Chemical Speciation of Heavy Metals in Sandy Soils

in Relation to Availability and Mobility

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Aan: Anneke, Daan en ..Jesse

Leef en beleef!
Er bestaat maar een ding in de kosmos
en dat is: het leven
De rest is illusie
illusie en niets dan illusie .....

uit: Het lelietheather; een jeugd in China
       Lulu Wang, Vassallucci, Amsterdam 1997

Stellingen

1. Indien competitie en complexering van zware metalen in de bodem niet meegenomen wordt bij modelberekeningen over uitspoeling, dan wordt de uitspoeling van deze metalen ten gevolge van milieu veranderingen niet goed geschat.

    Dit proefschrift

2. Het uitspoelen van calcium tijdens bodemverzuring heeft een positief effect op de vastlegging van cadmium in de bodem.

    Dit proefschrift

3. De suggestie van Janssen *et al.* (1997) dat ijzer(hydr)oxiden belangrijk zijn bij de koper speciatie in de bodem is onjuist.

    Janssen, R.P.T.; Pretorius, P.J.; Peijnenburg, W.J.G.M. & Van den Hoop M.A.G.T. *Determination of field-based partition coefficients for heavy metals in Dutch soils and the relationship of these coefficients with soil characteristics.* RIVM rapport 719101023.

    Dit proefschrift

4. Het laten ontstaan van een strooisellaag op een met koper verontreinigde grond heeft een verhoogde koper uitspoeling tot gevolg.

    Dit proefschrift

5. Het coaguleren van opgeloste organische stof hangt af van de waardigheid én de bindingssterkte van kationen.

    Dit proefschrift

6. Veranderend landgebruik zal een groot effect hebben op de beschikbaarheid en de mobiliteit van cadmium en koper in de bodem.

    Dit proefschrift

7. Voor het uitvoeren van urgentie bepalingen bij bodemsanering van met zware metalen verontreinigde grond is het essentieel, om naast een 'totaal' analyse, een extractie met een neutrale zout oplossing (bv. calciumchloride) uit te voeren.

8. Het toevoegen van EDTA of DTPA (synthetische complexvormers) aan calciumchloride extracties maakt het interpreteren van de data, letterlijk en figuurlijk, complexer.

9. Het verkleinen van de varkensstapel is niet alleen aan te raden vanwege de kans op varkenspest, maar ook vanwege de hoge koperbelasting van de Nederlandse bodem door toediening van deze mest.

10. Het beoogde effect van het reduceren van het kopergehalte in varkensvoer vanwege de hoge koperbelasting van de bodem via de mest is nagenoeg volledig te niet gedaan door de toename van het aantal varkens in dezelfde periode.

11. De beste milieumaatregelen zijn die waar geen beloningen of bekeuringen voor noodzakelijk zijn.

12. Als je het dal niet gezien hebt zul je nooit weten hoe hoog de bergen zijn.
    Chinees spreekwoord

13. Hoe sneller het vervoermiddel hoe langer het wachten bij de pont 'Lexkesveer'.

14. Technology is blind without analytical work!
    Prof. Dr. H.M. Ortner, Darmstadt.

15. Het plezier in een sport wordt mede bepaald door de gezelligheid na het sporten.

Stellingen behorend bij het proefschrift 'Chemical Speciation of Heavy Metals in Sandy Soils in Relation to Availability and Mobility' van Erwin J.M. Temminghoff, 18 maart 1998.

Voorwoord

De afgelopen vijf jaar heb ik een groot deel van mijn tijd besteed aan mijn promotie-onderzoek, waarvan een deel van de resultaten beschreven is in dit proefschrift. Veel mensen hebben een bijdrage geleverd aan de tot standkoming van dit proefschrift en hen wil ik dan ook graag bedanken in dit voorwoord.

Allereerst wil ik graag mijn promotor Frans de Haan bedanken. Hij was het die mij in 1987 promootte tot het volgen van een studie aan de LU. In 1992 was hij het opnieuw die mij stimuleerde om ook een promotie-onderzoek te gaan doen. Voor het vertrouwen dat hij al die jaren in mij gehad heeft ben ik hem zeer dankbaar. Ik hoop dat we nog lang vrienden blijven. Daarnaast wil ik graag mijn co-promotor Sjoerd van der Zee bedanken, die mij een grote mate van zelfstandigheid liet, hetgeen belangrijk was voor mijn ontwikkeling. Bij de verwerking van de resultaten was jij voor mij een belangrijke steun en kon jij mij op de juiste momenten stimuleren. Sjoerd, ik hoop dat we ook in de toekomst nog samen aan een paar onderwerpen blijven werken. Kees Koenders wil ik bedanken voor het in mij gestelde vertrouwen en de mogelijkheden die hij mij geboden heeft. Deze waren belangrijk voor het slagen van dit promotie-onderzoek.

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Abstract

Temminghoff, E.J.M. 1998. **Chemical Speciation of Heavy Metals in Sandy Soils in Relation to Availability and Mobility** Doctoral Thesis, Wageningen Agricultural University, Wageningen, The Netherlands, 183 pages.

The environmental risk of heavy metals which are present in soil at a certain total content is highly dependent on soil properties. Chemical speciation is a comprehensive term for the distribution of heavy metals over all possible chemical forms (species) in soil solution and in the solid phase. The chemical behaviour of heavy metals depends among others on the quantity and type of sorption sites at the solid surface (e.g. organic matter) and environmental conditions (e.g. pH, competitors, complexes). In this thesis, emphasis is given to the effects of pH, solid and dissolved organic matter, inorganic complexation, and calcium competition on the speciation of the heavy metals cadmium and copper in sandy soils. For cadmium, inorganic complexation (e.g. by chloride) is of great importance whereas for copper organic complexation (dissolved organic matter) (DOC) is more important with respect to availability and mobility. Copper binding by dissolved organic matter (DOC) and by (soil) solid organic matter could be described well with the Non-Ideal Competitive Adsorption (NICA) model and with the Two Species Freundlich (TSF) model using parameters derived from purified humic acid. Both models accurately predicted the copper concentration at different depths in a field. Leaching experiments revealed that copper mobility depends on DOC concentration. DOC coagulation was described as a function of complexed cations such as aluminium, calcium, copper and protons. The long term effect of changes in soil pH, and solid and dissolved organic matter on copper mobility are illustrated using a dynamic soil (solution) composition balance approach. Understanding of the chemical behaviour of cadmium and copper makes it possible to estimate the availabile and mobile contaminant fraction from routine accessible parameters such as total content, pH and organic matter.

Additional index words: heavy metals, cadmium, copper, groundwater quality, plant toxicity, dissolved organic matter (DOC), complexation.

Contents

Chapter 1

General Introduction

The European Union has an excess of crops, animals and animal products (Brouwer *et al.*, 1991). Due to this excess the policy of the EU is to decrease the agricultural areas in order to reduce the sales support of agricultural products (MacSharry plan). The aim of the EU is to abandon about 15 % of its agricultural areas (Ter Meulen-Smidt *et al.*, 1997). One of the possibilities is to change agricultural areas into nature reserve areas, by fallow land and/or forestation. These areas are supposed to have economical, ecological and/or recreational functions. The soils which should be abandoned first are the marginal soils which have low potential crop production or need high fertilization to attain acceptable crop yields. Sandy soils are for these reasons of most interest. The Netherlands is covered by sandy soils for more than 40 % of the total area (cf. Figure 1.1).

Large areas of soil are contaminated with heavy metals via fertilizers, waste disposal or atmospheric deposition. The use of fertilizers and atmospheric deposition via industry are main causes for heavy metal contamination in agricultural soils. Artificial (phosphate) fertilizers contain by nature among others trace amounts of cadmium; the cadmium content may range from 50 to 170 mg/kg of fertilizer (William & Davids, 1976).The use of contaminated harbour sludge for elevation of land in the western part of The Netherlands resulted in cadmium and copper contamination of soil (CCRX, 1985; CCRX, 1987). The use of animal manure is the most important diffuse copper source for soil copper contamination (CCRX, 1987). Copper is used as a feed additive for pigs to attain a higher feed conversion. More than 95 % of the copper added is found again in the pig excrements (Bremner, 1981). The copper content ranges from 381 to 499 mg/kg for dry pig manure (Hotsma *et al.*, 1996). Application

of pig manure as fertilizer resulted in maximum copper contamination levels of 1,500-2,000 g/ha/yr in the Seventies as was reported by Lexmond & De Haan (1977). Despite of the decrease of copper additions to feed since the early Eighties, the decrease of copper input into agricultural soils via pig manure has not diminished much because of a strong increase of the number of pigs at the same time.
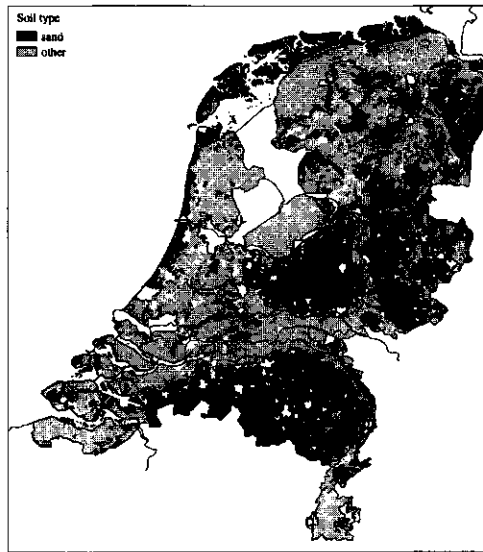
Figure 1.1.   Spatial distribution of sandy soils at a regional scale in the Netherlands (from: Tiktak, 1997).

Examples of other diffuse heavy metal (atmospheric) sources are combustion of fossil fuels, mining and smelting of non-ferrous ores (e.g. zinc smelters). Zinc smelters applied thermic procedures to extract zinc from ores for almost one century, which resulted in high emissions of cadmium and zinc into the atmosphere. In this way, in the Province Noord Brabant, an area ('De Kempen') of 350 km^2 has been contaminated with cadmium and zinc. Nowadays a different process is applied which decreased the

emission of cadmium and zinc considerably.

In Figure 1.2 the cadmium and copper content in the topsoil (0 - 20 cm) of the Netherlands are given. If we combine Figures 1.1 and 1.2 it is obvious that large sandy areas are contaminated to a level higher than 0.4 mg/kg for cadmium and higher than 10 mg/kg for copper. Continuation of intensive agriculture and industry will lead to a further increase of heavy metal contents in the topsoil. When the heavy metals become abundant in soil, adverse effects may occur. Due to toxicity, adverse effects may affect both soil organisms and plants *in situ*; this threatens soil ecology and agricultural yields as well. Also quality of agricultural products may adversely be affected without observable effects on yield; at the same time leaching may cause deterioration of the quality of ground water. Consequently, much research has been performed in order to quantify the effects of heavy metal contamination of soil.
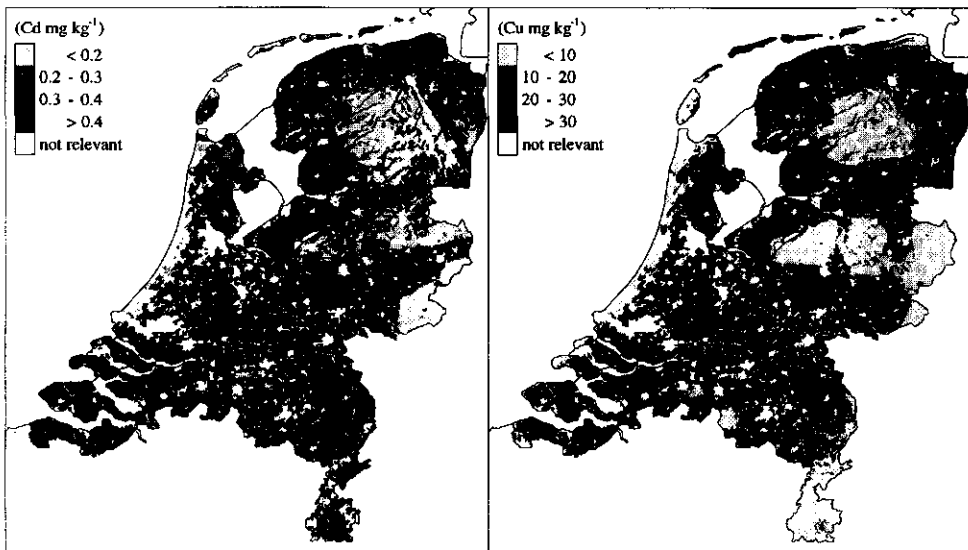
Figure 1.2. Cadmium and copper content in the topsoil of the Netherlands; based on 2544 observations in 1996 (Tiktak *et al.*, 1997).

It is well known that heavy metals may accumulate in soil as the result of chemical interactions with the solid phase (Lindsay, 1979; Sposito, 1989). This retention is a major factor which controls heavy metal biological availability as well as its mobility. Bioavailability of an element in a soil matrix is its capability to cause positive or negative effects on soil organisms, whereas mobility is related to transport through soil. The key factor appears to be the heavy metal concentration in the soil solution. Also for plants, the supply of heavy metals to the root system is governed by transport processes to roots and root hairs. The appearance of heavy metals in soil solution and solid phase in all possible chemical forms (species) is known as chemical speciation. Speciation depends on the heavy metal under consideration, and the composition of both the soil solution and the solid phase. Thus, pH, ionic strength and the presence of cations, anions, organic and inorganic ligands are determining parameters with regard to the soil solution. Types and quantities of primary, clay, and metal(hydr)oxide minerals, and chemical precipitates, as well as organic matter are important with regard to the solid phase. Chemical interactions between the solid and the solution phases of soil control the level at which metal concentrations are present in solution. Salt extractants, e.g. calcium nitrate, calcium chloride, sodium nitrate, and ammonium nitrate solutions, are used to provide a measure of the bio-available fraction for crops (Sanders *et al.*, 1987; Novozamsky *et al.*, 1993; Aten & Gupta, 1996). Unfortunately, it is hard to predict extractable quantities for different soil types and contaminant levels. Therefore, ascertainment of bio-availability and mobility still requires the understanding of chemical behaviour in the soil/extractant solution-system.

The conversion of agricultural areas to natural or forest areas and the resulting acidification by acid deposition may affect contaminant behaviour due to changes in biological, physical and chemical processes in soil. The chemical behaviour of heavy metals depends among others on the presence of sorption sites at the solid surface (e.g. organic matter) and environmental conditions (e.g. pH, competitors, complexes) as

mentioned. Due to changes in land use environmental conditions in soil will change. Hence, also heavy metal behaviour may change in time. Chemical parameters, which are subject to change, like organic matter content, pH, and calcium content, influence availability and/or mobility of heavy metals; these effects are discussed in this thesis.

(*i*)   As a result of forestation, an increase in solid and dissolved *organic matter* is probable. Litter fall and vegetation decomposition may lead to an increase of organic matter in the top soil. Two major types of organic compounds can be distinguished in the top soil, namely non-humic and humic substances (Stevenson, 1982). In soil systems the humic substances are predominantly insoluble and associated with the mineral phase. By decomposition of solid organic matter, dissolved organic matter (mostly expressed as Dissolved Organic Carbon (DOC)) is formed in the soil solution; major constituents of DOC are humic acids, fulvic acids, and relative small molecules like amino-acids and citric acid. (Schnitzer & Khan, 1978, Stevenson, 1982; Aiken *et al.*, 1985). Humic acids is the fraction of humic substances which is not soluble in water under acidic conditions (pH < 2) but becomes soluble at higher pH values; fulvic acids is the fraction that is soluble in water under all pH conditions. Both, solid and dissolved organic matter contain functional groups which may form complexes with metal ions (Stevenson, 1982; Perdue, 1987; Buffle, 1988). The reactivity of a functional group depends on its type and its environment (De Wit, 1992; Nederlof, 1992).

(*ii*)   Soil acidification is a natural process which may be accelerated by atmospheric deposition of SO_2, NO_x and NH_3. Soil acidification can exert itself in several ways: (a) by an increase of soil acidity or decrease of *pH*, (b) by a decrease of base saturation, (c) by an unbalanced availability of elements in the root environment, or by a decrease of the acid neutralizing capacity (ANC) of the soil (Van Breemen *et al.*, 1983). Dissolved organic matter (e.g. humic and fulvic acids), can lower soil pH values to less then 4 (Van Grinsven, 1986).

(*iii*)   To prevent crop yield reduction by acidity or aluminium toxicity, farmers control the pH regularly by adding lime, mostly in the form of calcium-carbonate. Termination of lime application leads to soil acidification (pH decrease). Besides the pH, also the *calcium* concentration in the soil solution decreases (Hesterberg, 1993).

Protons and calcium are competitors for heavy metal binding by soil organic matter and therefore important factors in relation to heavy metal availability and mobility.

Dutch Soil Protection Policy

Soil protection legislation intends to protect human health and the environment against adverse effects of soil contamination (VROM, 1994). In the Netherlands, in risk assessment approach, use is made of so called *reference* or *target* values and *intervention* values. Intervention values are referring to the maximum permissible risk (MRL) level whereas the target or reference values are the values with negligible risks (NRL). Intervention values are based on human toxicological and ecotoxicological considerations, whereas the target values are based on concentrations in natural environments. Although the two values originate from different perspectives, both are dependent on organic matter and clay content. Clay minerals contain by nature more heavy metals than other soil constituents and organic matter influences the soil bulk density; this explains why clay and organic matter are taken into account in the derivation of reference values (Lexmond & Edelman, 1987). The intervention values are also based on clay and organic matter content. However, in case of human toxicological and ecotoxicological risks other soil factors (e..g. pH, competition by major cations, complexation) may play an important role in relation to availability and mobility of contaminants in soil. Since speciation accounts for all these factors

speciation is an important tool in risk assessment (Figure 1.3).
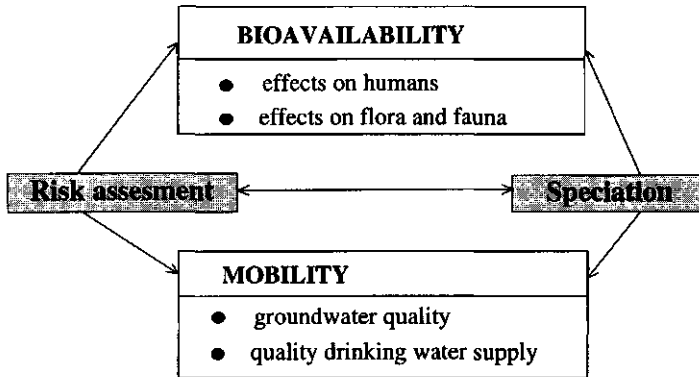
Figure 1.3. Relation scheme between risk assessment, speciation, bioavailability and mobility.

Research Objectives

As was outlined in the previous paragraph in soil the environmental risk of heavy metals which are present at a certain total content is highly dependent on soil properties. Quantification of this dependency is difficult because of the large number of soil properties involved.

The first objective of this thesis was to elucidate the effects of speciation of heavy metals in sandy soils, with emphasis on cadmium and copper, in relation to mobility and availability. Methods that seem promising with respect to availability and mobility are soil extraction with water, mild en strong extractants. Although these methods gives sometimes a good indication for bio-availability and mobility when

applying regression analysis, the value of the use of extractants is limited by the influence of various soil and soil solution parameters. Little is known about the chemical behaviour of cadmium and copper in such electrolyte soil solutions. If we can relate differences in extracted quantities with sorption, (in)organic complexation, competition by protons and other cations like calcium, it may be possible to *a priori* estimate the available and mobile contaminant fraction from the routine accessible parameters such as total content, pH and organic matter.

A second research objective is to derive heavy metal sorption models that adequately embrace the main phenomena for the binding by organic matter, since organic matter is the most reactive surface in sandy soils. After parametrization of these models for copper sorption by purified humic acid it is shown how sorption by other type of organic matter (i.e. solid (soil) and dissolved organic matter) can be described with a plausible adaptation of only two parameters. The applicability of the models developed for copper retention, and mobility is then assessed. In particular, it is shown that these models, after parametrization with *laboratory* experiments, adequately predict the copper retention and mobility in a soil profile *in the field*. Mobility of dissolved organic matter in soil is, among others, affected by coagulation. How coagulation is regulated by major cations (e.g. calcium) and in which way this affects the copper mobility was studied. The applicability of the approach is validated by comparing modelling results with data from column leaching experiments. Subsequently, model calculations are given to evaluate the effect of an increase of solid and dissolved organic matter and pH decrease (e.g. due to changes in land use) on copper retention and mobility. Effects of mixing or non-mixing of solid organic matter through the topsoil on copper mobility are also quantified.

Finally, this study aims at testing the ability of calciumchloride extractable copper concentrations of soil to indicate copper concentrations in plants. In this way this thesis addresses the importance of chemical speciation predicting availability and mobility of copper in soil.

Outline of this thesis

This thesis is a compilation of several articles, published in or submitted to international scientific journals. In Chapter 2 the chemical behaviour of cadmium in sandy soil is examined. Both low cadmium concentrations (linear adsorption) and high concentrations (non-linear adsorption) are considered. Sorption of cadmium by soil is described with a Three-Species-Freundlich (3SF) equation in which pH, complexation, calcium competition and ionic strength effects are taken into account.

In Chapter 3, the Three-Species-Freundlich (3SF) equation is applied to predict to what extent cadmium transport in a soil column experiment is influenced by chloride complexation, as well as by calcium competition. The predictions are compared with experimental data.

In Chapter 4 to 8 the chemical speciation of copper in acid sandy soil (solution) is investigated . The competition for 'free' copper between soil and dissolved organic matter (the latter consisting of both a humic fraction and a fulvic fraction) is studied in Chapter 4. We show the applicability of a Two Species Freundlich (TSF) equation, for modelling copper speciation in a sandy soil.

In Chapter 5, two heavy metal sorption models are presented, which both describe the copper and proton binding by purified humic acids. It was hypothesized that the sorption by other types of organic matter (i.e. solid soil organic matter and dissolved organic matter) can also be described with these models, requiring a plausible adaptation of a few parameters only. The models are validated for laboratory column experiments as well as for field data.

In Chapter 6, the coagulation of dissolved organic matter as affected by the cations aluminium, calcium, copper, sodium and protons is described. The mobility of dissolved organic matter was expected to be controlled by calcium. Predictions of copper binding by humic acid as affected by calcium as competitor are evaluated. The

applicability of the approach is shown by comparing modelling results with data from column experiments.

In Chapter 7, dynamic copper balances of a copper contaminated sandy soil due to changing solid and dissolved organic matter and pH are discussed. Speciation of copper and the subsequent multi-phase competition are incorporated in dynamic copper balances of a top soil. The calculations are used to show the effect of changes in soil properties (pH, solid and dissolved organic matter) on copper accumulation and leaching rates. Special emphasis is given to the effects of mixing and non-mixing of solid organic matter through the top soil.

In Chapter 8, the role of dissolved organic matter in relation to copper toxicity and copper uptake by ryegrass (*Lolium multiflorum L.*) Is described. Copper uptake and copper toxicity was investigated in relation to the 'free' copper ion concentration and the total copper concentration in $CaCl_2$ extracts of copper contaminated sandy soil at different pH values.

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Chapter 2

Speciation and Calcium Competition Effects on Cadmium Sorption by Sandy Soils at Various pH Levels

Co-authors: Sjoerd E.A.T.M. van der Zee & Frans A.M. de Haan

Abstract

The effects of Ca competition, ionic strength, inorganic complexation and pH on cadmium adsorption by a sandy soil were studied. Sorption of Cd was measured using four different electrolytes $CaCl_2$, $Ca(NO_3)_2$, $NaNO_3$ and $NaCl$ at a constant ionic strength (I) of 0.003 M at three different pHs, at variable Ca/Na ratio with a constant ionic strength of 0.03 and at variable ionic strengths between 0.003 and 0.3 M for two different pHs for $Ca(NO_3)_2$ and $NaNO_3$. The measured Cd sorption isotherms were non-linear. In the case of Cl as electrolyte anion, 13 % of the Cd in solution is complexed at $I=0.003$ (0.002 M Cl) and 91 % of Cd is complexed at $I=0.3$ (0.2 M Cl). If NO_3 is the anion, 0 % of Cd is complexed at $I=0.003$ and 11 % at $I=0.3$. The Cd complexes do not adsorb significantly. Ca competition, at an ionic strength of 0.03, reduced the Cd adsorption by 60 to 80 % compared with the case that Na is the cation. Increasing the ionic strength from 0.003 to 0.3 decreased Cd sorption by 60 % for $Ca(NO_3)_2$ and 25 % for $NaNO_3$ due to a decrease of the activity coefficient, increase of inorganic complexation and increase of Ca competition. A decrease of one pH unit reduces Cd sorption of about 75 %. Sorption of Cd by soil could be described adequately with the three-species Freundlich (3SF) equation in which pH, complexation, Ca competition and ionic strength effects were taken into account.

Introduction

Extraction with unbuffered salt electrolytes is recommended as a good measure of phyto-availability of heavy metals for plants (Hani and Gupta, 1982; Sanders *et al.*, 1987; Novozamsky *et al.*, 1993). The availability depends among others on soil type, pH, ionic strength, complexation by inorganic and organic ligands and competition with other cations. Various electrolytes such as $CaCl_2$ (0.01 - 0.1 M), $NaNO_3$ (0.1 M) and NH_4NO_3 (1 M) have been used as unbuffered extractants (Novozamsky *et al.*, 1993). Considerably different amounts of heavy metals are released into these extractants. These extracts provide different extracted quantities that are controlled by the chemical behaviour of the heavy metals. By studying the speciation in the extractant solutions these differences may be understood.

The effect of inorganic Cd-complexation by Cl and NO_3 on Cd adsorption by soil was shown by Boekhold *et al.* (1993). In the presence of 0.01 M $CaCl_2$ as electrolyte, about 52 % of the dissolved Cd was complexed with Cl and only 3 % with NO_3. A mixture of equimolar (0.005 M) $CaCl_2$ and $Ca(NO_3)_2$ solutions (Jopony & Young, 1994) give both CdCl and $CdNO_3$ complexes. Sanders *et al.* (1987) used 0.1 M $CaCl_2$, which resulted in a larger fraction of CdCl-complexes and improved Cd desorption from soil. The ionic strength in the soil solution in natural circumstances is significantly less than this solution. In addition to background electrolyte concentration and the effect of inorganic complexes, competition for sorption by Ca also occurs. Increasing the $CaCl_2$ concentration of the extractants results in increasing Cd desorption as was shown by Chardon (1984), Christensen (1984) and Petruzelli *et al.* (1985). Hendrickson & Corey (1981) showed an increase in selectivity coefficients K_{Ca}^{Cd} for increasing Ca concentrations for Ca-saturated soils. This dependence upon relative metal concentrations is apparently due to the heterogeneous composition of complexing sites in most soil systems and competition among the various cations present for these sites (Hendrickson & Corey, 1981). Competition between Cd and Ca

deminished Cd adsorption by 80 % in Ca-electrolyte as compared with a Na-electrolyte at an ionic strength of 0.03 M (Boekhold *et al.*, 1993). The presence of excess Na affects both Cd-sorption and Ca-desorption by soil since Ca is one of the major cations of the base saturation. This implies competition between Ca and Cd although using a Na-electrolyte. Little is known about the effect of the competition of cations (electrolytes) in combination with pH on (multi-component) sorption processes in soil.

The aim of this research is to understand and quantify the relative importance of Ca competition, complexation and ionic strength (in the range 0.003 - 0.3 M) at various pH on Cd adsorption by a sandy soil. Both small Cd concentrations (linear adsorption) as well as large concentrations (non-linear adsorption) are considered.

Theory

If we assume that pH and competition by Ca are the most important factors that affect Cd sorption by site S^-, the following reactions can be given as

$$S^- + Cd^{2+} + x\ H_2O \rightleftharpoons SCd(OH)_x^{1-x} + x\ H^+ \quad,\quad K_{Cd} \tag{2.1a}$$

and

$$S^- + Ca^{2+} + y\ H_2O \rightleftharpoons SCa(OH)_y^{1-y} + y\ H^+ \quad,\quad K_{Ca} \tag{2.1b}$$
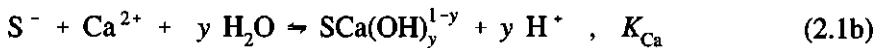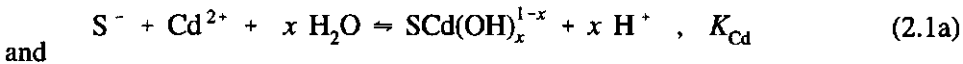
The factors x and y, which account for the (partial) hydrolysis of the surface complex, may have non-integer values because metal ion binding may lead to a decrease in the negative charge of, for example, the soil organic matter. This decrease may induce electrostatic interactions that cause a concomitant release of protons. These rather simplified equations are convenient because they have few parameters and account for both the pH-dependency of metal ion binding and competition with Ca in a fairly simple way. Adsorption of Cd by site S^- can be expressed as

$$\theta_{Cd} = \frac{Q_{Cd}}{Q_{Cd(max)}} = \frac{[SCd(OH)_x^{1-x}]}{[S^-] + [SCd(OH)_x^{1-x}] + [SCa(OH)_y^{1-y}]} \tag{2.2}$$

which can be rewritten as

$$\theta_{Cd} = \frac{\dfrac{K_{Cd}(Cd^{2+})}{(H^+)^x}}{1 + \dfrac{K_{Cd}(Cd^{2+})}{(H^+)^x} + \dfrac{K_{Ca}(Ca^{2+})}{(H^+)^y}} \tag{2.3}$$

In general, the soil surface may be regarded as being heterogeneous, with i different sites (S_i^-). Hence, a distribution of affinity constants ($K_{Cd^-}^i$ and $K_{Ca^-}^i$ values) is more realistic than single valued constants K_{Cd^-} and K_{Ca^-}-values.

A heterogeneous multi-component adsorption equation given by Koopal *et al.* (1994) is an equation of the Langmuir-Freundlich type and is called the Non-Ideal Competitive Adsorption (NICA) model:

$$\theta_l = \frac{Q_l}{Q_{l(max)}} = \frac{(\tilde{K}_l r_l)^{n_l}}{\sum_j (\tilde{K}_j r_j)^{n_j}} \cdot \frac{\left(\sum_j (\tilde{K}_j r_j)^{n_j}\right)^p}{1 + \left(\sum_j (\tilde{K}_j r_j)^{n_j}\right)^p} \tag{2.4}$$

where Q_l and $Q_{l,max}$ are the adsorbed quantity and the adsorption maximum of component l, $\tilde{K}_j$ is the median of the affinity constants (K_j^i) of component j, where j are all components including component l. Both n and p are heterogeneity parameters that are related to the width of the distributions of $\log K_j$ for the soil (organic matter). By r_j we denote the activity ratio of component j and protons, which for the present case is defined by

$$r_{Cd} = \frac{(Cd^{2+})}{(H^+)^x} \qquad ; \qquad r_{Ca} = \frac{(Ca^{2+})}{(H^+)^y}$$

This results in the following adsorption model for Cd

$$\theta_{Cd} = \frac{Q_{Cd}}{Q_{Cd(max)}} = \frac{\left(\tilde{K}_{Cd}\frac{(Cd^{2+})}{(H^+)^x}\right)^{n_{Cd}}}{\left\{\left(\tilde{K}_{Cd}\frac{(Cd^{2+})}{(H^+)^x}\right)^{n_{Cd}} + \left(\tilde{K}_{Ca}\frac{(Ca^{2+})}{(H^+)^y}\right)^{n_{Ca}}\right\}} \cdot \frac{\left\{\left(\tilde{K}_{Cd}\frac{(Cd^{2+})}{(H^+)^x}\right)^{n_{Cd}} + \left(\tilde{K}_{Ca}\frac{(Ca^{2+})}{(H^+)^y}\right)^{n_{Ca}}\right\}^p}{1 + \left\{\left(\tilde{K}_{Cd}\frac{(Cd^{2+})}{(H^+)^x}\right)^{n_{Cd}} + \left(\tilde{K}_{Ca}\frac{(Ca^{2+})}{(H^+)^y}\right)^{n_{Ca}}\right\}^p} \quad (2.5)$$

If we assume that the soil is almost saturated with Ca, the second term of the RHS of Equation (2.5), which is the sum of θ_{Cd} and θ_{Ca} is almost equal to θ_{Ca} because $\theta_{Cd} \ll \theta_{Ca}$. Both $\tilde{K}_{Cd}$ and $\tilde{K}_{Ca}$ are the median affinity constants of Cd and Ca respectively and n_{Cd} and n_{Ca} are the component specific nonideality parameters, and p is a measure of the width of the intrinsic surface heterogeneity. If $(Cd^{2+}) \ll (Ca^{2+})$, which is mostly the case in the natural environment, Equation (2.5) can be simplified to

$$\theta_{Cd} = = \frac{\left(\tilde{K}_{Cd}\frac{(Cd^{2+})}{(H^+)^x}\right)^{n_{Cd}}}{\left(\tilde{K}_{Ca}\frac{(Ca^{2+})}{(H^+)^y}\right)^{n_{Ca}}} \theta_{Ca} \qquad (2.6)$$

or after rearrangement

$$Q_{Cd} = K' (Cd^{2+})^{n_{Cd}} (Ca^{2+})^{-n_{Ca}} (H^+)^m \qquad (2.7)$$

In Equation (2.7) we defined

$$K' = Q_{Cd(max)} \theta_{Ca} \frac{(\tilde{K}_{Cd})^{n_{Cd}}}{(\tilde{K}_{Ca})^{n_{Ca}}} \qquad (2.8)$$

and

$$m = -(n_{Cd} \ x)+(n_{Ca} \ y) \tag{2.9}$$

Equation (2.7) we indicated by 3SF: the Three Species Freundlich model. This 3SF model is similar to an empirical equation given by Chardon (1984). The 3SF model is less general than the NICA model but easier to use because fewer parameters have to be derived. For the NICA model, Equation (2.4), for three components 16 parameters have to be derived in the case of a bimodal adsorption (Benedetti *et al.*, 1995). For the 3SF model only 4 parameters are needed.

In Equation (2.7) activities have to be used instead of concentrations. With the Davies extension of the Debye-Hückel equation (Bolt & Bruggenwert, 1978) and formation constants of Cl and NO_3 complexes with Cd (Sillén & Martell, 1971; Smith & Martell, 1981), the Cd concentration, [Cd], can be related with Cd^{2+} activity, (Cd^{2+}), as shown by Hendrickson & Corey (1981) and Boekhold *et al.* (1993)

$$(Cd^{2+}) = [Cd] \ f_{Cd} \ F \tag{2.10}$$

with

$$-\log f_{Cd} = 2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \tag{2.11}$$

and

$$F = \frac{[Cd^{2+}]}{[Cd_{total}]} = \frac{1}{1 + \sum_q K_q^I \ [X]^q} \tag{2.12}$$

in which f_{Cd} is the activity coefficient of Cd, F is the complexation coefficient, K_q is the formation constants of the Cd complexes with X (Cl⁻ or NO_3^-) at ionic strength I and [X] is the concentration of Cl⁻ or NO_3^- respectively. If the parameters K', n_{Cd}, n_{Ca} and m are known then the Cd^{2+} activity can be predicted with Equation (2.7) for known

total Cd content in the soil, Ca concentration and pH. The suggested equation accounts also for electrolyte composition, $CaCl_2$, $Ca(NO_3)_2$, $NaNO_3$ or $NaCl$, and electrolyte concentration (ionic strength).

Materials and methods

The sandy soil used in this study was from the vicinity of Wageningen and is similar to that used by Boekhold *et al.* (1993). Table 2.1 list the characteristic soil properties, including pH in 0.01 M $CaCl_2$, grain size distribution, organic carbon after wet oxidation by sulfochromic acid (Walinga *et al.*, 1992) and cation exchange capacity (CEC) and base saturation (according to the unbuffered 0.01 M $BaCl_2$ method), and total initial extractable Cd (0.43 M HNO_3). All methods are described in Houba *et al.*, 1995.

Table 2.1. Characteristics of the used soil.
pH $CaCl_2$ (0.01 M), Texture (%), organic matter (% C), Cation Exchange Capacity (mmol +/kg), Base saturation (mmol +/kg) and initial total Cd (mmol/kg) (0.43 M HNO_3).

pH-CaCl₂	4.2	CEC (mmol +/kg)	18
Particle size (%)		base saturation (mmol +/kg)	
> 50 μm	83	Na	0.0
< 50 μm	16	K	1.8
< 16 μm	8	Ca	8.8
< 2 μm	5	Mg	1.5
Organic C (%)	1.0	Total Cd (μmol/kg)	1.78

Adsorption isotherms were measured for Cd concentrations from 0 to 100 µmol/L at three pHs, pH 3.5, 4.0 and 5.0, by adding 0.1 M HNO_3 or 0.1 M NaOH to the soil suspension and equilibrating for 24 h before adding cadmium. As background electrolytes $CaCl_2$, $Ca(NO_3)_2$, $NaNO_3$ and $NaCl/NaNO_3$ were used, all at a constant ionic strength of 0.03. The pH titration curves of the soil were determined for the different electrolytes to know how much HNO_3 or NaOH was necessary to reach the desired pH. Besides the effect of Cl and NO_3, the effect of a divalent cation (Ca) with respect to a monovalent cation (Na) on Cd sorption was also measured. The Cd adsorption isotherms at three different pH levels and four different background electrolytes at constant ionic strength was called experiment A.

Cadmium adsorption at three concentrations, 4.4, 36 and 71 µmol/L, was also measured at ten different Ca/Na ratios at I=0.03 and at two pHs, 3.5 and 5.0. The extraction solution ratios of $Ca(NO_3)_2$ (0.01 M) : $NaNO_3$ (0.03 M) were 100:0 - 50:50 - 25:75 - 10:90 - 5:95 - 2:98 - 1:99 - 0:100. This we denote experiment B.

The effect of ionic strength on Cd adsorption was measured for five ionic strengths, 0.003 - 0.015 - 0.03 - 0.15 and 0.3 M. The background electrolytes were either $Ca(NO_3)_2$ or $NaNO_3$ and two pHs, 3.5 and 5.0. This we denote experiment C.

In all cases a soil:solution ratio of 1:5 was used. The (final) soil suspension was shaken end-over-end for 20 h at 20°C. After pH measurement the suspension was centrifuged at 10000 g for 15 min. The pHs were constant for each nominal state within 0.1 pH units for every concentration of electrolyte and cadmium. Cadmium was measured with Flame Atomic Absorption Spectrometry (FAAS) at 228.8 nm (Instrumentation Laboratory AA/AE spectrophotometer S11) with Smith-Hieftje background correction. Ca was measured with Flame Atomic Emission Spectrometry (FAES) at 622 nm (Eppendorf Elex 6361) using lanthanum as releasing agent (Houba et al., 1995).

Results and discussion

The effect of ionic strength (I) on the activity coefficient of Cd (f_{Cd}) as well as the effect of complexation by Cl and NO_3 on the complexation coefficient (F) is given in Fig. 2.1.
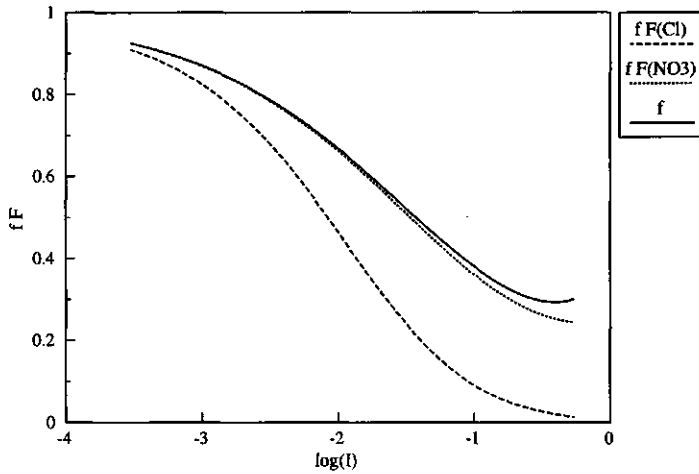
Figure 2.1. The effect of ionic strength (I) on the activity coefficient (f_{Cd}) and the effect of Cl and NO_3 complexation on the total coefficient (f_{Cd} F).

The complexation coefficient (F) is the fraction Cd^{2+} of the total Cd concentration in solution. The total coefficient (f_{Cd} F) is the combination of the activity and the complexation coefficient as given in Equation (2.10). The formation constants used are given in Table 2.2, which are taken from Smith & Martell (1981) and Sillén & Martell (1971). Increasing the ionic strength, without complexation, results in a decrease of the activity coefficient. Additional complexation by NO_3 has no influence on the total coefficient below I=0.01 (0.01 M NO_3), only a slight effect (1 to 11 % of the total coefficient) can be seen for I > 0.01. The effect of Cl complexation is much

stronger; complexation varies from 13 % of the total coefficient at I=0.003 to about 90 % at I=0.3. In the case of 0.001 M CaCl$_2$ 13 % of the Cd in solution is complexed with Cl as CdCl$^+$ complex, but in the case of 0.1 M CaCl$_2$ 59 % CdCl$^+$, 26 % CdCl$_2^0$ and 3 % CdCl$_3^-$ complexes (total 88 %) are formed of the total Cd in solution. The free Cd^{2+} activity depends both on ionic strength and electrolyte anion concentration.

Table 2.2. Formation constants of CdCl and CdNO$_3$ complexes at ionic strength 0.

	Cl	log (K_0)	NO$_3$	log (K_0)
	CdCl$^+$	1.98 [b]	Cd(NO$_3$)$^+$	0.31 [a]
	CdCl$_2^0$	2.60 [b]	Cd(NO$_3$)$_2^0$	0.00 [a]
	CdCl$_3^-$	2.40 [b]		
	CdCl$_4^{2-}$	2.50 [b]		

[a] Sillén & Martell, 1971
[b] Smith & Martell, 1981

Cadmium adsorption isotherms with different background electrolytes (experiment A) are given in Fig. 2.2a for the CaCl$_2$ and Ca(NO$_3$)$_2$ electrolyte and Fig. 2.2b for the NaCl and NaNO$_3$ electrolyte. For larger concentration ranges we deal with non-linear adsorption. In addition, effects of pH, inorganic complexation by Cl, and competition of Ca and Na with Cd are apparent in these figures. With increasing pH, adsorption decreased for all electrolytes. Cadmium adsorption is less for Cl-electrolytes because of CdCl complexes which apparently are not adsorbed significantly by the soil. In the case of 0.02 M chloride as much as 52 % of the Cd in solution is present as CdCl complexes. Calcium electrolytes (divalent cation) are stronger competitors then Na electrolytes (monovalent cation), so the soil adsorbed less Cd in the presence Ca was

used as background electrolyte than if Na was the electrolyte.
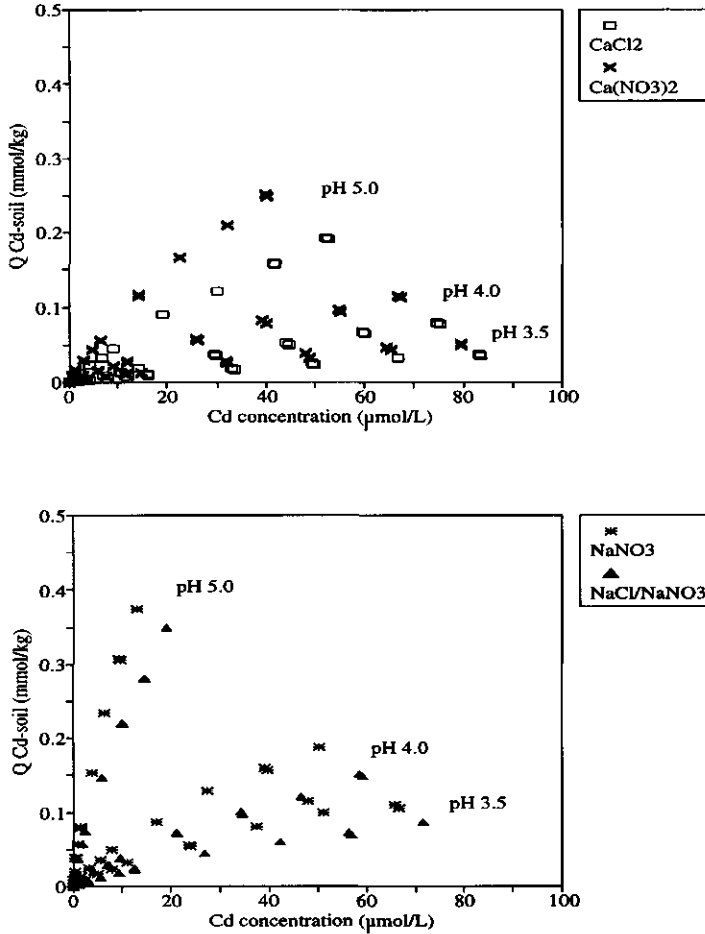
Figure 2.2. Adsorbed Cd (mmol/kg) as a function of the Cd concentration (μmol/L) at three pHs at 4 different electrolyte solutions; a) $CaCl_2$ and $Ca(NO_3)_2$ b) NaCl and $NaNO_3$ (experiment A).

If we do not take Ca competition into account, Euation (2.7) can be simplified

by

$$Q_{Cd} = K'' (Cd^{2+})^{n_{Cd}} (H^+)^m \tag{2.13}$$

where

$$K'' = K' (Ca^{2+})^{-n_{Ca}} \tag{2.14}$$

Equation (2.13) is the same as that used by Boekhold et al.(1993) and similar to the one of Jopony & Young (1994). Multiple regression results of Cd adsorption at different Cd^{2+} and different H^+ activities are given in Table 2.3.

Table 2.3. Multiple regression results at four different electrolytes, Ca and Na, with $\log(Q_{Cd\text{-soil}})$ as dependent variable and $\log(H^+)$ a nd $\log(Cd^{2+})$ as independent variables ($Q_{Cd\text{-soil}}$ in mol/kg and H^+ and Cd^{2+} in mol/L).

electrolyte	$\log K''$	n_{Cd}	m	r^2
Ca	-2.57	0.88 ± 0.02	-0.65 ± 0.02	0.99
Na	-2.93	0.81 ± 0.01	-0.75 ± 0.01	0.98

By taking Cd^{2+} activities instead of Cd concentrations the effect of inorganic complexation was eliminated. The pH factor (m) for the Ca-electrolyte was -0.65 and for the Na-electrolyte it was -0.75. These values are comparable with those of Anderson & Christensen (1988) and Boekhold et al. (1993) who found factors of -0.65 and -0.77 for Ca and -0.69 for Na as main cation. A much higher value for Na (-1.3) was found by Naidu et al. (1994) for Oxisols, which were high in Fe and Al oxides.

Electrolytes affect not only Cd sorption but also sorption of other cations (e.g. Ca). Hence, the electrolytes influence competition for sorption sites by these cations.

Approximately 50 % of the base saturation of the cation exchange capacity (CEC) is occupied by Ca, which means that Ca is an important competitor. The mean Ca concentrations in the soil extracts for all electrolytes and the pHs are given in Table 2.4.

Table 2.4. Ca concentrations in the soil extracts, for both electrolytes (Ca and Na) and three pHs (mean and standard deviation; mmol/L).

pH	Ca-electrolyte	Na-electrolyte
3.5	9.47 ± 0.19	0.38 ± 0.02
4.0	9.12 ± 0.24	0.32 ± 0.01
5.0	8.43 ± 0.21	0.13 ± 0.01

No differences were found between Cl and NO_3 as anion, and therefore the mean results for Ca and Na are given. *Adsorption* of Ca occurs for the Ca electrolytes (Ca concentration initial 10 mmol/L), and Ca *desorption* is observed if Na is the dominant cation. Also an effect of pH on the Ca concentration is visible. From this we conclude that the pH factor (m) disguises an effect of Ca competition on the adsorption of Cd. To assess the effect of Ca-competition, we measured Cd adsorption at different Ca/Na ratios at constant ionic stength (experiment B). The results are shown in Fig.2.3 for pH 3.5 and 5.0 and three Cd concentrations. An increase in the Ca/Na ratio (at constant I) diminishes Cd adsorption by a maximum of 60 % at both pH 5.0 and pH 3.5. If the decrease at a constant pH is affected only by Ca, a constant factor for Ca according to Equation (2.7) occur for each pH. At a constant pH Equation (2.7) can be adapted

$$Q_{Cd} = K''' (Cd^{2+})^{n_{Cd}} (Ca^{2+})^{-n_{Ca}} \tag{2.15}$$

where

$$K^{\prime\prime\prime} = K^{\prime} \, (H^+)^m \tag{2.16}$$

Results of multiple regression of the Cd adsorption at different activities of Cd^{2+} and Ca^{2+} are given in Table 2.5.
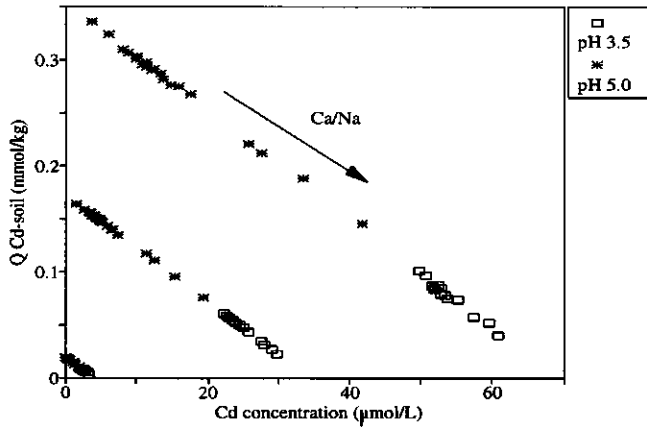
Figure 2.3. Adsorbed Cd (mmol/kg) as a function of the Cd concentration (μmol/L) at two pHs at variable Ca/Na ratio ($I=0.03$) (experiment B).

Table 2.5. Multiple regression results at two pHs with $\log(Q_{Cd\text{-soil}})$ as dependent variable and $\log(Ca^{2+})$ and $\log(Cd^{2+})$ as independent variables ($Q_{Cd\text{-soil}}$ in mol/kg and Ca^{2+} and Cd^{2+} in mol/L).

pH	$\log K^{\prime\prime\prime}$	n_{Cd}	n_{Ca}	r^2
3.5	-1.05	0.87 ± 0.02	0.33 ± 0.02	0.99
5.0	-0.50	0.82 ± 0.01	0.37 ± 0.01	1.00

The coefficients of determination show that the Cd adsorption can be described well with Equation (2.15). The negative coefficient for Ca indicates a decrease of adsorption of Cd as the Ca concentration increases. The slight difference between pH 3.5 and 5.0 is not significant. Therefore, a mean value of 0.34 for n_{Ca} was used between pH 3.5 and 5.0. Chardon (1984) found an average of 0.41 ± 0.07 for six different types of soil which corresponds with our findings. A new pH factor (m) is determined for the results of experiment A by taking the Ca^{2+} activity as well as Cd adsorption, Cd^{2+} and H^+ activity. A single pH factor of -0.69 was found for all four (i.e., both Na and Ca) background electrolytes, replacing values of -0.65 and -0.75 that were mentioned earlier.

Increasing the ionic strength (experiment C) yielded a decreased Cd adsorption (Fig. 2.4).
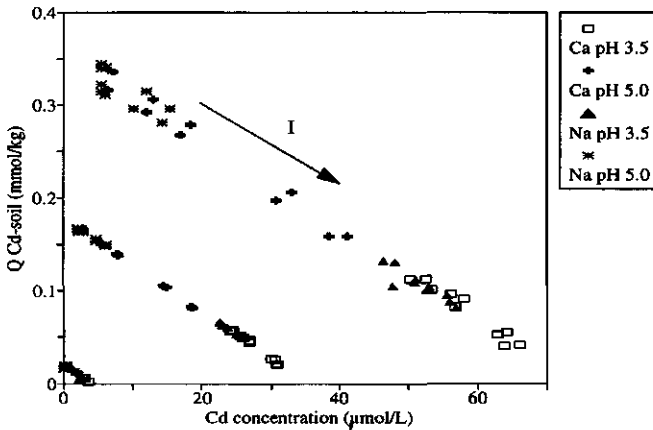
Figure 2.4. Adsorbed Cd (mmol/kg) as a function of the Cd concentration (µmol/L) at two pHs at variable ionic strength (I= 0.003 to 0.3) (experiment C).

The effect, for both pHs, is larger for Ca as electrolyte cation than for Na. For Ca as

the dominant cation, Cd adsorption diminished by a maximum of 60 %, and for Na the diminution was 25 %. If we eliminate, the effect of the ionic strength and complexation, by calculating Cd^{2+} activities and neglect the Ca competition but take the pH effect into account, Equation (2.13), the scatter of data is still large (Fig. 2.5). For the Ca electrolyte it is conceivable that the competition between Ca and Cd for sorption sites at increasing ionic strength also plays an important role. For the Na-electrolytes the Ca desorption from the soil increases at increasing ionic strength. Besides the total coefficient (f_{Cd} F), Ca competition should be taken into account for describing Cd adsorption at various ionic strength.
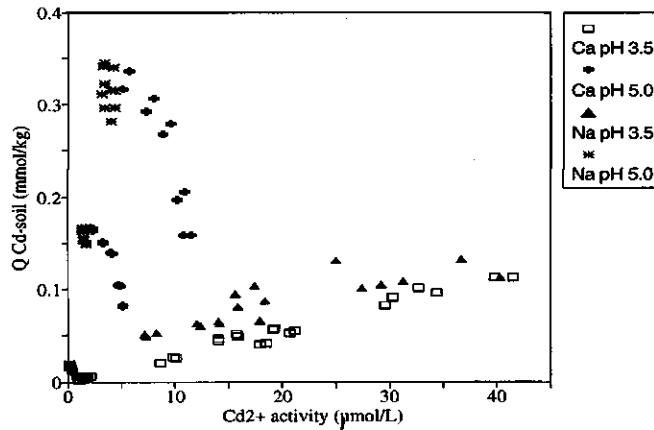
Figure 2.5. Adsorbed Cd (mmol/kg) as a function of Cd^{2+} activity (μmol/L) for results of experiment C (variable ionic strength).

If we take competition by calcium and protons into account the Cd adsorbed by the soil is given as a function of the product of $(Cd^{2+})^{0.85}$, $(H^+)^{-0.69}$ and $(Ca^{2+})^{-0.34}$), which is mean relation (Fig. 2.6). A straight line of data points is expected, for all electrolytes, ionic strengths and pHs, with a constant slope that equals K' (Equations (2.7) and (2.8)). Fig. 2.6a shows the results of the four different electrolytes at I=0.03

(experiment A), Fig. 2.6b shows the different Ca/Na ratios at I=0.03 (experiment B) and Fig. 2.6c shows the results of the ionic strength between 0.003 - 0.3 (experiment C). The data lie close to straight lines in all cases though with some scatter. The log K' and intercept of the data are given in Table 2.6. In all cases the same K' (-3.81 ± 0.02) is found. If we assume that Cd, Ca and protons adsorb on the same sites the result implies that the effects of pH, Ca competition and ionic strength on Cd-adsorption are explained succesfully with the 3SF equation.
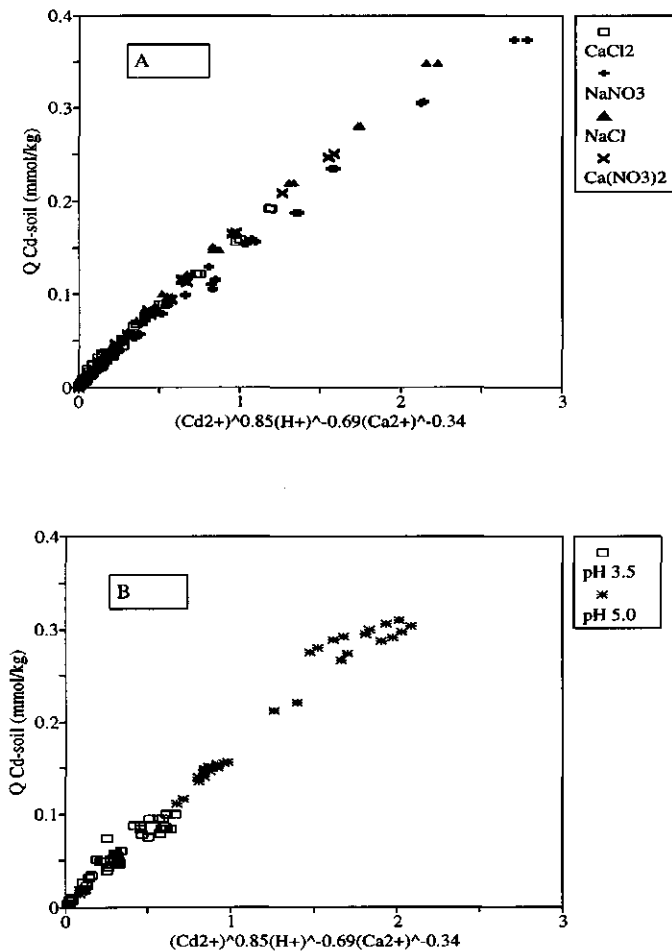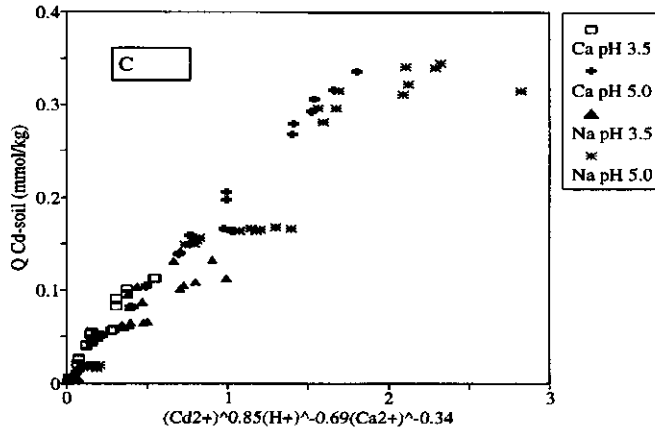
Figure 2.6. Adsorbed Cd (mmol/kg) as a function of $(Cd^{2+})^{0.85}(H^+)^{-0.69}(Ca^{2+})^{-0.34}$ for results of experiment A (Fig. 2.6a), experiment B (Fig. 2.6b) and experiment C (Fig. 2.6c).

Table 2.6. Slope and intercept values of the Cd adsorptions from experiment A, B and C (fig. 2.6) (Ca^{2+}, Cd^{2+} and H^+ in mol/L and $Q_{Cd\text{-soil}}$ in mol/kg; size of samples).

experiment	log K'	intercept	r^2	sample size
A (Fig. 2.6a)	-3.82 ± 0.01	5.0×10^{-6}	0.99	234
B (Fig. 2.6b)	-3.80 ± 0.01	3.9×10^{-6}	0.99	107
C (Fig. 2.6c)	-3.81 ± 0.02	1.1×10^{-5}	0.94	120
mean	-3.81 ± 0.02			

Conclusions

Sorption isotherms of Cd in suspension of an acid sandy soil were linear for small Cd concentration and non-linear for larger concentration ranges. Cadmium adsorption depend on inorganic complexation by Cl and NO_3, on competition by Ca, on ionic strength, and on pH. Where Cl was the main electrolyte anion, 13 % of the total dissolved Cd in solution was complexed with Cl at I=0.003 (0.002 M Cl), whereas at I=0.3 (0.2 M Cl) it was 88 %. When NO_3 was the main electrolyte anion none of the total Cd in solution was complexed at I=0.003 and 11 % at I=0.3. The 'free' divalent Cd^{2+} was adsorbed by soil in significant amounts, and the adsorption of CdCl or $CdNO_3$ complexes was negligible.

As a result of Ca competition the Cd adsorption was diminished by 60 to 80 % when $Ca(NO_3)_2$ was compared with $NaNO_3$ at a constant ionic strength of 0.03. A maximum diminution of Cd adsorption of 60 % was found for the effect of ionic strength between 0.003 and 0.3 for $Ca(NO_3)_2$ as background electrolyte. For $NaNO_3$ it was 25 %. An increase in ionic strength yielded a decreased Cd sorption as a result of a decrease in the activity coefficient, an increase of inorganic complexation and an increase in Ca competition. A decrease at pH 5 by one pH unit gave a decrease in Cd adsorption of about 75 %.

Effects of Ca competition, ionic strength, inorganic complexation and pH on Cd sorption by sandy soil can be described with the 3SF equation: with one equation all 461 data points could be described. We found a log K' value with very small standard deviation, i.e. K' = -3.81 ± 0.02, and the paramaters were n_{Cd} = 0.85, n_{Ca} = 0.34 and m = -0.65.

In different countries different electrolytes and electrolyte concentrations are employed for risk assesment. The 3SF equation can be used to calculate Cd sorption independent from electrolyte ($CaCl_2$, $Ca(NO_3)_2$, $NaNO_3$ or NaCl) and electrolyte concentration (ionic strength) both for the case of linear and nonlinear adsorption and

variable pHs. Hence, for sandy soil contaminated by Cd, the 3SF-equation may be helpful for comparing and understanding the different extracted quantities.

Acknowledgement

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Chapter 3

Mobility of Cadmium in Sandy Soils; Effects of Complexation and Competition

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Abstract

Batch and column experiments were carried out to study Cd transport through a sandy soil. Effects of pH inorganic complexation, pH and Ca competition on the mobility of Cd were shown and described with a three Species Freundlich equation (3SF). The measured Cd-breakthrough curves could be predicted well with the 3SF equation, if the exchange of the major cations Na and Ca is described with the Gaines-Thomas equation. Complexation of Cd by chloride as well as competition by Ca both enhance Cd mobility. This enhanced mobility can be very well predicted qualitatively.

Introduction

Risk assessment of heavy metal pollution of soils aims at predicting the fate of these compounds in the environment. Due to changes in environmental conditions, originally immobile heavy metals can be mobilized. This may pose a risk for ecological functioning, agricultural production and/or (ground)water quality. Understanding and prediction of soil chemistry and transport behaviour of contaminants is necessary to evaluate such potential risks.

The mobility of heavy metals in soils is related to their concentration in solution, which depends among others on pH, competition and complexation in solution. Due to complexation with dissolved organic matter (DOM) like humic and fulvic acids or inorganic complexation (e.g. Cl, NO_3^-) heavy metals can become more mobile. In cases with DOM we have to deal with facilitated transport in soils. Also soil pH appears to be an important parameter with respect to adsorption. A decrease of pH induces a decrease in Cd sorption (Christensen, 1984; Boekhold, 1993).

Competition by exchangeable major cations (e.g. Ca, Mg, K, Na) also affects the Cd sorption by soil (García-Miragaya & Page, 1976). Černík *et al.* (1994) described multicomponent transport of major cations in a clay soil. Their experimental data sets could be described by a single set of selectivity coefficients based on Gaines Thomas exchange for all major cations. For contaminants this can be rather problematic due to small sorption amounts with respect to these major cations.

The objective of the present study was to assess to what extent pH, complexation and Ca competition affect Cd mobility in sandy soils. Laboratory batch and column experiments were carried out for Cd in different background electrolytes. From the batch experiments, model parameters are derived to predict Cd transport. These predictions are compared with the experimental data.

Theory

The sorption behaviour of Cd is greatly influenced by the number of reactive sites in the soil (e.g. organic matter, metal(hydr)oxides and clay). For sandy soil, sorption can be described with the Freundlich equation (Kookana *et al.*, 1994). Many soil parameters are known which affect Cd-sorption. Due to inorganic (e.g. Cl⁻) and organic (e.g. humic- and fulvic acids) complexation the free cadmium (Cd^{2+}) concentration can decrease which influences sorption by the solid phase. In the case of 0.01 M CaCl$_2$ as background solution about 52 % of dissolved cadmium is complexed with Cl. pH and competition by other cations can influence the Cd-adsorption (Christensen, 1984). Boekhold *et al.* (1993) showed that Cd and protons may sorb onto the same sites. Besides protons, Ca competition can be important for Cd sorption if the reactive sites (cation exchange capacity) are predominantly occupied by Ca (Chardon, 1984; Temminghoff *et al.*, 1995). For different soils Cd adsorption decreased with an increase in ionic strength of the background electrolyte concentrtation (Naidu *et al.*, 1994).

From a heterogeneous multicomponent adsorption equation a simplified equation may be derived which is called the three Species Freundlich (3SF) equation (Temminghoff *et al.*, 1995). This equation explicitly accounts for Cd adsorption as it is affected by Cd and Ca activities and pH

$$Q_{Cd-soil} = K' \ (Cd^{2+})^{n_{Cd}} \ (Ca^{2+})^{-n_{Ca}} \ (H^+)^m \tag{3.1}$$

where $Q_{Cd-soil}$ is the Cd adsorbed by soil (mol/kg),(Cd^{2+}) and (Ca^{2+}) the Cd^{2+} and Ca^{2+} activity (mol/L), (H^+) the proton activity; 10^{-pH} (mol/L). K', n_{Cd}, $-n_{Ca}$ and m are the parameters.

In Eq (3.1) activities have to be used instead of concentrations. With the Davies extension of the Debye-Hückel equation (Bolt & Bruggenwert, 1978) and formation

constants of Cl and NO_3 complexes with Cd (Sillén & Martell, 1971; Smith & Martell, 1981), the Cd concentration, [Cd], can be related with Cd^{2+} activity, (Cd^{2+}), as shown by Boekhold *et al.*(1993) and Temminghoff *et al.* (1995)

$$(Cd^{2+}) = [Cd] f_{Cd} F \tag{3.2}$$

with

$$-\log f_{Cd} = 2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \tag{3.3}$$

and

$$F = \frac{[Cd^{2+}]}{[Cd_{total}]} = \frac{1}{1 + \sum_q K_q^I [X]^q} \tag{3.4}$$

in which f_{Cd} is the activity coefficient of Cd, F is the complexation coefficient, K_q is the formation constants of the Cd complexes with X (Cl^- or NO_3^-) at ionic strength I and [X] is the concentration of Cl^- or NO_3^- respectively.

If a column is percolated with Cd and Ca or Na as background electrolyte, Ca and Na are the major competiting cations. The exchange between Ca and Na can be described with the Gaines Thomas equation (Bolt, 1967; Černík *et al.*, 1994)

$$\frac{1}{2} CaS_2 + Na^+ \rightleftharpoons NaS + \frac{1}{2} Ca^{2+} \qquad K_{Ca}^{Na} = \frac{\dfrac{[NaS]}{S_t} (Ca^{2+})^{0.5}}{\left(\dfrac{2[CaS_2]}{S_t} \right)^{0.5} (Na^+)} \tag{3.5}$$

where CaS_2 and NaS denote adsorbed quantities (mol/kg), (Ca^{2+}) and (Na^+) denote the solution activities (mol/L) and K is the selectivity coefficient. The total available

sites, S_t, is defined by the Cation Exchange Capacity (CEC; mol_c/kg). From Eq (3.5) follows the Ca^{2+} activity needed in Eq (3.1).

To calculate transport, we solved the convection dispersion equation (CDE) for each of the solutes

$$\rho\frac{\partial Q(c)}{\partial t} \; + \; \theta\frac{\partial c}{\partial t} \; =. \; \theta D\frac{\partial^2 c}{\partial z^2} \; - \; \theta v\frac{\partial c}{\partial z} \tag{3.6}$$

where ρ is the soil bulk density (kg/m³), Q adsorbed amount of a component by soil for Ca and Na denoted by $[CaS_2]$ and $[NaS]$ in Eq (3.5) (mol/kg), t time (year), θ volumetric water fraction of the soil (m³/m³), D dispersion coefficient (m²/year), z distance (m) and v the inter-stitial water flow velocity (m/year). Eq (3.6) is solved for each solute (Cd, Ca, Na and Cl) with appropriate initial and boundary conditions (see next section). The first term of Eq (3.6) represents the quantities of solute that has reacted with the solid phase. Interactions between the dissolved species are given by a set of coupled algebraic equations for c.

Materials and Methods

For the batch and column experiments we used an acid sandy soil from the vicinity of Wageningen (Table 3.1). The sandy soil exist for the largest part out of quartz (83 %) and only a small clay fraction (5 %). From the base saturation we conclude that the main part of the CEC is occupied by Ca (49 %).

Batch experiments

Adsorption isotherms were determined at three pH levels (pH 3.5, 4.0 and 5.0) by adding 0.1 M HNO_3 or 0.1 M NaOH to the soil suspension and equilibrating for 24 h before adding cadmium. As background electrolytes 0.01 M $CaCl_2$, 0.01 M $Ca(NO_3)_2$,

0.03 M $NaNO_3$ and 0.02 M $NaCl$/0.01 M $NaNO_3$ were used, each at constant ionic strength of 0.03. These experiments are called experiment A. The effect on Cd sorption of Cl and NO_3 as well as the effect of a divalent cation (Ca) with respect to a monovalent cation (Na), was measured that way. Additionally, Cd adsorption was measured at ten different Ca/Na ratios at I=0.03 and two pH levels (3.5 and 5.0) and three total cadmium concentrations (22.3 - 178 and 356 μmol/L). The extraction solution ratios of $Ca(NO_3)_2$ (0.01 M) : $NaNO_3$ (0.03 M) were 100:0 - 50:50 - 25:75 - 10:90 - 5:95 - 2:98 - 1:99 - 0:100. These experiments are referred to as experiment B.

Table 3.1. Characteristic parameters of the used soil. pH $CaCl_2$ (0.01 M), Texture (%), organic carbon (% C) (Kurmies), Cation Exchange Capacity (mmol +/kg) (unbuffered $BaCl_2$), Base saturation (mmol +/kg) and initial 'total' adsorbed Cd (μmol/kg)(0.43 M HNO_3).

pH-$CaCl_2$	4.2	CEC (mmol +/kg)	18
Texture (%)		base saturation (mmol +/kg)	
> 50 μm	83	Na	0.0
< 50 μm	16	K	1.8
< 16 μm	8	Ca	8.8
< 2 μm	5	Mg	1.5
Organic C (%)	1.0	Total Cd (μmol/kg)	1.78

Column experiments

For the column experiments we used perspex columns with 4.5 cm in diameter and a length (L) of about 20 cm. Two columns were filled with 300 g of the sandy soil. A filter and a thin quartz sand layer were at the bottom of the column to prevent outflow of soil particles. Columns were saturated from below to prevent air inclusion. After

saturation the flow was directed downwards. After about one week of percolation with the background solutions (0.01 M $Ca(NO_3)_2$ and 0.01 M $CaCl_2$), to attain equilibrium, we percolated cadmium, with a concentration of 178 μmol/L, without changing the background electrolytes. Cd and pH were measured in the effluent. After cadmium breakthrough we changed the electrolytes. For the first column we changed from 0.01 M $Ca(NO_3)_2$ to 0.03 M $NaNO_3$ and for the second column we changed from 0.01 M $CaCl_2$ to 0.02M NaCl and 0.01 M $NaNO_3$ (Cl concentration and ionic strength remaining constant), without altering the Cd concentration of the feed solution. The soil density was 1.43 ± 0.02 g/cm^3. Cl was used as a tracer to determine the pore volume (PV) of the columns, which was 99 ± 2 ml, and the diffusion-dispersion coefficient, which was typically 0.050 m^2/year. The porosity ϕ was 0.47 ± 0.02. Flow rates of approximately 1.90 ± 0.05 ml/hour were used for all experiments. The Péclet number Pe ($=vL/D$) during the experiments was about 65. After measuring pH, the effluent was acidified and Cd was measured with FAAS at 228.8 nm (Instrumentation Laboratory AA/AE spectrophotometer S11 with Smith-Hieftje background correction). For the transport calculations we used the computer program ECOSAT, which was developed at the Wageningen Agricultural University (Keizer *et al.*, 1993) which combines one dimensional mass transport calculations with chemical speciation and state of the art (electrochemical) sorption models.

Results & Discussion

Cadmium adsorption isotherms with different background electrolytes and different pH values are given in Fig. 3.1. The isotherms are slightly nonlinear with respect to Cd concentration. In addition, effects of pH, inorganic complexation by Cl, and competition of Ca and Na with Cd are visible. At decreasing pH, adsorption decreases for all electrolytes. Cd adsorption is less for the Cl-electrolytes due to formation of

CdCl-complexes. These complexes are not (significantly) adsorbed by the soil. The complexation by Cl is much more important then complexation by dissolved organic matter (De Wit, 1992), so we neglected the DOM complexation. For the $CaCl_2$ electrolyte, 52 % of the Cd in solution is present as CdCl-complexes. Ca is a stronger competitor for sorption sites than Na. Hence, Cd adsorption is smaller if Ca instead of Na is used as background electrolyte cation.
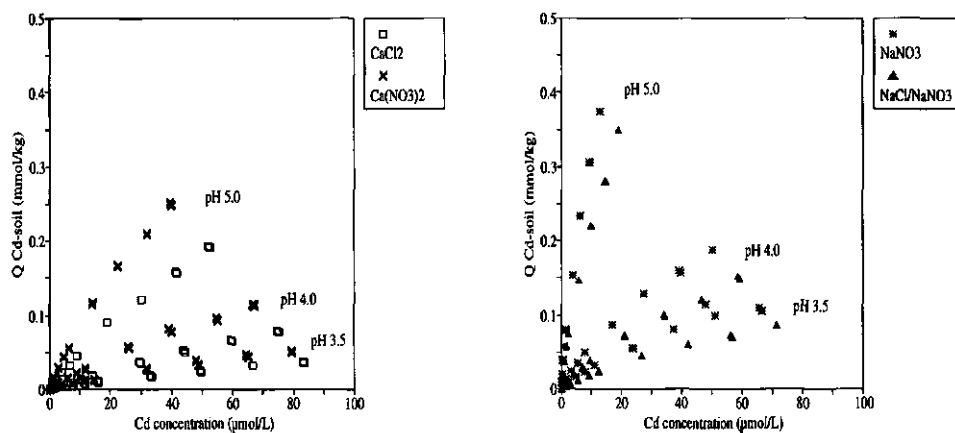
Figure 3.1. Adsorbed Cd as a function of the Cd concentration at 3 pH levels and four electrolyte solutions (experiment A); **a)** 0.01 M $CaCl_2$ and 0.01 M $Ca(NO_3)_2$ and **b)** 0.03 M $NaNO_3$ and 0.02 M $NaCl/0.01$ M $NaNO_3$.

To assess the effect of Ca-competition, we measured Cd adsorption at different Ca/Na ratios at constant ionic strength. The results are shown in Figure 3.2 for pH 3.5 and 5.0 and three Cd concentrations. An increase in the Ca/Na ratio (at constant I) reduces Cd adsorption by a maximum of 60 % for pH 5.0 as well for pH 3.5.
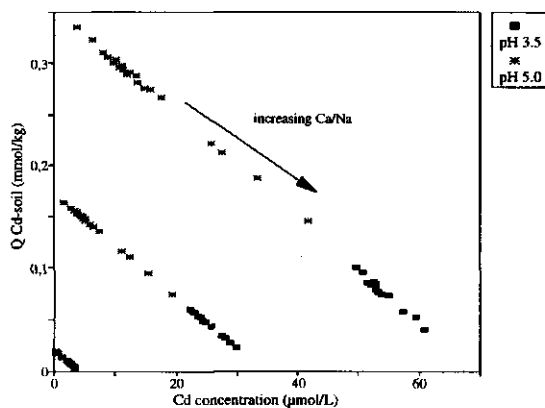
Figure 3.2. Adsorbed Cd as a function of the Cd concentration at two pH levels
and at variable Ca/Na ratio (experiment B).

The parameters for the 3SF equation (Eq (3.1)), which are determined with multiple regression, are $n_{Cd} = -0.85$, $n_{Ca} = -0.34$ and $m = -0.69$. In all cases activities were used. If we take competition by calcium and protons into account, Cd ad-sorbed as a function of the product of $(Cd^{2+})^{0.85}$, $(H^+)^{-0.69}$ and $(Ca^{2+})^{-0.34}$ should yield straight line with constant slope K'. In all cases the same K' (-3.81 ± 0.02) is found. If we assume that Cd, Ca and protons adsorb on the same sites the result implies that the effects of pH and Ca competition on Cd-adsorption are explained succesfully with the 3SF equation.

With the 3SF and transport equations, effects of complexation, pH and Ca competition on Cd mobility were calculated. In the case of inorganic complexation by Cl, the mobility increases by a factor 2 because 52 % of the total Cd in solution is complexed with Cl and does not adsorb. Decreasing pH by one gives an increase in mobility by a factor of 4 (0.01 M Ca has been used as background electrolyte). An increase in Ca concentration by a factor 100 shows a increase in mobility by a factor 5 at pH 4.5.
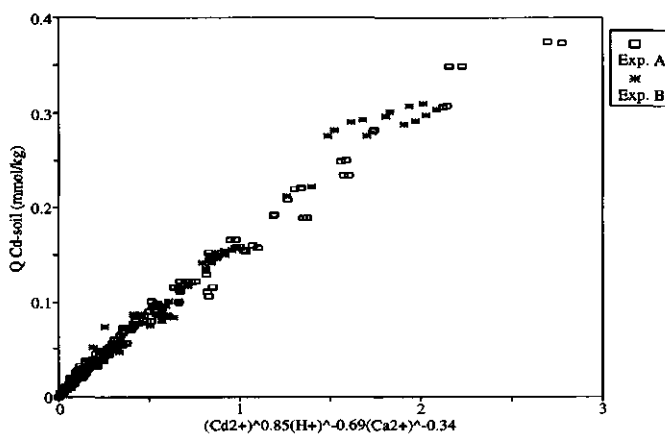
Figure 3.3. Adsorbed Cd as a function of $(Cd^{2+})^{0.85}(H^+)^{-0.69}(Ca^{2+})^{-0.34}$ for results of experiment A and B.

In Fig. 3.4 experimental data and predictions of Cd breakthrough curves (BTC) are given for 0.01 M $Ca(NO_3)_2$ and 0.01 M $CaCl_2$ as background electrolyte. The solid lines are the *predictions* from the 3SF model. In both cases the same constants are used. For $CaCl_2$ the formation of CdCl-complexes was incorporated in the model. pH was measured and was almost constant during the experiment. Due to the small (pore)water velocities we assumed virtual local equilibrium during Cd transport. The model qualitatively predicted Cd breakthrough with or without complexation reasonably well. Nevertheless we observe some discrepancies between numerical and analytical results that may be due to factors that were not accounted for (e.g. kinetics, small pH variations).
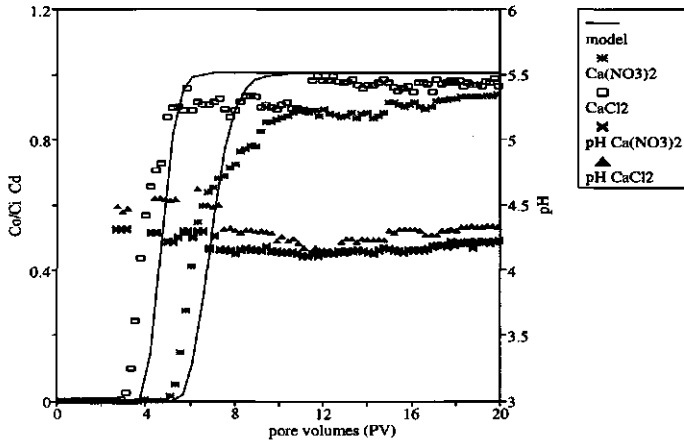
Figure 3.4. Experimental data and model calculations for the Cd breakthrough curves (BTC) and pH for two elctrolytes; 0.01 M CaCl$_2$ and 0.01 M Ca(NO$_3$)$_2$.

The effect of competition of Cd with Ca and Na as background electrolyte, both at an ionic strength of 0.03 are given in Fig. 3.5 for the experimental data as well for the model. After 30 pore volumes (arrow in Fig. 3.5) the electrolyte 0.01 M Ca(NO$_3$)$_2$ was changed to 0.03 M NaNO$_3$. After changing electrolytes a sharp peak of Cd and Ca was found in the effluent before the relative concentration (c_e/c_i) decreased, due to a reduction in Ca competition. Due to the decrease in Ca concentration an increase in Cd sorption appears. The small Cd peak can be explained by an increase in the salt concentration. We changed the electrolyte from 0.01 M Ca(NO$_3$)$_2$ to 0.03 M NaNO$_3$ which gives an increase in salt concentration by a factor 3 (the ionic strength of the influent was constant, I=0.03). Due to preferent adsorption an increase in ionic strength and Ca concentration exist for a short period (see Fig. 3.5). This saltfront increases the Cd concentration shortly before Cd sorption takes place. Similar saltfronts for major cations were found by Černík *et al.* (1994).
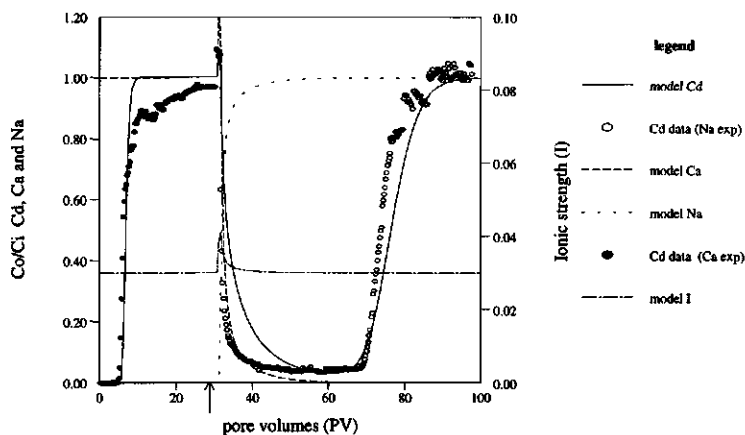
Figure 3.5. Experimental data and model calculations for Cd breakthrough curves (BTC) and background electrolytes $Ca(NO_3)_2$ followed (at arrow) by $NaNO_3$.

Due to the decrease in Ca competition the retardation factor of Cd decreased with a factor of 10 for the Na-electrolyte with respect to the Ca-electrolyte. The selectivity coefficient for Ca and Na K was 0.94 and was determined by integration of the breakthrough curve (BTC) of Ca (data not shown). The model qualitatively predicts the Cd breakthrough quite well although some discrepancies can be observed, possibly due to kinetic and small pH variations which are not taken into account.

Conclusions

The mobility of Cd was strongly influenced by pH, complexation and competition. With the proposed models, the three Species Freundlich (3SF) and the Gaines Thomas (GT) equation, the relative importance of these factors can be shown. By extrapolating

laboratory column experiments to field experiments special care should be taken. Calcium concentrations and pH should be taken into account to get a better prediction of the mobility of Cd under field conditions.

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Chapter 4

The Influence of pH on the Desorption and Speciation of Copper in a Sandy Soil

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Abstract

The effect of pH on copper desorption from a sandy soil and on complexation by dissolved organic fractions was studied, using a soil, with pH ranging from 4.3 to 5.6, which had been 'polluted' with copper a decade ago. For the desorption of extractable copper we used an unbuffered electrolyte solution (0.0033 M $Ca(NO_3)_2$; ionic strength 0.01 M). 'Free' copper was determined using an ion exchange resin method. Copper bound by dissolved organic matter was divided into a humic and a fulvic fraction using ultrafiltration. The Cu desorption isotherms were non-linear and dependent on pH. The (desorbed) extractable copper was less then 3 % of the total copper in soil. About 1 % of extractable copper was complexed with nitrate and free copper varied from 2 % (pH 5.7, 0.3 mmol/kg total Cu) to 9 % (pH 4.4, 3 mmol/kg total Cu). The remainder of extractable Cu was bound by dissolved organic matter. The amount of Cu bound by solid organic carbon (CuSOC) was almost equal to Cu bound by dissolved organic carbon (CuDOC) when both are expressed in mmol/g C, although there was a pH dependency. At low pH (4.4) Cu was predominantly bound by fulvic fraction and at pH 5.7 most was bound by humic fraction. Desorption of copper from soil, copper binding by humic and fulvic fraction (all different pH dependent) could be described adequately with the Two Species Freundlich (TSF)

equation. With this equation the competition between soil, fulvic fraction and humic fraction for free copper (Cu^{2+}) was shown.

Introduction

Adsorption and desorption processes, precipitation and dissolution of mineral copper influence the speciation behaviour of copper in soil. Speciation of copper in acid sandy soil is primarily regulated by sorption reactions. Precipitation and dissolution of copper is unlikely, except in soils which are calcitic or high in sulfide (Lindsay, 1979).

Depending on concentration, copper can be either a micronutrient or toxic for biota. Both beneficial and adverse effects depend on copper speciation in solution (Sunda & Gillespie, 1979; Van den Berg, 1984; McCarthy, 1987; Verweij, 1991). 'Free' copper (Cu^{2+}) is generally assumed to be the (most) bioavailable species. Therefore, this species predominantly controls whether we deal with deficiency or with toxicity of copper. Besides free copper, copper can be present in the form of inorganic complexes (e.g. with chloride, nitrate, hydroxy, sulfate) and organic complexes (e.g. with humic acid, fulvic acid, citric acid), which may be biologically unavailable (Baccini and Suter, 1979).

As a practical test to assess the bioavailability of heavy metals in soil an extraction with an unbuffered electrolyte solution has been recommended (Sanders *et al.*, 1987; Novozamsky *et al.*, 1992). Such an extraction method may be regarded as a measure for the easily extractable forms. For a chemical interpretation of the extraction, the speciation of the heavy metal should be assessed in the extract solution. Generally, Atomic Absorption Spectrometry (AAS) is used for measuring the total copper concentration in solution. From the total copper concentration in solution, the concentration of different inorganic complexes is relatively simple to calculate using (available) equilibrium constants (K-values) reported in literature. An illustration of

this approach was given by Boekhold *et al.* (1993) for Cd adsorption by sandy soil. For organic metal-complexes, speciation is usually difficult to assess because of the complexity and heterogenic nature of the organic compounds with many different types of sorption sites (Nederlof, 1992; De Wit, 1992).

The ion-exchange resin techniques were among the first methods employed to study complexes with humic and fulvic compounds by indirect measurement of 'free' copper (Baccini and Suter, 1979; Buffle, 1988). 'Free' copper ions are adsorbed by a cation resin and copper complexes do not. Lexmond (1980) used a cation acidic cation resin (Dowex 50W-X4) in the calcium form for a batch system of soil with resin. The advantage of the ion-exchange resin method used in a batch system is that a sufficiently long period can be used for equilibrium between 'free' copper and copper bound by soil and resin.

The soluble organic fraction of soil represents a complex system consisting of molecules that have a wide range of molecular weights, ranging from a few hundred for fulvic acids to several 100,000 for humic acids (Stevenson, 1982). The humic acid has more aliphatic chains and undergoes more condensation and adsorption reactions than the fulvic acid. The fulvic acid is more oxidized, resulting in a lager number of COOH group content, and larger charge and solubility (more hydrophilic) (Buffle, 1988). Ultrafiltration is one of the techniques which is generally accepted for fractionating dissolved organic matter on a molecular weight basis (Hoffman *et al.*, 1981; Staub *et al.*, 1984; Verweij, 1991). By choosing the right membranes it appeared feasible to distinguish between a fulvic fraction (mainly fulvic acids) and a humic fraction (mainly humic acids) (Buffle, 1988) and to distinguish the copper bound to this fractions.

The aim of this research is to study the speciation of copper in acid sandy soil (solution) and how this speciation depends on pH and Cu content. For soil we deal with competition between soil and dissolved organic matter, consisting of humic fraction and fulvic fraction, for 'free' copper. We show the applicability of an extended

Freundlich equation, for modelling the binding of copper by sandy soil, by dissolved organic matter (DOM) consisting of the humic fraction (HF) and the fulvic fraction (FF).

Theory

Adsorption or desorption of cations by soil occurs predominantly on (from) surfaces which are negatively charged, such as organic matter, clay and metal(hydr)oxides. Besides sorption by these solid phases, complexation of cations with inorganic species and dissolved organic matter (DOM) in the soil solution may also occur. Schematically, this can be represented for Cu desorption from soil by

$$Cu\text{-soil} \quad \rightleftharpoons \quad Cu^{2+} \tag{4.1a}$$

$$Cu^{2+} \quad \rightleftharpoons \quad Cu\text{-inorganic} \tag{4.1b}$$

$$Cu^{2+} \quad \rightleftharpoons \quad Cu\text{-organic (Cu-DOM)} \tag{4.1c}$$
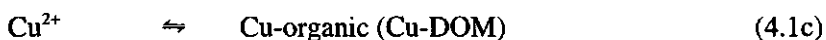
All these processes are regulated by the 'free' copper activity (Cu^{2+}). We deal with a competition between soil, dissolved organic matter and inorganic species for the free copper ion. The monovalent copper ion (Cu^{+}) is only relevant in strongly anaerobic soils.

If only Cu^{2+} and Cu-inorganic are present in solution, it is possible to calculate the Cu^{2+} activity using the equilibrium complexation constants (K^{0}) and the total concentrations of copper and inorganic components. Whereas for inorganic complexation the formation constants are available, this is seldom the case for organic complexes. Natural organic matter (dissolved or undissolved) is characterized by a wide range of functional groups that differ in their affinity for binding cations

(Nederlof, 1992). In soil we deal with competition of soil and dissolved organic matter (humic and fulvic compounds) for Cu^{2+} and other cations which will influence the Cu binding. By making several assumptions it is however possible to describe the Cu binding by soil humic and fulvic compounds with a relative simple model.

According to De Wit (1992) the metal binding to organic matter can be written as follows:

$$S_i^- + Cu^{2+} + x\ H_2O \rightleftharpoons S_iCu(OH)_x^{1-x} + x\ H^+ \tag{4.2}$$
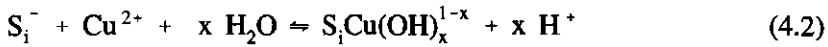
assuming a monodentate binding of the divalent copper ion with a site S_i. The factor (x) that accounts for the (partial) hydrolysis of the surface complex may have a non-integer value because binding of metal ions may lead to a decrease of the negative charge of the organic matter which may induce electrostatic interactions that cause a concomitant release of protons. This rather simplified equation is a convenient choice since it is characterized by a small number of parameters and accounts for the pH dependency of metal ion binding in a relative simple way. In the case of a Langmuir isotherm the (local) adsorption of Cu by site S_i^- can be expressed as

$$\theta_{Cu^{(i)}} = \frac{Q_{Cu}^{(i)}}{Q_{Cu(max)}^{(i)}} = \frac{[S_iCu(OH)1_x^{1-x}]}{[S_i^-] + [S_iCu(OH)_x^{1-x}]} = \frac{\dfrac{K_{Cu}^{(i)}.(Cu^{2+})}{(H^+)^x}}{1 + \dfrac{K_{Cu}^{(i)}.(Cu^{2+})}{(H^+)^x}} \tag{4.3}$$

However, humic substances have many different types of functional groups (S_i^-) each of which may bind metal ions to specific stoichiometry which not leads to a single equilibrium constant (K-value) but to distribution of K-values. When the difference between the consecutive K-values is small the overall adsorption of Cu on a continuous heterogeneous surface (Q_{Cu}) is given by a an integral function

$$Q_{Cu} = Q_{Cu(max)} \int_{\Delta log K_{Cu}} \frac{Q_{Cu}^{(i)}}{Q_{Cu(max)}^{(i)}} \, f(log K_{Cu}) \, d \, (log K_{Cu}) \tag{4.4}$$

where $f(log \, K_{Cu})$ is the distribution function of the affinity constants and $Q_{Cu}^{(i)}$ is the (local) adsorption which holds for parts of the surface with a certain affinity K_{Cu}. $\Delta log K_{Cu}$ is the relevant range of integration. $Q_{Cu(max)}^{(i)}$ and $Q_{Cu(max)}$ are the local and total Cu adsorption maximums respectively. If the distribution of $log \, K_{Cu}$ shows a nearly semi-gaussian function this integration can be solved analytically (Van Riemsdijk *et al.*, 1986). Which results in the Langmuir-Freundlich equation:

$$Q_{Cu} = Q_{Cu(max)} \cdot \frac{\left(\dfrac{\tilde{K}_{Cu} \cdot (Cu^{2+})}{(H^+)^x} \right)^n}{1 + \left(\dfrac{\tilde{K}_{Cu} \cdot (Cu^{2+})}{(H^+)^x} \right)^n} \tag{4.5}$$

where Q_{Cu} is the adsorbed amount Cu to organic matter (mmol/g), $Q_{Cu(max)}$ the adsorption maximum, n is related with the width of the distribution ($0 < n \le 1$) and $\tilde{K}_{Cu}$ the median of the $log \, K$ distribution. If we include the electrostatic interaction effect and also the competition effect of other cations in the soil solution for binding to organic matter in the affinity constants, the affinity constants have to be changed in conditional activity quotients (Perdue, 1987). At low Cu^{2+} activity this equation can be simplified to:

$$Q_{Cu} = Q_{Cu(max)} \cdot \left(\frac{\tilde{K}_{Cu} \cdot (Cu^{2+})}{(H^+)^x} \right)^n \tag{4.6}$$

which also can be written as

$$Q_{Cu} = K'_{Cu} \, (H^+)^m \, (Cu^{2+})^n \tag{4.7}$$

Where $K'_{Cu} = (\tilde{K}_{Cu})^n . Q_{Cu(max)}$ and $m = -x\,n$. Equation (4.7) we call the Two Species Freundlich (TSF) equation.

In view of the given background, the Two Species Freundlich equation that explicitly accounts for pH-effects, eq (4.7), is particularly useful for acid sandy soils where organic matter is the chemically most active surface. Hence, for soil we have

$$Q_{Cu-soil} = K'_{Cu-soil} \, (H^+)^{m_{Cu-soil}} \, (Cu^{2+})^{n_{Cu-soil}} \tag{4.8}$$

where $Q_{Cu-soil}$ is the adsorbed amount Cu (mol/kg soil), (Cu^{2+}) the 'free' copper ion activity (mol/L), (H^+) the proton activity (mol/L) and $K'_{Cu-soil}$, m, n are the parameters. These parameters depend on soil type and experimental conditions. Because the free Cu^{2+} ion is the dominant sorbing Cu-species, sorption is related with the Cu^{2+}-activity instead of the extractable copper concentration in solution. The extractable Cu concentration (Cu_{ex}), assessed by soil extraction with an unbuffered electrolyte (e.g. 0.0033 M $Ca(NO_3)_2$), exists of 'free' copper (Cu^{2+}), inorganic- and organic complexed copper:

$$[Cu_{ex}] = [Cu^{2+}] + [Cu\text{-}inorganic] + [Cu\text{-}organic] \tag{4.9}$$

Inorganic complexation by nitrate (used as the electrolyte anion in the experiments) that yields $Cu(NO_3)^+$ involves only 1 % of the total dissolved copper for the used NO_3^- and Cu concentrations according to the log K-values of Smith & Martell (1981). Hence, we conclude that inorganic complexation is negligible. The organic complexes are, however, rather important and can be quantified indirectly.

The 'free' copper ion activity can be quantified using a ion exchange resin

technique. A batch system with soil and resin can be represented by

$$Cu\text{-soil} \leftrightharpoons Cu^{2+} \leftrightharpoons Cu\text{-Resin} \tag{4.10}$$

Using a cation exchange resin Cu^{2+} will be adsorbed by the resin (Bacccini and Suter, 1979). Because Cu-complexes are hardly adsorbed by both soil and resin these complexes do not affect the equilibrium. The relationship between Cu^{2+} and Cu bound to the resin ($Q_{Cu\text{-resin}}$), *without* soil, is determined first and yields the copper resin adsorption isotherm or calibration curve. In the system with resin and *with* soil the copper bound to the resin is measured. Using the resin calibration curve we obtain the relationship between the Cu^{2+} activity and the amount of Cu sorbed by the soil. This sorbed amount is calculated as Cu 'total' initially adsorbed by the soil minus the extractable Cu concentration minus Cu adsorbed by the resin. By using eq (4.8) the relation between (Cu^{2+}), pH and $Q_{Cu\text{-soil}}$ can be calculated. Subsequently the Cu^{2+} activity can be calculated at the pH and $Q_{Cu\text{-soil}}$ of the $Ca(NO_3)_2$ extraction. From the Cu^{2+} and the extractable Cu concentration the copper bound to the dissolved organic matter can be calculated using eq (4.9) and neglecting Cu-inorganic.

By ultrafiltration a distinction can be made between a humic fraction and a fulvic fraction based on molecular weight fractionation. Soluble organic fraction of soil consists of molecules which have wide range of molecular weights, ranging from a few hundred for fulvic acids to several 100,000 for humic acids (Stevenson, 1982). The ultrafiltrate (using filters with a molecular weight cut off of 10,000) consists of 'free' copper (Cu^{2+}) and copper bound to the fulvic fraction (CuFF) (largely fulvic acids)

$$[Cu_{UF}] = [Cu^{2+}] + [CuFF] \tag{4.11}$$

where Cu_{UF} is the total copper concentration in the ultrafiltrate. The 'free' copper

concentration can be deduced from resin bound copper, whereafter the Cu bound to the fulvic fraction can be calculated. Likewise Cu bound to the humic fraction (CuHF) (largely humic acids) can be calculated with

$$[CuHF] = [Cu_{ex}] - [Cu_{UF}] \tag{4.12}$$

The concentration of dissolved organic matter (DOM) and fulvic fraction (FF) is measured as DOC, the dissolved organic carbon concentration (mg/L C).

The extractable Cu concentration in a soil extract solution can now be expressed as

$$[Cu_{ex}] = [Cu^{2+}] + K^{l}_{CuHF}(H^{+})^{m_{CuHF}}(Cu^{2+})^{n_{CuHF}} + K^{l}_{CuFF}(H^{+})^{m_{CuFF}}(Cu^{2+})^{n_{CuFF}} \tag{4.13}$$

With equation (4.8) and (4.13) the competition between soil, humic fraction and fulvic fraction for Cu binding can be calculated as a function of pH and the 'free' copper activity.

Materials and methods

Soil samples were taken from a field which has been used previously to study copper toxicity for maize (Lexmond, 1980). The soil was a Spodosol in a slightly loamy moderately fine sand. Four pH levels (i.e. pH-CaCl$_2$ 3.9, 5.0, 5.7 and 6.2) were established in 1982, followed by establishment of four total Cu levels (i.e. 0, 250, 500 and 750 kg/ha) at each pH-level (Lexmond, 1980). Soil samples were collected from the 16 plots, i.e. one for each pH/Cu combination, at a depth of 0 - 25 cm, air-dried and sieved (< 2 mm). Typical soil properties were measured, such as pH in 0.01 M CaCl$_2$, grain size distribution, organic carbon (analyzed according to Kurmies) and

cation exchange capacity (CEC) and base saturation using the unbuffered $BaCl_2$ method (all described in Houba *et al.*, 1988). The data are provided in Table 4.1 for each plot. Codes A, B, C, D designate the pH-levels and 1, 2, 3 ,4 designate the Cu-levels. The extraction with 0.43 M HNO_3 (soil:solution ratio 1:10) is assumed to yield the initial total amount adsorbed Cu (Houba *et al.*,1988). The 0.43 M HNO_3 extraction was done in triplicate.

Extraction with 0.0033 M Ca(NO₃)₂

The extraction with an unbuffered extraction solution gives an indication of the easily extractable Cu-species. For this purpose we used a 0.0033 M $Ca(NO_3)_2$ (ionic strength $I = 0.01$) at a soil : solution ratio of 1:4. The soil suspension was shaken end-over-end for 20 h at 20 °C after which the pH was measured in the suspension. After centrifugation at 10,000 g, the total Cu-concentration (Cu_{ex}) in the supernatant was measured using an atomic absorption spectrophotometer (Instrumentation Laboratory AA/AE spectrophotometer S11 with scale expansion, an air-acetylene flame and a wavelength of 324.7 nm). The detection limit was approximately 0.02 mg/l. The dissolved organic carbon (DOC) was measured with the fully automated SK^{12} (Skalar) TOC/DOC analyzer.

Ultrafiltration for copper fraction < 5nm

For ultrafiltration, 50 ml of the 0.0033 M $Ca(NO_3)_2$ extraction solution were used. The ultrafiltration was carried out under nitrogen pressure (300 kPa) in a filtration cell (Schleicher & Schüll UP050/S), using filters with a MWCO of 10,000 (Schleicher & Schüll AC61, pores < 5 nm). We assume that the filtrate contains only the free copper ion and copper bound to the fulvic fraction ([Cu^{2+}] and [Cu-FF]). The first 10 ml of the filtrate was discarded and the next 10 ml filtrate was used for analysis of Cu and DOC. Adsorption of Cu^{2+} by the filtration unit and the filters were tested by filtering a standard solution of 1 mg/L Cu in 0.0033 M $Ca(NO_3)_2$ at pH 5. Adsorption of Cu was

Table 4.1. Some characteristics of the soil used in the experiments.
pH CaCl$_2$, Texture (%), organic matter (% C), Cation Exchange Capacity (mmol +/kg), Base saturation (mmol +/kg) and 'total' Cu with standard deviation (mmol/kg).

Code	pH-CaCl$_2$	Texture (%)				organic C (% C)	CEC (mmol +/kg)	base saturation (mmol +/kg)				Cu-HNO$_3$ (mmol/kg)
		>50 µm	<50 µm	<16 µm	<2 µm			Na	K	Mg	Ca	
1 A	4.32	85.5	11.9	5.7	2.9	1.98	29.5	1.3	1.0	1.8	12.9	0.26 ± 0.005
2 A	4.32	85.3	12.3	6.2	2.2	2.20	33.2	1.3	1.0	1.8	13.9	1.19 ± 0.03
3 A	4.31	85.6	12.2	6.3	1.7	2.16	29.2	0.4	1.5	1.8	12.5	2.14 ± 0.01
4 A	4.25	85.6	12.3	6.3	3.4	2.15	30.5	1.3	1.0	1.8	11.9	2.95 ± 0.02
1 B	4.69	85.7	12.2	5.5	2.4	1.89	38.2	1.3	1.0	4.1	38.4	0.29 ± 0.002
2 B	4.56	84.6	13.4	6.9	2.9	2.02	35.5	1.3	1.0	2.5	20.5	1.24 ± 0.05
3 B	4.58	84.1	12.9	5.1	1.9	2.14	35.1	0.4	1.0	2.1	19.7	2.15 ± 0.01
4 B	4.59	84.4	13.3	6.2	2.4	2.02	23.3	1.3	1.5	1.8	18.1	3.03 ± 0.02
1 C	5.12	83.6	14.1	8.1	5.0	2.26	45.5	0.4	1.0	3.1	37.8	0.33 ± 0.003
2 C	5.06	83.4	13.9	7.5	3.8	2.34	42.6	1.3	1.0	2.5	31.2	1.29 ± 0.01
3 C	5.00	84.5	12.6	6.9	3.3	1.87	38.7	1.3	1.0	2.5	25.8	2.17 ± 0.02
4 C	4.95	83.7	13.9	8.1	5.0	2.07	43.5	0.4	1.5	2.5	30.0	3.18 ± 0.04
1 D	5.54	84.2	12.8	6.9	3.9	2.21	52.3	1.3	1.0	2.8	42.4	0.32 ± 0.005
2 D	5.46	83.9	14.0	7.4	3.8	2.24	56.6	0.4	1.0	5.4	56.4	1.28 ± 0.09
3 D	5.56	84.0	13.1	6.7	4.5	2.18	50.0	0.4	1.0	3.1	43.2	2.23 ± 0.05
4 D	5.49	84.3	12.9	6.3	3.3	2.10	52.7	1.3	1.0	2.8	41.2	3.11 ± 0.12
mean	-	84.5	13.0	6.6	3.3	2.11						
std	-	0.8	0.7	0.8	1.0	0.13						

negligible (< 2 %) if the first 10 ml of the filtrate was discarded.

Resin method for the free copper fraction

In soil we deal with large amounts of Ca derived from the base saturation of the soil (Table 4.1) and electrolyte solution (0.0033 M $Ca(NO_3)_2$). This implies that when using strongly acidic cation exchange resins (like Dowex 50WX8) Cu adsorption will be small due to competition with calcium. The selectivity coefficient K_{Ca}^{Cu} (BDH, 1981) is less than 1, i.e., the resin shows a preference for Ca. Important for the method is that the Cu adsorption by the resin has to be large, in the presence of high concentrations of Ca, in order to achieve accurate measurements of the adsorbed copper. Therefore we choose a weakly acidic resin with chelating properties (IRC-718; BDH, 1981), which preferently adsorbs heavy metals compared with calcium. The resin was already (partly) in the Ca-form. Before use the resin has been washed extensively with 0.0033 M $Ca(NO_3)_2$.

Soil samples of 20 g were shaken with 80 ml of 0.0033 M $Ca(NO_3)_2$ and 0.5 g of the resin. The resin was contained in a nylon netting bag (nyboldt PA-50/27, Kabel Zaandam) with a mesh size of 50 μm to keep coarse soil particles and root fragments apart from the resin. After 100 h end-over-end shaking at 20 °C the pH was measured. Then the resin bag was withdrawn from the soil suspension and the resin was removed from of the bag on a buchner funnel with a filter of nylon (nyboldt PA-350/36) using distilled water. Next the resin was washed free from soil by rinsing with distilled water. Copper was stripped in a polyethylene bottle by adding 25 ml 1 M HNO_3 to the resin and shaking for 2 h. The Cu concentration was measured by flame-AAS and the lower Cu concentrations by graphite furnace AAS (Varian SpectrAA 300). A resin calibration curve (Cu adsorption isotherm) was prepared by adding different Cu concentrations (0.0033 M $Ca(NO_3)_2$ electrolyte) to the resin without soil. In that case, the pH was kept constant using a pH stat titration unit (VIT 90 Video titrator, Radiometer). Calibration experiments were performed at 3 pH levels, i.e., pH 4, 4.5

and 5. The experiments with soil and resin required no pH stat due to the buffering capacity of the soil.

Results and discussion

Soil texture and organic carbon content results, shown in Table 4.1, were almost the same for all field plots. Means and standard deviations for the 16 plots were respectively for the fraction > 50 µm 84.5 ± 0.8 %, < 50 µm 13.0 ± 0.7 %, < 16 µm 6.6 ± 0.8 and < 2 µm (clay fraction) 3.3 ± 1.0. The organic carbon content (% C) was 2.11 ± 0.13. As the cation exchange capacity (CEC) was assessed with the unbuffered $BaCl_2$ method, the actual CEC is measured, i.e. the CEC at the soil pH. The CEC increases from 30.6 ± 1.5 mmol +/kg at pH 4.30 to 52.9 ± 2.4 at pH 5.5. From the base saturation we conclude that the main part of the CEC is occupied by Ca, 42 % at pH 4.3 and 86 % at pH 5.51.

The initial 'total' adsorbed Cu in the soil varied between 0.26 to 3.18 mmol/kg for the different treatments. Total Cu content was almost equal for each Cu level at all pH levels. Although for each Cu level a slight decrease in total Cu was seen as pH decreased, the differences were minor. This effect can possibly be explained by the fact that at lower pH Cu is more mobile and has been transported to deeper soil layers during the last decade.

In Fig. 4.1 Cu-desorption isotherms are shown at the four pH levels 4.3, 4.7, 5.2 and 5.7 as a function of the extractable copper concentration, Cu_{ex}, in the $Ca(NO_3)_2$ electrolyte. Copper desorption appears to be pH dependent. A decrease of 1 pH value gave an increase in the total extractable copper concentration of approximately a factor 2 for the considered range of pH values. The desorbed quantity was for all cases between 1 and 3 % of the total adsorbed copper, hence most copper remained adsorbed on the soil.
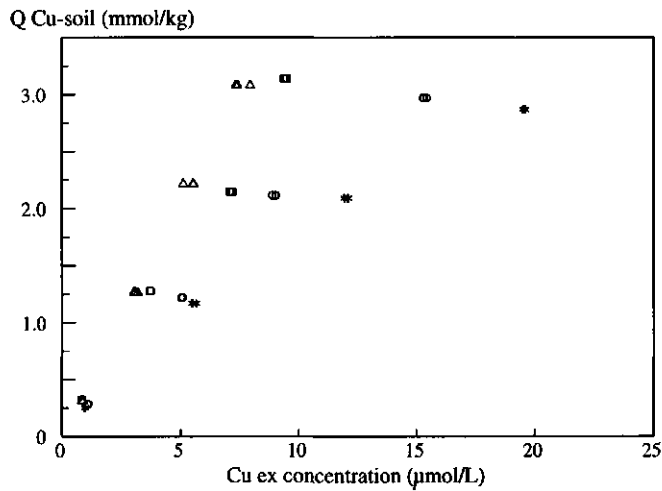
Q Cu-soil (mmol/kg)

Figure 4.1. Copper desorption isotherm; copper soil content ($Q_{Cu\text{-soil}}$ (mmol/kg)) as function of total extractable copper concentration (Cu_{ex} (μmol/L)) for 4 pH levels. $* = $ pH 4.3; $\circ = $ pH 4.7; $\square = $ pH = 5.2; $\triangle = $ pH 5.7.

After linearization of the Two Species Freundlich equation (4.8) by log transformation multiple linear regression can be used by taking $\log(Q_{Cu\text{-soil}})$ as response variable and pH and $\log(Cu_{ex})$ as regressor variables. Note that in this first approach instead of the free copper activity we took the extractable copper concentration. The results are given in Table 4.2. The coefficient of determination (r^2) of 0.99 shows that the Cu desorption can be described quite well with the TSF-equation. As our model suggests, all pH-effects are accounted for by the term $(H^+)^{-0.22}$. Hence, the ratio of $Q_{Cu\text{-soil}}$ and this factor shown as function of the extractable copper concentration should yield a single curve for all considered pH-values. As is shown in Figure 4.2 this appears to be the case.

Table 4.2. Multiple linear regression results of the $Ca(NO_3)_2$ extraction and the resin method by taking $log(Q_{Cu\text{-}soil})$ as dependent variable and pH and $log(Cu_{ex})$ or $log(Cu^{2+})$ as independent variables (using equation (4.6)). ($Q_{Cu\text{-}soil}$ in mol/kg and Cu_{ex} or Cu^{2+} in mol/L)

	Cu_{ex} ($Ca(NO_3)_2$)	Cu^{2+} (resin-method)
$log(K_{Cu\text{-}soil})$	1.13 ± 0.09	0.035 ± 0.004
$m_{Cu\text{-}soil}$	-0.22 ± 0.01	$-0.35 + 0.01$
$n_{Cu\text{-}soil}$	0.94 ± 0.01	0.70 ± 0.00
residue component (e)	0.00 ± 0.00	0.00 ± 0.07
coefficient of determination (r^2)	0.99	0.96
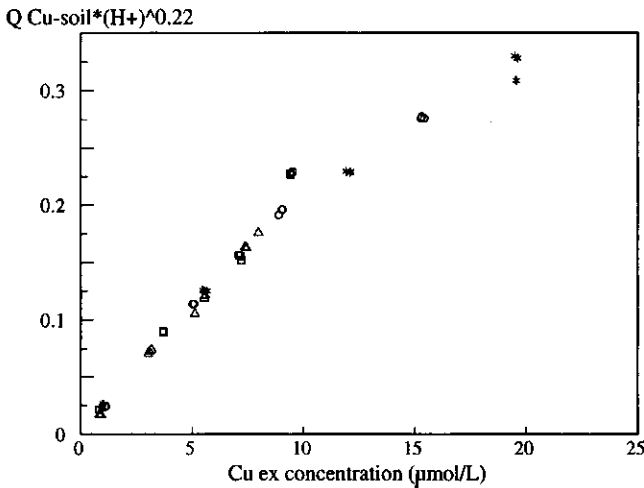
Figure 4.2. Product of the soil copper content ($Q_{Cu\text{-}soil}$ (mmol/kg)) and $(H^+)^{0.22}$ as function of the total extractable copper concentration (Cu_{ex} (µmol/L)). $*$ = pH 4.3; $\circ$ = pH 4.7; $\square$ = pH 5.2; $\triangle$ = pH 5.7.

However, because copper binding by acid soil and by dissolved organic matter is primarily regulated by the 'free' copper activity (Cu^{2+}), so Cu^{2+} should be used instead of Cu_{ex}.

The resin calibration curve shown in Figure 4.3, shows the relationship between Cu^{2+} and the resin adsorbed Cu, at pH 4.5, 5.0 and 5.5. At low Cu^{2+} concentrations the Cu adsorption shows a linear adsorption and is pH independent. The adsorption of Cu on IRC-718 resin can be described with the Langmuir equation

$$Q_{Cu-Resin} = \frac{Q_{Cu-Resin(max)} \; K_L \; (Cu^{2+})}{(1 \; + \; K_L \; (Cu^{2+}))} \tag{4.14}$$

The constants K_L and $Q_{Cu-Resin(max)}$ were calculated from the data shown in Figure 4.3 were $K_L = (1.04 \pm 0.25) * 10^5$ mol/l and $Q_{Cu-Resin(max)} = 0.987 \pm 0.002$ mmol/g. From the quantity of copper adsorbed by the resin, we can calculate the Cu^{2+} concentration between 10^{-5} and 5.10^{-8} M by interpolation. For smaller concentrations extrapolation is necessary.
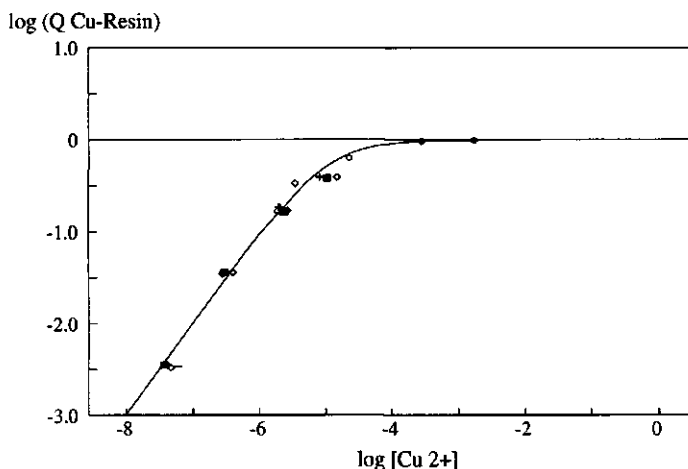
Figure 4.3. Cu resin calibration curve for three pH levels in 0.0033 M Ca(NO$_3$)$_2$. ■ = pH 4.5; + = pH 5.0; ◊ = pH 5.5.

Free copper activities in the soil solution determined with the resin method varied from 10^{-6} to 10^{-8} M. The resin experiments with soil shows a slight pH decrease with respect to the $Ca(NO_3)_2$ extraction. Since the Cu content in the soil was decreased significantly in the resin experiment (by adsorption on the resin), the results can not be compared directly to the $Ca(NO_3)_2$ extraction. Multiple regression gives a coefficient of determination (r^2) of 0.96 (Table 4.2), so 'free' copper desorption can be described quite well with the Two Species Freundlich equation. Besides that the $\log(K)$ value found by inserting 'free' copper in Eq.(4.8) is about 12 times smaller than the coefficient in terms of the extractable copper, also the pH dependency is larger. Other metals can also adsorb onto the resin (i.e. Fe, Al and Mn). Because the concentrations of these metals were quite small, it is unlikely that these metals affect copper binding by the resin. Adsorption of DOC by the resin has been measured by shaking DOC with and without resin. The difference showed that less than 5 % of the DOC initially present in the soil extract was adsorbed by the resin. With respect to the total copper adsorption by the resin this effect is insignificant on the calculated 'free' copper concentration.

The Two Species Freundlich model (Eq. (4.8)) can be used to calculate the free copper concentrations for a particular pH and copper content of the soil. For the $Ca(NO_3)_2$ experiments we calculated the 'free' copper activity and the Cu bound by dissolved organic matter (CuDOM) or carbon (CuDOC) (Eq. (4.7)). DOC concentrations decrease from 64 ± 3 mg/l C at pH 4.4, for all Cu levels, to 49 ± 3 mg/l C at pH 5.6. We assume that copper in soil is not bound by the mineral fraction of the solid phase but only by the (solid) soil organic matter (CuSOM) fraction. This implies that we can express CuSOM in terms of mmol/g C (soil organic carbon CuSOC) which was useful for comparison with CuDOC , which was also expressed in mmol/g C (Figure 4.4). The quantities of copper bound by solid and by dissolved organic carbon are almost equal at pH 5.7. At pH 4.4, CuDOC is approximately two times CuSOC, possibly due the fact that at low pH more fulvic acids are dissolved which

have a higher binding capacity (Buffle, 1988). However, the partitioning of Cu over solid and solution phases, depends much stronger on quantities of organic C in these two phases. The amount of SOC is approximately one hundred times higher than DOC for the $Ca(NO_3)_2$ extraction.
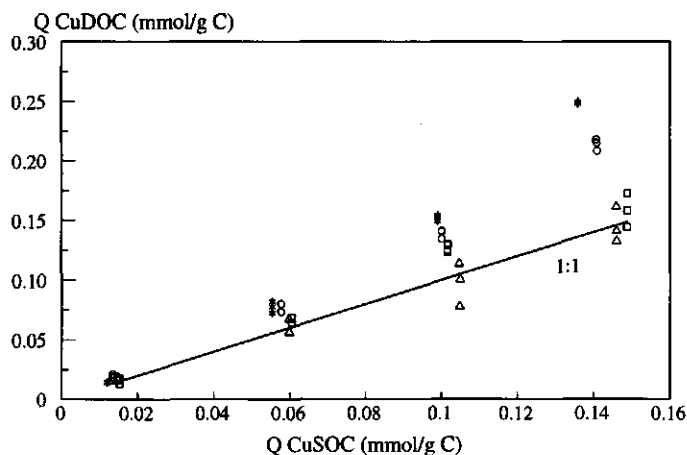
Figure 4.4.   Copper bound by dissolved organic carbon (CuDOC (mmol/g C)) as function of that bound by the solid phase (CuSOC (mmol/g C)). * = pH 4.3; ○ = pH 4.7; □ = pH = 5.2; △ = pH 5.7.

Using the ultrafiltration data, Cu bound by the fulvic (CuFF) and by the humic fraction (CuHF), at the pH levels of the soil, were calculated with eq (4.11) and eq (4.12). For the FF fractions the DOC changed from 42 ± 8 mg/l C at pH 4.4, for all Cu levels, to 28 ± 9 mg/l C at pH 5.7. DOC concentrations in the HF can be calculated by subtracting the FF from the total DOC. The humic fraction/fulvic fraction ratio is about 0.52 at pH 4.4 and 0.75 at pH 5.7. This reveals that at lower pH the fulvic fraction increases. This is reasonable since the definition for fulvic acid is the colored material which remains in solution after acidification (Stevenson, 1982).

   In Figure 4.5, free copper, copper bound to the fulvic fraction and copper bound

to the humic fraction are given as a percentage of the extractable copper in solution for the lowest (4.5a) and the highest copper (4.5b) content in the soil. Free copper ranged from about 9.0 % ($\approx 1.1*10^{-6}$ M Cu^{2+}) for soil 4A (low pH, high Cu content) to 1.7% ($\approx 1.5*10^{-8}$ M Cu^{2+}) for soil 1D (high pH, low Cu content). At low pH, more copper is bound by the fulvic fraction (75 - 85 %) than by the humic fraction (10 - 15 %) and at higher pH, more copper formed complexes with the humic fraction (50 - 60 %) than with fulvic fraction (35 - 45 %).
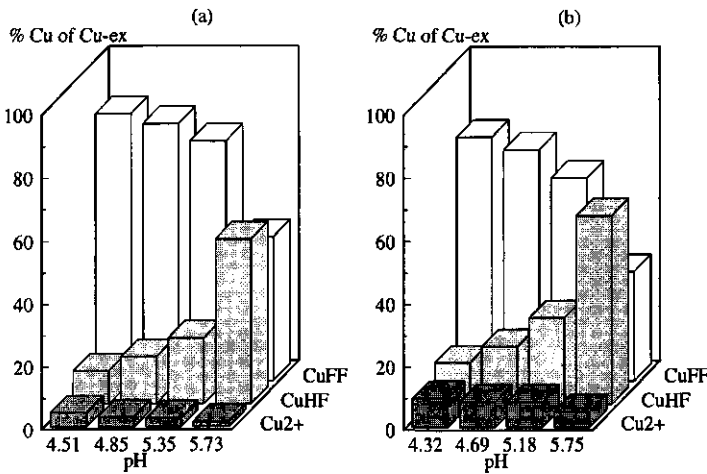
Figure 4.5. Different copper species as a percentage of the extractable copper concentration at four pH levels at 0.30 mmol/kg (a) and 3.07 mmol/kg (b) soil copper content.

Generally it is accepted that at increasing pH copper binding to humic or fulvic acids increases (Gamble *et al*, 1970; Buffle, 1988; De Wit, 1992). This seems to be in contradiction with the results presented here. However, in most cases the experiments have been done with either humic acids or fulvic acids. The complicating factor in our experiment is that we deal with a competition of three binding surfaces for free copper similar as described by Nederlof and Van Riemsdijk (1994). For these three surfaces

(soil, humic fraction and fulvic fraction) the calculated constants are given in Table 4.3. The pH factor (m) shows that as pH increases also the copper binding to soil, HF and FF increases. This agrees with the literature.

Table 4.3. Freundlich constants which have been used for the ECOSAT calculations for Cu-soil (mol/kg), CuHF (mol/L) and CuFF (mol/L).

	Cu-soil	CuHF	CuFF
$\log K'$	0.035	0.55	5.25
m	-0.35	-0.60	-0.05
n	0.70	0.70	1.00

To illustrate the effect of competition, speciation was calculated assuming 30 mg/l C for FF and 20 mg/l C for HF. For this we used the computer program ECOSAT (Keizer and Van Riemsdijk, 1993) which combines chemical speciation calculations with state of the art (electro chemical) sorption models. The results are shown in Figure 4.6, where we expressed Cu binding by fulvic- (4.6a) and humic (4.6b) fractions as a function of the Cu content in the soil. The TSF model and the used constants describe the data reasonably well. In the soil-HF-FF system, copper binding to the fulvic fraction decreases at increasing pH and the humic fraction increases, due to the different pH factors (m).
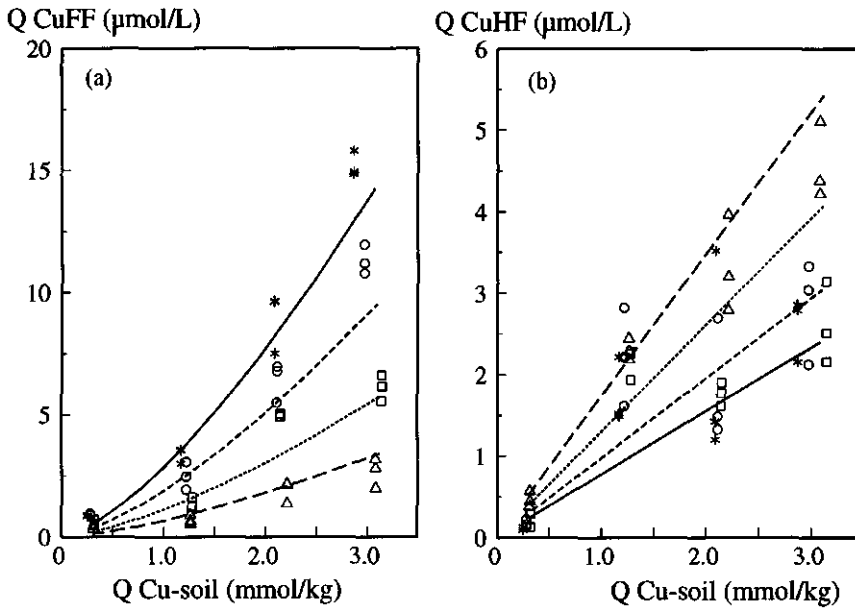
Figure 4.6. Copper binding by the fulvic fraction (a) and by the humic fraction
(b) (μmol/L) at four pH levels as a function of the soil copper
content (mmol/kg). — =model pH 4.3;   ---- = pH 4.7; ..... = pH
5.2; - - - = pH 5.7; * = ; measured pH 4.3; ○ = pH 4.7; □ = pH
5.2; △ = pH 5.7.

Conclusions

Desorption of copper in a sandy soil was dependent on pH and was non-linear within
a range of copper concentration from 0.3 to 3.1 mmol/kg soil. Copper desorption and
its pH dependency could be modelled with the Two Species Freundlich (TSF)
equation. Extractable copper concentration (Cu_{ex}) included 'free' copper (Cu^{2+}) and
copper complexed with dissolved organic matter (CuDOM). CuDOM could be

distinguished into copper complexed with fulvic fraction (CuFF) and humic fraction (CuHF) by ultrafiltration. As the soil pH decreased, the amount of copper desorbed from the soil increased. The amount of Cu bound by solid organic carbon (CuSOC) was almost equal to Cu bound by dissolved organic carbon (CuDOC) when both are expressed in mmol/g C, although there was a pH dependency. The partitioning of Cu over solid and solution phases, however, was much more dependent on quantities of organic C in these two phases. Decreasing soil pH resulted in an increase in 'free' copper and copper bound by the fulvic fraction, while copper bound by the humic fraction decreased. With the TSF equation competition between soil, humic and fulvic fraction for 'free' copper could be shown.

Acknowledgement

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Chapter 5

Copper Mobility in a Copper Contaminated Sandy Soil as Affected by pH, Solid and Dissolved Organic Matter

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Abstract

The effects of solid, dissolved organic matter and of pH on copper mobility in a copper contaminated sandy soil has been studied in the laboratory as well as in the field. The soil, with pH ranging from 3.8 to 5.7, had been polluted with copper in the range from 0.13 to 1.9 mmol/kg more than a decade ago. Copper bound by dissolved organic matter (purified humic acid) was determined by a Cu Ion Selective Electrode (Cu-ISE) in a pH range from 4 to 8 and free copper range from 10^{-4} to 10^{-12} mol/L. Column experiments were carried out to investigate the mobility of DOC itself and the effect of DOC on Cu mobility. Copper binding by dissolved organic matter (DOC) as well as copper binding by (soil) solid organic matter (SOC) could be described well with the non-ideal competitive adsorption (NICA) model and with the Two Species Freundlich (TSF) model. Both models could be used to *predict* the copper concentration at different depths in a field using the total Cu content, pH, solid and dissolved organic matter content. At pH 3.9 about 30 % of the Cu in solution was copper bound by DOC and at pH 6.6 CuDOC comprised of more than 99%. DOC mobility was very sensitive to pH and calcium concentration.

Introduction

Both in urban and agricultural areas, soil has accumulated heavy metals. These heavy metals may adversely affect soil ecology, agricultural production or product quality, and (ground)water quality. These effects are closely related to both the biological availability and the mobility of heavy metals, which in turn are controlled by the chemical speciation. The chemical behaviour of heavy metals depends on the presence of sorption sites at the solid surface of e.g. clay colloid, sesquioxides and organic matter. Additionally, soil solution parameters such as pH and the presence of competing or complexing ions influence heavy metal adsorption. Due to changes in e.g. land use or acidification these environmental conditions are subject to change. Hence, also heavy metal behaviour may change as a function of time.

In acid, sandy soil, organic matter is one of the most important solid phases that adsorb heavy metals such as Cu and Cd (Stevenson, 1982). Likewise, dissolved organic matter, mostly expressed as DOC, may significantly bind heavy metals such as copper (Benedetti *et al.*, 1995; Temminghoff *et al.*, 1994). Such copper-DOC complexes enhance copper mobility as well as their bio-availability (McCarthy & Zachara, 1989). Because the concentration of DOC may increase due to changes in land use, understanding of CuDOC binding becomes even more important. Separate studies of mobility of heavy metals and dissolved organic matter in soils has been studied extensively but the interactions between metal bound by soil, 'free' heavy metal ions and heavy metals bound by dissolved organic matter (DOC) and the influence of these interactions on heavy metal mobility in soil is not yet investigated much in detail.

To describe the binding of copper by organic matter, Benedetti *et al.* (1995) proposed the bimodal NICA model. They assessed the applicability of this model for purified humic acids in batch systems for a wide range of free metal ion concentrations and pH-values. Additionally, they suggested that their complicated model may be

simplified to less demanding ones that are appropriate for practical situations.

It is our scope to show that the information obtained for purified humic acids may be used for estimating Cu binding in real soil. We account for copper binding by both soil organic matter (denoted SOC) and dissolved organic matter (denoted DOC). Furthermore, we illustrate how the bimodal NICA model can be simplified significantly for both purified humic acid and soil without too much loss of accuracy for the present system. The applicability of the approach is shown by comparing modelling results with data from column leaching (laboratory) experiments and from observed accumulated copper as a function of depth *in situ* in the field.

Theoretical background

Both empirical and semi mechanistic models have been developed to describe heavy metals binding by soil and by dissolved organic matter. Recently, a semi mechanistic Non-Ideal Competitive Adsorption model (NICA) has been published which accounts for adsorption by heterogeneous surfaces such as (dissolved) organic matter (Benedetti *et al.*, 1995). This model can be characterized by the following isotherm equation:

$$Q_i = Q_{i(max,1)} \frac{(\tilde{K}_{i,1}c_i)^{n_{i,1}}}{\sum_j (\tilde{K}_{j,1}c_j)^{n_{j,1}}} \cdot \frac{\left[\sum_j (\tilde{K}_{j,1}c_j)^{n_{j,1}}\right]^{p_1}}{1+\left[\sum_j (\tilde{K}_{j,1}c_j)^{n_{j,1}}\right]^{p_1}} + Q_{i(max,2)} \frac{(\tilde{K}_{i,2}c_i)^{n_{i,2}}}{\sum_j (\tilde{K}_{j,2}c_j)^{n_{j,2}}} \cdot \frac{\left[\sum_j (\tilde{K}_{j,2}c_j)^{n_{j,2}}\right]^{p_2}}{1+\left[\sum_j (\tilde{K}_{j,2}c_j)^{n_{j,2}}\right]^{p_2}}$$

(5.1)

where Q_i and $Q_{i,max}$ are the adsorbed quantity and the maximum adsorption of component i (mol/kg organic matter), $\tilde{K}_j$ is the median of the affinity constants (K_j) of component j, where j includes component i. The parameter n reflects the non-ideal behaviour of component j and p reflects the intrinsic heterogeneity of the dissolved organic matter. By c_j we denote the concentration of component j (mol/L). Subscript

1 is considered to be related to the 'carboxylic' type groups and subscript 2 to the 'phenolic' type groups. Eq (5.1) has the advantages that it is valid over a wide pH range (2 - 10) and free metal ion concentration range (10^{-2} - 10^{-14} mol/L) and that it can easily be extended to the multi metal binding case.

In the natural environment with (mostly) low heavy metal concentration and intermediate pH levels ($4 \leq pH \leq 7$) the sorption by 'phenolic' groups (site 2) is less important than by 'carboxylic' groups (site 1). If we take only copper and proton competition into account eq (5.1) becomes

$$Q_{Cu} = Q_{Cu,max} \frac{(\tilde{K}_{Cu}c_{Cu})^{n_{Cu}}}{(\tilde{K}_{Cu}c_{Cu})^{n_{Cu}} + (\tilde{K}_{H}c_{H})^{n_{H}}} \cdot \frac{\left[(\tilde{K}_{Cu}c_{Cu})^{n_{Cu}} + (\tilde{K}_{H}c_{H})^{n_{H}}\right]^{p}}{1 + \left[(\tilde{K}_{Cu}c_{Cu})^{n_{Cu}} + (\tilde{K}_{H}c_{H})^{n_{H}}\right]^{p}} \tag{5.2}$$

For small Cu^{2+} concentrations and median pH values we may assume (Van Riemsdijk, 1994)

$$1 \gg (\tilde{K}_{H}c_{H})^{n_{H}} \gg (\tilde{K}_{Cu}c_{Cu})^{n_{Cu}} \tag{5.3}$$

In view of eq (5.3), eq (5.2) can be approximated by

$$Q_{Cu} = K' (c_{Cu})^{n_{Cu}} (c_{H})^{m_{H}} \tag{5.4}$$

where we defined

$$K' = Q_{Cu,max}(\tilde{K}_{Cu})^{n_{Cu}} (\tilde{K}_{H})^{n_{H}(p-1)} \tag{5.5}$$

and

$$m_{H} = n_{H}(p-1) \tag{5.6}$$

Eq (5.4) is a Two Species Freundlich equation (Temminghoff *et al.*, 1994).
In the case of heavy metal binding by sandy soils, where organic matter is the chemically most active surface, Q_i can be written as

$$Q_{i\text{-soil}} = f_{OM} \, Q_i \tag{5.7}$$

where $Q_{i\text{-soil}}$ is the adsorbed quantity of component i by soil (mol/kg soil) and f_{OM} the fraction or-ganic matter of the soil (kg/kg).

Experimental section

Humic acid extraction and purification

As a model substance for the binding studies onto organic matter we used purified humic acid that was extracted from forest floor material, taken from the Tongbersven forest (near Oisterwijk, NL). It has been used in previous studies and is described by Van Dobben *et al.* (1992) and Mulder *et al.* (1994). The upper 2 cm of the podzol B horizon from the forest floor material was collected in plastic bags. Upon return to the lab, the sample was homogenized, sieved (< 2 mm) and stored at 4 °C (field moist). The humic acid extraction was carried out according to the recommendation of the International Humic Substance Society (IHSS). The soil was extracted in N_2-atmosphere sequentially with 1.0 M NaOH and with 1.0 M HCl. After the NaOH extraction the solution was acidified to pH 1 with HCl and the precipitate was extracted once more with NaOH. The supernatant was again acidified to pH 1 with HCl. Subsequently the humic acid precipitate was treated twice with a mixture of HCl and HF, washed with demineralized water and dialysed (Spectra Por; MWCO 1000) against distilled water. The obtained humic acid was freeze dried and stored until use. Before use, each sample was dissolved in demi water. The 'hydrophobic' and 'hydrophilic' fractions (Leenheer, 1981), total copper and organic carbon were determined (Table 5.1)

Table 5.1. Some characteristic parameters of the purified humic acid.
(Total organic carbon content, copper content, 'hydrophobic' and 'hydrophilic' fraction)

C (%)	54
Cu (mg/g humic acid)	0.007
'hydrophobic' fraction[a]	97 % (185 mg/L humic acid)
'hydrophilic' fraction[a]	3 % (185 mg/L humic acid)

[a] No distinction is made between neutral, acid or base fraction.

Copper and proton binding by humic acid

Data for proton and copper binding to the humic acid were measured potentiometrically using a pH electrode (glass electrode; Radiometer) and/or a copper ion selective electrode (Cu-ISE; Orion 9429) and a double junction calomel reference electrode (Radiometer), all connected to a programmable Wallingford titrator (Kinniburgh *et al.*, 1995). All experiments were performed at 25 °C in 0.003 M $NaNO_3$ background electrolyte. The glass electrode was calibrated against two pH buffers of 4 and 7 (Radiometer). The Cu-ISE was linear for pCu between 3 and 13 ($r^2 = 0.9996$), using ethylenediamine for low Cu activities (Avdeef *et al.*, 1983; Benedetti *et al.*, 1995). The average of 14 calibrations, carried out for the sorption experiments, gave an average slope of 29.0 ± 0.2 mV/decade (97 % of theoretical Nerstian behaviour) and an average intercept, E_0, of 303 ± 5 mV which reveals the good quality of the electrode during the experiments.

The proton sorption experiment, between pH 3 and 11, started with 75 ml of 0.54 g/L DOC ($\simeq$ 1 g/L humic acid) and was titrated down to pH 3 with 0.1 M HNO3. Next 0.1 M NaOH was added in small amounts. Each addition was followed by 15 min waiting time until the drift criterium was less than 0.004 pH/min before a pH measurement was taken and a new addition was carried out.

Copper binding was measured at constant pH values of 4, 6 and 8 and started with 75 ml of 100 mg/L DOC ($\approx$ 185 mg/L humic acid). The sample was titrated to a certain pH and maintained for up to 12 h to stabilize the humic acid at that certain pH before Cu was added. To keep the pH at a certain level we used the pH stat mode of the titrator (Kinniburgh *et al.*, 1995). The concentration of free Cu was measured after the pH stat was maintained for 15 min and the drift criteria were less than 0.004 pH/min for the glass electrode (0.2 mV/min) and for the copper electrode 0.004 pCu/min (0.1 mV/min) before a new addition was carried out. The total Cu concentration in solution was calculated by the buret additions. The Cu binding by humic acid can be calculated by subtraction the Cu^{2+} from the total Cu concentration in solution. Above pH 6 also Cu hydroxide species should be taken into account (Benedetti *et al.*, 1995).

Contaminated soil

Soil samples were taken from a field near Wageningen in The Netherlands (Wildekamp site) which has been used previously to study copper speciation in the soil (solution) (Temminghoff *et al.*, 1994), copper toxicity for earthworms (Marinussen & Van der Zee, 1997) and long-term effects of copper and pH on the nematode community in an agroecosystem (Korthals *et al.*, 1996). The soil was a Spodosol in a slightly loamy moderately fine sand. The field contains a randomised block design of four copper concentrations and four pH adjustments in 6 * 11 m plots. Four pH levels coded A-D for pH_{KCl} 4.0, 4.7, 5.4 and 6.1 were established in 1982 using calcium carbonate or sulphur, followed by establishment of four total Cu levels coded 1-4 for 0, 250, 500 and 750 kg/ha, added as $CuSO_4$, at each pH-level. Methods of application are described in Lexmond (1980). pH and Cu levels where adjusted in the plough layer 0 - 0.40 m depth. We assumed that an equilibrium between the copper pollution and the soil has been more or less established since the 'pollution' occured more than 14 years ago. Every sixth year, pH levels were adjusted.

Table 5.2. Some characteristics and extraction results of the soil.
pH Ca(NO₃)₂, Texture (%), organic matter (OM; g/kg), 'total' Cu (Cu HNO₃; mmol/kg), exchangeable Cu concentration (Cu$_{ex}$; mmol/L) and DOC (mg/L). Cu HNO₃, DOC and Cu$_{ex}$ are a mean of three replicates with standard deviation.

Code	pH$_{Ca(NO_3)_2}$	Texture (%)				OM (g/kg)	Cu HNO₃ (mmol/kg)	Cu$_{ex}$ (μmol/L)	DOC (mg/L)
		>50	<50	<16	<2μm				
1A	3.81	85.5	11.9	5.7	2.9	33.0	0.485 ± 0.005	1.57 ± 0.02	9.0 ± 0.5
2A	3.88	85.3	12.3	6.2	2.2	36.7	1.007 ± 0.017	3.83 ± 0.04	9.9 ± 0.3
3A	3.92	85.6	12.2	6.3	1.8	36.0	1.675 ± 0.014	7.08 ± 0.14	10.2 ± 0.4
4A, 0-20	3.83	85.4	12.3	7.0	3.5	34.9	1.610 ± 0.043	10.3 ± 0.2	7.8 ± 0.3
4A, 20-40	3.90	84.8	12.1	7.1	3.4	35.0	1.768 ± 0.031	14.5 ± 0.2	8.8 ± 0.2
4A, 40-60	4.16	86.0	11.0	7.5	2.6	23.5	1.190 ± 0.068	8.81 ± 0.02	4.9 ± 0.2
4A, 60-80	4.51	88.3	9.3	6.6	3.2	10.6	0.191 ± 0.006	0.61 ± 0.09	2.0 ± 0.1
4A, 80-90	5.10	91.4	8.4	5.0	2.5	5.1	0.022 ± 0.002	0.13 ± 0.04	1.1 ± 0.1
1D	5.42	84.2	12.8	6.9	3.9	36.8	0.133 ± 0.009	0.18 ± 0.04	8.1 ± 0.2
2D	5.54	83.9	14.0	7.4	3.8	37.3	1.311 ± 0.049	1.62 ± 0.04	7.4 ± 0.3
3D, 0-20	5.74	85.8	11.1	7.2	3.8	37.8	1.887 ± 0.038	2.40 ± 0.08	11.4 ± 0.3
3D, 20-40	5.63	85.4	11.1	7.2	3.7	35.5	1.896 ± 0.022	3.16 ± 0.02	16.0 ± 0.9
3D, 40-60	5.55	86.3	12.3	7.7	3.8	21.7	0.206 ± 0.016	0.51 ± 0.08	11.7 ± 0.9
3D, 60-80	5.67	92.5	8.0	5.7	3.4	7.9	0.059 ± 0.009	0.26 ± 0.07	4.3 ± 0.3
3D, 80-90	5.91	95.3	5.1	3.9	2.7	3.8	0.013 ± 0.002	0.09 ± 0.03	1.9 ± 0.3
4D	5.25	84.3	12.9	6.3	3.3	35.0	2.604 ± 0.006	3.66 ± 0.21	7.7 ± 0.2

The field is cultivated in a crop rotation with corn, potatoes and oats. Soil samples were collected from the plots with the highest (code D) and lowest (code A) pH, for each pH/Cu combination, at a depth of 0 - 0.20 m. From two plots (4A and 3D), soil was sampled from the layers 0 - 0.20, 0.20 - 0.40, 0.40 - 0.60, 0.60 - 0.80 and 0.80 - 0.90 m. All soil samples were air-dried and sieved (< 2 mm). Typical soil properties, such as pH (0.001 M $Ca(NO_3)_2$), grain size distribution, organic matter by loss-on-ignition at 550 °C and the cation exchange capacity (CEC) using the unbuffered $BaCl_2$ method (Houba *et al.*, 1995) are provided in Table 5.2.

Copper desorption by soil

Batch experiments

The extraction of the soil samples with an unbuffered extractant (0.001 M $Ca(NO_3)_2$) gives an indication of the easily extractable Cu-species (Cu_{ex}) and the extraction with 0.43 M HNO_3 gives an indication of the totally adsorbed Cu (Cu_T) by the soil. For this purpose we used for both extractions a soil:solution ratio of 1:10. The soil suspensions were shaken end-over-end for 20 h at 25 °C after which the pH was measured in the suspensions for the 0.001 M $Ca(NO_3)_2$ extraction. After centrifugation at 10,000 g, the totally exchangeable Cu-concentration (Cu_{ex}) and the total Cu-concentration (Cu_T) in the supernatant was measured by flame AAS (Instrumentation Laboratory AA/AE spectrophotometer S11 with scale expansion). The detection limit was approximately 0.3 μmol/L. Samples below this detection limit were analyzed by graphite furnace AAS (Varian SpectrAA 300-Zeeman) with a detection limit of 0.03 μmol/L. The dissolved organic carbon (DOC) in the 0.001 M $Ca(NO_3)_2$ extracts was measured with the fully automated SK[12] (Skalar) TOC/DOC analyzer.

Column experiments

To show the effect of DOC concentration on Cu mobility column experiments were carried out with soils of plot 4A and 3D (layer 0 - 0.20 m). We used perspex columns 4.5 cm in diameter and about 20 cm long. Four columns were filled with 300 g of both

soils in duplicate. A filter and a thin quartz layer at the bottom of the column prevented outflow of soil particles. Columns were saturated from below with the background solution (0.001 M $Ca(NO_3)_2$) to prevent air inclusion, using a multi channel peristaltic pump (Gilson Minipuls III). The pH of the background solution was adjusted to pH 5.7 (soil pH) with 0.01 mol/L HNO_3 or NaOH. After saturation and 4 days incubation, the flow direction was changed into downwards. The top of the column was connected via a tube to the influent solution (0.001 M $Ca(NO_3)_2$; pH 5.7). A fraction collector (ISCO fraction collector) was used to collect the effluent samples of about 15 ml. Besides total Cu, we measured DOC and the pH in the effluent. After about 13 pore volumes (V/V_0), we changed the influent of the duplicates of each soil, 4A2 and 3D2, to 100 mg/L DOC (in 0.001 M $Ca(NO_3)_2$) without altering the influent of the other two soil columns, 4A1 and 3D1. The pH of the influent was adjusted to soil pH 3.9 and pH 5.7. After about 40 pore volumes, we changed the influent of the duplicates of each soil, 4A2 and 3D2, to 100 mg/L DOC in demineralized water (pH adjusted to 5.7) to investigate the Ca effect on DOC coagulation. The determined soil density was 1390 ± 70 kg/m^3 for the four columns. Breakthrough curves for chloride yield the pore volumes of the four columns, which was about 112 ml, and the diffusion-dispersion coefficient, which was typically 0.047 m^2/year. The porosity, ϕ, was about 0.51. Flow rates of approximately 3.1 ml/hour were used for all four column experiments. At the end of the experiment the soil columns were separated into layers of about 1.5 cm, dried and analyzed for total organic matter and total Cu.

Results and Discussion

Copper binding by purified humic acid is shown in Figure 5.1a for pH 4, 6 and 8 on logarithmic scales.
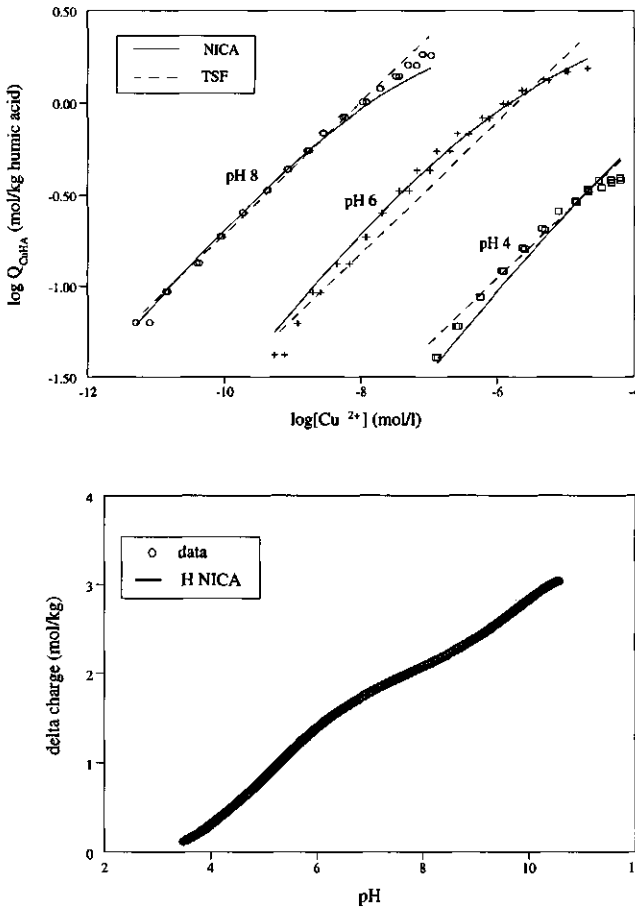
Figure 5.1. (a) Copper binding by DOC (purified humic acid) as a function of log(Cu^{2+}) at pH 4, 6 and 8 for data, the NICA and the TSF model at I=0.003 (0.003 M NaNO$_3$) (b) Proton binding by DOC (purified humic acid), calculated as delta charge, as function of pH (-log(H$^+$)) for data and the NICA model at I=0.003 (0.003 M NaNO$_3$).

Copper binding depends non-linearly on pH and Cu^{2+} concentration and is well

described by the (bimodal) NICA model (eq (5.2)) as well as the TSF model (eq (5.4)). The fitted parameters are given in Table 5.3a (NICA) and 5.3b(TSF).

Table 5.3a. Parameters for the NICA model to describe the copper binding by purified humic acid and soil organic matter at I= 0.003 and the values as found by Benedetti *et al.* (2) to describe Cu binding by purified peat humic acid (PPHA) at I=0.1.

	site 1		site 2	
	this study	Benedetti *et al*	this study	Benedetti *et al*
purified humic acid & soil organic matter				
$\log \tilde{K}_H$	5.12	4.60	9.78	9.34
$\log \tilde{K}_{Cu}$	5.40	3.40	10.82	8.17
n_H	0.81	0.93	0.83	0.57
n_{Cu}	0.46	0.52	0.46	0.30
purified humic acid				
p	0.57	0.47	0.58	0.68
$Q_{cu,max}$ (mol/kg)	2.18	2.48	1.54	1.93
soil organic matter				
p	0.50	-	0.50	-
$Q_{cu,max}$ (mol/kg)	0.65	-	0.46	-

purified humic acid

H; coefficient of determination (r^2) = 0.99998

Cu and H; coefficient of determination (r^2) = 0.98

soil organic matter

Cu and H; coefficient of determination (r^2) = 0.97

Table 5.3b. Parameters for the TSF model to describe the copper binding by purified humic acid and soil organic matter at I= 0.003. (Q_{Cu} in mol/kg, H^+ and Cu^{2+} in mol/L)

purified humic acid & soil organic matter	
n_{Cu}	0.36
purified humic acid	
m_H	-0.40
$\log K'$	-0.348
soil organic matter	
m_H	-0.58
$\log K'$	-1.77

purified humic acid
coefficient of determination (r^2) = 0.97
soil organic matter
coefficient of determination (r^2) = 0.93

The NICA model described the Cu adsorption slightly better because it accounts for an maximum adsorption. Proton binding by the purified humic acid is shown in Figure 5.1b where the relative charge is given as function of the pH. The fit by the NICA was excellent (r^2 = 0.99998). The fitted NICA parameters for protons are similar to those determined by Benedetti *et al.* (1995) despite that their humic acid is from a different location and that they used a different ionic strength (Table 5.3a). Copper median affinity constants ($\log \tilde{K}_{Cu}$) for both sites differ at least 2 units. This sugests that besides an ionic strength effect copper is stronger bound by our purified humic acid, than the purified peat humic acid used by Benedetti *et al.* (1995). The two sites shows similar proton non-ideal behaviour (n_H) towards the humic acid whereas for the purified peat humic acid the non-ideal behaviour is different for the two sites.

The concentration of copper extracted from the soil (Cu_{ex}), determined via 0.001 M $Ca(NO_3)_2$ extraction, corresponds to 'free' copper (Cu^{2+}), copper bound by dissolved organic matter (CuDOC) and copper bound by inorganic species. The Cu binding by the inorganic species (e.g. NO_3) is negligible. To assess the Cu^{2+} and CuDOC fractions, speciation techniques are necessary (Temminghoff et al., 1994). Assuming that Cu binding by dissolved organic matter behaves as Cu binding by humic acid, the 'free' Cu^{2+} can be calculated at every pH, Cu_{ex} and DOC concentration by either the NICA or the TSF model. In agreement with Kinniburgh et al. (1996) we assumed that Ca competition is negligible. Hence, for neither model we took Ca competition explicity into account. Dissolved organic carbon concentrations for all the 0 - 0.20 m top layer soil samples were equal (8.9 ± 1.4 mg/L). The calculated pCu^{2+} concentrations in the top layer varied from 5.1 (soil 4A) up to 9.9 (soil 1D). For sandy soils free copper (Cu^{2+}) has been shown to be in equilibrium with Cu bound by solid organic matter of the soil and by dissolved organic matter of the soil solution (Temminghoff et al., 1994). The Cu^{2+} binding by the (soil) solid organic matter in the top layer 0 - 0.20 m was also described by the NICA and TSF models where all parameters, except $Q_{cu,max}$ and the intrinsic heterogeneity (p), were kept constant compared with the Cu^{2+} binding by the humic acids (Table 5.3). By fitting only these two parameters for NICA (Table 5.3a) and the two corresponding parameters for TSF (Table 5.3b) we described the Cu^{2+} binding by soil for the layer 0 - 0.20 m (Figure 5.2). The maximum Cu sorption capacity for (soil) solid organic matter had to be reduced to 30 % of the $Q_{Cu,max}$ of the purified humic acid for both the TSF and the NICA model. This is plausible because the number of reactive sites (sites density) is probably smaller for solid organic matter than for dissolved organic matter since solid organic matter is less humified (Gooddy et al., 1995). For the NICA model the factor p had to be adjusted from 0.57 and 0.58 to 0.50 which indicates larger intrinsic heterogeneity of (soil) solid organic matter than purified humic acid. A change in

$Q_{cu,max}$ and parameter p gives a change in K' and m_H (see eq (5.5) and (5.6)) for the TSF model.
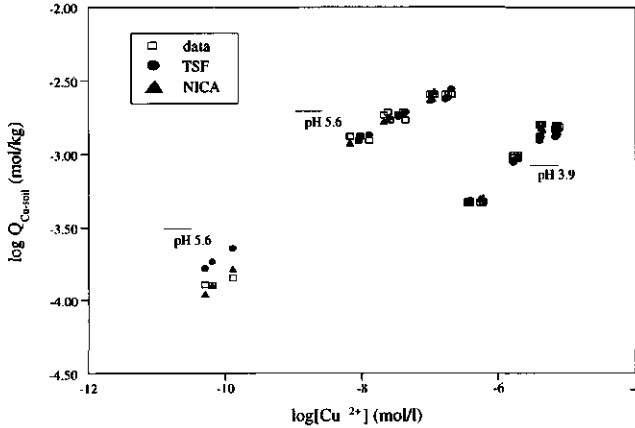
Figure 5.2. Copper desorption as a function of $\log(Cu^{2+})$ at the pH of the soil (solution) for data, the NICA and the TSF model at I=0.003 (0.001 M $Ca(NO_3)_2$).

The NICA and the TSF model described the desorption data excellently. Only at mean pH 5.7 and Cu^{2+} concentrations of approximately 10^{-10} mol/L the TSF model shows slight discrepancies.

Copper and DOC mobility in laboratory columns

In Figure 5.3 the total copper and DOC concentration and pH in the effluent of the columns are given for soil 4A1 (Fig. 5.3a), mean pH 3.9, and soil 3D1 (Fig. 5.3b), mean pH 6.6, as a function of leached pore volumes (V/V_0). The effluent pH for both columns is given in Figure 5.3c. The effluent pH differs from the soil pH (measured in batch), especially at high pH. At high pH the difference is about 1 pH while at low pH the difference is negligible. The Cu breakthrough curve (BTC) at pH 6.6 shows
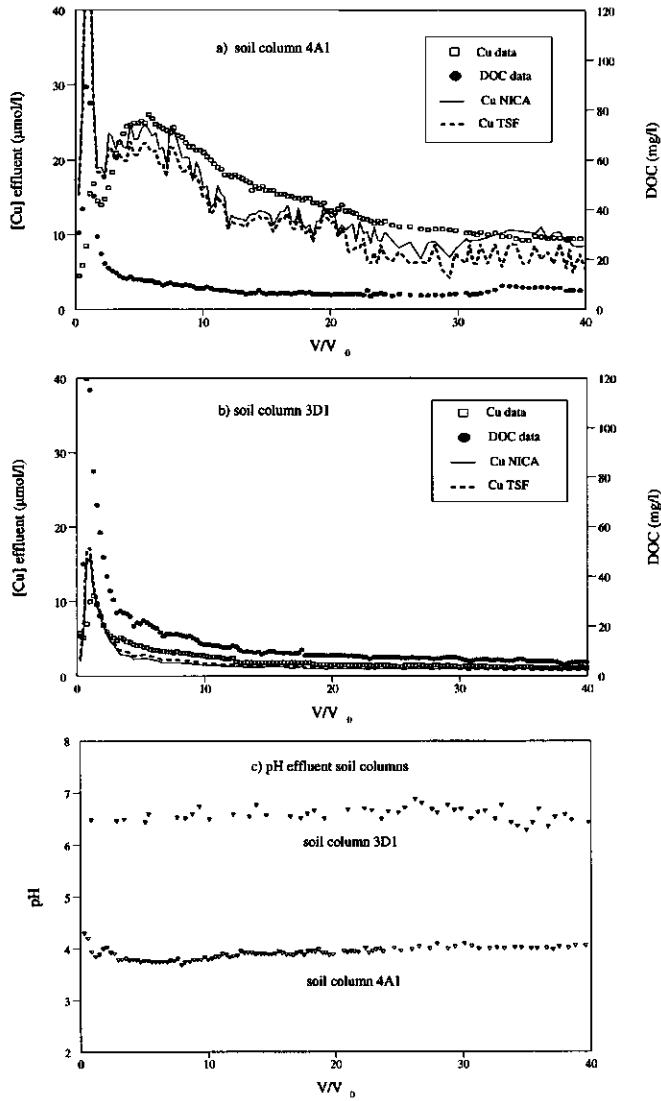
Figure 5.3. Copper and DOC concentration and pH in the effluent as a function of pore volumes for (a) soil column 4A1, (b) soil column 3D1 and (c) effluent pH for 4A1 and 3D1 for 0.001 M Ca(NO₃)₂ as influent (I=0.003). Line and dashed line is prediction of copper by NICA and TSF model respectively.

one Cu peak together with the DOC peak (Fig. 5.3b). At pH 3.9 two Cu peaks are visible, the first one at the same moment as the DOC peak, followed by a second Cu peak that corresponds with the decline of pH during the first pore volumes (Figure 5.4). The soil pH for soil 3D is 5.7 in batch whereas the mean pH of the effluent of column 3D is about 6.6. The Cu concentration at pH 3.9 reached a maximum of approximately 25 μmol/L Cu after 7 pore volumes and decreased slowly to 8 μmol/L after 45 pore volumes. At pH 6.6 the Cu concentration was 11 μmol/L (after 1 pore volume) and decreased fast below 5 μmol/L after 5 pore volumes. Maximum DOC concentration in the effluent was found after 1 pore volume both for pH 3.9 (83 mg/L DOC) and for pH 6.6 (120 mg/L DOC) and decreased fast to concentrations below 10 mg/L. The solid and the dashed lines are the Cu concentration predictions by the NICA and the TSF model in the effluent by taking both pH and DOC effects into account. The Cu concentration is predicted rather well for both models. The first peak for both pH values is slightly overestimated possibly due to non equilibrium during the first pore volume percolation in the columns. At pH 3.9 after about 10 pore volumes approximately 70 % of the total Cu in the effluent solution is Cu^{2+} and about 30 % is present as CuDOC, as calculated with the NICA and/or the TSF model. During the first ten pore volumes Cu^{2+} varied from 20 to 70 % due to changes in DOC and pH. At pH 6.6 only a small part of total Cu is present as Cu^{2+} (0.01 %) and most is of the form CuDOC (> 99 %).

In Figure 5.4 the duplicate columns 4A2 (Fig. 5.4a) and 3D2 (Fig. 5.4b) are given. The influent of the duplicate columns were changed after leaching 12.8 pore volumes from 0.001 M $Ca(NO_3)_2$ without DOC to 100 mg/L DOC ($\approx$ 185 mg/L humic acids) in 0.001 M $Ca(NO_3)_2$. This moment is indicated by the arrow in Figure 5.4. The pH of the effluent for these columns is given in Figure 5.4c and did not differ significantly from the effluent pH for soil columns 4A1 and 3D1 where the feed solution did not contain DOC. Hence, the effluent pH was not affected by humic acid in the influent. The Cu and DOC concentrations in the effluent during the first 12 pore
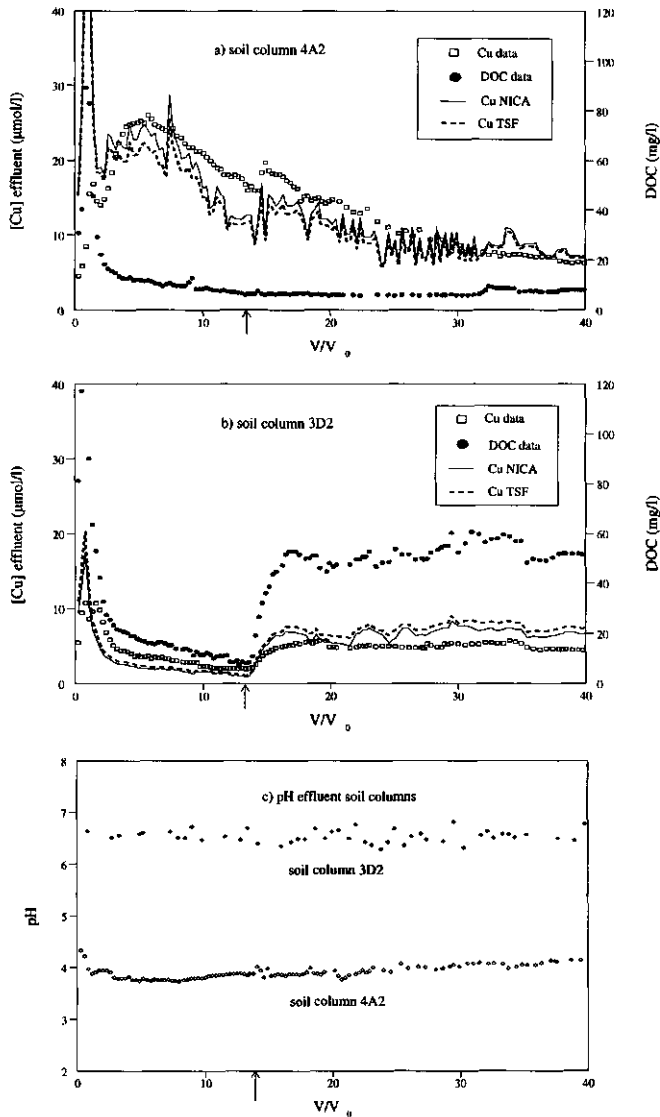
Figure 5.4. Copper and DOC concentration and pH in the effluent as a function of pore volumes for (a) soil column 4A2, (b) soil column 3D2 and (c) effluent pH for 4A2 and 3D2 for 0.001 M Ca(NO$_3$)$_2$ and (at arrow mark) 0.001 M Ca(NO$_3$)$_2$ and 100 mg/L DOC as influent (I=0.003). Line and dashed line is prediction of copper by NICA and TSF model respectively.

volumes were similar to the columns 4A1 and 3D1 (Fig. 5.3a and 5.3b). One pore volume after DOC was added to the feed solution the DOC concentration increased between 50 and 60 mg/L at pH 6.6 whereas at pH 3.9 no increase of DOC was found. This suggests that at pH 3.9 all humic acids and at pH 6.6 approximately 40 to 50 % is adsorbed or coagulated in the soil column. This is qualitatively in agreement with Parfitt *et al.* (1977) and Tipping (1981) who suggest that the DOC adsorption increases at decreasing pH. For low pH values, the charge of metal(hydr)oxides is more positive than for high pH, which favours the adsorption of negatively charged DOC. The quantity of DOC which was retained in the columns was so high that other processes could be involved. Ong & Bisque (1968) and Mulder *et al.* (1994) mentioned the possibility of DOC coagulation. Mulder *et al.* (1994) observed an increase in coagulation of DOC with a decrease in negative charge of DOC. This charge is influenced by cation binding to DOC, like aluminium, iron, calcium, copper and protons, where trivalent ions are more effective than divalent and mono valent ions in coagulating dissolved organic matter (Ong & Bisque, 1968). For decreasing soil pH, concentrations of many cations increase in the soil solution (e.g. Al, Cu) which explains possibly why beside some adsorption the humic acid coagulated completely in the column with pH 3.9 and only partly at pH 6.6. The Cu concentration at pH 6.6 increases after 13.8 pore volumes from 2 to 6 µmol/L due to an increase in DOC. An increase of DOC with a factor 8 gives an increase in copper by a factor 3 at pH 6.6. The NICA (solid line) and the TSF (dashed line) models predicted the increase of copper at increasing DOC concentration quite well.

To show the impact of Ca on DOC coagulation we changed the feed solution after 40 pore volumes to 100 mg/L DOC in demi-water that contains no Ca (indicated by arrow in Figure 5.5). Besides pH, Cu and DOC we measured the Ca concentration (Figure 5.5a, 5.5b and 5.5c) in the effluent. One pore volume after changing the feed solution composition, the Ca concentration decreased and the DOC concentration
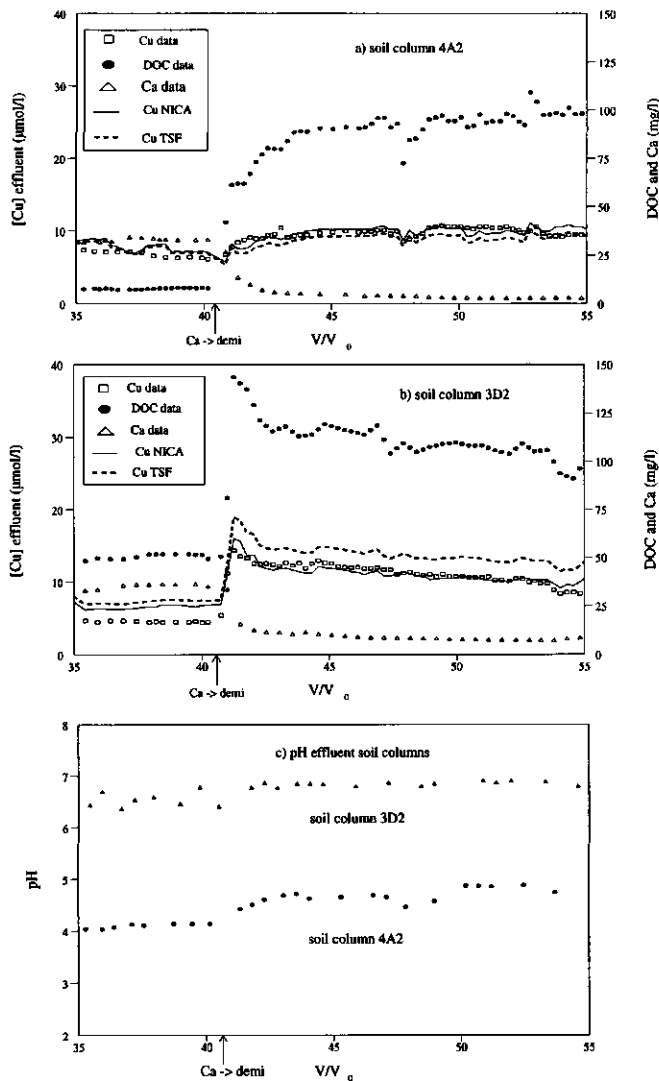
Figure 5.5. Copper, calcium and DOC concentration and pH in the effluent as a function of pore volumes for (a) soil column 4A2, (b) soil column 3D2 and (c) effluent pH for column 4A2 and 3D2 for 0.001 M $Ca(NO_3)_2$ and 100 mg/L DOC and (at arrow mark) demi-water and 100 mg/L DOC as influent (I = unknown). Line and dashed line is prediction of copper by NICA and TSF model respectively with parameters at I = 0.003.

increased simultaneously in the effluent for both columns. The pH increased for both columns slightly but especially at low pH. After a few pore volumes the effluent DOC concentration reached the feed DOC concentration (100 mg/L DOC) whereas the Ca concentration decreased only from 1 to 0.1-0.2 mmol/L. For column 3D2 the DOC concentration was during a short period even larger than the influent DOC concentration which suggests dissolution of coagulated DOC. This illustrates that DOC coagulation or DOC mobility is rather sensitive to small changes in Ca concentrations.

The effluent Cu concentrations for both columns were more or less the same (10 μmol/L) although the two soils differ of about 1.7 pH units. The NICA and the TSF model predicted the Cu effluent concentration at pH 6.6 quite well although the deviation for the NICA model is smaller than for the TSF model. At low pH we had to increase $Q_{Cu,max}$ for soil by a factor 2.5 for both models to get good agreement when demi-water was fed to the column. This may imply that in relative terms the Ca concentration at low pH is more important than at high pH, although the effect may be due to ionic strength changes also.

Due to coagulation the dissolved organic matter changed into (semi) solid organic matter and therefore increases the binding capacity of the soil. In Figure 5.6 the organic matter and the Cu profile for the four soil columns are given after the soil columns were separated in layers. In the case where DOC was not added to the feed solution solid organic matter remained more or less constant at both pH. When DOC was added to the feed solution, the solid organic matter became larger in the first two sampled layers of the columns for both pH levels due to coagulation. Coagulation is more likely than sorption because of the large increase of organic matter content in the first two layers of the columns. The solid organic matter increased from 35 g/kg soil up to 42 g/kg in the first sampled layer of the column at pH 3.9 and from 35 up to 39 g/kg at pH 6.6. Below the first two sampled layers no significant differences were found in solid organic matter content.

A decrease of copper content in the soil was found for all four columns and the copper content decreased most significantly in the first layer. About 32 % of the total copper was leached out at pH 3.9 and 12 % at pH 6.6 at a depth of 4.5 - 6.0 cm in the case no DOC was added to the feed. With DOC in the feed, about 28 % of the total copper was leached out at pH 3.9 and 20 % at pH 6.6 at a depth of 4.5 - 6.0 cm. This demonstrates the higher Cu mobility at low pH without DOC and that the increase in Cu mobility due to DOC is larger at high pH than at low pH.
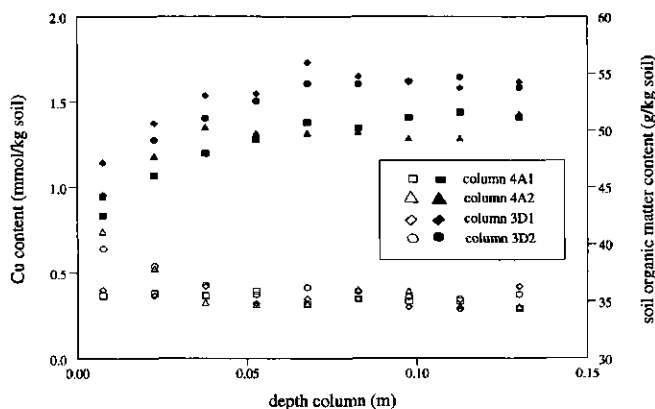
Figure 5.6. Copper (solid symbols) and solid organic matter (open symbols) content profiles in the four columns.

Copper mobility in the field

Dissolved organic matter (DOC), solid organic matter (SOC) content, pH and total Cu content vary with depth in the field (Table 5.2). Using parameters of Table 5.3 for describing Cu binding by DOC and Cu binding by (soil) solid organic matter (parameters only determined for the top layers 0 - 0.20 m) we predicted the extractable Cu concentration in the soil solution at each depth between 0 and 0.90 m with the NICA and the TSF models. In Figure 5.7 the predicted Cu_{ex} concentration is given as

a function of the measured Cu_{ex} concentration. The agreement is good for both models. For the NICA model the prediction was slightly better than the TSF model since the correlation coefficients were 0.97 and 0.93, respectively.
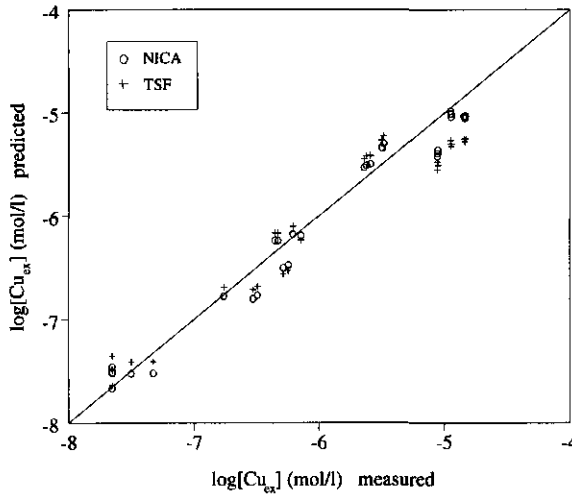
Figure 5.7. Extractable copper concentration calculated with the TSF and the NICA model in the Spodosol soil profile as a function of the measured exctractable copper concentration for five layers soil 4A and 3D till 0.9 m depth at I=0.003 (0.001 M $Ca(NO_3)_2$). Solid line is the 1:1 line.

Initially, soils of plot A and D with the same number had the same (total) Cu content in the plough layer but currently differences are observed. For soil 4A (low pH) total Cu content was already smaller than in soil 3D (high pH) in layer 0 - 0.40 m although the added Cu in 1982 was higher for soil 4A (750 kg/ha) than for soil 3D (500 kg/ha). However, below a depth of 0.40 m the copper content in soil 4A is much larger than in soil 3D (see Table 5.2). The extractable Cu concentration (Cu_{ex}), determined via 0.001 M $Ca(NO_3)_2$ extraction and the models, is for soil 4A (layer 0 - 0.20 m), about

five times larger than for soil 3D (high pH) which proofs the increase in Cu mobility at low pH.

Acknowledgements

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Chapter 6

DOC Mobility and DOC Coagulation in Relation to Copper Mobility in a Copper Contaminated Sandy Soil

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(submitted)

Abstract

The mobility and coagulation effects of dissolved organic matter and of pH on copper mobility in a copper contaminated sandy soil has been studied in the laboratory batch and column experiments. The soil, with pH ranging from 3.8 to 5.7, had been polluted with copper in the range from 0.13 to 1.9 mmol/kg more than a decade ago. Calcium and copper bound by dissolved organic matter (purified humic acid) was determined by a Ca and Cu Ion Selective Electrodes (Ca-ISE, Cu-ISE) in a pH range from 4 to 8 and free copper range from 10^{-4} to 10^{-12} mol/l Cu and 10^{-3} to 10^{-6} mol/l Ca. Copper binding by dissolved organic matter (DOC) as affected by calcium and pH could be *predicted* well with the non-ideal competitive adsorption (NICA) model. Coagulation of dissolved organic matter was affected by the amount of trivalent (Al) and divalent (Ca and Cu) cations in solution. The pH effect on coagulation was minor between pH 4 and 6. Coagulation differences in Ca and Cu concentrations could be explained by differences in Ca and Cu binding by dissolved organic matter. Copper binding by dissolved organic matter (DOC) as well as copper binding by (soil) solid organic

matter (SOC), both affected by calcium and pH, could be described well with the NICA model. Column experiments were carried out to investigate the coagulation and mobility of DOC, which enhanced Cu mobility, as affected by Ca and pH. Three processes, Cu desorption by soil, DOC coagulation and Cu complexation by DOC, act at the same time in the soil columns. All three processes with counteracting effects on Cu mobility are influenced by Ca and pH and could be adequately captured by the multicomponent NICA model.

Introduction

The contamination of the environment has become a matter of considerable concern. In areas with high intensity industry and agriculture, large concentrations of heavy metals may reach the soil by atmospheric deposition, animal manure, artificial fertilizer, or by waste diposal (sewage sludge). These contaminated sites are among others a potential risk for the groundwater quality and for the quality of the drinking water supply. The total heavy metal content are commonly used to indicate the soil contamination, the heavy metal concentration in solution however mostly determines the actual environmental exposure or risk. Heavy metal distribution between soil and solute is a key aspect in evaluating the environmental impact of copper addition to land. Despite the complexity of possible reactions, several important soil factors controlling the distribution of heavy metals between soil and solutes have been identified (Lindsay, 1979; Sposito, 1989). Due to changes in landuse changes will appear in the macro chemistry of the soil (e.g. pH, organic matter, calcium). These changes in the macro chemistry of the soil will afffect the behaviour of the accumulated heavy metals as well (Römkens et al., 1996). The importance of solid as well as dissolved organic matter on Cu mobility is shown by Temminghoff et al. (1997) The DOC concentration is partly controlled by calcium due to DOC sorption (Stevenson, 1982; Römkens et al., 1996). Calcium

can act as a bridge between the negatively charged DOC and negatively charged soil particles (clay, oxides). The negatively charged DOC can also adsorb directly to positively charged soil metal oxides like goethite (α-FeOOH) (Tipping, 1981; Spark *et al.*, 1997). Besides sorption of DOC coagulation of DOC by metal ions like aluminium and calcium takes place (Ong & Bisque, 1968; Tipping, 1984; Ares & Ziechman, 1988; Tambo *et al.*, 1989). DOC solubility depends on the hydration of the molecules, which is substantially diminished when ionised functional groups are neutralised by protonation and/or complexation with di- or tri-valent cations. Besides the valency also the radius of the hydrated ions is important (Ong & Bisque, 1968). For organic surface horizons Tipping and Woof (1990) showed that the solubility of humic substances decreases with decreasing negatively charge density. If the degree of neutralisation is sufficient high, the DOC solubility can be exceeded and DOC coagulates (Tipping & Ohnstad, 1984). Little is known of heavy metal (Cu, Ca, Al) binding by DOC in relation with coagulation and how these processes affect DOC mobility itself as well as enhance Cu mobility in a Cu contaminated soil.

Our aims are therefore to (*i*) determine the Ca and Cu binding by purified humic acid separately and to predict the Cu binding by purified humic acid in the presence of Ca by using the multi component bimodal NICA model; (*ii*) show how humic acid coagulation depends on aluminium, calcium, copper, sodium and protons (pH) (*iii*) show how these data can be used for estimating Cu binding by soil (organic matter) in the presence of Ca and protons as competitor; and (*iv*) show how DOC mobility in soil is regulated by Ca and how this affects Cu mobility. The applicability of the approach is shown by comparing modelling results with data from column leaching experiments.

Theoretical background

To describe heavy metals (specific) binding by (dissolved) organic matter the Non-Ideal Competitive Adsorption model (NICA) has been developed (Koopal *et al.*, 1994; Benedetti *et al.*, 1995; Kinniburgh *et al.*, 1996; Temminghoff *et al.*, 1997), which implicitly assumes an continuous distribution of site affinities. Two dimensional heterogeneity analysis clearly indicates that the metal binding follows a bimodal distribution characteristic of 'carboxylic' and 'phenolic' type groups (Rusch *et al.*, 1997). In terms the NICA model this agrees with:

$$Q_i = Q_{max,1} \frac{(\tilde{K}_{i,1} c_i)^{n_{i,1}}}{\sum_j (\tilde{K}_{j,1} c_j)^{n_{j,1}}} \cdot \frac{\left[\sum_j (\tilde{K}_{j,1} c_j)^{n_{j,1}} \right]^{p_1}}{1 + \left[\sum_j (\tilde{K}_{j,1} c_j)^{n_{j,1}} \right]^{p_1}} + Q_{max,2} \frac{(\tilde{K}_{i,2} c_i)^{n_{i,2}}}{\sum_j (\tilde{K}_{j,2} c_j)^{n_{j,2}}} \cdot \frac{\left[\sum_j (\tilde{K}_{j,2} c_j)^{n_{j,2}} \right]^{p_2}}{1 + \left[\sum_j (\tilde{K}_{j,2} c_j)^{n_{j,2}} \right]^{p_2}} \quad (6.1)$$

where Q_i is the adsorbed quantity of component i and and Q_{max} the maximum adsorption capacity of the organic matter (mol/kg organic matter), $\tilde{K}_j$ is the median of the affinity constants (K_j) of component j, where j includes component i. The parameter n reflects the non-ideal behaviour of component j and p reflects the intrinsic heterogeneity of the dissolved organic matter. By c_j we denote the concentration of the 'free' uncomplexed component j in solution (mol/L). Subscript 1 is considered to be related to the 'carboxylic' type groups and subscript 2 to the 'phenolic' type groups. Eq (6.1) has the advantages that it can describe data over a wide pH range (2 - 10) and free metal ion concentration range (10^{-2} - 10^{-14} mol/L) and that it can easily be extended to the multi metal binding case.

In the case of heavy metal binding by sandy soils, where organic matter is the chemically most reactive surface, Q_i can be written as

$$Q_{i\text{-soil}} = f_{OM} \, Q_i \quad (6.2)$$

where $Q_{i\text{-soil}}$ is the adsorbed quantity of component i by soil (mol/kg soil) and f_{OM} the fraction organic matter of the soil (kg/kg).

Without cations the humic acids are dissolved in water and their functional groups of the 'carboxylic' type and 'phenolic' type become more or less dissociated. Mutual repulsion of the negative functional groups occur and the humic acid will assume a stretched (hydrofilic) configuration. Binding of cations by the negatively charged groups, will cause a reduction of the repulsion in the polymer chain which favors coiling of the chain. This coiled structure geometry expels hydrated water and is known as the Fuoss effect (Ong & Bisque, 1968). The humic acids become more hydrofobic, and coagulation or flocculation occurs. Metal binding by humic acid can be calculated with the multicomponent bimodal NICA model.

Experimental section

Humic Acid Extraction and Purification
As a model substance for the binding studies to organic matter we used purified humic acid that was extracted from forest floor material, taken from the Tongbersven forest (near Oisterwijk, NL). It has been used in previous studies and is described by Van Dobben *et al.* (1992), Mulder *et al.* (1994) and Temminghoff *et al.* (1997).

Calcium, Copper and Proton Binding by Humic Acid
Data for proton binding to the purified humic acid (between pH 3 and 11) and Cu binding to the humic acid in 0.003 M $NaNO_3$ are available from an earlier study (Temminghoff *et al.*, 1997). In addition we measured potentiometrically: (*i*) Ca binding to the humic acid using a calcium ion selective electrode (Ca-ISE; Radiometer F2002) at three pH values (pH 5, 6 and 8). (*ii*) Cu binding to the humic

acid in the presence of Ca at pH 6 using a copper ion selective electrode (Cu-ISE; Orion 9429). For Ca and Cu binding to the humic acid we used the pH stat mode of the Wallingford titrator (Kinniburgh *et al.*, 1995). All experiments were performed at 25 °C in 0.003 M $NaNO_3$ background electrolyte or as given in the text. The glass electrode was calibrated against two pH buffers of 4 and 7 (Radiometer). The Cu-ISE was linear for pCu between 3 and 13 ($r^2 = 0.9996$), using ethylenediamine for low Cu activities (Avdeef *et al*, 1983; Benedetti *et al*, 1995; Temminghoff *et al.*, 1997). The Ca-ISE was linear for pCa between 2 and 5 ($r^2 = 0.994$). In natural soil environment calcium concentrations are expected between 10^{-6} and 10^{-2} M and from this point of view the range of the Ca-ISE is acceptable.

For experiment (*i*) the purified humic acid (1 g/l humic acid≈ 540 mg/L DOC) was titrated till a designated pH and maintained at this pH for up to 12 h to stabilize the humic acid before Ca was added (titrator pH stat mode). The concentration of free Ca was measured after the pH stat was maintained for 15 min and the drift criteria were less than 0.004 pH/min for the glass electrode (0.2 mV/min) and for the calcium electrode 0.004 pCa/min (0.1 mV/min) before a new addition of Ca. The total Ca concentration in solution was calculated by the buret additions. The Ca binding by humic acid can be calculated by subtraction of the 'free' Ca^{2+} concentration from the total Ca concentration in solution.

For experiment (*ii*) Cu binding to purified humic acid (185 mg/L humic acid ≈ 100 mg/L DOC) was determined in the absence of calcium (0 mmol/L) and in the presence of calcium (0.25 and 10 mmol/L) at pH 6. If necessary, $NaNO_3$ was added to establish an ionic strength of 0.003.

Humic Acid Coagulation

For the coagulation experiments the purifed humic acid at a concentration of 200 mg/L DOC was filtered through 0.45 μm filter (Schleicher and Schuell; NC45). The 0.45 μm is arbitrarily choosen but it is widely accepted (Buffle, 1988). Equal

amounts of the humic acid solution and Al, Cu, Ca and Na solutions, within the range of 10^{-7} to 10^{-2} M, are mixed. For Al, Cu and Ca the ionic strength was adjusted with $NaNO_3$ to be $I = 0.003$. In addition a coagulation experiment was carried out for Cu with 0.001 M $Ca(NO_3)_2$ as background electrolyte. The pH in all cases was fixed at pH 4 ± 0.2 with 0.005 M NaOH. In the case of Ca and Cu the same experiment was carried out at pH 6 ± 0.2. Next the solution was shaken end-over-end for 20 h at 25 °C after which the pH was measured in the suspensions. The suspension was again filtered over 0.45 µm and in the filtrate Cu, Ca, Al, Na and DOC were determined. Cu, Ca, Al and Na with ICP (Spectroflame; Spectro) and DOC with a TOC/DOC analyzer (SK^{12}; Skalar).

Calcium and Copper Desorption by Soil

Copper contaminated field

Soil samples (0-0.2 m) were taken from a copper contaminated field near Wageningen in The Netherlands (Wildekamp site) which has been used previously to study copper speciation in the soil (solution) (Temminghoff *et al.*, 1994 and 1997), copper toxicity both for earthworms (Marinussen *et al.*, 1997) and for springtails (Bruus Pedersen, in press), and long-term effects of copper and pH on the nematode community in an agroecosystem (Korthals *et al.*, 1996). The field consists of a randomised block design of four copper concentrations and four pH adjustments in 6 x 11 m plots. Four pH levels coded A-D for pH_{KCl} 4.0, 4.7, 5.4 and 6.1 were established in 1982 using calcium carbonate or sulphur, followed by establishment of four total Cu levels coded 1- 4 for 0, 250, 500 and 750 kg/ha, added as $CuSO_4$, at each pH level. Methods of application are described by Lexmond (1980). Typical soil parameters such as texture and organic matter content are given by Temminghoff *et al.* (1997).

Batch Experiments

The extraction of the soil samples with two unbuffered extractant (0.001 M

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$Ca(NO_3)_2$ and 0.003 M $NaNO_3$ gives indications of the easily extractable Cu species (Cu_{ex}) and the extraction with 0.43 M HNO_3 gives an indication of the total adsorbed Cu (Cu_T) by the soil. For this purpose we used for all three extractions a soil:solution ratio of 1:10 (w/V). The soil suspensions were shaken end-over-end for 20 h at 25 °C after which the pH was measured in the suspensions for the $Ca(NO_3)_2$ and $NaNO_3$ extractions. After centrifugation at 2,000 g, the easily extractable Cu concentrations (Cu_{ex}) and the total Cu-concentration (Cu_T) in the supernatant was measured by flame AAS (Instrumentation Laboratory AA/AE spectrophotometer S11 with scale expansion). The detection limit was approximately 0.3 µmol/L. Ca was measured in the $Ca(NO_3)_2$ and $NaNO_3$ extracts by flame AES (Eppendorf, Elex 6361). The dissolved organic carbon (DOC) in the 0.001 M $Ca(NO_3)_2$ and 0.003 M $NaNO_3$ extracts was measured with the TOC/DOC analyzer (SK^{12}; Skalar).

<u>Column Experiments</u>

To show the effect of Ca on DOC coagulation and (in)direct on Cu mobility, column experiments were carried out with soils of plot 4A and 3D (layer 0 - 0.20 m). We used perspex columns 4.5 cm in diameter and about 20 cm long which were filled with 300 g of both soils in duplicate. A filter and a thin quartz layer at the bottom of the column prevented outflow of soil particles. Columns were saturated from below with the initial background solution (0.003 M $NaNO_3$) to prevent air inclusion, using a multi channel peristaltic pump (Gilson Minipuls III). The pH of the background solution was adjusted to pH 5.7 (soil pH) with 0.01 mol/L HNO_3 or NaOH. After saturation and 4 days incubation, the flow direction was changed into downwards. The top of the column was connected via a tube to the initial feed solution (0.001 M $NaNO_3$; pH 5.7). A fraction collector (ISCO fraction collector) was used to collect the leached solution samples of about 15 ml. The determined soil density was 1319 ± 41 kg/m^3 for the four columns. Breakthrough curves for chloride yield the pore volumes of the four columns, which was 107 ± 5 ml, and the

diffusion-dispersion coefficient, which was typically 0.047 m^2/year. The porosity, ϕ, was about 0.47 which is under saturated conditions the same as the volumetric water fraction of the soil. Flow rates of approximately 3.1 ml/hour were used for all four column experiments. We changed the feed solution after certain periods (pore volumes ; V/V_0), for all four columns as given in Table 6.1. Besides total Cu and Ca, we measured DOC and the pH in the percolated fractions.

Table 6.1. Soil parameters and feed solution composition for all four columns. Cu_T (0.43 M HNO_3 extractable Cu) is a mean of three replicates with standard deviation.

Soil	$pH_{Ca(NO_3)_2}$	Cu_T (mmol/kg)	period I	period II	period III	period IV
4A1	3.83	1.610 ± 0.043	$NaNO_3$	$NaNO_3$	$Ca(NO_3)_2$	$Ca(NO_3)_2$ [a]
4A2	3.83	1.610 ± 0.043	$NaNO_3$	$NaNO_3$ + DOC	$Ca(NO_3)_2$ + DOC	$Ca(NO_3)_2$ + DOC [a]
3D1	5.74	1.887 ± 0.038	$NaNO_3$	$NaNO_3$	$Ca(NO_3)_2$	$Ca(NO_3)_2$ [b]
3D2	5.74	1.887 ± 0.038	$NaNO_3$	$NaNO_3$ + DOC	$Ca(NO_3)_2$ + DOC	$Ca(NO_3)_2$ + DOC [b]

electrolyte concentrations:
$NaNO_3$ (period I, period II) 0.003 M;
$Ca(NO_3)_2$ (period III) 0.0005 M;
$Ca(NO_3)_2$ [a] (period IV) 0.0001 M;
$Ca(NO_3)_2$ [b] (period IV) 0.0025 M;
DOC 100 mg/L.

Below an ionic strength 0.003 the ionic strength is adjusted with $NaNO_3$ to 0.003.

Results and Discussion

Calcium, Copper and Proton Binding by Humic Acid

Data and the bimodal NICA model description for proton and copper binding by purified humic acid are published elsewhere (Temminghoff *et al.*, 1997). The Ca binding by the purified humic acid is given in Figure 6.1 at pH 5, 6 and 8 on logarithmic scales. Ca binding depends non-linearly on pH and Ca^{2+} concentration and is well described by the (bimodal) NICA model (Eq (6.1)).
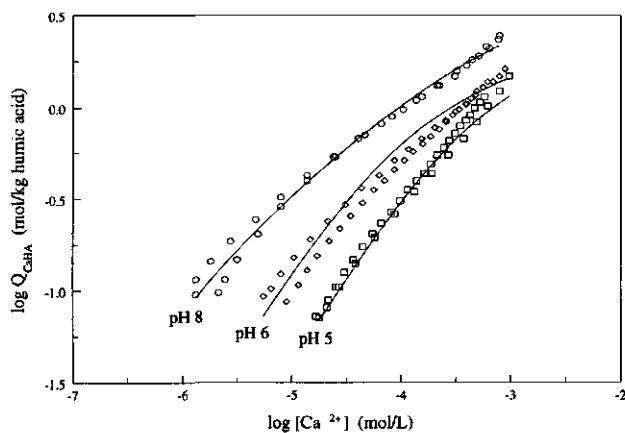
Figure 6.1. Calcium binding by DOC (purified humic acid) as a function of 'free' copper concentration ($[Cu^{2+}]$), on logarithmic scales, at pH 4, 6 and 8 for data symbols) and the NICA model (line) at I=0.003 (0.003 M $NaNO_3$). □ pH 5; ○ pH 6; ◇ pH 8.

The maximum binding capacity of the humic acid (Q_{max}), the intrinsic heterogeneity parameter p and the proton affinity constants (log $\tilde{K}_H$) are kept the same as presented earlier (Temminghoff *et al.*, 1997) and only the median Ca affinity constants for the 'carboxylic' type and 'phenolic' type sites (1 and 2) and the ion specific 'non ideal' behavior factor n_{Ca} for both sites are determined. The

parameters are given in Table 6.2 including the parameters for Cu and protons. The median Ca affinity constants (log $\tilde{K}_{Ca}$) are smaller than the median Cu affinity constants (log $\tilde{K}_{Cu}$). This suggests that the Ca binding is less than Cu binding by humic acid which is in agreement with literature (Benedetti *et al.*, 1995; Kinniburgh *et al.*, 1996). Whereas the ion specific 'non ideal' factors for both sites are almost equal for H and Cu, these are different for Ca.

Table 6.2. Parameters and standard deviations for the NICA model to describe the calcium, copper and proton binding by purified humic acid and soil organic matter at I= 0.003.

	site 1	site 2
purified humic acid & soil organic matter		
log $\tilde{K}_H$	5.12 ± 0.01	9.78 ± 0.00
log $\tilde{K}_{Cu}$	5.40 ± 0.02	10.82 ± 0.05
log $\tilde{K}_{Ca}$	3.57 ± 0.00	5.05 ± 0.11
n_H	0.81 ± 0.01	0.83 ± 0.01
n_{Cu}	0.46 ± 0.00	0.46 ± 0.01
n_{Ca}	0.95 ± 0.01	0.67 ± 0.05
purified humic acid		
p	0.57 ± 0.01	0.58 ± 0.01
Q_{max} (mol/kg)	2.18 ± 0.00	1.54 ± 0.01
soil organic matter		
p	0.63 ± 0.07	0.78 ± 0.10
Q_{max} (mol/kg)	0.63 ± 0.10	0.30 ± 0.17

purified humic acid

H; coefficient of determination (r^2) = 0.99998

Cu and H; coefficient of determination (r^2) = 0.98

Ca and H; coefficient of determination (r^2) = 0.98

soil organic matter

Cu, Ca and H; coefficient of determination (r^2) = 0.92

The multi component NICA model for H, Ca and Cu can now be used to *predict* the Cu binding by humic acid in the presence of Ca at every pH. In Figure 6.2 we show data and the prediction of Cu binding at pH 6 for three Ca concentrations; 0, $2.5.10^{-4}$ and 0.01 M. To calculate the competition the speciation program ECOSAT (Keizer & Van Riemsdijk, 1994) is used.
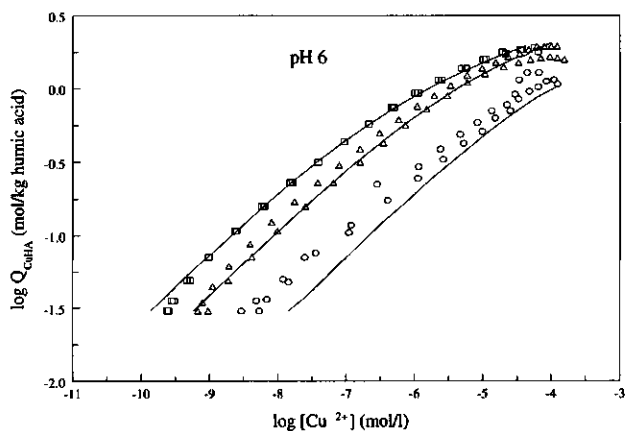
Figure 6.2. Copper binding by DOC (purified humic acid) as a function of 'free' copper concentration ($[Cu^{2+}]$), on logarithmic scales, at pH 6 and three Ca concentrations ; 0 M Ca, 0.25 mM Ca and 0.01 M Ca (total) for data (symbols) and the NICA model (line). The NICA model are the predictions with the use of parameters of Table 6.2. The ionic strength for 0 and 0.25 mM Ca is adjusted to I=0.003 with NaNO₃. □ 0 M Ca; △ 0.25 mM Ca; and ○ 10 mM Ca.

Due to Ca competition, Cu binding decreases with increasing Ca concentration. The prediction for 0 and 0.25 mM Ca is good. For 0.01 M calcium, either Cu binding is predicted slightly too large or Ca competition is sligthly overestimated. This difference may be partly due to differences in ionic strength which is 0.03 instead of 0.003 as used in other experiments. Another cause for discrepancy is that humic acids coagulate in the presence of 0.01 M Ca which possibly influences the Cu binding. The Ca competition on Cu binding is in the literature not unambiguously. Some show a considerable Ca competition on Cu binding by DOC (Hering & Morel, 1988; McKnight & Wershaw, 1994) whereas others observed a small Ca competition on Cu binding by DOC (Kinniburgh *et al.*, 1996). Kinniburgh however used very high purified peat humic acid concentrations (840 mg/L) and low total Ca concentrations ($\approx$ 1 mmol/L) which explains why only a small Ca competition effect was found. Simulations, with parameters of Kinniburgh *et al.* (1996), showed that at lower humic acid concentrations (100 mg/L DOC) and the same total Ca concentation as we used that significant Ca competition takes place but to a slightly less extent as we found.

Humic Acid Coagulation

In Figure 6.3 humic acid coagulation, expressed as a percentage of the initial Dissolvced Organic Carbon (DOC) concentration, is given as function of different metal concentrations (M) on a logarithmic scale at pH 4.

The results for a trivalent (Al^{3+}), two divalent (Ca $^{2+}$ and Cu $^{+}$) and a monovalent (Na^+) ion are shown. At a certain metal concentration the relative DOC concentration decreases rapidly due to humic acid coagulation. The almost total coagulation of the humic acid occurs in very small concentration ranges but differs for every cation. The trivalent ions are more effective in coagulation than the divalent ions, which are more effective than the mono valent ions, which is quantitatively in agreement with the coagulation theory (Ong & Bisque, 1968; Overbeek, 1972). The coagulation occurs at $\approx 10^{-4}$ mol/L Al, $\approx 10^{-3.3}$ mol/L Cu,

$\approx 10^{-2.5}$ mol/L Ca and not below 10^{-2} mol/L Na. Although Ca and Cu are both divalent ions the coagulation occurred at different Cu and Ca concentrations. Coagulation appears even earlier for Cu in 0.001 M $Ca(NO_3)_2$ compared to Cu in 0.003 M $NaNO_3$ (Figure 6.4a).
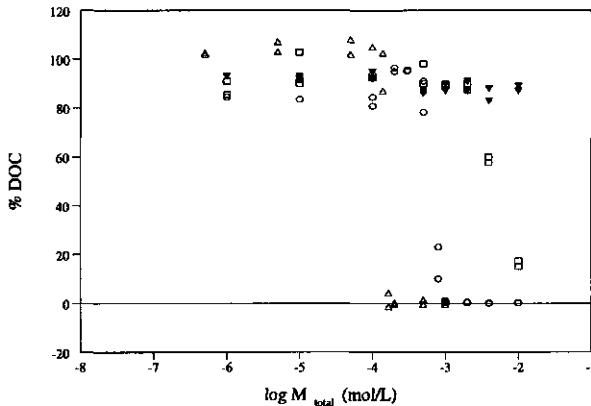
Figure 6.3. Humic acid coagulation, expressed as DOC percentage of initial DOC, as a function of total metal (Al, Cu, Ca or Na) concentrations (mol/L) at pH 4 on logarithmic scale. Ionic strength is 0.003 or higher (see text for details). △ Al; ○ Cu; □ Ca and ▼ Na.

The pH shows for Cu and Ca only a minor effect on coagulation between pH 4 and pH 6. With the NICA model the Cu and Ca binding by humic acid can be calculated to investigate as a first order approch the relation between Ca and Cu bound by humic acid and coagulation (Figure 6.4b). The coagulation occurs more or less at the same amount of Ca or Cu bound by the humic acid. Even for the mixtures of Cu and Ca, where the Cu and Ca bound by humic acid are added. The Cu binding by humic acid is much stronger than Ca binding (Table 6.2) which explains the earlier humic acid coagulation for Cu. In all cases the coagulation appeared between 1.0 and 1.8 mol/kg Ca and/or Cu binding by humic acid.
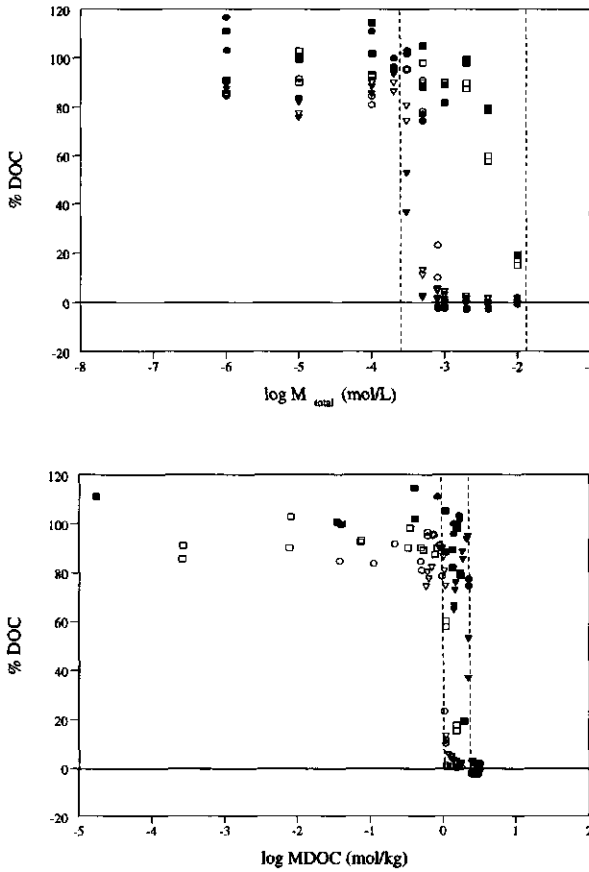
Figure 6.4. Humic acid coagulation, expressed as DOC percentage of initial DOC, as a function of **a)** total metal (Cu or Ca) concentrations at pH 4 and pH 6 and **b)** amount of Ca and Cu bound by humic acid, calculated with the NICA model. Both Cu and Ca concentrations (mol/L) and Ca and Cu bound by humic acid (mol/kg) are given on logarithmic scale. The ionic strength is 0.003 or higher (see text for details) □ Ca, pH 4; ○ Cu, pH 4; ■ Ca, pH 6; ● Cu, pH 6.▽ Cu and Ca, pH 4; ▼ Cu and Ca, pH 6.

Table 6.3. Extraction results of the Cu contaminated soil. 0.43 M HNO₃ extractable 'Total' Cu (Cu_T) and pH, extractable Cu (Cu_{ex}), Ca and DOC concentrations in 0.001 M Ca(NO₃)₂ and 0.003 M NaNO₃ (I=0.003).

| soil code	Cu_T mmol/kg	Ca(NO₃)₂				NaNO₃			
		pH	Cu µmol/L	Ca µmol/L	DOC mg/L	pH	Cu µmol/L	Ca µmol/L	DOC mg/L
1A	0.485 ± 0.005	3.92 ± 0.01	1.83 ± 0.12	879 ± 1	12.9 ± 0.2	4.18 ± 0.01	1.75 ± 0.23	15 ± 5	15.0 ± 0.2
2A	1.007 ± 0.017	3.99 ± 0.04	3.72 ± 0.12	862 ± 7	13.6 ± 0.3	4.18 ± 0.01	2.92 ± 0.14	19 ± 3	15.3 ± 0.1
3A	1.675 ± 0.014	4.02 ± 0.01	7.51 ± 0.6	872 ± 2	13.9 ± 0.1	4.18 ± 0.01	4.68 ± 0.00	29 2	15.7 ± 0.1
4A	1.610 ± 0.043	3.89 ± 0.02	11.5 ± 0.4	899 ± 2	12.0 ± 0.3	4.18 ± 0.01	5.96 ± 0.10	22 ± 1	13.4 ± 0.1
1D	0.485 ± 0.005	5.39 ± 0.01	- [a]	944 ± 10	9.1 ± 0.4	4.18 ± 0.01	- [a]	158 ± 2	14.9 ± 0.0
2D	0.485 ± 0.005	5.49 ± 0.01	1.89 ± 0.21	946 ± 4	9.7 ± 0.0	4.18 ± 0.01	3.24 ± 0.11	198 ± 37	15.6 ± 0.2
3D	0.485 ± 0.005	5.45 ± 0.03	2.51 ± 0.00	920 ± 1	10.6 ± 0.1	4.18 ± 0.01	4.68 ± 0.00	153 ± 2	17.0 ± 0.2
4D	0.485 ± 0.005	5.28 ± 0.02	3.63 ± 0.02	921 ± 4	9.5 ± 0.2	4.18 ± 0.01	6.33 ± 0.62	142 ± 5	15.7 ± 0.0

[a] below detection limit AAS.

Calcium and Copper Desorption by Soil

Batch Experiments

To investigate the effect of Ca on Cu desorption the soils were extracted with 0.001 M $Ca(NO_3)_2$ and 0.003 M $NaNO_3$. The ionic strength is in both cases 0.003. In Table 6.3 pH, Cu extractable, Ca and DOC concentrations are given including the total Cu content in the soil. For extraction with $NaNO_3$, the soil suspension pH was 0.2 - 0.4 pH units higher than for extraction with $Ca(NO_3)_2$. The DOC concentration in all soil extracts was slightly larger for $NaNO_3$ (15.3 ± 1.0 mg/L) than for the $Ca(NO_3)_2$ extraction (11.4 ± 1.8 mg/L). The initial Ca concentration of the 0.001 M $Ca(NO_3)_2$ was 1000 ± 3 μmol/L which implies that Ca *ad*sorption occurs in the case of $Ca(NO_3)_2$ extraction. The Ca adsorption is a sligthly higher at pH 4.0 than at pH 5.5. In the case of $NaNO_3$ as extraction solution Ca *de*sorption is observed, which is smaller at pH 4.0 than at pH 5.5. Ca desorption occurs of Ca that is intially bound by the soil (base saturation). Temminghoff *et al.* (1994) showed that for these sandy soils at pH 5.5 the (pH dependent) cation exchange capacity (CEC) is for about about 80 % occupied with Ca (21 mmol/kg Ca) whereas at pH 4.0 this is about 40 % (6 mmol/kg Ca).

At pH 4.0, the extractable Cu concentrations are larger for the $Ca(NO_3)_2$ extraction than for the $NaNO_3$ extraction. This would be expected since the divalent Ca is a stronger competitor than the monovalent Na. However, at pH 5.5 the $Ca(NO_3)_2$ extractable Cu concentrations are smaller than the $NaNO_3$ extractable Cu concentrations. This difference compared with pH 4.0 is shown in Figure 6.5a and can be explained by Cu complexation by DOC which is affected by Ca and H concentrations. With measured pH, extractable Cu, Ca and DOC concentrations and the NICA model the 'free' copper (Cu^{2+}) concentrations in the extracts can be calculated, if we assume that soil DOC behaves as humic acid. This procedure has been used before by Temminghoff *et al.* (1997). In Figure 6.5b the copper adsorbed by the soil ($Q_{Cu-soil}$) is given as a function of the calculated 'free' copper concentration on a logarithmic scale for both extracts.

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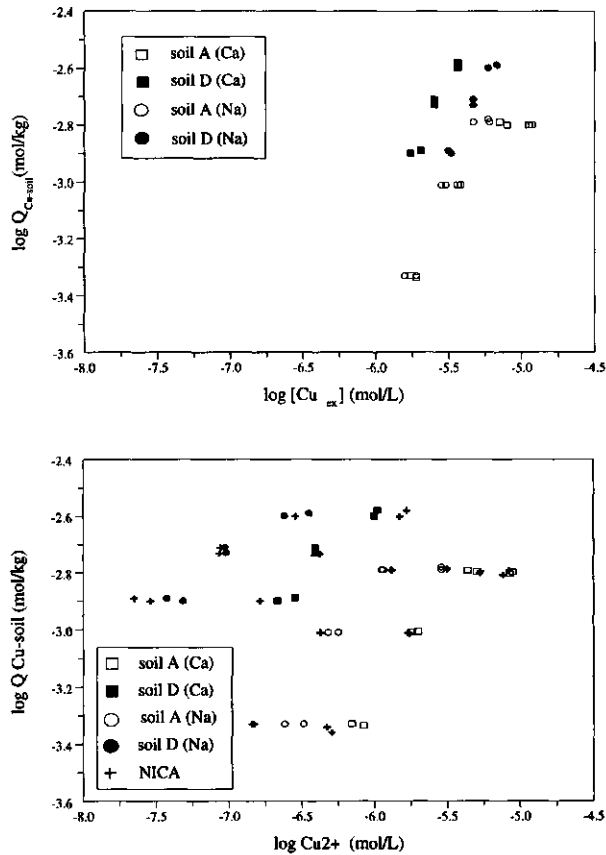
Figure 6.5. Copper (de)sorption ($Q_{Cu\text{-soil}}$; mmol/kg) as a function of a) extractable Cu concentration (log [Cu_{ex}]; mol/L) **b)** 'free' Cu concentration (log [Cu^{2+}]; mol/L) on logarithmic scales at the pH of the soil (solution) for 0.001 M Ca(NO$_3$)$_2$ and 0.003 M NaNO$_3$ (I=0.003 in both cases).

The 'free' copper concentration is larger for the Ca(NO$_3$)$_2$ extraction than for the NaNO$_3$ extraction at both pH levels which is in agreement with our expectations. The amount of Cu bound by DOC depends strongly by pH and Ca concentration.

At pH 4.0 the calculated copper bound by DOC was between 25 and 60 % of the total $Ca(NO_3)_2$ extractable Cu whereas for $NaNO_3$ this was between 50 and 85 %. At pH 5.5 70 to 88 % of the total $Ca(NO_3)_2$ extractable Cu was bound by DOC whereas for $NaNO_3$ this was between 95 and 99 %. Since organic matter is the most reactive solid component in sandy soils the calculated Cu^{2+} is in equilibrium with dissolved and solid (soil) organic matter. The organic matter content for the different soils are given by Temminghoff et al. (1997) The Cu^{2+} binding by the solid organic matter was also described by the NICA model (Eq (6.1) and (6.2)), where besides proton also Ca competition was taken into account. All parameters were kept constant except the maximum copper adsorption capacity (Q_{max}) and the intrinsic heterogeneity (p) of the organic matter (Table 6.2). By fitting only these two parameters we described the Cu^{2+} binding by (soil) solid organic matter with the NICA model (Figure 6.5b). The maximum Cu sorption capacity for (soil) solid organic matter had to be reduced between 20-30 % of the Q_{max} for both sites of the purified humic acid which is in agreement with earlier experiments (Temminghoff et al., 1997; Overbeek, 1972). The intrinsic heterogeneity factor p of the organic matter needed only sligth adjustments which shows that the intrinsic heterogeneity of the soil solid organic matter and the humic acid are of the same order of magnitude. The NICA model described the Cu binding by the soil solid organic matter excellent at different pH and Ca concentrations.

Column Experiments

The effect of Ca on DOC coagulation and Cu mobility is shown in Figure 6.6. Figures a, b, c and d show the Cu and DOC concentrations in the leached solutions as a function of percolated porevolumes (V/V_0) for column 4A1, 4A2, 3D1 and 3D2. In the Figures e, f, g and h, the pH and Ca concentrations in the leached solutions are shown for the same columns. For each column experiment four periods are distinguished which are separated by dashed lines in Figure 6.6.
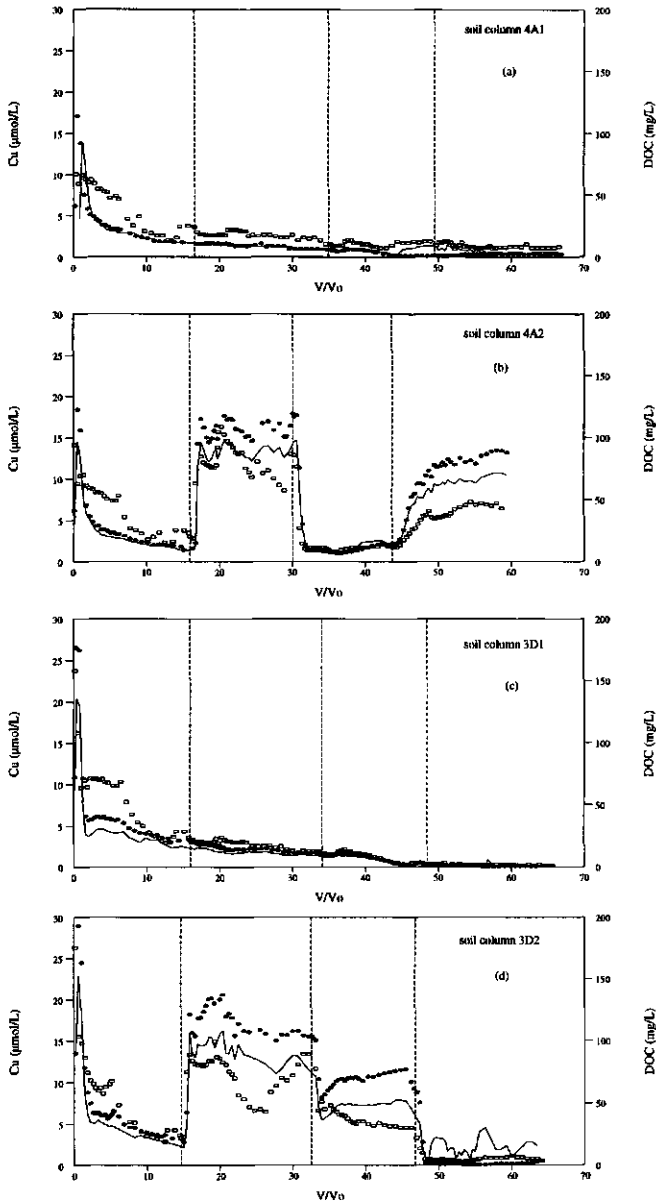
Figure 6.6. Copper and DOC concentrations (Figure a, b, c and d) and Ca concentrations and pH (Figure e, f, g and h) in the percolate as a function of pore volumes for soil column 4A1, 4A2, 3D1 and 3D2 for different
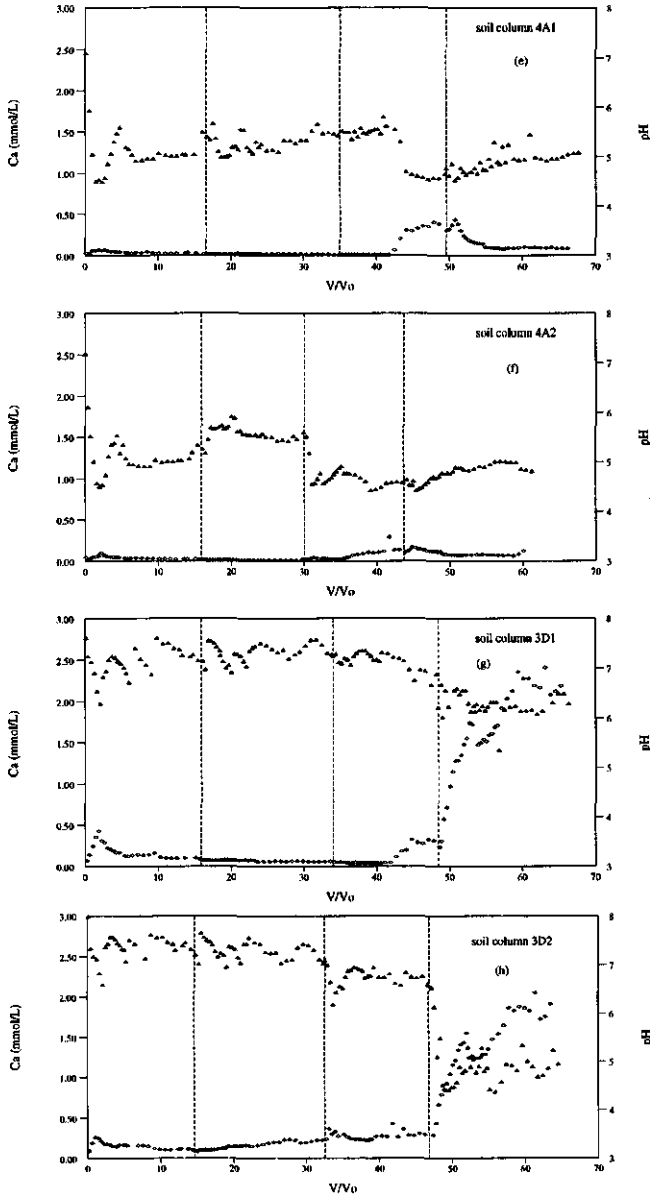
background electrolytes at different periods (expressed by dashed line) as given in Table 6.1. □ Cu, μmol/L; ● DOC, mg/L; ▲ pH; ◊ Ca, mmol/L. Solid line are predictions with the NICA model.

During each period a different feed solution was used as given in Table 6.1. Columns 4A1/4A2 and 3D1/3D2 are duplicates. For the first period the duplicate columns were leached by the same 0.003 M $NaNO_3$ electrolyte and give similar results. For DOC, the concentration shows a narrow peak of 125 mg/L for soil column 4A1/4A2 and 180 mg/L for soil column 3D1/3D2 after about 1 pore volume (V/V_0). The Cu breakthrough curves also show one peak which is a sligthly broader than the DOC peak. At the end of period I, the Cu concentrations for all four columns were almost the same and varied between 3 and 5 µmol/L. The DOC concentration at the end of period I was about 10 mg/L at pH 5.3 and 20 mg/L at pH 7.3. At pH 5.2, the Ca concentration is about 22 µmol/L whereas at pH 7.3 the Ca concentration is about 100 µmol/L. This difference of Ca concentrations can be understood with the results of the batch experiments, since the (pH dependent) CEC of the soil is largely occupied with Ca.

Soil batch pH values and soil column pH values differ despite that the same electrolyte (0.003 M $NaNO_3$) was used. The differences of pH are about 1 pH unit for soil 4A and about 2 pH units for soil 3D. Using the pH, DOC, and Ca concentrations in the leached solutions, we *predicted* the Cu concentrations in these solutions. At each pH, DOC and Ca concentration of the percolate both Cu desorption by (soil) solid organic matter and Cu adsorption by DOC were calculated using the NICA model, with parameters of Table 6.2 and the speciation program ECOSAT (Keizer & Van Riemsdijk, 1994). The Cu concentrations in the leached solutions predicted by the model are given in the Figures by a solid line. The NICA model predicted the Cu concentrations rather well although slight discrepancies were found during the first pore volumes.

For the periods II, III, and IV, 100 mg/L DOC (humic acid) was added to the feed solutions of columns 4A2 and 3D2 whereas no DOC was added to the feed solutions for columns 4A1 and 3D1. During period II the 0.003 M $NaNO_3$ was maintained as background electrolyte. For both pH levels, the DOC breakthrough

was very fast as is shown in Figure 6.6b and 6.6d. After 1 pore volume the DOC concentrations were equal to the initial feed DOC solution which indicates that no significant DOC adsorption occurs in the columns. Simultaneously with DOC breakthrough, the Cu concentrations increased from about 3 to values ranging from 10 till 15 µmol/L whereas they decreased to 2 µmol/L in columns 4A1 and 3D1. This reveals that due to leaching of 100 mg/L DOC, Cu leaching was enhanced by a factor 5 till 8 for both pH 5.2 and pH 7.3. The Ca concentration in the percolate increased by a factor 2 simultaneous with the DOC increase in column 3D2 (pH 7.3) whereas in column 4A2 no increase of Ca was found despite the DOC increase. This suggests that at pH 7.3 Ca competes with Cu for binding by DOC whereas at pH 5.2 this is negligible. The NICA model predicted the Cu concentrations in the leached solutions rather well for period II as affected by DOC at different pH levels.

To investigate the DOC coagulation by calcium the feed solution for the columns was changed from 0.003 M $NaNO_3$ into 0.0005 M $Ca(NO_3)_2$ in period III, whereas the ionic strength was maintained at 0.003 (the same as during period I) by addition of 0.0015 M $NaNO_3$ to the feed solution. For the columns 4A2 and 3D2 100 mg/L DOC was present in the feed solution. In batch experiments DOC coagulation occurs at Ca concentrations above 3 mmol/L, for both pH 4 and pH 6 (Figure 6.4). Already at the relatively small Ca concentration in the feed solution (0.5 mmol/L Ca) compared to the batch experiments the DOC concentration in the percolates decreased within 2 pore volumes from about 110 to 10 mg/L for column 4A2 (Fig. 6.6b). These DOC concentrations are the same as the DOC cocentrations in column 4A1 (Fig. 6.6a) for which no DOC was added to the feed solution which shows that the additionally injected DOC was completely retained in column 4A2. At pH 7.3 (column 3D2) the DOC concentrations decreased within 2 pore volumes to 70 - 80 mg/L at the relatively small Ca concentration in the feed solution. About 20 to 30 % of the initial DOC concentration in the feed solution was retained in the

column at pH 7.3. DOC coagulation by calcium appeared in column experiments at smaller concentration (0.5 mmol/L Ca) that in batch eperiments (3 mmol/L Ca) and was pH dependent. Partial coagulation took place at pH 7.3 and total coagulation at pH 5.3. A possible cause that in column experiments (total) coagulation occurs at smaller Ca concentrations than was observed for the batch experiments may be the desorption of other previously soil-bound di- and trivalent cations (e.g. Mg, Cu, Al). These cations can affect DOC coagulation as is shown in Figure 6.3 for Ca, Cu, and Al. Simultaneously with the DOC decrease the Cu concentrations in the percolates decreased for both pH values. The Cu mobility is partly regulated by the DOC concentration in the leached solutions and partly by the Ca concentration. A sharp Ca breakthrough occurred after about 8 pore volumes (V/V_0) in period III for column 4A1 and 3D1 (Fig. 6.6e and 6.6g) whereas the Ca breakthrough is less sharp for the columns, 4A2 and 3D2, with DOC in the feed solution (Fig. 6.6f and 6.6h). Together with the steep Ca increase the DOC and pH decreased for both columns 4A1 and 3D1. For column 4A1 (pH 5.3) the Cu concentration in the percolate *increased* whereas the Cu *de*creased for column 3D1 (pH 7.2). Three processes, Cu desorption by soil, DOC coagulation and Cu complexation by DOC, act at the same time and all three processes are influenced by Ca and the pH. It appears that at small pH, Cu desorption by soil is dominant whereas at large pH Cu complexation by DOC is dominant. The good prediction by the NICA model of the Cu concentration in the leached solutions reveals that the effects of pH, DOC and Ca on Cu speciation are adequateley captured by the model.

In period IV the three processes that depends on pH and Ca concentration (Cu desorption by soil, DOC coagulation and Cu binding by DOC) with counteracting effects on Cu mobility are investigated some more in detail. Thus, in period IV the Ca concentration of the feed solution was decreased to 0.1 mmol/L for the columns 4A whereas for the columns 3D the Ca concentration was increased to 2.5 mmol/L. For columns 4A1 and 4A2 the Ca concentration

decreased slowly (Fig. 6.6e and 6.6f). For column 4A2 simultaneously the DOC and Cu concentration increased slowly (Fig. 6.6b) which reveals that the DOC as well as the Cu breakthrough is regulated by the Ca concentration. For column 3D2 the DOC concentration in the percolate decreased very fast from 70 mg/L to 2 mg/L due to the increased Ca concentration in the feed solution. The Cu decreased simultaneously with the decrease of DOC from 5 to 1 µmol/L (Fig. 6.6d). Although the Ca concentration increased by a factor 5 the Cu concentration decreased by a factor 5 which again shows that at high pH Cu binding by DOC is predominant for Cu mobility. The predicted Cu concentrations in the percolate by the NICA model agreed well with our observations and shows that pH, DOC and Ca effects on Cu speciation (Cu desorption by soil and Cu binding by DOC) in soil are adequateley captured by the model.

To investigate the DOC coagulation in the column experiments the DOC percentage of the initial DOC concentration in the feed solution for colums 4A2 and 3D2 during period II, III and IV is given as a function of the metal binding (Cu and Ca) by DOC in Figure 6.7 similarly as was done in Figure 6.4b. To enable these calculations with the NICA model, the Cu^{2+} desorption by the (soil) organic matter at each leached solution pH and Ca concentration is used. In case that Ca concentrations of the leached solutions are smaller than the Ca feed concentration, the latter was used since the Ca front where the DOC coagulation occurs still resides in the column. Also results of column experiments by Temminghoff *et al.* (1997) are shown. The DOC coagulation in column experiments appears to be in agreement with the batch experiments although at small pH the coagulation occurs at a sligthly smaller calculated metal binding content.
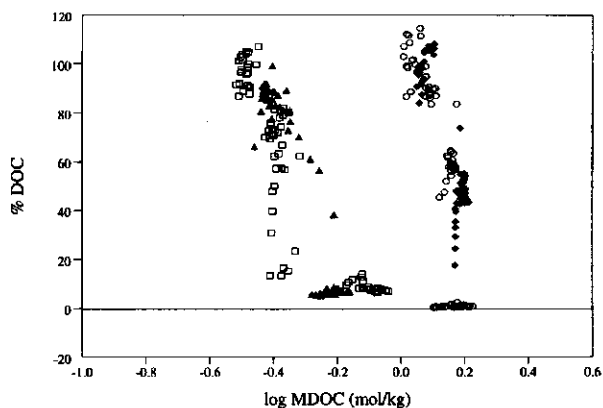
Figure 6.7. Humic acid coagulation in column experiments 4A2 and 3D2 during periods II, III and IV. Coagulation, expressed as DOC percentage of initial DOC, as a function of the amount of Ca and Cu bound by DOC (MDOC) as calculated with the NICA model in mol/kg on logarithmic scale (see text for details). □ column 4A2; ○ 3D2. Data for ▲ soil 4A and ◆ soil 3D are taken from Temminghoff *et al.*, 1997.

Acknowledgements

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Chapter 7

Dynamic Copper Balances of Contaminated Sandy Soil as Affected by Changing Solid and Dissolved Organic Matter and pH

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Abstract

Changing land use from arable farming to forestry results in increasing soil organic matter content and H^+ solution concentrations. Effects of organic matter increase and pH decrease on copper speciation and consequent copper mobility are modeled for different land use change scenarios by incorporating the Two Species Freundlich equation in dynamic balances for copper in soil. The land use change scenarios show that copper accumulation in soil may appear harmless at first, but may adversely affect soil biology and groundwater quality later. Such effects depend on the copper input history of the soil (agricultural use) and also to a large extent on the question whether the litter is mixed through the topsoil or not (forestry). In a land use change scenario with high copper input history, after 50 years, Cu leaching is about 4 times higher if the litter remains on top of the topsoil than in the cases of mixing litter through the topsoil or continuing high-input agriculture. The increase of the Cu^{2+} activity in the land use change scenarios as compared with continued agriculture (factor 30 and 750 for the mixed and non-mixed case, respectively) due to decreasing pH is apparent.

Introduction

Agricultural productivity in Europe is characterized by overproduction in relation to markets, considerable differences in productivity over the continent, and different potentials for increases in productivity under present technological conditions. Therefore, large areas of European agricultural land are being taken out of production according to 'set-aside' schemes (Brouwer *et al.*, 1991). An important land use change is changing arable land into forests. A majority of these forests are to be planted on soils with a relatively low potential for agricultural production. In the Netherlands, these areas consist largely of sandy soils with a low buffering capacity. 'The buffering capacity of soil with respect to soil contamination may be defined as its capacity to delay the negative effects of the contaminant's presence because of inactivation' (De Haan, 1996). In case of changing land use, slow alterations gradually reduce the buffering capacity and predispose the system to adverse effects (Stigliani *et al.*, 1991).

Forestation will lead to a decrease in soil pH (due to termination of regular lime applications), an increase in the soil organic matter content (due to lower pH and and higher input of organic material without the removal of harvest products). Soil acidification is a natural process that can be strongly enhanced by atmospheric deposition of SO_2, NO_x, and NH_3. Soil acidification rates depend primarily on acid input rates and the soil acid neutralizing capacity. On a limed agricultural field that was later abandoned and converted into deciduous woodland, the pH of the plough layer decreased from pH 7 to 4.2 over 100 years (Johnston *et al.*, 1986). Hesterberg (1993) modeled changes in the solubility of some trace metals in soil as a result of acidification and found that zinc, cadmium and aluminum solubilities increased exponentially with decreasing pH and calcium concentrations after liming stops.

Soil organic matter (expressed as SOC; solid organic carbon) originates from decaying plant and animal products that have been converted to a more or less

stable product (humus). Mineralization of organic matter and recycling of nutrients by plants is essential in the relationship between soil and the above-ground biosphere (Stevenson, 1982). Composition and turnover of organic matter have a profound bearing on the physical and chemical properties of the soil (Schulin *et al.*, 1995).

Accumulation of heavy metals in soil may cause problems if soil is to permanently fulfil its functions in agricultural production, in environmental processes, and as a habitat of numerous organisms. The biological availability and the mobility of heavy metals are controlled by their chemical speciation *i.e.*, the distribution of the total metal content over all possible chemical forms (species) that are present in the solid, the liquid, and the biotic phases of soil (Temminghoff *et al.*, 1997a). Adsorption of the 'free' heavy-metal ion on each soil component (soil particles, (in)organic ligands, biota) depends on factors like pH and competition. The 'free' metal ion fraction in the soil solution is often the most bioavailable fraction whereas heavy-metal complexes are often important with respect to mobility (Plette, 1996; Temminghoff *et al.*, 1997a). Excess amounts of heavy metals may interfere with essential microbiological soil functions, like organic matter decomposition, nitrogen fixation, and nitrification. This may have substantial impacts on the entire ecological dynamics of soil. In turn, bioavailability of heavy metals in soil will strongly depend on biotic processes. Inhibition of litter decomposition tends to increase the storage capacity of heavy metals by SOC, because SOC may have a high (specific) binding capacity for heavy metals. If stable complexes of heavy metals and organic matter are formed, the toxic effect of these metals in contaminated acid soils may be reduced (Brümmer *et al.*, 1986). Decomposition of SOC may strongly affect the redox potential due to oxidation and the pH of the solution by producing organic acids and carbon dioxide. Through decomposition processes, dissolved organic matter (expressed as DOC; dissolved organic carbon) concentrations in the soil solution

increase and these DOC compounds form soluble complexes with various heavy metals. In that way, the complexation of sorbed metal species by soluble organic ligands can enhance heavy-metal mobility (Häni *et al.*, 1996).

The extent to which heavy metals are mobile in an (acid) sandy soil depends on pH, the amounts sorbed by the SOC, and on the extent to which metal-DOC complexes are formed. Copper-DOC complexes are known to be important for enhancing copper (Cu) mobility and bioavailability in sandy soil (Temminghoff *et al.*, 1997a,b). Since the concentration of DOC may increase due to land use changes, the understanding of Cu-DOC binding is very important in this context (Temminghoff *et al.*, 1994).

In this paper, we study the effect of increasing (solid and dissolved) organic matter and decreasing pH with regard to Cu accumulation and mobility in soil. For this purpose, the speciation of Cu and the consequent multi-phase competition (Cu complexation with SOC and DOC) are taken into account in dynamic Cu balances of the topsoil. In these dynamic soil balances, the organic matter dynamics influence the soil bulk density as well. In this way, we develop an integrated approach in which Cu speciation in solution is calculated with a well defined speciation model and incorporated in the dynamic soil balance.

We consider two extreme possibilities of how the system's boundaries develop after changing land use from arable farming to forestry. On the one hand, the fallen litter is considered to be mixed completely throughout the topsoil (*i.e.*, the former plough layer) by biological action (*e.g.*, earthworms, springtails, etc.). On the other hand, the same amount of organic matter as in the case of mixing accumulates on top of the soil by the formation of a litter layer, which is thus considered to be separate from the former plough layer. The Cu balances of the top 0.3 m (litter layer not taken into account) are compared for the two cases.

Theory

A balance of heavy metals in the topsoil relates the rates of change in heavy-metal content, input and output and can be given by:

$$\frac{dG}{dt} = A - L - U \tag{7.1}$$

In equation 7.1, the change in total heavy metal content in soil (dG/dt) depends on the input rate at the soil surface (A), the leaching rate at the lower boundary of the system (L) and the removal rate by harvesting plants (U). The topsoil is taken to be homogeneously mixed, which implies that the SOC and Cu contents do not show vertical variation within the system.

Leaching (L) and crop uptake (U) of heavy metals are related to the metal concentration in the soil solution which depends on sorption characteristics. Both empirical and semi-mechanistic models have been developed to describe heavy-metal adsorption by heterogeneous surfaces such as soil, (dissolved) organic matter and organisms. A semi-mechanistic Non-Ideal Competitive Adsorption (NICA) model was developed by Koopal *et al.* (1994). At median pH ranges and low heavy-metal concentrations the NICA equation can be simplified to a Two Species Freundlich equation (TSF) if only proton competition with one heavy metal is taken into account (Temminghoff *et al.*, 1997b):

$$Q_{Cu} = K' \, (Cu^{2+})^{n_{Cu}} \, (H^+)^{m_H} \tag{7.2}$$

Here, Q_{Cu} is the adsorbed quantity of Cu by organic matter (mol/kg), H^+ and Cu^{2+} are solute concentrations in mol/l and K', n_{Cu}, and m_H are parameters that are quantified in Table 7.1.

Table 7.1. Parameters for the TSF model to describe copper binding by Dissolved Organic Matter (DOC) and Soil Organic Matter (SOC) at I=0.003 (from Temminghoff *et al.*, 1997b).

	DOC	SOC
n_{Cu}	0.36	0.36
m_H	-0.40	-0.58
$\log K'$	-0.348	-1.77

Temminghoff *et al.* (1997b) were able to describe both Cu binding by DOC and Cu binding by SOC with the NICA and the TSF model. At pH 3.9, about 30% of the total Cu in solution was complexed Cu-DOC. At pH 6.6, Cu-DOC comprised more than 99%. Furthermore, Temminghoff *et al.* (1997b) used both (NICA and TSF) models to *predict* the Cu concentration in the soil solution at different depths (0-0.9 m) under field conditions from the total Cu content, pH, SOC, and DOC contents.

We model the adsorption of Cu onto SOC and DOC with the TSF equation (Eq. 7.2) in the calculation of dynamic Cu balances in soil. Using the parameter values from Table 7.1, the distribution of Cu between SOC (Q_{CuSOC}; mol/kg SOC) and DOC (Q_{CuDOC}; mol/kg DOC) and free Cu^{2+} (mol/l) is calculated. The amount of adsorbed Cu on the soil solid phase (Q_{Cusoil}; mol/kg soil) is derived from the amount of Cu adsorbed on SOC by accounting for the mass fraction of SOC (f_{SOC}):

$$Q_{Cu-soil} = f_{SOC} \, Q_{CuSOC} \tag{7.3}$$

The CuDOC concentration (mol/l) is related to Q_{CuDOC} according to:

$$[CuDOC] = Q_{CuDOC} \, [DOC] \, 10^{-6} \tag{7.4}$$

where [DOC] is the DOC concentration in the soil solution (mg/l).

Using equations 8.2 - 8.4, the leaching rate (L) can be related to the total Cu concentration in the soil solution ($Cu_{sol} = Cu^{2+} + CuDOC$):

$$L = \frac{\theta v(Cu_{sol})}{l_p} \qquad (7.5)$$

where v is the interstitial water flow velocity (1 m/yr), θ is the volumetric water content of the soil (0.3 m³/m³), and l_p is the plough layer thickness (0.3 m). Here, we consider only vertical solute transport. The values of θ, v, and l_p are taken to be representative for an 'average Dutch situation' in this paper.

Crop uptake rate is expressed here according to the relationship

$$U = B\ G^m \qquad (7.6)$$

with the plant uptake rate coefficient (B) and total soil Cu content (G) (cf. Kuboi et al., 1986). Based on Moolenaar & Lexmond (1998), we take $m = 1$ and $B = 5\ 10^{-4}$ (1/yr) for Cu offtake by an arable crop rotation. The solution of the differential balance equation (Eq. 7.1) is approximated numerically using the 4th order Runge-Kutta method (Press et al., 1986).

Moolenaar et al. (1997) developed a method for calculating heavy-metal balances, in which changes in soil composition are explicitly accounted for by calculating mass balances of heavy metals and of the main soil constituents at the same time. In this dynamic soil composition balance (DSCB) approach, the dynamics in soil composition are reflected in changing organic matter, clay and non-clay fractions of the plough layer. These fractions determine the soil bulk density and hence the plough layer weight. The effect of changing SOC content on the soil bulk density (ρ: g/m³) is modeled according to an empirical relation based on data gathered by Van Wijk & Beuving (1984):

$$\rho = \frac{1}{(0.6+3f_{SOC})} \tag{7.7}$$

The resulting Cu-soil content (expressed on unit mass: mmol/kg) is calculated by dividing the Cu content expressed on unit volume (mmol/m^3) by the new soil bulk density (ρ_{new}; kg/m^3) and by using a correction factor (*i.e.*, ρ_{new}/ρ_{old}) for constant plough layer thickness in the case of mixing. According to McBride *et al.* (1997), any attempt to predict Cu solubility or leachability as a function of soil properties must quantify the factors that affect organic matter solubility. We derived the relationship between DOC concentrations (mg/l), SOC content (%), and pH based on the measurements of SOC, DOC, and pH in a Cu contaminated sandy soil carried out by Temminghoff *et al.* (1997b). After logarithmic transformation, linear regression was carried out which resulted in the following equation:

$$\log(DOC) = 0.07 + 0.923\log(SOC) + 0.084pH \tag{7.8}$$

The correlation is good (coefficient of determination $r^2 = 0.82$) since important factors that determine the DOC concentration (*i.e.*, SOC and pH) are taken into account in this equation. The DOC concentration can be regulated by many factors like charge of DOC, binding onto metal (hydr)oxides and clay, and coagulation (Tipping & Woof, 1990). Therefore, extrapolation of Eq. 7.8 to other cases than the field used by Temminghoff *et al.* (1997b) should be carried out with caution.

In accordance with values measured by Johnston *et al.* (1986) and by Römkens & De Vries (1994), we assume that within 50 years after arable land is converted into forest the pH will decrease non-linearly from 6 to 4. This acidification pattern is simulated by a net yearly (linear) increase in the soil solution of 2 µmol H$^+$ per liter.

For all calculations it is assumed that arable farming or forestry are practised

on the sandy soil which is described by Temminghoff *et al.* (1997b). The initial Cu soil content is 15 mg/kg (0.24 mmol/kg), which is a common value for Cu contents in Dutch sandy arable soil (Van Drecht *et al.*, 1997).

Scenarios

Three agricultural scenarios are defined to show different developments of soil Cu contents resulting from Cu input of manure and Cu output with crop offtake. One scenario serves as a 'base scenario' (a) because both Cu input and output by crop offtake are defined set equal to zero. The moderate Cu input (200 g/ha) scenario (b) is based on application of cow manure. The high Cu input (800 g/ha) scenario (c) resembles the use of pig manure for continuous maize culture. Input rates for scenarios b and c are taken from Anonymous (1997). Agricultural scenarios (a-c) are assumed to have a constant pH (6) and SOC content (3%) resulting from management practices like liming, growing catch crops and manure applications.

After forestation, a situation where the litter is homogeneously mixed through the former plough layer by biological action and a situation where a separate litter layer is formed on top of the soil are distinguished. If mixing occurs, the SOC content of the topsoil increases linearly from 3-10% in 50 years. If a separate litter layer is formed, the SOC content remains constant (3%) whereas the newly formed litter layer is a source of fresh DOC input to the topsoil. Copper and SOC are assumed to remain uniformly distributed throughout the topsoil and the amount of DOC formed is equal in the mixed and non-mixed case. In the case of mixing litter through the topsoil, increasing SOC results in decreasing soil bulk density of the topsoil from about 1450 to 1100 (kg/m^3) in 50 years (according to Eq. 7.7).

As a result of land use change, SOC, DOC and pH change as well. To

quantify the effects of these changes separately, first calculations were carried out with increasing SOC (from 3 to 10%) at constant pH (*i.e.*, 6) in scenario (d) and with decreasing pH (from 6 to 4 in 50 years) at constant SOC content (*i.e.*, 3%) in scenrio (e).

Finally, in scenario (f), agricultural practice with 100 years of high Cu inputs is followed by land use change with both decreasing pH and increasing SOC content during 50 years. Scenario (f) shows the changes in Cu speciation and accumulation for both the situation with and without litter being mixed through the topsoil.

Results

Agriculture

Figure 7.1 shows the development of Cu-soil content (mmol/kg) in agricultural scenarios (a-c). In the scenarios with Cu input (b and c), the increasing Cu-soil contents show that the Cu input rates are higher than the respective sums of the leaching and crop offtake rates. In the case of moderate (200 g Cu/ha) and high (800 g Cu/ha) input, the Cu-soil content increases from 0.25 to 0.28 and 0.49 mmol/kg after 100 years, respectively. Leaching losses in base scenario (a) are small as is shown by the very slow Cu depletion rate from 0.24 to 0.22 mmol/kg in this soil. Losses by leaching and crop offtake both increase from about 30 (g/ha) to 40 and 70 (g/ha) in 100 years in the moderate and high input cases, respectively.

The speciation of Cu in soil is calculated according to Eqs. 7.2 and 7.3. In the agricultural scenarios, the pH and SOC content remain the same and thus the amount of Cu adsorbed by SOC (CuSOC) increases with increasing Cu content in the soil and also the CuDOC concentrations follow the same pattern as the CuSOC contents. In the agricultural scenarios, the CuDOC concentrations are almost equal

to the total amount of Cu in soil solution (Cu_{sol}) since > 99% of all Cu in solution is present as CuDOC.
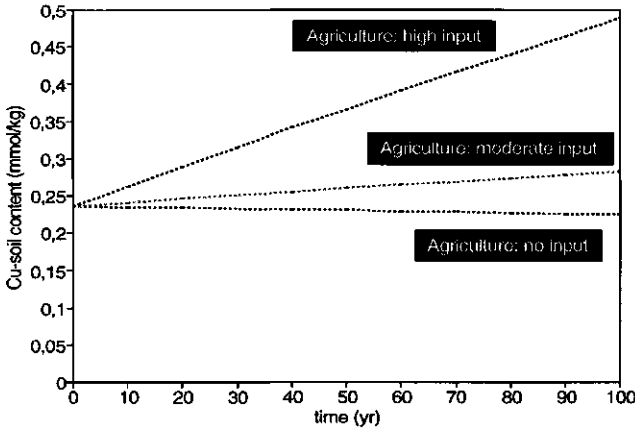
Figure 7.1. The development of the Cu-soil content in agricultural scenarios with high (800 g/ha), moderate (200 g/ha) and zero Cu input.

pH, SOC, and DOC changes

In the case of land use change, pH, SOC and DOC are subject to change. The SOC content of the topsoil increases linearly from 3-10% in 50 years. The developments of pH and DOC are shown in Figs. 7.2 and 7.3, respectively. The DOC concentrations are calculated by substituting pH and SOC contents in Eq. 7.8. In the agricultural scenarios, SOC content and pH (Fig. 7.2) remain constant and so the DOC concentration remains constant as well (10 mg/l: Fig. 7.3). Due to the relatively fast pH decrease in the first 5 years after land use change (Fig. 7.2), the DOC concentration decreases at first and increases only after several years (due to increasing SOC content) up to 20 mg/l (scenario f). The case where the pH remains constant with increasing SOC content (scenario d) results in the highest DOC concentrations (30 mg/l). If, at decreasing pH, the SOC content is kept constant

(scenario e), the DOC concentration decreases to 7 mg/l after 50 years (Fig. 7.3).
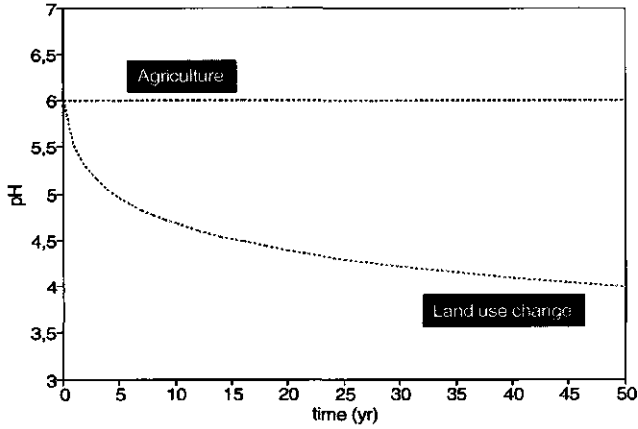
Figure 7.2.   The development of pH during 50 years in the case of agriculture and land use change.
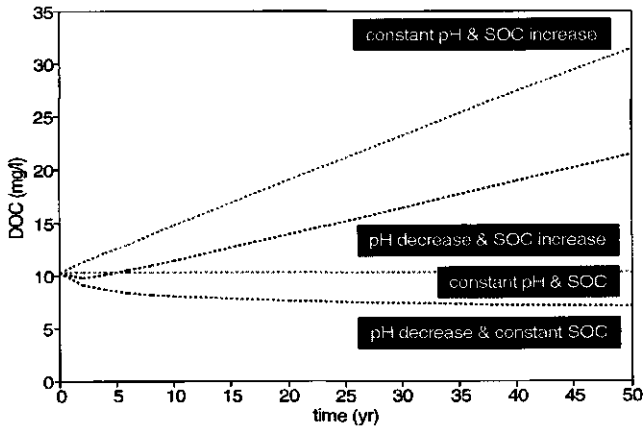
Figure 7.3.   The development of the DOC concentration during 50 years in the case of constant and decreasing pH and constant and increasing SOC content.

Land use change

scenario d

In the case of changing land use, litter falls on top of the former plough layer. First, agricultural base scenario (a) is compared with land use change scenario (d) in which the initial soil Cu content equals 0.24 mmol/kg (no Cu input history) and in which the pH is kept constant at 6. With these calculations the effect of increasing SOC are quantified. Figures 7.4a and 7.4b show the developments of the Cu-soil and CuSOC contents, respectively. In the mixed case, the SOC increases throughout the whole topsoil (0.3 m) and the Cu-soil content slightly differs from the situation where the litter remains on top of the soil (0.230 and 0.224 mmol/kg after 50 years, respectively) as is shown in Fig. 7.4a.
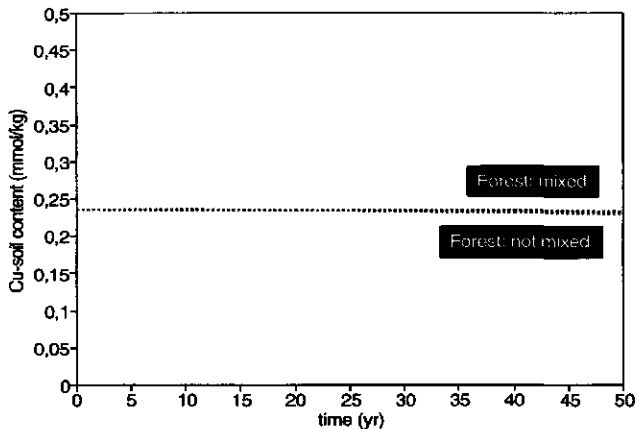
Figure 7.4a. The development of the Cu-soil content in the case of forestry (no Cu input history) with litter mixed and not mixed throughout the topsoil.

In case of mixing, less Cu is available for leaching. The bulk of the amount of Cu present in soil remains adsorbed by SOC due to the constant pH value in this scenario. Therefore, the case of not mixing results in slightly lower Cu-soil contents.

However, the Cu-SOC content in the mixed case decreases strongly (Fig. 7.4b). More SOC is available for Cu adsorption after mixing and thus Cu-SOC (expressed as mmol/kg SOC) is 'diluted' which is not the case if litter is not mixed.
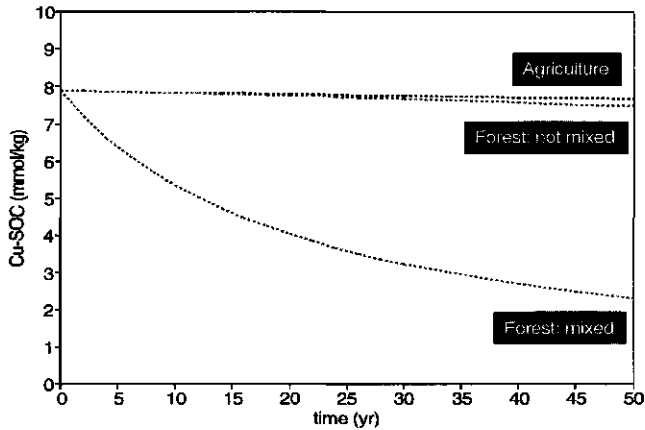
Figure 7.4b. The development of the Cu-SOC content in the case of agriculture and of forestry (no Cu input history) with litter mixed and not mixed throughout the topsoil.

Without mixing, scenario (d) results in slightly lower Cu-SOC contents than the agricultural base scenario (Fig. 7.4b). Although the SOC content is the same in both cases, higher DOC concentrations are present in scenario (d) due to the litter layer.

Figure 7.4c shows that as a result of mixing the Cu solute concentrations do not increase as fast as in the non-mixing scenario, because due to mixing more binding sites on SOC are available. Consequently, the leaching rate is more than 3 times higher if the topsoil were not mixed compared with the mixed case after 50 years. The agricultural base scenario has the lowest leaching rate (Fig. 7.4c) and consequently the highest Cu-soil content (0.230 mmol/kg) after 50 years.
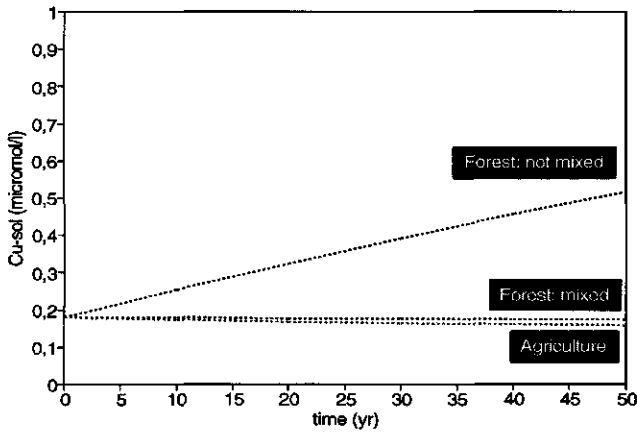
Figure 7.4c. The development of the total Cu solute concentration (Cu_{sol}) in
the case of agriculture and of forestry (no Cu input history) with
litter mixed and not mixed throughout the topsoil.

Because of relatively low DOC concentrations in the case of agriculture (Fig. 7.3),
the Cu solute concentrations in the agricultural scenario are the lowest. In all three
scenarios (a, d mixed, d not-mixed), 99% of the total Cu in solution is present in
the form of Cu-DOC.

scenario e
The Cu adsorption by SOC and consequently the Cu-soil content decrease slightly
over time due to the effect of decreasing pH (6 to 4) and constant SOC content
(3%) in scenario (e). After 50 years, the Cu-soil content of scenario (e) still equals
about 0.23 mmol/kg.
Due to decreasing pH, Cu solute concentrations (Cu_{sol}) increase almost two times
compared with the case of constant pH after 50 years (Fig. 7.5). This is caused by
Cu redistribution from the solid phase (Cu-SOC) to the solute phase (CuDOC and
Cu^{2+}). In the scenario with decreasing pH, the percentage of complexed Cu-DOC in

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the dissolved phase decreases from 99% to 87% in 50 years. The percentage of Cu^{2+} ions thus increases in the case of decreasing pH. The competition between H^+ and Cu^{2+} adsorption onto SOC and DOC determines the resulting Cu^{2+} concentration according to Eq. 7.2.
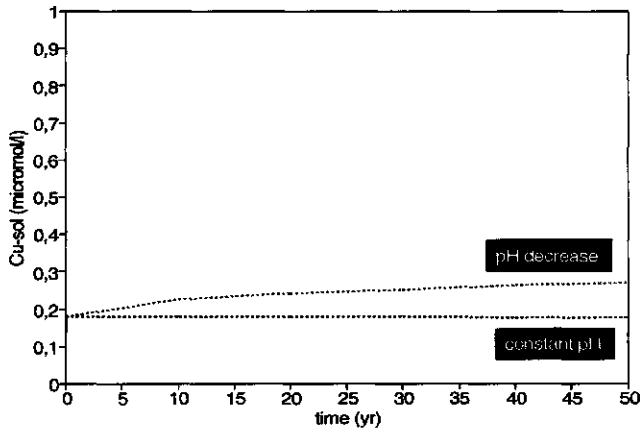
Figure 7.5. The effect of pH decrease on the development of the total Cu solute concentration (Cu_{sol}) in the case of forestry (no Cu input history) with constant SOC content.

scenario f

Figure 7.6a shows the development of Cu-soil contents for the case in which first high-input agriculture is practised for 100 years and there after land use change occurs for another 50 years. The land use change scenario with a high-input history is studied for the situation that both the pH decreases from 6 to 4 and the SOC content increases from 3 to 10% in the case of mixing litter throughout the topsoil. If the litter remains on top of the soil, SOC content remains constant at 3%, but DOC increases up to 20 (mg/l) as in the mixed case.
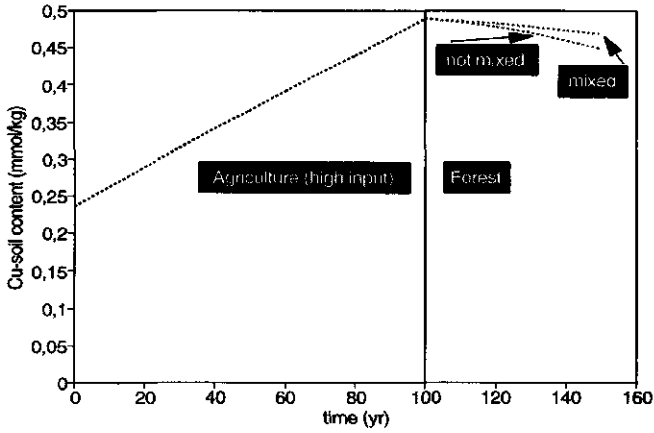
Figure 7.6a. The development of the Cu-soil content in the case of agriculture (high Cu input) followed by forestry with the litter mixed and not mixed throughout the topsoil.
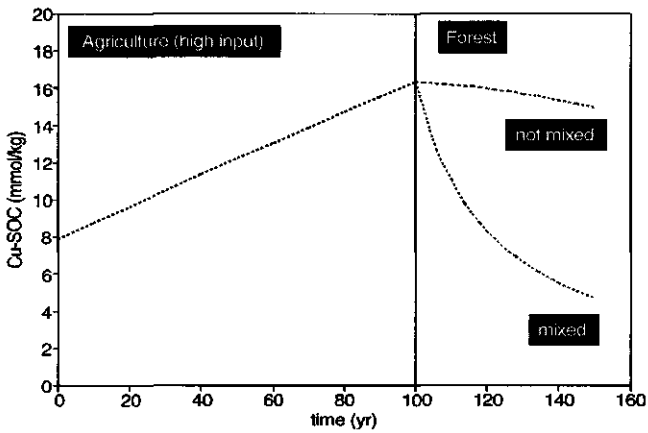
Figure 7.6b. The development of the Cu-SOC content in the case of agriculture (high Cu input) followed by forestry with litter mixed and not mixed throughout the topsoil.

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During high-input agriculture, the Cu content increases from 0.24 to 0.49 mmol/kg. If land use change starts, the manure inputs discontinue and the Cu-soil content decreases due to increasing leaching losses both in the case of mixing and non-mixing. However, Cu-soil decreases at a lower rate in the case of mixing (Fig. 7.6a).

With regard to Cu-SOC, the amount of Cu adsorbed onto SOC slowly decreases in the case of non mixing (Fig. 6b), because the Cu-soil content decreases at constant SOC content. The Cu-SOC content decreases much faster if mixing occurs because of 'dilution' of Cu-SOC.

In Figure 7.7, the mobile Cu concentrations are shown during 100 years of high-input agriculture and during 50 years if arable land were changed to forestry (with both pH decrease and SOC increase) in the case of mixing and not mixing.

Figure 7.7. The development of the total Cu solute concentration (Cu_{sol}) in the case of agriculture (high Cu input) followed by forestry with litter mixed and not mixed throughout the topsoil.
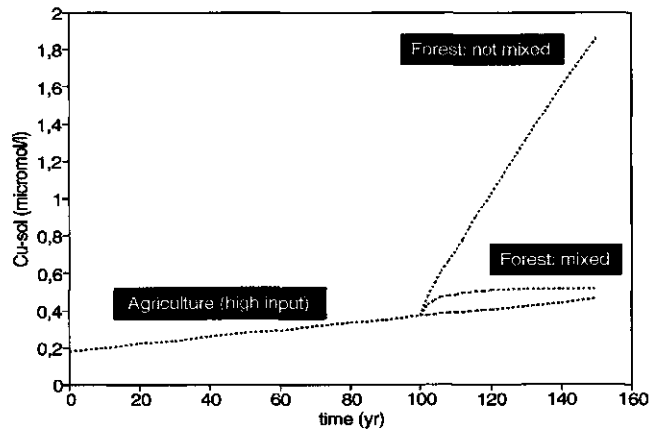
In the case of agricultural land use, CuDOC comprises 99% of total Cu in solution. After land use change, the contribution of Cu-DOC to the total amount of Cu in

solution (Cu_{sol}) is 86% in the non-mixing scenario and 98 in the mixing scenario after 50 years.

At decreasing pH and increasing SOC content, the DOC concentration increases. Consequently, CuDOC concentrations increase. The combination with the more pronounced Cu redistribution from the solid phase to the solute phase in the case of not mixing results in higher Cu_{sol} concentrations. Due to land use change, the Cu mobility clearly increases and the value of Cu_{sol} after 50 years would be almost 1.1 (mixing) and 4 (non-mixing) times higher than if high-input agriculture were to be continued (Fig. 7.7). The pCu^{2+} (*i.e.*, $-\log[Cu^{2+}]$; (mol/l)) decreases from 9.72 at year 100 to 9.46, 7.99, and 6.59 at year 150 in the agricultural, the mixed, and the non-mixed case, respectively. These values are of the same order of magnitude as those found by Temminghoff *et al.* (1997b) at pH values 4 and 6. The large increase of the Cu^{2+} activity in the land use change scenarios as compared with continued agriculture (factor 30 and 750 for the mixed and non-mixed case, respectively) due to decreasing pH is apparent.

In the case of mixing, the Cu_{sol} concentrations start to decrease slowly after year 140 (Fig. 7.7). If the calculations would be continued, the Cu_{sol} concentrations of the agricultural scenario and of the mixed case would be the same at year 175. Continued agriculture results in increasing soil Cu contents ($Cu_{sol} = 0.6$ µmol/l at year 250) and hence in higher leaching rates than those occurring in the mixed case. The Cu_{sol} concentrations in case of non-mixing reach a maximum after about 230 year (at $Cu_{sol} = 2.8$ µmol/l) and the Cu_{sol}-concentrations decrease slowly afterwards.

At year 150, the Cu-soil content equals 0.61, 0.47, and 0.45 mmol/kg in the agricultural, the mixed, and the non-mixed case, respectively. Clearly, the Cu-soil content is lowest and the Cu leaching rate is highest in the case of land use change with a litter layer that remains separate from the rest of the topsoil.

Discussion & Conclusions

By incorporating the Two Species Freundlich equation into a dynamic Cu balance of soil, it was possible to show the main effects of changing pH and soil organic matter (SOC and DOC) contents with respect to Cu speciation and the consequences for Cu mobility, bioavailability, and accumulation in a sandy soil after changing land use from arable farming to forestry.

In the case of continuing agriculture, groundwater quality will not be threatened at first. However, in that case the total soil Cu content may increase rapidly and the land use change scenarios showed that such accumulation may appear harmless at first, but may adversely affect soil biology (through increased uptake by soil flora and fauna) and groundwater quality (through increased leaching) later due to higher Cu availability and mobility.

After land use change, the size and type of the heavy-metal flows change. Fertilization will stop but deposition may continue at higher rates due to different characteristics of the forest canopy compared with the arable crops. The input of Cu by deposition may thus not be negligible compared to the amount of Cu that is already present in the topsoil, as is assumed in this paper. Because the litter layer will be newly formed, we neglected CuDOC leaching from this layer in our calculations. Depending on the role of atmospheric Cu deposition (and subsequent foliar uptake and sorption onto leaves), the Cu input to the topsoil, its impact on distribution in the humus layer and the mineral soil profile, and subsequent leaching may be underestimated.

The organic matter dynamics show two extremes of how the soil organic matter content and the dissolved organic carbon concentrations might develop in the course of time in order to clarify the relative importance of mixing litter through the topsoil. The rate at which adverse effects may occur depends to a large extent on whether the litter is mixed through the topsoil by biological action or not.

In the end, continuing high-input agriculture may result in more adverse effects (due to Cu accumulation and leaching) than changing to forestry where litter is mixed through the topsoil.

The non-mixing situation was shown to result in the highest Cu concentrations in the soil solution. The calculations showed that the Cu_{sol} after 50 years would be 4 times higher while the Cu^{2+} concentration would be 750 times higher than if high-input agriculture would be continued. These results show that speciation changes drastically and because the ionic form is also the most bioavailable one, these inter-species effects are very important.

Acknowledgement

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Chapter 8

Copper Speciation in Sandy Soil in Relation to
Copper Uptake and Copper Toxicity by Ryegrass
(*Lolium multiflorum L.*)

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Abstract

The effects of soil solid, dissolved organic matter and of pH on copper availability for ryegrass (*Lolium multiflorum L.*) in a copper contaminated sandy soil has been studied. The soil, with pH 4.5 and 5.7, had been polluted with copper in the range from 0 to 1.7 mmol/kg. For the desorption of extractable copper an unbuffered electrolyte solution ($CaCl_2$) at two different concentrations (0.01 and 0.001 M) was used. For the 'total' adsorbed copper we used 0. 43 M HNO_3. 'Free' copper was calculated well in the unbuffered electrolyte solutions with the NICA model. The Cu desorption isotherms were non-linear and dependent on pH, and Ca concentration. Copper uptake by ryegrass increases at increasing total Cu content in the soil but is dependent on soil pH. Yield reduction was observed at different extractable Cu concentrations for both $CaCl_2$ extracts. In the case of 'free' copper, yield reduction was observed above a single critical Cu^{2+} concentration. The Cu uptake by ryegrass is neither linear with regard to Cu^{2+} concentration nor with yield in case of copper toxicity.

Introduction

Copper can be either a micro nutrient or a toxic element which depends on the copper concentration. Whether, positive or negative effects occur depends on the speciation of Cu in the soil and in the plant. Speciation of metals in soil can be defined as the distribution of the total metal content over the possible chemical forms (species) in the solid, the liquid or the biotic phases (e.g. plants) of soil. The chemical behaviour of heavy metals in soils depends on the sorption capacity of the soil which is determined by the (reactive) solid surfaces of e.g. clay minerals, metal(hydr)oxides and organic matter. The availability of heavy metals for plants is affected by many environmental conditions such as soil type, pH, ionic strength, complexation by (in)organic ligands and competition with other cations. Extraction with unbuffered salt electrolytes such as $CaCl_2$ and $NaNO_3$ has been recommended as a measure of availability of heavy metals for plants in view of the good correlation between extracted metal and plant/crop tissue concentration (Hani & Gupta, 1982; Sanders *et al.*, 1987; Novozamsky *et al.*, 1993; Aten & Gupta, 1996). By studying the speciation in the soil suspension extraction, differences between quantities extracted by different chemicals or from different soil samples may be understood which can give more insight in the behaviour of heavy metals in soil. The 'free' metal ions are probably the most bioavailable heavy metals species for e.g. plants and micro organisms whereas the heavy metal complexes are usually important for mobility (Sposito, 1986; Buffle, 1988; McCarthy & Zachara, 1989). Changes in 'free' metal concentrations (Cd and Zn) as a function of time gave the best correlations with changes in plant uptake (accumulated) of these metals which suggest that plants mainly absorb 'free' metal ions from soil solution (Hamon *et al.*, 1995). Lorenz *et al.* (1997) however suggest that the Cd^{2+} and Zn^{2+} in the rhizospere differ from the Cd^{2+} and Zn^{2+} outside the rhizosphere. Therefore they conclude that the prediction of the Cd concentration in the plant was not improved

by taking Cd^{2+} and Zn^{2+} instead of the total Cd and Zn in the soil solution. Cabrera *et al.* (1988) have shown by water culture experiments that the Cd uptake was reduced in presence of humic acid due to the formation of Cd-humic acid complexes which were not taken up by the plant. Complexation of cadmium with humic acid is relatively small with respect to copper. In the case of copper more than 99 % of the copper in the soil solution can be complexed with dissolved organic matter (Sanders, 1982) although this depends among others on pH and Ca concentration (Temminghoff *et al.*, 1997). Recently McLaughin *et al.* (1997) suggested that charge ans size of the complexes are as important as the speciation in solution and that the uptake can be even more efficient in the presence of small organically complexed species, particularly if these have a neutral or positive charge. Small heavy metal complexes can be taken up by plant roots or enhance 'free' metal uptake through enhance diffusion through root membranes.

Additionally, plant related factors affect copper uptake, such as: (*i*) the extent to which Cu has been adsorbed by roots from the labile reserves of the soil; (*ii*) the mobility of Cu within the plant; (*iii*) the environmental conditions (e.g. nutrients); (*iv*) the growth rate of the plant; (*v*) the stage of plant growth can affect Cu uptake (Jarvis, 1981); (*vi*) the water uptake by the plant for transpiration (Hamon *et al.*, 1995); (*vii*) mechanisms to avoid heavy metal uptake (excluders) or heavy metals detoxification in the plant (Woolhouse & Walker, 1981). All these factors complicate the understanding of heavy metal uptake and make it difficult to give straightforward answers about fytotoxicity.

The aim of this research is to study how pH, calcium competition and dissolved organic matter (DOC) affect (*i*) the speciation of copper in acid sandy soil (solution) in 'free' copper and copper bound by DOC concentrations and (*ii*) the Cu uptake and Cu toxicity by ryegrass (*Lolium multiflorum L.*). For soil we deal with competition between soil, dissolved organic matter and plant roots for 'free' copper. We show the applicability of a Non Ideal Competitive Adsorption (NICA) model

for modelling the copper speciation in a sandy soil. Next we test which Cu species is most relevant with respect to Cu uptake and Cu toxicity for ryegrass.

Theoretical background

Both empirical and semi mechanistic models have been developed to describe heavy metal binding by soil and dissolved organic matter. Recently, a semi mechanistic Non-Ideal Competitive Adsorption model (NICA) has been proposed which accounts for adsorption by heterogeneous surfaces such as dissolved organic matter (Koopal *et al.*, 1994; Benedetti *et al.*, 1995, Kinniburgh *et al.*, 1996) and soil organic matter (Gooddy *et al.*, 1995; Temminghoff et al., 1997). This model is given by the following isotherm equation

$$Q_i = Q_{max,1} \frac{(\bar{K}_{i,1}c_i)^{n_{i,1}}}{\sum_j (\bar{K}_{j,1}c_j)^{n_{j,1}}} \cdot \frac{\left[\sum_j (\bar{K}_{j,1}c_j)^{n_{j,1}}\right]^{p_1}}{1 + \left[\sum_j (\bar{K}_{j,1}c_j)^{n_{j,1}}\right]^{p_1}} + Q_{max,2} \frac{(\bar{K}_{i,2}c_i)^{n_{i,2}}}{\sum_j (\bar{K}_{j,2}c_j)^{n_{j,2}}} \cdot \frac{\left[\sum_j (\bar{K}_{j,2}c_j)^{n_{j,2}}\right]^{p_2}}{1 + \left[\sum_j (\bar{K}_{j,2}c_j)^{n_{j,2}}\right]^{p_2}} \quad (8.1)$$

where Q_i is the adsorbed quantity of component i by organic matter and Q_{max} the maximum adsorption capacity of the organic matter (mol/kg organic matter). Organic matter has many different types of reactive functional groups each of which may bind metal ions according to a specific stoichiometry. This leads to a distribution of *K*-values. Therefore, $\tilde{K}_j$ is the median of the affinity constants (K_j) of all components j, including component i. The parameters n and p are related with the width of the affinity constants distribution where the parameter n reflects the non-ideal behaviour of component j and p reflects the intrinsic heterogeneity property of the organic matter. By c_j we denote the concentration of the 'free' uncomplexed component j in solution (mol/L). Subscript 1 is considered to be related to the 'carboxylic' type groups and subscript 2 to the 'phenolic' type groups.

With the NICA model and the parameters, which are determined for the model substance humic acid, the 'free' Cu activity can be calculated from the organic matter content, pH and total copper content (Temminghoff *et al.*, 1997).

At constant plant stress factors (e.g. water content, light intensity, nutrient availability), the plant yield is assumed to be only dependent on the water evapotranspiration and is given by

$$Y = \gamma \int E_p dt \qquad (8.2)$$

where Y is the plant yield, E_p the water transpiration rate and γ a constant. If yield reduction occurs due to copper toxicity only, Eq 8.2 can written as

$$Y = \gamma \ f \ (Cu) \int E_p dt \qquad (8.3)$$

where $f(Cu)$ is a correction factor $(0 \leq f(Cu) \leq 1)$ that represents yield reduction due to copper toxicity. At low Cu concentrations the yield is not affected by copper and $f(Cu)=1$. The Cu uptake by plants can be either an active (plant regulated) or an passive (solution concentration regulated) process. In case copper uptake is an active process, the plant regulates uptake such that it meets its demands but avoids toxic effects. If copper uptake is passive, the supply of bio-available copper fractions in water taken up to meet the transpirative demands controls copper uptake. In the latter case, the copper uptake rate (U) depends linearly on the concentration of bio-available copper species and water uptake rate, provided copper toxicity does not occur. As the bio-available species are yet unknown, we hypothesize therefore

$$U = \beta \ E_p \ (Cu)_a \qquad (8.4)$$

where $(Cu)_a$ is the bio-available copper species concentration. When buffering

processes occur, $(Cu)_a$ is relatively time-independent and may be taken out of the integral of cumulative uptake (A)

$$A = \int U dt = \beta \ (Cu)_a \int E_p dt \tag{8.5a}$$

For the bio-available species, we test several alternatives based on our understanding of copper speciation in the soil solution and assume that the $CaCl_2$ extractions correspond closely enough with the soil solution. The species that may represent $(Cu)_a$ are 'free' copper (Cu^{2+}), total copper (Cu_T), extractable copper (Cu_{ex}), and copper complexed with dissolved organic matter (CuDOC). For each of these species we require both that yield reduces at one particular (critical) concentration and that a linear dependency with U as proposed by Eq(8.4) holds. If these requirements are not met, the particular species is assumed not to be singly responsible for copper uptake or that copper uptake is not passive. In view of the non-linear dependencies between on one hand Cu_T, CuDOC, and Cu_{ex} and on the other hand Cu^{2+} it is clear that if the earlier ones control uptake we obtain

$$A = \alpha \ (Cu^{2+})^{n_p} \int E_p dt \tag{8.5b}$$

Only if $Cu_a = Cu^{2+}$, we obtain $n_p = 1$. A special case is obtained if copper adsorbs onto the root surface as first step of uptake, similar as the case considered by Plette *et al.* (1996) for micro-organisms. Only if the root surface behaves similar as soil organic matter (i.e., same pH, Ca, and ionic strength dependencies), we are able to test Eq(8.5b) using our Cu-speciation model.

To normalize our data, we consider copper tissue concentration in the plant (C_p) by dividing Eq. (8.5b) by the plant yield (Y); or

$$C_p = \frac{A}{Y} = K_p \ (Cu^{2+})^{n_p} \tag{8.6a}$$

or in general

$$C_p = K_p^a \, (Cu)_a \tag{8.6b}$$

where $K_p = \alpha/\gamma$.

Materials and methods

Pot experiment

The sandy soil that has been adjusted to two different pH levels since about 1950 was part of an experimental field in Wageningen. From two plots (A and B) soil was sampled in 1980 from the layer 0 - 0.20 m. Both soil samples were air-dried and sieved (< 2 mm). Typical soil properties given in Table 8.1 are pH in 0.01 M $CaCl_2$, grain size distribution, organic matter by loss of ignition at 550 °C, cation exchange capacity (CEC) and base saturation (according to the unbuffered 0.01 M $BaCl_2$ method), and total initial extractable Cd (0.43 M HNO_3). The analytical methods are described in Houba *et al.*, (1995).

The pot experiment study in 1996 was conducted in the greenhouse using 2 L plastic pots. A copper range was established by adding, reagent grade $Cu(NO_3)_2$, at rates equivalent to 0. 12.5, 25, 50 and 100 mg/kg Cu per pot. To ascertain the same ionic strength and nitrate concentrations in all the treatments, $Ca(NO_3)_2$ was added in equivalent quantities. Besides Cu and Ca, 2 mmol/kg potassium phosphate was added as a phosphate fertilizer. Each Cu treatment was carried out in duplicate. The soil moisture was finally adjusted to 60 % of the maximum water holding capacity (126 ml/kg dry soil). After covering the top with a thin layer of quartz sand 2 g of ryegrass seeds (*Lolium multiflorum L.*) was distributed on the surface. The pots were transferred to the greenhouse with a temperature of 20 °C, relative

humidity of 60 %, and illumination at an intensity of 400 W/m^2 by HPL grow lamps for 16 h/d. The moisture content was registered daily by weighing each pot and maintained constant throughout the experiment. After six weeks, the grass was harvested and weighed immediately (wet). The grass was dried in an oven at 70 °C for 24 h, weighed (dry) and ground in a stainless steel grinder. The Cu concentration in the grass was determined with ICP (Spectro Flame) after digestion with HNO$_3$, H$_2$O$_2$ and HF (Novozamsky *et al.*, 1993).

Table 8.1. Soil characteristics of the sandy soils.
pH CaCl$_2$ (0.01 M), Texture (%), organic matter (%), Cation Exchange Capacity (mmol +/kg), Base saturation (mmol +/kg) and initial total Cu (0.43 MHNO$_3$; mmol/kg).

	Soil A	Soil B		Soil A	Soil B
pH CaCl$_2$	4.5	5.7	CEC (mmol +/kg)	18	42
Particle size (%)			*base saturation* (mmol +/kg)		
> 50 μm	83	81	Na	0.0	0.5
< 50 μm	16	18	K	1.8	3.1
< 16 μm	8	9	Ca	8.8	33.8
< 2 μm	5	5	Mg	1.5	2.8
Organic matter (%)	2.5	2.3	Total Cu (mmol/kg)	0.14	0.14

Soil experiments

Soil samples were taken from each pot with a small auger. The samples were air dried, sieved through a 2 mm sieve and stored in plastic bags before analysis. Extractions were done with HNO$_3$ as well as CaCl$_2$. The unbuffered CaCl$_2$ extractant was done at two concentrations (0.001 and 0.01 M) which give an

indication of the easily extractable Cu-species (Cu_{ex}). The extraction with 0.43 M HNO_3 gives an indication of total amount of Cu adsorbed (Cu_T) by the soil. For alle three extractions a soil:solution ratio 1:10 w/V) was used. The soil suspensions were shaken end-over-end for 20 h at 25 °C after which the pH was measured in the suspensions for the $CaCl_2$ extraction. After centrifugation at 3,000 g, the easily extractable Cu-concentration (Cu_{ex}) and the total extractable Cu-concentration (Cu_T) in the supernatant were measured by flame AAS (Instrumentation Laboratory AA/AE spectrophotometer S11 with scale expansion). The detection limit was approximately 0.3 µmol/l. Samples below this detection limit were analyzed by graphite furnace AAS (Varian SpectrAA 300-Zeeman) with a detection limit of 0.03 µmol/l. The dissolved organic carbon (DOC) in the $CaCl_2$ extracts was measured with the fully automated SK^{12} (Skalar) TOC/DOC analyzer.

Results and discussion

The fresh yield of the ryegrass plants varied between 61 g/pot (high pH and low Cu content of the soil) and 3 g/pot (low pH and high Cu) whereas the dry matter weight varied between 9.5 and 0.3 g/pot (Table 8.2). In all cases the dry:wet plant material ratio was constant (0.17 ± 0.05) although at very low yields (< 3 g/pot wet weight) the ratio varied between 0.11 and 0.40, even within dulplicates. The Cu uptake varied between 0.15 mmol/kg (high pH and low Cu content in soil) and 2.3 mmol/kg (low pH and high Cu content in soil) (Table 8.2).

Table 8.2. Yield (Y) and plant tissue copper concentration Ryegrass.

soil code	Yield (dry) g/pot	Cu plant mmol/kg
1A	8.88 ± 0.05	0.182 ± 0.008
2A	9.25 ± 0.23	0.292 ± 0.008
3A	7.61 ± 0.28	0.424 ± 0.030
4A	3.48 ± 0.66	0.654 ± 0.007
5A	0.71 ± 0.53	2.287 ± 0.026
1B	10.6 ± 0.5	0.155 ± 0.002
2B	9.96 ± 0.27	0.217 ± 0.006
3B	10.7 ± 0.4	0.263 ± 0.009
4B	9.79 ± 1.01	0.315 ± 0.008
5B	9.23 ± 0.74	0.446 ± 0.011

In Table 8.3 results of the different soil extractions are given. The total extractable Cu concentration (Cu_T) varied between 11 and 170 µmol/l (0.11 and 1.70 mmol/kg soil) and were similar for the two soil pH levels. The Cu concentrations in the unbuffered salt extracts depends on Ca concentration, soil pH and total Cu content. Cu_{ex} varied from 0.2 µmol/l (high pH low Cu content) till 12 µmol/l (low pH and high Cu) in 0.001 M $CaCl_2$ and varied from 0.1 till 21 µmol/l in 0.01 M $CaCl_2$. The pH differs slightly between the two $CaCl_2$ extracts; between 4.7 and 6.0 for 0.001 M $CaCl_2$ and 4.5 and 5.7 for 0.01 M $CaCl_2$. The DOC concentration in $CaCl_2$ extracts was constant for each Ca concentration (10.9 ± 2.7 mg/l at 0.001 M $CaCl_2$ and 5.8 ± 1.7 at 0.01 M $CaCl_2$). In the $CaCl_2$ extracts also the Ca concentration was determined to be 1.91 ± 0.07 mmol/l for the 0.001 M

CaCl$_2$ and 9.84 ± 0.19 mmol/L for the 0.01 M CaCl extracts. This indicates, that Ca desorbed from the soil at 0.001 M Ca whereas no change is obeserved for the 0.01 M Ca extracts.

Table 8.3. Total copper content and copper CaCl$_2$ extractable results of soil A and B (mean ± std).

soil code	Cu$_T$ mmol/kg	0.01 M CaCl$_2$			0.001 M CaCl$_2$	
		pH	Cu$_{ex}$ mol/L		pH	Cu$_{ex}$ mol/L
1A	0.139 ± 0.006	4.56	0.18 ± 0.02		4.84	0.16 ± 0.00
2A	0.305 ± 0.009	4.55	1.17 ± 0.10		4.79	0.81 ± 0.00
3A	0.511 ± 0.001	4.51	2.67 ± 0.13		4.76	1.78 ± 0.08
4A	0.903 ± 0.010	4.46	6.70 ± 1.31		4.70	4.22 ± 0.05
5A	1.670 ± 0.066	4.41	29.1 ± 1.5		4.62	12.1 ± 0.1
1B	0.140 ± 0.013	5.73	0.25 ± 0.03		6.07	0.16 ± 0.02
2B	0.318 ± 0.017	5.75	0.49 ± 0.06		6.07	0.56 ± 0.05
3B	0.529 ± 0.030	5.74	0.80 ± 0.07		6.06	1.27 ± 0.48
4B	0.847 ± 0.046	5.71	1.16 ± 0.03		6.03	2.01 ± 0.64
5B	1.598 ± 0.002	5.62	2.51 ± 0.34		5.92	4.49 ± 0.22

At low pH, more copper was extracted with 0.01 M CaCl$_2$ whereas at high pH more copper was extracted with 0.001 M CaCl$_2$. At first sight this results seems strange. More extractable copper would be expected in 0.01 M CaCl$_2$ due to the higher Ca concentration. Using the measured pH, extractable Cu, Ca and DOC concentrations, 'free' copper (Cu^{2+}) concentrations in the extracts were calculated

with the NICA model. We assumed that the dissolved soil organic matter (expressed as DOC) behaves as humic acid. This procedure has been used before by Temminghoff *et al.* (1997). The used NICA parameters are given in Table 8.4.

Table 8.4. Parameters and standard deviations for the NICA model to describe the calcium, copper and proton binding by purified humic acid and soil organic matter at I= 0.003.

	site 1	site 2
purified humic acid & soil organic matter		
$\log \tilde{K}_H$	5.12 ± 0.01	9.78 ± 0.00
$\log \tilde{K}_{Cu}$	5.40 ± 0.02	10.82 ± 0.05
$\log \tilde{K}_{Ca}$	3.57 ± 0.00	5.05 ± 0.11
n_H	0.81 ± 0.01	0.83 ± 0.01
n_{Cu}	0.46 ± 0.00	0.46 ± 0.01
n_{Ca}	0.95 ± 0.01	0.67 ± 0.05
purified humic acid		
p	0.57 ± 0.01	0.58 ± 0.01
Q_{max} (mol/kg)	2.18 ± 0.00	1.54 ± 0.01
soil organic matter		
p	0.57 ± 0.07	0.58 ± 0.10
Q_{max} (mol/kg)	0.56 ± 0.07	0.55 ± 0.08

purified humic acid

H; coefficient of determination (r^2) = 0.99998

Cu and H; coefficient of determination (r^2) = 0.98

Ca and H; coefficient of determination (r^2) = 0.98

soil organic matter

Cu, Ca and H; coefficient of determination (r^2) = 0.86

The differences in ionic strength are rather small and therefore no corrections are made. The 'free' Cu (Cu^{2+}) concentration varied between 0.02 and 10.8 µmol/L. In Figure 8.1 the copper sorbed by the soil ($Q_{Cu-soil}$) is given as a function of the calculated 'free' copper concentration on a logarithmic scale for both extracts. The 'free' copper concentration is larger for the 0.01 M $CaCl_2$ extraction than for the 0.001 M $CaCl_2$ extraction at both pH levels which is in agreement with our expectations. At high pH and low Cu content about 99 % of the Cu in 0.001 M $CaCl_2$ and 94 % in 0.01 M $CaCl_2$ is complexed with DOC whereas at low pH and high Cu content only 31 % is complexed with DOC in 0.001 M $CaCl_2$ and 5 % in 0.01 M $CaCl_2$. The different fractions in Cu bound by DOC can be explained by the differences in Ca and proton competition, and by differences in DOC concentration.
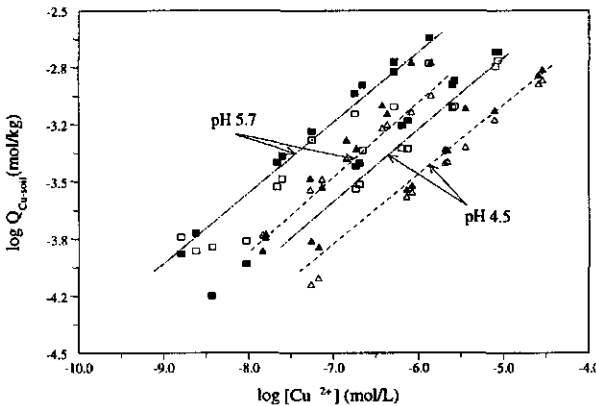
Figure 8.1. Copper (de)sorption ($Q_{Cu-soil}$; mmol/kg) as a function of the 'free' Cu concentration ([Cu^{2+}]; mol/L) on logarithmic scales at the pH of the soil (solution) for 0.001 M and 0.01 M $CaCl_2$. □ data and ■ model 0.01 M $CaCl_2$; △ data and ▲ model 0.001 M $CaCl_2$.

The Cu^{2+} sorption by sandy soil, where solid soil organic matter is the most

reactive surface, can also be described by the Non Ideal Competitive Adsorption (NICA) model as described earlier by Temminghoff et $al.$ (1997) by taking H^+, Ca^{2+} and Cu^{2+} competition into account (Table 8.4). All parameters were kept constant except Q_{max}. The maximum adsorption capacity for (soil) solid organic matter had to be reduced to 26 % of the Q_{max} for site 1 and to 36 % for site 2 of the purified humic acid which is in agreement with earlier experiments (Temminghoff et $al.$, 1997). Since solid organic matter is less humified the number of reactive sites (sites density) is probably smaller for solid organic matter than for dissolved organic matter (Gooddy et $al.$, 1995). The intrinsic heterogeneity factor p of the organic matter needed no adjustments which shows that the intrinsic heterogeneity of the soil solid organic matter and the humic acid are of the same order of magnitude. The NICA model described the Cu binding by the soil solid organic matter well at different pH, Ca and Cu concentrations although slight discrepancies are observed beween model and data for 0.01 M $CaCl_2$ solution, possibly due to differences in ionic strength. The model calculations for solid and dissolved soil organic matter are used to compare the extractable Cu concentration (Cu_{ex}), the 'free' Cu concentration (Cu^{2+}), and Cu bound by dissolved organic matter (CuDOC) in relation to the Cu uptake and Cu toxicity for ryegrass.

Since Cu^{2+} is often assumed to be the most bio-available fraction (McCarthy & Zachara, 1989), we investigated whether the calculated Cu^{2+} concentration is a better predictor for both Cu uptake and Cu toxicity. In Fig. 8.2 (dry) yield (Y) and plant tissue copper concentration (C_p) are given as a function of the calculated Cu^{2+} concentration in both $CaCl_2$ extracts (all at logaritmic scale). Yield reduction due to Cu toxicity occurs for both $CaCl_2$ extracts if the Cu^{2+} concentration exceeds pCu^{2+} = 6.0. Only slight discrepancies for Cu uptake are found between the two extraction solutions at low Cu^{2+} concentrations. The Cu uptake is on logaritmic scales linear with the Cu^{2+} concentrations for 0.01 M and 0.001 M $CaCl_2$ in the Cu^{2+}-range where no yield reduction (toxicity effect) was observed whereas the Cu uptake is

not linear in the Cu^{2+}-range where yield reduction (toxicity effect) was observed.
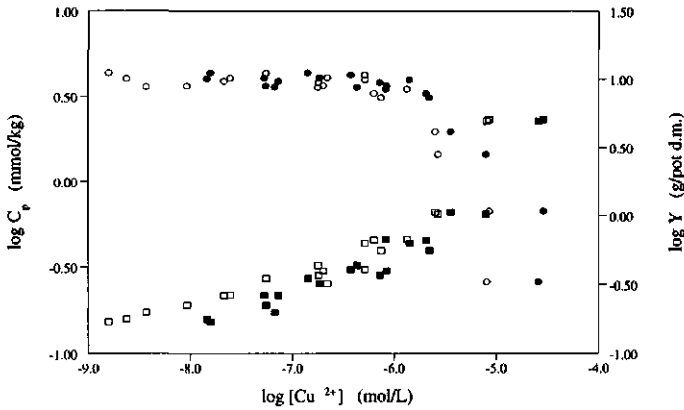
Figure 8.2.   Plant tissue copper concentration (C_p) and plant yield (Y) at two
pH levels as a function of extractable 'free' copper (Cu^{2+}) for
0.01 M and 0.001 M $CaCl_2$, all on logarithmic scales. Open
symbols 0.001 M, and closed symbols 0.01 M $CaCl_2$; □ and ■
plant tissue copper concentration ; ○ and ● plant yield.

Therefore the regression analysis in Table 8.5 are only carried out for the results
where no yield reduction was observed. The hypothesis that the plant tissue Cu
concentration is directly related to the Cu^{2+} concentration in the $CaCl_2$ extracts and
the evapotranspiration possibly has to be rejected since the slope of the relationship
between the Cu concentration in the plant (C_p) and the Cu^{2+} concentration in
solution is 0.21 (0.01 M $CaCl_2$) and 0.16 (0.001 M $CaCl_2$) and not 1.0 as would be
expected for passive Cu^{2+} uptake (cf. Table 8.5). These powers might suggest that
copper complexes with dissolved organic matter (CuDOC), or that uptake occurs
directly from the soil surface, or that adsorption to the plant roots is an intermediate
step to uptake.

Table 8.5. Summary of linear least squares lines to represent uptake of copper by yegrass without yield reduction as functions of extractable copper concentration.

Extraction	$\log K_p$	n_p	r^2
0.43 M HNO₃			
Cu_T	1.14 ± 0.08	0.39 ± 0.06	0.75
0.01 M CaCl₂			
Cu_{ex}	1.67 ± 0.05	0.37 ± 0.03	0.92
Cu^{2+}	0.83 ± 0.05	0.21 ± 0.02	0.89
CuDOC	1.29 ± 0.12	0.30 ± 0.08	0.49
0.001 M CaCl₂			
Cu_{ex}	1.19 ± 0.06	0.29 ± 0.03	0.84
Cu^{2+}	0.57 ± 0.05	0.16 ± 0.01	0.91
CuDOC	1.29 ± 0.08	0.30 ± 0.04	0.77

Therefore, we show C_p and Y as a function of CuDOC in Fig. 8.3. In view of the different CuDOC levels that indicate yield reductions and the power $n_p < 1$ (Table 8.5), CuDOC as such can not be identified as the bio-available species. For the same reasons, a combination of Cu^{2+} and CuDOC (through Cu_{ex}) and also uptake directly from the soil surface (Cu_T) have to be declined.

In the case of 0.01 M CaCl₂, the correlation between extractable Cu concentration (Cu_{ex}) and the plant tissue Cu concentration (C_p) was 0.92 which demonstrates the good suitability of 0.01 M CaCl₂ as a single measure of the bio-available heavy metal in the soil (Fig. 8.4 and Table 8.5). Similar results were found for 0.001 M CaCl₂ although the correlation was slightly less (0.84). Furthermore, the yield (Y) reduction is observed above a single Cu_{ex} concentration for 0.01 M CaCl₂ and different soil pH values whereas this is not the case for 0.001

M CaCl$_2$. A single critical Cu$_{ex}$ concentration would be expected if Cu$_{ex}$ (= Cu^{2+} + CuDOC) is a measure of the bio-available fraction.
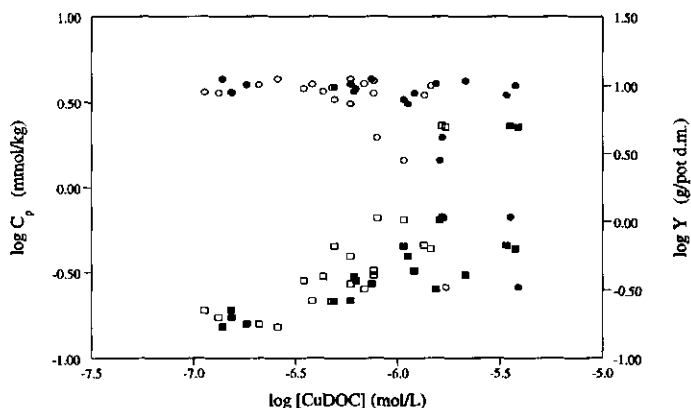
Figure 8.3. Plant tissue copper concentration (C_p) and plant yield (Y) at two pH levels as a function of extractable copper bound by DOC (CuDOC) for 0.01 M and 0.001 M CaCl$_2$, all on logarithmic scales. Open symbols 0.001 M, and closed symbols 0.01 M CaCl$_2$; □ and ■ plant tissue copper concentration; ○ and ● plant yield.

In all investigated cases (Cu^{2+}, CuDOC and Cu$_{ex}$) a slope smaller than 1.0 was found (Table 8.5). McLaughlin *et al.* (1997) found a slope of 1.0 for the regression between Cd uptake by lettuce and the 'free' Cd^{2+} concentration in solution in hydroponic experiments. In the presence of organic acids a slope of 0.39 between Cd concentration in the plant and calculated 'free' Cd^{2+} concentration in solution was found. It was concluded that possibly small Cd-complexes can be taken up. Possibly, in the case of such experiments with Cu also small CuDOC complexes may be taken up. However the behaviour of Cu is different from Cd whereas also the uptake of lettuce can be different from ryegrass. Also the Cu

speciation in the CaCl$_2$ extracts may differ from the rhizosphere due to excretion of (organic) acids by the roots. The excretion of organic acids by roots is known in the case of phosphate (Hoffland *et al.*, 1990) and iron (Römheld & Marschner, 1981) deficiency. To investigate the Cu speciation in the rhizosphere was not the primary objective of this work.
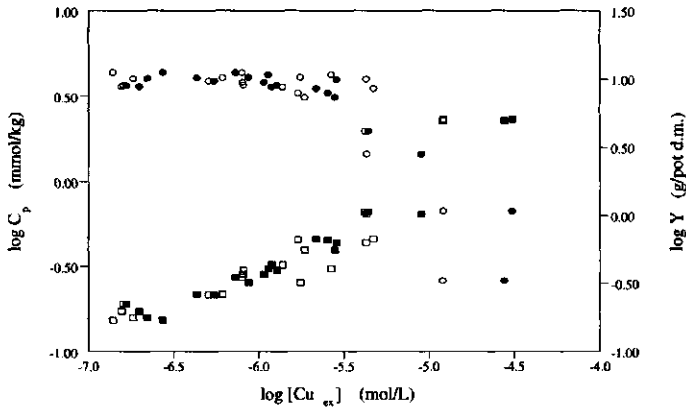
Figure 8.4. Plant tissue copper concentration (C_p) and plant yield (Y) at two pH levels as a function of extractable copper (Cu$_{ex}$) for 0.01 M and 0.001 M CaCl$_2$, all on logarithmic scales. Open symbols 0.001 M, and closed symbols 0.01 M CaCl$_2$; □ and ■ plant tissue copper concentration; ○ and ● plant yield.

Also in the case of (Cu$_T$) a good correlation between the 'total' extractable Cu concentration (0.43 M HNO$_3$) and the plant tissue copper concentration (C_p) and/or the yield (Y) of the ryegrass is not found (Fig. 8.5 and Table 8.5). Linear regression analysis of the HNO$_3$ extractable Cu concentration and the Cu uptake gave a regression coefficcient of only 0.75 (Table 8.5). Moreover the yield reduction starts at different HNO$_3$ extractable Cu concentration for different soil pH values.
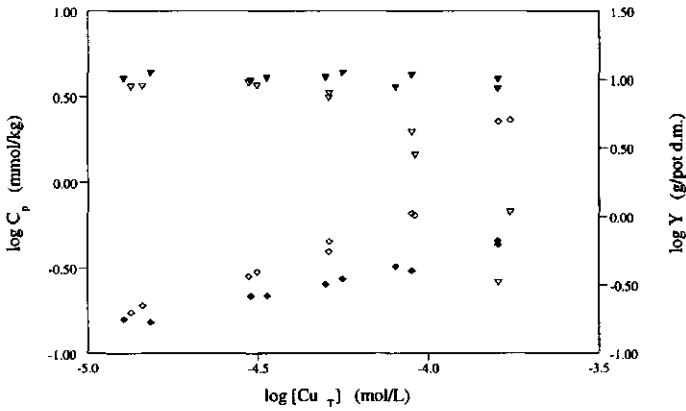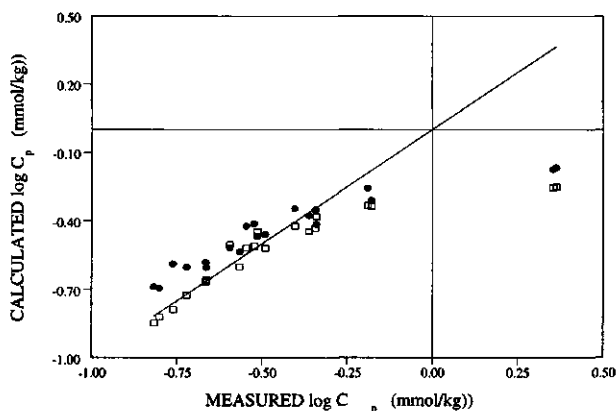
Figure 8.5. Plant tissue copper concentration (C_p) and plant yield (Y) at two pH levels as a function of 'total' 0.43 M HNO$_3$ extractable copper (Cu$_T$), all on logarithmic scales. $\Diamond$ and $\blacklozenge$ plant tissue copper concentration; $\triangledown$ and $\blacktriangledown$ plant yield. Open symbols pH 4.5 and closed symbols pH 5.7.

For known total Cu content in soil, solid and dissolved organic matter content, and pH the 'free' copper concentration (Cu^{2+}) in the soil solution for both CaCl$_2$ extracts is calculated with the NICA model (Eq(8.1)) whereas the Cu uptake by the plant is calculated with Eq(8.6). The average model parameter values for both extracts are 0.56 ± 0.07 for K_p and 0.16 ± 0.01 for n_p ($r^2 = 0.81$). In Fig. 8.6 the calculated Cu concentration in the plant is given as a function of the measured Cu concentration in the plant. The predictions with both models are rather good. Large discrepancies are found in case of yield reduction. The predictions are slighty better for the 0.001 M CaCl$_2$ extract than for the 0.01 M CaCl$_2$ extract.

Figure 8.6. Calculated plant tissue copper concentration as a function of the measured plant tissue copper concentration. $\square$ 0.001 M $CaCl_2$; $\bullet$ 0.01 M $CaCl_2$; line 1:1.

Conclusions

Copper uptake by ryegrass increases at increasing total Cu content in the soil and depent on soil pH. Yield reduction due to Cu toxicity starts at different concentrations for different background electolytes but in the case of the 'free' copper (Cu^{2+}) concentration a single concentration is observed above which yield reduction was obeserved for ryegrass. Speciation of Cu in the soil (solution) can be excellently described with the NICA model by taking total Cu content, pH, Ca concentration, solid and dissolved organic matter into account. The extractable Cu concentration in the soil solution was affected by pH, DOC and Ca concentration. The Cu concentration in ryegrass is not linear with the 'free' copper concentration during yield reduction. Furthermore, no single copper species could be identified whose concentration regulates copper uptake by ryegrass assuming passive copper uptake.

Acknowlodgement

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Samenvatting

Binnen de Europese Unie (EU) hebben we te maken met een overproduktie van gewas, vlees en andere dierlijke produkten zoals melk en boter. Het beleid van de Europese Unie is dan ook de laatste jaren gericht op het reduceren van deze overproduktie in de lidstaten (MacSharry plan). Voor Nederland houdt dit in dat het landbouwareaal met minimaal 15 % terug gedrongen moet worden. Een van de mogelijkheden is om deze gebieden in te richten als natuur- en/of bos gebieden. Ten gevolge van het veranderen van het landgebruik gaan allerlei chemische, fysische en biologische bodemprocessen plaats vinden. Deze processen kunnen vervolgens allerlei invloeden hebben op verontreinigingen die reeds in de bodem aanwezig zijn. In dit proefschrift zijn een aantal effecten van het veranderend landgebruik op mobiliteit en beschikbaarheid van de zware metalen cadmium en koper in zandgronden onderzocht. Verhoogde cadmium en kopergehalten komen in landbouwgronden o.a. voor door het gebruik van meststoffen (kunstmest, dierlijke mest, slib) en door atmosferische depositie (bv. 'De Kempen').

Gronden die als eerste in aanmerking komen om uit produktie te worden genomen zijn de zgn. marginale gronden. Marginale gronden zijn met name zandgronden aangezien deze relatief gezien het minst vruchtbaar zijn en daardoor hoge bemestingsgiften vereisen voor optimale gewasopbrengsten. Met name de zandgronden die reeds verontreinigd zijn met zware metalen kunnen ten gevolge van veranderend landgebruik een risico vormen voor mens en milieu.

Het inrichten van landbouwgebieden als natuurgebied gaat gepaard met het stoppen bemesten en bekalken van de bodem waardoor op lange termijn verschraling van de bodem zal plaats vinden. Tegelijk met het stoppen van de bemesting neemt de toevoer van in meststoffen aanwezige zware metalen af. Naast bemesting wordt in de landbouw ook kalk (o.a. calciumcarbonaat) aan de bodem toegevoegd om de zuurtegraad van de bodem (pH) te stabiliseren. Optimale gewasopbrengsten worden bij zandgronden verkregen bij neutrale of licht zure pH. Ten gevolge van natuurlijke

bodem verzuring (via mineralisatie) en zure atmosferische depositie gaat de bodem pH dalen en spoelt o.a. het aanwezige calcium uit naar het grondwater. Door blad- en naaldval en het afsterven van vegetatie zal er een toename van organische stof plaats vinden. Door chemische omzettingen en microbiële afbraak wordt van de (vaste) organische stof onder andere opgeloste organische stof gevormd waarvan humus- en fulvozuren de meest bekende fracties zijn. In dit proefschrift is gekeken naar de effecten van verandering in pH, opgeloste en vaste organische stof en calcium in de bodem op de mobiliteit en beschikbaarheid van cadmium en koper in zandgronden.

Speciatie van zware metalen in grond is een term die duidt op de distributie van de totale hoeveelheid metaal over alle mogelijke chemische vormen (speciës) in de vaste en de vloeibare fase van de bodem. Deze speciatie hangt af van het metaal, de samenstelling van de vaste fase en de bodemoplossing. Ten aanzien van de vaste fase zijn klei, metaal(hydr)oxiden,organische stof belangrijke parameters terwijl voor de bodemoplossing pH, ionsterkte, en de aanwezigheid en aard van andere kat- en anionen en organische complexvormers (bv. opgeloste organische stof) belangrijk zijn.

In zandgronden worden de zware metalen cadmium en koper hoofdzakelijk gebonden door organische stof (H 2 t/m H 7). Deze vastlegging bepaalt in grote mate de beschikbaarheid van cadmium en koper voor organismen en de snelheid en de concentratie waarmee deze metalen uitspoelen naar het grondwater. Deze vastlegging wordt o.a. beïnvloed door milieucondities zoals pH en calcium concentratie (H 2 en H 6). De hoeveelheid metaal gebonden aan de vaste (organische) stof, ook wel geadsorbeerde hoeveelheid genoemd, is in evenwicht met de totale concentratie aan metalen in oplossing. De totale concentratie in oplossing wordt bepaald door de som van de 'vrije' metaal ionen en de gecomplexeerde metaal ionen in oplossing. In het geval van cadmium is anorganische complexering met chloride van groot belang (H 2 en H 3) terwijl voor koper juist de organische complexering van groter belang is (H 4 t/m H 8). In de aanwezigheid van 0.002 M chloride (Cl) is ca. 13 % van de totale hoeveelheid Cd in oplossing gecomplexeerd met Cl waarbij $CdCl^+$ en $CdCl^0$ de

belangrijkste complexen zijn. In het geval van 0.2 M Cl is maar liefst 91 % van het cadmium in oplossing gecomplexeerd. De competitie met calcium en protonen bepalen tevens in belangrijke mate de hoeveelheid cadmium in oplossing. Bij hoge pH is er relatief veel calcium geadsorbeerd aan de vaste organische stof terwijl bij lage pH relatief weinig calcium geadsorbeerd zit aan de organische stof. De hoeveelheid cadmium in oplossing wordt dus o.a. bepaald door calcium en protonen. Calcium competitie reduceert de cadmium vastlegging aan de onderzochte grond met 60 tot 80 % ten opzichte van natrium als dominant kation bij een constante ionsterkte van 0.003 (H 2). Bij toenemende ionsterkte neemt de cadmium vastlegging aan organische stof af met 60 % in het geval van calcium en 25 % voor natrium. De cadmium vastlegging neemt met 75 % af bij één pH eenheid afname voor de onderzochte zandgrond. Alle verkregen meetdata kunnen uitstekend beschreven worden met het drie Species Freundlich (3SF) model waarbij rekening gehouden wordt met zoutsterkte, calcium competitie, pH en Cl complexering. De cadmium mobiliteit onder invloed van anorganische chloride complexering en calcium competitie is aangetoond met laboratorium kolom proeven (H 3). Voor de gebruikte zandgrond en een chloride concentratie van 0.02 M in het percolaat neemt de Cd mobiliteit met een factor twee toe t.o.v. geen chloride in het percolaat hetgeen m.b.v. van het 3SF model voorspeld kan worden (H 3). De cadmium mobiliteit wordt tevens sterk beïnvloed door de competitie met calcium en natrium. Bij extrapolatie van laboratorium kolom proeven naar veldproeven moet zowel de anorganische complexering, de calcium concentratie als de pH meegenomen worden om tot een betere schatting te komen t.a.v. Cd uitspoeling onder veldomstandigheden.

In het geval van anorganische complexen zijn evenwichtsconstanten, die het evenwicht tussen het 'vrije' metaalion en anorganische metaal complexen beschrijven, redelijk tot goed bekend. Echter in het geval van metaal binding aan opgeloste organische stof zijn de evenwichtsconstanten niet bekend. Opgeloste organisch stof bestaat hoofdzakelijk uit humus- en fulvozuren welke negatief geladen groepen

bevatten, zoals carboxyl- en fenolische hydroxyl-achtige groepen. Aan deze negatief geladen groepen kunnen zich relatief gemakkelijk positief geladen ionen binden, zoals protonen, koper en calcium (H 4 t/m H 7). De ionen gaan onderling een competitie aan om de aanwezige bindingsplaatsen. Bij lage pH bijvoorbeeld is de binding van koper geringer dan bij hoge pH.

Opgeloste en vaste organische stof concurreren met elkaar voor het aanwezige koper. Ten gevolge van deze competitie kunnen resultaten verkregen worden die op basis van de stoffen afzonderlijk niet verwacht zouden worden. De competitie tussen humus- en fulvozuren (opgeloste organische stof) en vaste organische stof voor koper laat zien dat ondanks verlaging van de pH de koperbinding aan fulvozuur kan toenemen terwijl de koperbinding aan fulvozuur afzonderlijk afneemt bij verlaging van de pH (H 4). In H 5 zijn de resultaten van de koper- en proton binding aan gezuiverd humuszuur (HA) voor een groot pH- en kopertraject gegeven. Het humuszuur is geëxtraheerd uit een bosgrond volgens een procedure van de 'International Humic Substance Society (IHSS)'. De koperbinding is sterk pH afhankelijk en niet lineair. Twee modellen zijn gebruikt om de data te beschrijven nl. het Niet-Ideaal Competitief Adsorptie (NICA) model en het daaruit afgeleide (vereenvoudigde) Twee Species Freundlich (TSF) model. Beide modellen beschrijven de data goed. In het geval van het NICA model zijn voor het beschrijven van de koper binding aan humuszuur 12 parameters nodig terwijl voor het TSF model slechts 3 parameters nodig zijn, hetgeen de eenvoud van het TSF model aan geeft. Een groot aantal van de parameters in het NICA model, zoals de mediaan affiniteits constanten en de ionspecifieke niet idealiteits parameters, zijn echter constanten en moeten dus gelden onder een groot aantal omstandigheden. Door nu deze parameters constant te veronderstellen en alleen de maximaal aantal bindingsplaatsen en de heterogeniteitsparameter van de organische stof aan te passen is getracht de koperdesorptie in een zandgrond te beschrijven. De maximaal aantal bindingsplaatsen en de heterogeniteits parameter van de organische stof zijn aangepast aangezien het aannemelijk is dat vaste organische stof relatief

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minder reactieve bindingsplaatsen heeft en qua samenstelling heterogener is. Door alleen deze twee parameters te variëren wordt de koperdesorptie uitstekend beschreven in schudproeven voor bekende vaste en opgeloste organische stof, totaal koper gehalte en pH met zowel het NICA als het TSF model. De voorspellende mogelijkheden van beide modellen zijn getoetst m.b.v. kolomproeven in het laboratorium, welke goed overeen komen met de gemeten concentraties (H 5). In het geval de calciumconcentratie ook verandert in de bodem kan deze interactie meegenomen worden in het NICA model aangezien dit een multi-component model is (H 6). Dit is echter niet mogelijk voor het TSF model.

De opgeloste organische stof concentratie (meestal weergegeven als DOC ('Dissolved Organic Carbon' aangezien de koolstof concentratie een goede maat is voor de opgeloste organische stof concentratie) en dus indirect ook de hoeveelheid koper in de bodemoplossing wordt sterk beïnvloed door de concentratie aan divalente en trivalente kationen zoals calcium, koper en aluminium. opgeloste organische stof coaguleert uit in de bodem door binding van o.a. calcium, koper en aluminium ionen aan de opgeloste organische stof (H 6). De mate van coaguleren hangt af van de concentratie van de ionen in oplossing en van de bindingsterkte van de ionen aan de opgeloste organische stof. De volgorde van coagulatie voor de onderzochte ionen is aluminium, koper, calcium en vervolgens natrium. Middels kolom proeven is aangetoond hoe gevoelig de opgeloste organische stof mobiliteit is voor kleine variaties in calcium en pH. De koper concentratie die afhankelijk is van zowel het totaal koper gehalte, de pH, de calcium en de opgeloste organische stof concentratie wordt goed voorspeld m.b.v. het NICA model (H 6). Ook in het veld beschrijven zowel het NICA als het TSF model de relatie tussen totaal en opgelost koper, vast en opgelost organische stof en de pH voor een zandprofiel goed (H 5). Voorspellingen van het multi-component transport van o.a. koper, calcium, pH en opgeloste organische stof is helaas nog niet mogelijk aangezien over o.a. de vorming en de mobiliteit van opgeloste organische stof in de bodem nog te weinig bekend is. Dit kan

en moet dan ook een belangrijk punt voor vervolg onderzoek zijn.

Om, op grond van aannames over toekomstige ontwikkelingen, voorspellingen te doen over de koperspeciatie in een zandgrond zijn scenariostudies uitgevoerd. Modelberekeningen voor een landbouwgrond die uit produktie is genomen, waarbij rekening gehouden is met een toename in vaste en opgeloste organische stof en pH daling, laten zien dat de totale koper concentratie na 50 jaar in de bodemoplossing slechts een geringe toename laat zien (factor 4) terwijl de 'vrije' koper concentratie (Cu^{2+})met een factor 750 toeneemt t.o.v. een landbouwgrond die niet uit produktie is genomen (H 7). Het al of niet gemengd raken van de organische stof rijke strooisellaag door de (licht) verontreinigde bovengrond bepaalt in sterke mate de koperuitspoeling. Indien de strooisellaag zich niet mengt met de bovengrond is de koperuitspoeling hoger (factor 4) dan als er wel menging van de strooisellaag optreedt door de bovengrond. De modelberekeningen tonen aan dat de koperspeciatie in een zandgrond verandert als gevolg van veranderend landgebruik waarbij de effecten veel sterker zijn voor de 'vrije' koperion concentratie dan voor de totale koperconcentratie in oplossing.

De speciatie van koper in een zandgrond in relatie tot biologische beschikbaarheid is getoetst voor het gewas Engels raaigras ((*Lolium multiflorum L.*) (H 8). De koper opname bij raaigras neemt toe met toenemend totaal koper gehalte in de grond. Bij eenzelfde totaal koper gehalte in de grond en afnemende pH neemt de koperopname bij het raaigras toe. Het begin van gewasopbrengst derving (verlies) werd geconstateerd bij verschillende koper concentraties geëxtraheerd met ongebufferde electrolietoplossingen ($CaCl_2$). Echter in het geval van de 'vrije' koper (Cu^{2+}) concentratie is één concentratie gevonden waarbij gewasopbrengst derving begon op te treden. De koperopname door raaigras is niet lineair met name tijdens gewasopbrengst derving.

Risico-evaluatie gebaseerd op bodemextractie met ongebufferde neutrale electroliet oplossingen zou nader onderzochtmoeten worden op de bruikbaarheid voor andere zware metalen en andere gronden. Nationale en internationale organisaties, die

zich bezig houden met het standaardiseren van meetmethoden, zijn bezig om bodemextractiemethoden zoveel mogelijk te standaardiseren.

De resultaten van dit proefschrift kunnen gebruikt worden bij zogenaamde risico beoordeling t.a.v. biologische beschikbaarheid en mobiliteit van verontreinigingen in de bodem op basis van de huidige routinematig verkregen parameters zoals totaal gehalte, pH en organische stof. Recent is door het kabinet besloten tot de uitvoering van een interdepartementaal beleidsonderzoek (heroverweging) bodemsanering en is door o.a. het ministerie van VROM het beleidvernieuwingsproces (BEVER) bodemsanering gestart (Tweede Kamer, 1997)*. Een van de belangrijke punten in de koerswijziging is de saneringsmaatregelen af te stemmen op het gewenste gebruik (functiegericht saneren). Een belangrijk aspect hierbij is het maken van een onderscheid in mobiele en immobiele verontreinigingen. Voor cadmium en koper is in dit proefschrift aangegeven onder welke omstandigheden de metalen relatief mobiel cq immobiel zijn.

* Tweede Kamer. 1997. Interdepartementaal beidsonderzoek: bodemsanering. Vergaderjaar 1996-1997, 25411, nr. 1.

Curriculum vitae

Erwin Temminghoff werd op 2 juli 1959 geboren in Hengelo (O). Nadat hij zijn middelbare school diploma's had behaald begon hij in 1978 zijn studie HBO-A met de afstudeerrichting analytische chemie aan de toenmalige S.L.P. te Hengelo (O). Na het behalen van het diploma in 1980 vertrok hij naar Arnhem alwaar hij de studie HBO-B, eveneens met de afstudeerrichting analytische chemie, aan de O.L.A.N. begon. Tijdens deze studie, waarvan hij in 1983 het diploma behaalde, heeft hij stage gelopen op de Landbouwuniversiteit Wageningen bij de vakgroep Bodemkunde en plantenvoeding. In november 1983 kreeg hij een aanstelling als analist bij dezelfde vakgroep sectie chemische grond- en gewasanalyse waarna hij in 1986 'verhuisde' naar de sectie bodemhygiëne en bodemverontreiniging. In 1987 vertrok hij, samen met prof. Frans de Haan, voor 3 maanden naar de Brawaijaja Universiteit in Malang (Indonesië) voor het mede verzorgen van een 'shortcourse on pollution of soil & water in East-Java'. Na terugkomst begon hij in september 1987, naast zijn baan als analist, de studie Milieuhygiëne aan de Landbouwuniversiteit. In 1992 studeerde hij af in de richting bodemkwaliteitsbeheer met de afstudeervakken grond & gewasanalyse en bodemverontreiniging.

In 1992 kreeg hij een aanstelling als toegevoegd onderzoeker bij de 'vakgroep' Bodemkunde en plantenvoeding, sectie bodemhygiëne en bodemverontreiniging. Gedurende de vijf jaar die volgden heeft hij onderzoek uitgevoerd op het gebied van speciatie van zware metalen in de bodem in relatie tot biologische beschikbaarheid en mobiliteit, waarvan de belangrijkste resultaten in dit proefschrift zijn beschreven. Naast zijn promotieonderzoek was hij tevens hoofd van het Bodemchemie laboratorium op de vakgroep. In 1997 werd hij na fusie van het Bodemchemie en het Centraal laboratorium bij de 'vakgroep' hoofd van het nieuw gevormde Centraal laboratorium. Sinds januari 1998 is hij in dienst bij het departement Omgevingswetenschappen, sectie Bodemkunde en plantenvoeding, leerstoelgroep Bodemscheikunde en chemische grond & gewasanalyse als universitair docent.