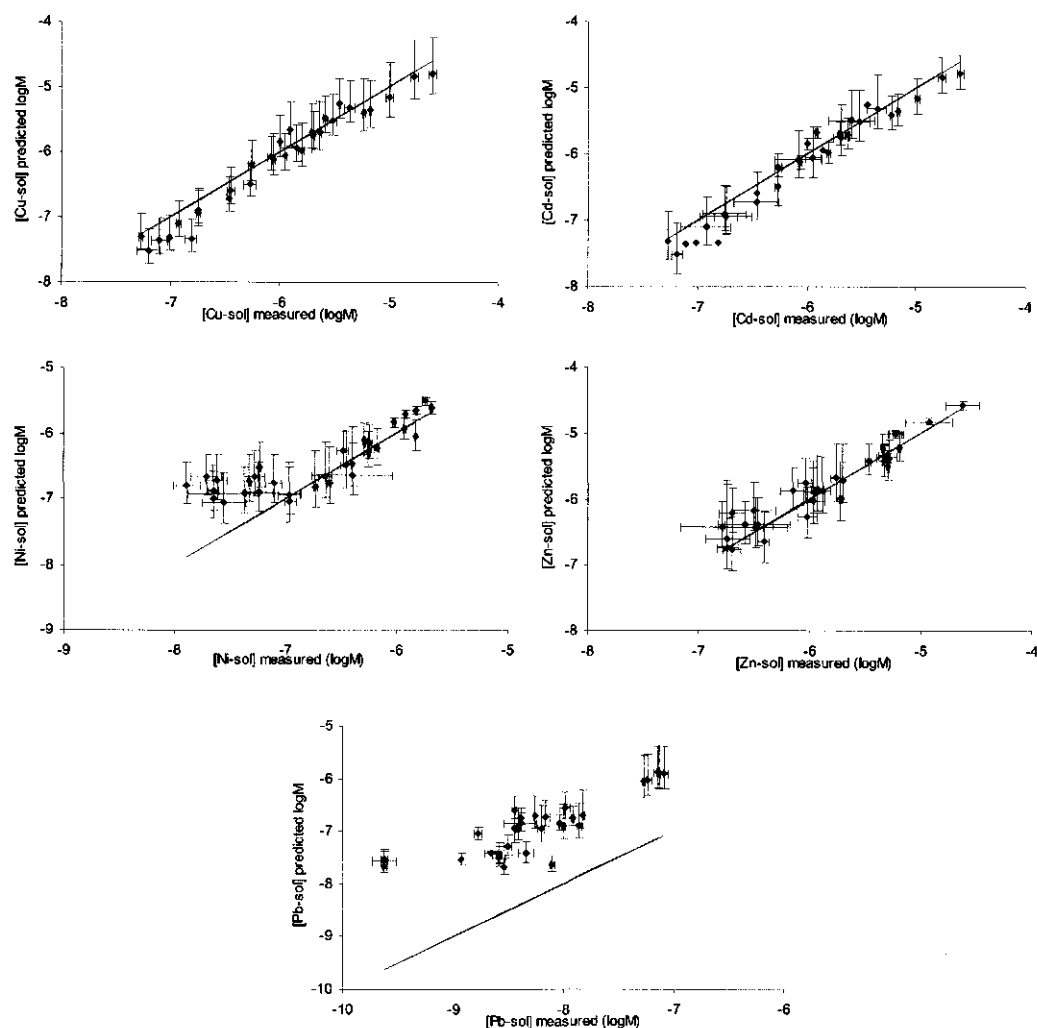


Figure 3. Comparison of dissolved metal content predicted and measured in the soil solution (♦ model predictions at the mean clay charge of 0.25 mol/kg and site density of SOM equals to 31% of the generic humic acid. The vertical error bars are model predictions with extreme clay charge and site density of SOM. The horizontal error bars are the standard deviations of the metal activity measured; —1 to 1 line).

The agreement between the model predicted and the measured dissolved concentrations of Cu and Cd is very good (Figure 3). This can be expected from the reasonable prediction of the free ion activities (Weng et al., 2001a) and the complexation with DOM of these metals.

For Zn and Ni, the estimated concentrations of dissolved metal agree with the measurements reasonably well for most of the samples, except for some samples of soil 3D and 4D at larger depth. For these samples, the model predicts larger free Zn^{2+} and Ni^{2+} concentration than measured. The overestimation of Zn and Ni solubility is largely due to the overestimation of their free ion activity in these soils (Weng et al., 2001a). In the previous paper, we have suggested that a possible reason for the discrepancy between the predicted and measured Zn^{2+} and Ni^{2+} activity in these samples might be the formation of Zn-Al and Ni-Al layered double hydroxide (LDH), which are more stable at near neutral pH values (Ford and Sparks, 2000; Roberts et al., 1999). The predicted concentration of the dissolved Pb is generally 0.5-2.1 log-unit larger than measured. The disagreement is due to the overestimation of Pb^{2+} activity and the overestimation of Pb complexation with DOM. The Pb^{2+} activity predicted with the model is generally 0.2-1.4 log-unit larger than the measurement. Note that in our previous paper the discrepancy found was 0.5-2.5 log-unit (Weng et al., 2001a), which is incorrect. This is because the NICA-Donnan parameters used for Pb were incorrect due to an error in the previous version of the database.

Besides the prediction of the dissolved metal concentrations, the multi-surface model gives an estimation of each sorbent contribution to metal solubility control in soils. The model predicted that the metal that is bound by DOM is only a small fraction of the metal that is bound to all the soil sorbents (SOM, clay, iron hydroxides and DOM). Among the total bound metal, only 0.3-2.9% Cu, 0.6-4.8% Cd, 0.3-2.1% Zn, 0.3-2.0% Ni, and 0.2-2.8% Pb are DOM-complexed. Compared to metal binding to the other soil sorbents, the contribution of DOM is not important. The free ion activity in these soils is therefore largely determined by metal binding to the solid phase (Weng et al., 2001a). Sauvé et al. (2000b) found that the addition of the dissolved organic matter to their equation $\text{pCd}^{2+} = 5.14 + 0.61\text{pH} - 0.79\log(\text{total Cd})$ improved R^2 by less than 2%. The relative contribution of SOM, clay and iron hydroxides to the metal activity control has been discussed previously (Weng et al., 2001a).

Although metal binding to DOM doesn't contribute significantly to the control of metal activity in soil, it can affect the solubility of metals to a considerable extent. The measurements show that the complexation with DOM can increase the concentration of dissolved metals by more than two orders of magnitude. Due to the non-linearity and pH-dependency of the metal binding to DOM, the effects of the complexation with DOM are

more significant at lower free metal activity and at higher pH. Any factors that lead to an increase in the DOM concentration will enhance the solubility and mobility of the metals.

pH-dependency of metal solubility and mobility

The significance of DOM complexation in soil solution influences the pH dependency of the solid-solution distribution of metals. When DOM complexed species is the dominant fraction of the metal in the solution, the pH effects on the solid-solution distribution of the metal will be less obvious than that on the free ion activity. This is because the binding of the metal to both the solid phase and the DOM is pH dependent. The increased binding to DOM at higher pH compensates to a certain extent the decrease of the free metal concentration.

In Figure 4, the pH dependency of the dissolved metal concentration measured in the soils is compared to that of the free ion activity. It shows that the difference in the pH dependency of the dissolved and free concentration is bigger for Cu and Pb, for which the DOM complexed fraction is more important, than for Cd, Zn and Ni, where the complexation with DOM is less significant. Sauvé et al. (2000a) studied the pH dependency of the partitioning coefficient (K_d) of Cu, Cd, Zn, Ni and Pb and found that the pH dependency of K_d values is in the order of $Cu < Pb < Cd < Zn < Ni$.

As has been noted in our previous paper (Weng et al., 2001a), the increased solubility of metals by acidification leads to enhanced metal leaching from the soil during the 16 year period. When comparing the total metal content in the surface layer (0-20 cm) for the low pH soils (soils A) and the high pH soils (soil D), it follows that the amount in the low pH soils is 8-24%, 56%, 69% and 66% smaller for Cu, Cd, Zn and Ni respectively than in the high pH soils. As for Pb, there is little difference observed in the average total Pb content in the surface layer at the low and high pH. The enhanced leaching by acidification is more significant for metals such as Cd, Zn and Ni, which have larger solubilities and are less complexed with DOM, than for metals such as Cu and Pb, which have smaller solubility and are more in the DOM-complexed form.

We did a very simple static balance calculation for the metals in the top 20 cm layer to roughly estimate how much decrease in the total metal content might have resulted from the increased metal solubility by acidification. It is known that the precipitation surplus in the area is on average 300 mm/year, and the dry bulk density of the surface soil is about 1350

kg/m³. We assumed that the soluble metal concentration was constant during the 16 years period, and calculated the decrease in the total metal concentrations in the low pH soil (soil A) in comparison to that in the high pH soil (soil D). In Table 2, the estimated decrease in the total metal content due to acidification was compared to those measured. Both the

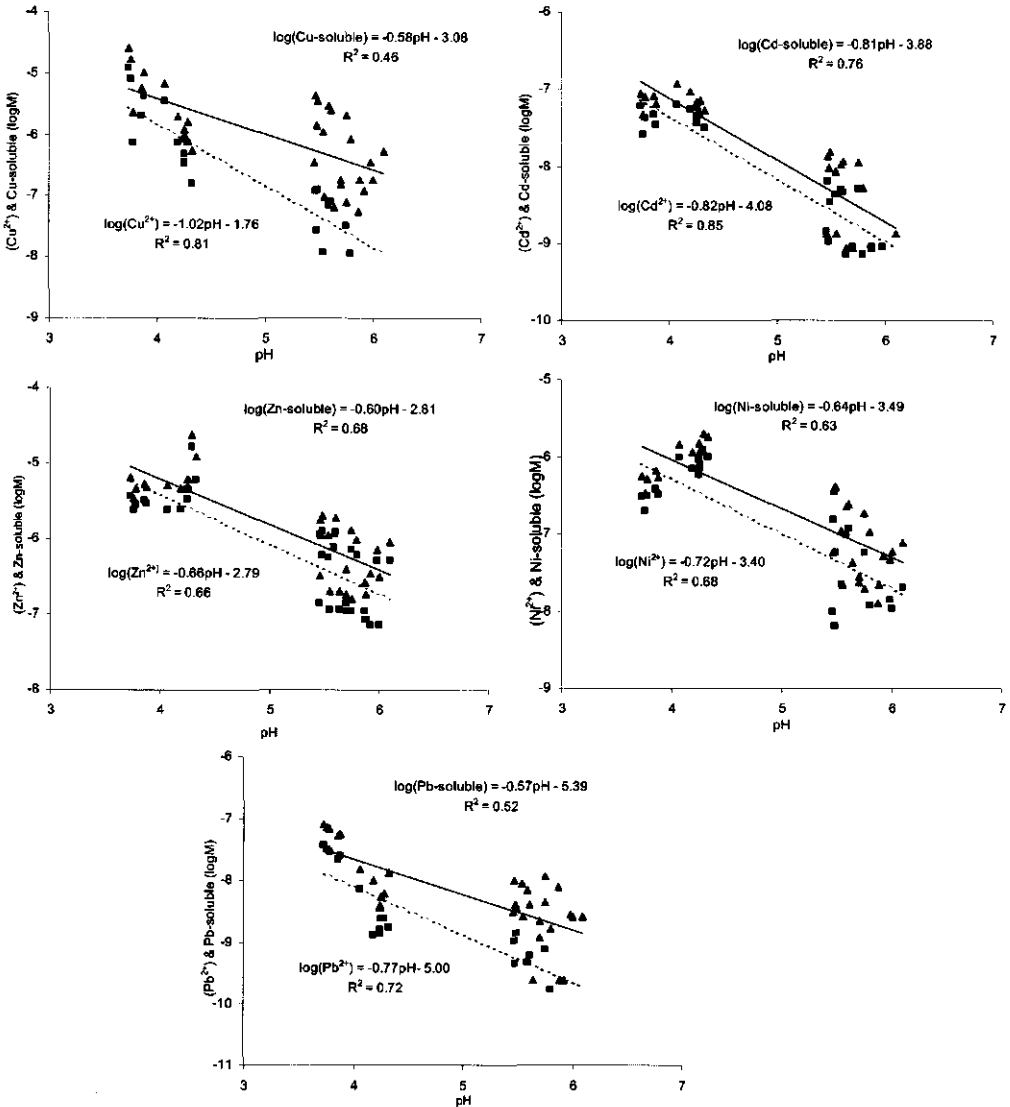


Figure 4. pH dependency of the dissolved metal concentration and free metal activity (\blacktriangle dissolved metal concentration; \blacksquare free metal activity; — regression line of the dissolved metal concentration; ---- regression line of the free metal activity).

Table 2. *Decrease in the metal content in soil by acidification (comparison between the low pH soil (soil A) and high pH soil (soil D))*

	Increase in metal concentration in solution due to acidification measured (μM)	Decrease in total metal content predicted ($\mu\text{mol/kg}$) based on the difference in the measured solution concentration	Decrease in total metal content (2M HNO_3) ($\mu\text{mol/kg}$) measured
Cu (0 kg CuSO_4/ha)	1.22	21.7	57.8
Cu (250 kg CuSO_4/ha)	3.85	68.4	84.0
Cu (500 kg CuSO_4/ha)	7.21	128.2	354.3
Cu (750 kg CuSO_4/ha)	12.62	224.4	533.4
Cd (average of four Cu treatments)	0.06	1.1	1.3
Zn (average of four Cu treatments)	3.17	56.4	110.6
Ni (average of four Cu treatments)	0.29	5.2	16.8
Pb (average of four Cu treatments)	0.05	0.9	0.6

calculation and the measurement show that there has been little Pb leaching because of its very small solubility. For other metals, the calculation indicates that the increased leaching by acidification explains on average 52% of the observed decrease in metal content. The systematic underestimation of the leaching can largely be explained by the fact that the solution concentrations directly after acidification would have been larger than the measured concentrations after 16 years, which have been used for the calculation.

Chapter 6

Interpretation of Humic Acid Coagulation and Soluble Soil Organic Matter Using a Calculated Electrostatic Potential

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Abstract

The coagulation of humic substances and its role in controlling the solubility of organic matter in soils are not well understood. We therefore studied the physico-chemical behaviour of purified humic acid from forest soil coagulated with Na, Ca, Cu, Al at pH 4 and 6, and then modelled the behaviour with the Non Ideal Consistent Competitive Adsorption Donnan model (NICA-Donnan). We found that the coagulation of humic acid occurs when the Donnan potential is less negative than -0.08 V. Based on this result, an empirical relation between the Donnan potential of humic acid and its concentration in solution was derived. In addition, the Donnan potential of the dissolved organic matter in the soil solution of six soil profiles from forests was calculated using the NICA-Donnan model under the assumption that all the dissolved organic matter behaves as humic acid. The measured concentration of dissolved organic matter also decreases in a soil profile, as the calculated potential becomes less negative. The results are in many cases in semi-quantitative agreement with the predicted concentration based on the humic acid coagulation experiment. Acid soils contain more dissolved organic matter, which may result from the presence of a fairly large fraction of more soluble organic molecules, such as fulvic acid.

Introduction

Dissolved organic matter (DOM) present in soil solution, natural aquatic systems, and wastewater is important for biogeochemical processes and for human health. It can strongly influence the cycling and fate of nutrients (such as N and P) and contaminants (inorganic and organic). Despite much research in the last decade, our knowledge of the formation and fate of dissolved organic matter in soils and its response to changing environmental conditions is still fragmentary and often inconsistent (Kalbitz et al., 2000).

Dissolved organic matter is a complex mixture of many molecules, and it is usually operationally defined as the organic matter that passes a 0.45- μm filter. A large portion of it in the soil solution is present as humic substances (humic and fulvic acids) (Thurman, 1985). Other organic compounds include macromolecular hydrophilic acids and identifiable organic compounds such as carbohydrates, carboxylic acids, and amino acids. Most of the macromolecules of humic substances fall within the colloidal range (0.001-1.0 μm). The modern view of the colloidal nature of humic substances is that they consist of rather long chain molecules, can form three-dimensional cross-linked structure, and can adopt the configuration of a flexible coil or gel in solution (Hayes et al., 1989; Stevenson, 1994). Under certain conditions, such as low pH and large concentration of salt, humic colloids become unstable and start to coagulate and form aggregates. Concentration of cations, such as Al^{3+} , Ca^{2+} and Cu^{2+} , pH and ionic strength are found to affect the coagulation of humic acid (Tipping and Ohnstad, 1984; Stevenson and Vance, 1989; Temminghoff et al., 1998).

The organic matter from forests is an important source of the dissolved organic matter in the natural environment (Michalzik and Matzner, 1999). Concentrations of the dissolved organic carbon (DOC) in soil solutions from forest surface layers are normally found in the range of 10 to 300 mg/l. Immobilisation, rather than biodegradation, is mainly responsible for maintaining small concentrations of dissolved carbon in the mineral soil and preventing the loss of organic matter into stream water (Qualls and Haines, 1992). The immobilisation of organic matter in soil, especially mineral soils, has been ascribed mainly to its adsorption to the surface of solids. Many different surfaces including those of Fe and Al oxides (Davis and Gloor, 1981; Tipping, 1981; Gu et al., 1994; Kaiser et al., 1997; Filius et al., 2000), clay minerals (Murphy et al., 1990; Baham and Sposito, 1994) and soils (Jardine et al., 1989; Kaiser et al., 1996) have been indicated.

Besides the uncertainty about the exact mechanisms by which organic matter adsorbs on soil mineral surfaces, the extent to which the adsorption regulates the concentration of dissolved organic matter is unknown. Soils vary in the relative content of organic matter to the area of reactive minerals. The maximum adsorption of unfractionated dissolved organic carbon on to Al and Fe oxides and hydroxides ranges from 0.2 to 2.2 mg/m surface area (Kalbitz et al., 2000). It is likely that clay minerals and oxides in soil are to a certain extent coated with organic matter. When there is much reactive soil organic matter in relation to mineral surface, as in the upper forest floor, there will be insufficient reactive mineral area to explain the relationship between immobile and mobile organic matter. Precipitation or coagulation could be important in mediating the concentration of dissolved organic matter in such situations. This is supported by the preferential retention of the hydrophobic organic matter and higher molecular weight organic matter to soils (Davis and Gloor, 1981; Qualls and Haines, 1992; Kaiser et al., 1996). The solubility of organic matter in soils was found to be related to adsorbed concentration of cations, *e.g.* Al^{3+} and Ca^{2+} , (Skylberg and Magnusson, 1995). The authors suggested that the adsorption of organic matter on mineral surfaces could not explain its immobilisation in organic horizons.

If coagulation effects are important then the surface charge and the extent of the diffuse part of the double layer around the molecules will be relevant. Tipping & Woof (1990, 1991) proposed a model for the release of humic substances in acid organic soils based on the electrical charge (Tipping and Woof, 1990, 1991). In their model, the soil humic substances are considered to be of two types: mobile and immobile. The potentially mobile organic matter comprises several fractions, each having a different solubility. The tendency of each fraction to pass into solution is then determined by its electrostatic charge, calculated using a humic ion-binding model. The more negative the charge, the greater is the extent of release of potentially mobile humic substances into the solution. Recently, this model has been used in the modelling of the solid solution partitioning of organic matter in three forest soils (Lofts et al., 2001). Although the model can give a reasonable explanation of the data of the dissolved organic matter after the model parameters have been fitted, it provides little insight about the mechanisms by which the material is aimed.

Another humic ion-binding model, the NICA-Donnan (Non Ideal Consistent Competitive Adsorption Donnan) model (Kinniburgh et al., 1999), combines specific binding (NICA) with simple ion-exchange due to electrostatic effects (Donnan) and takes into account proton

and multi-metal binding, the heterogeneity of binding sites, ion-specific non-ideality, and variable stoichiometry. Using this model, we have investigated the conditions under which purified humic acid coagulates in the laboratory, and compared the concentration of dissolved organic matter in forest soil solution with coagulation of humic acid. Our aim was to improve our understanding of the mechanisms that determine the concentration of dissolved organic matter in the field. We report the results below.

Materials and methods

Coagulation of purified forest humic acid

Batch experiments of the coagulation of purified forest humic acid with the cations Na^+ , Ca^{2+} , Cu^{2+} and Al^{3+} have been carried out. Most of the data have been reported by Temminghoff *et al.* (1998). The humic acid was extracted from the B horizon of a forest floor material from the Tongbersven forest in the Netherlands following the International Humic Substance Society (IHSS) procedures, and filtered through a 0.45- μm membrane. Equal amounts of the humic acid solution (200 mg/l dissolved C) and the solution containing the cations were mixed. The total concentration of humic acid in the final solution was 100 mg/l dissolved C. The concentration of the cations varied from 10^{-7} to 10^{-2} M. When the ionic strength in the solution containing Ca^{2+} , Cu^{2+} or Al^{3+} was less than 3 mM, it was adjusted to 3 mM with NaNO_3 . The pH was adjusted to 4.0 or 6.0 with NaOH and HNO_3 . For Cu and Al, experiments were also carried out in 1 mM $\text{Ca}(\text{NO}_3)_2$ background at pH 4.0 (Al, Cu) and pH 6.0 (Cu). The solutions were shaken for 20 hours at 25°C, after which the pH was measured in the suspension. The suspension was filtered over a 0.45- μm membrane (Schleicher & Schuell, NC45), and in the filtrate, the concentrations of Na, Ca, Cu, Al and dissolved C were determined. The Na, Ca, Cu and Al were measured with ICP-OES (Spectros, Spectro Flame) and the dissolved C with a TOC-analyser (SK12, Skalar).

Data sets of soil solution samples from forest areas

For this paper we studied two sets of data on samples of soil solution from forest. The first set was from two Podzol profiles in Simon's Wood and Crowthorne Wood in the south of England, sampled and analysed in 1992, and reported by Goody *et al.* (1995). Both profiles are acid sandy and under pine forest. The Crowthorne Wood profile has a thicker layer of humus than the Simon's Wood profile, and the site is directly under the canopy of a tree. The clay-rich sands at the base of the Simon's Wood profile resulted in an increased cation exchange capacity (CEC), although the total organic matter content is small. The soil

solution was extracted from the field-moist samples by centrifuging at 30 000 g, at 4°C for 35 minutes. The extract was filtered through a 0.45-µm membrane. Concentrations of elements were measured by ICP-AES or ICP-MS. The concentration of dissolved C was determined by a TOC-analyser. They measured the pH of the solution obtained by eluting 5 cm³ of deionised water slowly through a small column containing 10 g soil. For more information of the soils and methods, see Gooddy *et al.* (1995). The important properties of the soil and soil solution of Simon's Wood and Crowthorne Wood are listed in Table 1.

Table 1. Soil and Soil Solution Properties of Crowthorne Wood and Simon's Wood Profiles (Gooddy *et al.*, 1995)

Profile	Horizon	Depth (cm)	Soil organic matter ^a (%)	pH	Soil solution			
					DOC ^b (mg/l)	Ca (mM)	Al (mM)	ionic strength ^c (mM)
Crowthorne	FH	10-0	90.4	3.23	226.8	0.27	0.057	3.3
	A1	0-4	15.7	2.96	266.4	0.27	0.085	4.4
	Ea1	4-10	2.8	3.14	171.6	0.22	0.066	3.7
	Bh1	10-13	8.3	3.80	171.6	0.29	0.077	3.1
	Bh2	13-20	3.4	2.96	152.4	0.39	0.083	4.5
	Bh	20-29	2.4	3.17	110.4	0.39	0.078	4.6
	Bs	29-38	2.2	3.45	92.4	0.36	0.24	5.6
	C1	38-52	2.2	3.89	58.8	0.35	0.20	4.4
	C2	52-65	1.0	4.15	51.6	0.38	0.38	6.6
	C3	65-80	0.2	4.20	48.0	0.31	0.85	11.8
Simon's Wood	C4	80-102	0.2	4.12	69.6	0.16	1.60	22.8
	FH	3-0	55.4	3.48	91.2	0.15	0.024	1.7
	A1	0-6	3.8	3.67	94.8	0.10	0.033	1.8
	Ea1	6-11	1.6	3.65	70.8	0.10	0.043	2.0
	Ea2	11-16	1.0	3.80	61.2	0.60	0.072	1.5
	Bh(Bs)	16-19	4.0	3.84	78.0	0.20	0.081	1.5
	Bs(Bh)	19-22	6.4	4.26	66.0	0.30	0.100	1.3
	C1	22-32	2.3	4.11	19.2	0.70	0.016	1.3
	C2	32-42	1.0	3.88	10.6	0.80	0.004	1.6
	C3	42-52	1.4	4.15	10.3	0.40	0.011	1.8

^a measured with loss-on-ignition; ^b DOC=dissolved organic carbon; ^c ionic strength calculated from the salt content in the solution

The other set of data was taken from Van Breemen *et al.* (1988), who monitored the biogeochemical properties of an oak woodland soil (Hackfort) in the Netherlands for 3 years (1981-1984). Four plots with different soil characteristics were selected in the Hackfort forest. Hackfort A (Gleysol) is an acid brown loamy soil with calcareous subsoil starting at 80 cm below the soil surface. Hackfort B (Humic Cambisol) is an acid brown sandy soil with

Table 2. Soil and soil solution properties of Hackfort A, B, C and D (means with standard errors in brackets) (Breemen et al., 1988)

Profile	Horizon	Depth (cm)	Soil organic matter ^a (%)	Soil solution					
				measurements	pH	DOC ^b (mg/l)	Ca (mM)	Al (mM)	ionic strength ^c (mM)
Hackfort-A	A0	0	84	11	3.51 (0.10)	42.8 (7.6)	0.34 (0.15)	0.044 (0.019)	3.3 (1.2)
	A1	10	6.2	8	3.36 (0.08)	55.2 (7.7)	0.27 (0.06)	0.123 (0.041)	2.8 (0.7)
	B1	20	1.8	9	3.58 (0.10)	41.7 (7.5)	0.25 (0.03)	0.282 (0.108)	3.8 (0.7)
	B2	40	0.6	6	3.78 (0.15)	25.5 (6.3)	0.31 (0.04)	0.767 (0.131)	6.2 (1.1)
	C1g	60	0.2	11	4.63 (0.23)	19.2 (6.7)	1.29 (0.40)	0.017 (0.006)	6.8 (1.9)
	C2g	90	0.2	15	7.05 (0.39)	22.5 (17.3)	2.39 (0.70)	0.007 (0.009)	10.4 (2.2)
Hackfort-B	A0	0	94	11	3.96 (0.18)	80.1 (22.8)	0.18 (0.14)	0.012 (0.009)	2.7 (1.4)
	A1/B21	10	6.0	7	3.38 (0.11)	49.4 (9.1)	0.12 (0.03)	0.077 (0.011)	2.0 (0.4)
	B22	40	5.0	8	4.05 (0.16)	21.7 (12.6)	0.19 (0.02)	0.506 (0.072)	5.0 (3.1)
	C11g	90	0.2	9	4.01 (0.23)	27.6 (19.7)	0.25 (0.26)	0.971 (0.767)	6.7 (4.1)
Hackfort-C	A0	0	82	9	3.92 (0.56)	234.6 (348.4)	0.18 (0.06)	0.019 (0.015)	3.1 (1.6)
	A1	10	4.6	7	3.78 (0.14)	55.4 (29.3)	0.13 (0.07)	0.245 (0.052)	2.7 (0.8)
	B23	60	1.0	10	4.12 (0.13)	17.4 (4.7)	0.19 (0.03)	0.265 (0.036)	3.0 (0.2)
	C1g	90	0.2	13	4.12 (0.19)	26.2 (14.9)	0.20 (0.08)	0.407 (0.133)	3.7 (0.8)
Hackfort-D	A1	10	6.6	7	7.66 (0.19)	33.4 (7.4)	1.60 (0.20)	0.011 (0.011)	5.6 (0.7)
	AC	20	6.0	7	7.56 (0.21)	39.2 (15.3)	3.68 (1.84)	0.009 (0.009)	6.9 (1.7)
	C1g	40	0.4	9	7.55 (0.20)	28.8 (9.3)	5.34 (2.67)	0.006 (0.007)	9.2 (1.8)
	IIB22tb	60	0.4	11	7.22 (0.18)	25.1 (8.5)	6.20 (3.10)	0.002 (0.011)	11.6 (1.4)
	IIB22sb	90	0.2	14	7.42 (0.22)	22.6 (12.1)	7.42 (3.71)	0.002 (0.003)	13.0 (1.6)

^a soil organic matter measured with loss on ignition for the forest floor; for the mineral horizon measured with potentiometry after wet combustion in a mixture of phosphoric and chromic acid; ^b DOC=dissolved organic carbon; ^c ionic strength calculated from the salt content in the solution

calcareous subsoil below 120 cm. Hackfort C (Gleyic Arenosol) is a moderately acid yellowish brown sandy soil without calcareous material. Hackfort D (Mollic Gleysol) is a grey sandy soil that is calcareous throughout. Soil solution in the mineral horizon was

collected monthly by the means of high flow porous ceramic cups (Soil Moisture Cup, Santa Barbara, California) at 10, 20, 40, 60 and 90 cm depth. The soil solution at the surface was sampled by means of a filter plate placed immediately below the organic surface layer. The filter plate consists of an Acropor filter (0.2 μm Gellmann Inc.). The pH and the dissolved C in the soil solution were measured. Part of the solution was acidified with HCl to pH 2 or 3 and used to determine element concentration. Aluminium was determined with an autoanalyser (Technicon AAII). Concentrations of Ca, Mg, K and Na were measured with AAS (Perkin Elmer). Here we have used the soil solution data measured in 1983, and each measured value was considered separately. More detailed description of the profiles and methods can be found in Van Breemen *et al.* (1988). The important properties of the soil and soil solution from the Hackfort A, B, C and D are listed in Table 2.

Modelling method

The physico-chemical behaviour of humic acid and organic matter in the soil solution was modelled to find out the effect of the physico-chemical characteristics on the coagulation of humic acid and the concentration of dissolved organic matter. We assumed that the later behaves like humic acid with respect to cation and proton binding.

The semi-mechanistic NICA-Donnan model (Kinniburgh *et al.*, 1999) was applied to simulate the behaviour of humic acid in response to the change of pH, salt concentration, specifically and non-specifically bound cations. In it, the humic acid molecule is viewed as a three-dimensional gel phase (Benedetti *et al.*, 1996a; Kinniburgh *et al.*, 1999). The oxygen-containing functional groups in the humic acid, mainly carboxylic (COOH) and phenolic (OH) groups, can protonate and deprotonate and can bind cations. In using the Donnan model, we assume that at each electrical charge Q (mol/kg), the overall electro-neutrality of the gel phase is entirely preserved by the penetration of salt ions in the gel phase (Benedetti *et al.*, 1996b; Kinniburgh *et al.*, 1999):

$$\frac{Q}{V_D} + \sum_{i=1}^n Z_i (C_{D,i} - C_i) = 0, \quad (1)$$

where V_D (l/kg) is the volume of the Donnan gel phase, $C_{D,i}$ (mol/l) is the concentration of component i with the charge Z_i in the Donnan phase, and C_i (mol/l) is its concentration in the external solution.

The charge of the humic acid leads to an electrostatic Donnan potential Ψ_D (V). The component concentration in the Donnan phase C_{iD} is related to its concentration in the solution C_i according to the Boltzmann accumulation factor:

$$C_{iD} = C_i \exp\left(-\frac{Z_i F \Psi_D}{RT}\right), \quad (2)$$

where F is Faraday's constant (coulomb/mol), R is the gas constant (J/mol K), and T is the temperature (K).

Benedetti *et al.* (1996b) showed that the Donnan volume (V_D) of humic acid decreases with increasing ionic strength (I) and used the following empirical relation to estimated the Donnan volume:

$$\log_{10}(V_D) = a - b \log_{10}(I), \quad (3)$$

where a and b are constants. The NICA type model has been used to describe metal binding to natural organic matter in soils using parameters derived from purified humic or fulvic acids (Goody *et al.*, 1995; Benedetti *et al.*, 1996a; Temminghoff *et al.*, 1997). The general equation of the bimodal NICA type model can be written as:

$$\begin{aligned} Q_i = Q_{\max 1} \times \frac{n_{i1}}{n_{H1}} \times \frac{(\tilde{K}_{i1} C_{iD})^{n_{i1}}}{\sum_i (\tilde{K}_{i1} C_{iD})^{n_{i1}}} \times \frac{\left\{ \sum_i (\tilde{K}_{i1} C_{iD})^{n_{i1}} \right\}^{P_1}}{1 + \left\{ \sum_i (\tilde{K}_{i1} C_{iD})^{n_{i1}} \right\}^{P_1}} \\ + Q_{\max 2} \times \frac{n_{i2}}{n_{H2}} \times \frac{(\tilde{K}_{i2} C_{iD})^{n_{i2}}}{\sum_i (\tilde{K}_{i2} C_{iD})^{n_{i2}}} \times \frac{\left\{ \sum_i (\tilde{K}_{i2} C_{iD})^{n_{i2}} \right\}^{P_2}}{1 + \left\{ \sum_i (\tilde{K}_{i2} C_{iD})^{n_{i2}} \right\}^{P_2}}, \quad (4) \end{aligned}$$

where the subscripts 1 and 2 relate to the weak proton affinity, mainly carboxylic-type and strong proton affinity, mainly phenolic-type sites respectively. The term Q_{\max} is the site density, Q_i is the total amount of ion i bound chemically to reactive groups, and \tilde{K}_i is the median affinity for ion i . The term C_{iD} is the concentration of ion i in the Donnan phase. The quantities p and n_i reflect the heterogeneity of the humic substances and the non-ideal behaviour of ion i respectively.

The total amount of cation bound is the sum of the amount of specifically bound according to Equation (4) and what is bound in the Donnan phase according to Equation (2). For more detailed description of the NICA-Donnan model see Kinniburgh *et al.* (1999). In this paper, the NICA-Donnan model parameters of generic humic acid (Milne *et al.*, 2001) are used in the calculation (see Table 1, Appendix). All parameters are kept constant for both humic acid in the coagulation experiment and dissolved organic matter in the forest soil solution. We did the modelling with the chemical speciation code ECOSAT (Keizer and Van Riemsdijk, 1994).

Results and discussion

Coagulation of purified forest humic acid

The results of the coagulation experiment show that, at a certain total ion concentration and pH, the concentration of dissolved C decreases rapidly due to the coagulation of humic acid (Figure 1a). As discussed by Temminghoff *et al.* (1998), the almost total coagulation of the humic acid occurs over a very small concentration range but differs for every ion and pH. At the same total concentration, the trivalent Al^{3+} is more effective in coagulation than the divalent Ca^{2+} and Cu^{2+} , which are more effective than the monovalent Na^+ . The valence effect on the stability obeys the so-called Schulze Hardy rule. The coagulation occurs at about 10^{-4} M Al, $10^{-3.3}$ M Cu, $10^{-2.5}$ M Ca and not below 10^{-2} M Na (Temminghoff *et al.*, 1998). The pH shows minor effects on the coagulation at pH 4 and pH 6. At the same metal content, the solubility of humic acid is somewhat larger at pH 6 than at pH 4. The pH effects are less important for Cu^{2+} than for other cations.

To find the crucial physico-chemical factor that determines the humic acid coagulation, cation adsorption to humic acid was calculated with the NICA-Donnan model using the generic parameters of humic acid (Milne *et al.*, 2001). Figure 1b shows the amount of dissolved humic acid in relation to the amount of cation adsorbed. The amount of cations adsorbed to the humic acid at which coagulation happens depends on the cation and pH. The coagulation starts when the amount of total metal adsorbed is about 1.7 mol/kg Ca^{2+} , 1.9 mol/kg Al^{3+} , 2.7 mol/kg Cu^{2+} at pH 4, and 3.3 mol/kg Ca^{2+} , 2.8 mol/kg Al^{3+} and 3.7 mol/kg Cu^{2+} at pH 6. Compared with that at pH 4, coagulation at pH 6 occurs when more cation is adsorbed on the humic acid. Copper binds to humic acid more strongly than Ca^{2+} . Even though coagulation of humic acid started at a smaller total concentration of Cu than Ca in the experiment, there is more Cu than Ca bound at the starting point of the coagulation. It

shows that the amount of bound metal is not the only factor that determines the coagulation of humic acid. Other important factors such as the type of binding (chemical or electrostatic), pH and ionic strength play a role.

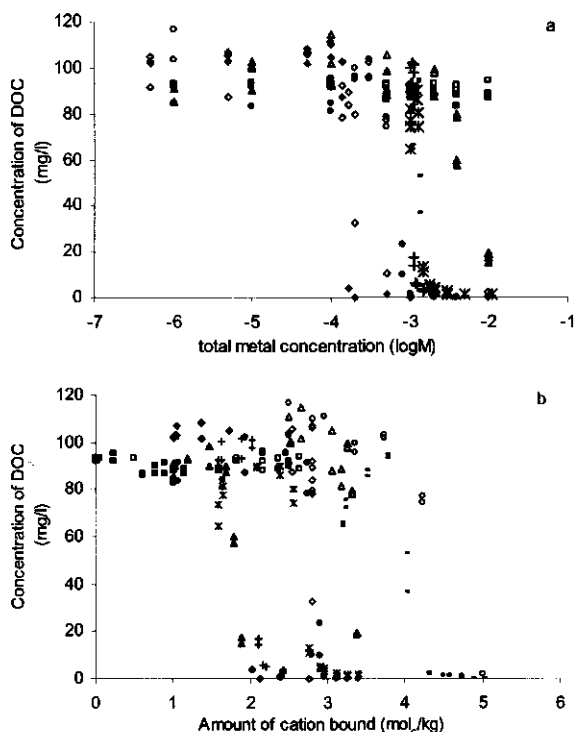


Figure 1. The concentration of DOC as a function of (a) the logarithm of the total concentration of cations expressed in mol/l and (b) the adsorbed amount of cations on the humic acid expressed in mol/kg (■ Na^+ pH4; □ Na^+ pH6; ▲ Ca^{2+} pH4; △ Ca^{2+} pH6; ● Cu^{2+} pH4; ○ Cu^{2+} pH6; ◆ Al^{3+} pH4; ◇ Al^{3+} pH6; + $\text{Al}^{3+} + \text{Ca}^{2+}$ pH4; * $\text{Cu}^{2+} + \text{Ca}^{2+}$ pH4; _ $\text{Cu}^{2+} + \text{Ca}^{2+}$ pH6).

The NICA-Donnan calculation shows that under the experimental conditions, the humic acid was negatively charged. This negative charge leads to a negative Donnan potential of the humic acid molecule. The calculated Donnan potential of the humic acid in the coagulation experiment is in the range of -0.24 to -0.03 V. The concentration of the dissolved humic acid against its Donnan potential is plotted in Figure 2a. We found that the coagulation of humic acid starts to occur when the negative Donnan potential has become less negative. The concentration of humic acid that remained in the solution depends on the Donnan potential.

Except for the treatment of Al at pH 6, coagulation starts at a Donnan potential of about -0.08 V, and the dissolved C decreases drastically from -0.08 to -0.05 V regardless of the type of the cation and pH. The response of coagulation to the Donnan potential with Al^{3+} at pH 6 differs obviously from the other treatments, including Al^{3+} at pH 4. The exceptional situation for Al^{3+} at pH 6 could be because $\text{Al}(\text{OH})_3$ precipitates. In this case the adsorption of humic acid to $\text{Al}(\text{OH})_3$ leads to a smaller solubility of humic acid. This so-called 'sweep' coagulation phenomenon (Gregory, 1978) commonly takes place in water treatment using salts of Al and Fe.

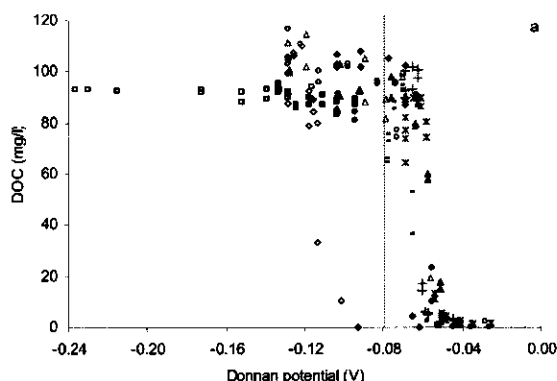


Figure 2a. The effect of the Donnan potential on the coagulation of humic acid

(■ Na^+ pH4; □ Na^+ pH6; ▲ Ca^{2+} pH4; △ Ca^{2+} pH6; ● Cu^{2+} pH4; ○ Cu^{2+} pH6; ◆ Al^{3+} pH4; ◇ Al^{3+} pH6; + $\text{Al}^{3+} + \text{Ca}^{2+}$ pH4; * $\text{Cu}^{2+} + \text{Ca}^{2+}$ pH4; x $\text{Cu}^{2+} + \text{Ca}^{2+}$ pH6; dashed line: starting point of coagulation).

Because the Donnan potential is calculated from the chosen concentration of cations and pH, it is therefore appropriate to apply regression of the concentration of dissolved C on the Donnan potential. We derived an empirical regression model from the coagulation data of humic acid ignoring the treatment of Al^{3+} at pH 6. This equation quantifies the relation between the concentration of dissolved organic C (DOC) and the Donnan potential, when the calculated Donnan potential is less negative than -0.08 V, at which coagulation started to occur in the experiment (Figure 2b):

$$\log_{10}(\text{DOC}) = -52.0 \psi_D - 1.85, \quad (5)$$

where DOC is in mg/l and the Donnan potential ψ_D is in V. The initial concentration of dissolved C in all experiments was 100 mg dm^{-3} . Considering the empirical nature of the

equation and the lack of data beyond 100 mg/l, one should be careful not to apply the equation beyond the conditions for which it has been tested. Note that the equation explains the data imperfectly ($R^2=0.72$). However, it does give a single logical explanation for all the experimental results of humic acid coagulation, independent of the type of cation, pH and ionic strength. This finding accords in principle with the flocculation theory of colloids, the DLVO theory. The deviation of the data from the model could be due to the steep slope of the decrease of dissolved C in combination with the experimental errors in the measurement.

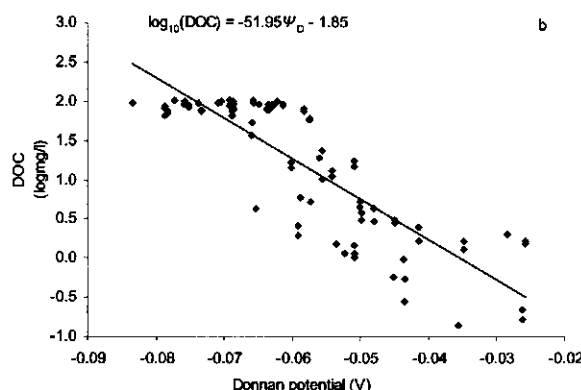


Figure 2b. *The relation between the common logarithm of DOC, expressed in mg/l and Donnan potential. (◆ measured concentration of DOC in the coagulation experiment; — regression of the concentration of logDOC on Donnan potential)*

Using this relation of humic acid coagulation and the Donnan potential, we can assess the effects of various factors on the solubility of humic acid. It follows from the data that coagulation starts when there is less Ca bound to the humic acid than Cu. Copper and calcium show an enormous difference in binding behaviour. Calcium binds weakly chemically compared with Cu, and its pH-dependency in the chemical binding is much less than for Cu. The pH-dependency is directly linked to the exchange ratio of protons upon binding of the metal (Benedetti et al., 1996a; Kinniburgh et al., 1999). This implies that the reduction of the negative charge upon binding of a Ca^{2+} ion is much bigger than for Cu^{2+} . In other words, more Cu is bound chemically to humic acid to obtain the same change in charge than in case of Ca at the same pH. Another important factor is the cation exchange that takes place in the Donnan phase. The electrostatic potential will be less negative for a given humic

acid charge and pH (including changes in charge due to specific binding) the more the ions with larger valence are involved in the charge compensation in the Donnan phase. Adding the same amount of Ca or Cu to humic acid with NaNO_3 as background electrolyte will lead to a larger ratio of Ca in the Donnan phase than for Cu, because Cu binds much more strongly chemically to the reactive groups of the humic acid. We can conclude the above discussion by stating that the chemically weakly bound Ca^{2+} ion plays a much more significant role in coagulating humic acid than Cu^{2+} in terms of amount metal bound. However, in terms of total metal added, Cu is more effective due to its much stronger binding. The NICA-Donnan model can be used to describe the experimental facts both conceptually and quantitatively.

Organic matter in soil solution

In the six forest soil profiles studied (data sets of Breemen et al., 1988; Gooddy et al., 1995) the pH of the soil solution ranges from very acidic (pH less than 3.0) to neutral or weakly alkaline (pH 7.7). The most acid samples were in the Crowthorne Wood profile. The concentration of dissolved C is between 10-266 mg/l, with the smallest in the bottom layer of Simon's Wood and the largest in the top layer of Crowthorne Wood. In each profile, the concentration of dissolved organic C decreases with depth. The same trend was found in other studies such as that by Michalzik & Matzner (1999) in a spruce ecosystem. Concentrations of Ca and Al in the soil solution were in the range of 10^{-5} - 10^{-3} and 10^{-6} - 10^{-3} M respectively. Although many laboratory studies show that the release of dissolved C from organic soil is positively related to pH (Kalbitz et al., 2000), no such relationship was found in these samples of forest soil (Figure 3). The largest concentrations of dissolved C are observed at low pH and large Al concentration.

The Donnan potential of the dissolved organic matter in these soil solutions was calculated with the NICA-Donnan model on the assumption that all dissolved organic matter is humic acid. The effect of pH, adsorption of Ca and Al and salt concentration was considered. The Donnan potential calculated ranges from -0.10 to -0.04 V. To compare with the regression in the coagulation experiment, Equation (5), we computed a regression of the concentration of the dissolved organic C on the Donnan potential for these soil data. In Figure 4, the relation for the soil data is shown and compared with that of Equation (5) derived from the humic acid coagulation experiment (the dashed lines).

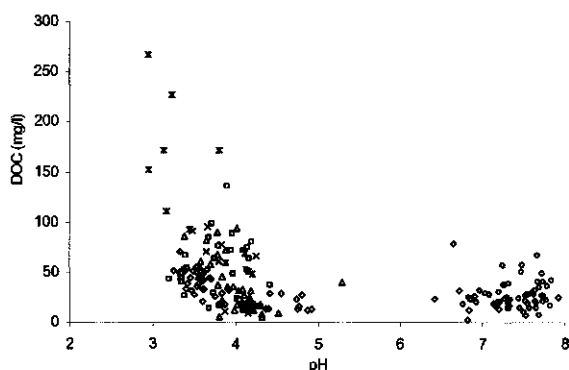


Figure 3. *DOC concentration in the soil solutions as a function of the soil pH*

(* Crowthorne Wood; × Simon's Wood; ◇ Hackfort A; □ Hackfort B; △ Hackfort C; ○ Hackfort D).

The results of the Crowthorne Wood profile are given in Figure 4a. The Donnan potential of the dissolved organic matter calculated ranges from -0.07 to -0.04 V. The results suggest that the dissolved C in the soil solutions decreases as the Donnan potential becomes less negative. Compared with the coagulation of humic acid, the slope of the decrease is less (-24.0 against -52.0) and the intercept is larger (+0.63 against -1.85). The results show that in this soil, the measured dissolved C is larger than that expected due to the coagulation of humic acid. The larger concentration in this profile may be due to the presence of organic compounds that are more soluble than humic acid, e.g. fulvic acid, amino acids, etc. This can be the consequence of the dense vegetation of the site. The Crowthorne Wood profile was sampled directly under the tree canopy.

In the Simon's Wood profile, the Donnan potential calculated ranges from -0.08 to -0.07 V. We observed a relation between the concentration of dissolved organic C and the Donnan potential except for the base horizons (Figure 4b). In the base horizons of the Simon's Wood profile, the measured concentrations are much less than the others, even though the Donnan potential is more negative. The explanation of this disagreement can be attributed to the enrichment of clay in this part of the profile (Goddy et al., 1995). The process that controls the concentration of dissolved organic matter might be different in the clay rich soils, where the adsorption of organic matter to clay minerals might be the controlling factor leading to the small concentration. In addition to oxides and hydroxides, clay minerals are also

important adsorbents for dissolved C in soils. As shown in Figure 4b, the concentration of dissolved C in the upper horizons in the Simon's Wood profile decreases, as the Donnan potential becomes less negative. The concentration is close to that predicted by the coagulation of humic acid.

In the Hackfort profiles, the concentration of dissolved organic C varied strongly among the repeated measurements at the same place during the year (Table 2). Figure 4c to 4f show the dependency of dissolved C on the Donnan potential in the profiles of Hackfort A, B, C and D. We observed a correlation between the concentration and the Donnan potential in the profiles of Hackfort B, C and D. The correlation in the Hackfort D profile is not as significant as in the Hackfort B and C profiles, probably because of the narrow range of the Donnan potential in it. In the Hackfort B and C profiles, Donnan potentials that are more negative than -0.08 V were calculated. For these samples, Equation (5) is not applicable.

In the Hackfort B, C and D profiles, the concentration of dissolved C decreases with a less negative Donnan potential. Compared with the correlation in the humic acid coagulation, the slope is less (-15.7 to -36.7 against -52.0) and the intercept is larger (+0.60 to -1.00 against -1.85), similar to that in the profiles of Simon's Wood and Crowthorne Wood. In the Hackfort B and C profiles, the regression line of the soil solutions crosses the line of humic acid coagulation at about -0.07 V of the Donnan potential. In these two acid sandy soils, the concentration of dissolved organic C is normally larger than that controlled by humic acid coagulation at less negative Donnan potential. This can be explained by the existence of the organic molecules that are more soluble than humic acid. In the profile of Hackfort D, the measured concentration of dissolved organic C is close to that predicted due to humic acid coagulation. The pH in this profile is between 7.2 and 7.7. You *et al.* (1999) have shown that humic acid is the most important constituent of dissolved organic matter at close to neutral pH, whereas at acidic pH, fulvic acid dominates.

The absence of a correlation between the concentration of dissolved organic C and the Donnan potential in the Hackfort A profile (Figure 4c) could be the result of the big changes of the soil properties through this profile. The soil is acid at the surface and calcareous from 80 cm downwards. The pH ranges from 3.4 to 7.1. As above, pH can have an effect on the

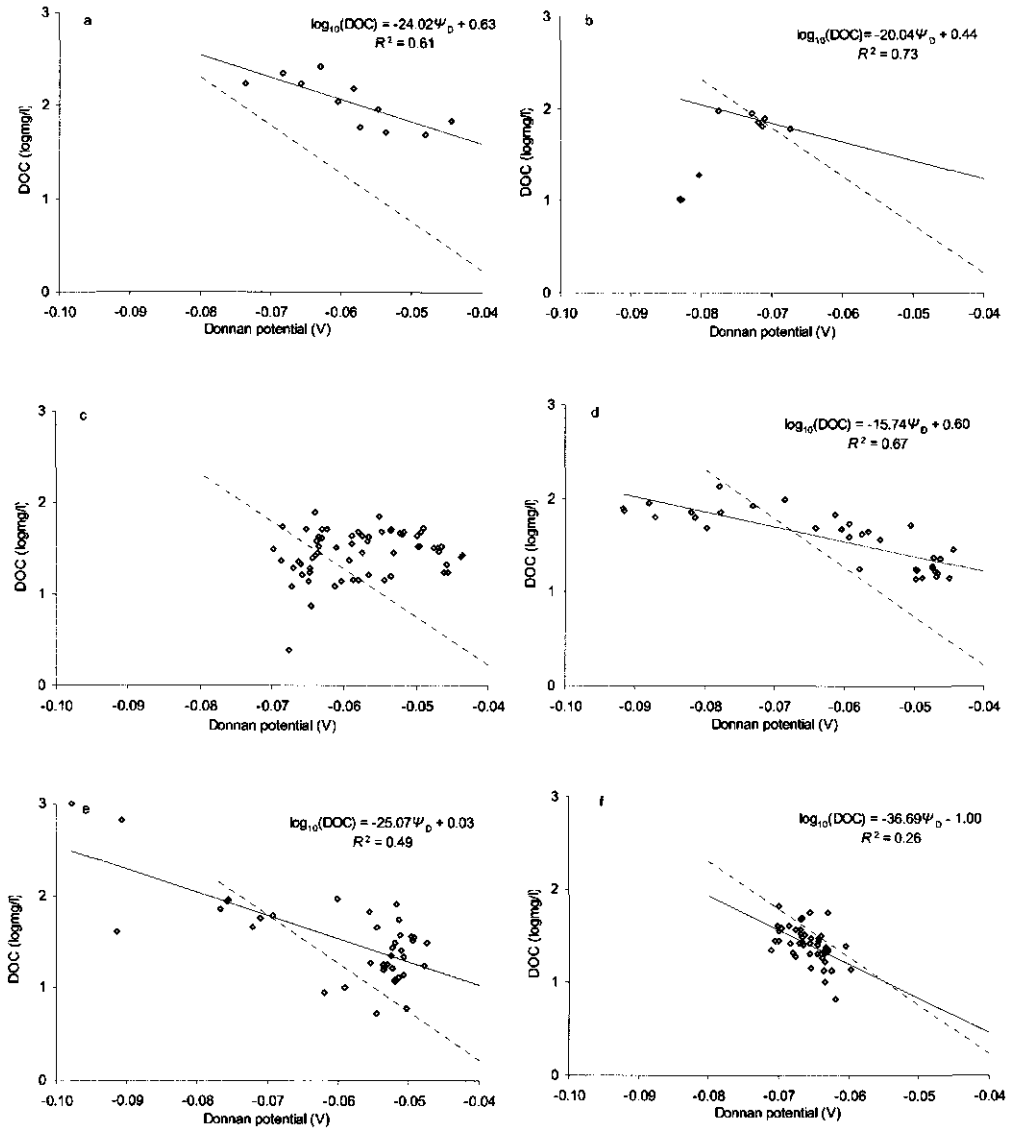


Figure 4. DOC concentration in soil solutions as a function of the calculated Donnan potential (a) Crowthorne Wood; (b) Simon's Wood; (c) Hackfort A; (d) Hackfort B; (e) Hackfort C; (f) Hackfort D (\diamond measured DOC in soil solution; \blacklozenge measured DOC at the bottom of the Simon's Wood profile that are not considered in the regression; — regression line of the DOC in soil solution; ---- calculated DOC concentration based on Equation (5)).

composition of dissolved organic matter. In the other soil profiles studied, the differences in the dependency of dissolved organic C on the Donnan potential can also be the result of the variation in the composition of the organic matter, which in turn depends on its origin, the biological community and the environment. The change of the composition of dissolved organic matter with pH may explain the broad picture of the pH effects as observed in Figure 3, showing the largest concentration of dissolved organic C at low pH and the largest dissolved Al concentration, which we did not expect from the coagulation theory.

Conclusions

We have examined the control of humic acid solubility and concentration of dissolved organic matter by coagulation from a physico-chemical point of view and compared the amount of organic matter in solutions of forest soils with results from coagulation studies. The results show that the coagulation of purified humic acid depends on the Donnan potential calculated according to the NICA-Donnan model. We found an empirical linear relation between the logarithm of the concentration of the dissolved organic C and the Donnan potential, Equation (5). The solubility of humic acid is smaller when the Donnan potential is less negative.

In five out of the six soil profiles studied, we observed a correlation between the concentration of dissolved organic C and the Donnan potential. The trend of the relation is the same as for the coagulation of humic acid, i.e. the concentration of dissolved organic C decreases when the Donnan potential is less negative. However, the correlation differs from profile to profile, probably because of the differences in the composition and properties of dissolved organic matter. The results show that in the acid sandy soils, the concentration of dissolved organic matter is often larger than that predicted by the coagulation of humic acid when the calculated Donnan potential is less negative than about -0.07 V. This could be due to the presence of a fairly large fraction of organic molecules that are more soluble than humic acid, for instance fulvic acid. Under these conditions (acid sandy soil, Donnan potential less negative than -0.07 V), the coagulation of humic acid can in principle occur, and the coagulation process may contribute to the control, at least in part, of the concentration of dissolved organic matter in the soil solution. The adsorption mechanism may contribute to the control of dissolved organic matter with smaller molecular weight such as fulvic acid. In acid soil with a calculated Donnan potential more negative than -0.07 V, or in the neutral and weakly alkaline soil, the measured concentration to dissolved organic C

was close to or less than that controlled by the coagulation of humic acid. More attention to the composition of dissolved organic matter and to the processes that likely control its various fractions may help us to understand better of the factors that are important.

Chapter 7

Transport of Humic and Fulvic Acid in Relation to Metal Mobility in a Copper Contaminated Acid Sandy Soil

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Co-authors Ellen P. M. J. Fest, Jeroen Fillius, Erwin J. M. Temminghoff, Willem H. Van Riemsdijk

Abstract

The transport of inorganic and organic pollutants in water and soil can be strongly influenced by the mobility of natural dissolved organic matter (DOM). In this paper, the transport of a humic acid (HA) and a fulvic acid (FA) in a copper contaminated acid sandy soil was studied. The data showed that the transport behaviour of HA differed from that of FA. The breakthrough curves (BTCs) of HA were characterised by a rapid relatively sharp front followed by a plateau at a lower HA concentration than in the influent solution. The increase of the Ca concentration decreased the HA concentration further. Compared to HA, the BTCs of FA were retarded and showed an extended tailing, approaching complete breakthrough. The increase of the Ca concentration decreased the FA concentration only temporarily. Based on our model calculation, the characterisation of HA transport could be explained by the coagulation of HA largely upon the binding of Al. The increase of the Ca concentration resulted in further coagulation of HA because of the increased Ca adsorption, which occurred mainly in the Donnan phase. For FA, the adsorption to the soil matrix was more likely the process that controls its solubility and mobility. The mobility of Al and Cu in the soil column was closely related to the solubility and transport of the dissolved organic matter in soil solution. The concentration of Ca in the effluent was lower than in the influent because Ca was retained in the soil due to the retardation of HA and FA and due to the compensation of the other cations released from the soil to the solution.

Introduction

The partitioning and mobility of organic matter play an important role in the transport of contaminants (inorganic and organic) in the natural environment. Organic matter can enhance (when dissolved) or retard (when in the solid matrix) the transport of contaminants through the soil (Carter and Suffet, 1983; McCarthy and Zachara, 1989; Stevenson, 1994; Benedetti et al., 1995; Jordan et al., 1997; Temminghoff et al., 1998). Risks of enhanced transport of contaminants occur when the concentration of dissolved organic matter (DOM) in soil increases. The mobility of DOM in soil is governed by both the chemistry of the bulk solution and the composition of the soil solid phase, where the former determines DOM dissolution properties, and the latter controls the extent of DOM adsorption (Weigand and Totsche, 1998).

Dissolved organic matter (DOM) is a complex mixture of many molecules and is usually operationally defined as the organic matter that passes a 0.45 μm filter. A large portion of the DOM in the soil solution is present as humic acid (HA) and fulvic acid (FA) (Thurman, 1985). The other organic compounds include macromolecular hydrophilic acids and identifiable organic compounds such as carbohydrates, carboxylic acids, and amino acids (Herbert and Bertsch, 1995).

In spite of the complex nature of DOM, it is often treated as a single component in the studies of its adsorption and transport on various soil, clay and oxides surfaces; relatively few studies have explicitly considered DOM as a complex mixture, with adsorption behaviour varying from one sub-component to another (Gu et al., 1996). In the breakthrough curves (BTCs) of the natural organic matter, shoulder formation is a common phenomenon (Weigand and Totsche, 1998), which may be due to a fractionation of DOM into sub-components according to differences in reactivity during the transport. In the study of the transport of the DOM in columns containing aquifer sediments, Dunnivant *et al.* (1992) found that the hydrophobic constituents of DOM were preferentially adsorbed, while hydrophilic components were rapidly transported.

Reduction of DOM concentration, in the presence of many different surfaces including Fe and Al hydroxides (Davis and Gloor, 1981; Tipping, 1981; Gu et al., 1994; Kaiser et al., 1997; Filius et al., 2000), clay minerals (Murphy et al., 1990; Baham and Sposito, 1994) and soils (Jardine et al., 1989; Kaiser et al., 1996) have been reported. The immobilization of

DOM by soils, especially mineral soils, has been mostly ascribed to its adsorption to soil surfaces. Dunnivant *et al.* (1992) speculated that because the hydrophobic DOM was preferentially adsorbed in the column experiment, the multi-process adsorption of DOM via direct association with the solid phase and the hydrophobic binding processes between DOM components on the solid and DOM components in solution were important in controlling DOM transport. Despite intensive research in the last decade, our knowledge of the formation and fate of DOM in soils and its response to changing environmental conditions is still fragmented and often inconsistent (Kalbitz *et al.*, 2000).

In this paper, we studied the transport behaviour of humic acid (HA) and fulvic acid (FA) in an acid sandy soil, and their response to the changes in the Ca concentration in the bulk solution. It is not our intention to simulate the transport process with transport modelling. Instead, our focus is to understand the major factors that are involved in the HA and FA transport with the help of breakthrough curves and speciation model calculations. With this study, we aim to get more insight into the various mechanisms that control the solubility and mobility of different DOM sub-components.

Materials and methods

Humic and fulvic acid

The materials of humic acid (HA) and fulvic acid (FA) used here were purified from the B-horizon of a forest soil (Tongbersven in Oisterwijk, the Netherlands) and the Bs-horizon of a peat Podzol (Strichen Association) respectively following the IHSS (International Humic Substance Society) procedures. The carbon content of the HA is 54%, while in the FA it is 40%. More extensive description of the materials can be found elsewhere (Filius *et al.*, 2000; Temminghoff *et al.*, 1997).

Soil sample

Table 1. *Soil characteristics*

Soil	pH	CEC (mmol/kg)	Clay ($<2\ \mu\text{m}$) (%)	SOM (%)	Fe-oxalate (g Fe/kg)	Fe-DCB (g Fe/kg)	Total Cu (2M HNO ₃) ($\mu\text{mol/kg}$)
4A (0-20cm)	3.76	20.5	4.2	3.9	2.02	2.34	1713.6

The soil sample was collected in June 1998 from a field near Wageningen in the Netherlands (Wildekamp site). In 1982, the field site was established as a randomised block design of four pH adjustments (nominal pH: 4.0, 4.7, 5.4 and 6.1) and four copper concentrations (0, 250, 500, and 750 kg CuSO₄/hectare). The pH levels were established using calcium carbonate or sulphur. In 1988, the pH levels were readjusted to their nominal values (Lexmond, 1980; Korthals et al., 1996).

The surface layer (0-20 cm) sample from the treatment 4A (nominal pH 4.0, 750 kg CuSO₄/hectare) was used in the column experiment. The field soil sample was air-dried and sieved (<2 mm). The content of soil organic matter (SOM) was measured by loss-on-ignition at 550°C. Clay content (<2 µm) was measured by sieve and pipette method. Cation exchange capacity (CEC) was determined by unbuffered 0.01 M BaCl₂ method (Houba et al., 1997). Iron fractions in DCB (dithionite-citrate-bicarbonate) and ammonium oxalate – oxalic acid extractions, and Cu content in 2 M HNO₃ (SSR=1:10) extractions were measured with ICP-OES (Spectros, Spectro Flame). These results are given in Table 1.

Column experiment

The Perspex columns in the experiment have a diameter of 4.5 cm and a length of 20 cm. Each column was filled with 300 g of the air-dried soil sample. At the bottom of the column, a filter paper and a thin layer of quartz sand were added to prevent the soil particles from leaching. The pore volume (pv) of the columns was 115 ± 7 ml. Flow rate of 3 ml/hour was used for all the columns in the experiment. The influent solutions for the column experiment were prepared from concentrated stock solutions of Ca(NO₃)₂, HA and FA. The pH of the percolation solution was adjusted to 5.0±0.1 with HNO₃ and NaOH.

The columns were saturated from below using a peristaltic pump (Gilson Minipuls 3) with the initial percolation solution, e.g. 0.5 mM Ca(NO₃)₂ to prevent air inclusion. After saturation and 6 days of preconditioning, the flow direction was changed to downwards and the influent solution entered the column at the top. The scheme of the column experiment is given in Table 2. Previous to period I, the columns were preconditioned with 0.5 mM Ca(NO₃)₂. In period I the background of the influent was 0.45 mM Ca(NO₃)₂ and contained about 120 mg C/l of HA or 160 mg C/l of FA. At the pore volume of 15.5, the experiment was shifted from period I to II. Period II was characterised by an increase of the Ca(NO₃)₂

concentration to 0.92 mM at the same HA and FA concentration, and this period lasted for 15 pore volumes.

Table 2. *Scheme of the column experiment*

Columns	Period I	Period II
blank	0.5 mM $\text{Ca}(\text{NO}_3)_2$	1 mM $\text{Ca}(\text{NO}_3)_2$
HA	0.45 mM $\text{Ca}(\text{NO}_3)_2$ + 120 mg/l DOC (HA)	0.92 mM $\text{Ca}(\text{NO}_3)_2$ + 120 mg/l DOC (HA)
FA	0.45 mM $\text{Ca}(\text{NO}_3)_2$ + 160 mg/l DOC (FA)	0.92 mM $\text{Ca}(\text{NO}_3)_2$ + 160 mg/l DOC (FA)

A fraction collector (ISCO Retriever IV) was used to collect the leached solution in fractions of 15 ml. The concentration of dissolved organic carbon (DOC) in the leached solution samples was measured with a SK-12 analyser (SKALAR). The pH was measured with a PHM84 Research pH-meter. The concentrations of Ca, Cu, Al and Fe were measured with ICP-OES (Spectros, Spectro Flame).

Modelling method

The semi-mechanistic consistent NICA-Donnan model (NICA=Non Ideal Competitive Adsorption) (Kinniburgh et al., 1999) is one of the most advanced models to describe proton and metal binding to humic substances and the influence of the binding on the physico-chemical characteristics of humic substances. The NICA-Donnan model combines specific binding (NICA) with simple ion-exchange due to the electrostatic effects (Donnan) and takes into account proton and multi-metal binding, binding site heterogeneity, ion specific non-ideality and variable stoichiometry.

The oxygen-containing functional groups in the humic acids, mainly carboxylic ($-\text{COOH}$) and phenolic ($-\text{OH}$) groups, can protonate and deprotonate and can complex cations. In the Donnan model, the humic molecules are viewed as a three-dimensional gel phase (Benedetti et al., 1996b; Kinniburgh et al., 1999). It is assumed that at each electrical charge, the overall electro-neutrality of the gel phase is entirely preserved by the penetration of salt ions in the gel phase (Benedetti et al., 1996a; Kinniburgh et al., 1999). The charge of the humic acid leads to an electrostatic potential around the molecule, which in the Donnan model is called the Donnan potential (Ψ_D).

The NICA type model has been used to describe metal binding to natural organic matter in soils using parameters derived from purified humic or fulvic acids (Gooddy et al., 1995; Benedetti et al., 1996a; Temminghoff et al., 1997, 1998). In this paper, we used the NICA-Donnan model to calculate the metal binding to HA and FA in the influent and effluent solutions and their charge and Donnan potential. It was assumed that the HA and FA used behave generically and the generic parameters (see Table 1, Appendix) (Milne, 2000; Milne et al., 2001) were used in the calculation. The measured pH, total concentrations of Ca, Al, Cu and DOC in the influent and effluent solutions were used as the input data. The calculation was carried out with the chemical speciation code ECOSAT (Keizer and Van Riemsdijk, 1994).

Results and discussions

General features

As schematically demonstrated in Figure 1, the column experiment involved a multi-component transport problem. Prior to the start of period I, the ion binding sites on the soil matrix (organic matter, clay) were occupied mainly by H, Ca and Al. In the influent solutions containing HA or FA, H and Ca were partly bound to the HA and FA and partly present as free ions. When the percolation began, several processes occurred, such as the ion adsorption/desorption to/from the solid matrix and the DOM, the coagulation and adsorption of HA and FA, and the dissolution/precipitation of soil minerals. The breakthrough curves of such a multi-component system shows in principle multiple fronts. Theoretically, the number of fronts is equal to the amount of components that have independent interaction with each other and that can be transported (Černík et al., 1996). However, in practice often not all fronts are clearly observed.

In the experiment, the columns have been leached for almost 20 pore volumes with 0.5 mM $\text{Ca}(\text{NO}_3)_2$ solution before the start of period I. In this preconditioning phase, the DOC concentration of all the columns was about the same, approximately 7 - 8 mg/l, and remained constant during period I and II in the blank (no HA or FA added) column (data not shown). In Figure 2-a, the BTCs of the reduced concentration of DOC during period I and II is shown as a function of the number of pv for the FA and HA column. The BTCs of the total concentration of Al, Cu, Fe and Ca in the effluent solution are shown in Figure 2-b to 2-e. In these figures, the dashed lines at about 15.5 pv indicate the change in the influent composition from period I to II (see Table 2).

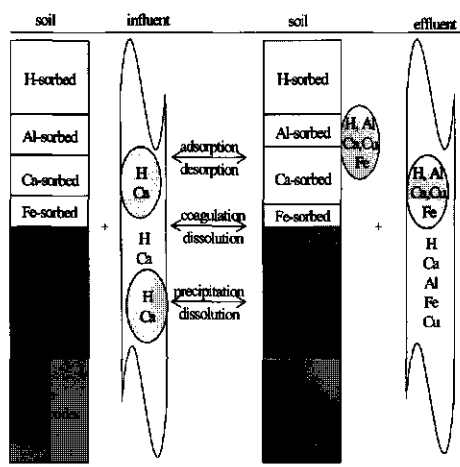


Figure 1. *Schematic description of the multi-component transport system in the column experiment (dark circle indicates DOM and DOM retained in the column with ions bound)*

The pH in the effluent was not constant during the experiment (Figure 2-f). The pH in the HA and FA columns were more stable than in the blank, probably because of the buffering of HA or FA added. The big increase of pH could not be explained by the HA and FA adsorption to the soil, because the increase of pH in the blank column was even bigger than in the HA and FA columns. The increase in pH during the experiment was mostly likely the result of the reduction of nitrate and iron. The fluctuation of the pH was linked to the replacement of peristaltic tubing during the experiment, which might lead to a variation of the redox condition in the columns.

As is shown in Figure 2-a, the initial phase of the DOC breakthrough in period I in the HA column was very fast with very little retardation. After approximately 2 pv, the HA concentration in the effluent reached a plateau at a DOC concentration between 72-79 mg/l, which equalled roughly 60-66% of the influent DOC. After the increase of the Ca concentration in period II, the DOC concentration in the effluent showed a small increase followed by a sharp decrease. After a few pv, the DOC concentration fluctuated around 35-55 mg/l, which was about 29-46% of the DOC in the influent and was lower than in the first period. The observed type of breakthrough might be due to the multi-component nature of

the transport process, which in this case was probably also linked to the coagulation of HA, as we will show below.

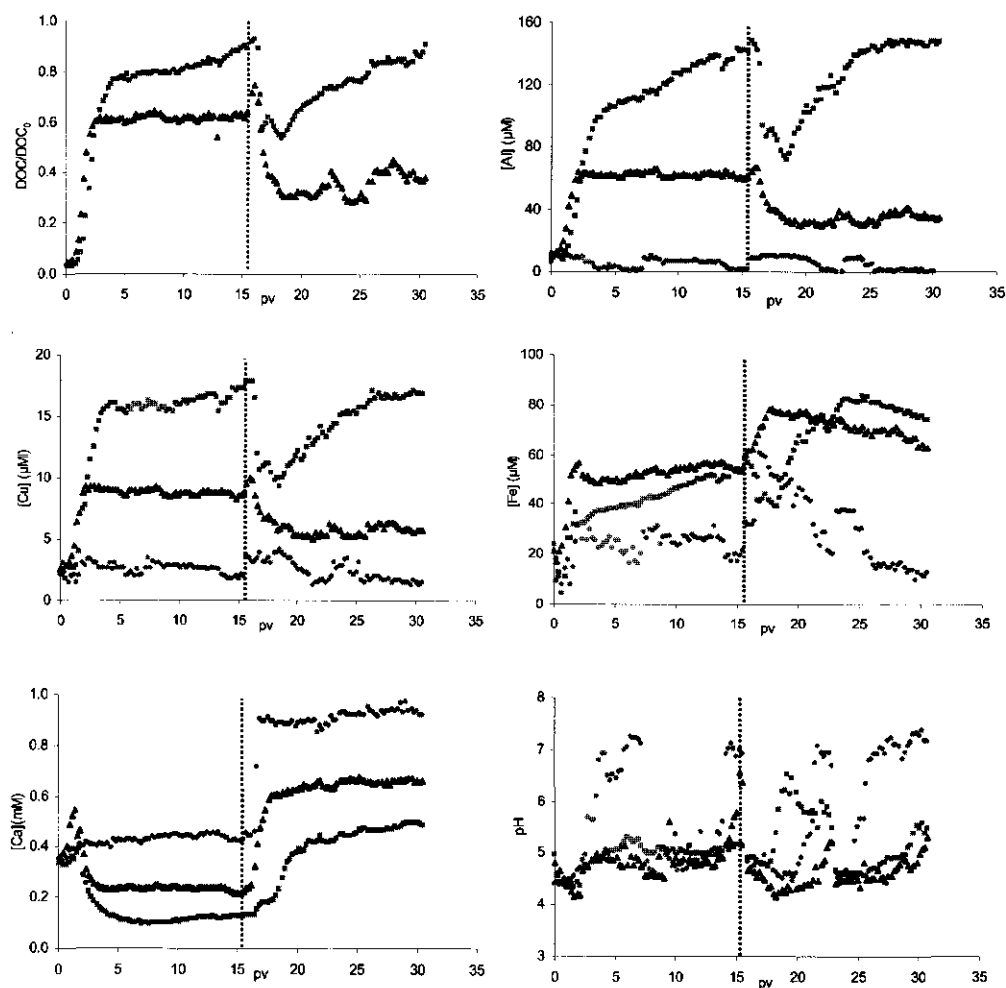


Figure 2. Breakthrough curves of (a) reduced DOC; (b) Al; (c) Cu; (d) Fe; (e) Ca; (f) pH. (• blank; ▲ HA; ■ FA).

Solubility and transport of HA

Humic substances contain functional groups such as carboxylic and phenolic group, which form a polyelectrolyte in water (Ong and Bisque, 1968). Under certain conditions, such as low pH and high salt level, humic colloids become unstable and starts to coagulate and form

aggregates. Cations such as Al^{3+} , Ca^{2+} and Cu^{2+} , pH and ionic strength are found to affect the coagulation of humic acid (Stevenson and Vance, 1989; Temminghoff et al., 1998; Tipping and Ohnstad, 1984). In one soil column experiment with HA it has been found that the mobility of HA was very sensitive to pH and Ca concentration, and the authors hypothesised that the coagulation of HA was the reason for the reduced DOC concentration (Temminghoff et al., 1997). In a recent paper of Zysset & Berggren (2001), a near steady state of DOC at approximately 75% of the concentration in the input was achieved in a column experiment with podozal Bs-horizons. The authors concluded that the reaction mechanisms might be precipitation of metal-organic complexes or physical sorption of dissolved organic matter on previously sorbed organic matter.

In the study of the coagulation data with the same humic acid material as used in this paper, Weng *et al.* (Accepted) found that humic acid started to coagulate when the electrostatic potential of the molecules calculated using the NICA-Donnan model, became less negative. They derived an empirical regression relation from the coagulation data of the HA:

$$\log(\text{DOC}) = -52.0(\Psi_D) - 1.85, \quad (1)$$

in which DOC is in mg/l and the Donnan potential (Ψ_D) in volt (V).

Following the same approach, the electrostatic potential of HA in the column experiment was estimated (see Materials and Methods, Modelling methods). In the calculation, the binding of Fe was neglected. Because of the reduced condition, most of the Fe in solution would be Fe^{2+} . According to the NICA-Donnan parameters for Fe^{2+} adsorption to HA, it is weakly specifically bound. The Fe^{2+} concentration was small compared to the major cation Ca^{2+} , therefore its influence on the calculated Donnan potential of HA was negligible. The ion of Fe^{3+} is strongly bound to HA, however, the concentration of this ion is normally very low. If we assume that goethite control the concentration of Fe^{3+} , the concentration of Fe^{3+} in the effluent solution would be lower than 10^{-12} M. The calculation results, including the amount of protons and cations bound, the electrostatic charge and the Donnan potential of HA are given in Table 3. In period I (excluding the first 2 pv), the charge and the Donnan potential of HA in the effluent solution were at the average of -1.76 mol/kg and -0.079 V. They were less negative than in the influent solution, e.g. -2.24 mol/kg and -0.084 V. Compared to the influent solution, the amount of protons and Ca bound to HA was less,

mainly because of the competition with Al. However, because most of the Al and Cu was chemically bound, while Ca was mostly electrostatically bound, the binding of Al and Cu to HA led to a less negative charge and potential of HA despite of the decreased adsorption of H and Ca.

In period II, the calculated Donnan potential of HA in the effluent solution after the first 2 pv averaged at -0.065 V, which was less negative than in the effluent solution during period I (-0.079 V). Compared to period I, the amount of adsorbed H and Cu was more or less the same. However, the amount of Ca bound was increased due to the increase of the Ca concentration in the influent solution, and the adsorbed Al decreased because of the increased competition with Ca. The calculated charge of the HA did not change very much compared to that in period I (-1.67 vs. -1.76 mol/kg). However, the Donnan potential of HA in period II was less negative than in period I, mainly because of the increase in ionic strength.

Table 3. *Physico-chemical characteristics of HA calculated using the NICA-Donnan model (average over the calculated results for individual samples)*

Characteristics	Period I		Period II	
	influent	effluent (except the first 2 pv)	influent	effluent (except the first 2 pv)
charge (mol/kg)	-2.24	-1.76	-2.32	-1.67
Donnan potential (V)	-0.084	-0.079	-0.073	-0.065
cations adsorbed (mol _e /kg)		2.79 H ⁺		2.90 H ⁺
	3.37 H ⁺	1.37 Ca ²⁺	3.20 H ⁺	1.74 Ca ²⁺
	2.34 Ca ²⁺	1.18 Al ³⁺	2.50 Ca ²⁺	0.90 Al ³⁺
		0.12 Cu ²⁺		0.14 Cu ²⁺

In the study of the batch coagulation experiment of HA, it was found that coagulation of HA might occur at a Donnan potential less negative than -0.08 to -0.07 V when the initial DOC concentration was 100 mg/l (Weng et al., Accepted). In this column experiment, the calculated Donnan potentials of HA in period I were -0.084 V and -0.079 V in the influent and effluent solution respectively and they were beyond or very close to the limitation of the data from which Equation (1) was derived. Therefore Equation (1) could not be applied reliably to predict the DOC concentration in this period. For period II, the equation was applicable and the predicted DOC concentration in the influent solution was 88 mg/l, which

means some coagulation of HA might already have occurred in the influent. The predicted DOC concentration in the effluent solution of period II varied from 36 mg/l to 77 mg/l, which was close to those measured, *e.g.* 35-55 mg/l. In Figure 3, the predicted DOC concentration in the effluent solution in period II is compared to the experimental data and the agreement is reasonable. The fluctuation of HA concentration in period II corresponded mostly to the pH variations during that time.

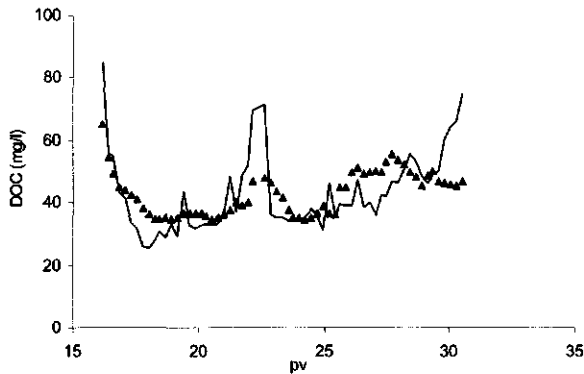


Figure 3. Comparison of predicted DOC using Equation (1) with measured DOC for the HA column in period II. (\blacktriangle measured; — modelled).

The calculations showed that the binding of Al to HA resulted in a less negative Donnan potential of the HA molecules in the effluent solution than in the influent solution in period I. The increase of the Ca concentration in period II reduced the absolute magnitude of the Donnan potential even further. The less negative electrostatic potential induced partial coagulation of HA, and therefore the decrease of the DOC concentration in the effluent solution. The reasonable agreement between the predicted and measured DOC concentration in period II and the shape of the BTCs of HA indicated that a coagulation phenomenon was most likely the process that controlled HA solubility and transport in this acid soil. The analysis suggests that full breakthrough can only be expected after the aluminium activity has been decreased to a substantially lower level due to adsorption to added HA and leaching. However, the Al activity is expected to remain high for a very long period due to dissolution/weathering reactions. Because of the coagulation process, fractionation of the HA might have occurred that led to the retention of more insoluble part of the material. Similar phenomena can be expected to happen in the field, for instance when the solution

from the surface humus layer in a forest, which may contain a high concentration of DOC, enters the mineral soil underneath.

Adsorption and transport of FA

The BTCs of FA differed from that of HA. The DOC concentration in the effluent of the FA column increased fast at the beginning (the first 4 pv) followed by a long tail during the rest of period I to almost complete breakthrough (90%) (Figure 2-a). In period II, the increase of the Ca concentration led to an immediate decrease of the DOC concentration during about 0.5 pv. Then a small increase was seen for just another 0.5 pv, after which the DOC concentration decreased further. After the first 2.5 pv, the DOC concentration started to increase gradually. At the end of the experiment, 90% of the initial DOC concentration was found in the effluent. Note that after the fast increase in period I and the fast decrease in period II, the BTCs of the FA showed the same sort of gradual tailing. Eventually complete breakthrough might be expected if the experiment had been extended for somewhat longer.

The BTCs of FA found here were very similar to the BTCs of DOM transport through a column filled with aquifer material (Dunnivant *et al.*, 1992) and the goethite-coated quartz sand (Weigand and Totsche, 1998), all characterised by an initial rapid concentration increase followed by extended tailing. Differing from HA, the coagulation is not the likely mechanism for the retardation of FA in the column experiment. The molecules of FA are smaller than HA and have a higher negative charge for the same solution conditions. The calculated average Donnan potential of FA was -0.136 and -0.112 V in period I and II respectively, which was more negative than the potential of HA. Moreover, the Van der Waals attraction force is less for FA than for HA because of the smaller molecular weight of FA. Therefore, the coagulation of FA happens not as easy as for HA. The breakthrough of FA reflected the adsorption of FA to the soil matrix. Dunnivant *et al.* (1992) suggested three processes that may contribute to the extended tailing of the observed DOM BTCs during adsorption: (i) non-linear adsorption. (ii) time-dependent adsorption. (iii) multi-component adsorption and transport.

The different responses of the HA and FA BTCs to the changes in Ca concentration in the influent solution (Figure 2-a) indicate different mechanisms. The increase in Ca concentration led to a lower DOC concentration in the HA column, while the reduction of the DOC concentration in the FA column was only temporarily. When the Ca concentration was increased in period II, the adsorption capacity of the soil increased mainly due to

electrostatic effects and more FA could be adsorbed, resulting in the sharp decrease of the DOC concentration at the beginning of period II. However, as shown in Figure 2-a, the extra adsorption capacity was readily filled approaching a new equilibrium, leading to almost complete breakthrough. The increase of the humic substances adsorption to iron oxides as a function of cation concentration was also found by Tipping (1981). By using the CD-MUSIC model to describe FA binding on goethite, Filius *et al.* (2000) gave a general explanation of this phenomenon: When the FA and oxide surface are oppositely charged (at acid pH), the surface charge of the oxide will be neutralised by FA. Multivalent cations like Ca^{2+} can decrease the negative charge of the FA and increase the positive charge of the oxide surface. Therefore, more FA is needed before the charge of the oxide is neutralised resulting in enhanced adsorption.

From the data of DOC concentrations in the influent and effluent solutions, we calculated that about 250 mg DOC/kg soil was bound in the column in period II. Compared to the soil organic matter content (3.98 %), the increased adsorption of FA was very small (0.016%). The small increase of the FA concentration that was observed at the beginning of period II (Figure 2-a) might be a result of the pH increases in the FA column at that time (Figure 2-f). The adsorption of FA on goethite is pH dependent and the adsorption is stronger at lower pH for the pH range of this experiment.

Changes in the concentration of the cations

The BTCs of Al and Cu (Figure 2-b, 2-c) showed the same trend as found for the DOC in both the HA and FA columns. In the preconditioning phase, the concentrations of Al and Cu in the effluent were relatively small (about 10 μM Al and 5 μM Cu). As period I began, due to the binding of Cu and Al to the added humic or fulvic acids, the total concentration of dissolved Al and Cu increased. According to the calculation using the NICA-Donnan model (data not shown), the fraction of organically bound Al and Cu in the effluent solution in both the HA and FA columns increased fast at the beginning of period I, following the increase of HA and FA concentration. Because the organically bound Al and Cu were the dominant species in the effluent solution, the BTCs of Al and Cu were similar to that of HA and FA. The concentrations of dissolved Al and Cu were higher in the FA than the HA column because of the higher FA concentration in solution. The solubility of dissolved organic matter plays a more important role than the type of DOM in the control of mobility of metals that are strongly bound.

The Fe breakthrough (Figure 2-d) differed from that of Al and Cu. The increase of the Ca concentration in period II led to a smaller (HA) or approximately equal (FA) concentration of Al and Cu, but a larger Fe concentration. It indicated that Fe was mostly in the form of Fe^{2+} and it was mainly electrostatically bound in the soil matrix. The larger Ca concentration in period II resulted in more Fe release to the solution because of the stronger competition with Ca for the binding to soil sites such as organic matter and clay. If Fe^{3+} was the dominant species, one would expect similar breakthrough curves as for Al and Cu because Fe^{3+} is strongly bound to organic matter.

The Ca breakthrough (Figure 2-e) also differed from that of Al and Cu. For the HA column, at the start of period I, the Ca concentration showed an initial increase for 1.5 pv followed by a decrease and then reached a plateau. The steady state concentration (0.24 mM) was about 50% of the input Ca concentration (0.45 mM). After the switch from period I to period II, the concentration of Ca increased due to the increased concentration in the influent, but remained lower than the concentration in the influent (0.65 mM vs 0.92 mM). The changes of the Ca concentration in the FA column were similar to that in the HA column, but at a lower concentration (around 0.13 mM at the end of period I and 0.49 mM at the end of period II). Differing from the breakthrough of DOC, there was no indication that the Ca concentration would approach complete breakthrough during the experiment.

The increase in the Ca concentration at the beginning of period I was because of the higher concentration of free Ca^{2+} in the soil in the preconditioning phase than in the influent solution containing HA and FA. The following decrease of the Ca concentration to a level lower than that in the influent could be due to two reasons. First, Ca was retained in the solid matrix together with the coagulated or adsorbed HA or FA, leading to a Ca concentration reduction in the solution. The NICA-Donnan calculation showed that the Ca that was coagulated with HA was about 0.05 mM in period I and 0.12 mM in period II at the steady state. The Ca that was retained with the adsorbed FA was estimated at 0.02mM and 0.07 mM in the FA column at the end of period I and II respectively. With the FA approaching the complete breakthrough, the Ca that was retained in the column with adsorbed FA diminished, therefore a slight increase of the Ca concentration in the effluent was observed at the end of period I and II in the FA column.

The remaining decrease in the calcium concentration was due to the increased binding to the soil solid phase. Many factors influence this binding. The increase in pH led to a decrease in the binding of aluminium and protons to soil organic matter, resulting an increase in Ca binding. In addition to this, the competition with Fe^{2+} also influences the calcium binding. The decrease in Ca concentration could be rationalised by a simplified calculation based on the electroneutrality of the solution phase, which should be obeyed. The extra decrease in the Ca concentration, in addition to the Ca that was associated with the retained HA or FA was then due to the increase in the concentration of Al, Fe and Cu, which was compensated by a charge equivalent decrease of the Ca in solution.

In this paper, we showed that the BTCs of HA differed from that of FA and as well its response to changes in Ca concentration in the influent solution. In this acid soil, the solubility and mobility of FA was higher than HA at both low and high Ca concentrations. Model calculations showed that a coagulation process was very likely controlling the mobility of HA, while the adsorption mechanism might be important for FA immobilisation. We have also shown that in order to understand better the mobility of DOC in natural porous media it is essential to study changes in speciation in the pore fluid as well as changes in the solid phase speciation.

Chapter 8

Phytotoxicity and Chemical Speciation of Nickel in Soil: the Effects of pH and Soil Characteristics

(Submitted)

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Abstract

In this paper, pot experiments with three different soils, *i.e.* a sandy soil, a sandy soil with a relatively high content of organic matter and iron hydroxides and a clay soil, were conducted to study the phytotoxicity of Ni to oats and the effects of pH and soil characteristics. The EC_{50} of spiked Ni in the decreasing of the mass of the straw were between 0.7 and 22.5 mmol/kg soil, varying by a factor of 32 with the type of soil and pH (pH range 4.7-7.0). The toxicity of Ni in terms of total Ni increased with decreasing pH in all the soils. The results showed that one unit increase in pH by liming could reduce the Ni toxicity by a factor of 2-6. The effects were bigger at near neutral pH than at lower pH. The difference in the toxicity of Ni in the three soils reflected the various extent of Ni bioavailability, and corresponded to the difference in the soil binding capacities for Ni measured in a batch desorption experiment. With the simulation calculations using a multi-surface speciation model, the effects of pH and soil characteristics on the chemical speciation of Ni in the soils were studied. The results showed that soil organic matter binds Ni much stronger than clay and iron hydroxides at a relatively low pH. At close to neutral pH, iron hydroxides became an important sorbing surface. The EC_{50} of Ni in the 0.01M $CaCl_2$ extraction of all the soils was in the range of 24-58 μ M varying by a factor of about 2. Nickel concentration in the extraction with 0.01M $CaCl_2$ was closely related to the plant uptake and to the growth response and was a much better indicator of the bioavailability of Ni than the total Ni concentration in the soils.

Introduction

Soil pollution with heavy metals is a potential threat to the environment. It can be harmful to the plants and other organisms and it can lead to contamination of groundwater and surface water. When a certain content limit of heavy metals is exceeded, remediation measures have to be taken to remove the pollutants or to reduce the risk. Common techniques for soil remediation include excavation, extraction, phytoremediation and immobilization. In situ immobilization is a relatively mild approach and it is physically and economically more feasible than excavation and extraction, especially when dealing with extensive areas (Osté et al., 2001).

Both indigenous and added metals in the soils are distributed over various chemical species in both the solid and solution phases. Not all forms of metals are equally available to plants and organisms and subjected to transport. It has been established that under most circumstances, the activity (or concentration) of the “free” metal ion is the key factor in determining metal bioavailability and toxicity (Parker and Pedler, 1997). The dissolved metal pool reflects the soil metal fraction that could potentially be leached from the soil to groundwater and surface water (Sauvé et al., 2000a). In situ immobilization decreases the metal concentration in solution, and therefore reducing its mobility and toxicity.

Raising the soil pH by adding lime is a well-known practice of in situ immobilization. Soil pH is connected closely to the chemical processes of precipitation, sorption and complexation, and it is the main factor influencing the speciation and availability of heavy metals. Soils and sediments usually contain mixtures of several reactive surfaces, which bind heavy metals. The binding of heavy metals to these surfaces is recognized as being important in controlling the activity of metal ions. Colloidal particles of soil organic matter (SOM), clay silicates and metal hydroxides, which have large surface area and are often electrically charged, are considered important adsorptive surfaces to bind heavy metals. The pH effects on metal binding to these surfaces differ with respect to metals, type of surfaces and metal concentrations. For example, it has been found that one unit increase in pH produced almost a 25-fold decrease of zinc concentration in the solution containing goethite (Barrow et al., 1989), but the effect was much smaller for the solution containing soils (Barrow and Whelan, 1998). The relative importance of the soil sorbents in the control of metal speciation has consequences to the pH effects on metal speciation in a specific soil.

The relative importance of soil surfaces in the binding of heavy metals is often studied using sequential extractions (e.g. Tessier et al., 1979; Tack and Verloo, 1995) and statistical relationships between the sorption and soil properties (e.g. McLaren and Crawford, 1973; King, 1988b; McBride et al., 1997). However, as pointed out by Zachara *et al.* (1992), all these methods have their limitations. The contribution of individual sorbents may be difficult or impossible to experimentally identify (Mattigod and Zachara, 1996). Another approach is to predict the metal speciation in soil using adsorption and ion-exchange models for the various soil constituents (Cowan et al., 1992; Tipping, 1994; Vermeer et al., 1999; Voegelin et al., 2001; Weng et al., 2001a). The advantage of this kind of mechanistic approach is its ability to predict metal partitioning in various soils under different conditions of the bulk solution chemistry. A better understanding of the mechanisms of metal speciation can be very useful for the assessment of the consequences of the changes in environmental conditions such as pH on metal behavior.

Basic data on the phytotoxic concentrations in soils of metals such as zinc, copper, nickel and chromium to common crop plants are lacking (McGrath, 1995). The comparisons of biological effects, speciation measurement and simulation using a multi-surface model are rare. The aim of this research was to link the toxicity, extractable concentration of Ni, and the soil characteristics by comparing the results of the pot experiments, the batch desorption experiment and the model simulations. With the combination of the various techniques, we intend to gain more insight in the bioavailability and toxicity control of Ni in soils and the effects of pH.

Materials and Methods

Experiments

Pot experiments were carried out in two series. In the first series, three different soils were investigated: a sandy soil (SS), a sandy soil with a relatively high content of organic matter and iron hydroxides (OMFe) and a clay soil (CS). In this series, the biomass of the plant and desorption of Ni were measured after the pot experiment, but not the Ni concentration in the plant. In the second series, pot experiments were carried out using the sandy soil (SS). After the pot experiments, the concentrations of Ni in the plant were measured, in addition to the biomass and desorption of Ni. Soil samples were taken from various experimental test fields

in the Netherlands. The field soil samples were air-dried and sieved (<2 mm). The major soil characteristics are listed in Table 1.

Table 1. *Soil characteristics*

Soil	Organic mater (%) (loss on ignition)	Clay (%) (<2 μ m)	Fe-total (%) (<i>aqua</i> <i>regia</i>)	Fe- oxalate (%)	Ni-total (mmol/kg) (<i>aqua</i> <i>regia</i>)	pH- KCl	Field moist capacity (ml/kg)
SS	4	4	0.6	0.2	0.09	4.0	165
OMFe	8	6	13.1	6.6	0.05	4.9	231
CS	4	36	3.3	0.8	0.65	5.4	258

The design of the treatment was an incomplete factorial experiment with 3 replicates (Table 2). Appropriate amount of the dehydrated calcium hydroxide ($\text{Ca}(\text{OH})_2$) was added to change the soil pH. Nickel was spiked by adding the stock solution of $\text{Ni}(\text{NO}_3)_2$ to achieve the nominal Ni content (Table 2). In the first pot experiment, each pot contained 1.6 kg sandy soil (SS), or 1.2 kg soil rich in organic matter and iron hydroxides (OMFe) or 1.5 kg clay soil (CS). In the second pot experiment, each replicate contained 2.5 kg air-dried sandy soil SS. After adding Ni solution, deionized water was added to each soil sample to a total moisture volume of 200 ml or 300 ml in the first and second experiment respectively. The soils were left in plastic bags, stored in the dark at an ambient temperature (first experiment October; second experiment June, the Netherlands) in a greenhouse and incubated for 4 weeks.

After 4 weeks of incubation, the soils were fertilized with 2.2 or 5.8 mmol MgSO_4 /pot and 4.6 or 8.6 mmol KH_2PO_4 /pot in the first or second experiment respectively. In the first experiment, a solution of KNO_3 was added to the soils that received less than 1.70 mmol $\text{Ni}(\text{NO}_3)_2$ /kg soil to a total N level of 5.4 mmol N/pot. In the second experiment, a solution of $\text{Ca}(\text{NO}_3)_2$ was added to balance the nitrogen concentration to the same level of 6.81 mmol $\text{Ni}(\text{NO}_3)_2$ /kg soil, namely 34 mmol N/pot. In the first experiment, nitrogen was fertilized for the second time in the form of $\text{Ca}(\text{NO}_3)_2$ five weeks after sowing at a dosage of 40 mmol N/pot to the soils that received less than 13.63 mmol $\text{Ni}(\text{NO}_3)_2$ /kg soil. It was assumed that at a large Ni dosage, the Ni toxicity is so severe that the difference in N content in the soil

will not have much effect on the growth. Deionized water was added to all the soil samples to its field capacity (Table 1). The soil was then transferred into PVC pots.

Table 2. Treatments of the pot experiment

Soil	Normal pH	Ni-spiked (mmol/kg soil)						
		0	0.10	0.21	0.43	0.85	1.70	3.41
SS (second experiment)	4	0	0.10	0.21	0.43	0.85	1.70	3.41
	5	0	0.21	0.43	0.85	1.70	3.41	6.81
	6	0	0.43	0.85	1.70	3.41	6.81	13.63
	7	0	0.85	1.70	3.41	6.81	13.63	27.26
SS (first experiment)	4.5	0	0.10	0.21	0.43	0.85	1.70	3.41
	5.5	0	0.21	0.43	0.85	1.70	3.41	6.81
	6.5	0	0.85	1.70	3.41	6.81	13.63	27.26
OMFe	4.9	0	0.43	0.85	1.70	3.41	6.81	13.63
	5.9	0	1.70	3.41	6.81	13.63	27.26	54.51
	6.9	0	1.70	3.41	6.81	13.63	27.26	54.51
CS	5.4	0	0.21	0.43	0.85	1.70	3.41	6.81
	6.2	0	0.53	1.06	2.13	4.26	8.52	17.04
	7.0	0	1.70	3.41	6.81	13.63	27.26	54.51

In the second experiment, 170 gram of clean fine quartz sand was spread on the top of the soil in each pot to make a germination layer. No such sand layer was made in the first experiment. Oats (*Avena sativa* L.) were used as the test plant, and 18-20 seeds were sown to each pot. The pots were covered with a plastic sheet until the seeds germinated. After germination, seedlings were thinned to 10 and 11 per pot in the first and second experiment respectively. The plants were grown in a greenhouse and water content at field capacity was maintained by weighing the pots and adding deionized water every day.

The first experiment lasted for 6.5 weeks (November-December) and the second for 6.0 weeks (July-August) until harvesting. The plants were cut directly above the soil surface, rinsed with water and dried at 70-75°C. The dry weight was measured. From the second experiment, a sub-sample of the plant material was digested according to a procedure described by Novozamsky et al. (1996), and the concentration of Ni was measured with ICP-

OES (Spectros, Spectro Flame). The data of the Ni concentration in the plant will be discussed in a following paper.

From each pot a soil sample consisting of 4-5 cores using a small gouge auger was taken. The soil samples were dried in the air or at 40°C in the first and second experiment respectively, and sieved (2 mm). Desorption of Ni was measured by mixing 3 gram of soil with 30 ml 0.01M CaCl₂ and shaking end-over-end at 20°C for 22 hours. pH of the suspensions was measured with a pH meter (PHM92 LAB). The suspensions were centrifuged at 3000 rpm for 15 minutes. Concentration of Ni in the solution was measured with flame AAS. Concentration of dissolved organic carbon (DOC) was measured with a fully automated TOC/DOC analyzer (SK12, Skalar, Netherlands).

Ecotoxicological statistics

We used the logistic model without hormesis effect (positive biological effect at low concentration) (Hoekstra, 1993) to describe the exposure response of oats to Ni:

$$E(\%) = \frac{1}{1 + (c/EC_{50})^n}, \quad (1)$$

in which E(%) is the ratio of the response of the biota at the chemical concentration (c) to the response when c=0. EC₅₀ and n are model parameters. EC₅₀ indicates the chemical concentration that reduces the average response to 50% of its value under control circumstances. The model parameters EC₅₀ and n were estimated for the total Ni spiked in soil, Ni concentration in the 0.01M CaCl₂ soil extraction and Ni concentration in the straw of oats respectively by curve fitting.

Speciation modeling

The pot experiments were done for the three soils at different Ni dosage and pH, therefore the comparison of their binding capacity for Ni based on the desorption data was not straightforward. For this reason, the two-species Freundlich model was employed to describe Ni binding to the soils. The Freundlich equations were derived by carrying out regression using the desorption data. In this regression, the indigenous Ni was neglected, because the amount of indigenous Ni in the SS and OMFe soil was small compared to those added. The clay soil contained more indigenous Ni than in the other two soils, however only

less than 0.3% of it was extractable with 0.01 M CaCl_2 , and probably most of it existed in the minerals. With the Freundlich equations derived, the binding capacity for Ni of the three soils could be compared for the same conditions (pH and Ni dosage).

Although the empirical Freundlich equation allowed us to compare the binding capacity of the soils, it could not explain the mechanisms that led to various binding capacity in the soils. Therefore we applied a multi-surface model to predict Ni speciation in soil, to estimate the role of soil binding surfaces in the control of Ni speciation and the pH effects. This multi-surface model was recently proposed by Weng *et al.* (2001a), which employs advanced sorption and cation exchange models and default binding parameters. This model has been used to predict the free ion activity of Cu^{2+} , Cd^{2+} , Zn^{2+} and Ni^{2+} in the sandy soil SS, over the pH range of 3.7-6.1 with reasonable success (Weng *et al.*, 2001a).

The model considers soil as a set of independent sorption surfaces (Weng *et al.*, 2001a). Metal binding to the soil organic matter, to clay and to the amorphous and crystalline iron hydroxides are calculated using the NICA-Donnan model (Kinniburgh *et al.*, 1999), Donnan model, two site surface complexation diffuse double layer model (Dzombak and Morel, 1990) and the Charge Distribution Multi-Site Complexation (CD-MUSIC) model (Hiemstra and Van Riemsdijk, 1996; 1999) respectively. Detailed description of the multi-surface model can be found in Weng *et al.* (2001a).

In this paper, we assumed that the total amount of Ni spiked was reactive in the adsorption to the soil surfaces, while in the paper of Weng *et al.* (2001a) the 2 M HNO_3 extractable metal was assumed as the reactive fraction. Humic acid was used as an analogue for the soil organic matter (SOM), and the average site density of SOM was estimated as 31% of that of the generic humic acid (Weng *et al.*, 2001a). Illite was taken as a representative of clay silicate, because it is an important aluminum silicate mineral in most soils of the Netherlands (Kuipers, 1984). The average charge of clay was assumed to be 0.25 mol/kg (Weng *et al.*, 2001a) and it was independent of pH. The amount of amorphous iron hydroxides was estimated as the oxalate extractable Fe. The surface area of amorphous iron hydroxides was assumed to be the same as that of HFO, *i.e.* 600 m^2/g (Dzombak and Morel, 1990). The amount of crystalline iron hydroxides was estimated as the difference between the total (*aqua regia*) and the oxalate extractable Fe. Due to the lack of the CD-MUSIC parameters

for Ni binding to goethite, Ni binding to crystalline iron hydroxides was estimated in the same way as for the amorphous iron hydroxides but with a lower surface area of $100 \text{ m}^2/\text{g}$.

Nickel speciation in the soils was estimated with this multi-surface model by assuming that the adsorption of Ni to the soil solid surfaces was controlling its ion activity. The dissolved concentration of Ni was controlled by the ion activity and the complexation with carbonate and dissolved organic matter (DOM). The complexation with DOM was calculated using the NICA-Donnan model by assuming that 30% of DOM was humic acid and 30% of DOM was fulvic acid and the rest of DOM was inert. The calculation was carried out for the situation of 0.01 M CaCl_2 extraction. The competition of Ca and Al for the binding was considered, and the activity of Al^{3+} was assumed to be controlled by gibbsite. The model parameters used in this calculation can be found in the Supporting Information of Weng *et al.* (2001a). The calculation was done with the computer program ECOSAT (Keizer and Van Riemsdijk, 1994).

Results and discussions

Toxicity of Ni in soil

Nickel is a ubiquitous element and has been detected in soil, water and air as both a natural component and a pollutant introduced by human activities. Nickel concentration in soil is mostly in the range of $10\text{-}1000 \text{ mg/kg}$ (Leeper, 1978). Terrestrial plants take up Ni from soil mainly by their roots. The necessity of Ni as a plant nutrient in soybeans, chickpeas and temperate cereals has been illustrated (Eskew *et al.*, 1984; Brown *et al.*, 1987). However, high burden of Ni in the living medium of organisms may cause deleterious effects.

In the pot experiments, symptoms of Ni toxicity started appearing a few days after germination and increased in severity with time and Ni concentration. Most or all the plants at the highest Ni concentration in each pH series died before harvest. The typical Ni toxicity symptom of oats, white necrosis longitudinal stripes between the veins, was observed at high Ni dosages. For instance, in the second experiment with the sandy soil, this symptom appeared on the leaves of the treatments with Ni concentration higher than 0.43 , 0.85 , 1.7 and 3.41 mmol/kg soil at the nominal pH of 4, 5, 6 and 7 respectively. Chlorosis occurred at pH above 6 and became more serious with increasing concentration of Ni. Brown colored

diffuse necrosis was observed at high Ni concentration. The chlorosis and diffuse necrosis on the leaves at high pH and Ni levels tended to obscure the symptom of white stripes on the leaves. The growth of oats was depressed by Ni, which resulted in less tillers and shorter and weaker straws. According to Crooke (1954), necrosis was a specific Ni effect, whereas the chlorosis was due to iron deficiency. Antagonism between Fe and Ni in the plant might be responsible for the chlorosis in oats.

Table 3. Toxicity of Ni in the terms of total spiked and 0.01 M CaCl₂ extracted (in the brackets are standard errors)

	Nominal pH	Average pH-CaCl ₂	Dry weight of the control (g/pot)	Ecotoxicological parameters					
				Total Ni spiked			Ni in 0.01M CaCl ₂		
				EC ₅₀ (mmolNi/kg soil)	n	R ²	EC ₅₀ (μM)	n	R ²
SS2	4	4.7	18.3 (1.1)	0.72 (0.03)	4.0	0.997	24 (1)	2.6	0.997
	5	5.2	18.4 (0.6)	1.32 (0.02)	5.8	1.000	29 (1)	3.3	1.000
	6	6.0	19.3 (0.8)	4.10 (0.46)	6.3	0.978	31 (6)	2.8	0.980
	7	6.8	17.8 (1.5)	9.95 (0.58)	8.5	0.997	25 (3)	4.5	0.997
SS1	4.5	4.8	7.7 (0.7)	0.80 (0.05)	4.5	0.942	25 (3)	3.0	0.937
	5.5	5.6	6.8 (0.6)	2.33 (0.19)	5.2	0.953	38 (5)	3.2	0.938
	6.5	6.2	6.9 (1.1)	4.94 (0.53)	7.9	0.962	40 (9)	3.8	0.962
OMFe	4.9	5.0	8.7 (1.4)	4.22 (0.27)	4.5	0.954	58 (7)	2.3	0.955
	5.9	5.6	8.5 (1.1)	5.64 (0.43)	4.7	0.960	47 (2)	6.2	0.979
	6.9	6.2	7.6 (2.7)	10.8 (1.24)	3.2	0.907	55 (8)	2.3	0.908
CS	5.4	5.7	4.9 (0.6)	3.37 (1.35)	19.2	0.838	47 (6)	5.1	0.834
	6.2	6.4	6.8 (0.8)	6.03 (0.56)	4.8	0.916	35 (6)	2.4	0.917
	7.0	7.0	5.8 (1.1)	22.5 (3.68)	6.8	0.868	34 (16)	5.6	0.870

The biomass yield was much larger in the second experiment than in the first (see Table 3), probably due to the presence of more soil and fertilizers and higher temperature and more daylight in the second experiment. If we compare the yield of different soils in the first experiment for the controls (no Ni spiked), it follows that the plant grew better in both sandy soils (SS and OMFe) than in the clay soil (CS) (F-test, $p=0.004$). The pH didn't show a

significant effect on the biomass production for each soil when no Ni was added (F-test, SS1 $p=0.366$, OMFe $p=0.751$, CS $p=0.257$, SS2 $p=0.378$).

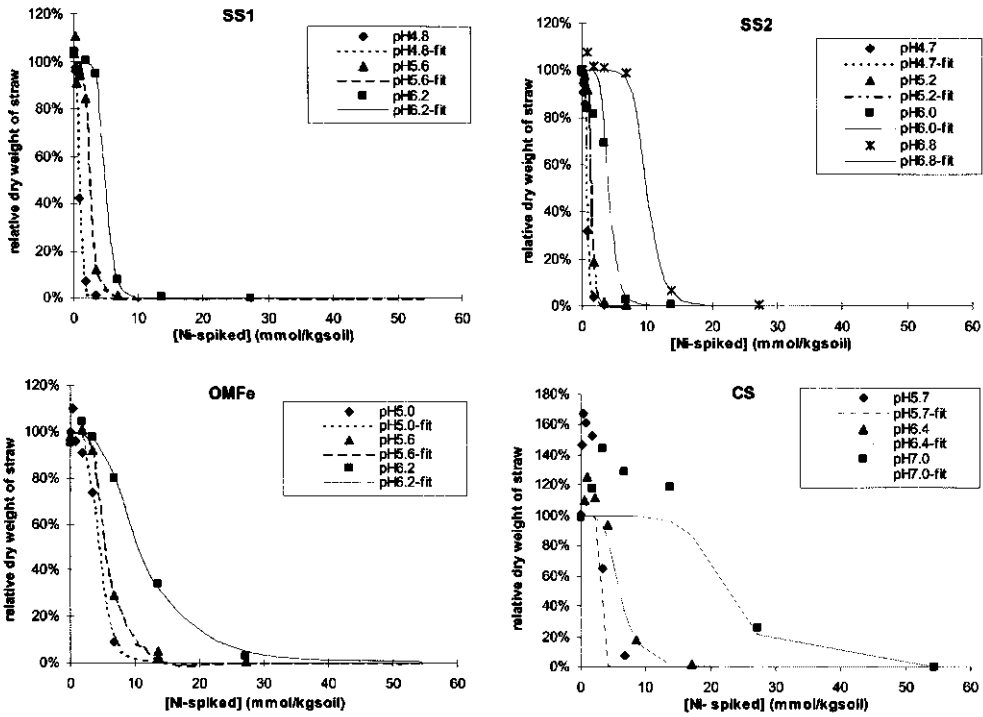


Figure 1. *Relative dry weight of the oats straw as a function of the amount of Ni added to the soils (points are the measurements, lines are the fitted curve to the ecotoxicological model)*

As can be seen from Figure 1, Ni in the soil depressed the dry matter yield of oats significantly at sufficient high Ni dosages in the two pot experiments with three different soils. There was no obvious hormesis effect of Ni in the two sandy soils, but the hormesis effect was observed in the clay soil. In all three soils, the toxicity of Ni decreased with increasing pH. The data was fitted to the toxicity model and the estimated model parameters of total Ni spiked to the soil are listed in Table 3. The model could explain the data reasonably ($R^2>0.84$), but the fit was less good for the clay soil because of the hormesis effect that was neglected in the model.

The EC_{50} of total Ni in the three soils varied between 0.7-22.5 mmol/kg depending on type of the soil and the pH (Table 3, Figure 2). For the sandy soil SS, the EC_{50} of Ni spiked varied from 0.72 to 9.95 mmol/kg for the pH range of 4.7 to 6.8 (pH measured in 0.01 M $CaCl_2$, see Table 3). There was no significant difference between the results in the two experiments for the same soil SS (Figure 2), even though the biomass production was larger in the second experiment. For the other sandy soil OMFe, the EC_{50} of Ni spiked ranged from 4.22 to 10.8 mmol Ni/kg for pH 5.0-6.2. The EC_{50} in the OMFe soil were much larger than in the sandy soil SS and the clay soil CS, indicating a lower bioavailability and toxicity of Ni in the OMFe soil. For the clay soil, the EC_{50} varied from 3.37 to 22.5 mmol/kg for pH 5.7-7.0. At pH below 6.4, the EC_{50} of Ni spiked in the clay soil was comparable to that in the sandy soil SS. But the EC_{50} in the clay soil at pH 7 was very large (22.5 mmol/kg) (Figure 2). For the three soils, each unit increase in pH led to an increase in the EC_{50} of total Ni by a factor of 2-6. The pH effects were generally larger at high pH than at low pH.

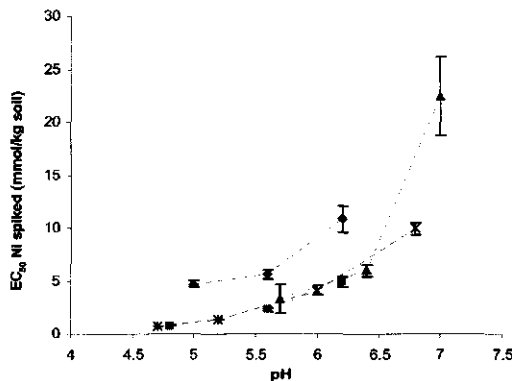


Figure 2. EC_{50} of Ni spiked in the soils in the reduction of the dry weight of oats straw (■SS1, ◆OMFe, ▲CS, *SS2)

Desorption of Ni

A batch experiment of Ni desorption using 0.01 M $CaCl_2$ extraction was conducted to study the distribution of Ni in these soils. It was observed that within one nominal pH series, the pH in the 0.01M $CaCl_2$ soil solution decreased with the increase of Ni concentrations due to the competitive adsorption of Ni with protons (data not shown). The DOC concentration in the 0.01M $CaCl_2$ solution of these soil samples was in the range of 10-25 mg/l. The partitioning ratio of Ni between the solid and solution phase depended on the pH and type of

the soil. In these samples, 0.7%-52% of the spiked Ni was recovered in the 0.01 M CaCl₂ extraction. From the desorption data, the two-species Freundlich models were derived:

$$\log[\text{Ni-soil}]=-2.96+0.67\log[\text{Ni-CaCl}_2]+0.73\text{pH}, (R^2=0.98) \text{ (SS1)}$$

$$\log[\text{Ni-soil}]=-1.89+0.77\log[\text{Ni-CaCl}_2]+0.60\text{pH}, (R^2=0.99) \text{ (SS2)}$$

$$\log[\text{Ni-soil}]=-0.88+0.61\log[\text{Ni-CaCl}_2]+0.43\text{pH}, (R^2=0.99) \text{ (OMFe)}$$

$$\log[\text{Ni-soil}]=-2.73+0.78\log[\text{Ni-CaCl}_2]+0.73\text{pH}, (R^2=0.99) \text{ (CS)}$$

in which [Ni-soil] is in mmol/kg and [Ni-CaCl₂] in mM. As indicated by the regression coefficient (R^2), the empirical Freundlich model could describe the Ni binding in the individual soils very well. With these equations, we could calculate and compare the ability of the three soils in retaining Ni for the same pH and Ni concentration.

In Figure 3, the sorption isotherms are shown for the three soils in the first experiment at pH 4.0 and 7.0. The isotherms showed that the binding capacity for Ni was similar for the sandy soil SS and the clay soil. The large amount of clay in the clay soil didn't significantly increase its ability to bind Ni. However, the sandy soil rich in organic matter and iron hydroxides OMFe showed a stronger binding capacity for Ni than the two other soils at the relatively low pH (pH 4.0). The difference became much smaller and even disappeared at the neutral pH (pH 7.0). According to the Freundlich equations, at the same Ni-CaCl₂ concentration, a unit increase in pH led to 5.4 times more Ni retained in the SS (first experiment) and CS soils and 2.7 times more in the OMFe soil. This is in agreement with the data obtained by Barrow & Whelan (1998) who found that adsorption of Ni to a loamy sandy soil increased by 3-5 fold with one unit increase in pH.

It was noted that the concentration of Ni-CaCl₂ was slightly larger in the sandy soil SS from the first experiment than in the second under the same conditions (data not shown). This could be due to the difference in the way that the soil samples were prepared before the desorption analysis. In the first experiment, the soil sample was dried in air, whereas in the second experiment the sample was dried at 40 °C.

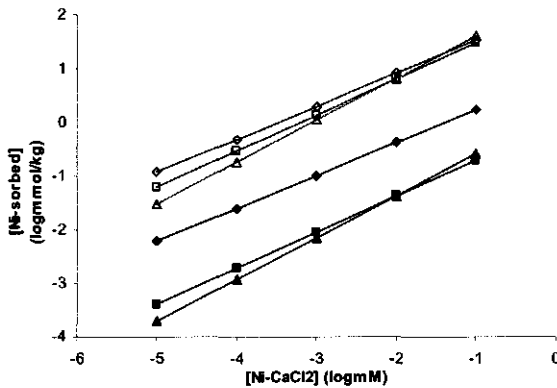


Figure 3. Sorption isotherms of Ni at pH 4 and 7 in the three soils calculated using the Freundlich equations derived from the data of Ni desorption by 0.01M CaCl₂ (■ SS1 pH4, ◆ OMFe pH4, ▲ CS pH4, □ SS2 pH7, △ OMFe pH7, ◇ CS pH7)

The results of desorption experiment corresponded well with the Ni toxicity observed in the pot experiments. The similar EC₅₀ of Ni in the sandy soil SS and the clay soil (Figure 2) is in good agreement with their similar binding capacity (Figure 3). The EC₅₀ of Ni in the OMFe soil is larger than in the two other soils, which could be explained by the stronger binding capacity of this soil as the desorption experiment demonstrated. Although the empirical Freundlich model can help us to link the soil binding capacity to the Ni toxicity in the soil, it provides little insight into the mechanisms of Ni binding and the role of the soil characteristics in Ni speciation. The questions such as why the high clay content in the clay soil did not lead to less extractable Ni, which one might expect from the metal binding potential of clay, cannot be answered, neither the observation of Barrow and Whelan (Barrow and Whelan, 1998) that the pH dependency of metal retention was smaller in soil than could be explained from binding to goethite. For these purposes, the speciation calculation using mechanistic models can lead to a better understanding, as we will show below.

Modeling Ni Speciation

In Figure 4, the concentrations of Ni in the 0.01M CaCl₂ extraction predicted using the multi-surface model were compared to those measured. The predicted concentrations were generally somewhat higher than the measurements.

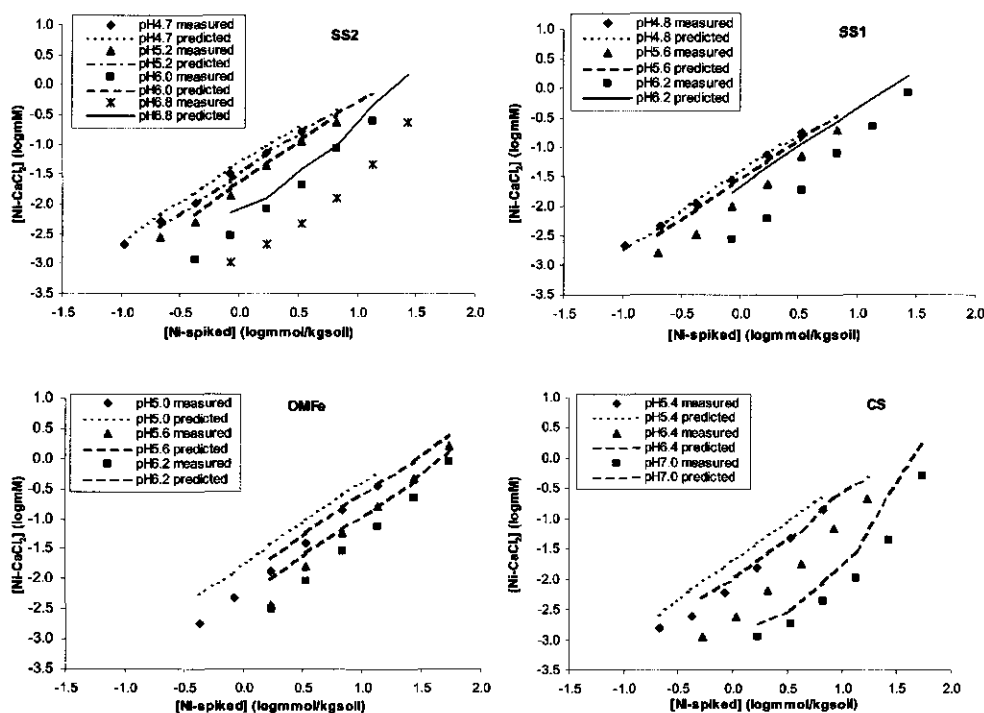


Figure 4. Comparison of Ni concentration in 0.01 M CaCl₂ measured and predicted using the multi surface model (points are the measurements, lines are the predictions)

For the sandy soil SS in the first experiment, the concentration was perfectly predicted for the series of pH 4.8. The predictions were 0.3 and 0.6 log-unit higher than the measurements for the series of pH 5.6 and pH 6.2. For this soil in the second experiment, the predicted concentration was on the average 0.1, 0.2, 0.7 and 0.9 log-unit higher than the measurements for the pH series of 4.7, 5.2, 6.0 and 6.8 respectively. For this soil, the model gave good predictions for relatively low pH, but underestimated Ni retention in the soil at high pH.

Compared to the sandy soil SS, the OMFe soil contained about 2 times more soil organic matter, 1.5 times more clay and 30 times more iron hydroxides. The predicted concentrations of Ni-CaCl₂ in this soil were on the average 0.4 log unit higher than the measurements at all the three pH series (pH5.0, 5.6 and 6.2). The clay soil contained about the same amount of organic matter as in the sandy soil SS, but 9 times more clay and 4 times more iron

hydroxides. The predicted Ni-CaCl₂ concentrations in the clay soil were on the average 0.3, 0.6 and 0.4 log unit higher than the measurements at pH of 5.7, 6.4 and 7.0 respectively.

Table 4. Predicted contribution of soil sorbents to the binding of Ni using the multi-surface model (part of the samples)

Soil	Ni spiked mmol/kg soil	Contribution to total Ni bound		
		soil organic matter	clay	iron hydroxides
SS2 pH4.7	0.10	97.5%	2.4%	0.0%
	0.43	95.6%	4.3%	0.1%
	1.70	89.8%	10.1%	0.1%
SS2 pH6.8	0.85	54.3%	0.7%	45.0%
	3.41	39.4%	1.0%	59.6%
	13.63	51.1%	3.8%	45.1%
OMFe pH5.0	0.43	95.8%	1.8%	2.4%
	1.70	92.8%	3.6%	3.6%
	6.81	88.9%	6.9%	4.2%
OMFe pH6.2	1.70	54.0%	0.7%	45.3%
	6.81	45.5%	1.3%	53.2%
	27.26	34.9%	2.1%	63.0%
CS pH5.7	0.21	86.2%	9.7%	4.1%
	0.85	76.2%	16.6%	7.1%
	3.41	64.4%	30.0%	5.6%
CS pH7.0	1.70	12.0%	0.8%	87.2%
	6.81	7.8%	0.9%	91.3%
	27.26	14.1%	7.2%	78.7%

The underestimation of Ni retention in the sandy soil SS by the multi-surface model at close to neutral pH has been noticed in the earlier work using the multi-surface model (Weng et al., 2001a). The authors hypothesized that the formation of Ni-Al layered double hydroxide (LDH) (Roberts et al., 1999) might be the reason for the discrepancy at close to neutral pH. However, as will be shown below, the calculations predict a relatively large importance of binding to iron hydroxides at high pH. Since no Ni binding parameters for goethite are available in the CD-MUSIC model and since little is known about the effects of the adsorbed

organic matter on the oxides on the metal binding, the discrepancy may also be caused by an underestimation of the binding to metal hydroxides.

In Table 4, the model estimation of the contribution of the soil surfaces, e.g. soil organic matter, clay and iron hydroxides, to the binding of Ni are given for the lowest and highest pH series for each soil. The results showed that in the three soils, the soil organic matter was the controlling phase of Ni speciation for the conditions of 0.01M CaCl_2 experiment at relatively low pH ($\text{pH} < 6$), even in the clay soil. In this pH range, the content of organic matter in the soil would be the key factor in determining Ni speciation and toxicity. The relatively weak binding capacity of clay for Ni compared to soil organic matter made it a less important surface for Ni speciation. This can explain the results that the EC_{50} of Ni in the OMFe soil was generally larger than that in the sandy soil SS and the clay soil (Figure 2). At $\text{pH} > 6$, both soil organic matter and the iron hydroxides are predicted to be important. The model showed that at pH 7 most of the Ni is bound to the iron hydroxides in the clay soil. According to the model, Ni binding to the iron hydroxides has a stronger pH dependency than soil organic matter. One unit increase in pH leads to more than 20 times more binding on the iron hydroxides, but less than 2 times on organic matter. The binding capacity of the iron hydroxides is larger than that of the soil organic matter at close to neutral pH.

Toxicity and Bioavailability of Ni in Relation to Ni Concentration in 0.01M CaCl_2 Extraction

In Figure 5, the biomass of the oats straw is shown as a function of the Ni concentration in 0.01 M CaCl_2 extraction. In the three soils, the plant biomass decreased dramatically with the increase of the extractable Ni concentration. At a concentration close to 300 μM Ni- CaCl_2 , there was almost no growth of the plant. The fitted EC_{50} (Table 3) of extractable Ni in the three soils was in the range of 24-58 μM and varied by only a factor 2. No obvious trend of pH dependency was found for the EC_{50} of Ni extracted by 0.01M CaCl_2 . It was only noted that the EC_{50} was generally slightly larger in the OMFe soil than in the two other soils.

After the second pot experiment, the Ni concentration in the oats straw was analyzed. In Figure 6, the concentration of Ni in the straw is plotted against the concentration of Ni extracted by 0.01 M CaCl_2 . The Ni uptake in the plant could be explained reasonably using the two-species Freundlich equation:

$$\log[\text{Ni-straw}] = 2.23 + 0.98 \log[\text{Ni-CaCl}_2] - 0.04 \text{pH}, (R^2 = 0.94)$$

in which $[\text{Ni-straw}]$ is in mmol/kg and $[\text{Ni-CaCl}_2]$ is in mM. As can be seen from Figure 6 and this equation, the tissue content of Ni was closely related to the Ni concentration measured in the 0.01 M CaCl_2 extraction. No obvious pH dependency was observed.

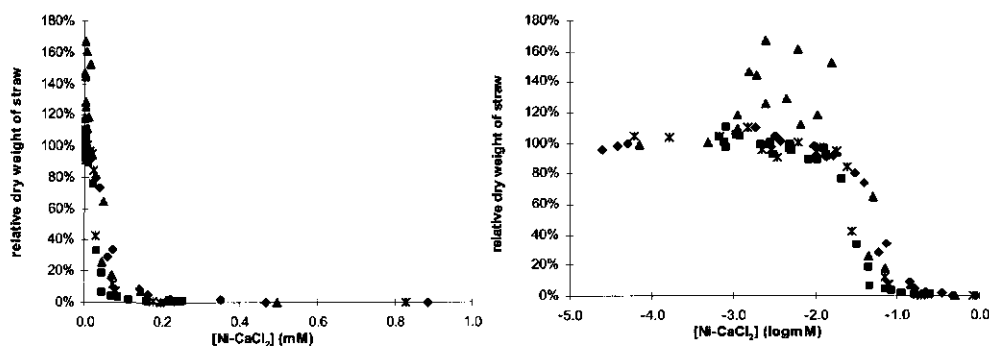


Figure 5. Relative dry weight of oats straw as a function of Ni concentration measured in 0.01 M CaCl_2 soil extraction (■ SS1, ◆ OMFe, ▲ CS, * SS2)

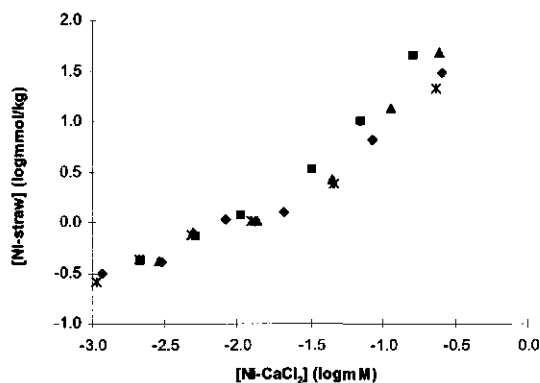


Figure 6. Concentration of Ni in the straw of oats grown in the sandy soil SS in the second pot experiment as a function of Ni concentration measured in 0.01 M CaCl_2 soil extraction (■ pH 4.7, ▲ pH 5.4, ◆ pH 6.2, * pH 6.8)

As early as the 1970s, a close correlation was found between the concentrations of Al and Mn in 0.01 M CaCl_2 extracts of acidic soils and toxicity to plants (Hoyt and Nyborg, 1971a; 1971b). Later this method was used to study the bioavailability of heavy metals (Zn, Cu, Ni), which had accumulated in soils as a result of human activities (Houba et al., 1996; 1990;

Novozamsky et al., 1993). The metal concentration that is achieved after the soil is suspended with CaCl_2 is controlled by desorption (including ion exchange) and/or solubility of mineral phases. Because the electrolyte concentration stays practically constant, the metal concentration reflects the differences in binding strength or solubility between different soils (Houba et al., 1996). The results found in this research supported the suggestion of Houba *et al.* (Houba et al., 1996; 1990) that extraction with 0.01 M CaCl_2 could be a simple way to determine metal bioavailability and toxicity.

Conclusions

It was found that Ni at high concentrations was toxic to oats grown in soil, causing toxicity symptoms and reduction of growth. The EC_{50} of total Ni spiked in soil varied widely in the range of 0.7-22.5 mmol/kg, depending on soil type and pH. At the same pH, the Ni toxicity was the lowest in the OMFe soil, which was characterized by the highest content of organic matter and iron hydroxides among the three soils. The toxicity of Ni at pH below 6.5 was quite similar for the other two soils, the sandy soil and the clay soil, which contained the same amount of soil organic matter. The pH affected Ni toxicity significantly in the pot experiment, and in all soils Ni toxicity decreased with increasing pH. One unit increase in pH led to an increase in the EC_{50} of spiked Ni by a factor of 2-6.

The two-species Freundlich model could well describe Ni binding in the soils and the effects of pH. These empirical equations showed that the OMFe soil had a stronger Ni binding capacity than the SS and CS soils. The clay soil showed similar Ni binding capacity to that of the sandy soil. One unit increase in pH led to 3-5 times more Ni binding in the soils. The desorption results of Ni using 0.01 M CaCl_2 corresponded with the observations of the different Ni toxicity in the three soils in the pot experiments.

With the predictions using the multi-surface model, we found that soil organic matter binds Ni more strongly than clay in 0.01M CaCl_2 (more than 10 fold). The calculated Ni binding to iron hydroxides at relatively low pH is not important. But the pH dependency of Ni binding to iron hydroxides is stronger than that of soil organic matter. At a pH close to neutral, the binding capacity of iron hydroxides surpasses that of soil organic matter and becomes a very important binding surface. The discrepancy of the model prediction and measured

concentration of Ni in 0.01 M CaCl_2 at close to neutral pH could be due to the formation of precipitates or due to present inaccuracies in the oxide binding models.

The EC_{50} values of the extractable Ni in 0.01 M CaCl_2 was in the range of 24-58 μM . The Ni uptake by the plant, represented by the Ni content in the straw, was closely related to the Ni concentration in the 0.01 M CaCl_2 extraction, highlighting the possibility to use this extraction as an indicator of the bioavailability and toxicity of Ni in soils.

Chapter 9

Comparison of pH effects on phytotoxicity and plant uptake of Nickel from solution culture and soil solution

(Submitted)

Co-authors: Theo M. Lexmond, Anke Wolthoorn, Erwin J. M. Temminghoff, Willem H. Van Riemsdijk

Abstract

The effects of pH on the bioavailability and toxicity of Ni to oats were studied with a solution culture experiment, and the results were compared with those from the previous soil pot experiments. With the increase in pH, the toxicity of Ni was intensified in the solution culture, but was alleviated in the soils in terms of the total Ni concentration. The EC_{50} of Ni in the nutrient solution decreased from 23 to 1.7 μM at pH 4-7, varying by a factor of 14. However, no such pH dependency has been found for the EC_{50} of Ni in the 0.01M CaCl_2 soil extractions, which was in the range of 58-24 μM . Using a Donnan membrane technique, the speciation of Ni in the 0.01 M CaCl_2 extraction of the soil samples taken from the pot experiments was analyzed. Similar to the solution culture, the EC_{50} of free Ni^{2+} in the 0.01 M CaCl_2 soil solution (44-10 μM) decreased with increasing pH, but they were generally higher than the EC_{50} of Ni^{2+} in the solution culture. The EC_{50} of Ni in the oats straw from the solution culture were between 1.2 and 2.8 mmol/kg, similar to the EC_{50} of Ni in the oats grown in a sandy soil (1.6-2.5 mmol/kg), indicating that the metal concentration in the biota is a better indicator for metal toxicity than the total metal concentration in the media. The effects of pH on Ni uptake from the sandy soil could be predicted reasonably well with the quantitative approach using the results of Ni binding to the soil and Ni uptake from the nutrient solution. The model approach shows that the pH effects on Ni binding to the soil exceed the pH effects on the Ni uptake, therefore a decrease of Ni uptake and toxicity in soil is predicted with increasing pH.

Introduction

Due to the harmful impacts of a high metal burden on organisms, it is crucial to interpret the relationship between exposure levels and biological effects in order to develop environmental protection criteria for heavy metals. In the ecotoxicology tests, the effects of heavy metals on biota are usually related to the total metal concentration. However, it has been found that the relationship between the total metal concentration and the effects on biota is not straightforward, but depends on factors such as the nature of the media, pH and ionic strength. pH affects metal toxicity profoundly, and the effects of pH on metal toxicity depend on the type of media in which the biota is present while being exposed to the metal. It is common to find that the toxicity of metal for plants growing in soils decreases with increasing pH (Lexmond, 1980; Smith, 1994; Wallace et al., 1977). In contrast, when the plants were grown in solution, the increase of pH often intensified the biological effects of the metals (Crooke et al., 1954; Lexmond and Vorm, 1981; Hatch et al., 1988).

Speciation and bioavailability are the key issues in the risk assessment of heavy metals to biota in the environment. Compared to the total metal concentration, the free-ion-activity model (FIAM) (Campbell, 1995; Morel, 1983) provides a better basis for predicting the availability and toxicity of metals. According to the FIAM model, the free-metal-ion activity is the parameter that determines the physiological effects. Several authors have stressed the fact that other solution parameters apart from the metal activity will affect the availability, such as pH and Ca concentration (Campbell, 1995; Meyer et al., 1999; Plette et al., 1999; Schamphelaere and Janssen, 2002). Metal interactions with organisms can be understood by considering an organism as an assemblage of reactive ligands (Morel, 1983).

Nederlof & Van Riemsdijk (Nederlof and Van Riemsdijk, 1995) and Plette *et al.* (Plette et al., 1999) proposed a quantitative model to calculate the bioavailability of heavy metals in terrestrial and aquatic systems. They assumed that uptake or sorption of metal ions by biota present in a complex system like soil can be regarded as the result of competition for binding of that metal ion by all reactive components, including the biota. They chose the relatively simple extended Freundlich equation to describe ion binding to various components to illustrate the principle. The main assumption is that all interactions with the metal are mediated via the activity of the free metal ion in solution. The pH can influence the uptake of metals in at least two ways: by affecting metal speciation directly and by affecting metal binding or uptake by the biological surface. A biotic surface, for instance a plant root, may

have a pH dependency in terms of binding that is in the same direction as for the soil surfaces (increased binding at increased pH), but differs in the magnitude of the effect. This will imply that the metal ion distribution is shifting at increasing pH towards the biotic system or the soil surface, depending on the relative magnitude of the effects on the biota and soil, which may result in a higher or lower toxicity of the metal ion. The authors suggested that the concept of the quantitative model might be a valuable tool in predicting quantitatively the metal ion uptake or sorption by the biota present in a complex system and to predict the relative change in availability due to environmental changes. However, the approach has so far only been tested for sorption to biotic surfaces and not by comparing it with uptake data. The bioavailability of metals can only be understood when the interactions of the metal ion in the soil-solution interface and in the biota-solution interface are both taken into account.

In our previous work on pH effects on Ni phytotoxicity to oats, we conducted pot experiments with three different soils, a sandy soil (SS), a sandy soil containing more organic matter and iron hydroxides (OMFe), and a clay soil (CS) (Weng et al., submitted). We found that an increase in pH decreased the uptake and toxicity of Ni in the soils. In a batch experiment of Ni adsorption/desorption using 0.01 M CaCl_2 solution following the pot experiments, it was found that the increase of pH led to stronger binding of Ni to the soils. The pH effects on both the sorption to soil and the uptake and toxicity to plants in the pot experiments were of approximately the same order of magnitude. Based on the total Ni concentration measured in the 0.01 M CaCl_2 extraction, no significant pH effects on Ni uptake and toxicity were observed. It was not known why there were no such effects: either it was a result of a lack of pH dependency of Ni uptake by the plant, or due to the counterbalance of pH effects on Ni uptake and speciation in the solution.

In this paper we describe experiments conducted in a solution culture with oats to study if pH affects Ni uptake by the plant and the direction and magnitude of the effects. The results of the solution culture experiment are compared to those of the soil pot experiments (Weng et al., submitted). We used a Donnan membrane technique to analyze the speciation of Ni in the soil solution of 0.01 M CaCl_2 , to find out the pH effects on Ni speciation in the soil solution (Temminghoff et al., 2000; Weng et al., 2001b). Using the experimental results, the ability of the quantitative model for the prediction of Ni uptake by the plant in the soil-

solution system is tested. The model approach will also be used to try to explain the opposing pH effects on Ni phytotoxicity in the nutrient solution and in the soils.

Materials and methods

Solution culture experiment

To eliminate the influence of the soil, we conducted a solution culture experiment to investigate the effects of pH on the uptake and toxicity of Ni to oats, and to establish a quantitative macroscopic model of Ni uptake. The stock solutions of nutrients were prepared from analytical pure reagents. The final concentrations of the nutrients in the solution culture are listed in Table 1. Nickel was added to the nutrient solution from the stock solution of NiSO_4 to achieve the nominal Ni concentrations (Table 2). pH was maintained by continuous titration with 0.1 M NaOH and 0.05 M H_2SO_4 .

Table 1. Concentration of nutrients in the solution culture

Nutrients	Final concentration	Nutrients	Final concentration
$\text{Ca}(\text{NO}_3)_2$	1.32 mM	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	1.82 μM
KNO_3	1.34 mM	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.06 μM
MgSO_4	0.54 mM	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.15 μM
KH_2PO_4	56 μM	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	0.02 μM
H_3BO_3	9.0 μM	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}^*$	1.8 μM

* $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ stock solution was made freshly every time before use

Table 2. Treatments of the solution culture experiment

pH	Ni concentration (μM)							
4.0	0		4.3	8.5	17.0	34.1	68.1	136.3
5.0	0		2.1	4.3	8.5	17.0	34.1	68.1
6.0	0	1.1	2.1	4.3	8.5	17.0	34.1	
7.0	0	0.5	1.1	2.1	4.3	8.5	17.0	

The test plant, oats (*Avena sativa* L.) were sown in moist quartz sand (180 ml pure water/kg sand) in PVC trays, and cultured in climate chambers at 22°C, 60% relative humidity, and a 16 hour light / 8 hour dark regime for 7 days before being transferred to the nutrient solution. Each treatment contained 50 l of nutrient solution in a PVC container, to which 32 seedlings were transplanted and 2 of them were removed 3 days later. The plants grew in the climate

chamber at 16 hours light, 22°C / 8 hours dark, 14°C and 60% relative humidity. Solutions were continuously aerated and refreshed every 2 days (at weekends, every 3 days).

After 1, 2 and 3 weeks, 3 replicates of plant samples each containing 3 seedlings were sampled randomly from each treatment. The straw and root were separated after rinsing with water then dried at 75°C, and the dry weight was measured. A sub-sample of the plant material was digested according to a procedure described by Novozamsky et al. (1996), and the concentration of Ni was measured with ICP-OES (Spectros, Spectro Flame).

Determine Ni speciation in the soil solution using the Donnan membrane technique

Temminghoff *et al.* (2000) and Weng *et al.* (2001b) have described the method of the (soil column) Donnan membrane technique. The design of the cation exchange cell was described by Temminghoff *et al.* (2000). In the cell, a cation exchange membrane (BDH Laboratory Supplies, England) is used to separate the substrate solution (donor) and a blank salt solution (acceptor). The membrane has a matrix of polystyrene and divinylbenzene with sulphonic acid groups, which are fully deprotonated at pH>2. Before analysis, the membrane is prepared by shaking first with 0.1 M HNO₃ followed by pure water and the same solution that will be used as the acceptor solution.

Both the donor and the acceptor solution are circulated over the membrane surface continuously by pumping. When the Donnan membrane equilibrium is reached, samples from both sides are taken and concentrations of the target and reference cations are measured. The concentration of the free target cation, in this case free Ni²⁺, is calculated based on the theory of Donnan membrane equilibrium that the charge corrected ratios of the cation activity in both sides of the membrane are equal (Fitch and Helmke, 1989):

$$(a_{td}/a_{ta})^{1/Z_t} = (a_{rd}/a_{ra})^{1/Z_r}, \quad (1)$$

where a_{td} and a_{ta} are the activity of the target cation in donor and acceptor solution and Z_t is its charge, and a_{rd} , a_{ra} and Z_r are the analogous quantities for the reference cation. In the Donnan membrane analysis with soil samples, potassium can be used as the reference cation, since K is naturally present in soil and it forms very weak complexes with most ligands in the soil solution (Weng *et al.*, 2001b).

Soil samples from the pot experiments described in our previous paper (Weng et al., submitted) were used to determine Ni speciation in the 0.01 M CaCl_2 soil solution using the Donnan membrane technique linked to a soil column. In the pot experiments, a sandy soil (SS), a sandy soil containing higher amount of organic matter and iron hydroxides (OMFe) and a clay soil (CS) were used. The soils have been brought to various pH and Ni levels by liming and spiking $\text{Ni}(\text{NO}_3)_2$. Oats have been grown in pots containing these soils for 6-6.5 weeks. After harvesting, a soil sample consisting of 4-5 cores was taken from each pot. The soil samples were dried at 40°C or in air and sieved through 2 mm. For the sandy soil SS, the samples from all the treatments in the second pot experiment (Weng et al., submitted) were analyzed for the free Ni^{2+} concentration in the soil solution using the Donnan membrane technique. For the OMFe and CS soil, two samples from each pH series that contained a total Ni concentration close to the EC_{50} values were selected for the analysis. In the analysis, 100 g dry soil sample was used to prepare the soil column. The soil column was equilibrated with 200 ml of 0.01 M CaCl_2 solution. The same electrolyte solution was used as the acceptor solution (18 ml). Samples were taken after 2 and 3 days. The donor solution was filtered over 0.45 μm . pH, concentration of dissolved organic carbon (DOC) and concentrations of K, Ca and Ni were measured.

pH was measured with a pH-meter. Concentration of dissolved organic carbon (DOC) was measured with a fully automated TOC/DOC analyzer (SK12, Skalar, The Netherlands). The concentrations of the macro-elements (Ca, K) were measured using ICP-OES (Spectro, Spectro Flame), and concentrations of Ni were measured using ICP-MS (Perkin-Elmer, Elan 6000).

Ecotoxicological statistics

We used the logistic model without hormesis effect (positive biological effect at low concentration) (Hoekstra, 1993) to describe the exposure response of oats to Ni:

$$E(\%) = \frac{1}{1 + (c/\text{EC}_{50})^n}, \quad (2)$$

in which $E(\%)$ is the ratio of the response of the biota at the chemical concentration (c) to the response when $c=0$. EC_{50} and n are model parameters. EC_{50} indicates the chemical concentration that reduces the average response to 50% of its value under control circumstances. The model parameters EC_{50} and n were estimated by curve fitting.

Quantitative model

Nederlof & Van Riemsdijk (1995), and Plette *et al.* (1999) proposed a conceptual model to calculate the bioavailability of heavy metals in terrestrial and aquatic systems. The main assumption is that all interactions with the metal are mediated via the activity (concentration) of the free metal ion in solution. In the quantitative application of the conceptual approach, the competitive binding of metal and proton ions to the soil solid phase Q_{M-soil} and the amount bound to a biota surface, in this case the amount taken up by a plant when grown during a certain period under specified condition, $Q_{M-biota}$, are described by the two-species Freundlich equation as:

$$Q_{M-soil} = K_s [M^{2+}]^{m_s} (H^+)^{a_s}, \quad (3)$$

$$Q_{M-biota} = K_b [M^{2+}]^{m_b} (H^+)^{a_b}, \quad (4)$$

in which K is a constant related to the number of binding sites and their affinity for protons and metal ions, $[M^{2+}]$ represents the free metal ion concentration (activity) in the solution. (H^+) is the proton activity, m and a are empirical parameters. The subscript s and b relate to the soil phase and the biota respectively. Plette *et al.* (1999) pointed out that the K value and the exponents m and a are soil/organism specific, as the amount and type of binding sites will vary. The total amount of metal in the soil/plant system is often approximately equal to the amount of metal bound to the soil, $Q_{M-soil} \approx Q_{M-total}$. Metal binding to biota can thus be expressed as a function of total metal in soil and pH by combining Equations (3) and (4):

$$Q_{M-biota} = K_b K_s^{\left(\frac{m_b}{m_s}\right)} Q_{M-total}^{\left(\frac{m_b}{m_s}\right)} (H^+)^{\left(a_b - a_s \frac{m_b}{m_s}\right)} \quad (5)$$

The equation illustrates that the direction of the pH effect depends on both soil and plant factors. In this paper, we used the logarithmic form of the Freundlich equation to describe Ni binding to the soil and uptake by plant. Nickel uptake by the plant was expressed as the Ni concentration in the plant measured after harvesting the plants grown either in the solution culture or pot experiments.

Results and discussions

Toxicity of Ni in nutrient solution, in soil and in 0.01M CaCl₂ soil solution

In the solution culture experiment, symptoms of Ni toxicity started appearing a few days

after transplanting and increased in severity with time and rate of Ni application. The typical Ni toxicity symptom of oats, white necrosis longitudinal stripes between the veins, appeared on the leaves of the treatments with Ni concentration higher than 17.0, 8.5, 8.5 and 4.3 μM at the nominal pH of 4, 5, 6 and 7 respectively. Chlorosis occurred at pH 6 and pH 7 and became more serious at higher Ni concentration. Fine root development was stunted by Ni addition. The color of roots was darker at higher pH and Ni levels. Similar symptoms have been observed in the previous pot experiments.

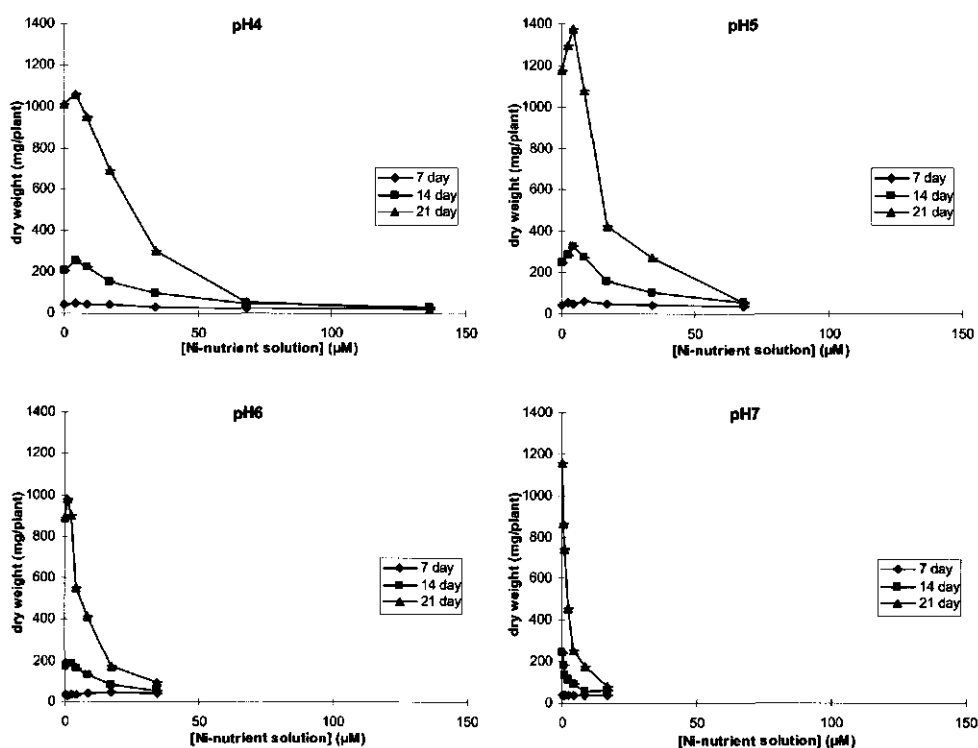


Figure 1. *The relative dry weight of the oats straw after grown in the nutrient solution for 1, 2, and 3 weeks*

The dry weight of the straw after 1, 2 and 3 weeks growing in the nutrient solution is shown in Figure 1. The biomass was decreased by Ni at all Ni concentrations except for a few treatments with less than 4.3 μM Ni at pH 4, 5, and 6. In these treatments, the yield was higher than that of the control. The toxicity of Ni in the nutrient solution was different at various pH. The decrease of the biomass at low pH was more gradual than that at high pH (Figure 1 & 2). Based on the dry weight of the straw after 3 weeks, the calculated EC_{50} of Ni

in the nutrient solution was 23.0, 14.7, 6.6 and 1.7 μM for pH 4, 5, 6, and 7 respectively (Table 3). Each unit increase in pH led to 2-4 times decrease in the EC_{50} value.

According to the chemical speciation calculation using the computer program ECOSAT (Keizer and Van Riemsdijk, 1994), in which the formation of the hydrolysis and carbonate species of Ni were accounted for, the free Ni^{2+} ion comprised 95-86% of the total Ni in the nutrient solution at pH 4 to pH 7. Most of the complexed Ni was associated with sulfate at low pH and with carbonate at high pH. The calculated EC_{50} of free Ni^{2+} in the nutrient solution was 21.9, 13.9, 6.3 and 1.4 μM for pH 4, 5, 6, and 7 respectively (Figure 3), and can be expressed as a function of: $\log \text{EC}_{50}\text{-Ni}^{2+} = 3.02 - 0.39\text{pH}$ ($R^2 = 0.94$). These results confirm that the free ion concentration is not a constant indicator of metal bioavailability and toxicity, and that metal toxicity in a nutrient solution is rather strongly influenced by the solution pH. The $\log \text{EC}_{50}$ of Ni^{2+} in the nutrient solution found in this work decreased with pH at the same slope as that of the critical $\log \text{Cu}^{2+}$ activity found by Lexmond & Van der Vorm (1981). The pH effects on Ni toxicity in the nutrient solution is opposite to that on the Ni toxicity in the soils studied. As we have found in the pot experiments, the toxicity of Ni in soil decreased with increasing pH. The EC_{50} of total Ni in the three soils studied varied between 0.7-22.5 mmol/kg and increased by 2-6 times with each unit increase in pH (Weng et al., submitted). The direction of the pH effects on metal toxicity depends on the type of media in which the plant grows.

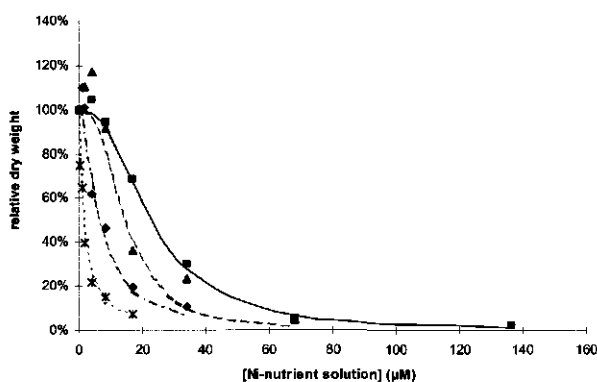


Figure 2. *The relative dry weight of the straw measured after 3 weeks in the solution culture and the fitted curves to the ecotoxicological model (\blacksquare pH4, \blacktriangle pH5, \blacklozenge pH6, $*$ pH7, — fitted curve pH4, — — fitted curve pH5, - - - fitted curve pH6, - · - fitted curve pH7)*

Table 3. Toxicity of Ni in the nutrient solution and in the straw from both the solution culture and the pot experiment (based on the dry biomass of the straw)

Solution culture									Pot experiment with the sandy soil		
pH	Dry weight of the straw of the control g/plant	ecotoxicological parameters of Ni in nutrient solution			ecotoxicological parameters of Ni in straw				ecotoxicological parameters of Ni in straw		
		EC ₅₀ (μ M)	n	R ²	EC ₅₀ (mmol/kg)	n	R ²		EC ₅₀ (mmol/kg)	n	R ²
4	1.011 (0.133)	23.0 (0.9)	2.81	1.00	2.30 (0.13)	3.14	0.99		2.49 (0.10)	2.42	1.00
5	1.175 (0.036)	14.7 (2.0)	2.61	0.97	2.84 (0.14)	5.28	0.99		1.86 (0.03)	4.21	1.00
6	0.891 (0.070)	6.6 (1.2)	1.63	0.97	2.66 (0.20)	4.35	0.96		1.93 (0.35)	2.64	0.99
7	1.156 (0.077)	1.7 (0.2)	1.13	1.00	1.18 (0.03)	2.16	1.00		1.64 (0.11)	7.07	1.00

We have observed before that the 0.01M CaCl₂ soil extraction was closely related to the toxicity of Ni in the soils and was a better indicator of the bioavailability than the total Ni concentration in the soils (Weng et al., submitted). The EC₅₀ of Ni in the 0.01M CaCl₂ soil extraction varied by only a factor of 2 between 24 and 58 μ M. Differing from the EC₅₀ of Ni in the nutrient solution, no obvious pH dependency was observed for the EC₅₀ of Ni in the 0.01M CaCl₂ soil extraction.

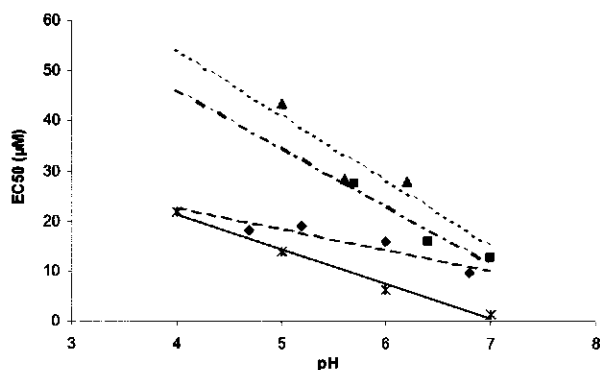


Figure 3. Comparison of the EC₅₀ of free Ni²⁺ in the nutrient solution and in the 0.01M CaCl₂ soil solution (◆ SS2, ▲ OMFe, ■ CS, * nutrient solution, — trend line nutrient solution, — — trend line SS2, - - - trend line OMFe, ---- trend line CS)

Uptake of Ni from the nutrient solution and the 0.01M CaCl₂ soil extract

The Ni concentration in the oats from the solution culture varied between 0.07-49 mmol/kg dry weight in the root and 0.02-25 mmol/kg in the straw. In Figure 4, the concentration of Ni in the root and straw was plotted against the Ni concentration in the nutrient solution. Nickel is considered relatively mobile in the plant compared to some other heavy metals such as Cd (Sajwan et al., 1996). Our results show that still more Ni was retained in the root than in the straw. The ratio of Ni in the root to that in the straw was between 1.4 and 23, and the difference became bigger with the increase in pH.

The uptake of Ni by oats from the solution culture depends on pH (Figure 4). Each unit increase in pH between pH 4 and 6 led to an increase of Ni concentration in the straw by up to 2.6 times. Further increase of pH from pH 6 to 7 did not show an effect on the Ni concentration in the straw. The pH dependency of Ni uptake was bigger for the root than for the straw. Each unit increase in pH led to up to 3.4 times more Ni in the root. At pH 6 and 7, the pH dependency of Ni uptake in the root became obscured at large Ni dosage (Figure 4). The measured concentration of Ni in the oats can be reasonably described with the two-species Freundlich model. The fitted models for Ni in the straw and root of oats grown in the solution culture are:

$$\log[\text{Ni-straw}] = 1.17 + 0.65 \log[\text{Ni-nutrient solution}] + 0.10 \text{pH}, (R^2 = 0.95) \quad (6)$$

$$\log[\text{Ni-root}] = 1.12 + 0.70 \log[\text{Ni-nutrient solution}] + 0.27 \text{pH}, (R^2 = 0.90) \quad (7)$$

in which Ni in the straw and root is in mmol/kg; Ni in the nutrient solution is in mM. The agreement is better for the straw than for the root.

In the pot experiment with the sandy soil SS, the concentration of Ni in oats straw was determined after 6 weeks of treatment and it varied between 0.03-34 mmol/kg. In contrast with Ni uptake from the nutrient solution, Ni uptake in the pot experiment based on the Ni concentration in the 0.01 M CaCl₂ extraction did not show a clear pH dependency (Figure 4) (Weng et al., submitted). The Freundlich model derived for the Ni uptake in the pot experiment is as the following:

$$\log[\text{Ni-straw}] = 2.23 + 0.98 \log[\text{Ni-CaCl}_2] - 0.04 \text{pH}, (R^2 = 0.94) \quad (8)$$

in which Ni in the straw is in mmol/kg and Ni in CaCl₂ is in mM. The absence of a pH dependency of Ni uptake for Ni in the 0.01M CaCl₂ soil solution can not be explained by the observation in the solution culture. We will come back to this point later.

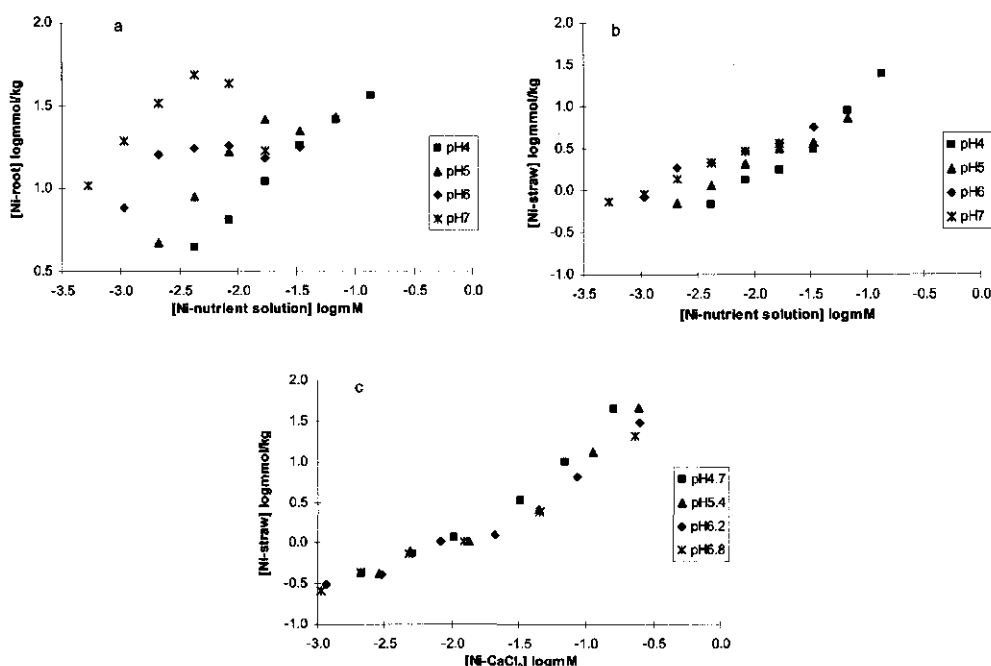


Figure 4. *Ni* concentration in the root (a) and straw (b) of oats after 3 weeks growing in the solution culture as a function of *Ni* concentration in the nutrient solution; *Ni* concentration in the oats straw (c) after 6 weeks in the pot experiment using the sandy soil as a function of *Ni* concentration in the 0.01M CaCl_2 .

In the solution culture experiment, the *Ni* concentrations in straw at which *Ni* toxicity symptoms appeared were 1.75-2.95 mmol/kg. According to Welch (1981), the normal *Ni* concentration range in plants is 0.2-85 $\mu\text{mol/kg}$, and the toxic concentrations in plants are usually of the order of 426-852 $\mu\text{mol/kg}$. It has been found that the *Ni* toxicity symptom appeared at the concentration in oats of 1.38-1.62 mmol/kg in solution culture and 1.93-1.94 mmol/kg in the soil experiment (Crooke, 1956; Crooke and Inkson, 1955).

The growth response (dry weight of straw) to the concentration of *Ni* in the straw measured after the solution culture and the pot experiment with the sandy soil is shown in Figure 5. The estimated EC_{50} of *Ni* in the straw in the solution culture were in the range of 1.2-2.3 mmol/kg (Table 3). They are very similar to those calculated for the pot experiment, e.g. 1.6-2.5 mmol/kg (Table 3). The EC_{50} of *Ni* in the straw varied by about 3 times in the solution culture and by 1.5 times in the pot experiment, and they tended to decrease with increasing pH. This may suggest that the total *Ni* concentration in the tissue is not the only factor in

determining the biological response. The effects of a certain Ni content in the straw seems to be affected by other environmental conditions as well. However, compared to the variation of the effective Ni concentration in the medium, the tissue Ni concentration is still a more direct indicator of the toxicity.

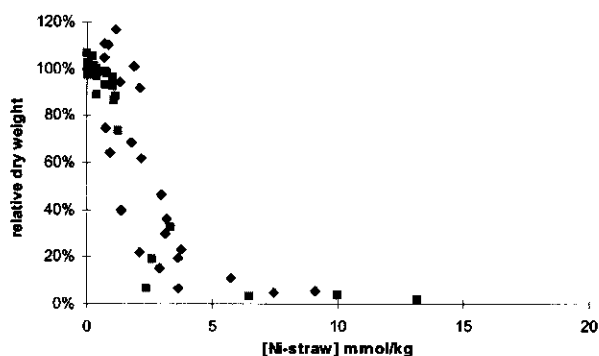


Figure 5. Relative dry weight of the straw vs. the Ni concentration in the straw (■ pot experiment, ◆ solution culture)

Free Ni^{2+} in the 0.01M CaCl_2 soil solution

Using the soil column Donnan membrane technique, Ni speciation in the 0.01M CaCl_2 solution in equilibrium with the soil samples was measured. The free Ni^{2+} concentration was calculated from the measured concentrations of Ni in the donor and acceptor solutions using Equation (1), in which potassium was used as the reference cation. In this measurement, the pH of the soil solution varied between 4.4 and 7.3, and the DOC concentration ranged from 34 to 91mg/l. Generally, the DOC concentration increased with increasing pH. In these soil solution samples, the free Ni^{2+} ranged from almost 100% to about 20% of the total dissolved Ni. The fraction of free Ni^{2+} decreased with increasing pH and increased with the total concentration of dissolved Ni. The concentration of Ni that was complexed with inorganic ligands including carbonate was calculated with ECOSAT using the measured free Ni^{2+} concentration. The total inorganic complexes of Ni was at the maximum about 20% of the total Ni in the solution at high pH. The difference between the total concentration of dissolved Ni and the inorganic Ni was considered as Ni that was bound to dissolved organic matter (DOM). The DOM complexed Ni ranged from almost 0% to about 60% in the soil solution. The following equation was derived from the analytical data:

$$\log[\text{Ni}^{2+}] = 0.76 + 1.09\log[\text{Ni}-\text{CaCl}_2] - 0.14\text{pH}, (R^2=0.98) \quad (9)$$

in which the concentration of free Ni^{2+} and Ni in 0.01 M CaCl_2 are in mM. The agreement of the prediction using this equation with the measurement is good. Both the increased binding affinity of Ni to DOM and the increased concentration of DOC at higher pH account for the stronger decrease of the free Ni^{2+} fraction in the soil solution than in the nutrient solution.

Using Equation (9), the Ni toxicity in the pot experiment (EC_{50}) in terms of free Ni^{2+} in the soil solution was calculated from the EC_{50} of Ni in the 0.01M CaCl_2 solution and the pH. The estimated EC_{50} of free Ni^{2+} in the soil solutions ranged from 44-10 μM and they are compared to the EC_{50} of free Ni^{2+} in the nutrient solution in Figure 3. The results showed that, the toxicity of Ni^{2+} in both the nutrient solution and the soil solution decreased with increasing pH. Compared with that in the nutrient solution, the pH effect was less strong for the sandy soil SS, but the pH effects were stronger for the soil OMFe and the clay soil. In general, the EC_{50} of free Ni^{2+} in the 0.01 M CaCl_2 soil solution were larger than the EC_{50} of Ni^{2+} in the nutrient solution. The absence of pH dependency of plant uptake of Ni in the 0.01 M CaCl_2 soil solution observed in the pot experiments can be explained by the Ni speciation in the soil solution. The decrease of free Ni^{2+} concentration in the 0.01 M CaCl_2 soil solution at increased pH counterbalanced the increased uptake by the plant.

The discrepancy between the toxicity of Ni^{2+} in the nutrient solution and in the 0.01 M CaCl_2 soil solution could besides other possible reasons be due to the difference between the 0.01 M CaCl_2 soil solution and the pore water. The CaCl_2 extract is expected to give a higher free metal ion concentration than in the pore water, due to the increased competition of calcium with the metal ion for the binding to soil and the decrease of the activity coefficient. The larger EC_{50} of free Ni^{2+} in the OMFe and CS soils than in the SS soil (Figure 3) could be due to the larger CEC of the OMFe and CS soils. Therefore there was more Ni in the OMFe and CS soils that could be replaced by the Ca added.

Testing the quantitative model

With the data of the solution culture experiment and the pot experiment using the sandy soil, we can test the quantitative model proposed by Nederlof & Van Riemsdijk (1995), and Plette *et al.* (1999). From the results of the solution culture, the Ni concentration in the straw can be expressed as a function of the free Ni^{2+} concentration in the nutrient solution and pH:

$$\log[\text{Ni-straw}] = 1.15 + 0.65 \log[\text{Ni}^{2+}] + 0.11 \text{pH}, (R^2 = 0.95) \quad (10)$$

in which [Ni-straw] is in mmol/kg and $[\text{Ni}^{2+}]$ is in mM. Because most of the Ni in the nutrient solution was present as free Ni^{2+} , replacing Ni concentration in the nutrient solution with the concentration of free Ni^{2+} made little difference between Equation (6) and (10).

As found in the Donnan membrane analysis, the free Ni^{2+} concentration in the 0.01M CaCl_2 extract is given by Equation (9). If we combine Equation (9) and (10), the two-species Freundlich equation of Ni uptake in the oats straw from Ni in the 0.01 M CaCl_2 soil solution is derived:

$$\log[\text{Ni-straw}] = 1.64 + 0.71 \log[\text{Ni-CaCl}_2] + 0.02 \text{pH}, \quad (11)$$

From the experiments with the sandy soil, the following Freundlich equation of Ni adsorption to the SS soil has been derived in 0.01M CaCl_2 (Weng et al., submitted):

$$\log[\text{Ni-soil}] = -1.89 + 0.77 \log[\text{Ni-CaCl}_2] + 0.60 \text{pH}, (R^2 = 0.99) \quad (12)$$

in which [Ni-soil] is in mmol/kg and [Ni- CaCl_2] is in mM. By following the quantitative model and combining Equation (11) and (12), the Ni uptake from the sandy soil is predicted:

$$\log[\text{Ni-straw}] = 3.41 + 0.92 \log[\text{Ni-soil}] - 0.53 \text{pH}, \quad (13)$$

The resulted Equation (13) indicates that the pH effect on the binding to the soil exceeds the effect on plant uptake, and therefore a decrease of Ni uptake and toxicity in soil can be predicted at increased pH.

In the pot experiment with the sandy soil, the measured Ni concentration in the straw was a function of:

$$\log[\text{Ni-straw}] = 3.66 + 1.08 \log[\text{Ni-soil}] - 0.63 \text{pH} (R^2 = 0.94) \quad (14)$$

In Equation (14), the 0.95 confidence range for the factor of pH dependency is between -0.73 and -0.53. The predicted factor of pH dependency in Equation (13), e.g. 0.53, falls in this range. In Figure 6, the predicted Ni uptake from the sandy soil is compared to the measurement. The predicted lines are slightly shifted compared to the measurements, especially at lower Ni content in the soil. However, the discrepancy is within 0.5 log-unit.

This discrepancy can be the result of many factors. One possible major reason might be the difference between the 0.01M CaCl_2 extractable Ni and Ni in the pore water. We have noted that the EC_{50} of free Ni^{2+} in the 0.01M CaCl_2 extraction were generally higher than the EC_{50} of free Ni^{2+} in the nutrient solution. The competition of Ca with Ni for the binding to the soil will result in a higher free Ni^{2+} concentration in the 0.01 M CaCl_2 soil solution than in the

actual pore water in the pot experiment. Using the free Ni^{2+} concentration in the 0.01M CaCl_2 soil solution to predict Ni uptake by the plant thus may lead to some overestimation of the uptake, due to the overestimation of the free Ni^{2+} concentration in the pore water. Other reasons that might lead to the discrepancy include the neglect of the some factors that may play a role in affecting Ni toxicity. For instance the competition of Ca with Ni for the uptake by the plant. The Ca concentration in the solution culture, from which the Ni uptake equation was derived and used in the quantitative model, can be different from that in the pore water. And the concentration of Ca in the pore water may not be the same for the soil at various pH.

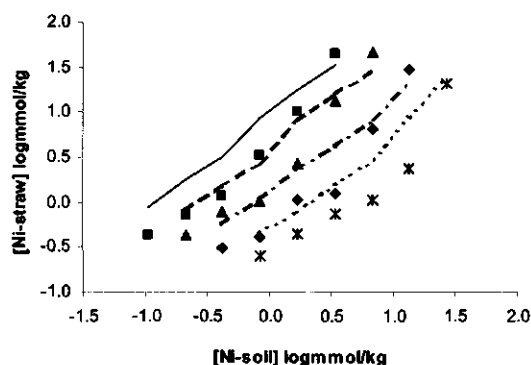


Figure 6. Comparison of Ni uptake from the sandy soil predicted using the quantitative model and measured after 6 weeks of the pot experiment (■ pH4.7 measured, ▲ pH5.4 measured, ◆ pH6.2 measured, * pH6.8 measured, — pH4.7 predicted, — — pH5.4 predicted, - - pH6.2 predicted, ---- pH6.8 predicted)

In spite of the small discrepancy between the prediction of the plant uptake of Ni using the quantitative model and the measurement, the effects of pH on Ni uptake in soil can be quite reasonably estimated with the quantitative model. The model also helps to better understand the mechanisms of the effects of environmental factors on the availability of metal ions. The results proved that the measuring of the Ni concentration in the 0.01M CaCl_2 soil extraction is a simple way to estimate the toxicity and availability of Ni in the soils. In order to fully understand the effects of pH we have shown that it is essential to measure or calculate the free nickel concentration in a 0.01M CaCl_2 extracted soil solution.

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Appendix

Table 1. Parameters of NICA-Donnan model (Milne, 2000; Milne *et al.*, 2001)

<i>Generic Humic Acid</i>				
Electrostatic Donnan b value in Eq. $\log V_D = a + b \log I$	-0.49			
	low affinity or carboxylic type site		high affinity or phenolic type site	
site density $Q_{\max, H}$ (mol/kg)	3.15		2.55	
heterogeneity p	0.62		0.41	
ion specific parameters	affinity $\log K_1$	non-ideality n_1	affinity $\log K_2$	non-ideality n_2
H	2.93	0.81	8.00	0.63
Ca	-1.37	0.78	-0.43	0.75
Al	-1.05	0.40	8.89	0.30
Fe(III)	5.00	0.30	17.5	0.25
Cu	2.23	0.56	6.85	0.34
Cd	-0.20	0.73	2.37	0.54
Zn	0.11	0.67	2.39	0.27
Ni	-0.26	0.64	1.0	0.55
Pb	1.26	0.60	4.86	0.69

<i>Generic Fulvic Acid</i>				
Electrostatic Donnan b value in Eq. $\log V_D = a + b \log I$	-0.57			
	low affinity site		high affinity site	
site density $Q_{\max, H}$ (mol/kg)	5.88		1.86	
heterogeneity p	0.59		0.70	
ion specific parameters	affinity $\log K_1$	non-ideality n_1	affinity $\log K_2$	non-ideality n_2
H	2.34	0.66	8.60	0.76
Ca	-2.17	0.85	-3.29	0.83
Al	-4.11	0.42	12.16	0.31
Fe(III)	6.0	0.25	36	0.19
Cu	0.26	0.53	8.24	0.36
Cd	-0.99	0.68	0.73	0.50
Zn	-3.84	0.67	-0.73	0.61
Ni	-2.07	0.65	2.03	0.53
Pb	-1.22	0.60	6.87	0.70

Table 2. Parameters of Humic Acid Ion Binding Model VI (Tipping, 1998)

Parameter	Humic acid	Fulvic acid	Comments
M	15000	1500	molecular weight
r (nm)	1.72	0.80	radius
n_A (mol/g)	3.3×10^{-3}	4.8×10^{-3}	number of type A groups
n_B (mol/g)	1.65×10^{-3}	2.4×10^{-3}	$= 0.5 \times n_A$
pK_A	4.1	3.2	median proton dissociation constant for type A groups
pK_B	8.8	9.4	median proton dissociation constant for type B groups
ΔpK_A	2.1	3.3	range factor for pK_A
ΔpK_B	3.6	4.9	range factor for pK_B
P	-330	-115	electrostatic parameter
f_{prB}	0.50	0.42	proximity factor for bidentate sites
f_{prT}	0.065	0.03	proximity factor for tridentate sites
ΔLK_1	2.8	2.8	range factor for metal binding
$\log K_{MA}$			
Mg	0.7	1.1	Intrinsic equilibrium constants for monodentate binding at type A sites. Values for type B sites are obtained from the relation: $\log K_{MB} = 3.39 \log K_{MA} - 1.15$ ($r^2 = 0.80$)
Al	2.6	2.5	
Ca	0.7	1.3	
Fe(III)	2.5	2.4	
Cu	2.0	2.1	
Ni	1.1	1.4	
Zn	1.5	1.6	
Cd	1.3	1.6	
Pb	2.0	2.2	
ΔLK_2			
Mg	0.12		Strong binding site term, obtained from the relation: $\Delta LK_2 = 0.55 \log K_{NH_3}$ ($r^2 = 0.66$), where K_{NH_3} is the equilibrium constant for complexation with NH_3
Al	0.46		
Ca	0.0		
Fe(III)	2.20		
Cu	2.34		
Ni	1.57		
Zn	1.28		
Cd	1.48		
Pb	0.93		

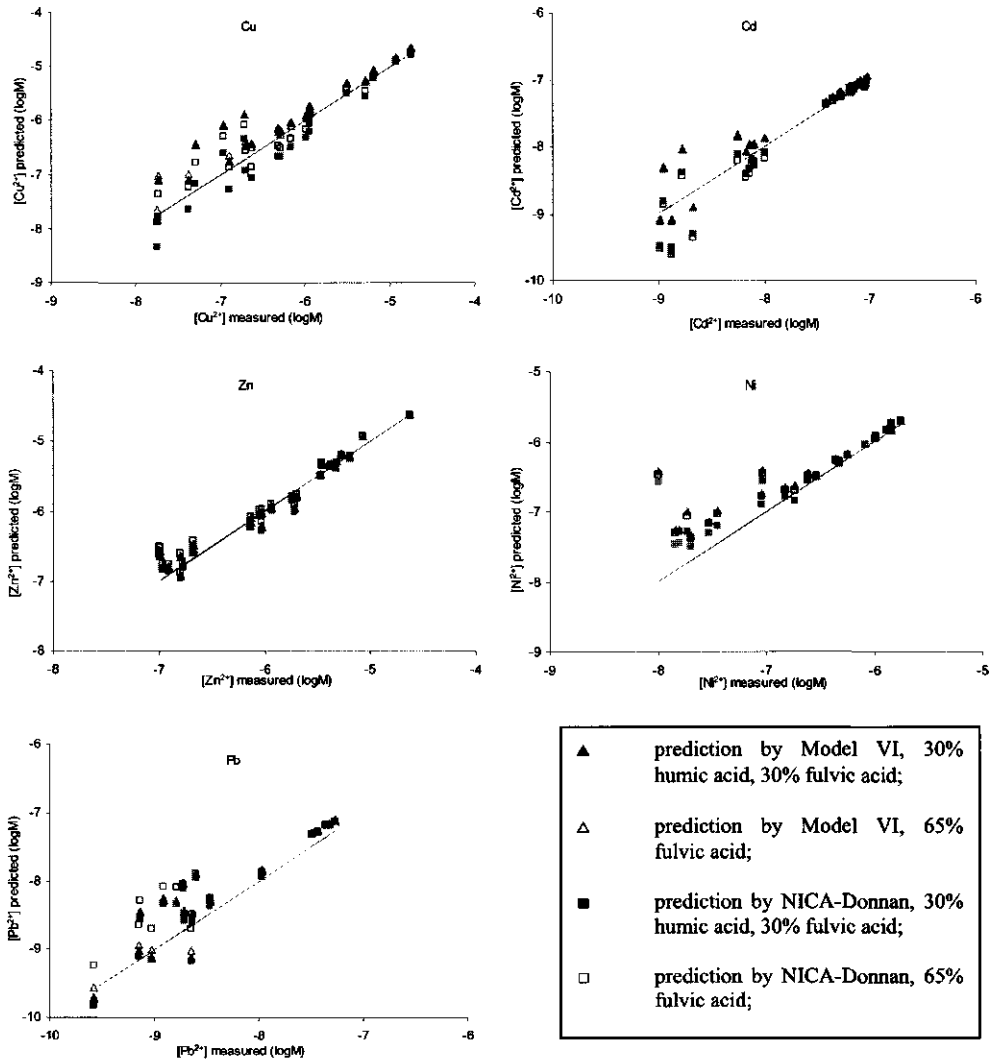
Table 3. Parameters of Two Site Surface Complexation Diffuse Double Layer (DDL) model for HFO (Dzombak & Morel, 1990)

Surface area: $6 \times 10^3 \text{ m}^2/\text{kg}$			
S ₁ -OH site: $0.056/\text{nm}^2$			
S ₂ -OH site: $2.255/\text{nm}^2$			
surface species	logK ₀	surface species	logK ₀
S ₁ -OH ⁰	0	S ₂ -OH ⁰	0
S ₁ -OH ₂ ⁺	7.29	S ₂ -OH ₂ ⁺	7.29
S ₁ -O ⁻	-8.93	S ₂ -O ⁻	-8.93
S ₁ -PO ₄ ²⁻	17.72	S ₂ -PO ₄ ²⁻	17.72
S ₁ -HPO ₄ ⁻	25.39	S ₂ -HPO ₄ ⁻	25.39
S ₁ -H ₂ PO ₄ ⁰	31.29	S ₂ -H ₂ PO ₄ ⁰	31.29
S ₁ -OHCa ²⁺	4.97	S ₂ -OCa ⁺	-5.85
S ₁ -OCu ⁺	2.89	S ₂ -OCu ⁺	0.60
S ₁ -OCd ⁺	0.47	S ₂ -OCd ⁺	-2.90
S ₁ -OZn ⁺	0.99	S ₂ -OZn ⁺	-1.99
S ₁ -ONi ⁺	0.37	S ₂ -ONi ⁺	-2.50
S ₁ -OPb ⁺	4.65	S ₂ -OPb ⁺	0.30

Table 4. Parameters of CD-MUSIC model for goethite (Hiemstra & Van Riemsdijk, 1996, 1999 and personal communication)

110 face			021 face			
surface area: $4.5 \times 10^4 \text{ m}^2/\text{kg}$			surface area: $5 \times 10^3 \text{ m}^2/\text{kg}$			
$\text{FeOH}^{0.5}$ site: $3.0/\text{nm}^2$			$\text{FeOH}^{0.5}$ site: $3.75/\text{nm}^2$			
$\text{Fe}_3\text{O}^{0.5}$ site: $3.0/\text{nm}^2$			$\text{Fe}_h\text{OH}^{0.5}$ site: $3.75/\text{nm}^2$			
species parameters						
surface species	$\log K_0$	site 1	site 2	0-plane	1-plane $C_1 = 1.02 \text{ F/m}^2$	2-plane $C_2 = 5 \text{ F/m}^2$
$\text{FeOH}^{0.5}$	0	$1\text{FeOH}^{0.5}$		0	0	0
$\text{FeOH}_2^{+0.5}$	9.2	$1\text{FeOH}^{0.5}$		1	0	0
$\text{FeOHK}^{+0.5}$	-1.0	$1\text{FeOH}^{0.5}$		0	0	1
$\text{FeOH}_2\text{NO}_3^{-0.5}$	8.2	$1\text{FeOH}^{0.5}$		1	0	-1
$\text{Fe}_3\text{O}^{0.5}$	0	$1\text{Fe}_3\text{O}^{0.5}$		0	0	0
$\text{Fe}_3\text{OH}^{+0.5}$	9.2	$1\text{Fe}_3\text{O}^{0.5}$		1	0	0
$\text{Fe}_3\text{OK}^{+0.5}$	-1.0	$1\text{Fe}_3\text{O}^{0.5}$		0	0	1
$\text{Fe}_3\text{OHNO}_3^{-0.5}$	8.2	$1\text{Fe}_3\text{O}^{0.5}$		1	0	-1
$\text{Fe}_h\text{OH}^{0.5}$	0.0	$1\text{Fe}_h\text{OH}^{0.5}$		0	0	0
$\text{Fe}_h\text{OH}_2^{+0.5}$	9.2	$1\text{Fe}_h\text{OH}^{0.5}$		1	0	0
$\text{Fe}_h\text{OHK}^{+0.5}$	-1.0	$1\text{Fe}_h\text{OH}^{0.5}$		0	0	1
$\text{Fe}_h\text{OH}_2\text{NO}_3^{-0.5}$	8.2	$1\text{Fe}_h\text{OH}^{0.5}$		1	0	-1
$\text{FeOHCa}^{+1.5}$	3.55	$1\text{FeOH}^{0.5}$		0.2	1.8	0
$\text{FeOPO}_3^{-2.5}$	20.8	$1\text{FeOH}^{0.5}$		0.25	-2.25	0
$(\text{FeO})_2\text{PO}_2\text{H}^{-1}$	35.7	$2\text{FeOH}^{0.5}$		0.9	-0.9	0
$(\text{FeO})_2\text{PO}_2^{-2}$	29.4	$2\text{FeOH}^{0.5}$		0.39	-1.39	0
$(\text{Fe}_h\text{O})_2\text{PO}_2\text{H}^{-1}$	35.7	$2\text{Fe}_h\text{OH}^{0.5}$		0.9	-0.9	0
$(\text{Fe}_h\text{O})_2\text{PO}_2^{-2}$	29.4	$2\text{Fe}_h\text{OH}^{0.5}$		0.39	-1.39	0
$\text{FeOHCu}^{+1.5}$	8.62	$1\text{FeOH}^{0.5}$		0.83	1.17	0
$\text{FeOHCuOH}^{+0.5}$	3.03	$1\text{FeOH}^{0.5}$		0.83	0.17	0
$\text{Fe}_h\text{OHCu}^{+1.5}$	8.62	$1\text{Fe}_h\text{OH}^{0.5}$		0.83	1.17	0
$\text{Fe}_h\text{OHCuOH}^{+0.5}$	3.03	$1\text{Fe}_h\text{OH}^{0.5}$		0.83	0.17	0
$(\text{FeOH})_2\text{Cd}^{+1}$	6.98	$2\text{FeOH}^{0.5}$		0.71	1.29	0
$(\text{FeOH})_2\text{CdOH}^0$	-2.94	$2\text{FeOH}^{0.5}$		0.71	0.29	0
$(\text{Fe}_h\text{OH})_2\text{Cd}^{+1}$	6.98	$2\text{Fe}_h\text{OH}^{0.5}$		0.71	1.29	0
$(\text{Fe}_h\text{OH})_2\text{CdOH}^0$	-0.32	$2\text{Fe}_h\text{OH}^{0.5}$		0.71	0.29	0
$(\text{FeOH})_2\text{Pb}^{+1}$	9.75	$2\text{FeOH}^{0.5}$		1.15	0.85	0
$(\text{Fe}_h\text{OH})_2\text{Pb}^{+1}$	9.75	$2\text{Fe}_h\text{OH}^{0.5}$		1.15	0.85	0
$(\text{FeOHFe}_3\text{O})\text{Zn}^{+1}$	8.01	$1\text{FeOH}^{0.5}$	$1\text{Fe}_3\text{O}^{0.5}$	0.83	1.17	0
$(\text{FeOHFe}_3\text{O})\text{ZnOH}^0$	-1.0	$1\text{FeOH}^{0.5}$	$1\text{Fe}_3\text{O}^{0.5}$	0.83	0.17	0
$(\text{Fe}_h\text{OH})_2\text{Zn}^{+1}$	6.63	$2\text{Fe}_h\text{OH}^{0.5}$		0.83	1.17	0
$(\text{Fe}_h\text{OH})_2\text{ZnOH}^0$	-2.38	$2\text{Fe}_h\text{OH}^{0.5}$		0.83	0.17	0

Figure 1. Comparison of the free ion concentration in the soil solutions measured and predicted by Model VI and NICA-Donnan



Summary

Introduction

Interactions between metals ions and the biogeo-surfaces in soil and water are important in the control of the speciation, therefore the bioavailability and mobility of heavy metals. These interactions are also important in determining the solubility and mobility of the natural organic matter, which in turn influences the solubility of heavy metals. Better understanding and quantification of the interactions between the metal ions and the biogeo-surfaces in soil and water are the basis for an improved quantitative risk assessment of heavy metals in the environment. In this thesis, both experimental and modelling approaches are employed to obtain a better understanding of the processes that affect heavy metal interactions with the soil organic matter (solid and dissolved), clay, iron hydroxides and plant. The aim is also to get more insight in the relative importance of the various phases on the metal speciation, bioavailability and mobility.

Donnan membrane technique

It is commonly believed that the free metal ion is the key factor in the determination of metal availability. However, accurate measurement of the free metal ion is difficult, especially for trace metals present in very low concentrations (less than micro-molar) in natural systems. The recently developed Donnan membrane technique can measure the concentrations in solution in the presence of inorganic and organic complexing agents. We have developed this method further to make it applicable for analyzing soil samples. The major development is the linkage of a soil column with the Donnan cell. The operational aspects of the method, including equilibrium time, buffering capacity and correction for differences in ionic strength were investigated and optimized. The method was applied to determine concentrations of free Cu^{2+} , Cd^{2+} , Pb^{2+} and Zn^{2+} in the soil solution of 15 soil samples. Compared with other speciation methods, the Donnan membrane technique has the advantage of allowing the measurement of several elements simultaneously and it minimizes the disturbance of substrate. The detection limit of the Donnan membrane technique in its present form is about 10^{-9} M. This method can be applied to study the biogeochemical behavior of metals in soils, sediments and other solid materials.

In the natural waters including soil solutions, aluminum is a strong competitor for the heavy metals to the binding on colloidal particles such as organic matter. The study of Al speciation is of interest for the assessment of soil and water quality. For the measurement of "free" aluminum (Al^{3+}), the Donnan membrane technique was tested by measuring Al^{3+} in aluminum-fluoride solutions and gibbsite suspensions. It shows that the Donnan membrane technique can measure free Al^{3+} reliably up to 10^{-9} M and the equilibration takes 3-4 days. Aluminum binding to humic acid (HA) purified from a forest soil was measured using either the Donnan membrane technique or gibbsite suspension. Results were compared with those predicted with the NICA-Donnan model. The predictions using the generic parameters without fitting were in reasonable agreement with the measured data. In addition, the Donnan membrane technique was used to determine Al binding to dissolved organic matter (DOM) in the solutions of 24 soil samples at pH interval of 3-7. Measurements agree well with the predictions using the NICA-Donnan model assuming 30% of DOM is humic acid and 30% is fulvic acid. With this model, the effects of pH and DOM changes on the concentration of Al in 81 soil solutions were predicted reasonably without adjustment of model parameters. The comparison between the results of analysis and the modeling provides a mutual validation for the two methods.

Multi-surface model

Although the measurement provides the most direct, and probably the most reliable information of metal speciation, it has limitations such as the detection limit that is often above the concentration of the metal ion. In addition, the distribution of heavy metals over the various solid surfaces is difficult to be determined experimentally. Without a model, the effects of the changes in environmental conditions on metal speciation can not be predicted quantitatively using only the analytical approach. In this research, a multi-surface model is used to estimate the contribution of various sorption surfaces to the control of heavy metal activity in sandy soil samples at pH 3.7-6.1 with different sorbent contents. This multi-surface model considers soil as a set of independent sorption surfaces, *i.e.* organic matter (NICA-Donnan), clay silicate (Donnan) and iron hydroxides (DDL, CD-MUSIC). The activities of Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} and Pb^{2+} in equilibrium with the soil have been measured using the Donnan membrane technique. The metal activities predicted by the model agree with those measured reasonably well over a wide concentration range for all the metals of interest except for Pb. The modelling results suggest that soil organic matter is the most important sorbent that controls the activity of Cu^{2+} , Cd^{2+} , Zn^{2+} and Ni^{2+} in these sandy soils.

When metal loading is high in comparison with soil organic matter content, the contribution of clay silicates to metal binding becomes more important. Adsorption to iron hydroxides is found not significant in these samples for Cu, Cd, Zn and Ni. However, for Pb the model estimates strong adsorption on iron hydroxides. The model predicts that acidification will not only lead to increased solution concentrations, but also to a shift towards more nonspecific cation-exchange type binding especially for the metals Cd, Zn and Ni. Lowering the pH has led to a loss of 56% of Cd, 69% of Zn and 66% of Ni during 16 years due to increased leaching.

The complexation of heavy metals with dissolved organic matter (DOM) in the environment influences the solubility and mobility of these metals. Using a Donnan membrane technique we measured the complexation of Cu, Cd, Zn, Ni and Pb with DOM in the soil solution at pH 3.7-6.1. The results show that the DOM-complexed species is generally more significant for Cu and Pb than for Cd, Zn and Ni. The ability of two advanced models for ion binding to humic substances, *e.g.* Model VI and NICA-Donnan, in the simulation of metal binding to natural DOM was assessed by comparing the model predictions with the measurements. Using the default parameters of fulvic and humic acid, the predicted concentrations of free metal ions from the solution speciation calculation using the two models are mostly within one order of magnitude difference from the measured concentrations. Furthermore, the solid-solution partitioning of the metals was simulated using the multi-surface model, in which metal binding to soil organic matter, dissolved organic matter, clay, and iron hydroxides were accounted for using adsorption and cation exchange models (NICA-Donnan, Donnan, DDL, CD-MUSIC). The model gave a reasonable estimation of the dissolved concentration of all the metals of interest except for Pb. The solubility of the metals depends mainly on the metal loading of the soil sorbents, pH and the concentration of inorganic ligands and DOM in the soil solution.

Solubility and mobility of organic matter

The interactions between the metal ions and the natural organic matter are not only important for the metal distribution, but also for the solubility and mobility of organic matters. The coagulation of humic substances and its role in controlling the solubility of organic matter in soils are not well understood. We therefore studied the physico-chemical behaviour of purified humic acid from forest soil coagulated with Na, Ca, Cu, Al at pH 4 and 6, and then modelled the behaviour with the NICA-Donnan model. We found that the coagulation of

humic acid occurs when the Donnan potential is less negative than -0.08 V. Based on this result, an empirical relation between the Donnan potential of humic acid and its concentration in solution was derived. In addition, the Donnan potential of the dissolved organic matter in the soil solution of six soil profiles from forests was calculated using the NICA-Donnan model under the assumption that all the dissolved organic matter behaves as humic acid. The measured concentration of dissolved organic matter also decreases in a soil profile, as the calculated potential becomes less negative. The results are in many cases in semi-quantitative agreement with the predicted concentration based on the humic acid coagulation experiment. Acid soils contain more dissolved organic matter, which may result from the presence of a fairly large fraction of more soluble organic molecules, such as fulvic acid.

The transport of inorganic and organic pollutants in water and soil can be strongly influenced by the mobility of natural dissolved organic matter (DOM). In this thesis, the transport of a humic acid (HA) and a fulvic acid (FA) in a copper contaminated acid sandy soil was studied. The data showed that the transport behaviour of HA differed from that of FA. The breakthrough curves (BTCs) of HA were characterised by a rapid relatively sharp front followed by a plateau at a lower HA concentration than in the influent solution. The increase of the Ca concentration decreased the HA concentration further. Compared to HA, the BTCs of FA were retarded and showed an extended tailing, approaching complete breakthrough. The increase of the Ca concentration decreased the FA concentration only temporarily. Based on our model calculation, the characterisation of HA transport could be explained by the coagulation of HA largely upon the binding of Al. The increase of the Ca concentration resulted in further coagulation of HA because of the increased Ca adsorption, which occurred mainly in the Donnan phase. For FA, the adsorption to the soil matrix was more likely the process that controls its solubility and mobility. The mobility of Al and Cu in the soil column was closely related to the solubility and transport of the dissolved organic matter in soil solution. The concentration of Ca in the effluent was lower than in the influent because Ca was retained in the soil due to the retardation of HA and FA and due to the compensation of the other cations released from the soil to the solution.

Interpretation of the toxicological data of Ni

The experimental and the modelling approaches developed are helpful in improving the quantitative risk assessment of the heavy metals. Using the modelling and measuring

methods developed, the results of the pH effects on the nickel toxicity to plant is interpreted and studied in more detail. Pot experiments with three different soils, *e.g.* a sandy soil, a sandy soil with a relatively high content of organic matter and iron hydroxides and a clay soil have been conducted to study the phytotoxicity of Ni to oats and the effects of pH and soil characteristics. The EC_{50} of spiked Ni in the decreasing of the mass of the straw were between 0.7 and 22.5 mmol/kg soil, varying by a factor of 32 with the type of soil and pH (pH range 4.7-7.0). The toxicity of Ni in terms of total Ni increased with decreasing pH in all the soils. The results showed that one unit increase in pH by liming could reduce the Ni toxicity by a factor of 2-6. The effects were bigger at near neutral pH than at lower pH. The difference in the toxicity of Ni in the three soils reflected the various extent of Ni bioavailability, and corresponded to the difference in the soil binding capacities for Ni measured in a batch desorption experiment. With the simulation calculations using the multi-surface speciation model, the effects of pH and soil characteristics on the chemical speciation of Ni in the soils were studied. The results showed that soil organic matter binds Ni much stronger than clay and iron hydroxides at a relatively low pH. At close to neutral pH, iron hydroxides became an important sorbing surface. The EC_{50} of Ni in the 0.01M $CaCl_2$ extraction of all the soils was in the range of 24-58 μM varying by a factor of about 2. Nickel concentration in the extraction with 0.01M $CaCl_2$ was closely related to the plant uptake and to the growth response and was a much better indicator of the bioavailability of Ni than the total Ni concentration in the soils.

Further, the effects of pH on the bioavailability and toxicity of Ni to oats have been also studied with a solution culture experiment, and the results were compared with those from the soil pot experiments. Opposite to the pot experiment, with the increase in pH, the toxicity of Ni was intensified in the solution culture. The EC_{50} of Ni in the nutrient solution decreased from 23 to 1.7 μM at pH 4-7, varying by a factor of 14. No such pH dependency has been found for the EC_{50} of Ni in the 0.01M $CaCl_2$ soil extractions, which was in the range of 58-24 μM . Using the Donnan membrane technique, the speciation of Ni in the 0.01 M $CaCl_2$ extraction of the soil samples taken from the pot experiments was analysed. Similar to the solution culture, the EC_{50} of free Ni^{2+} in the 0.01 M $CaCl_2$ soil solution (44-10 μM) decreased with increasing pH, but they were generally higher than the EC_{50} of Ni^{2+} in the solution culture. The EC_{50} of Ni in the oats straw from the solution culture were between 1.2 and 2.8 mmol/kg, similar to the EC_{50} of Ni in the oats grown in a sandy soil (1.6-2.5 mmol/kg), indicating that the metal concentration in the biota is a better indicator for metal

toxicity than the total metal concentration in the media. The effects of pH on Ni uptake from the sandy soil could be predicted reasonably well with the quantitative approach using the results of Ni desorption from the soil and Ni uptake from the nutrient solution. The pH effects on Ni binding to the soil exceed the pH effects on the Ni uptake, therefore a decrease of Ni uptake and toxicity in soil is predicted at increasing pH.

Concluding remarks

In this research, the interactions between the metal ions and the biogeo-surfaces are studied from several aspects, which are linked by comparison of measurement with modelling, distribution with solubility, speciation with toxicity.

The developed Donnan membrane technique is proven to be a useful analytical technique for the determination of metal speciation in soil and water samples. The major limitation of this technique at present is the detection limit constrained by the ICP-MS. The concentrations of the heavy metals in the soil solution and in the waters are often below this detection limit. Further research is needed to improve the method to make it capable to measure lower concentrations.

The multi-surface model approach developed in this research has been validated against the measured free metal activity and metal concentration in soil solution of a sandy soil for Cu, Cd, Zn, Ni and Pb and of two sandy soils and a clay soil for Ni. Validation and improvement of this model approach can be achieved after comparing the predictions with the measurements for more different soils. The model calculations have shown that the metal binding to the major soil surfaces: soil organic matter, clay and iron hydroxides, are important in the control of metal speciation in the soils. At this stage of the modelling, the interactions between the various surfaces and their effects on the metal binding are neglected. The binding of metals is calculated as the additive results to the various surfaces. In addition, metal binding to oxides and clay are treated in a simpler way compared to soil organic matter. The effects of the binding of many anions on the metal binding to oxides are not yet accounted for. Further research is necessary to improve the modelling approach and to make it closer to the situation in the field.

Samenvatting

Introductie

De interacties tussen metaalionen en biogeo-oppervlakken in grond en water zijn belangrijk bij de buffering van de speciatie, en daarom van belang voor de biologische beschikbaarheid en mobiliteit van zware metalen. Deze interacties zijn eveneens van belang bij het bepalen van de oplosbaarheid en mobiliteit van natuurlijke organische stof, welk op zijn beurt de oplosbaarheid van zware metalen weer beïnvloedt. Een beter begrip en kwantificering van de interacties tussen metaalionen en biogeo-oppervlakken in bodem en water zijn de basis voor een verbetering van de kwantitatieve risico beoordeling van zware metalen in het milieu. In dit proefschrift zijn zowel experimenten en modelconcepten toegepast om een beter inzicht te krijgen in de processen die de zware metalen interacties beïnvloeden tussen bodem organische stof (vast en opgelost), klei, ijzer(hydr)oxiden en planten. Het doel is tevens inzicht verkrijgen in het relatieve belang van verschillende fasen op de metaalspeciatie, biologische beschikbaarheid en mobiliteit.

Donnan membraan techniek (DMT)

Het is algemeen aanvaard dat het 'vrije' metaalion de sleutelfactor is in de bepaling van de metaalbeschikbaarheid. Echter, accurate metingen van 'vrije' metaalionen zijn moeilijk, speciaal voor metaalionen bij lage concentraties (lager dan micromolair) in natuurlijke systemen. De recentelijk ontwikkelde Donnan membraan techniek kan zware metaal concentraties meten in oplossing in de aanwezigheid van anorganische en organische complexvormers. De techniek is verder ontwikkeld om het toepasbaar te maken voor bodemmonsters. De belangrijkste ontwikkeling is de koppeling van een grondkolom met de Donnan cel. De operationele aspecten van de methode, inclusief evenwichttijd, bufferend vermogen en correcties voor verschillen in ionsterkte, zijn onderzocht en geoptimaliseerd. De methode is toegepast voor het bepalen van 'vrij' Cu^{2+} , Cd^{2+} , Pb^{2+} en Zn^{2+} in de bodemoplossing van 15 grondmonsters. Vergeleken met andere speciatie methoden heeft de Donnan membraan methode het voordeel dat het de mogelijkheid heeft om simultaan verschillende vrije metaalionen te meten waarbij het bodemsubstraat nagenoeg niet wordt verstoord. De detectielimiet van de Donnan membraan techniek is ongeveer 10^{-9} M. De techniek kan worden toegepast bij het bestuderen van het biogeochemisch gedrag van metalen in grond, sediment en andere vaste stoffen.

In natuurlijke wateren, inclusief bodemoplossingen, is aluminium een sterke competitor voor zware metalen ten aanzien van binding aan colloïdale deeltjes zoals organische stof. De studie naar Al speciatie is van belang voor de beoordeling van bodem en waterkwaliteit. Voor de meting van 'vrij' aluminium (Al^{3+}) is de Donnan membraantechniek getoetst door middel van het meten van Al^{3+} in een aluminiumfluoride oplossing en gibbsietsuspensies. Hieruit bleek dat de Donnan membraantechniek 'vrij' Al^{3+} kan meten tot 10^{-9} M en dat de evenwichtinstelling ongeveer 3 tot 4 dagen duurt. Aluminiumbinding aan humuszuur (HA), gezuiverd van een bosgrond, is gemeten door gebruik te maken van de Donnan membraantechniek of de gibbsiet suspensie. De resultaten zijn vergeleken met de voorspellingen van het NICA-Donnan model. De voorspellingen met generieke parameters (zonder aanpassing) kwamen goed overeen met de gemeten data. Tevens is de Donnan membraantechniek gebruikt voor het bepalen van Al binding aan opgeloste organische stof (DOM) in bodemoplossingen van 24 grondmonsters in een pH range van 3-7. De metingen komen goed overeen met de voorspellingen van het NICA-Donnan model waarbij is aangenomen dat 30 % van DOM is humuszuur en 30 % fulvozuur. Met dit model wordt het effect van de pH- en DOM-veranderingen op de Al concentraties redelijk goed voorspeld voor 81 bodemoplossingen zonder hiervoor modelparameters aan te passen. De vergelijking tussen de analyse resultaten en de modelberekeningen geeft de mogelijkheid om de twee methoden te valideren.

Multi-oppervlak model

Alhoewel metingen de meest directe en waarschijnlijk de meest juiste informatie geven van metaalspeciatie, blijven er beperkingen ten aanzien van de detectielimiet, die vaak boven de natuurlijke metaalionen concentratie ligt. Tevens is de verdeling van zware metaalionen over de verschillende reactieve vaste oppervlakken moeilijk experimenteel te bepalen. Zonder een model kunnen de effecten van veranderingen in milieuomstandigheden op de metaalspeciatie niet kwantitatief worden voorspeld. In dit onderzoek is een multi-oppervlak model gebruikt om een schatting te kunnen maken van de bijdrage van de diverse bindingsoppervlakken die de metaalionen activiteit reguleren in zandgronden met een pH range van 3,7-6,1 en verschillende hoeveelheden bindingscomponenten. Het multi-oppervlak model benadert de bodem als een set van onafhankelijke bindingsoppervlakken, te weten organische stof (NICA-Donnan), klei silicaten (Donnan) en ijzer(hydr)oxiden (DDL, CD-MUSIC). De activiteiten van Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} en Pb^{2+} in evenwicht met de bodem zijn gemeten met de Donnan membraantechniek. De metaalactiviteiten voorspeld met behulp van het model

komen goed overeen met de gemeten concentraties over een grote range voor alle gemeten metalen met uitzondering van Pb. De modelberekeningen geven aan dat bodem organische stof de meest belangrijke bindingscomponent is die de activiteit van Cu^{2+} , Cd^{2+} , Zn^{2+} and Ni^{2+} reguleert in deze zandgronden. Wanneer de hoeveelheid metaal hoog is in vergelijking met het organisch stof gehalte dan wordt de bijdrage van klei silicaten belangrijker. Adsorptie aan ijzer(hydr)oxiden is niet significant in deze monsters voor Cu, Cd, Zn en Ni. Echter voor Pb schat het model sterke adsorptie aan ijzer(hydr)oxiden. Het model voorspelt dat bodemverzuring niet alleen zal leiden tot een toename in metaalconcentraties maar ook tot een verschuiving naar meer niet-specifieke kation uitwisseling type van binding, vooral voor de metalen Cd, Zn en Ni. Verlaging van de pH met ruim 2 eenheden heeft geleid tot een afname in de zandgronden van 56 % voor Cd, 69 % van Zn en 66% van Ni gedurende 16 jaar door toegenomen metaaluitspoeling

De complexering van zware metalen met opgeloste organische stof (DOM) in het milieu beïnvloedt de oplosbaarheid en de mobiliteit van deze zware metalen. De complexering van de zware metalen Cu, Cd, Zn, Ni en Pb met DOM in bodemoplossing, bij een pH range van 3,7-6,1, is gemeten door gebruik te maken van de Donnan membraan techniek. Uit de resultaten bleek dat deze DOM-complexen over het algemeen significant vaker voorkomen voor Cu en Pb dan voor Cd, Zn en Ni. Deze data maakt het mogelijk om twee geavanceerde modellen voor ionbinding aan organische stof, te weten de Model VI en NICA-Donnan, met elkaar te vergelijken ten opzichte van de metingen. Door gebruik te maken van generieke parameters voor fulvo- en humuszuren blijken de twee modelvoorspellingen van de 'vrije' metaalionen concentraties in de meeste gevallen niet meer dan een log eenheid van de gemeten waarden te verschillen. Tevens is de verdeling van de zware metalen over de vaste stof en oplossing gesimuleerd door gebruik te maken van het multi-oppervlak model, waarbij bodem organische stof, opgeloste organische stof, klei en ijzer(hydr)oxiden zijn meegenomen voor adsorptie en kationuitwisseling modellen (NICA-Donnan, Donnan, DDL, CD-MUSIC). Het model gaf een redelijk goede schatting van de opgeloste concentraties van alle zware metalen behalve voor Pb. De oplosbaarheid van zware metalen hangt voornamelijk af van de bodembindingscomponenten, pH en de concentratie van anorganische liganden en DOM in de bodemoplossing.

Oplosbaarheid en mobiliteit van organische stof

De interactie tussen metaalionen en natuurlijke organische stof is niet alleen belangrijk voor de metaaldistributie maar ook voor de oplosbaarheid en mobiliteit van organische stof. De coagulatie van humusbestanddelen en zijn rol in het reguleren van de oplosbaarheid van organische stof is niet duidelijk. Daarom werd het fysisch-chemisch gedrag van gezuiverd humuszuur van een bosgrond bestudeerd middels coagulatie-experimenten met Na, Ca, Cu en Al bij pH 4 en 6. Vervolgens werd het coagulatiegedrag gemodelleerd met het NICA-Donnan model. Coagulatie van humuszuur vond telkens plaats bij een Donnan potentiaal lager dan $-0,08\text{V}$. Op basis van deze resultaten werd een empirische relatie tussen de Donnan potentiaal van humuszuur en zijn concentratie in oplossing afgeleid. Vervolgens werd de Donnan potentiaal van opgeloste organische stof in bodemoplossing van zes bosgrond bodemprofielen berekend met behulp van het NICA-Donnan model met de aanname dat alle opgeloste organische stof zich gedraagt als humuszuur. De gemeten concentratie van opgeloste organische stof neemt af in een bodemprofiel als ook de berekende potentiaal minder negatief is. De resultaten zijn in veel gevallen in kwantitatief opzicht in overeenstemming met de voorspelde concentratie gebaseerd op het humuszuur coagulatie-experiment. Zure gronden bevatten meer opgeloste organische stof, hetgeen mogelijk veroorzaakt wordt door de relatief grote fractie aan makkelijk oplosbare organische zuren, zoals fulvozuren.

Transport van anorganische en organische verontreinigingen in water en grond kunnen sterk beïnvloedt worden door de mobiliteit van natuurlijk opgeloste organische stof (DOM). In dit proefschrift werd het transport van een humus zuur (HA) en een fulvozuur (FA) in een met koper verontreinigende zandgrond bestudeerd. De meetresultaten laten zien dat het transport gedrag van HA verschilt van FA. De doorbraakcurven (BTC's) van HA worden gekarakteriseerd door een relatief scherp front gevolgd door een plateau bij een lagere HA concentratie dan in de influentoplossing. Een toename van de Ca concentratie laat de HA concentratie verder dalen. Ten opzichte van HA zijn de BTC's van FA sterker geretardeerd en vertonen een sterke tailing richting een complete doorbraak. Een toename in de Ca concentratie laat de FA concentratie slechts tijdelijk dalen. Gebaseerd op onze modelberekeningen kon het HA transport verklaard worden door de coagulatie van HA ten gevolge van Al binding. Een toename van de Ca concentratie resulteerde in een verdere HA coagulatie ten gevolge een toenemende Ca binding, welke hoofdzakelijk plaats vindt in de Donnan fase. Wat betreft FA lijkt de adsorptie aan de bodemmatrix een meer logisch proces

dat de oplosbaarheid en mobiliteit reguleert. De mobiliteit van Al en Cu in de grondkolom was nauw gerelateerd aan de oplosbaarheid en het transport van opgeloste organische stof in de bodemoplossing. De concentratie van Ca in het effluent was lager dan in de influent concentratie aangezien Ca achter bleef in de kolom ten gevolge van de retardatie van HA en FA en door de compensatie van andere kationen die van de grond naar de oplossing zijn gegaan.

Interpretatie van de toxicologische data van Ni

De ontwikkelde experimentele en model benaderingen zijn bruikbaar bij de verbetering van een kwantitatieve risico beoordeling van zware metalen. Door gebruik te maken van de modellen en de ontwikkelde meetmethoden zijn de resultaten van de pH effecten op nikkeltoxiciteit van planten meer in detail bestudeerd. Voor het bestuderen van nikkel fytotoxiciteit op tarwe en de effecten van pH en bodem karakteristieken hierop zijn potexperimenten uitgevoerd met drie verschillende gronden, nl. een zandgrond, een zandgrond met een relatief hoog gehalte aan organische stof en ijzer(hydr)oxiden en kleigrond. De EC_{50} van toegevoegd Ni ten opzichte van de afname van de gewasopbrengst lag tussen de 0,7 en 22,5 mmol/kg, oftewel variërend met een factor 32 afhankelijk van grondtype en pH (pH range 4,7 - 7,0). De toxiciteit van Ni, in termen van totaal Ni, neemt toe met afnemende pH voor alle gronden. De resultaten laten zien dat het verhogen van de pH met een eenheid, middels bijvoorbeeld bekalken, de Ni-toxiciteit kan gereduceerd worden met een factor 2-6. De effecten zijn groter bij neutrale pH dan bij zure pH. De verschillen in de Ni toxiciteit van de drie gronden komen overeen met de verschillen in Ni beschikbaarheid en corresponderen met de verschillen in bindingscapaciteiten van Ni gemeten met behulp van desorptie experimenten. Met behulp van simulatie berekeningen, waarbij het multi-oppervlak model is gebruikt, zijn de effecten van pH en bodemkarakteristieken op de chemische speciatie van Ni bestudeerd. De resultaten laten zien dat bodem organische stof Ni veel sterker bindt dan klei en ijzer(hydr)oxiden bij relatief lage pH. Bij nagenoeg neutrale pH worden ijzer(hydr)oxiden een belangrijk bindingsoppervlak. De EC_{50} van Ni in de 0,01 M $CaCl_2$ extracten van alle gronden was in de range van 24-58 μM , en varieerde met een factor van ongeveer 2. Nikkel concentraties in de 0,01 M $CaCl_2$ waren nauw gerelateerd aan de plantopname en aan de groei respons en was dus een veel betere indicator voor de biologische beschikbaarheid van nikkel dan het totaal gehalte van nikkel in de grond.

Tevens zijn de effecten van pH op de biologische beschikbaarheid en toxiciteit van Ni op tarwe bestudeerd in een watercultuur experiment en deze resultaten zijn vergeleken met de resultaten van de potexperimenten. De toxiciteit van Ni in watercultuur oplossingen neemt toe met de toename van de pH hetgeen tegengesteld is van de potexperimenten. De EC_{50} van Ni in de voedingsoplossing neemt af van 23 tot $1,7 \mu\text{M}$ bij een pH tussen 4 en 7, oftewel variërend met een factor 14. Echter er is geen pH afhankelijkheid gevonden voor de EC_{50} van Ni in de $0,01\text{M CaCl}_2$ grondextracten, welke in de range van $58\text{--}24 \mu\text{M}$ lagen. Door gebruik te maken van de Donnan membraan techniek is de speciatie van Ni in $0,01\text{M CaCl}_2$ grondextracten van de potexperimenten geanalyseerd. Vergelijkbaar met de watercultuur oplossingen nam de EC_{50} van 'vrij' Ni^{2+} in de $0,01 \text{ M CaCl}_2$ grondextracten af ($44\text{--}10 \mu\text{M}$), maar lag in het algemeen hoger dan de EC_{50} van 'vrij' Ni^{2+} in de watercultuur oplossingen. De EC_{50} van Ni in de tarwe plant van de watercultuur oplossingen lag tussen 1,2 en de $2,8 \text{ mmol/kg}$, hetgeen vergelijkbaar is met de EC_{50} van Ni in de tarwe die gegroeid is op een zandgrond, hetgeen aangeeft dat het totaal metaal gehalte in de biota een betere indicator is voor metaal toxiciteit dan het totaal metaal gehalte in het medium waar de plant in groeit. De effecten van pH op de Ni-opname van de zandgrond kon redelijk goed voorspeld worden met een kwantitatieve benadering waarbij gebruik gemaakt is van de Ni-desorptie van de grond en Ni-opname van de watercultuur oplossing. De pH effecten op de Ni binding aan de grond zijn sterker dan de pH effecten op de Ni opname waardoor een afname van de Ni-opname en de toxiciteit in grond is voorspeld bij toename van de pH.

Conclusies en opmerkingen

In dit onderzoek, zijn de interacties tussen metaal ionen en biogeo-oppervlakken bestudeerd vanwege diverse aspecten welke gekoppeld zijn met de vergelijking tussen metingen met modellen, distributie met oplosbaarheid en speciatie met toxiciteit.

De ontwikkelde Donnan membraan techniek heeft bewezen een bruikbare analytische techniek te zijn voor de bepaling van metaalspeciatie in grond en watermonsters. De grootste limitering van deze techniek is op dit moment de detectielimiet die bepaald wordt door de ICP-MS. De concentratie van zware metalen in de bodemoplossing en in wateren liggen vaak lager dan deze detectielimiet. Meer onderzoek is nodig om de methode te verbeteren om het bruikbaar te maken voor het meten van nog lagere concentraties.

Het multi-oppervlak model benadering, ontwikkelt in dit onderzoek, is gevalideerd door het meten van de 'vrije' metaal activiteit en de totaal metaal concentratie in bodemoplossing en van een zandgrond voor Cu, Cd, Zn, Ni en Pb en voor twee zandgronden en een kleigrond voor Ni. Validatie en verbetering van het model kunnen worden bereikt door het vergelijken van de voorspellingen en de metingen voor meer verschillende gronden. De modelberekeningen hebben aangetoond dat de metaalbinding aan de bodemcomponenten: organische stof, klei en ijzer(hydr)oxiden, de belangrijkste in het reguleren van de metaalspeciatie in grond. Op dit moment zijn bij het modelleren de interacties tussen de verschillende bodemcomponenten en de effecten hiervan op de metaalbinding zijn niet meegenomen. De totale binding van metalen is berekend als de som van de binding aan de afzonderlijke componenten. Tevens is de binding aan oxiden en klei op een eenvoudiger manier meegenomen in vergelijking tot organische stof. Met de effecten van de binding van veel anionen op de metaalbinding aan oxiden is op dit moment nog geen rekening gehouden. Meer onderzoek is nodig om de modelbenadering te verbeteren en om de veldsituatie beter te benaderen.

土壤和水中金属离子与生物、矿物表面的相互作用 定量风险评估的基础

论文摘要

研究背景

金属离子与土壤和水中生物及矿物表面的相互作用在控制其化学形态分布上起着重要作用。这一相互作用也影响到天然有机物的可溶性和迁移性，从而影响重金属的溶解性。对于土壤和水中的金属离子与生物、矿物表面相互作用的深入理解和量化计算，是重金属环境风险定量评估的基础。本论文运用实验和模型的方法，以更好地了解影响重金属和土壤有机物、粘土矿物、铁氢氧化物及植物相互作用的因素，同时揭示各土壤成份在控制金属分布、生物有效性及迁移性的相对重要性。

Donnan膜方法

自由态金属离子常被看作决定金属生物有效性的关键。但是，精确测定自由态金属离子是困难的，特别是天然样品中的微量元素，其浓度常常很低(低于纳摩尔浓度)。近来发展的Donnan膜方法可以测定含有无机、有机复合剂溶液中的离子浓度。本论文进一步发展了这一方法使之适应于土壤样品的分析。主要的改进是将土壤柱与Donnan平衡室连接起来。并对诸如平衡时间、缓冲能力、及离子强度的校正等方面进行了研究和优化。应用这一方法，我们测定了15个土样中 Cu^{2+} 、 Cd^{2+} 、 Pb^{2+} 、 Zn^{2+} 的浓度。与其它的测定方法相比，Donnan膜法具有可同时测定多个元素的优点，并最大程度上减少了对待测液平衡的干扰。现阶段的Donnan膜法的检测下限为 10^{-9}M 左右。这一方法可用于研究金属离子在土壤、沉积物及其它固态物中的生物、地球化学行为。

在天然水体包括土壤溶液中，铝对重金属在土壤有机物等胶体颗粒表面的吸附有很强的竞争作用。研究铝的化学形态有助于土壤和水体质量评估。通过测定铝-氟溶液和氢氧化铝悬浮液中铝离子(Al^{3+})的浓度，我们检验了Donnan膜法测定自由态铝离子的可行性。结果显示，Donnan膜法能可靠的测定高于 10^{-9}M 的 Al^{3+} 的浓度，平衡时间为3-4天。利用Donnan膜法或氢氧化铝悬浮液我们测定了铝在森林土壤中提取的腐质酸上的吸附，并将测定结果与NICA-Donnan模型预测结果进行了比较。结果显示，使用未经调整的原系数所作的预测和测定结果吻合良好。此外运用Donnan膜法，我们也测定了pH在3-7范围的24个土样溶液中铝在可溶有机物(DOM)上的吸附。所测结果与在假设30

%的DOM为腐质酸, 30%的DOM是富丽酸的条件下NICA-Donnan模型预测较好的吻合。使用这一模型较好的预测了pH和DOM浓度的变化对81个土壤溶液中铝浓度变化的影响。分析与模型结果的比较为这两种方法提供了双向检验。

多种表面模型

尽管测定提供了金属化学形态的最直接的数据, 但直接测定有其局限性, 比如检测下限常高于实际浓度。而且, 重金属在各固态表面的分布, 难以通过实验确定。仅靠分析的方法不采用模型计算, 不能定量预计环境条件变化对金属化学形态的影响。本研究采用一多种表面模型, 估算了有不同含量吸附表面、pH值在3.7-6.1之间的沙土样品中, 各吸附表面在控制重金属离子活度上的相对重要性。这一多种表面模型把土壤看作含有一组各自独立的吸附表面的集合体。吸附表面包括: 有机质(NICA-Donnan模型), 硅酸盐粘土矿物(Donnan模型)和铁氢氧化物(DDL, CD-MUSIC模型)。采用Donnan膜法, 测定了这些土样中与土壤保持化学平衡的 Cu^{2+} 、 Cd^{2+} 、 Zn^{2+} 、 Ni^{2+} 、 Pb^{2+} 的离子活度。除去铅例外, 在很大浓度范围上模型预测的离子活度与所测定的结果吻合较好。模型结果显示, 在这些沙土样中, 土壤有机物是控制 Cu^{2+} 、 Cd^{2+} 、 Zn^{2+} 、 Ni^{2+} 活度的最重要的吸附相。当与土壤有机物含量相比金属总含量较高时, 金属在粘土矿物上的吸附才变得较为重要。在这些样品中, 铁氢氧化物对 Cu^{2+} 、 Cd^{2+} 、 Zn^{2+} 、 Ni^{2+} 的吸附不占主要地位。但据模型预测铁氢氧化物可较强地吸附 Pb^{2+} 。模型预计土壤酸化不仅导致溶液中金属浓度的增加, 而且使吸附倾向于非特异性离子交换状态, 特别是对 Cd^{2+} 、 Zn^{2+} 、 Ni^{2+} 影响更大。在16年期间, pH值降低导致的淋洗增加使土壤中Cd、Zn、Ni的含量分别降低了56%、69%、66%。

自然环境中重金属与可溶性有机物(DOM)的络合会影响这些金属的溶解性和移动性。使用Donnan膜法, 我们测定了pH值在3.7-6.1之间的土壤溶液中Cu、Cd、Zn、Ni、Pb与DOM的络合。结果显示与DOM的络合对Cu、Pb比对Cd、Zn、Ni更重要。通过比较模型预测值和测定结果, 检验了两个描述离子在腐植质上吸附的先进模型: ModelVI和NICA-Donnan, 模拟金属在天然可溶性有机物上吸附的能力。采用这两个模型使用富丽酸和腐质酸的原系数进行了溶液化学形态计算, 所得到的自由态离子的浓度与测定值的差别绝大多数在一个数量级内。另外应用多种表面模型模拟了金属的固-液态分配。其中, 运用吸附和离子交换模型计算了金属离子在土壤有机物(NICA-Donnan), 可溶性有机物(NICA-Donnan), 粘土矿物(Donnan), 和铁氢氧化物(DDL, CD-MUSIC)上的吸附。模型较好的估计了除Pb外的其它金属的溶液浓度。金属的可溶性主要取决于金属相对土壤吸附相的含量、pH值和土壤溶液中无机络合物及DOM浓度。

有机质的溶解性和移动性

金属离子与天然有机质的相互作用不仅对金属的分布很重要,而且影响到有机质的溶解性和移动性。腐植质的凝聚过程及其在控制土壤有机物溶解性的作用尚未得到很好地理解。因此我们研究和利用NICA-Donnan模型模拟了森林土壤中提取的腐植酸在pH4和6下被钠、钙、铜、铝凝聚时的物理化学行为。我们发现,当腐植酸的Donnan电势高于-0.08伏(绝对值减少)时将会发生凝聚。基于这一结果回归得到腐植酸的Donnan电势与其在溶液中的浓度的经验关系式。此外,假设可溶性有机物为腐植酸,应用NICA-Donnan模型计算了6个森林土壤层面土壤溶液中DOM的Donnan电势。当所计算的电势绝对值减小时,所测定的同一土壤各层面中DOM浓度也减少。在多数情况下,测定结果与基于腐植酸凝聚的结果所作的预测值半定量吻合。酸性土壤中含有较多的可溶性有机物,可能是由于大量的溶解性强的有机物如富丽酸存在的结果。

水与土壤里的有机、无机污染物的迁移受到天然可溶性有机质的移动性的很大影响。在本论文中,研究了一铜污染酸性沙土中腐质酸(HA)和富丽酸(FA)的迁移。数据显示HA的迁移行为不同于FA。HA的穿透曲线(BTC)的特征为一快的、较陡的前锋,跟随一低于进液HA浓度的平顶。进液中钙浓度的提高进一步降低了HA的浓度。与HA相比,FA的穿透曲线滞后,并有长的拖尾,趋近于完全穿透。钙浓度的增加,只使FA的浓度暂时降低。基于我们的模型计算,HA迁移的特征很大程度上可由铝吸附引起的HA的凝聚来解释。钙浓度的提高使吸附的钙增加(主要在Donnan相),从而使HA进一步凝聚。对FA来说,在土壤介质上的吸附更可能是控制其溶解性和移动性的机制。铝和铜在土柱中的移动性与土壤溶液中可溶性有机物的溶解性和移动性密切相关。由于HA和FA的滞留,和补偿从土壤释放到溶液中的其它阳离子,钙被存留于土壤中,所以淋出液中钙浓度低于进液。

镍毒性数据的解释

上述的实验与模型手段有助于提高重金属的定量风险评估。运用这些方法,我们更详细地研究和阐述了pH值对镍的植物毒性的影响结果。已有的盆栽实验结果显示了镍对燕麦的植物毒性及pH和土壤特性的影响。该实验采用三种不同的土壤:沙土、含较多有机质和铁氢氧化物的沙土、粘土。降低茎杆生物量的镍的 EC_{50} 值在0.7和22.5mmol/kg之间,因土壤和pH(4.7-7.0)的不同,相差32倍。以全镍含量表示的镍毒性在所有土壤中随pH的升高而降低。结果显示,施用石灰使pH每升高一个单位,镍毒性降低2-6倍。接近中性pH的效果大于在较低pH时的效果。三种土壤中镍的不同毒性反映了镍的不同程度的生物有效性,也与在解吸实验中所测定的不同土壤吸附镍的能力相对应。应用多种表面模型的模拟计算,研究了pH和土壤特性对镍在土壤中化学形态分布的影

响。结果指出,在较低pH下,土壤有机质吸附镍的能力高于粘土矿物和铁氢氧化物。在接近中性pH时铁氢氧化物成为重要的吸附表面。0.01M CaCl_2 土壤提取液中镍的 EC_{50} 值在24-58微摩尔之间,变化范围大约为2倍。0.01M CaCl_2 土壤提取液中镍的浓度与植物的吸收和生长反应密切相关,是较于土壤中全镍含量更好的生物有效性的指示指标。

通过一溶液栽培实验及与土壤盆栽实验的比较,我们进一步研究了pH对镍在燕麦上的生物有效性和毒性。与盆栽实验相反,pH值的升高强化了溶液栽培中镍的毒性。营养溶液中镍的 EC_{50} 值在pH4-7时为23-1.7微摩尔,相差14倍。而0.01M CaCl_2 土壤提取液中镍的 EC_{50} 值在24-58微摩尔之间,未发现类似的pH相关性。使用Donnan膜法,分析了盆栽土样0.01M CaCl_2 提取液中镍的化学形态分布。与溶液培养结果相似,0.01M CaCl_2 土壤提取液中自由态 Ni^{2+} 离子的 EC_{50} 值(10-44微摩尔)也随pH的增高而降低,但普遍高于溶液培养中自由态 Ni^{2+} 离子的 EC_{50} 值。溶液栽培后燕麦组织中镍的 EC_{50} 值在1.2-2.8mmol/kg,近似于栽培于沙土中的燕麦中镍的 EC_{50} 值(1.6-2.5mmol/kg),表明生物体内的金属含量比较于介质中金属的总含量来说能更好地指示金属的毒性。使用镍从土壤上的解析结果和植物从营养液中吸收镍的结果,运用定量方法,可较好地预测pH对植物从土壤中吸收镍的影响。pH对镍在土壤上吸附的影响超过对植物吸收镍的影响,因此,pH增加预示着土壤中镍的吸收和毒性的降低。

结尾评述

本论文从几个方面研究了金属与生物、矿物表面的相互作用。通过比较测定与模拟、分布与溶解性、化学形态与毒性而贯穿。

所发展的Donnan膜法被证明为测定土壤和水样品中金属形态分布的有用方法。目前这一技术的主要局限性是其由ICP-MS制约的检测下限。土壤溶液和水中的重金属浓度常常低于检测下限。需要进一步的研究来完善这个方法使其能测定更低的浓度。

本研究所提出的多种表面模型已被测定的一沙土溶液中铜、镉、锌、镍、铅,和两种沙土及一粘土中镍的离子浓度和溶液浓度所验证。对更多不同土壤的测定值和模型计算值的比较,可进一步验证这一模型。模型计算结果显示金属在土壤主要表面:土壤有机质、粘土矿物、和铁氢氧化物上的吸附,对控制其在土壤中的分布起重要作用。在现阶段,模型尚未考虑不同表面的相互作用及其对金属吸附的影响。另外,与土壤有机物相比,对金属在粘土矿物和铁氢氧化物上吸附的处理还比较简化,还没有将阴离子对金属在氧化物上吸附的影响考虑在内。需要进一步的研究来完善这一模型使之更接近于实际环境中的情况。

Epilogue

The thesis that is laying in your hands now is a result of several years' work. Reading literature, working in the lab, calculating and modelling, discussing, long time writing behind the computer... a period full of learning, thinking, inspiration and enthusiasm. Now the thesis is finished, but life and research will go on.

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Liping Weng

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Liping Weng was born on the 29th January, 1965 in Tianjin, China. After finishing high school in 1982, she studied Biology in Nankai University (China) and received her BSc. of plant physiology in 1986 and MSc. of plant nutrition in 1989. During 1989 and 1996, she worked at Tianjin Soil Science Institute (China) as a research fellow. In 1995, she had a 3 months workshop in Japan about soil management. In 1996, she came to Wageningen, the Netherlands. She studied Environmental Science in Wageningen University and got her MSc. with distinction in 1998. From 1998 to 2002, she was a research assistant (AIO) in the Soil Quality group of Wageningen University. The important results of her research during this period are presented in this thesis. After getting her Ph.D, she will continue her research in the Soil Quality group of Wageningen University as a postdoc.

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