

The effects of changing land use on the behavior of copper in the soil

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Voorwoord

De literatuurstudie die nu voor u ligt is uitgevoerd in het kader van mijn studie Milieu-Biologie aan de Rijks Universiteit Groningen (RUG). Deze literatuurstudie is verricht in de maanden september en oktober 1994 op het DLO Instituut voor Agrobiologisch en Bodemvruchtbaarheidsonderzoek (AB-DLO) te Haren.

In deze literatuurstudie wordt een beeld geschetst van de te verwachten effecten van bebossing op de mobiliteit van koper in voormalige landbouwgronden. Dit is momenteel een zeer actueel onderwerp, aangezien door hervormingen in de landbouwpolitiek van de Europese Gemeenschap circa 30% van het huidige landbouwareaal uit productie wordt genomen en gedeeltelijk wordt bebost.

Graag dank ik hierbij Paul Römken en Jan Dolfing voor hun inhoudelijk waardevolle en enthousiaste begeleiding.

Gerwin Koopmans

Samenvatting

Landgebruiksverandering heeft grote gevolgen voor bodemparameters zoals pH, organische stofgehalte en de Ca^{2+} -concentratie in het bodemvocht. In deze literatuurstudie worden de interacties tussen bovengenoemde bodemparameters en de gevolgen van deze interacties voor de oplosbaarheid en mobiliteit van koper in de bodem beschreven wanneer voormalige landbouwgronden worden bebost. Als gevolg van het beëindigen van de onderhoudsbekalking zullen de bodem-pH en de Ca^{2+} -concentratie in het bodemvocht dalen. Verder zal er zich door de aanleg van een bos een strooisellaag ontwikkelen. Dit organische materiaal zorgt voor een constante bron van opgeloste organische koolstof (DOC; Dissolved Organic Carbon). Als gevolg van deze veranderingen (lagere bodem-pH, lagere Ca^{2+} - en hogere DOC-concentratie) zal de oplosbaarheid en mobiliteit van het tot nu toe in de bodem geïmmobiliseerde koper toenemen. Bij een dalende bodem-pH neemt de oplosbaarheid van koper toe, vooral bij pH-waarden lager dan 4.5. Bij pH-waarden hoger dan 4.5 is DOC in staat om koper te mobiliseren door het vormen van stabiele oplosbare Cu-DOC complexen. In aanwezigheid van Ca^{2+} daalt zowel de DOC- als de Cu-concentratie in het bodemvocht, als gevolg van een verhoogde adsorptie aan de vaste bodembestanddelen. Ca^{2+} is in staat om als een brug te fungeren tussen het negatief geladen DOC en de overwegend negatief geladen bodembestanddelen, vooral onder zwak-zure omstandigheden. Door een afname van de Ca^{2+} -concentratie, wanneer voormalige landbouwgronden worden bebost, blijven de Cu-DOC complexen echter in oplossing. Doordat de Cu-DOC complexen een hoge mobiliteit bezitten t.o.v. de vrije ion-vorm van koper kan een deel van het gecomplexeerde koper uiteindelijk uitspoelen naar het grondwater.

Als conclusie kan gesteld worden dat als gevolg van het beëindigen van de onderhoudsbekalking, wanneer voormalige landbouwgronden worden bebost, de Ca^{2+} -concentratie zal dalen, waardoor de DOC- en Cu-concentraties in het bodemvocht zullen stijgen. De verhoogde mobiliteit en concentraties van koper kunnen leiden tot het optreden van toxische effecten bij planten en bodemorganismen en een verhoogde uitspoeling naar het grondwater.

Summary

The conversion of agricultural land to forest directly affects important soil parameters such as soil pH, organic matter content and Ca solution concentration. In this literature review the interactions between the above-mentioned soil parameters and the implications of these interactions for the solubility and mobility of copper in the soil in case of forestation of agricultural land are discussed. Termination of liming will result in decreases in the soil pH and the concentration of Ca in the soil solution. On the other hand, the organic matter content and the DOC solution concentration will increase. Because of these changes in soil parameters the solubility and mobility of copper will increase. Copper has accumulated in the topsoil of agricultural land as a result of farming. With decreasing soil pH, the solubility of copper increases, especially at pH values lower than 4.5. At pH values higher than 4.5, DOC is able to solubilize copper resulting in the formation of aqueous Cu-DOC complexes. The availability of Ca^{2+} reduces both the DOC and copper solution concentration as a result of adsorption to the solid phase, especially at near neutral pH. This behaviour is attributed to the formation of cation bridges. However, due to the decrease in Ca^{2+} solution concentration in case of converting agricultural land to forest, the Cu-DOC complexes remain in solution. Because of the high mobility of the complexed copper in soil compared to the free ionic form of copper, a fraction of the complexed copper may ultimately leach to the groundwater.

It is concluded that due to the termination of liming when agricultural land is changed into forest, the Ca^{2+} solution concentrations will decrease which results in increasing DOC and copper solution concentrations. The increased copper mobility and solution concentrations may induce toxic effects in plants and soil organisms, and may cause enhanced leaching to the groundwater.

1. Introduction

The agricultural policy of the European Community (EC) has recently been reformed in an attempt to reduce the agricultural surpluses and expenses (Bertels, 1993). Large areas used for arable crop and dairy production are being taken out of production and are converted to other purposes. One of the options of changing land use is to convert these areas to new forests that have economical (wood production), ecological (habitat function and CO₂ buffer) and/or recreational functions (Römkens et al., in review). Conversion of agricultural land to forest in the EC is estimated at 8.5 million hectares from 1985 to 2020 (Stigliani & Salomons, 1993). A major part of these forests are to be planted on the less productive soils exhibiting low potential for agricultural purposes (Römkens & Nummerdor, in prep.).

As a result of excessive application of animal manure and sewage sludge, both used as fertilizers and soil amendments, the total heavy metal content (e.g. Cu, Cd and Zn) of most agricultural soils is elevated (Van Driel & Smilde, 1990). The heavy metal content of present agricultural soils is high, compared to forest soils. Van Driel et al. (1991) measured an average Cu content of 10 mg per kg in agricultural soils (0-30 cm soil layer), whilst Römkens (in review) observed an average Cu content of 2.21 mg per kg in forest soils (0-30 cm soil layer). Despite the higher heavy metal content of agricultural soils, soil solution concentrations are much lower than those in forest soils (Römkens & Salomons, 1993). Due to the near neutral pH and low dissolved organic carbon (DOC) content of agricultural soils, a major part of the applied heavy metals is adsorbed to solid soil components like clay minerals, Fe- and Al-(hydr)oxides and organic matter (Römkens & Salomons, 1993; Römkens & Nummerdor, in prep.).

High concentrations of heavy metals may induce toxic effects after uptake by soil organisms and plants. The bio-availability of heavy metals determines the toxicity for soil organisms and plants. In present agricultural soils, a major part of the applied heavy metals is stored in the topsoil resulting in a low bio-availability. However, a decrease in pH or an increase in DOC can lead to an increase in soil solution concentration and may result in an enhanced bio-availability of heavy metals or enhanced leaching of heavy metals towards groundwater storage (Hesterberg, 1993; Römkens & Nummerdor, in prep.).

Forestation will induce major changes in soil parameters such as soil pH, Ca and DOC. Agricultural soils are limed to maintain soil pH at a level beneficial to crops (near neutral pH). Consequently, termination of liming will cause a decrease in soil pH (Hesterberg et al., 1992). Especially non-calcareous sandy soils with low buffering capacity and a low clay content are susceptible to enhanced acidification (Hesterberg, 1993). Johnston et al. (1986) measured a decrease in soil pH of the 0-23 cm soil layers from pH 7 to 4.2 over a period of 100 years, when limed agricultural land was converted to deciduous forest.

Also the Ca solution concentration will decrease since the main source (lime) has been terminated. The role of Ca as the main cation in solution will be taken over by Al. The Al solution concentration, at pH values below 4.2, will increase due to an increase in the solubility of Al (hydr)oxides (Reuss & Walthall, 1990).

On the other hand, the organic matter content is expected to increase, due to the development of an organic horizon (Ah, Oh) at the soil surface. This also means an increase in DOC content in the soil solution.

These changes in soil parameters (pH and DOC) will affect the behaviour of stored heavy metals. A direct result of soil acidification is that the heavy metal solubility increases (Hesterberg, 1993). The ability of soil (hydr)oxides, solid organic matter and DOC to adsorb heavy metals decreases as pH decreases, due to a reduction in the net negative surface charge (Kuo & Baker, 1980; Buffle, 1988).

It has been shown that DOC enhances the solubility and mobility of heavy metals (König et al., 1986; Ahmrein et al., 1992). At near neutral pH, complexation decreases the net positive surface charge of the heavy metal, thereby reducing the electrostatic attraction between the complexed heavy metal and the negatively charged soil surface. Especially Cu exhibits a strong affinity for binding to DOC and forms stable aqueous complexes with organic ligands (Stevenson, 1991; Apte & Day, 1993). The complexation of heavy metals also affects toxicity. In general, the toxicity of heavy metals decreases with an increasing degree of complexation (Van der Werff, 1981). Plants predominantly take up heavy metals in the free ionic form (Kuiters & Mulder, 1993^b).

Agricultural soils exhibiting low potential for agricultural purposes are converted to forest first. These areas consist largely of non-calcareous sandy soils with a low organic matter and clay content and, hence a low buffering capacity. Therefore, in case of conversion of agricultural land to forest the soil pH is expected to decrease rapidly. On the other hand, the DOC content is expected to increase due to the development of an organic horizon. Figure 1 shows the observed changes in soil pH and DOC concentration in solution in eight mixed forests of different age on sandy soils in case of conversion of former agricultural land to forest.

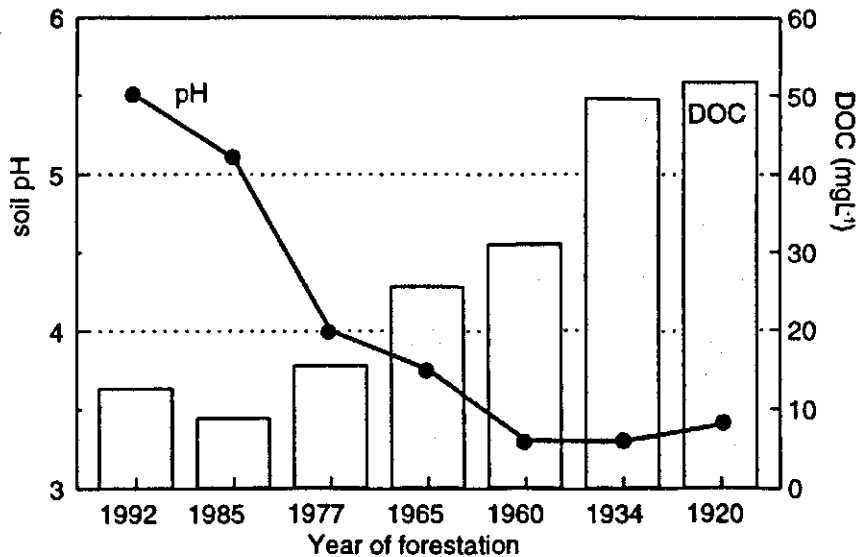


Figure 1. Change in soil pH and DOC concentration (0-30 cm soil layer) as a result of forestation of arable land (Römken & De Vries, in press).

The heavy metal content of agricultural soils is elevated as result of a net accumulation going on for many years. Consequently, it can be expected that in case of a conversion of agricultural land to forest even higher Cu concentrations occur in the soil solution, compared to nature forest soil solution (Salomons, in press).

As mentioned before, the complexation of Cu by DOC affects both toxicity and mobility in the soil. It is therefore important to know which soil parameters control the DOC solution concentrations (Römken et al., in review). Adsorption of DOC to the surface of soil minerals is strongly pH-dependent (Jardine et al., 1989; Gu et al., 1994). Due to a decrease in pH, the negative surface charge of the DOC will decrease, which results in an enhanced adsorption to the negatively charged surface of soil minerals. Also polyvalent cations like Ca^{2+} and Al^{3+} are able to enhance the adsorption of DOC to the solid phase (Randtke & Jepsen, 1982). In the presence of these cations, the DOC solution content is reduced as a result of the formation of cation bridges (Tipping, 1981; Tipping & Cooke, 1982; Schulthess & Huang, 1991). By acting as a bridge between the dissociated functional groups of DOC and the negatively charged soil surfaces (especially clay particles, Si and Mn oxides), Ca^{2+} and Al^{3+} are capable of reducing the concentration of DOC in soil solution (Tipping, 1981; Tipping & Cooke, 1982). The process of cation bridging is stronger at near neutral pH values than at low pH values due to the reduction in net negative surface charge of the soil constituents as pH decreases (Römken et al., in review). In limed agricultural soils, Ca^{2+} is the main cation in solution that can affect the DOC solution concentration. Until now it has been assumed that the main effect of Ca on Cu was through a cation exchange mechanism; Ca competes with Cu for binding sites on DOC (Inskeep & Baham, 1983). However, a mechanism proposed by Römken et al. (in review) implies that Ca^{2+} controls the DOC solution content at near neutral pH by cation bridging. Thereby, Ca^{2+} may indirectly regulate the concentration of heavy metals (e.g. Cu) that strongly bind to DOC.

The purpose of this literature study is to review those soil parameters that control both Cu mobility and speciation. This study attempts to combine several main soil parameters, including pH, DOC and Ca, and an evaluation of the overall effect of the interactions between these soil parameters on the behaviour of Cu will be made. In chapter 2, the different sources of Cu pollution are briefly described, followed by a description of the different phases among which Cu is distributed in the soil. The pertinent soil parameters which affect the distribution processes of Cu between the different phases in the soil are briefly discussed in chapter 3. The interactions between pH, Ca and DOC and the implications of these interactions for Cu mobility are discussed in chapter 4. A case study involving the effects of the conversion of agricultural land to deciduous forest on the mobility and speciation of Cu in a sandy soil is described in chapter 5, and is used to evaluate the interactions between the main soil parameters discussed in the preceding chapters.

2. Copper in soils

2.1. Sources of copper

As a result of a continuously increasing degree of industrialization during the last 200 years, the production, use and release of heavy metals into the environment has increased enormously (Wilmoth et al., 1991). Global data provided by Nriagu & Pacyna (1988) estimate that the annual amount of Cu released to the general soil environment approximates 971×10^3 tons.

Several sources of Cu pollution of soils related to agricultural and industrial activities can be distinguished. The main sources are (Thornton, 1979):

- past and present-day metalliferous mining and smelting;
- coal residues (fly ash and solid wastes);
- other industrial emissions and effluents;
- waste material;
- traffic;
- dry and wet deposition;
- animal manure and sewage sludge;
- commercial fertilizers, pesticides and lime.

Not all of these sources contribute similar amounts of Cu to all soils. The majority of the contributions are direct inputs to the soil system; the amount of Cu can be controlled by applying a given quantity to a certain area. Only imissions from metalliferous mining and smelting activities and traffic can be considered as inputs from outside the soil system; Cu is imported via the atmosphere.

The total annual supply of Cu to agricultural soils in the Netherlands has been estimated at approximately 776 to 970 tons (Van Eerd & Stiggelbout, 1992; Fraters, 1991). The main sources of Cu in Dutch agricultural soils are animal manure and sewage sludge. The annual Cu supply due to the application of animal manure and sewage sludge has been estimated at 750 and 31 tons, respectively (Van der Hoek, 1987; Van Eerd & Stiggelbout, 1992). The contribution of pig manure to the total amount of Cu supplied by animal manure has been estimated at 430 tons (Van der Hoek, 1987; Van Eerd & Stiggelbout, 1992). Pig manure and sewage sludge are both used as fertilizers and soil amendments because of their beneficial constituents like nitrogen, phosphate and organic matter (Van Driel & Smilde, 1990). The application of pesticides and commercial fertilizers and atmospheric deposition are considered as less important sources (Stoop et al., 1993).

Cu balance sheets for agricultural soils are presented in Figure 2. They show a considerable imbalance between losses and supply of Cu. The inputs of Cu have recently been decreased due to a reduction in both the Cu concentration of pig manure and sewage sludge, as well as the use of animal manure and pesticides. However, the situation of net accumulation described had been going on for many years and therefore the Cu content of agricultural soils is still elevated.

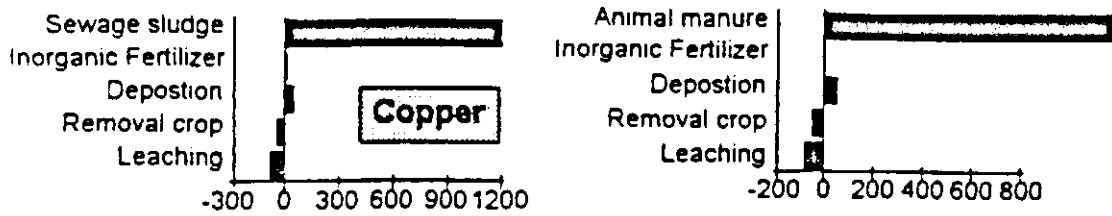


Figure 2. Cu balance sheets for agricultural soils, for scenarios which include either animal manure or sewage sludge application ($\text{g ha}^{-1} \text{y}^{-1}$) (Van Driel & Smilde, 1990).

Table 1 shows the average Cu contents in Dutch agricultural soils. Locally Cu concentrations exceed these values as a result of excessive application of pig manure and sewage sludge or river and/or harbour sediments.

Table 1. Average Cu contents (mg kg^{-1}) in Dutch agricultural soils¹.

	Van Driel & Smilde ² (1981)	Van Toor & Van der Vleuten ³ (1990)
clay	20.0	34.9
sand	11.0	13.0
peat	28.0	21.1

¹ adapted from Stoop et al. (1993)

² sampling depth 0 to 30 cm

³ sampling depth 0 to 25 cm

Van Toor & Van der Vleuten (1990) reported that the Cu concentrations exceed the reference values for unpolluted soils in 15.5% of the agricultural soils. Reference values for heavy metals have been laid down by the Dutch Ministry of Environmental Protection, i.e. upper limits for heavy metal concentrations in soil at which all soil functions still perform normally. The reference values for Cu (in mg kg^{-1}) can be derived from equation 1 (Van Driel & Smilde, 1990):

$$\text{Cu} = 15 + 0.6(\text{L} + \text{H}) \quad (1)$$

(L = %particles < 2 μm ; H = %humus)

2.2. Speciation of copper in soils

Due to the considerable differences in main soil forming factors (parent material, time, climate, geomorphology and human influence) between soils, Cu behaves quite differently in different soils. Even within a given soil, the mobility and solubility of Cu varies considerably with depth, due to a large heterogeneity in soil properties such as pH and organic matter content.

Three different phases are distinguished within the soil: solid, solution and organic phase. Due to the variability in soil properties Cu is distributed among these phases (Shuman, 1991^b).

Solid phase

Three main fractions of Cu can be distinguished within the solid phase (Shuman, 1991^b; Stevenson, 1991):

- adsorbed Cu;
- secondary precipitates;
- Cu present in primary minerals.

Usually the adsorbed fraction contributes the smallest amount of Cu to the total Cu content, compared to the other fractions within the solid phase (Römken et al., 1993). Despite its small contribution to the total Cu content, the adsorbed fraction is considered to be the most reactive. The equilibria between Cu present in secondary precipitates and primary minerals and the solution phase are considered to be slow compared to adsorption reactions. Therefore, it has been assumed that these fractions hardly affect the equilibrium between Cu present in the solid and solution phase (Shuman, 1991^a). The main adsorbing phases in soils are: clay minerals, Mn, Al and Fe (hydr)oxides and organic matter (Harter, 1991). Furthermore, clay or other inorganic solid surfaces can be coated with an organic layer resulting in the formation of additional adsorption sites (Davis & Leckie, 1978; Dalang et al., 1984).

Solution phase

The solution phase contains a minor part of the total Cu content of soils. However, it is considered to be the most important phase in the soil system (Römken et al., 1993). It is assumed that the soil solution acts as an intermediate for the transport of Cu between the solid phase and soil organisms and plants (Sposito, 1989). Furthermore, the solubility of Cu is considered to be indicative of bioavailability (Hesterberg, 1993). The solution phase is also important with regard to the amounts of Cu that are potentially leached to lower soil horizons and ultimately the groundwater. Three main fractions within the solution phase can be distinguished (Shuman, 1991^b, Stevenson, 1991):

- free Cu ions (Cu^{2+});
- complexes with inorganic ligands (e.g. Cl^- , NO_3^-);
- complexes with organic ligands (both solubilized and colloidal, e.g. DOC).

The distinction between the different fractions of Cu in the soil solution is of considerable importance because the chemical speciation mainly determines the rate and extent of redistribution between the different phases and fractions, and affects toxicity to soil organisms and plants.

Organic phase

A part of the total Cu content present in the soil is stored in living or dead organic biomass. The decomposition of dead organic biomass by microorganisms leads to the release of Cu to the solid or solution phase. The rate at which Cu is released depends upon conditions affecting microbial activity. Uptake of Cu present in soil solution by living soil organisms or plants may be an important mechanism in removing Cu from the solution phase and can affect the equilibrium between the solid and solution phase (Römken et al., 1993).

3. Soil parameters

The distribution of Cu between the different phases and fractions in soil can be characterized as a dynamic equilibrium. This equilibrium is influenced by numerous soil parameters, which directly or indirectly affect the distribution processes of Cu. Only the pertinent soil parameters will be described below, including pH, redox potential, CEC, organic matter and salinity.

3.1. pH

The cation adsorption mechanisms involving proton exchange are highly pH-dependent. Results obtained by Kuo & Baker (1980) showed a reduction in heavy metal adsorption, including Cu, at lower pH values due to a decrease in the net negative surface charge. As pH decreases, the net negative surface charge will decrease as result of protonation of soil (hydr)oxides and dissociated functional groups of organic matter. Other pH-induced changes which affect distribution of metals are (Sposito, 1989):

- a change in the hydrolyzation of the metals, changing their affinity for specific surface sites;
- increased dissolution of especially Al (hydr)oxides results in elevated Al concentrations in solution (pH 4.2-2.8) (Reuss & Walthall, 1990). The elevated Al concentration induces a competition effect between Al and other metal species for specific bonding sites.

The pH largely depends on the buffering capacity of a soil. Table 2 shows the relationships between pH and buffering processes in the soil.

Table 2. Buffering mechanisms in soils¹.

pH range	Buffer mechanism
2.4-3.8	Fe buffer
3.0-4.8	Al buffer
4.2-5.0	cation exchange
>5.0	silicate buffer
6.5-8.3	CaCO ₃ dissolution

¹ adapted from Robarge and Johnson (1992)

Non-calcareous sandy soils with a low organic matter content have a low buffering capacity and are therefore susceptible to more rapid acidification (Hesterberg, 1993).

3.2. Redox potential

In well-aerated soils, O_2 is the main electron acceptor. As the O_2 concentration decreases, due to O_2 consumption by microorganisms for respiration, the role of O_2 as main electron acceptor is taken over by other electron acceptors such as: NO_3^- , Mn^{2+} , Fe^{3+} and SO_4^{2-} (Locher & De Bakker, 1991). The redox potential (E_h) decreases with decreasing O_2 concentration. Alterations of the redox potential affect the mobility of metals in two different ways. First, the valence of metals can be altered as result of changing E_h . For example, under reducing conditions Fe^{3+} is transformed to Fe^{2+} . Since the reduced ions are more soluble, increased concentrations of those metals will be observed in solutions of reduced soils (Salomons, in press). Secondly, under reducing conditions sulphate reducing-bacteria form sulphide, which precipitates with metals (Salomons, in press) Other effects of changing the E_h include the enhanced dissolution of Mn and Fe (hydr)oxides resulting in a decrease in the number of specific adsorption sites under reducing conditions. The enhanced Mn and Fe concentrations lead to a competition between these species and other cations for similar adsorption sites (Römkens et al., 1993).

Oxic conditions prevail in well-aerated soils, such as agricultural soils, resulting in relatively constant high E_h . Therefore, the Cu mobility and solubility in agricultural soils is not affected by alterations of E_h .

3.3. CEC and organic matter

The CEC of the soil is mainly determined by the clay, soil (hydr)oxides and organic matter content. An increase in these soil constituents results in an increase in CEC (Sposito, 1989). Also a soil parameter such as pH affects the CEC of the soil. For example, due to lowering of the pH the net negative surface charges of these soil constituents will decrease thereby reducing the electrostatic attraction between these soil constituents and heavy metals.

The CEC of sandy soils is mainly determined by the presence of organic matter, due to the low to very low clay content (Locher & De Bakker, 1991). Soil organic matter mainly occurs in an insoluble form tightly bound to soil minerals and acts as a sink for Cu due to its high CEC (Kuiters & Mulder, 1993^b). The main functional groups of organic matter in adsorbing heavy metals are carboxylic and phenolic hydroxyl groups. After proton dissociation, these groups are able to adsorb heavy metals. The dissociation of these functional groups increases with increasing pH resulting in an elevated net negative surface charge. This leads to an enhanced adsorption of heavy metals. The proton dissociation constants (pK_a) for carboxylic groups of organic matter range from 4.5 to 4.8 (Römkens & Bril, in press). This means that 50% of the carboxylic groups are dissociated in the pH region from 4.5 to 4.8. The pK_a 's of phenolic hydroxyl groups of organic matter range from 8.3 to 8.7 (Römkens & Bril, in press).

3.4. Salinity

Alterations of the salinity as induced by the application of large amounts of animal manure change heavy metal retention in several ways (Römkens et al., 1993). By increasing the total ionic strength, the partial activity of the heavy metals is reduced. This lower activity may lead to an increase in desorption in order to restore the equilibrium situation. Due to the increase

in total ionic strength, concentrations of other cations in solution are increased as well. The presence of enhanced concentrations of other cations induces a competition effect for adsorption sites between the heavy metals and the major cations in solution. The presence of complexing inorganic ligands (e.g. CO_3^{2-}) enhances complex formation. It has been shown that with increasing ionic strength, the above-mentioned mechanisms indeed cause a decrease in amounts of heavy metals that are retained from soil solution (Cabaniss & Shuman, 1988; Ahmrein et al., 1992).

However, due to management changes in case of a conversion of agricultural land to forest the application of animal manure will be terminated and, hence the total ionic strength of the soil solution is expected to be relatively constant. It is therefore expected that changes in salinity will play only a minor role in regulating the Cu mobility and solubility in case of forestation of former agricultural land.

4. Copper, pH, calcium and DOC

As stated before, DOC can affect the Cu concentrations in the soil solution. It is therefore important to know which mechanisms control the DOC solution concentration in a given soil. Soil pH and availability of polyvalent cations seem to be the major soil parameters controlling the DOC concentration in soil solution. The effect of DOC on Cu solubility and mobility will be described below, as well as the interactions between two soil parameters, viz. soil pH and availability of cations on the one hand and DOC on the other, and the implications of these interactions for the Cu solution concentrations.

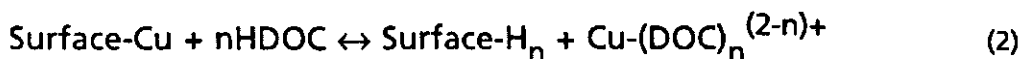
4.1. Interaction between copper and DOC

Only a small part of the soil organic matter is present in soil solution as DOC. DOC is derived from the decomposition of dead organic biomass. Because living organisms contain a large number of different organic compounds, their degradation leads to a complex mixture of organic molecules with widely varying physical and chemical properties (Apte & Day, 1993).

DOC mainly consists of humic substances (60 to 80%). Humic substances are the most important heavy metal complexing species and can be subdivided into the humic fraction, which precipitates as pH decreases, and the fulvic fraction which remains in solution (Apte & Day, 1993). The fulvic acids contain the low molecular weight fraction of DOC with an average molecular weight of approximately 1000, whereas the humic acids contain the high molecular weight fraction with an average molecular weight of higher than 2000 (Buffle, 1988).

A major part of the DOC contains aliphatic and aromatic molecules. Both species contain carboxylic (-COOH) and phenolic hydroxyl (-OH) groups. Approximately 90% of the potential binding sites is attributed to these carboxylic and phenolic hydroxyl groups (Apte & Day, 1993). Amongst divalent metals, Cu exhibits one of the highest affinities for binding to DOC. Cu is able to form strong bonds with ligands containing oxygen, nitrogen and sulphur (Apte & Day, 1993).

Numerous studies showed that due to the high affinity of DOC for complexing Cu, DOC enhances the solubility and mobility of Cu (Davis, 1984; Bergkvist, 1987; Ahmrein et al., 1992; Japenga et al., 1992; Kuiters & Mulder, 1993^{a,b}). The DOC present in soil solution competes with the solid phase for the Cu ions, causing a decrease in Cu adsorption by soil constituents such as clay minerals, Fe and Al (hydr)oxides and organic matter. The mobilization of Cu by DOC is modelled according to:



Consequently, a major part of the Cu in soil solution is present as organic complexes (Hodgson et al., 1965, 1966; Kerven et al., 1984). Hodgson et al. (1965) measured that 76 to 99% of the total Cu amount in soil solution was present in the organically bound form. Due to the complexation of Cu by DOC, the net positive charge of Cu decreases compared to the free ionic form of Cu. Thereby, the electrostatic attraction between Cu and the predominantly negatively charged soil surface is reduced, resulting in an enhanced Cu mobility in the soil.

Apart from the total amount, also the DOC composition has a strong influence on the Cu solubility and mobility in the soil. König et al. (1986) observed that Cu mainly interacted with the low molecular weight DOC which was not easily adsorbed by the mineral soil surfaces. Schulthess & Huang (1991) hypothesized that fulvic acids (i.e. the low molecular weight fraction of DOC) have a higher number of adsorption sites than humic acids (i.e. the high molecular weight fraction of DOC). Hence, the low molecular weight DOC is more reactive than the high molecular weight DOC which may result in an increased sorption of Cu in the soil solution. Results obtained by Guggenberger et al. (1994) showed that Cu was especially adsorbed by the hydrophilic fraction of the DOC. Because heavy-metal binding by organic matter can be regarded as an ion exchange process between protons and heavy metal ions on acidic functional groups (McBride, 1989), the larger extent of Cu adsorbed by hydrophilic acids is probably due to their higher exchange capacity (Guggenberger et al., 1994). With decreasing pH, the relative importance of the hydrophilic acids increased due to the reduced solubility of the less polar hydrophobic acids (Guggenberger et al., 1994). These less polar hydrophobic acids are more susceptible for a H^+ -initiated adsorption to soil constituents compared to the more polar hydrophilic acids.

In general, the Cu hydrophilic acid complexes were retained to a lesser extent by the soil constituents compared than the hydrophobic acids resulting in an enhanced Cu mobility (Guggenberger et al., 1994). Also Jardine et al. (1989) observed that of the total amount of DOC sorbed to the soils, over 80% consisted of hydrophobic acids and less than 20% of hydrophilic acids.

4.2. Interaction between pH and DOC and implications for Cu mobility

Studies performed by Jardine et al. (1989) and Gu et al. (1994) showed that the adsorption of DOC to the mineral surfaces is strongly pH-dependent, with DOC adsorption increasing as pH decreases. Especially Al, Fe and Mn (hydr)oxides have been found to act as a major adsorbent for DOC because of their significant anion exchange capacity (Schulthess & Sparks, 1987; Jardine et al., 1989; Gu et al., 1994). Figure 3 shows the pH-dependent adsorption of DOC to Fe (hydr)oxide at different background solutions.

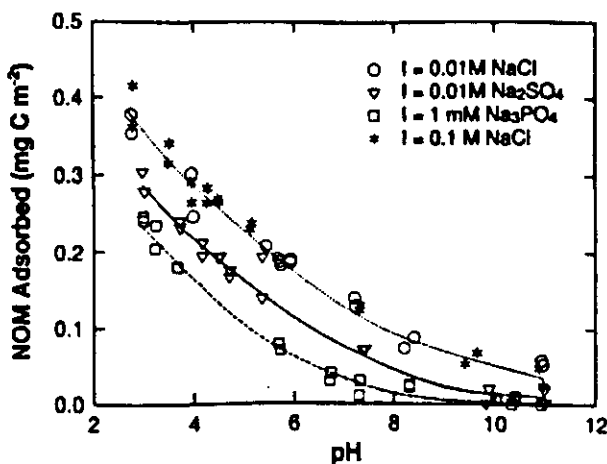
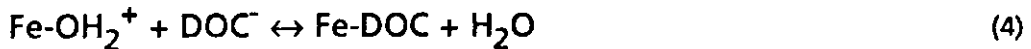


Figure 3. pH dependence of the adsorption of natural organic matter (NOM) to Fe (hydr)oxide at different background solutions (Gu et al., 1994).

It was hypothesized that DOC adsorbs to the mineral surface by anion exchange, involving electrostatic interaction between the DOC molecule and the mineral surface (Davis & Gloor, 1981; Liang et al., 1993). This mechanism was modelled in the following reaction:



Due to a decrease in soil pH, the DOC molecules will be protonated resulting in a reduction of the net negative surface charge of the DOC. Thereby, the electrostatic repulsion between the DOC and the negatively charged soil surface will decrease as well, resulting in an enhanced adsorption of the DOC. However, Jardine et al. (1989) observed significant DOC adsorption at pH values > 7. In this higher pH region, the DOC molecules will be ionized and have predominately negative charges, as is the surface of most soil minerals. The DOC molecules must overcome large electrostatic repulsion during adsorption in this high pH region. Therefore, it was concluded by Jardine et al. (1989) that other mechanisms than cation exchange are also operative. Jardine et al. (1989) proposed that physical adsorption mechanisms such as Van der Waals forces and electrostatic attraction between dipole molecules contribute significantly to the DOC adsorption by the soil. This was supported by the preferential adsorption of the hydrophobic fraction of the DOC to the soil minerals. On the other hand, Gu et al. (1994) and Murphy et al. (1994) concluded that the DOC adsorption to (hydr)oxide surfaces was mainly due to the ligand exchange mechanism between the carboxylic and the phenolic hydroxyl functional groups of the DOC and soil Fe and Al (hydr)oxides. Also results obtained by Tipping (1981) favoured a mechanism involving ligand exchange of DOC with H₂O and OH⁻ of surface Fe-OH₂⁺ and Fe-OH groups respectively. These ligand exchange mechanisms were modelled accordingly:



The soil pH directly affects the DOC content in the soil solution and thereby indirectly alters the Cu solubility and mobility. Kuiters & Mulder (1993^a) reported that with a decrease in soil pH, Cu mobilization was significantly lower due to an increase in the adsorption of the DOC to the soil surface and a decrease in the complexing capacity of the DOC. Inskeep & Baham (1983) and Davis (1984) measured a decrease in the Cu adsorption to Al (hydr)oxides in the higher pH region (pH > 6.5), due to the formation of Cu-DOC complexes in solution. Figure 4 shows the adsorption of Cu to Al (hydr)oxide as a function of pH and DOC.

Davis (1984) reported that the free ionic Cu content in solution decreased at pH > 4.5 because of the formation of organic complexes. The Cu-DOC complexes dominated the Cu speciation completely in the pH range from 4.5 to 8.

König et al. (1986) and Römken & Nummerdor (in prep.) also found that the Cu solution concentration was controlled by DOC at higher pH values. König et al. (1984) measured that at pH > 3.7 the mobilization of Cu by DOC determined the Cu solution concentration. Römken & Nummerdor (in prep.) observed that Cu solution concentration reached minimum levels around pH 4.5 and increased at both higher and lower pH values. At lower pH values (pH < 4.5) Cu solution concentration was controlled by pH. Because of the decrease in net negative surface charge of the adsorbents, electrostatic attraction between Cu and the adsorbents decreases as well. This means that with a decreasing pH (pH < 4.5) Cu solution concentration increases. At pH > 4.5 Cu solution concentration was controlled by DOC. Due to the formation of aqueous Cu-DOC complexes, Cu solution concentration increases at pH > 4.5.

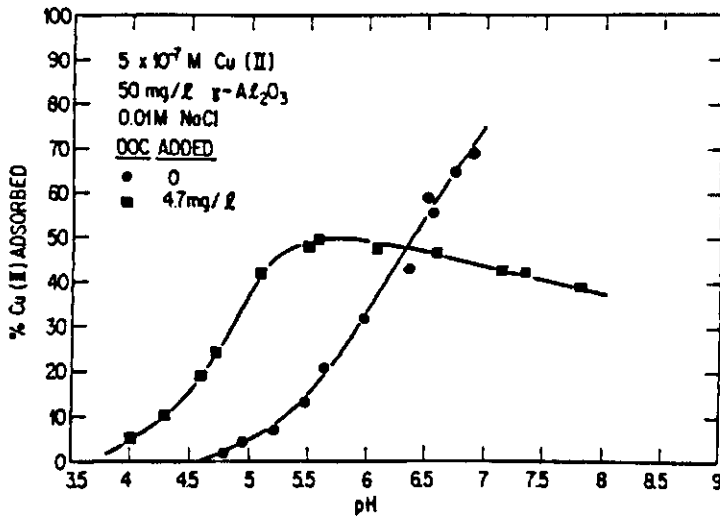


Figure 4. Adsorption of Cu to Al (hydr)oxides ($50 \text{ mg}\cdot\text{L}^{-1}$) suspended in 0.01 M NaCl solution as a function of pH and DOC (Davis, 1984).

4.3. Interactions between Ca and DOC

The presence of polyvalent cations can enhance the adsorption of DOC to various types of surfaces (e.g. clays and (hydr)oxides) (Randtke & Jepsen, 1982). Edwards & Bremner (1967) suggested that polyvalent cations can link the DOC with clay minerals resulting in the formation of a clay-cation-DOC complex. The cation acts as a bridge between the dissociated functional groups of the DOC and the negatively charged soil surfaces (especially clay minerals and Si and Mg oxides).

The cation bridging mechanism is stronger at near neutral pH values than at lower pH values, because of the reduction in the net negative surface charge of both the DOC and the soil constituents (Römken et al., in review). Also the affinity of the metal to form complexes with the DOC determines the ultimate effect of the cation bridging mechanism. If the positive charge of the metal is compensated by the DOC, no charge is available to act as a bridge between the organic ligand and the soil surface. This is likely to be the case for Cu which forms very stable aqueous complexes with DOC in solutions. The stability constant ($\log K_d$) for the formation of Cu-DOC complexes approximated 7.85 (at pH 8) (Mantoura et al., 1978). The $\log K_d$ values for the interaction between Ca^{2+} and Mg^{2+} on the one hand and DOC on the other approximated 3.65 and 3.81, respectively (at pH 8) (Mantoura et al., 1978), indicating that Ca^{2+} and Mg^{2+} exhibit a less strong affinity for binding with DOC than to Cu. Due to the less strong complexing properties of Ca^{2+} and Mg^{2+} , the positive charge of these cations is not fully compensated through binding with DOC. Thereby, Ca^{2+} and Mg^{2+} can potentially affect the DOC solution concentration.

At high Ca^{2+} concentrations flocculation and/or precipitation of a Ca-DOC complex can also reduce the DOC solution concentration. In general, Ca^{2+} concentrations in agricultural soils are beyond the concentration at which flocculation and/or precipitation occurs (Hesterberg et al., 1993). After the application of lime, the Ca^{2+} concentration may temporary exceed the

concentration at which DOC is removed from the soil solution by precipitation and/or flocculation processes (40 to 100 mg·L⁻¹ Ca²⁺; Römken & Bril, in prep.)

Tipping (1981) observed that the adsorption of DOC to Fe-(hydr)oxides in the presence of the cations Ca²⁺ and Mg²⁺ at pH 7 was approximately twice as high as in the system without these cations. The increased sorptive capacity of the Fe (hydr)oxides was attributed to the co-adsorption of Ca²⁺ and Mg²⁺ to the surface of the Fe (hydr)oxides. It was hypothesized that the sorbed Ca²⁺ and Mg²⁺ cations compete with the Fe (hydr)oxide for adsorbing the anionic groups on the DOC and that such competition is more effective at high adsorption densities. This could result in the anionic groups on the DOC making fewer contacts per molecule with the Fe (hydr)oxide surface which then is able to adsorb more DOC molecules. Tipping & Cooke (1982) measured, in agreement with the previously mentioned study (Tipping, 1981), that the amount of DOC sorbed to a certain type of clay mineral (goethite) coated with Fe (hydr)oxides is larger in the presence of Ca²⁺ and Mg²⁺ than compared to Fe (hydr)oxides without Ca²⁺ and Mg²⁺ additions. Also a decrease in the negative electrophoretic mobility of the complex with increasing Ca²⁺ solution concentration was observed. Figure 5 shows the dependence of the electrophoretic mobility on the DOC concentration at various Ca²⁺ concentrations at constant pH (6.7 ± 0.1).

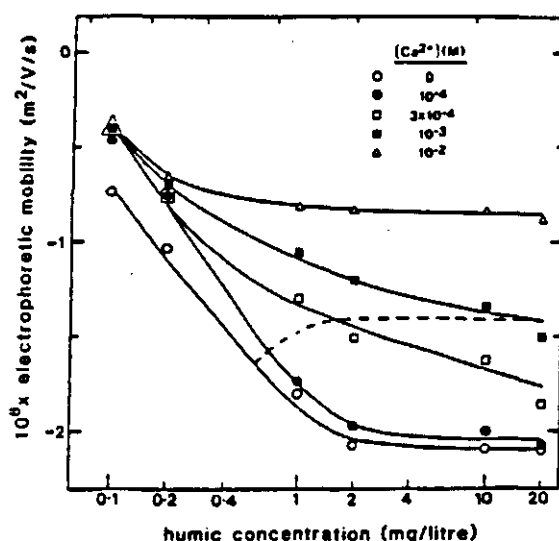


Figure 5. Dependence of the electrophoretic mobility of goethite on the DOC and Ca²⁺ concentrations, at pH 6.7 ± 0.1. All suspensions contained 0.01 M NaCl. The dashed line is a qualitative flocculation boundary: suspensions above the line were flocculated at the time when the mobilities were measured, those below it dispersed (Tipping & Cooke, 1982).

Clay minerals, coated with Fe (hydr)oxides, become negatively charged because of the adsorption of DOC. The magnitude of the negative surface charge decreases with increasing solution concentrations of the divalent cations Ca²⁺ and Mg²⁺. The cations Ca²⁺ and Mg²⁺ interact with the negatively charged functional groups of the DOC, which are not involved in adsorptive reactions with the Fe (hydr)oxide surface. As a result of this interaction the electrostatic repulsion between the adjacent adsorbed DOC molecules is reduced and, hence more DOC molecules can potentially adsorb to the Fe (hydr)oxide surface. This process is likely to occur within the higher pH region, due to dissociation of the functional groups of the DOC at these pH values.

Also the results of Römken et al. (in review) and Römken & Nummerdor (in prep.) showed that at near neutral pH the DOC solution content depends on the availability of Ca²⁺. With

increasing Ca^{2+} solution concentration, the DOC solution content decreased due to adsorption to soil constituents or precipitation processes. The formation of Ca-DOC complexes was found to be pH-dependent, with $K_{\text{Ca-DOC}}$ increasing as pH increased.

Murphy et al. (1994) reported that at high pH (pH 6.5) and in the presence of di- or trivalent cations, a ternary surface complex was formed between the Fe or Al (hydr)oxide, the cation and the dissociated functional groups of the DOC. In the presence of Ca^{2+} , the adsorbed DOC molecule may adopt a more condensed structure, due to intra-site cation bridging between the negatively charged functional groups of the DOC molecule. It was hypothesized that Ca^{2+} facilitates the exposure of the hydrophobic binding sites to the soil solution by cation bridging (Tipping & Cooke, 1982) or by neutralizing ionized sites on the DOC (Tipping & Cooke, 1982; Zachara et al., 1994), leading to an increase in the adsorption of hydrophobic organic compounds (Murphy et al., 1994). Murphy et al. (1994) indeed measured an increase in the adsorption of hydrophobic organic compounds to the clay mineral associated DOC in the presence of Ca^{2+} . Figure 6 shows the adsorption of dibenzothiophene onto clay (kaolinite) coated with peat humic acid in the presence and absence of Ca^{2+} at pH 4.5.

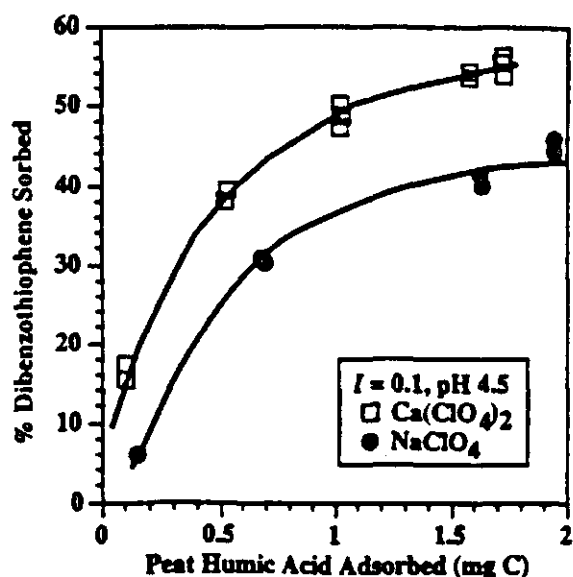


Figure 6. Comparison of dibenzothiophene sorption to kaolinite coated with peat humic acid in high electrolyte (0.1), Ca^{2+} or Na^+ , solution at pH 4.5 (Murphy et al., 1994).

Also the composition of the DOC influences the amount of DOC adsorbed through the cation bridging mechanism. Schulthess & Huang (1991) observed an enhanced humic acid adsorption above pH 4, particularly to Si oxides, through a hypothesized cation bridging mechanism. Conversely, the presence of cations did not enhance fulvic acid adsorption to Si oxide. This was attributed to the fact that fulvic acids have a significantly higher number of adsorption sites than humic acids, which results in the formation of bidentate complexes with the cation. The fulvic acid adsorption sites are very effective in competing with the Si oxide adsorption sites for binding with the cation. The positive charge of the cation is fully compensated through the formation of fulvic acid-cation complexes. Thereby, no charge is available to act as a bridge between the fulvic acid and the negatively charged Si-oxide surface. Therefore, the fulvic acid-cation complex exhibits very weak interaction with the Si oxide surface.

4.4. Implications of Ca-DOC interaction for the Cu concentration in the soil solution

DOC can adsorb to inorganic soil minerals containing hydroxylated Al, Fe or Mn sites (Tipping, 1981; Tipping & Cooke, 1982; Murphy et al., 1994). Due to the formation of organic coatings, the physical and chemical properties of the underlying soil mineral can be completely masked (Hunter, 1980). The adsorbed DOC is capable to interact with heavy metals present in the solution phase via surface complexation reactions. Soil mineral associated DOC can increase heavy metal adsorption by contributing additional, potentially high affinity complexing sites (Davis & Leckie, 1978; Davis, 1984; Zachara et al., 1994). Heavy metals may have a larger affinity (e.g. Cu) for coordination with the chelating group of the adsorbed DOC than with the (hydr)oxide surface sites.

Dalang et al. (1984) investigated the adsorption and complexation phenomena in the ternary system Cu-fulvic acid-kaolinite. Their results showed that the adsorption of fulvic acid only slightly increased the adsorption of Cu, as a result of the formation of complexes between the sorbed fulvic acid and Cu. The relative independence of the adsorption processes of fulvic acid and Cu to kaolinite seems to indicate that fulvic acid and Cu bind to different sites. Results of McBride (1991) showed that Cu is probably not adsorbed at the edges but at one or both faces of the kaolinite particles. Consequently, there may be enough space for the adsorption of fulvic acid to the surface of kaolinite without interfering the adsorption process of Cu. Dalang et al. (1984) also observed that the adsorption of fulvic acids did not result in a loss of its complexing properties. This indicates that the adsorption of fulvic acid does not block the complexing sites of fulvic acid for Cu. Also Zachara et al. (1994) found that few metal complexing sites on the DOC or (hydr)oxide surfaces were consumed in the adsorption of DOC.

The availability of polyvalent cations in soil solution can increase the adsorption of DOC to soil surfaces at near neutral pH, which may result in an enhanced adsorption of Cu. Römken et al. (in review) found that the addition of Ca^{2+} significantly reduced both the DOC and the Cu solution concentration. Figure 7 shows the Cu solution concentration as a function of pH and different electrolyte solutions in the presence of DOC.

The increased removal of DOC has been attributed to the formation of cation bridges. The decrease in Cu concentration cannot be explained with cation exchange processes: in this case an increase in the Ca content should lead to an increase in the Cu solution content as well due to a competition effect between Ca and Cu for binding sites on the DOC (Inskeep & Baham, 1983). The cation exchange mechanism was modelled according to:



Römken et al. (in review) proposed that the DOC removed from the solution by Ca contains the most reactive groups which also contain the largest part of the complexed Cu. The results of Römken et al. (in review) indicate that Ca and Cu apparently occupy different sites on the DOC. This is supported by a study performed by Hering & Morel (1988). Both Cu and Ca exhibit high affinity towards binding DOC but no competitive effects were observed between Cu and Ca. Hence, it was concluded that different ligand sites must be involved in Cu and Ca binding. Figure 8^{a,b} shows the effect of Ca on Cu titrations of humic acids as a function of total Cu.

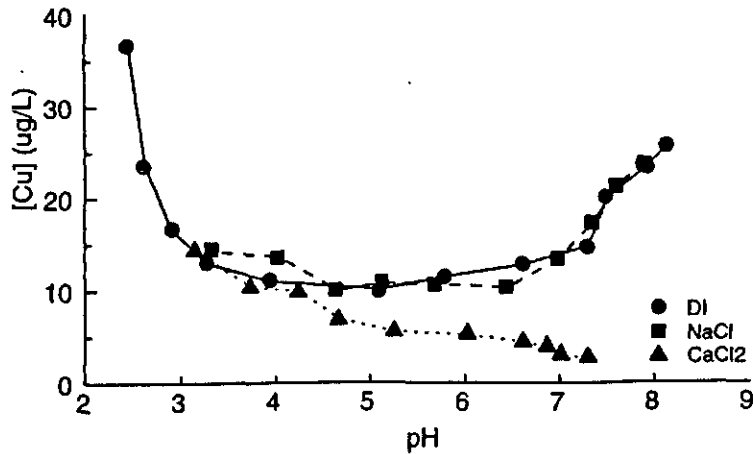


Figure 7. The Cu solution concentration as a function of pH and different electrolyte solutions (de-ionized water (DI), 0.05 N NaCl, 0.05 N CaCl₂) in the presence of DOC (25 mg l⁻¹) (Römken & Nummerdor, in prep.).

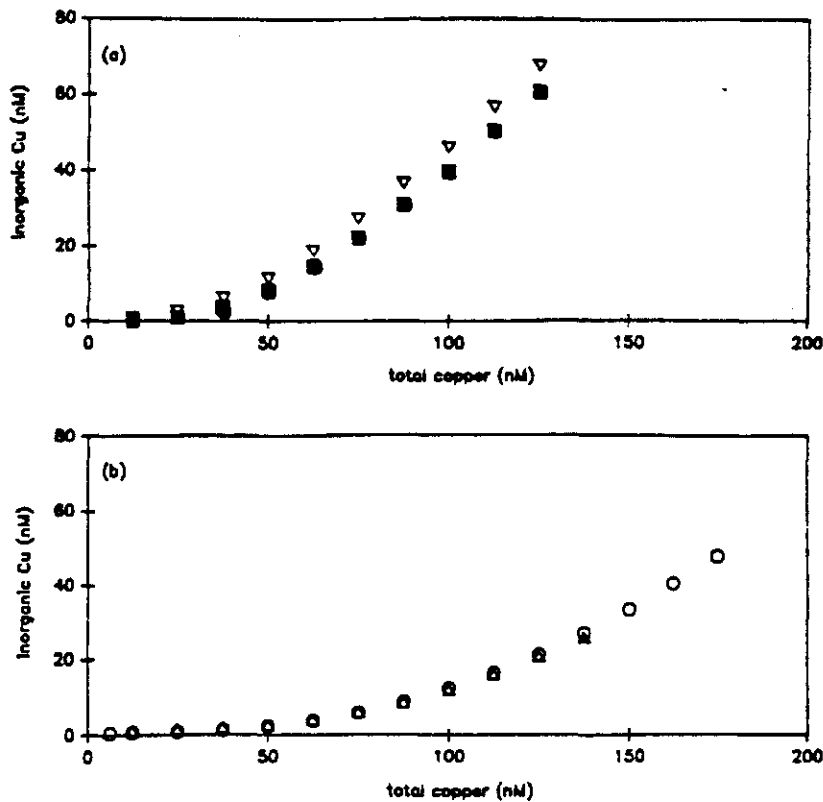


Figure 8^{a,b}. Effect of Ca on Cu titrations of humic acid (a) 0.3 mg l⁻¹, (solid square) no Ca, (open triangle) 10⁻² M Ca, and (b) 0.6 mg l⁻¹, (open circle) no Ca, (open triangle) 10⁻² M Ca (Hering & Morel, 1988).

Cabaniss & Shuman (1988) also reported only slight competition between Cu and Ca for binding sites on the DOC. Results of McKnight & Wershaw (1989) showed a decrease in Cu complexation at low Ca concentration.

However, no further decrease in Cu complexation was observed at increasing Ca

concentrations. This behaviour was attributed to the structural heterogeneity of the Cu binding sites on the DOC and competition of Cu and Ca for only a small fraction of the binding sites with no competition for other binding sites.

5. Case study

Agricultural land is taken out of production and converted to mixed forest after years of intensive farming. Large inputs of animal manure and sewage sludge to the soil caused the Cu content to increase considerably (Van Driel & Smilde, 1990). Especially the less productive soils with low potential for agricultural purposes are converted to forest first (e.g. non-calcareous sandy soils). These soils are characterized by a low organic matter and clay content and, hence a low buffering capacity (Hesterberg, 1993). Therefore, the soil pH is expected to decrease considerably. As a result of liming the soil pH was maintained at values around 5.5 to 6. After termination of liming, as a result of management changes, the soil pH will drop to values around 3.5 to 4 within 60 years (see chapter 1, Figure 1). These pH values are considered natural in many Dutch forests on sandy soils (De Bakker, 1979). Due to the elimination of the only source of Ca in non-calcareous soils (lime), the Ca concentration in the soil solution will decrease considerably. Converting agricultural land to forest can affect both the composition and the amount of soil organic matter. In young forests, leaf litter is sparse and therefore DOC might not be important (Hesterberg et al., 1992). However, as a forest matures a rich organic horizon (Ah, Oh) develops at the soil surface. This organic horizon acts as a source of DOC in the soil solution. Therefore, the DOC solution concentration will increase considerably (see chapter 1, Figure 1).

Due to these changes in soil parameters, the behaviour of Cu accumulated in the topsoil during farming will alter significantly.

The decrease in soil pH is small during the first decade of forestation and is expected to drop to a value around 4.5 within 10 years (Römkens & De Vries, in press). At pH values higher than 4.5, the Cu concentration is controlled by DOC present in the soil solution (Römkens & Nummerdor, in prep.). This means that DOC is able to increase the amount of Cu in solution through the formation of stable aqueous Cu-DOC complexes. The positive charge of Cu is fully compensated through binding with DOC. Therefore, the electrostatic attraction between the complexed Cu and the negatively charged soil surface will decrease, resulting in an enhanced Cu mobility in the soil. Within 30 to 40 years, the soil pH will further drop to values below 4. In this pH region the Cu solution concentration is controlled by the soil pH (Römkens & Nummerdor, in prep.). This means that a decrease in soil pH causes the Cu solution concentration to increase.

Especially the smaller DOC molecules play an important role in solubilizing Cu (König et al., 1986), probably due to the higher number of adsorption sites compared to larger molecules (Schulthess & Huang, 1991). The smaller DOC molecules are retained to a lesser extent by the soil than the larger DOC molecules (König et al., 1986). Guggenberger et al. (1994) observed that Cu preferentially binds to hydrophilic acids present in soil solution. The hydrophilic acid-Cu complexes are very mobile in the soil due to the low amount of hydrophilic acids sorbed by the soil compared to hydrophobic acids (Guggenberger et al., 1994). With decreasing soil pH, the relative importance of the hydrophilic fraction is expected to increase (Guggenberger et al., 1994).

The availability of Ca^{2+} can increase the adsorption of DOC to the solid phase (Tipping, 1981; Tipping & Cooke, 1982) by acting as a bridge between the negatively charged DOC and the negative charge of the soil surface. This process is likely to occur within the higher pH region (near neutral pH) compared to the lower pH region, due to the decrease in net negative surface charge as pH decreases. Because of the preferential binding of Cu to DOC, Ca^{2+} indirectly affects the Cu concentration in soil solution. However, due to the termination of liming the Ca^{2+} solution concentration will decrease dramatically. Because of the diminishing Ca bridging effect, the solubility of DOC will increase in case of converting agricultural land to forest, and will lead to an increase in DOC solution concentration.

Consequently, it can be expected that within the first 10 years of forestation of former agricultural land, the Cu solution concentration and bio-availability will increase. Due to the decrease in soil pH and the increasing DOC concentration, the solubility of Cu increases resulting in increasing Cu solution concentrations. The major part of the Cu in the soil solution, will be present in the organically complexed form. Kerven et al. (1984) measured that of the total Cu amount in soil solution, 60 to 90% was present as organic complexes at natural pH values (3.4 to 3.5). Due to the decrease in Ca^{2+} solution concentration the DOC will remain solubilized, resulting in an enhanced Cu mobility in the topsoil. Due to the complex formation with DOC, the mobility of the DOC-bound Cu is high compared to the mobility of the free ionic Cu. The stable aqueous Cu-DOC complexes will leach to lower soil horizons. Whether the Cu-DOC complex in lower soil horizons will remain in solution or will be retained by the soil surface depends on factors such as the local pH and organic matter content. De Bakker (1979) reported that the pH in Cb horizons (depth 120 to 125 cm) of non-calcareous sandy soils approximated 4.7. This means that a fraction of the Cu-DOC complexes remains solubilized at lower depth and, hence this fraction may ultimately leach to the groundwater.

It can be concluded that the termination of liming will lead to lower Ca^{2+} solution concentrations and consequently higher DOC and Cu solution concentrations which in turn may induce toxic effects in plants and soil organisms and/or enhanced leaching of Cu to the groundwater.

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