Proton buffering and metal mobility in Dutch sandy soils

- modeling laboratory and field data -

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Ellen P.M.J. Fest

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Abstract

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Recently, advanced geochemical models have become available to describe solid/ solution partitioning of cations between various reactive surfaces in soils and soil solutions. These geochemical models can reproduce the behavior of heavy metals in soils. Since large areas struggle with diffuse heavy metal pollution, these models may also be used to predict the possible effects of land use changes on accumulated heavy metals. In this study, geochemical models have been tested on both laboratory and field data, considering important properties of the soil in relation to heavy metal binding.

Both the desorption of heavy metals and soil pH as a result of acidification of the soil have been studied under laboratory conditions. The results of acidification experiments have been described by a combination of geochemical models. Below pH 4, the model underestimated the pH, because the buffering by Al-hydroxide minerals was not incorporated in the modeling approach. Model predictions, however, gave satisfying results; the model was able to reproduce pH and heavy metal concentrations over a wide pH range and metal content.

In sandy soils, the behavior of heavy metals is largely controlled by the soil organic matter (solid and dissolved). Distribution of organic matter between the solid and solution phase is essential for adequate predictions of total dissolved metal concentrations. The effect of solution extraction, solid/solution ratio, pH and storage time on the DOC composition and extractability of DOC and metals was studied. In general, the metal/DOC ratio decreased at increasing solid/ solution ratio, indicating that additional released DOC at higher solid/solution ratio has a lower metal binding capacity. Furthermore, the extracted DOC mainly comprised of fulvic acids and small hydrophilic acids.

At an experimental site, leaching of heavy metals under field conditions was studied for 22 years. The Cd, Ni and Zn content decreased significantly during the studied period in the low pH (~pH 4) plot, whereas the Cu and Pb content stayed rather constant throughout the years. Transport calculations show a good prediction of the leaching of Cd, Ni Pb and Zn after 22 years. Field plots with elevated Cu content, however, showed a strong decrease of Cu content after 22 years, which was not influenced by pH. The considerable leaching of Cu could not be predicted by the model under reasonable assumptions of soil properties. Most likely, Cu distribution over all binding sites in the top soil layer takes several years after application of Cu.

The effect of land use and groundwater depth on Al, pH and DOC concentration in groundwater of Dutch sandy soils has also been studied in this research. Both pH and DOC concentration play a major role in the speciation of Al in solution. Complexation of Al with DOC is shown to be an important factor for Al concentrations, especially at high DOC concentrations as was found for agricultural-phreatic groundwater.

The current available advanced geochemical models can be applied to a broad range of soil-metal studies as was shown by the results of this thesis. However, the assumptions and simplifications necessary for each application should be considered carefully. The applied geochemical modeling in this thesis is a powerful tool for scenario studies considering the bio-availability and mobility of heavy metals.

Keywords: proton buffering, heavy metals, sandy soil, organic matter, metal speciation, humic acid, fulvic acid. aluminum, groundwater.

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> Soms zijn de zee en ik alleen
> En is zij net als iedereen
> Als ik onder haar golven wil
> Dan laat ze mij er niet doorheen
> Dat is de zee
> En eigenlijk zijn wij allemaal net zo
> Dat we ver onder de spiegel willen gaan
> Naar daar waar alle liefde zit
> Maar we zijn te bang om 't toe te staan
>
> Wie neemt me mee?
> Wie durft te beginnen?
> Wie laat mij zien hoe mooi een mens kan zijn van binnen?
> Wie leidt de weg?
> Wie durft te voelen?
> Ik draag het licht en jij hebt 't zicht
> Kom met me mee en hou van de zee
>
> *- John Ewbank - Trijntje Oosterhuis - De zee -*

CHAPTER 1

General introduction

Ellen P.M.J. Fest

1.1 Introduction

An increasing agricultural area is set aside and converted into nature. This conversion leads to changes in soil properties, like increase of organic matter content, acidification or decline of nutrient content. To quantify effects of potential acidification of these soils, understanding of the proton buffering is necessary. Former agricultural soils can have elevated metal contents as a result of the manure and fertilizer application as well as from local pollution sources. Mobility and related transport of metals in acidifying soils is relevant with respect to the protection of groundwater resources and surface waters. Sandy, non-calcareous soils are susceptible to acidification and consequently to metal leaching from these soils. These recent newspaper headings "Cadmium in groundwater Belgian border districts" (Spits, 2007) and "Uranium found in groundwater close to old dumping sites in Brabant" (De Volkskrant, 2007) show that still problems with heavy metal pollution occur and emphasize the importance of understanding the behavior of heavy metals in soils. The complexity of the interaction between metal ions and soil particles is reflected in Figure 1.1. Metal ions can be present in adsorbed or free form and the various particles can also interact with each other. Consequently, modeling studies on the behavior of heavy metals under natural conditions can provide useful understanding of the behavior of these metals. Natural soils are more and more considered as a combination of different sorbing surfaces. This study shows the application of mechanistic modeling in prediction of heavy metal behavior in sandy soils. In addition, the focus in soil risk assessment shifts more and more towards bioavailable fractions of pollutants in contrast to the current legislation based on total contents.

Knowledge on behavior and speciation of metals in soils could be very useful for practical application in relation to various environmental studies and policy plans. The applied mechanistic modeling approach in the present study can be used to determine the chemical form of the contamination present in soil, groundwater and surface water. The present approach is not restricted to land soils but can also be applied to aquatic systems like lakes and rivers, describing the exchange of substances between e.g. the river bed and the surrounding water. In perspective of the European Water Framework Directive (EWFD) (in Dutch: 'KaderRichtlijn Water') surface water and groundwater have to meet certain quality criteria. For water councils the bioavailability of both metals and organic con-

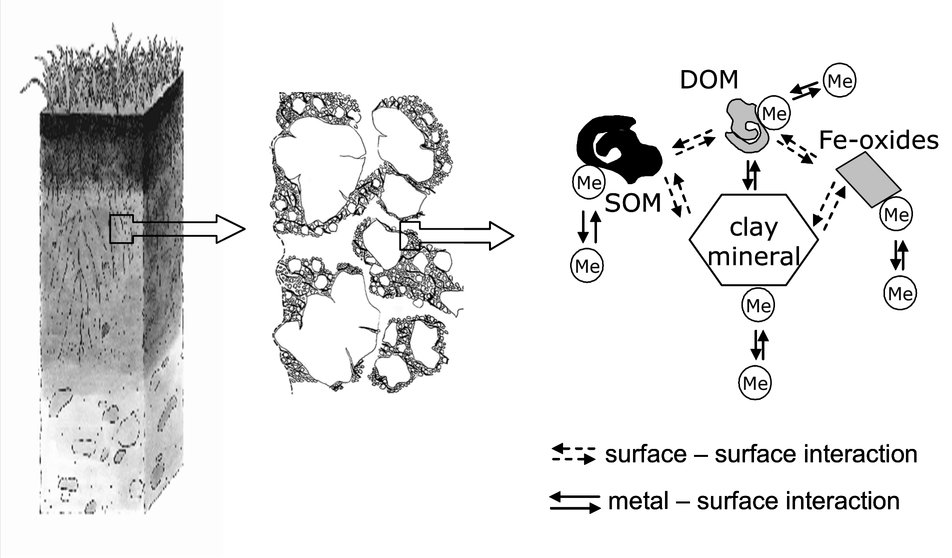

Figure 1.1: A schematic visualization of the interactions between the soil system (various reacting surfaces) and reactive metals in the soil system (SOM = soil organic matter; DOM = dissolved organic matter).

taminants is an important consideration with respect to the efficient use of the 'environment-euro' efficiently. Furthermore, for land soils, scenario based studies could give insight in effects of land use changes (nature development, inundation of floodplains etc.) on existing contaminations. Such scenario studies considering the bio-availability and mobility of heavy metals can be of interest for water councils, landscape managers, nature conservation organizations and local and regional authorities and fit in large policy plans like 'Groen voor Blauw projecten', 'Ruimte voor de Rivier' and realization of the 'Ecologische Hoofdstructuur'.

1.2 Land use changes

As a result of EU policy to reduce both arable crop production and dairy products, more and more arable lands are taken out of production and converted into forests, pasture, heath lands or wetlands. Figure 1.2 shows that for the Netherlands about 0.04% of the country area (~14,000 ha) was withdrawn from agriculture in the period 1999 - 2000. This set aside area was partly converted into forest and partly converted into other types of nature (e.g. wetlands or heather). Afforestation of agricultural land can affect soil properties because liming and fertilization are terminated. The termination of these activities results in acidification, depletion of base cations and accumulation of organic matter in the soil (Andersen *et al.*, 2002). Furthermore, also the areas with intensive livestock breeding have been reconstructed as a result of the swine fever outbreak in 1997. Within this integrated area development the major themes were e.g. environment, nature and landscape (Boonstra *et al.*, 2007).

Soil acidification by mineralization, root respiration and proton exudation (De Vries and Breeuwsema, 1986; Strobel *et al.*, 2001) can be enhanced by atmospheric deposition of acidifying substances (SO_2, NO_x and NH_3). Since 1980 the potential acid deposition has been decreased with 50% for the Netherlands as a result of the decreased SO_2-emission (Figure 1.3). Intensive agriculture results in locally increased N-deposition (RIVM, 2001). The soil matrix is able to buffer incoming protons by exchanging protons for other cations. Various buffering substances play a role in the overall buffering process, each at different pH levels (Table 1.1). In sandy soils that are low in clay content and contain some organic matter, protons are mainly buffered by ion binding processes to natural organic matter (humic substances) and weathering of amorphous and crystalline compounds. Protons can easily and quickly be exchanged by ion exchange. However,

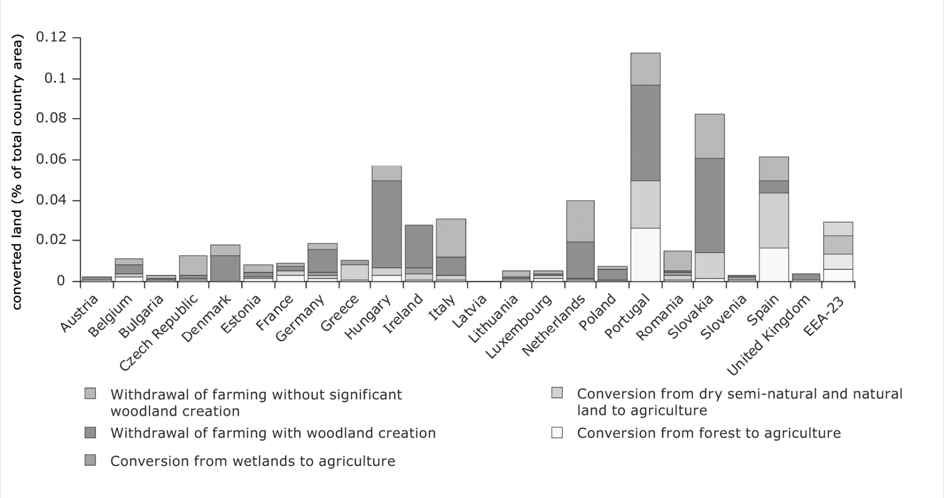

Figure 1.2: Conversions between agriculture, forest and natural land (in ha yr^{-1}) for the period 1999-2000 expressed as % of the total country area (Copyright EEA, Copenhagen, 2005; http://www.eea.europa.eu).

this process strongly decreases the base saturation of the soil (CEC-Ca/Mg + $2H^+$ ↔ CEC-H_2 + Ca/Mg^{2+}). At low pH and low base saturation of the soil, dissolution of organic and inorganic amorphous Al-hydroxides becomes the dominant proton buffering process. Furthermore, below pH 3.8 the dissolution of Fe-(hydr) oxides starts playing a role in the buffering of protons.

Termination of lime application and conversion of arable fields to forest results in acidification of the soil as a result of the above mentioned processes. Römkens *et al.* (1995) showed that the pH of forested former arable fields (sandy soils) decreased from a pH of about 6 to 4 in a period of 30 to 40 years. This pH decrease indicates that the soil acidifies relatively fast, because sandy soils have a relatively low buffering capacity. Another study (Andersen *et al.*, 2002) showed significant differences in pH between arable fields and comparable forested fields. The soil was more acid in the forest fields; the acidification was limited to only the A and B horizon, indicating that the acidification front had not reached the C horizon during the 34 years of forestation. Johnston *et al.* (1986) showed that an arable plot that was transformed into deciduous woodland showed a considerable decrease of the pH, from 7.1 to 4.2 in 100 years. The contribution of acidifying processes was estimated and direct after transformation of the arable land (~1890) the soil derived natural proton sources turned out to be the largest contributor to acidification of the soil. Later on (~1980) deposition of acidifying substances was the most important proton source for these soils.

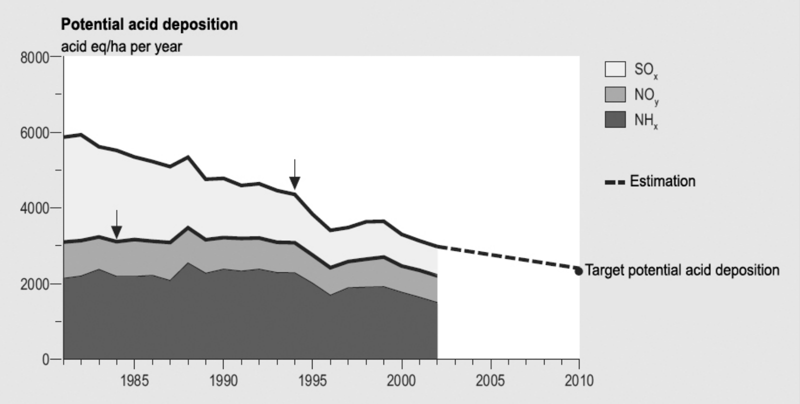

Figure 1.3: Trends of acidifying deposition in the Netherlands since 1980 and target for potential acid deposition in 2010. Contribution of various acidifying substances (SO_x, NO_y and NH_x) is shown (RIVM, 2004).

A shift from agricultural practices to natural vegetation can also lead to development of a litter layer. An increase in litter production affects also the DOC production, resulting in increased leaching rates of DOC from the O-layer (Fröberg *et al.*, 2005).

Besides these naturally occurring processes like the decrease in pH and the development of a litter layer, specific circumstances can be created in order to develop a certain type of nature. For instance, restoration of peat bogs requires hydrological measures. Often natural vegetation requires soils with a low nutrient status. To create circumstances for these kinds of nature, the soils need to become poorer; this can be achieved by removing the top soil. Upon removal of the fertile upper layer a nutrient poorer layer will become the toplayer. Wetting of soils can cause an increase in pH, an increase in organic matter content, an increase in DOC and results in a decrease of the redox status (Ter Meulen-Smidt *et al.*, 1996). All these changes in soil properties will have an effect on the behavior of heavy metals present in the soil. Naturally occurring processes as well as processes created by human intervention need to be considered in predicting the effects of nature development on sandy soils with elevated metal contents.

Table 1.1: Buffering substances in the soil and their pH range (from Bloom, 2000).

buffering substance	pH range	proton accepting/releasing reaction
magnesiumcarbonate ($MgCO_3$)	> 9.5	precipitation and dissolution
soil organic matter	3.5 – 10	ionization of carboxyl and phenolic groups
Fe/Al-(hydr)oxides, allophane, imogolite and silicate clay edges	3.5 – 10	ionization and protonation of surface hydroxyl groups
limestone ($CaCO_3$)	7 – 9.5	dissolution and precipitation
permanent charge on silicate clay minerals	3.5 – 5	ion exchange of H^+ and Al^{3+} with base cations
$Al(OH)_3$ – soil organic matter	5 – 8	precipitation of organic bound Al^{3+} as $Al(OH)_3$ of dissolution of $Al(OH)_3$ by organic acids
interlayer Al in 2:1 clays	5 – 7	precipitation or dissolution of interlayer $Al(OH)_3$
Al – soil organic matter	< 5	carboxyl H^+ exchange with Al^{3+}
irreversible dissolution of high activity silicate clays and allophane	< 3.5	consumption of H^+ upon dissolution of Al^{3+}
very slow irreversible weathering of primary silicate minerals	3 – 10	consumption of H upon dissolution of Ca^{2+}, Mg^{2+}, Na^+ and K^+

1.3 Elevated metal contents/ diffuse metal pollution

During the past several decades the soil heavy metal content in the Netherlands has increased as a result of atmospheric deposition, application of waste products and sewage sludge, application of manure and fertilizer and deposition of river sediments. This widespread diffuse contamination of soils with heavy metals is mostly caused by long-term supply of low amounts. Figure 1.4 gives an indication of the diffuse pollution of soil by various metals; this figure shows the percentage of soil samples within a certain area that is above the Dutch target value for soils.

Copper and Zn end up in animal manure because these metals are added to the cattle feed in order to enhance various body functions, e.g. the digestion of food. However, only a small fraction of the added Cu and Zn is taken up in the animal's body and the major fraction of the dietary Cu is thus excreted (90-95%;

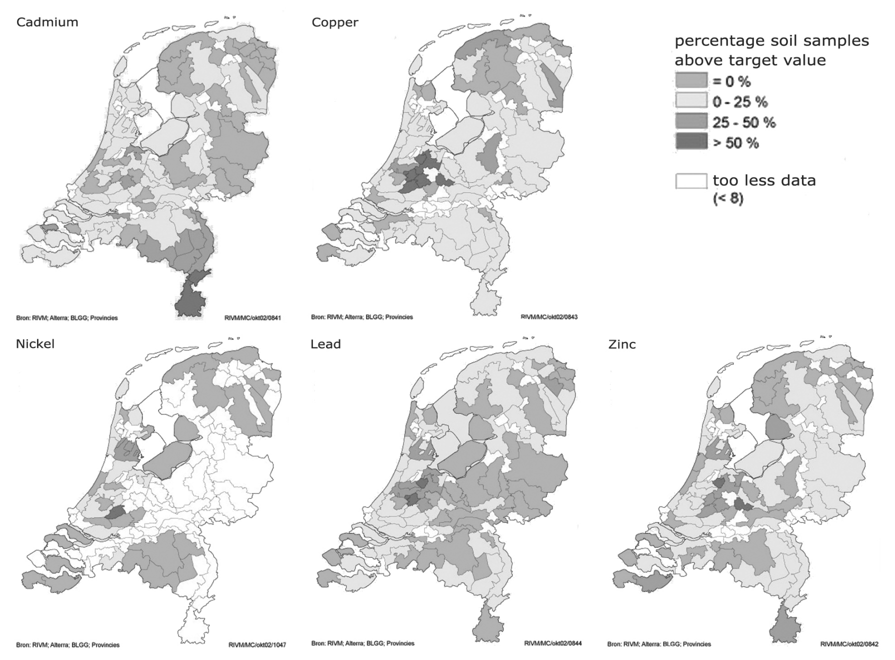

Figure 1.4: Overview of the diffuse metal pollution in the upper soil layer in the Netherlands. Areas show the distribution of samples (from monitoring networks) above the Dutch target value for the heavy metals Cd, Cu ,Ni, Pb and Zn (taken from (Van Drecht *et al.*, 1996)). Soil samples have been taken from agricultural and natural fields.

(Payne *et al.*, 1998)). In this way, the application of manure on agricultural fields can result in increased Cu and Zn contents in these soils. A study by Brock *et al.* (2006) showed that Cu and Zn have been accumulated in soils with repeated manure applications; however the Cu and Zn levels did not yet reach toxicity levels. Also inorganic fertilizers often contain heavy metals (e.g. Cd, Cu, Zn) and are widely applied on agricultural fields (Moolenaar and Lexmond, 1998).

Large areas along the Dutch – Belgium border show elevated heavy metal contents in soils as a result from the non ferrous metal industry that was situated in this area since the 19th century. Activities at the metallurgy plants like ore melting caused the spreading of metals like Zn, Cd, Pb and Cu in a wide region (Bosmans and Paenhuys, 1980). Emitted metals were transported into the surrounding areas by water and wind. Deposited metals can be in the form of primary metal bearing mineral, slag particles, metal particles and metal oxides (Hilber *et al.*, 2007). Nowadays, most metal smelters have been closed or modernized their processes and reduced their emission of metals (Horckmans *et al.*, 2006).

Table 1.2 shows that atmospheric deposition was the major source of Pb deposition. Removing Pb from petrol has resulted in a drastic decrease in the Pb-deposition. Concentrations of Pb have declined from 55 ng m^{-3} in 1990 to less than 10 ng m^{-3} in 2005 (MNP, 2006).

Besides manure application and atmospheric deposition, heavy metals can also enter the agricultural soils via flooding and addition of sludge. For example the river water of the Rhine transports yearly about 3 million tons of sediments to the Netherlands (Schröder, 2005) and that in the Netherlands $40 \cdot 10^6$ m^3 of sediments have to be dredged every year (Vermeulen, 2007). With these sedi-

Table 1.2: Relative contribution of fertilizer application and atmospheric deposition to the diffuse load of metals of agricultural soils in 1989 (Van Drecht *et al.*, 1996).

sources	**Cd**	**Cu**	**Pb**	**Zn**
	- - - - - - - -	- - - - (%) - - - -	- - - - - - - -	- - - - - - - -
manure	30	88	17	73
inorganic fertilizer	55	3	8	14
atmospheric deposition	13	3	71	5
other	2	6	4	8

ments also heavy metals are deposited in the floodplains, riverbeds, harbors and lakes. The dredged sediments have been widely applied to agricultural fields because of the high nutrient content of the sediments. For centuries, these sediments have been used as natural fertilizer, but since the late 1970s it became clear that the river sediments were heavily polluted and application of the sediments on agricultural land was no longer permitted (Vermeulen, 2007).

1.4 Modeling adsorption of metals in soils

At first, a distinction should be made between the total amount of heavy metals present in the soil and the amount of metals that plays a role in solid/solution partitioning. Metals can be present incorporated in the mineral particles of the soil. These metals are unavailable for exchange processes with the soil solution. Also as a result of ageing, metals can become unavailable. This process is ascribed to the slow incorporation of metals in oxide structures (Degryse *et al.*, 2003). Only extreme conditions, like strong destructive solutions can destroy these formations and increase the availability of the heavy metals (Gupta *et al.*, 1996; Gleyzes *et al.*, 2002). To identify the reactive metal content of the soil, often 2 M HNO_3 (Weng *et al.*, 2001a; Kalis *et al.*, 2007) or 0.43 M HNO_3 (Boekhold *et al.*, 1993; Tipping *et al.*, 2003; Dijkstra *et al.*, 2004; Römkens *et al.*, 2004) are used. Furthermore, the various reacting fractions of heavy metals in soils are often measured with sequential batch extractions, in which a series of extractions solutions are applied. Every extraction solution is considered to extract a certain fraction of the metals based on a certain binding strength. However, these fractions are operationally defined, and exact chemical form in which the metals are present (speciation) is not reflected (Voegelin *et al.*, 2003).

Besides total reactive metal content, major interest is concerned on the actual concentrations of metals and their chemical form (speciation) in the soil solution (speciation). Numerous approaches have been used to measure metal speciation in the soil solution and surface waters (Van Leeuwen *et al.*, 2005; Sigg *et al.*, 2006; Kalis *et al.*, 2006a) Besides, several extraction methods have been in use as a measure for the available metal concentration in the soil (Gupta *et al.*, 1996; Houba *et al.*, 1996; Van Erp *et al.*, 1998; Gleyzes *et al.*, 2002).

To predict solid/solution partitioning of metals empirical models have been derived from various datasets (Anderson and Christensen, 1988; Elzinga *et* *al.*, 1999; Sauvé *et al.*, 2000; Römkens *et al.*, 2004; Meers *et al.*, 2006). These empirical models relate metal concentrations in soil solution with the total metal content and various soil properties (e.g. pH, OM content and clay content). In order to get reliable model parameters, the model should be derived from a dataset covering a wide range of soils and concern only a few input parameters (Römkens *et al.*, 2004). However, for every element the relation between metal content and metal concentration has to be derived. And as results of the single species relationships, the competition with protons and other cations is not taken into account in such relationships. Furthermore, no distinction is made between specific and electrostatic binding of the metal ions on the adsorption sites. These regression relationships are therefore less suitable to predict effects of changes in soil properties, like pH and solution composition.

At present, more sophisticated models, describing the metal sorption on soil particles from a more mechanistic point of view, are available. These surface complexation models (SCMs) have shown to be able to describe metal binding on specific surfaces like organic matter, clay and Fe-oxides (e.g. Dzombak and Morel, 1990; Hiemstra and Van Riemsdijk, 1996; Bradbury and Baeyens, 1997; Tipping, 1998; Kinniburgh *et al.*, 1999). When assuming that the soil consists of various sorbing surfaces, single SCMs can be combined to describe the total sorption onto the soil surface. This idea of combining the single sorption models to describe the total soil surface was already studied by Bibak (1994) and further tested by Vermeer *et al.* (1999). They investigated the sorption of metals on pure metal oxides and humic acid (HA) and on a mixture of these substances. Moreover, it was shown by Pagnanelli *et al.* (2006) that proton and Pb binding on a mixture of clay minerals could be predicted by the sorption onto single clay minerals. However, Vermeer (1999) concluded that some deviations occur from the additivity rule resulting from the mutual effect of the sorption surfaces on each others their binding affinities. The idea that a combination surface complexation models can describe the metal binding properties of soil systems was further examined by several research groups (Tipping *et al.*, 1995; Weng *et al.*, 2001a; Cancès *et al.*, 2003).

At this moment there are two important models describing the surface complexation of metals onto organic matter in soils, viz. NICA-Donnan (Kinniburgh *et al.*, 1999) and Model VI (Tipping, 1998). An important difference between these two model is the assumption on the distribution of the functional groups of the organic matter. The NICA-Donnan model assumes a continuous distribution of the functional groups (Kinniburgh *et al.*, 1999) while Model VI assumes a discrete distribution of the functional groups of the organic matter (Tipping, 1998). Besides the specific binding to the functional groups, both models also account for the electrostatic binding as a result of the negative charge of the humic molecules; electrostatic binding is described by both models also in a different way. These models have been shown to be able to describe metal binding on isolated FA and HA from soils and waters (e.g. Christensen *et al.*, 1999; Pinheiro *et al.*, 2000; Osté *et al.*, 2002a). Both SCMs take into account the competition between cations and heterogeneity of organic matter. To apply these models to a wide variety of organic matter, generic parameters have been derived from large datasets (Tipping, 1998; Milne *et al.*, 2001; Milne *et al.*, 2003).

For the complexation of metals with Fe-oxides often a distinction has been made between crystalline and amorphous oxides. One way to calculate metal sorption on Fe-oxides is the CD-MUSIC model (Hiemstra and Van Riemsdijk, 1996; 1999). This advanced SCM takes the variation in reactivity of oxygen groups into account. The charge of the adsorbed ions is divided over a surface and an intermediate plane. The model is thoroughly tested for the adsorption of cations and anions on goethite (e.g. Rietra *et al.*, 2001; Weerasooriya *et al.*, 2002; Ponthieu *et al.*, 2006; Stachowicz *et al.*, 2006). Recently the model was tested for metal ion binding to both crystalline (goethite) and amorphous (HFO) Fe-oxides (Ponthieu *et al.*, 2006) and constants have been derived for Fe-oxides as a whole. Besides the CD-MUSIC model the complexation of metal ions with Fe oxides can also be described with the model from Dzombak and Morel (1990), the two site surface complexation diffuse double layer (DDL) model. Dijkstra *et al.* (2004) used this model to account for the total sorption on Fe oxides in contrast to Weng *et al.* (2001a). Weng *et al.* (2001a) used this model only for the adsorption on hydrous ferric oxide (HFO); HFO is assumed to be a model substance for the amorphous forms of Fe oxides in the soils. The above shown differences in model choice showed that it is not straightforward which model should be used. The used models should have a minimum number of adjustable parameters and therefore a large dataset of generic parameters should be available for application in field situations (Ponthieu *et al.*, 2006).

The binding to clay silicates such as kaolinite, illite, chlorite and montmorillonite is often based on thermodynamic cation exchange models (Bolt, 1982). Furthermore, Bradbury and Baeyens (1997) developed a model for metal sorption on Na-montmorillonite taking into account cation exchange and surface complexation mechanisms. However, in the multi-surface modeling approach sorption onto clay is accounted purely electrostatic (Tipping *et al.*, 1995; Weng *et al.*, 2001a). Following Weng *et al.* (2001a), the sorption of metals onto clay minerals is described by a Donnan model. This approach is justified by the fact that at lower pH (< 6) the electrostatic interaction is the main process for sorption on clay minerals. At higher pH, specific sorption of metal ions onto the edges of the clay minerals becomes more important but is assumed to play a minor role in the studied samples (Weng *et al.*, 2001a). And besides, the clay content in the studied sandy soils is very low and therefore considered less important.

In this study we followed the approach of Weng *et al.* (2002b) to describe proton buffering of soil samples and combined multi-component metal (de) sorption. A conceptual scheme of the modeling approach, the so-called multi-surface model is shown in Figure 1.5. With this multi-surface model approach we are able to gain insight in the effects of changes in soil properties such as pH, organic matter content or metal content. Until now, only metal concentration have been predicted at constant pH, however with this multi-component approach it is possible to predict also the pH from the distribution of protons over the various surfaces and the soil solution.

At present more and more progress has been achieved in the application of mechanistic modeling of the interaction between the various soil surfaces. For instance, humic molecules (HA and FA) can bind strongly on (hydr)oxides and these associations occur as colloids in soil systems and surface waters (Van Riemsdijk *et al.*, 2006). Both particles are present in natural soils and affect each others metal binding affinity as a result of mutual interaction. For many years numerous studies have been conducted on the interaction between humic molecules and metal-oxides in which theories were developed further (Tipping, 1981; Davis, 1982; Murphy *et al.*, 1992; Gu *et al.*, 1994; Spark *et al.*, 1997; Vermeer *et al.*, 1998; Filius *et al.*, 2000; Weng *et al.*, 2006). Weng *et al.* (2005) distinguish models that do not take electrostatic interaction between humics and Fe-oxides into account, models that make assumptions on the amount of surface species including electrostatic interactions and models that originally have been developed for adsorption of polyelectrolytes on surfaces. Recently, progress has been made in the modeling of the interaction between humic molecules and metal-oxides by combining the NICA-Donnan model with the CD-MUSIC model (Van Riemsdijk *et al.*,

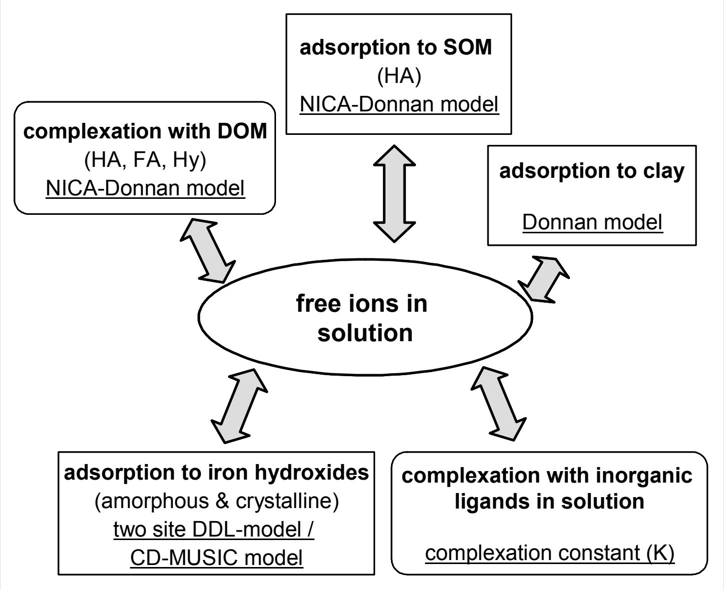

Figure 1.5: Conceptual scheme of the multi-surface model. (modified from Weng *et al.* (2002)).

2006). Although major steps have been made in de the development of the modeling of the humic – Fe-oxide interaction, these interactions have not been taken into account yet in the modeling work of this thesis.

1.5 Policy / Soil critical limits

With the Lekkerkerk affaire in 1980 (Van de Griendt and Janssen, 2004), the first serious soil pollution case in the Netherlands, the research on soil pollution increased enormously and the discussion on soil quality regulations started and still soil pollution and related effects receive serious attention. Since then several soil quality standards have been formulated. At first, the ABC values had been derived in 1982. After that, the ABC values have been followed up by reference values in 1988. These standards were based on the presence of heavy metals in "not polluted" areas, mainly natural areas. Standardization for clay and organic matter content was also introduced to compare the different soil types in the Netherlands. Subsequently, the eco-toxicological knowledge increased and based on that the target and intervention values (1991/1994) have been derived. Eventually soil remediation objectives (1999) have been introduced. For every type of land use, soil standards have been derived, which indicate only the minimal level of soil quality necessary for that type of land use (Souren, 2006).

All these standards have in common that they relate total metal content in soil samples to the soil standards. In practice not the total metal content in soil samples determines the risk of the contamination, but the speciation of the metal is the relevant parameter in risk assessment.

There is growing evidence that the free metal ions are the most available forms for uptake by organisms, the so called bioavailable fraction (Kalis *et al.*, 2006b). Furthermore, the mobile metal fraction is of great interest for the transport of metals further downward in the soil. So, therefore the actual metal concentration in the soil solution is of great importance in soil risk assessment. Both leaching of metals to groundwater and surface water and uptake of metals by organisms are thus highly dependent on the speciation and distribution of metals over the soil surface and soil solution.

The multi surface model, as discussed earlier, could predict risks of metal leaching upon changes in the land use. This study focuses on the change from agricultural land into natural land, but other changes are also possible and can be approached in the same way. Effects of land use changes are determined by the type of nature that will be developed and needs thorough characterization of the occurring changes upon nature development. After defining changes in soil properties upon nature development, the total effect on metal leaching of these changes can be predicted. As discussed before, in case of nature development on former agricultural soils, the pH will drop and the organic matter content will build up. These changes could lead on the one hand to increased metal mobility as a result of the lower pH and the increased amount of DOC in the soil solution. On the other hand the total adsorption surface increases as a result of the increased organic matter content. With the approach presented in this thesis it is possible to predict the overall effect of these changes on the metal mobility in soils.

The use of mechanistic modeling and the multi surface approach can subsequently also be of interest for the derivation of new soil policy. This modeling approach provides insight in the distribution of metals over the various soil surfaces, which can differ enormously between the various soil types. In order to extrapolate this molecular approach to macro scale studies the amount of model parameters should be limited to general soil characteristics determined by standard techniques. Generic parameters for all used mechanistic models should be available for all relevant metals.

Furthermore, as a result of this total system approach in potentially redox reactions can also be taken into account, which makes application of this modeling approach possible for application to sludge and sediments. This could be a very powerful methodology for determining effects of sludge application on soils.

1.6 Outline of the thesis

The overall objective of this thesis is to test the applicability of mechanistic modeling of proton and metal behavior in sandy soils in the context of land use changes. First, the application of mechanistic modeling was shown in laboratory experiments and applied to field data. Second, DOC was studied in both laboratory experiments and field data and its importance in modeling metal behavior was shown.

Following this introductory chapter (**chapter 1**), **chapter 2** focuses on the acidification of sandy soil samples in a laboratory experiment. Soil samples with different pH and metal content were acidified by adding acid to the soil solution at successive steps. pH, cation concentration and metal leaching were modeled with the multi-surface modeling approach. Up till now the multi-surface model was only used at fixed pH, but in this chapter we showed that this multi-surface model is able to predict the pH change upon acid addition. Besides, the effect of increased amount of acidification in the system on macro elements (Ca, Mg and Al) and heavy metals (Cd, Cu, Ni, Pb, Zn) was predicted.

The importance of the amount of DOC and its composition for metal speciation is shown in **chapter 3**. DOM and metal concentrations were studied by different extraction methods. Salt concentration and solid/solution ratios were varied. Furthermore, the amount and composition of DOM in combination with free metal concentrations were studied in a soil column experiment. To study the free metal concentration the soil column was combined with a Donnan Membrane Technique (DMT) cell. Samples from a long term field experiment with different pH levels and metal content were used.

In **chapter 4 and 5**, we tested the applicability of mechanistic modeling for metal leaching in field situations. The leaching of heavy metals from a sandy, agricultural field was studied for 22 years. Heavy metals (Cd, Cu, Ni, Pb and Zn) were present in this field at background level, and also Cu contaminated plots are present. Leaching of heavy metals was predicted assuming that organic matter was the major sorbing phase. The sensitivity of the model predictions was tested for changes in pH, organic matter content and DOC concentration. These soil properties showed variation in the field during the studied time period and are also expected to be important variables in land use changes.

Finally, **chapter 6** focused on the speciation of Al in groundwater at different land use types and at different depths. Al is an important cation in environmental research because of its potential toxicity at elevated concentrations. The speciation of Al was calculated by taking besides inorganic complexation also the organic complexation with DOC into account. Free Al concentrations were compared to the solubility of various forms of Al containing minerals, like gibbsite and amorphous $Al(OH)_3$.

> Yesterday is history, tomorrow a mystery.
> Today is a gift. That’s why we call it the present!
> *- Winnie the Pooh -*

CHAPTER 2

Proton buffering and metal leaching in sandy soils

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Abstract

Recent developments in acidification research focused on the leaching of metals from contaminated soil. In this paper the buffering of sandy soils upon acidification is studied in relation to the release of major (Al, Ca, Mg) and trace metals (Cu, Cd, Ni, Zn) from the soil reactive surface. The buffering process and the (de) sorption of metals are described with a mechanistic multisurface model, expressing the sorption onto different soil surfaces (organic matter, clay, Fe (hydr)-oxides). The pH of sandy soil samples is predicted upon proton addition in combination with the behavior of major and trace metals. Acidification of contaminated sandy soil samples, with different pH levels and metal contents, is performed in a flow-through reactor by flushing the samples with acid solution. Acidification has taken place in successive steps of proton addition and followed by sampling. Prediction of pH upon acidification with a multisurface model gives satisfying results for all samples studied. The pH is modeled reasonably well between pH 6 and 4. Below pH 4 the predicted pH values are slightly too low, probably due to the buffering by Al-containing minerals (e.g., Al hydroxide), which are not included in the model. Desorption of major and trace metals upon pH decrease is, in general, predicted well, within a factor of 1-5 on a linear scale. Overall prediction of proton buffering in combination with desorption of metals in sandy soil samples, over a wide pH range and metal content, is done quite well for the studied metals with the multisurface model.

2.1 Introduction

In view of groundwater protection it is of great importance to predict the effect of acid deposition on the soil and further transport of acid pore water to aquifers. Although acid deposition has decreased in many parts of the world during the past decade, the soil still receives a considerable amount of acid (e.g., 3000 eq acid (ha yr)$^{-1}$ in the Netherlands) (RIVM, 2004). Until now soil pH was usually assumed constant for metal mobility predictions, but for estimating the effect of acid deposition on metal mobility it is also necessary to predict the pH. For example, agricultural areas are set aside and will be converted to, for example, forests. Under agricultural use the pH of these soils is buffered by liming but these soils will acidify after abandoning as a result of natural and anthropogenic acidification (Hesterberg, 1993; Römkens and De Vries, 1995; Moolenaar *et al.*, 1998). Agricultural soils often have elevated heavy metal contents in addition to atmospheric deposited metals due to the application of fertilizers such as manure and sludge for many years (Hesterberg, 1993; Römkens and Salomons, 1998).

Often solid/solution partitioning of heavy metals in soil is described using empirically derived relations between metal concentration and various soil properties (e.g., pH, soil organic matter (SOM), CEC, clay, total metal content) (Elzinga *et al.*, 1999; Sauvé *et al.*, 2000; Tipping *et al.*, 2003; Voegelin and Kretzschmar, 2003; Römkens *et al.*, 2004). The advantage of this method is the relatively simple way to predict metal concentrations using a small set of soil properties. From a mechanistic point of view a so-called multisurface model is introduced, based on the additivity of the adsorption onto different surfaces occurring in soil samples (Davis *et al.*, 1998; Weng *et al.*, 2001a; Weng *et al.*, 2002b; Cancès *et al.*, 2003; Tipping *et al.*, 2003; Dijkstra *et al.*, 2004). This means that every surface in the soil sample contributes to the adsorption of ions in the same way as when the surface is isolated. The adsorption of ions to the different surfaces is described by surface complexation models (SCMs) developed for the binding to a specific single surface, e.g., NICA-Donnan (Kinniburgh *et al.*, 1999), Model VI (Tipping, 1998), and CD-MUSIC (Hiemstra and Van Riemsdijk, 1996; , 1999). Good results have been achieved in predicting metal concentration with this multisurface approach for a wide pH range and for different metal contents, but still the pH is assumed constant in the model. To predict the effect of acidification of soils and aquifers on the pH it is necessary to describe proton binding on different soil surfaces as a function of acid input.

Acidification has been studied extensively during the past 30 years, but the research mainly focused on the effect of acid rain on trees and the increased Al concentrations in acid forest soils. A brief overview of the acidification research is given by Mol *et al.* (2003). Several studies showed that Al desorbs from both the organic and inorganic pool under acid conditions (Berggren and Mulder, 1995; Van der Salm *et al.*, 2000; Gustafsson *et al.*, 2001), while others assume that only $Al(OH)_3$ mobilizes Al under acid conditions (Hansen and Postma, 1995; Weng *et al.*, 2001a; Kjøller *et al.*, 2004). Besides the role of the solid phase (organic and inorganic) the Al solubility is also influenced by DOM, forming insoluble complexes under specific conditions (Jansen *et al.*, 2002). Lofts and coauthors (2001b) tried to predict pH and Al concentrations in acid forest soils, assuming that Al solubility is controlled by sorption to organic matter. They show good descriptions of pH and Al solubility with WHAM-S (Tipping, 1994) (model V (Tipping and Hurley, 1992)), but fitting is necessary for every single soil horizon.

To predict the effect of acid deposition on soils, the proton buffering of sandy soils at different pH levels is studied. This study focuses on noncalcareous sandy soils with a field pH from 6 to 4, which will experimentally be acidified to pH 3. Proton buffering will be characterized by reactions with various solid phases, without considering the slow weathering of minerals. Above pH 4 proton adsorption is considered to be the main buffering process, and below pH 4 the main proton buffering process is assumed to be the dissolution of minerals, resulting in increased Al concentrations. The aim of this study is two-fold: (i) to determine proton and metal binding/release on different soil surfaces as a buffer mechanism between pH 6 and 3 with a mechanistic multisurface model and predict the soil pH upon acid addition, and (ii) to predict major metal (Al, Ca, Mg) and trace metal (Cd, Cu, Ni, Zn) concentrations upon acid addition. A distinction is made between major and trace metals because the major metals are affecting proton adsorption by competitive binding. Therefore, an acidification experiment is performed in the laboratory and these results are compared with field data. Samples are taken from an experimental field site characterized by a pH range together with a range of copper contents, established more than 20 years ago. The experimental results, both pH and metal concentrations, are modeled with the multisurface model as described by Weng *et al.* (2001a), using general soil characteristics and generic model parameters completely without fitting any parameter.

2.2 Model description

For modeling the speciation of metals in soils, a multisurface approach introduced by (Lofts and Tipping, 1998; Weng *et al.*, 2001a; Weng *et al.*, 2002b; Cancès *et al.*, 2003; Dijkstra *et al.*, 2004; Lumsdon, 2004) was used. Weng and coauthors (Weng *et al.*, 2001a; 2002b) used the approach to calculate the distribution of trace metals over the reacting surfaces (i.e., soil organic matter, clay minerals, and amorphous and crystalline iron oxides), as well as the effect of dissolved organic matter on the metal speciation in solution. Dijkstra and coauthors (2004) also used this modeling approach. They left out the distinction between amorphous and crystalline Fe (hydr)oxides, but included the adsorption to amorphous Al hydroxides using an elevated amount of hydrous ferrous oxide (HFO) as a substitute. Distribution of metals and protons over the soil and the soil solution was calculated. Another study (Cancès *et al.*, 2003) takes SOM, HFO, and hydrous manganese oxides (HMO) into account as reacting solid surfaces. This combination of surfaces shows good predictions of metal concentrations in a soil column experiment. In this study we choose to follow the approach of Weng and coauthors (2001a). The interaction between inorganic and organic surfaces, which can influence the proton and metal adsorption to these surfaces (Vermeer *et al.*, 1999; Lumsdon, 2004; Weng *et al.*, 2005), is not taken into account in the present study.

The modeling work is performed with the computer program ECOSAT (Keizer and Van Riemsdijk, 1998). The equilibrium between the sorption on the different surfaces and the solution composition are calculated by the model, by combining the used surface complexation models. Binding to organic matter (solid and dissolved) is described with the NICA-Donnan model (Kinniburgh *et al.*, 1999). Humic acid is taken as a reference substance for solid organic matter (SOM) with a maximum binding capacity (Q_{max}) of 31% relative to pure humic acid (Weng *et al.*, 2001). Previous research showed that some researchers assumed dissolved organic matter (DOM) to consist of 100% total reactive surface for proton and metal binding (Cancès *et al.*, 2003; Dijkstra *et al.*, 2004), while others assumed DOM to have a certain inert part (Lofts *et al.*, 2001a; Weng *et al.*, 2001a; Tipping *et al.*, 2003). In this study we followed the approach of Weng *et al.* (2001a) in which DOM consists of 65% fulvic acid and 35% inert organic matter. Generic parameters of the NICA-Donnan model for humic acid and fulvic acid are used (Milne *et al.*, 2001; Milne *et al.*, 2003). Both SOM and DOM are assumed to exist for

50% of organic C (Schnitzer and Khan, 1978; Dijkstra *et al.*, 2004). The amount of DOM is based on the average dissolved organic carbon (DOC) concentration throughout the experiment (15 mg DOM L^{-1}).

The sorption onto clay mineral surfaces is described with a Donnan model as has been done by others (Tipping, 1994; Weng *et al.*, 2001a; Dijkstra *et al.*, 2004). This model simulates the nonspecific (electrostatic) sorption onto a negatively charged clay mineral surface. We take 0.25 mol kg^{-1} as an average for the charge of the surface; the Donnan volume is set at 1 L kg^{-1}, assuming that illite is a representative clay for the used samples (Breeuwsma *et al.*, 1987). The exact clay mineral composition is not known for the used soil samples, and other clay minerals could affect the charge of the clay surface (Bain *et al.*, 2003). The amount of clay surface is based on the clay content in the samples determined with the sieve and pipet method (Houba *et al.*, 1997).

Iron hydroxides are divided into two types of surfaces, i.e., amorphous and crystalline Fe (hydr)oxides. HFO was assumed to be the model surface for the amorphous Fe (hydr)oxides and binding to this surface will be described with the two-site diffuse double layer surface complexation model (DDL) (Dzombak and Morel, 1990; Weng *et al.*, 2001a). Goethite was taken as a model surface for crystalline Fe (hydr)oxides. Binding to goethite is described with the CD-MUSIC model (Hiemstra and Van Riemsdijk, 1996; 1999). Parameters for both the DDL and CD-MUSIC models are taken from Weng *et al.* (2001a). Unfortunately both databases are not complete for all metals studied in this research (for DDL Mg and Al parameters are missing and for CD-MUSIC Mg, Al, and Ni parameters are missing). However, lacking binding constants will result in only a small underestimation of the total binding for some metals and corresponding overestimation of binding of other metals and protons, when Fe (hydr)oxides are assumed not to be the major binding surface for the studied ions in this system (Weng *et al.*, 2001a). Parameters of the used sorption models are given in Appendix I. The amounts of amorphous and crystalline Fe are taken from Weng *et al.* (2001a), based on DCB (dithionite-citrate-bicarbonate) and oxalate-extractable iron (Houba *et al.*, 1997). For the exact calculation procedure of the amounts of goethite and HFO from the Fe (hydr)oxide content see Weng *et al.* (2001a).

The first step in modeling the behavior of protons in the acidification experiment is to calculate the initial total amount of protons in the system at the initial pH. The second step in modeling is to calculate the pH with an increasing amount of protons in the system due to the acid additions. The total amount of protons at each addition step is calculated from the total proton content of the system (calculated) at the previous step decreased with the amount of protons taken away by sampling and increased with the amount of protons added at the corresponding step in the experiment. The total amount of metals in the system is also corrected for the amount of metals taken away by sampling during each step.

2.3 Experimental section

Soil samples were taken from the Wildekamp experimental field established in 1982 (Lexmond, 1980; Temminghoff *et al.*, 1997) near Wageningen. This pasture field consists of randomized plots with different pHs (4.0, 4.7, 5.4, and 6.1) and Cu levels (addition of 0, 250, 500, and 750 kg $CuSO_4$ per hectare).

Samples at a depth of 0-20 cm were taken in September 2002 from the plots with high (H) and low (L) pH combined with a low (I) and high (II) Cu-level, resulting in 4 different samples namely high pH-low Cu (H-I), high pH-high Cu (H-II), low pH-low Cu (L-I), and low pH-high Cu (L-II). Several samples were taken from each plot and mixing of the subsamples resulted in a representative sample for each plot. Some soil characteristics were determined and are shown in Table 2.1, including sample codes. Soil samples were air-dried and sieved (< 2 mm) before analysis. The listed pH values were measured in a 0.01 M $CaCl_2$ suspension (Houba *et al.*, 2000). Actual cation exchange capacity (CEC) was determined with an unbuffered $BaCl_2$ solution (Houba *et al.*, 1997). The amount of exchangeable metals (Ca, Mg, Na, K, and Al) was measured in the $BaCl_2$ extract. Organic matter content was determined by loss-on-ignition (Houba *et al.*, 1997). The amounts of Fe (hydr)oxides (amorphous and crystalline) and clay are also given in Table 2.1. The reactive metal content was determined by 0.43 M HNO_3 extraction (soil/solution ratio (SSR) 1:10). This method was used by others (Boekhold *et al.*, 1993; Tipping *et al.*, 2003; Dijkstra *et al.*, 2004; Römkens *et al.*, 2004) as a measure for the active metals.

Acidification experiments were performed with the four soil samples described above. All samples were air-dried and sieved (< 2 mm). Those 4 samples have resulted in a duplicate for the high (H) and low (L) pH samples and for low (I) and high (II) Cu samples. A flow-through reactor was used based on Grolimund *et al.* (1995). The reactor system consisted of a column containing the

Table 2.1: Characteristics of the soil samples used (mean with standard deviation in brackets (n=2))[a]

	low pH- low Cu	high pH- low Cu	low pH- high Cu	high pH- high Cu
sample code	L-I	H-I	L-II	H-II
pH-CaCl$_2$	4.1 (0.01)	5.3 (0.04)	3.9 (0.02)	5.2 (0.21)
CEC (mmol$_+$ kg^{-1})	16.2 (0.16)	35.2 (2.28)	15.5 (0.07)	29.5 (1.10)
exchangeable metals (mmol$_+$ kg^{-1})				
Ca	4.54 (0.23)	26.17 (1.68)	3.12 (0.05)	17.95 (2.75)
Mg	1.50 (0.09)	6.01 (0.70)	1.09 (0.03)	3.70 (2.79)
K	0.05 (0.05)	0.32 (0.04)	0.07 (0.03)	0.71 (0.66)
Na	0.02 (0.03)	0.05 (0.02)	0.07 (0.06)	0.07 (0.12)
Al	10.4 (-)	1.6 (-)	8.9 (-)	1.8 (-)
OC (%)	3.1 (0.1)	3.4 (0.0)	3.3 (0.0)	3.4 (0.1)
clay (%)[b]	4.2 (-)	4.2 (-)	4.2 (-)	4.3 (-)
Fe-OX (g Fe kg^{-1})[b]	2.08 (-)	2.02 (-)	2.23 (-)	2.10 (-)
Fe-DCB (g Fe kg^{-1})[b]	2.34 (-)	2.34 (-)	2.28 (-)	2.28 (-)
metal content				
Cu (mmol kg^{-1})	0.49 (0.00)	0.12 (0.00)	1.24 (0.00)	1.32 (0.01)
Cd (µmol kg^{-1})	0.69 (0.00)	1.69 (0.01)	0.31 (0.01)	1.30 (0.04)
Zn (µmol kg^{-1})	26.3 (0.32)	104.4 (1.59)	15.6 (1.74)	53.5 (0.29)
Ni (µmol kg^{-1})	3.6 (0.01)	10.3 (0.20)	2.0 (0.05)	11.4 (0.3)

[a] Explanation of used methods is given in the text.

[b] Clay content and Fe-content (oxalate and DCB extractable) are taken from Weng *et al.* (2001a) since Fe-(hydr)oxides and clay content are expected to be constant in time (< 25 yr).

soil sample. From a reservoir the acid solution was circulated through the soil column. Pumps were responsible for circulating the solution and Teflon tubing connected various parts. From previous research it appeared that shaking of soil particles with acid could lead to higher dissolution rates due to abrasion of the surfaces (Van Grinsven and Van Riemsdijk, 1992). Therefore we haven chosen to use this flow-through approach in which the soil sample was flushed continuously with the solution without moving the soil particles. Another advantage was that the reservoir could be used to measure the pH, to take samples and to add new solution to the system.

The soil samples were equilibrated with 0.01 M NaCl before acidification by circulating this solution for 24 h. The acidification experiment consisted of a number of repeated steps of acid addition, down to at least pH 3. During each step the samples were injected with a HCl solution and 0.01 M NaCl as background electrolyte. Protons were added in successive steps of 0-10 mmol kg^{-1} soil, leading to a total amount of added protons after the final addition of 40 mmol kg^{-1} soil for the low pH samples and 50 mmol kg^{-1} soil for the high pH samples.

After each acid addition the acid solution was flushed through the sample for 24 h at a rate of 4 mL min^{-1}, resulting in about 165 times flushing of the total solution through the column per addition. From tests with this system 24 h seemed to be long enough to reach a (semi-) equilibrium, although slow dissolution processes will continue. These slow acid buffering processes were beyond the scope of this study. After the equilibrium period, the pH was measured and part of the solution was removed. The sampled solution was filtered with a 0.45 µm nitrate-cellulose membrane filter and analyzed for major metals (Al, Ca, Mg, K, Na) (ICP-OES, SPECTRO Spectroflame), trace metals (Cu, Cd, Pb, Ni, Zn, Mn, Fe) (ICP-MS, Perkin-Elmer Elan 6000), and DOC (TOC analyzer, Skalar SK12).

2.4 Results and discussion

A clear difference of at least one pH unit in pH-$CaCl_2$ is found between the high pH and the low pH samples (Table 2.1). The difference between the high and low pH samples is also shown in the actual CEC, because at low pH more protons are bound to the organic matter, neutralizing part of the CEC. In the high pH samples, Ca is the major metal on the particle surface in contrast to the low pH samples in which Al is the major metal on the particle surface. The contribution of K and Na to the total exchangeable metals is very low in both high (H) and low (L) pH samples. The amount of clay and organic matter is almost equal in the four samples and this holds also for the content of Fe (hydr)oxides (amorphous and crystalline). In addition to the pH, the samples vary also in Cu content (Table 2.1). The high pH-high Cu (H-II) sample does have a Cu content about ten times higher than the high pH-low Cu sample (H-I), whereas at low pH (L-I and L-II) the difference in Cu content is only 2.5 times. The low Cu (I) samples show a difference in Cu content, with the low pH sample (L-I) having a higher Cu content than the high pH sample (H-I). A closer look at the other trace metals (Cd, Zn, Ni) shows a distinctly higher metal content for the high pH samples, because at low pH a considerable amount of these metals is leached out. This was also expected for the low Cu (I) samples; we expect some pollution from neighboring plots, because this difference is not found by others (Temminghoff *et al.*, 1994; Weng *et al.*, 2001a). The observed difference in Cu content is found back in the leaching during acidification. For the high Cu (II) samples, samples with almost equal Cu content were chosen, so the difference between the low and high pH samples is not found in these samples.

Proton buffering

The acidification experiments show the effect of an increasing amount of added protons on the solution pH (Figure 2.1); a gradual decrease of the pH upon acid addition is observed. For the low pH (L) samples the total decrease in pH is less than for the high pH (H) samples, because low pH samples already start at pH 4 and slowly decrease to pH 3 and lower. The pH of the high pH samples decreases from 6 to 3 as a result of 50 mmol protons added per kg of soil. This amount of acid seems quite high for acid deposition in natural environments, but is necessary to reach levels of pH 3 in the experiment. From yearly deposition data in The Netherlands (5500 acid eq (ha yr)$^{-1}$ in 1982 decreasing to 3000 acid eq (ha yr)$^{-1}$ in 2002 (RIVM, 2004)) it is calculated that the cumulative amount of protons that is deposited in The Netherlands is about 28 mmol kg^{-1} in 20 years, considering protons to influence the upper 20 cm. This shows that the amount of protons added in the experiment is almost twice as much as what was atmospherically deposited in the last 20 years. With the current acid deposition (~3000 acid eq (ha yr)$^{-1}$) this period would even be longer (~50 years). This calculation depends, of course, thoroughly on the local acid deposition and the thickness of the soil layer that is considered.

In the inset of Figure 2.1 the high pH samples (H) are shifted in a way that the behavior of H and L samples can be compared below pH 4.5. This means that the experimental data points of the H samples are shifted 20 mmol kg^{-1} to the left. Comparing the behavior of the H and L samples below pH 4.5 in the laboratory and the field, it is found that both curves end at the same pH with equal amounts of protons added (below pH 4.5). But between the starting and ending point the curves show a slightly different shape. The low pH samples (L) tend to give a stronger decrease in the beginning of acidification, while the high pH samples (H) show a more gradual decrease during acidification, probably because the occupation of the soil reactive surface is different for the H and L samples. This

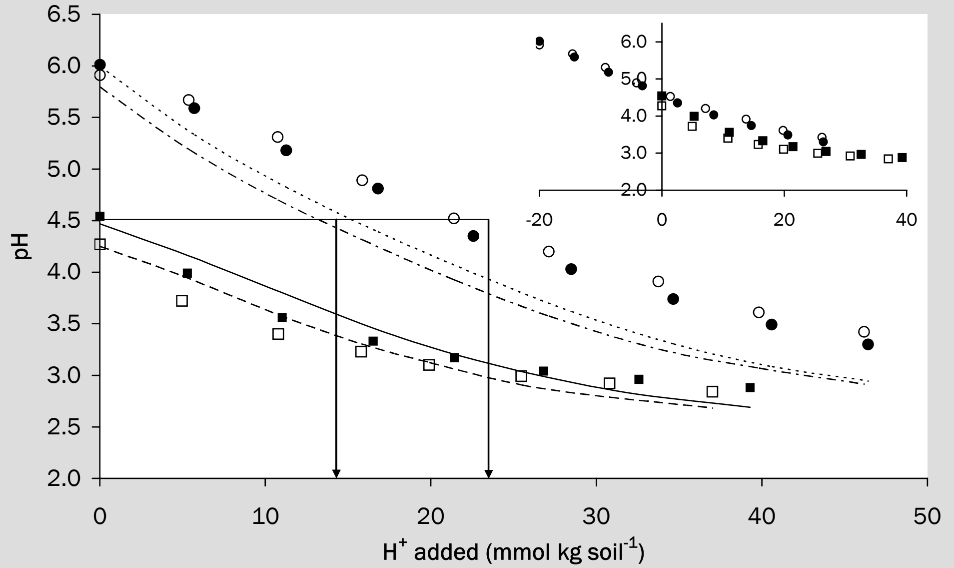

Figure 2.1: pH in soil solution as a function of protons added to the samples during the acidification experiment. Experimental results: ■ L-I; □ L-II; ●H-I; ○ H-II. Model predictions: the black line represents L-I, the black dashed line represents L-II, the black dotted line represents H-I, and the black dashed-dotted line represents H-II. Arrows indicate amount of protons needed to acidify high pH samples to ~pH 4.5 for both experimental and modeling results. Inset: experimental results for H-samples shifted 20 mmol kg^{-1} to the left.

implies that the effect of acidification in the field (L samples) has not resulted in a clear difference in buffering behavior at low pH (pH < 4) compared with samples acidified in the lab experiment.

As a result of acidification, cations are exchanged for protons on the soil reactive surface of the soil samples, leading to a decrease of the actual CEC. The difference between the actual CEC of the high and low pH samples is about 15-20 mmol kg^{-1} (Table 2.1) and this is almost equal to the amount of protons added to the high pH samples to reach pH 4.5 (~20 mmol kg^{-1}). This implies that acidification to pH 4.5 in the lab resulted in the same decrease in actual CEC as observed in the field. Proton binding by surface complexation may thus be considered the main buffering process between pH 6.5 and 4.

Modeling proton buffering

Combining the general soil properties together with the model parameters in the multisurface model and using the increasing amounts of protons added to the soil samples, the pHs of the system during acidification can be calculated by the model. The results of these calculations are shown by the lines in Figure 2.1. Prediction of pH for the low-pH samples is done quite well, with a small overestimation at the beginning of the acidification and a small underestimation of the pH at the end. The pH prediction for the high pH samples shows immediately from the beginning an underestimation of the pH, meaning that too few protons are exchanged with cations. This underestimation might suggest that the total binding capacity of the surfaces used in the model is too low. First we have to take a look at the behavior of the major metals, to get a better idea about what is responsible for the underestimation of the pH.

Figure 2.2 shows the leaching of major metals (Ca, Mg, Al) during the acidification experiments. For those three metals the total amount of leached metals increases during acidification, but some difference is shown between the metals and the different samples. Both Ca and Mg seem to reach a plateau value, which can be explained by the running out of exchangeable cations. In contrast, Al tends to increase exponentially, because Al can also be released during dissolution of Al-containing minerals. Dissolution of, e.g., Al hydroxides starts playing a role in buffering below pH 4 (Ulrich, 1991); in Figure 2.2c pH 4 is indicated by the arrows and shows the moment when the Al concentration starts to increase.

Due to the multicomponent character of the model, the behavior of major metals upon acidification is also described by the model. The Ca concentration is predicted very well for the low pH samples (L), but for the high pH samples the concentration is modeled too high. The overprediction arises from the predicted high initial concentration, as the trend during acidification is quite good. The prediction of the Mg concentration shows a slightly different result: a considerable difference is shown between the 2 high pH (H) samples, which is due to the large difference in Mg content (6.0 and 3.7 mmol kg^{-1}).

In Table 2.2 the distribution of the protons and the metals over the different specified surfaces is presented for the initial situation and after acidification based on the model calculation. If Ca and Mg in the high pH samples are examined in the initial situation, it is found that clay is an important binding surface besides organic matter, whereas the other metals are mainly adsorbed to organic

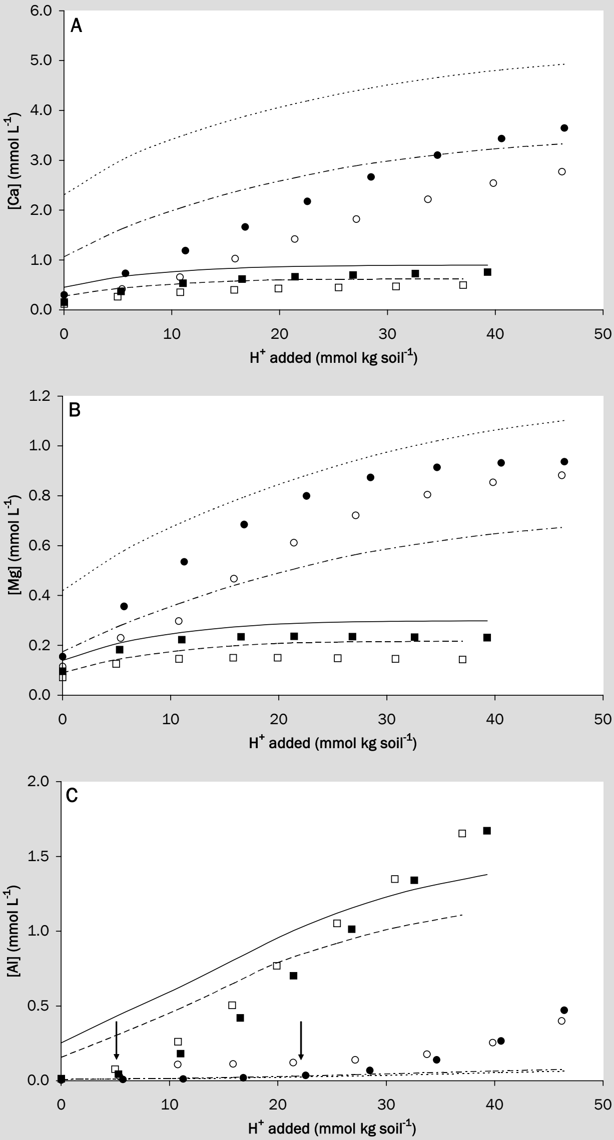

Figure 2.2: Cumulative concentration of major cations in the soil solution as a function of total protons added to the samples during the acidification experiment: (A) Ca, (B) Mg, and (C) Al. Experimental results: ■ L-I; □ L-II; ●H-I; ○ H-II. Model predictions: the black line represents L-I, the black dashed line represents L-II, the black dotted line represents H-I, and the black dashed-dotted line represents H-II. The arrows refers to pH 4 condition for low pH samples (L) and high pH samples (H).

matter. Probably the explanation for the deviation of the pH prediction in those high pH samples lies in this observation. Due to a possible underestimation of the surface charge of clay, less binding capacity on clay is available in the model compared to the samples, resulting in more competition between the protons and Ca and Mg for the surface sites on organic matter. This effect is not seen in the low pH samples because less Ca and Mg are bound to the soil reactive surface. Increase of the surface charge for the clay surface will result in reduction of the binding capacity of organic matter because the total capacity of reactive surface must be constant and equal to the measured CEC. Another way to improve the pH prediction is increasing the binding capacity of organic matter. As was shown by Weng and coauthors (2001) the binding capacity of organic matter is found for the same samples to be between 16 and 46% of the maximum binding capacity of humic acid. Somewhat higher values for the reactive fraction of organic matter are found by Cancès *et al.* ((2003); 50%), Dijkstra *et al.* ((2004); 46 ± 14%) and Gustafsson *et al.* ((2003); 18-84%). Increasing binding capacity of SOM to 46% of the maximum binding capacity of HA implicates a decrease in the surface charge of clay to keep the total exchange capacity constant. This gives an improved prediction of pH and a better prediction of the initial Ca and Mg concentration. As a result of the increased available surface of organic matter more adsorption sites for metals are available and therefore the metal leaching is reduced somewhat (see Appendix I). The increase of the binding capacity of organic matter will have a less pronounced effect on the prediction of the pH for the low pH samples. An underestimation of the CEC could be responsible for the deviation between predicted pH and experimental results as a result of the applied method to determine CEC (Benedetti *et al.*, 1996). A remark must be made regarding the sorption of cations to clay. An electrostatic binding model is used to predict binding of cations onto clay (for low pH levels), although with this model cation exchange at specific adsorption sites is not taken into account (Baeyens and Bradbury, 1997; Bradbury and Baeyens, 1997).

Besides Ca and Mg, the third studied major metal, Al plays a role in proton buffering, through exchangeable Al and dissolution of Al-containing minerals. The effect of Al on pH might be smaller than assumed because released Al from Al (hydr)oxides could again be sorbed on the soil reactive surface releasing protons and other cations. Not enough Al is present at the soil reactive surface to reach the measured concentrations (Figure 2.2c); therefore it is assumed that dis-

Table 2.2: Distribution (%) of sorbed protons and metals and protons and metals complexed with DOM over the specified surfaces in the initial situation and after acidification based on the model calculations.[a]

		Step 0					Step end				
		Fe-ox. (crys)	*clay*	*Fe-ox. (am)*	*SOM*	*DOM*	*Fe-ox. (crys)*	*clay*	*Fe-ox. (am)*	*SOM*	*DOM*
L-I	H	<1	<1	**7**	**91**	<1	<1	**2**	**8**	**89**	<1
	Ca	<1	**36**	<1	**63**	<1	<1	**57**	<1	**43**	<1
	Mg	<1	**30**	<1	**69**	<1	<1	**54**	<1	**45**	<1
	Al	<1	**23**	<1	**76**	<1	<1	**63**	<1	**36**	<1
	Cu	<1	<1	<1	**99**	<1	**1**	**5**	<1	**94**	<1
	Cd	<1	**2**	<1	**67**	**31**	<1	**10**	<1	**55**	**35**
	Ni	<1	**3**	<1	**97**	<1	<1	**25**	<1	**74**	<1
	Zn	<1	**4**	<1	**96**	<1	<1	**28**	<1	**72**	<1
L-II	H	<1	<1	**6**	**92**	<1	<1	**2**	**7**	**90**	<1
	Ca	<1	**36**	<1	**63**	<1	<1	**57**	<1	**42**	<1
	Mg	<1	**32**	<1	**68**	<1	<1	**54**	<1	**45**	<1
	Al	<1	**26**	<1	**73**	**1**	<1	**63**	<1	**36**	**1**
	Cu	**1**	<1	<1	**98**	<1	**1**	**8**	<1	**90**	<1
	Cd	<1	**2**	<1	**68**	**30**	<1	**8**	<1	**57**	**35**
	Ni	<1	**3**	<1	**97**	<1	<1	**23**	<1	**77**	<1
	Zn	<1	**4**	<1	**96**	<1	<1	**25**	<1	**74**	<1
H-I	H	<1	<1	**3**	**96**	<1	<1	**1**	**7**	**91**	<1
	Ca	<1	**24**	<1	**75**	**1**	<1	**61**	<1	**38**	<1
	Mg	<1	**16**	<1	**83**	<1	<1	**60**	<1	**39**	<1
	Al	<1	<1	<1	**99**	<1	<1	**61**	<1	**38**	**1**
	Cu	<1	<1	<1	**100**	<1	<1	**2**	<1	**97**	<1
	Cd	<1	<1	<1	**79**	**20**	<1	**16**	<1	**51**	**33**
	Ni	<1	<1	<1	**99**	<1	<1	**39**	<1	**61**	<1
	Zn	<1	<1	**2**	**97**	<1	<1	**44**	<1	**55**	<1
H-II	H	<1	<1	**3**	**96**	<1	<1	**2**	**7**	**90**	<1
	Ca	<1	**26**	<1	**73**	**1**	<1	**67**	<1	**32**	<1
	Mg	<1	**19**	<1	**80**	<1	<1	**66**	<1	**33**	<1
	Al	<1	<1	<1	**99**	<1	<1	**71**	<1	**28**	**1**
	Cu	<1	<1	**1**	**98**	<1	<1	**14**	<1	**84**	<1
	Cd	<1	<1	<1	**76**	**23**	<1	**15**	<1	**50**	**36**
	Ni	<1	<1	<1	**99**	<1	<1	**46**	<1	**53**	<1
	Zn	<1	<1	<1	**99**	<1	<1	**48**	<1	**51**	<1

[a] Fractions larger than 1% are shown in bold. Fe-ox. (crys) refer to crystalline Fe-(hydr)oxides and Fe-ox. (am) refer to amorphous Fe-(hydr)oxides.

solution of Al-containing minerals plays a role. However this is not taken into account in present study. To improve the prediction of proton buffering the dissolution kinetics of Al-containing minerals need to be taken into account below pH 4.5.

Desorption of heavy metals

The elegancy of the approach presented is that it leads straightforwardly to the calculation of the trace metal concentrations associated with the pH change. The results for Cu are shown in Figure 2.3a for all four samples. The model describes the experimental results well: the trend is very good and the final concentrations are within a factor 1.5. Care should be taken if pH is not predicted exactly right, e.g. a slightly underestimated pH will result in slightly too high predicted metal concentrations. However, the model shows very good predictions for a wide

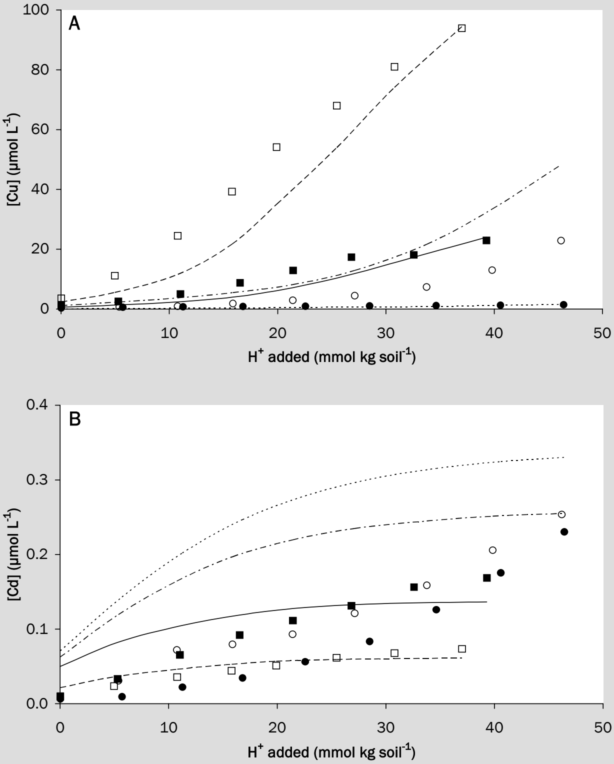

Figure 2.3: Continued on the next page

range of initial Cu contents, varying from 0.12 to 1.32 mmol kg^{-1}. Soil organic matter is the main binding surface for Cu (Table 2.2). At low Cu contents relatively less Cu desorbs as a result of acidification in relation to high Cu contents (Table 2.3) due to a stronger binding at lower Cu contents.

As shown for Cu, the concentrations of other metals (like Zn, Cd, Ni) are also calculated upon acidification with the multisurface model. The trend of the Cd concentration (Figure 2.3b) is predicted wrong at high pH. According to the model the Cd concentration seems to reach a maximum level at the end of the

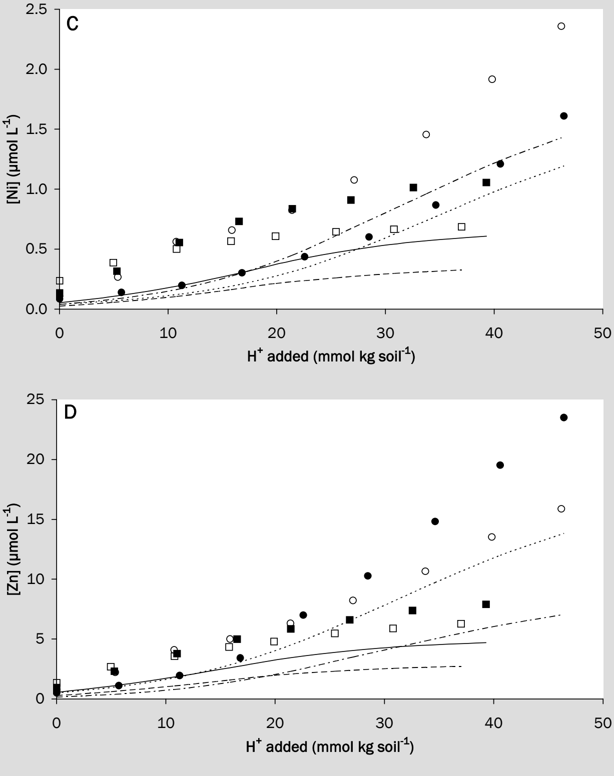

Figure 2.3: Cumulative concentration of heavy metals in the soil solution as a function of total protons added to the samples during the acidification experiment: (A) Cu, (B) Cd, (C) Ni, and (D) Zn. Experimental results: ■ L-I; □ L-II; ●H-I; ○ H-II. Model predictions: the black line represents L-I, the black dashed line represents L-II, the black dotted line represents H-I, and the black dashed-dotted line represents H-II. The arrows refers to pH 4 condition for low pH samples (L) and high pH samples (H).

experiment, which suggests an exhaustion of Cd on the soil reactive surface. This is shown in Table 2.3; according to the model calculation almost all Cd is leached out during the experiment. When Table 2.2 is consulted it is found that Cd is sorbed for a distinct part to DOM. Since DOM is taken away by sampling, a substantial amount of Cd is assumed to be taken away by sampling. Probably the total amount of DOM taken away during the experiment is too high, because an average concentration of DOM during the experiment is taken as a constant amount of DOM per step.

The model predicts the Ni concentration (Figure 2.3c) quite well for the high pH-low Cu (H-I) sample. For the high pH-high Cu (H-II) sample the Ni concentration is slightly underestimated (less than a factor 2), whereas the trend of the model predictions agrees with the experimental results. The same is observed for the low pH (L) samples. Organic matter appears to be the main binding surface for Ni according to Table 2.2. Table 2.3 shows that a considerable amount of Ni has been leached during acidification (~70%), except for sample H-I (~50%).

The model shows a reasonable prediction of the Zn concentration for the low pH (L) samples (Figure 2.3d). The model prediction for the high pH (H) samples shows an underestimation of the Zn concentration by a factor of 2.5, however the trend of the predictions is quite reasonable. A possible reason for the underestimation of the leached Zn could be the dissolution of Zn layered double hydroxides (Zn-LDH). These precipitates could be present in soil samples at near neutral pH and will dissolve when the pH decreases (Voegelin and Kretzschmar, 2005). As for Cu and Ni, organic matter is the main binding surface for Zn (Table 2.2). After acidification, a considerable amount of Zn was leached (57-84%, Table 2.3).

Using a multisurface model to predict pH upon acidification gives encouraging results, but a more detailed study of the binding surfaces and determination of them could improve the results. The concentrations of the major and trace metals studied are in most cases predicted well, but some are underestimated. The NICA-Donnan parameters for organic binding are derived from a small dataset for some metals, so the accuracy of the parameters can be doubted. Another reason for the discrepancy is that the initial content of reactive metal is not always estimated correctly. For Cd, adsorption to DOM appears to be the reason for the bad prediction of the trend. SOM is the main binding surface for the metals in these soils, because of the large binding capacity. This is also valid for the proton binding, and the OM content of this type of soils is therefore of great

Table 2.3: Percentage reactive trace metals (Cu, Cd, Ni, Zn) leached out during the acidification experiment.[a]

sample	Cu (%)	Cd (%)	Ni (%)	Zn (%)
L-I (low pH-low Cu)	18	98	78	84
L-II (low pH-high Cu)	30	97	74	82
H-I (high pH-low Cu)	5	96	48	57
H-II (high pH-high Cu)	23	99	70	73

[a] The total amount of reactive metal was determined by a 0.43 M HNO_3 extraction.

importance. The way the OM content is measured and the calculation of the binding site capacity strongly influence the model results. Better characterization of soil organic matter may improve the modeling. The clay content is important in the Ca and Mg exchange with protons, therefore it is suggested to study the clay fraction of the samples in more detail together with the applied adsorption model. The amount of dissolved organic matter (15 mg L^{-1}) was too low compared to the amount of OM in the experiments to have a large influence on the proton and metal binding, except for Cd. Although Fe oxides have a small contribution to the binding of protons and metals, they are included in the model for further research on soil samples with less organic matter present. In real field systems the acidification and buffering are influenced by heterogeneity, preferential flow conditions, and kinetic constraints, which complicate the application of the used modeling approach. Trace metal concentrations are predicted within a factor of 1-5 on a linear scale over a wide pH range and metal content. The major advantage of this approach is that acidification effects could be predicted with a mechanistic model without any fitting for specific soil samples; just some general characteristics are needed.

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Acknowledgments

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> Happiness is when what you think, what you say and
> what you do, are in harmony
> - *Mahatma Gandhi* -

CHAPTER 3

Solid/solution partitioning of DOC and heavy metals in soils: effects of extracting solution, solid/solution ratio, pH and storage time

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submitted

Abstract

In sandy soils the behavior of heavy metals is largely controlled by soil organic matter (solid and dissolved organic matter; SOC and DOC). Therefore, knowledge of the partitioning of organic matter between the solid phase and soil solution is essential for adequate predictions of the total dissolved metal concentration in the soil solution. At present, only a few studies have incorporated solid/solution partitioning of organic matter in metal mobility predictions. In order to gain more insight in the behavior of DOC, we have studied the effect of the extraction solution, solid/solution ratio, pH and storage time on the extractability of DOC and related metal concentration in the soil solution. Furthermore, the composition of the DOC was measured and free metal concentrations were analyzed in the soil solution with the Donnan Membrane Technique. Extraction solution, solid/solution ratio and pH affected the extracted amount of both DOC and metals. The DOC concentrations were highest in pore water and decreased further from water extracts to $CaCl_2$ extracts. In general, with increasing solid/solution ratio the metal/DOC ratio decreased, which indicated that the increased DOC at higher solid/solution ratios had a lower average metal binding capacity than DOC released at the lowest solid/solution ratio. Storage time of the samples greatly affected the extracted amount of DOC; the DOC concentration of samples that had been stored for a long period of time (> 20 yr) can be 10 times higher than for samples stored for less than one year. The extracted DOC is comprised mainly of fulvic acids (FA) and hydrophilic acids. Humic acids (HA) played a minor role in the DOC, which is in contrast to the often used assumptions on the DOC compositions in modeling studies. The composition of DOC is also affected by the soil pH; at low pH the contribution of FA to the total DOC concentration is lower because more FA is adsorbed to Fe-oxides in the soil. Speciation calculations assuming that DOC comprised of HA, FA and citric acid (as a model substance for hydrophilic acids) showed that for Cu the citrate-bound Cu could be up to 20% of the total Cu in solution. This study shows that more research is needed to gain more insight in the composition, concentration and behavior of DOC under field conditions in order to improve the prediction of metal leaching in the field.

3.1 Introduction

In the previous century, soils have been burdened with heavy metals by atmospheric deposition, fertilizer and manure application, sewage sludge application and river flooding. These sources have resulted in increased metal contents in soils. Land use changes affecting soil properties such as pH and organic matter, may lead to increased mobility and/or bioavailability of these accumulated metals. At present, soil risk assessment focuses more and more on the solid/solution partitioning of pollutants rather than on total metal contents in soil systems. In order to predict these risks it is necessary to understand the solid/solution partitioning of metals at varying soil conditions.

Since some metals (Cu, Pb) show a high sorption affinity for organic matter (both solid and dissolved), the solid/solution partitioning of organic matter is an important process contributing to the mobility of these metals. Soil properties, such as organic matter and metal content can be measured by laboratory measurements. However, the dissolved organic matter (DOM) concentration in the soil solution varies throughout the year (Lumsdon *et al.*, 2005). At present, mechanistic modeling has made important progress in describing processes in soils, such as heavy metal mobility (Tipping *et al.*, 1995; Temminghoff *et al.*, 1997; Weng *et al.*, 2002b), proton buffering (Fest *et al.*, 2005), the solid/solution partitioning of organic C (Lumsdon, 2004) and interaction between Fe-oxides and organic substances (Weng *et al.*, 2005; 2006). This mechanistic modeling has also been applied to municipal solid waste incineration (MSWI) bottom ash (Dijkstra *et al.*, 2006). To incorporate heavy metal binding onto DOM, still assumptions have to be made about the DOM concentrations and composition in soil solutions. Those assumptions are mainly based on extractions of soil samples and literature results.

The metal binding capacity and affinity of organic matter depends on its structure. However, reliable data on the composition of solid and dissolved organic matter (e.g. HA and FA content) in soils is most often lacking. In previous studies, various assumptions were made for the composition of solid organic matter. Weng *et al.* (2001a) calculated that the binding capacity of solid organic matter ranged from 16% to 46% of the binding capacity of humic acids (HA). Others studies (Tipping *et al.*, 1995; Schröder *et al.*, 2005) used a slightly different approach to estimate SOM in soil samples; these authors assumed that 50% of the SOM was present as HA or FA and that the rest of the SOM was inert. However, in some cases the amount of active humic substances (HA and FA) can be even much lower, as has been shown by Tipping *et al.* (1995). In a mineral soil only 10% of the SOM was apparently present as active humic substances (HA and FA).

DOM is operationally defined as a complex mixture of organic molecules with different sizes and structures, which passes a filter with a pore size of 0.45 μm (Kalbitz *et al.*, 2000). DOM consists for a major part of HA and FA; the rest of the DOM is comprised of smaller molecules such as carbohydrates and carboxylic acids and macromolecular hydrophilic acids (Herbert and Bertsch, 1995). As a result a wide variety of assumptions about the DOM composition has been used to model metal binding on DOM in soil samples. For instance, Cancès *et al.* (2003) assumed that DOM consisted for 50% of FA and for 50% of HA to model metal speciation in soil solutions. However, other studies expected only a part of the DOM to be reactive for metal binding, e.g. 50% FA and 50% inert (Lofts and Tipping, 2000; Tye *et al.*, 2004), or 65% FA and 35% inert (Bryan *et al.*, 2002; Weng *et al.*, 2002b; Tipping *et al.*, 2003; Guthrie *et al.*, 2005).

Dried soil samples are generally used in soil research because of the standard regulations for soil analyses or because of the necessity to store samples. Although it is well known that drying of soils samples affects soil properties (Bartlett and James, 1980; Walworth, 1992), it is hard to avoid. The natural process of drying and rewetting of soils generates a flush in respiration and results in a release of soluble C in the soil (Merckx *et al.*, 2001), but such a release can also be the result of the osmotic shock and lysis of microbial cells (Thurman and Haygarth, 2001). Research by Kaiser and others (2001) showed that air-dried (forest) soil samples released more DOC than fresh samples (4.5 times higher) and that the DOC of the air-dried soil samples appeared to have a larger fraction of hydrophilic DOC (~70%). Koopmans *et al.* (2006) found that drying of soil samples resulted in increased DOC concentrations in soil extractions and that this also resulted in higher extractable P from the soil samples. Tack *et al.* (2006) showed that heavy metal concentrations increased after a drying period of the soil samples. They attributed this increase to the higher solubility of organic matter and, pH effects caused by rewetting of dried soil samples.

The aim of this study is two-fold: (i) To study the effect of the composition of the extraction solution and solid/solution ratio on the amount and composition of extractable DOC. (ii) To study the effect of extraction solution, solid/solution ratio and DOC concentration on the solubility and speciation of heavy metals. Since soil pH and storage time differ between the soil samples, effects of these sample properties were included in this study.

To study the effect of extraction solution and solid/solution ratio on the DOC concentration and heavy metal solubility, we extracted soil samples from a long-term field experiment with water and 0.01 M $CaCl_2$ at different solid/ solution ratios. In addition, the DOC concentration and metal solubility was measured in porewater to account for more actual field concentrations. To gain more insight in the extracted DOC and metal concentrations we performed an additional experiment to study the DOC composition in the soil solution as well as the free metal concentration in the soil solution. For this purpose, we performed a soil column experiment which was connected to a Donnan Membranre Technique (DMT cell (Temminghoff *et al.*, 2000; Weng *et al.*, 2001b)). The effluent of the soil column was analyzed for its composition of humic acids, fulvic acids and smaller, hydrophilic acids (Van Zomeren and Comans, 2004). The DMT cell was used to measure the free metal concentration in the effluent. Subsequently, we predicted the free metal concentration in the soil solution by taking into account the total metal concentration in the soil solution and the measured DOC composition by using a mechanistic geochemical model.

3.2 Materials & Methods

Samples

We used in this study soil samples from the Wildekamp experimental field. This field has previously been used to study the behavior of copper in these soils (Temminghoff *et al.*, 1997; Weng *et al.*, 2001a; Fest *et al.*, 2005) and the effect of copper on the soil fauna (Korthals *et al.*, 1996; Marinussen and Van der Zee, 1997; Tobor-Kaplon *et al.*, 2006). This experimental field was established in 1982 and has since then been used for crop production (maize, potato and oats in rotation). Four pH levels (pH-KCl: 4.0, 4.7, 5.4 and 6.1) have been established by calcium carbonate or sulphur application. At each pH level, four Cu levels have been introduced (addition of 0, 250, 500 and 750 kg $CuSO_4$ per ha). All these applications (in 1982) were performed in a randomized plot design with plots of 6 x 11 m. Methods of application can be found in Lexmond (1980). Samples were taken from fields with the highest and lowest Cu level at both high (6.1) and low (4.0) pH. Samples were named after their field characteristics, viz. L stands for low pH, H stands for high pH, I stands for low Cu level, and II stands for high Cu level. Since the establishment in 1982 of the experimental field, samples were taken regularly from the upper 20 cm of the soil. For this study we used samples from 1986 and 2005 to study the effect of storage on the DOC concentration and composition. After sampling in 1986 and 2005 the soil samples were dried at 40 °C, sieved (< 2 mm) and stored at room temperature until analysis.

Soil characteristics

Soil organic matter content was determined by loss-on-ignition (Houba *et al.*, 1997). Metal content was determined by 0.43 M HNO_3 extraction (solid/solution ratio (SSR) 0.1 kg L^{-1}). This method has been used as a measure for the amount of reactive metals in soil samples in other studies (Boekhold *et al.*, 1993; Tipping *et al.*, 2003; Dijkstra *et al.*, 2004; Römkens *et al.*, 2004). Concentrations of cations in the HNO_3 extract (Cu, Cd, Zn, Ni, Pb, Al, Fe, Ca, Mg, K, Mn, and Na) were measured by ICP-AES (IRIS). pH was determined in a 0.01 M $CaCl_2$ extract (Houba *et al.*, 2000). These soil characteristics are shown in Table 3.1.

Soil extractions at various SSR and ionic strength

To study the effect of the solid/solution ratio and the ionic strength on the extractable amount of DOM and metals, extractions of the soil samples were performed at various solid/solution ratios with water and $CaCl_2$ as an extraction solution. Solid/solution ratios of 1:10, 1:5 and 1:2 were tested for both water and 0.01 M $CaCl_2$ as an extraction solution. For the water extraction we used the same procedure as for the $CaCl_2$ extraction (Houba *et al.*, 2000). pH was measured in a settling soil suspension in the various extracts. Samples were analyzed for DOC by a TOC analyzer (Skalar SK12), and for metals by ICP-MS after filtration (0.45 µm aquatron TOC free) and acidification (0.014 M HNO_3) of the solution. Pore water was extracted from the samples by centrifugation (Bufflap and Allen, 1995). The pore waters were obtained by first equilibrating previously dried samples with water at field capacity during 24 hours and by subsequent centrifugation in Teflon beakers at 6000 rpm for 30 minutes. The porewater was analyzed for pH, DOC and metal concentration.

Soil column DMT experiment

To study solid/solution partitioning and related metal speciation, a soil column experiment was performed. The column outlet was connected to a DMT cell to be able to measure the free metal concentration in the soil solution. An extensive description of the DMT cell and the experimental setup can be found in the work of Temminghoff *et al.* (2000) and Weng *et al.* (2001b), respectively. The soil column DMT experiment was performed with samples from 1986 and 2005 with high and low pH and Cu content.

Perspex columns were filled with 100 g of air-dried soil. Salt solution (0.002 M $Ca(NO_3)_2$) was pumped from the reservoir (polyethylene bottle) into the column. We have chosen for 0.002 M $Ca(NO_3)_2$ as background salt solution for a better agreement with the ionic composition in the field (Weng *et al.*, 2001b; Schröder *et al.*, 2005). The solution entered the column at the bottom and left the column at the top. After transport through the soil column, the solution was flushed through the donor side of the DMT cell and finally returned to the reservoir. For a schematic setup of the column experiment we refer to Weng *et al.* (2001b). We used 200 ml of the salt solution to recirculate through the soil sample, which resulted in a SSR of 1:2. The acceptor side of the DMT cell was continuously recirculated with the same salt solution (18 mL) from another reservoir. To decrease the detection limit for the free metal ions, purified HA was added to the acceptor solution (Kalis *et al.*, 2006b). The salt solution was percolated through the column at a rate of 2.0 $cm^3\ min^{-1}$; the solution was pumped through the DMT cell at a rate of 2.5 $cm^3\ min^{-1}$ (Weng *et al.*, 2001b). All materials used for the soil column DMT experiment were thoroughly washed with acid and water before use. Although, Weng *et al.* (2001b) showed that 24 hours are sufficient to reach equilibrium over the Donnan membrane, we also have to obtain equilibrium in the soil column. Therefore, aliquots were taken from both the donor and acceptor solution after 48, 96 and 168 hours. Copper, Cd, Ni, Pb and Zn concentrations were measured by ICP-MS (Perkin-Elmer; Elan 6000); Ca, K, Na and Al concentrations were analyzed by ICP-AES (Spectro; Spectroflame); and DOM was analyzed by a TOC analyzer (Skalar; SK12). DOM composition (HA, FA and hydrophilic fraction) was quantified by a batch procedure developed by Van Zomeren and Comans (2004). This procedure is based on the currently recommended guidelines for organic matter characterization from the IHSS (Thurman and Malcolm, 1981; Swift, 1996). Speciation calculations were performed with the computer program

ECOSAT (Keizer and Van Riemsdijk, 1998), using generic parameters for metal complexation with HA and FA for the NICA-Donnan model (Milne *et al.*, 2003) and thermodynamic parameters for inorganic complexation (Lindsay, 1979; Allison *et al.*, 1991; Morel and Hering, 1993).

3.3 Results and discussion

The samples clearly show the different pH and copper levels that were selected for this study (Table 3.1). The L-samples showed a pH around 4 and the H-samples have a pH varying around 5. Every 6 years the pH values have been re-adjusted to their nominal value. The organic matter content of all samples has decreased since 1986, because the application of organic fertilizer has been stopped since the construction of the experimental field. The difference between the I and II samples is clearly shown by the amount of reactive Cu in these samples. The I-plots did not receive any Cu during the construction of the field in contrast to a high load on the II-plots. The Cu content in the II samples (high Cu) decreased in 20 years from 2.88 to 1.44 mmol kg^{-1} and this decrease is attributed to leaching of copper from the top soil to deeper layers. Leaching of metals from this experimental field has been studied in further detail in another study (Fest *et al.*, 2007b). The decrease in the content of Cd, Ni and Zn seems to be dependent on the pH level. Low pH (L) samples show a major decrease in the Cd, Ni and Zn content between 1986 and 2005 in contrast to the high pH samples (H). The leaching of Cu does not show this pH dependency. The high pH samples (H) show a slightly higher Pb content than the low pH (L) samples. Furthermore, the Pb content has remained constant over the last 20 years.

Effect of extraction solution on DOC concentration

The amount of DOC extracted with water was higher for all samples and all extraction ratios than the amount extracted with $CaCl_2$, which is in agreement with recent findings by Amery *et al.* (2007). The higher DOC concentrations in the water extract compared to the $CaCl_2$ extract ranged from 3% for the low pH-1986 (L-II_{1986}) sample up to 150% for the high pH-2005 (H-II_{2005}) sample. Römkens and Dolfing (1998) showed that extracted DOC from the same soils precipitated under influence of increasing Ca concentration. 30% of the DOC precipitated at a Ca concentration of 0.01 M. Weng *et al.* (2002d) showed that the coagulation of dis-

Table 3.1: General soil characteristics (pH in 0.01M $CaCl_2$, OM content (loss-on-ignition) and reactive (0.43M HNO_3) metal content (Cd, Cu, Ni, Pb and Zn) of the studied soil samples (L-I$_{1986}$: sample with low pH and low Cu from 1986; L-II$_{1986}$: sample with low pH-high Cu from 1986; L-I$_{2005}$: sample with low pH and low Cu from 2005; L-II$_{2005}$: sample with low pH-high Cu from 2005; H-I$_{1986}$: sample with high pH and low Cu from 1986; H-II$_{1986}$: sample with high pH-high Cu from 1986; H-I$_{2005}$: sample with high pH and low Cu from 2005; H-II$_{2005}$: sample with high pH-high Cu from 2005). Standard deviation is given between the brackets.

sample	pH	OM	Cu	Cd	Ni	Pb	Zn
		(%)	(mmol kg^{-1})	- - - - - - - - (µmol kg^{-1}) - - - - - - - -			
L-I$_{1986}$	4.0 (0.0)	3.7 (-)	0.29 (0.00)	1.9 (0.0)	9.2 (0.2)	85.5 (1.4)	77.7 (1.6)
L-II$_{1986}$	4.0 (0.0)	3.9 (-)	2.20 (0.03)	1.6 (0.1)	10.2 (0.8)	87.6 (4.9)	65.8 (5.7)
L-I$_{2005}$	4.0 (0.0)	3.1 (-)	0.42 (0.01)	0.6 (0.0)	0.4 (0.0)	79.9 (1.9)	20.3 (0.3)
L-II$_{2005}$	3.9 (0.0)	3.2 (-)	1.11 (0.02)	0.6 (0.0)	0.6 (0.1)	86.8 (3.1)	23.3 (1.1)
H-I$_{1986}$	5.3 (0.0)	3.7 (-)	0.09 (0.00)	2.5 (0.0)	9.8 (0.1)	104.0 (0.4)	144.2 (0.2)
H-II$_{1986}$	4.8 (0.0)	3.6 (-)	2.88 (0.02)	2.6 (0.0)	33.3 (0.1)	103.8 (1.0)	171.7 (0.2)
H-I$_{2005}$	5.5 (0.0)	2.7 (-)	0.21 (0.01)	2.0 (0.2)	9.6 (0.9)	93.4 (7.7)	99.9 (6.2)
H-II$_{2005}$	5.3 (0.0)	3.0 (-)	1.44 (0.09)	2.3 (0.1)	17.1 (1.5)	100.6 (6.7)	111.0 (7.7)

solved humic acid is related to the Donnan potential. The difference between the concentration in the water and $CaCl_2$ extract appeared to be the largest at high pH when comparing samples from the same year.

The 2005 samples only show a small difference in DOC concentration between the two studied pH levels (L-II$_{2005}$ and H-II$_{2005}$) and these samples with limited storage time show a significant lower DOC concentration than the samples from 1986 (L-II$_{1986}$ and H-II$_{1986}$). Storage of the samples since 1986 seemed to have affected the organic matter properties of the samples, resulting in increased DOC concentrations. Therefore, the composition of the DOC was studied and results are discussed below in the DOC composition section.

To which extent extracted DOC concentrations represent actual DOC contents in field situations is still unknown, because moisture content of the soil and salt concentration vary throughout the soil and the year. Lumsdon *et al.* (2005) showed that the DOC concentration, measured in situ, varied significantly throughout the year. Furthermore, geochemical model calculations showed that this seasonal variation could only partly be explained by the geochemical controls of DOC in the soil. Therefore, biological processes also have a significant effect on the DOC concentrations in the soil solution (Lumsdon *et al.*, 2005).

Effect of solid/solution ratio on DOC concentration

DOC concentrations increased almost linearly with the solid/solution ratio for both extraction solutions (Figure 3.1). The 1986 samples showed for both extractions a strong increase in DOC concentration, whereas for samples from 2005 the increase is smaller. However, a small difference can be seen between the high and low pH sample from 1986; the low pH sample (L-II_{1986}) showed the highest DOC concentration. This pH effect in the 1986 samples is still not understood. The 2005 samples did not show any difference in the extracted DOC concentration, so the pH did not seem to affect the DOC concentration in these samples. Transformation of the DOC concentrations into DOC content per kg soil resulted for all samples in decreasing content of DOC at increasing solid/solution ratio, while this decrease was larger for the water extractions compared to the $CaCl_2$ extractions. This effect can be related to the highly variable salt concentration when only water was used as extraction solution. Therefore results from extractions at different solid/solution ratios should be interpreted with care.

DOC concentrations were also measured in extracted pore water. Very high DOC concentrations (>1000 mg L^{-1}) were found at this high SSR. Results (Figure 3.1C) show a linear increase for the 1986 samples on a log scale. Transforming concentration in amounts per kg soil showed a small decrease for the 1986 samples in both the $CaCl_2$ and water extraction upon increasing solid/solution ratio. However, DOC content in the porewater for samples with limited storage time (2005) was found to be lower (~30 mg C kg $soil^{-1}$) than the contents found by the $CaCl_2$ (43-74 mg C kg $soil^{-1}$) and water extraction (95-132 mg C kg $soil^{-1}$) probably as a result of the variation in Ca concentration between these extraction solutions. This result shows that DOC contents found with water extractions can not be directly extrapolated to porewater concentrations, while DOC contents found by $CaCl_2$ extraction appeared to provide a reasonable measure for DOC content of the porewater.

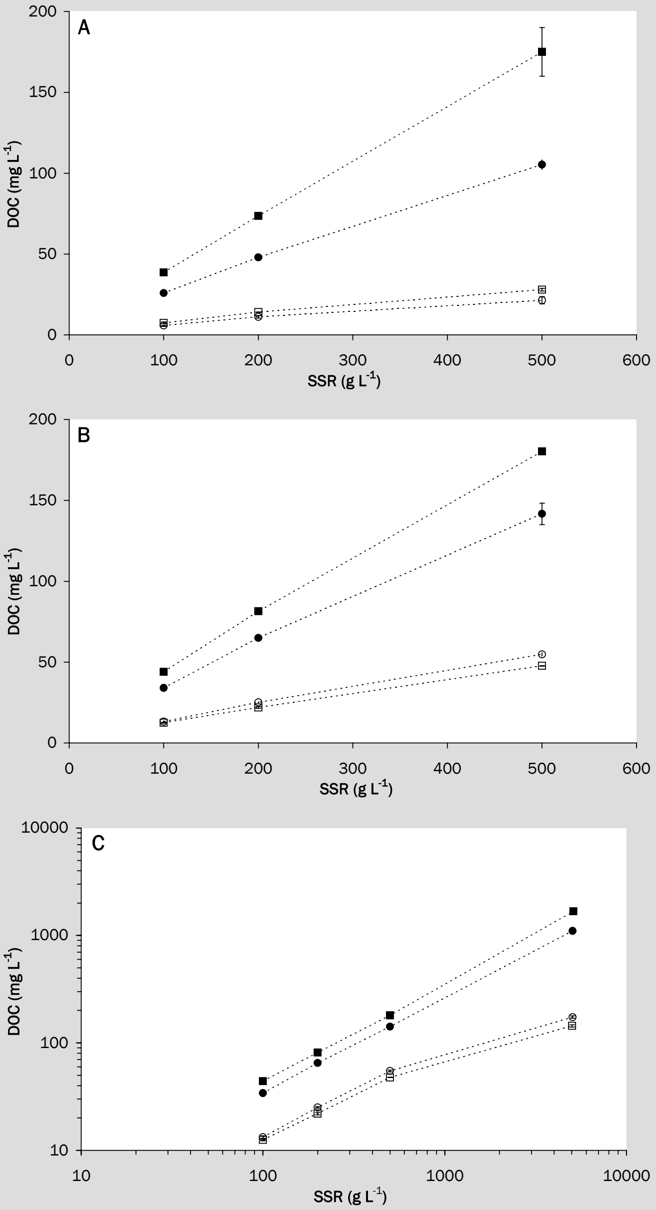

Figure 3.1: DOC concentration (mg kg^{-1} soil) in the soil extracts as function of the solid/solution ratio (g_{soil} $L_{solution}^{-1}$) between the soil sample and the extraction solution. A) 0.01 M $CaCl_2$; B) water; C) water including pore water plotted on double log scale (■ L-II_{1986}, □ L-II_{2005}, ●H-II_{1986}, ○ H-II_{2005}). Standard deviations are shown by the error bars.

DOC composition

To study the effects of storage and pH on DOC concentrations, we have performed a soil column experiment in combination with a DMT cell. The solution from the soil column-DMT experiment was analyzed for the DOC composition (humic acid, fulvic acid and hydrophilic acid fraction) and results are shown in Table 3.2. The differences in total DOC concentration, found between the 1986 and 2005 samples, were in agreement with the results from the $CaCl_2$ and water extractions; measured DOC concentrations were in the range found with the other two extraction solutions. The Cu-level of the samples did not show any effect on the DOC concentrations; concentrations for the same pH level and year did not show a large difference between the high and low Cu level.

The contribution of HA to the DOC in the soil solution is for all samples very low, at most 2% of the total DOC. The absolute amount of HA was higher for the 1986 samples and this was also valid for FA and hydrophilic acids. But on the other hand the relative contributions of the various DOC fractions were quite comparable between the samples stored since 1985 and their equivalents from 2005. The concentration FA is higher at high pH compared to the low pH samples. Weng *et al.* (2002a) concluded that the mobility of FA is mainly determined by adsorption on the solid phase while the mobility of HA is mainly determined by the coagulation of the HA with multivalent cations. The adsorption of FA will be less strong at higher pH and this can explain the difference in FA concentration between the high and the low pH sample. Since the Ca concentration in this experiment was constrained by the salt concentration in the circulating solution, the Ca concentration did not vary much between the samples and therefore the differences in HA concentration are less pronounced.

The relative contribution of FA varies between 20-40% of the total C in the soil solution. In case of the low pH samples the hydrophilic acid fraction is very large (80%), whereas this fraction at high pH is somewhat lower (60%). These results show that the DOC in solutions mainly consists of FA and hydrophilic acids and that HA was a minor fraction. These findings showed that the assumptions on DOC composition in modeling studies (e.g Lofts and Tipping, 2000; Weng *et al.*, 2002b) do not agree with the actual DOC composition. In particular, these studies tend to largely overestimate the contribution of HA to the total DOC concentration. Also, the contribution of the hydrophilic acid fraction has not been taken into account yet. Studies on metal biding by low molecular

Table 3.2: Total DOC concentration and the concentrations of the three DOC fractions (HA, FA and hydrophilic acids (Hy)) and their relative amount in the soil solution from DMT-soil column experiment (L-I$_{1986}$: sample with low pH and low Cu from 1986; L-II$_{1986}$: sample with low pH-high Cu from 1986; L-I$_{2005}$: sample with low pH and low Cu from 2005; L-II$_{2005}$: sample with low pH-high Cu from 2005; H-I$_{1986}$: sample with high pH and low Cu from 1986; H-II$_{1986}$: sample with high pH-high Cu from 1986; H-I$_{2005}$: sample with high pH and low Cu from 2005; H-II$_{2005}$: sample with high pH-high Cu from 2005).

sample	DOC	HA	FA	Hy	% HA	% FA	% Hy
	(mg C L^{-1})				%		
L-I$_{1986}$	166	1	31	134	0.8	18.7	80.5
L-II$_{1986}$	160	2	25	133	1.3	15.8	82.8
L-I$_{2005}$	12	0	2	10	0.2	17.6	82.2
L-II$_{2005}$	13	0	2	11	0.9	15.5	83.6
H-I$_{1986}$	93	1	39	53	1.3	41.8	56.9
H-II$_{1986}$	111	2	37	72	2.1	33.1	64.8
H-I$_{2005}$	14	0	6	8	0.8	40.9	58.3
H-II$_{2005}$	14	0	5	9	2.0	33.9	64.1

weight organic acids (Mench *et al.*, 1988; Qin *et al.*, 2004) have shown that these small organic molecules often present in the rhizosphere, are able to form complexes with metals in the soil solution. It is therefore plausible that the hydrophilic acid fraction of DOM is also capable of complex formation with metals in soils. However, there are indications that this fraction binds metals to lesser extent than the FA and HA fraction, but since the exact reactivity of these hydrophilic acids in metal binding is still unknown, this fraction can not a priori be ignored when studying metal availability in soils.

Effect of extraction solution on metals

Extracting soil samples with a salt solution influences the local equilibrium between the metals sorbed to the soil solid surface (SOM, clay and Fe (hydr)oxides), the free metals and the metals sorbed to the DOM (Weng *et al.*, 2002b). Using $CaCl_2$ to extract metals from soil samples, results in a rather well defined medium where the calcium ions compete with the metal ions for binding to both the solid phase and the DOM. Furthermore, the Ca concentration also affects the solubility of DOM, which also influences the distribution of metals over the soil and the solution (Römkens and Dolfing, 1998).

Figure 3.2A and B show the Cd concentrations in respectively the $CaCl_2$ and the water extraction. The Cd concentration increased for most samples linearly with increasing DOC concentration in both the $CaCl_2$ and the water extract. Free metal activity is determined by the equilibrium with the solid phase whereas the total metal concentration depends on the free metal and the complexation with DOC. The Cd concentrations in the $CaCl_2$ extract (0.01-0.23 μmol L^{-1}) were much higher than in the water extract (0.00-0.03 μmol L^{-1}). Also, in the $CaCl_2$ extract a small difference between the samples with different pH levels was found; at the high pH level (H-sample) the Cd concentrations were somewhat higher compared to the low pH samples (Figure 3.2A). This finding is likely to be the result of the higher complexation with DOC at high pH, because from the viewpoint of the solid phase the Cd^{2+} activity would be higher at the lowest pH level. The latter pH effect was only found for the 1986 samples in the water extract (Figure 3.2B). The less pronounced pH effect in the water extract is probably due to the varying salt concentration obtained by a water extraction. For these sandy soils, the salt concentration depends on the soil properties, in contrast to the $CaCl_2$ extraction in which the salt concentration is largely enforced by the extraction solution.

Comparison of the results for Cd and Cu (Figure 3.2A/B and Figure 3.2C/D) indicate that these metals do not behave identical. For Cu, a pH effect is clearly visible in the $CaCl_2$ extract (Figure 3.2C) and is less clear in the water extract. Cu concentrations in the $CaCl_2$ extract are higher at low pH (L-samples) than at high pH (H-samples) and this was found for both the 1986 and the 2005 samples. The results of the water extraction (Figure 3.2D) showed that the Cu concentration was linear related to the DOC concentration in the water extract. The strong pH dependency of the Cu concentration in a $CaCl_2$ extract was also found by (Temminghoff *et al.*, 1998) and was attributed to the strong effect of Ca on the equilibrium between Cu ions and the solid surface at low pH. For Cd, the expected pH effect was not found in the $CaCl_2$-extract. Probably, the competition of Ca ions masked the effect of pH on the solid/solution partitioning of Cd.

Also for Pb (Figure 3.2E), the pH effect is clearly visible in the $CaCl_2$ extract, showing the highest concentration at low pH. This showed that also the Pb concentration is influenced by the local competition between protons, Ca-ions and Pb-ions at the solid phase. However, in the water extract a difference between the 1986 and 2005 samples is apparent, probably affected by the DOC composition and its affinity for Pb (Figure 3.2F). The samples stored since 2005 showed a higher Pb/DOC ratio than the samples from 1986. This was also pronounced in the $CaCl_2$ extract, but only for the low pH samples. This difference between Pb concentration in the 1986 and 2005 samples could be explained by increased immobilization of Pb during storage.

The behavior of Zn was identical with Cd in both extractions. For Ni however, high pH samples (H-samples) showed higher concentrations than the low pH samples (L-samples), indicating that the effect of increased complexation with DOC at high pH dominated over the increased free metal concentration at low pH. The same effect was also found for Ni in the water extract.

The results of the metal extractions do not show equal behavior of the studied metals in the two extraction solutions, water and 0.01 M $CaCl_2$. From these observations, we conclude that in most cases the increased DOC complexation at higher pH exceeds the increase in free metal concentration at low pH, resulting in higher total metal concentrations for the high pH samples. However, in a few cases (Cd and Zn in water, and Cu and Pb in $CaCl_2$) concentrations for the low pH samples (L-samples) were higher compared to their high pH equivalent.

Effect of solid/solution ratio on metal concentration

In the previous paragraph the effect of the two extraction solutions was already discussed and it was mentioned that the metal concentration increased in most cases linearly with the DOC concentration. The increased DOC concentration was related to the various extraction ratios. In general the metal-DOC ratio decreased with increasing solid/solution ratio, indicating that the extra released DOC at higher solid/solution ratio had a lower metal binding capacity than DOC released at lowest solid/solution ratio. One exception was found for Pb in the water extract. The metal-DOC ratio increased with increasing solid/solution ratio to some maximum ratio.

Modeling metal speciation

In the DMT experiment both the total metal and free metal concentrations were measured in the soil solution; results are given in Appendix II. The contribution of free metal to the total metal concentration in the soil solution differed between

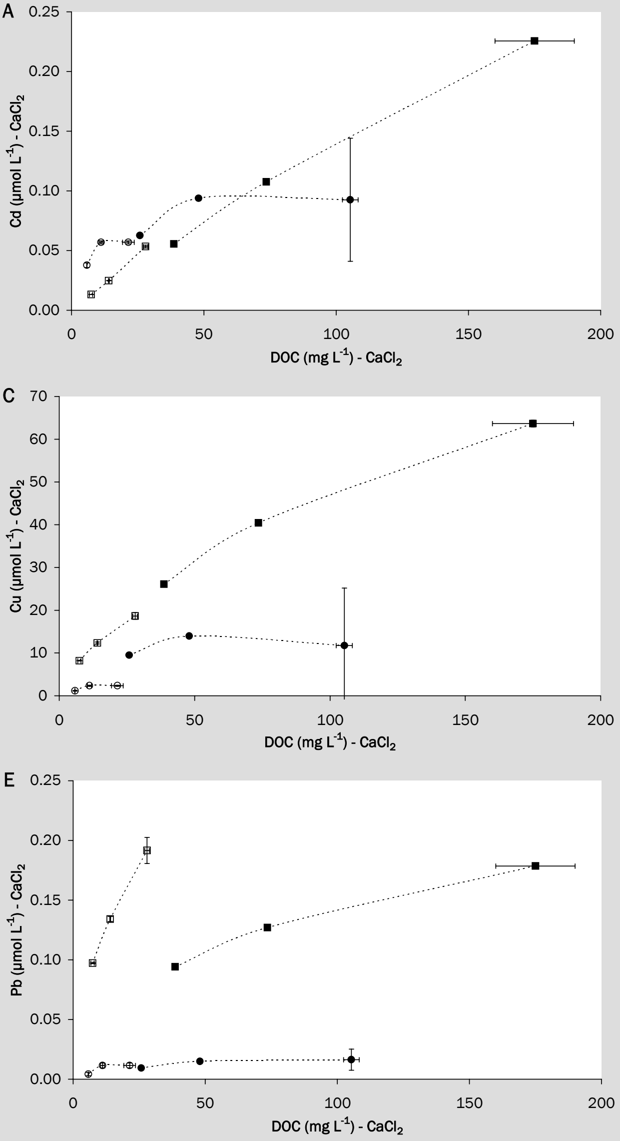

Figure 3.2 A,C,E: Cd, Cu and Pb concentration in the 0.01 M $CaCl_2$ extract plotted as function of the total DOC concentration. DOC concentration because of the increasing solid/solution ratio (see Figure 3.1) A) Cd concentration in the 0.01 M $CaCl_2$ extract; C) Cu concentration in the 0.01 M $CaCl_2$ extract; E) Pb concentration in the 0.01 M $CaCl_2$ extract (■ L-II$_{1986}$, □ L-II$_{2005}$, ●H-II$_{1986}$, ○ H-II$_{2005}$). Standard deviations are given by the error bars.

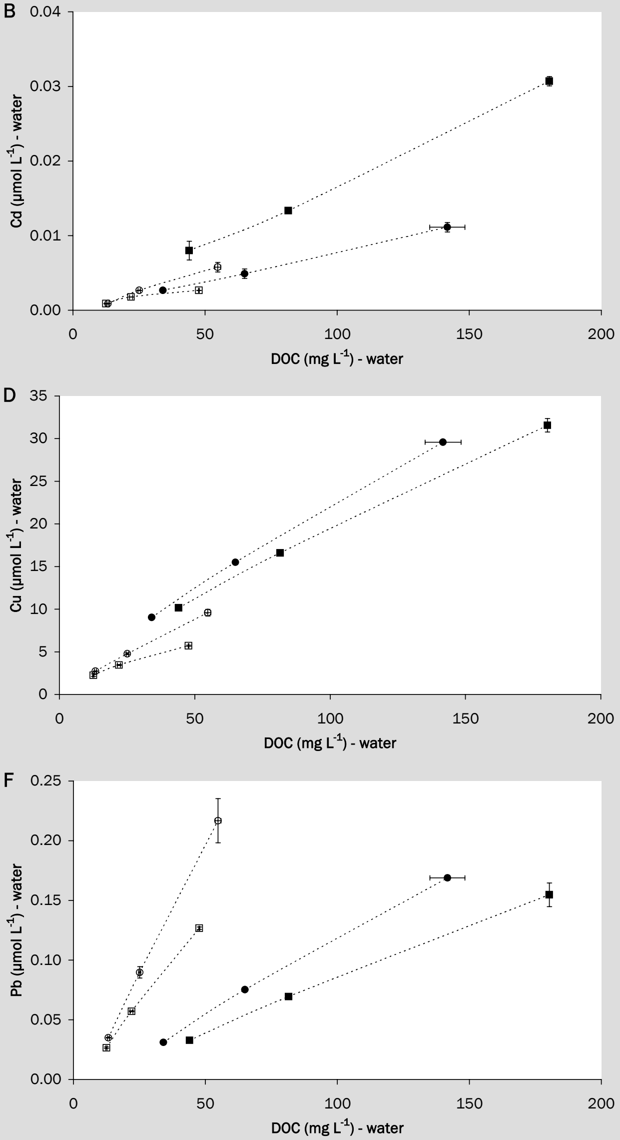

Figure 3.2 B, D, F: Cd, Cu and Pb concentration in the water extract plotted as function of the total DOC concentration. DOC concentration because of the increasing solid/solution ratio (see Figure 3.1) B) Cd concentration in the water extract; D) Cu concentration in the water extract; F) Pb concentration in the water extract (■ L-II$_{1986}$, □ L-II$_{2005}$, ●H-II$_{1986}$, ○ H-II$_{2005}$). Standard deviations are given by the error bars.

the various metals and the soil pH. At low pH (L-samples) most Cd was present in its free ionic form; however at higher pH (H-samples) less than 50% of the total Cd was present as Cd^{2+}. The larger free metal fraction at low pH, which was also found for Cu, Ni and Zn, is due to the lower effective affinity of DOM for Cd at low pH. In the case of Pb, a very small percentage of the total Pb in solution was in the form of Pb^{2+}.

Speciation in the soil solution was predicted with the NICA-Donnan model by using the solution composition (total metal and major cation concentration, DOC concentration and pH). The measured DOC composition (HA, FA and hydrophilic acids) was used to calculate speciation in the donor solution of the DMT-soil column experiment. We distinguish two assumptions, first we assume that all hydrophilic acids are inert and second, that the hydrophilic acids have binding properties similar to citric acid. Citric acid is often found as a component of low organic acids in soil samples (Van Hees *et al.*, 2001b; Qin *et al.*, 2004). Furthermore, we have also studied the altenative assumptions that all DOC is reactive and consists for 50% of HA and for 50% of FA (Cancès *et al.*, 2003) and that only half of the DOC is present as FA (Lofts and Tipping, 2000). Predicted free metal concentrations are plotted versus the measured free metal concentration in Figure 3.3 (Cd, Cu and Pb) and Appendix II (Ni and Pb).

For Cd, all predictions were within one log unit of the measured Cd^{2+} concentration (Figure 3.3A). Best predictions for pCd were found when the measured DOM composition (only HA and FA) was used. Addition of citric acid as complexing agent resulted in a small decrease in predicted Cd^{2+} concentration compared to the assumption that hydrophilic acids were inert. DOC composition from literature (50% HA-50% FA or 50% FA) resulted for Cd mostly in an underprediction of the Cd^{2+} concentration.

Most predictions for Cu lie within the range of one order of magnitude from the measured Cu^{2+} concentration and are higher than the measured concentrations. Only for the assumption that all DOC is reactive (50% HA-50% FA) some underpredictions of the Cu^{2+} were found. These results showed that the measured DOC composition can not completely account for the total complexation of Cu in the soil solution. This observation could be explained in two ways, first the Cu binding affinity for HA and/or FA is too low. Since the generic parameters of the NICA-Donnan model (Milne *et al.*, 2001; 2003) cover a wide variety of HA and FA, the underprediction of free Cu concentrations suggest that the binding capacity of this specific dissolved organic matter was underestimated by the generic parameters. Milne *et al.* (2001) found for FA a Q_{max1} of 8.76 and a Q_{max2} of 7.77 as maximum values from the total dataset. Using these values of Q_{max}, the calculation of Cu^{2+} concentration was improved (Figure 3.3B). These results suggest that the dissolved organic matter was in this case not sufficiently described by the generic parameters and, therefore that the use of specific binding parameters would be preferred. A second explanation can be the role of the hydrophilic acids. These small acids could play an important role in the complexation of Cu in the soil solution. Results in Figure 3.3B showed that taking into account complexation with citric acid could improve the prediction of the Cu^{2+} concentration, providing a significant amount of complexing groups.

Predictions of Pb^{2+} concentrations were very poor. Variation of the DOC composition showed a large effect on the predicted Pb^{2+} concentration. Overall the Pb^{2+} concentration was highly overpredicted. One reason might be that competition of Al and Fe with Pb for binding to HA and FA in the soil solution is overestimated and thus results in overpredicted Pb^{2+} concentrations. The overestimation of the competition can be due to the presence of Al and Fe in the soil solution as colloids (Al/Fe-oxides) instead of monomeric metal ions. Prediction of Pb^{2+} without Al and Fe competition resulted in some cases to lower Pb^{2+} predictions (Figure 3.3C). Besides the competition effect Pb can also be adsorbed to these nanoparticles and this fraction will lower the free Pb concentration in the solution. This effect may thus qualitatively explain the observed overprediction of the free lead concentration. The overestimation of the Pb^{2+} concentration could also be explained by the complexation of $PbPO_4$ complexes on oxide surface, which have not been taken into account in the prediction. Incorporating the adsorption of these complexes was shown to improve prediction of Pb^{2+} in floodplain soils (Schröder *et al.*, 2005).

Ni^{2+} concentrations (see Appendix II) were highly overpredicted at low Ni^{2+} concentrations ($<10^{-7}$ mol L^{-1}). The complexation with DOC was highly underestimated, mainly in the case of the high pH samples. This underestimation was also found by Weng *et al.* (2002b) and Van Laer *et al.* (2006), indicating that the model parameters for both the NICA-Donnan model and Model VI underestimate the Ni complexation with DOC or as suggested for lead, that adsorption onto inorganic (nano)colloids plays a significant role. Conversely, prediction of Zn^{2+} concentrations were in good agreement with the measurements. In some

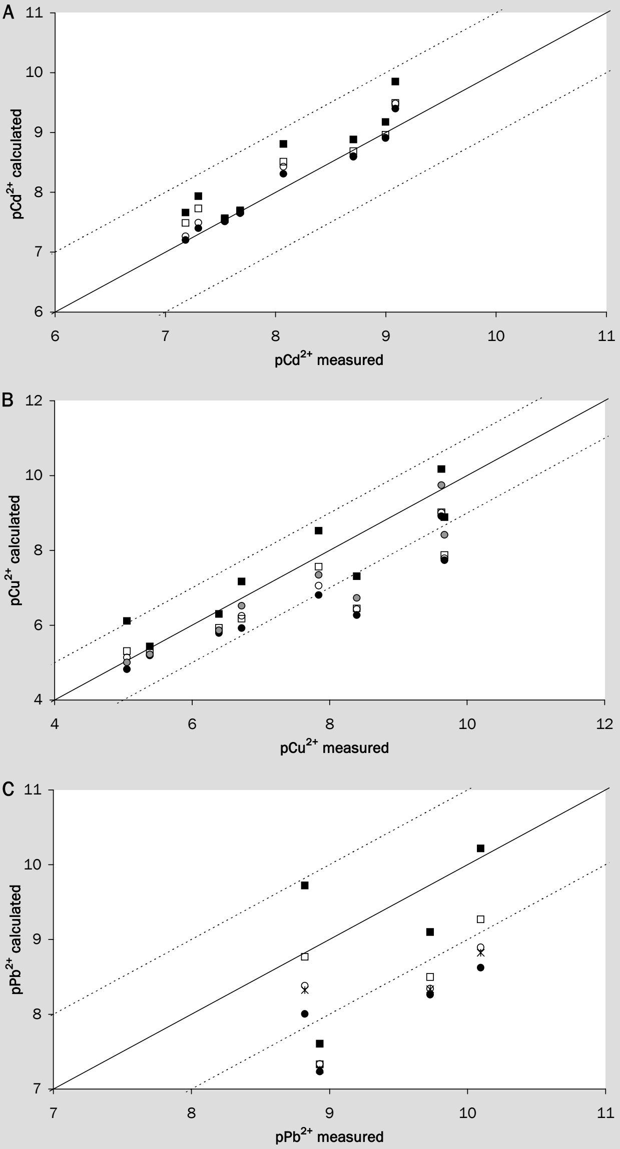

Figure 3.3: Calculated free metal concentrations plotted versus the measured free metal concentrations. Symbols show different DOC compositions in speciation calculations (● HA-FA measured, ○ HA-FA-citric acid, ■ 50%HA-50%FA, □ 50%FA, ● Q_{max} FA adjusted (only for Cu); ○ HA-FA measured without Fe and Al competition (only for Pb)). The solid line shows the 1 to 1 relation, whereas the dotted lines represent the one log variation. A) Cd; B) Cu; C) Pb.

cases the complexation with citric acid improved the prediction of the Zn^{2+} concentration compared to the situation with inert hydrophilic acids.

Figure 3.4 shows the distribution of Cd, Cu and Pb over the various species present in the solution phase (complexed with HA, FA and citrate and the free metal and inorganic complexed form). This distribution is shown for the model prediction under the assumption that the hydrophilic acids behave like citrate. Cd was mainly present as Cd^{2+} or bound to FA; HA and citric acid did not contribute significantly to the binding of Cd in the soil solution. For Cu, Cu complexed to FA is the most important form of Cu in the soil solution; one exception is found for the low pH soils from 2005 (L_{2005}) in which Cu^{2+} is the major species in the soil solution. But also HA and citric acid contributed to the speciation of Cu in the soil solution. In some cases the complexation of Cu with citric acid could make up to more than 20% of the total Cu in the soil solution. Ni and Zn were mainly present as Ni^{2+} and Zn^{2+}, but for the 1986 samples, which do have a high hydrophilic acid content, the binding to citric acid is significant (see Appendix II). Pb (Figure 3.4C) seemed to be mainly bound to the organic substances in the soil solution, with an exception for the low pH samples from 2005 (L_{2005}).

3.4 Conclusions

Soil DOC extractions with water and $CaCl_2$ show that extracted amounts of DOC were not only affected by the extraction solution but also by the pH and the solid/solution ratio. Related metal concentration were also affected by these variables. Therefore, DOC concentrations in various solutions and solid/solution ratios should be interpreted with care. Storage of the soil samples resulted in increased amounts of DOC. The amount of DOC in the 1986 samples is up to a factor of 10 higher than in the samples that were only stored since 2005 due to an increase in both fulvic acids and hydrophilic acids. Further research on field DOC concentrations is necessary in order to obtain a better understanding of the role of DOC in metal leaching in field situations.

The behavior of the studied heavy metals differs per metal. In general the metal-DOC ratio decreased with increasing solid/solution ratio. This finding indicates that at higher solid/solution ratio, which is closer to the situation in the field, the DOC had a lower metal binding affinity than at lower solid/solution ratios. The prediction of the free metal concentration showed in general a reason-

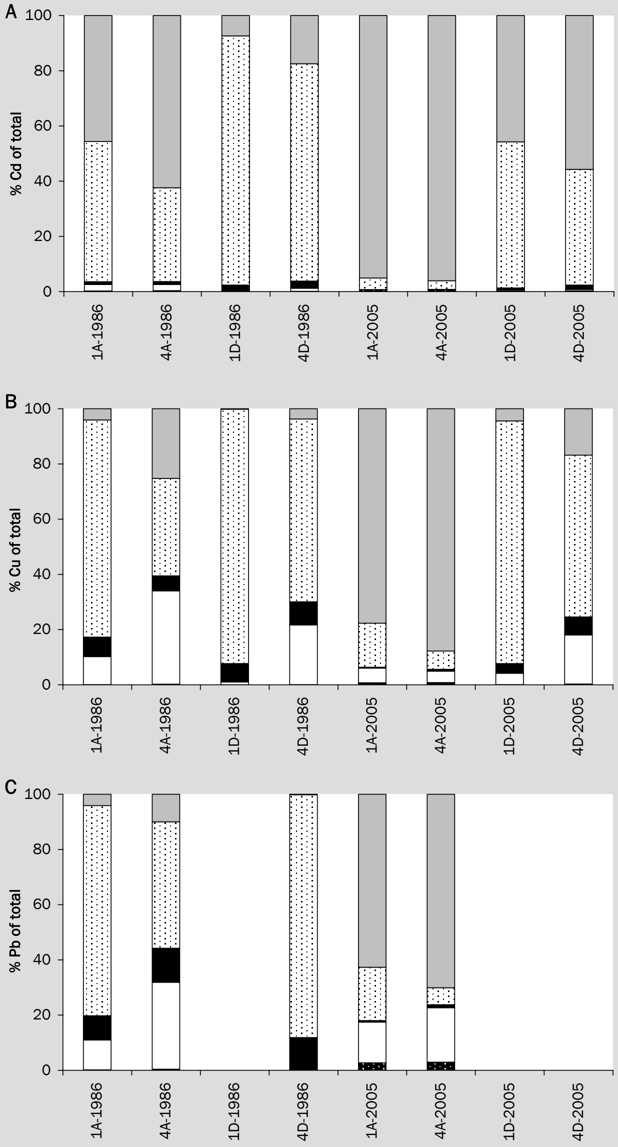

Figure 3.4: Speciation of metals in the donor solution calculated with the measured DOC composition (HA-FA-citric acid) shown as percentage of total metal concentration in solution; light blue bar: free metal; white bar with blue dots: metal bound to FA; blue bar: metal bound to HA; white bar: metal bound to citric acid (representing hydrophilic acids); blue bar with white dots: inorganic metal species; A) Cd; B) Cu, C) Pb.

able agreement with the measured free metal concentrations; however some exceptions occurred for Ni and Pb. These exceptions could be related to the adsorption onto inorganic colloids in the soil solution and more attention should be paid to this possibly important process. The use of the measured DOC composition to predict free metal concentration gave good results, including HA, FA and citric acid. Citric acid was used as a model substance for the hydrophilic acids. The binding on citric acid seemed to be important for Cu, because for some samples this binding could make up for 20% of the total Cu in solution. On the other hand, more specific NICA-Donnan parameters are necessary in stead of the used generic parameters for an optimal prediction of free metal concentrations based on the measured amounts of HA and FA.

This study showed that a large fraction of the soil DOC consist of hydrophilic acids (e.g. citric acid) that can potentially contribute, significantly to the complexation of metals such as Cu and Pb. Therefore more research is needed to unravel the molecular composition and metal binding capacity of this hydrophilic acid fraction in order to provide a better quantitative understanding of its role in metal leaching from soils. Besides the necessity to use specific NICA-Donnan parameters for this study, also more research is needed on the generic parameters for improving predictions of Ni complexation and the competitive role of Al and Fe on metal complexation on DOC.

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> Pijn is tijdelijk, opgeven voor altijd
> *- Lance Armstrong in ‘Elke seconde telt’ -*

CHAPTER 4

Metal leaching from a sandy soil: results from a long-term field experiment and model predictions

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submitted

Abstract

Advanced adsorption modeling shows more and more promise to predict both total and free metal concentrations in the soil solution in equilibrium with the solid phase. In this study, leaching of heavy metals (Cd, Cu, Ni, Pb and Zn) from the Wildekamp experimental (agricultural) field is presented and compared to model predictions. The considered heavy metals were present at background levels and studied at two pH levels for a period of two decades. The multi-component leaching of the studied heavy metals has been calculated using an advanced adsorption model (NICA-Donnan) assuming that organic matter is the most important sorptive phase for these heavy metals. The Cd, Ni and Zn content decreased significantly during the studied period in the low pH plot, whereas the Cu and Pb content stayed rather constant throughout the years. Transport calculations show a good prediction of the leaching of Cd, Ni Pb and Zn after 22 years, whereas the observed increase in the Cu content is not predicted by the model. The increase in the Cu content can be attributed to the pollution of these plots by the neighboring plots, which have higher Cu contents as a result of intentional addition of Cu. The successful model predictions indicate the potential of this approach for scenario type calculations. The pH dependence of the metal leaching is highest for those metal ions that do not form strong complexes to DOC in these fields like Cd, Ni and Zn.

4.1 Introduction

Increased concentrations of the reactive fraction of heavy metal ions present in soils are the result of various anthropogenic activities. These increased reactive metal contents form a potential risk for adjacent surface waters and underlying groundwater in the case of leaching and for plants and organisms living in and on these soils due to increased bioavailability. To quantify effects of changing soil properties (as a result of e.g. changing land use), knowledge on solid/solution partitioning and speciation of metals is necessary to be able to predict metal bioavailability and mobility. Recent studies show that metal binding onto various soil surfaces (clay, organic matter and Fe-oxides) can be described by combining different advanced adsorption models (Weng *et al.*, 2001a).

Several studies show the importance of dissolved organic matter (DOM) for metal mobility in soils (McCarthy and Zachara, 1989; Temminghoff *et al.*, 1997; Weng *et al.*, 2002b); therefore, the solid/solution partitioning of organic matter should be considered when metal mobility is studied. DOM represents a complex mixture of organic molecules with varying size, shape and chemical reactivity. The operational definition of DOM is the organic matter that passes a 0.45 μm filter. A major part of DOM consists of humic acids (HA) and fulvic acids (FA), which are used as model substances in modeling metal binding to DOM (McCarthy and Zachara, 1989; Temminghoff *et al.*, 1997; Weng *et al.*, 2002a).

Metals sorbed onto DOM can become unavailable for transport when DOM coagulates under the influence of a change in the ionic composition of the solution (Ong and Bisque, 1968) or when it binds to solid surfaces in soils (Filius *et al.*, 2000). Lofts *et al.* (2001a) developed a model for solid/solution partitioning of organic matter in forest soils and with this model repeated leaching is described reasonably well. However, Lumsdon *et al.* (2005) showed that geochemical controls cannot fully explain the variation of DOM concentration in the soil solution throughout the year. They conclude that the solid/solution partitioning of DOM during the season is also influenced by biological processes. Several studies (Ong and Bisque, 1968; Tipping and Ohnstad, 1984; Temminghoff *et al.*, 1998; Osté *et al.*, 2002b; Weng *et al.*, 2002d show the effect of Ca on the coagulation of DOM; Ca concentrations higher than 10^{-3} M seem to have a major effect on the solubility of DOM. Therefore, it is uncertain whether extractions with 0.01 molar $CaCl_2$ are a good predictor of the availability of metals in soils (Sanders *et al.*, 1987; Smilde *et al.*, 1992; Van Erp *et al.*, 1998) or of metal leaching from soils. We will test in this paper in how far mechanistic adsorption modeling is a useful tool to predict leaching and actual concentrations in soils after long periods of time as a function of the pH of the soil.

Leaching of metals from soils has been studied in short term column experiments (Temminghoff *et al.*, 1997; Degryse *et al.*, 2007) and batch extractions (Voegelin *et al.*, 2003; Dijkstra *et al.*, 2004). Column leaching studies sometimes focus on the hydrological modeling of metal transport in those columns (Cerník *et al.*, 1994; Camobreco *et al.*, 1996). Very few long-term field experiments on the leaching of metals that are either present semi-naturally or have been added on purpose, are available at present.

The aim of this paper is two-fold: (i) to study metal (at background level) leaching from an agricultural field at two different pH levels for a period of 22 years; (ii) to test an advanced modeling approach for prediction of metal leaching and to show the sensitivity of the calculations for some soil properties that change over time in the experiments (pH, OM, DOC concentration). We studied the effect of pH, organic matter content and metal content in an experimental, agricultural field by analyzing soil samples taken at different times between 1983 and 2005. This experimental field consists of plots with different pH levels with different amounts of Cu added at the start of the experiments. Solid/solution partitioning of the heavy metals is predicted with the NICA-Donnan model assuming that organic matter is the main adsorption surface for the studied metals in this sandy soil. Furthermore, the leaching of various heavy metals in the studied field soils is predicted using simplified transport calculations.

4.2 Materials and Methods

Samples

Soil samples from the Wildekamp experimental field (Temminghoff *et al.*, 1994; Korthals *et al.*, 1996) were used in this study. This experimental field has previously been used to study behavior of copper in these soils (Temminghoff *et al.*, 1997; Weng *et al.*, 2001a; Fest *et al.*, 2005) and the effect of copper on the soil fauna (Korthals *et al.*, 1996; Marinussen and Van der Zee, 1997; Tobor-Kaplon *et al.*, 2006). This experimental field consists of randomized plots with four pH levels (pH-KCl: 4.0, 4.7, 5.4 and 6.1) combined with four Cu levels (addition of 0, 250, 500 and 750 kg $CuSO_4$ per ha). The pH levels have been established by application of calcium carbonate or sulphur. Every six years the pH is readjusted to their nominal levels. All these applications were performed in a randomized plot design with plots of 6 x 11 m. Methods of application can be found in Lexmond (1980). The Cu levels were introduced in 1982 and the pH levels were established several years before. Since 1982 the experimental field is in use for crop production (maize, potato and oats in rotation).

In this paper, we use samples from two non Cu polluted plots; one with a nominal pH of 4.0 (further mentioned as pH-4 plot) and one with a nominal pH of 6.1 (further mentioned as pH-6 plot). Since the establishment of the experimental field, samples were taken regularly from the upper 20 cm of the soil. This sampling resulted in a series of samples from the years: 1983, 1985, 1986, 1989, 1992, 1995, 1998, 2001, and 2005. After sampling the samples were dried at 40 °C, sieved (< 2 mm) and stored at room temperature until further analysis.

Soil characteristics

Soil organic matter content was determined by loss-on-ignition (Houba *et al.*, 1997). Reactive metal content (Cd, Cu, Ni, Pb and Zn) was determined by 0.43 M HNO_3 extraction (solid/solution ratio (SSR) 0.1 kg L^{-1}), which was used as a measure for the amount of reactive metals in soil samples in other studies (Boekhold *et al.*, 1993; Tipping *et al.*, 2003; Dijkstra *et al.*, 2004; Römkens *et al.*, 2004) and measured by ICP-AES (IRIS). Soil pH and DOC concentration and in the soil samples were determined by 0.01 M $CaCl_2$ extraction (Van Erp *et al.*, 1998; Houba *et al.*, 2000). DOC was measured by TOC analyzer (Skalar SK12).

Leaching calculations

The leached amount of metals since the establishment of the experimental field was calculated by transport calculations. Calculations were performed with the chemical equilibrium program ECOSAT (Keizer and Van Riemsdijk, 1998). Transport in the water phase was calculated by one dimensional flow. For simplicity we assumed a system with a constant flux and moisture content. The average flux was set at a value of 350 mm $year^{-1}$ which is for the relevant climatic conditions in between the net precipitation surplus for maize and arable land on sandy soils (Willems *et al.*, 2005). The volumetric water content at field capacity was assumed to be 0.20, resulting in a solid/solution ratio of 6.75 kg L^{-1}. Also soil properties, like pH and organic matter content were set constant to simplify calculations. Furthermore, no significant deposition of heavy metals was expected since 1982. In the top layer of these sandy soils the main sorption surface for heavy metals appears to be organic matter. Weng *et al.* (2001a) already showed that the contribution of clay and Fe-hydroxides to the sorption of the studied heavy metals was low (< 10%). Total exchangeable metal content is based on the measured metal content with a 0.43 M HNO_3 extraction. The reactive amount of organic matter is based on the amount of organic matter in the soil samples determined by loss-on-ignition. The organic matter is assumed to be all humic acid and the binding capacity was lowered (31% of Q_{max}) according to Weng *et al.* (2001a). The transport calculations were performed for a period of 22 years, from 1983 (first sampling) to 2005 (last sampling). Since the total salt concentration and composition in the soil solutions varies throughout the year, an average concentration of 0.01 M $CaCl_2$ was enforced in the system. Leaching calculations were performed for the first 20 cm of the soil. After calculating 22 years of leaching the remaining metal content was averaged over the this layer.

4.3 Results and Discussion

Field experiment

Trends of the considered soil properties will be discussed in this part, but exact results of the soil properties are given in the appendix. The pH (0.01 M $CaCl_2$) of the soil samples showed some variation over time. However, this does not give information on the variation of the pH during one year in the field. The pH of the pH-4 plot, stayed rather constant since 1982. In contrast, the pH of the pH-6 plot show more fluctuations varying from 6.2 to 5.5 with an average of 5.6. The fluctuations in pH of the pH-6 plot are larger in the first 10 years than in the last 10 years. The fluctuations of the pH are the combined result of natural acidification and repeated liming (every six years) of the plots. The plots were limed to compensate for the acidification and to raise the pH back to its nominal value. However, the applied liming at the pH-6 plot did not result in the initial value, suggesting that the applied liming of the pH-6 plot every six years was in this case not enough to bring the pH back to its intended value.

The organic matter content decreased gradually in both fields since 1983. The organic matter content has decreased in the pH-4 plot from 3.8% to 3.1% and in the pH-6 plot from 3.7% to 2.7%. This decrease of the organic matter content is the consequence of the termination of organic fertilizer application since the construction of the field experiment and the agricultural practice. Besides, the DOC concentration (0.01 M $CaCl_2$) in the soil samples also shows an enormous decrease since 1982. The concentration decreases with a factor 5. The behavior of the DOC in these samples was studied in detail by Fest *et al.* (2007a). That study shows that the measured DOC concentration is affected by the storage time. Mineralization continued during storage and rewetting of the samples causes lysis of microbial cells and these processes lead to increased amounts of mainly small hydrophilic molecules and FA after long periods of storage.

The reactive Cu content shows an increase between 1982 and 2005 for both plots; the Cu content doubled in the pH-6 plot and tripled in the pH-4 plot. This increase of the Cu content is ascribed to the spreading of Cu from neighboring plots, which contain artificially increased levels of Cu (Fest *et al.*, 2007c). Control samples contain 0.16 mmol Cu kg^{-1}, which is somewhat lower than the Cu content of pH-4 and pH-6 plot.

The other studied heavy metals (Cd, Zn, Ni, and Pb) were not artificially elevated and considerable leaching is visible for some of these metals depending on the pH of the plots. Cadmium and Zn show an initial (1983) higher metal content in the pH-6 plot. This is due to the fact that the pH levels were established already before 1982 inducing already increased leaching for the low pH. Relative leaching was highest for Cd, Ni and Zn for the pH-4 plot, indicating the pH effect on the leaching of these metals.

The Pb content has stayed rather constant over the past 22 years (pH-4 plot) or has slightly decreased (pH-6 plot). The binding of Pb to the soil surfaces is much stronger than the binding of the other metals. The binding to Fe oxides in combination with PO4 complexation has been suggested to explain the stronger binding of Pb in soils rather than expected based on Pb-organic matter interaction only (Schröder *et al.*, 2005). The reactive metal content as determined by 0.43 M HNO_3 extraction may result in too high estimated loadings when ascribed only to the organic matter fraction. Perhaps also the deposition affected the reactive Pb content, especially in the first years after the construction of the experimental field when the deposition of Pb was still considerable. In 1990 the concentration of Pb in the air was 53 ng m^{-3}, but since then the Pb concentration in the air decreased enormously as a result of the reduced emission of Pb from traffic. At present, the Pb concentration is around 8 ng m^{-3} (MNP, 2006).

Leaching predictions

The leaching of the five studied metals from the studied fields has first been calculated using the average pH over time, the initial organic matter content and the DOC concentration found by 0.002 M $Ca(NO_3)_2$ extraction (DMT experiment (Fest *et al.*, 2007a)). The sensitivity of the leaching predictions have been tested for variations in pH, OM and DOC. Results of these leaching predictions are shown in Figure 4.1 for the pH-4 plot and in Figure 4.2 for the pH-6 plot. The various assumptions used for the leaching calculations are given in Table 4.1.

Prediction 1 shows for both the pH-4 plot as well as the pH-6 plot a reasonable prediction of the metal leaching. Only the increase in Cu content was not predicted by the model, because the deposition of Cu from surrounding plots was not taken into account in the model calculation. This first prediction shows that the metal leaching is predicted well with this modeling approach using general soil properties and some reasonable assumptions. Also the effect of pH is predicted very well as shown by the difference in leaching between the two pH levels.

However, to gain more insight in the sensitivity of the leaching for changes in soil properties we tested the leaching predictions under varying soil properties like found in this field experiment. Because the pH in the $CaCl_2$-extract

Table 4.1: Soil properties used in the various leaching predictions shown in Figure 4.1 and 4.2.

	pH-4 plot			*pH-6 plot*		
	pH	OM (%)	DOC (mg C L^{-1})	pH	OM (%)	DOC (mg C L^{-1})
prediction 1	4.0	3.8	11.9	5.6	3.7	11.6
prediction 2	3.8	3.8	11.9	5.1	3.7	11.6
prediction 3	4.3	3.8	11.9	6.2	3.7	11.6
prediction 4	4.0	3.0	11.9	5.6	2.7	11.6
prediction 5	4.0	3.8	100	5.6	3.7	100

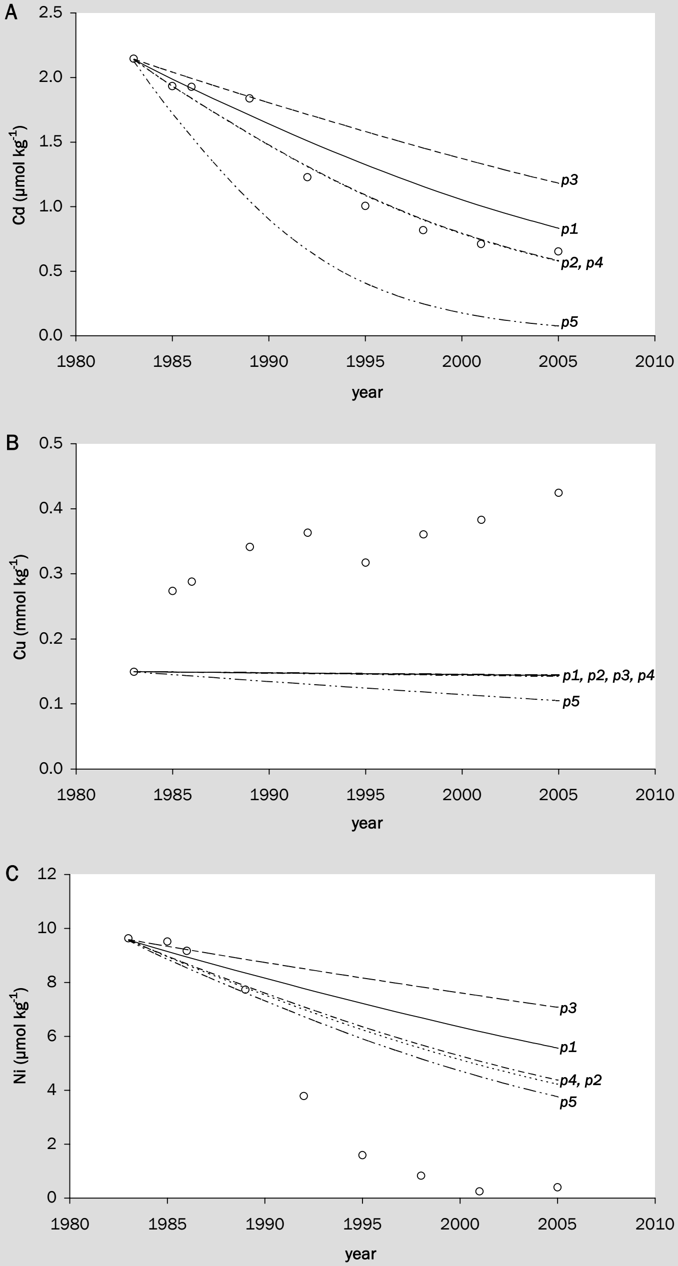

Figure 4.1: Continued on the next page.

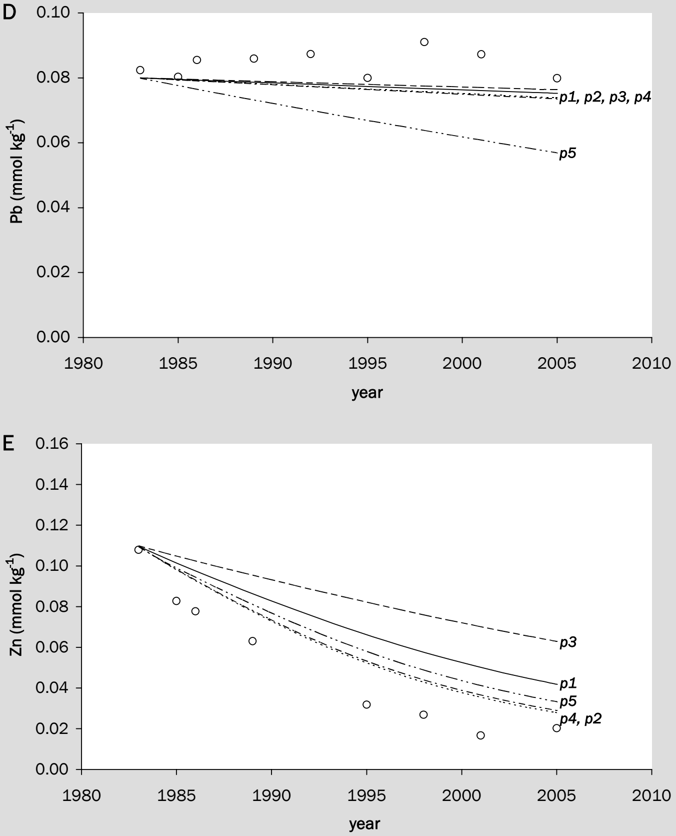

Figure 4.1: Metal content in the pH-4 plot as function of time. Field data are shown by the open circles and leaching predictions are indicated by the lines; straight line: prediction 1; dotted line: prediction 2; dashed line: prediction 3; dashed dotted line: prediction 4; dashed double dotted line: prediction 5. For soil properties used for the various predictions see Table 4.1. A: Cd; B: Cu; C: Ni; D: Pb; E: Zn.

varies somewhat since 1983 and because the pH in the field will also vary, the leaching prediction has been tested on its sensitivity for pH changes on metal leaching. Leaching is predicted taking the lowest (prediction 2) and the highest (prediction 3) measured pH per field. The effect of pH is largest for the leaching predictions of Cd, Ni and Zn in the pH-4 plot (Figure 4.1). In the pH-6 plot the effect of pH on the leaching of Cd, Ni and Zn is less than in the pH-4 plot (Figure 4.2). The pH sensitivity for both Cu and Pb is low compared to the other studied heavy metals and the pH level (pH-4 an pH-6 plot) of the plot does not affect this sensitivity. The reason for this is that the pH dependence of the binding to the DOC and to the soil is similar, which leads to a very low pH effect in case most of the dissolved metal ions are bound to DOC (Plette *et al.*, 1999). These predictions (prediction 2 and 3) show that when the pH is highly variable throughout the year that this can have a substantial effect on the leaching of the pH sensitive metals (Cd, Ni and Zn). However, one should realize that the salt level will also affect the pH during the season. Wet periods are needed for transport and wet periods create lower salt levels, leading to an increase in pH. The sensitivity for organic matter content has also been tested, because the OM content of the field plots changed during the studied period. A decrease in the organic matter content with time will enhance the leaching, because fewer binding sites are available. A decrease of the organic matter of about 1% unit was found on a total initial content of about 4%. The effect of a decreased organic matter content is shown in Figure 4.1 and 4.2 by prediction 4. Again the effect of the decreased organic matter content is largest for the pH-4 plots and has primarily an effect on the leaching of Cd, Ni and Zn in the pH-4 plot. Leaching of Cu and Pb increases only very slightly when the organic matter content was lowered. The effect of lowering organic matter is more pronounced at low pH because competition with protons for adsorption sites is relatively more important with decreasing available sorption sites.

In addition to the sensitivity for changes in pH and OM content, the DOC concentration is expected to affect the leaching of the metals in the soil, especially for those metals that have a strong affinity for organic matter, like Cu and Pb. The DOC concentration has been increased almost 10 fold to 100 mg L^{-1} for prediction 5. This concentration is based on pore water extractions of these samples (Fest *et al.*, 2007a). Since these pore water concentrations were performed with dried soil samples it is unclear how representative these results are. Römkens *et al.* (2004) derived a regression equation in which the DOC concentration is a function of the organic matter content, the pH and the solid/solution ratio. Application of this regression equation to the studied plots, results in DOC concentrations at a field solid/solution ratio of 100-200 mg C L^{-1}, which is considerably higher than the experimentally derived DOC concentrations. Contrary to this are the DOC concentrations found by Temminghoff *et al.* (1998) in a column experiment. These column experiments performed with the same soil samples show DOC concentra-

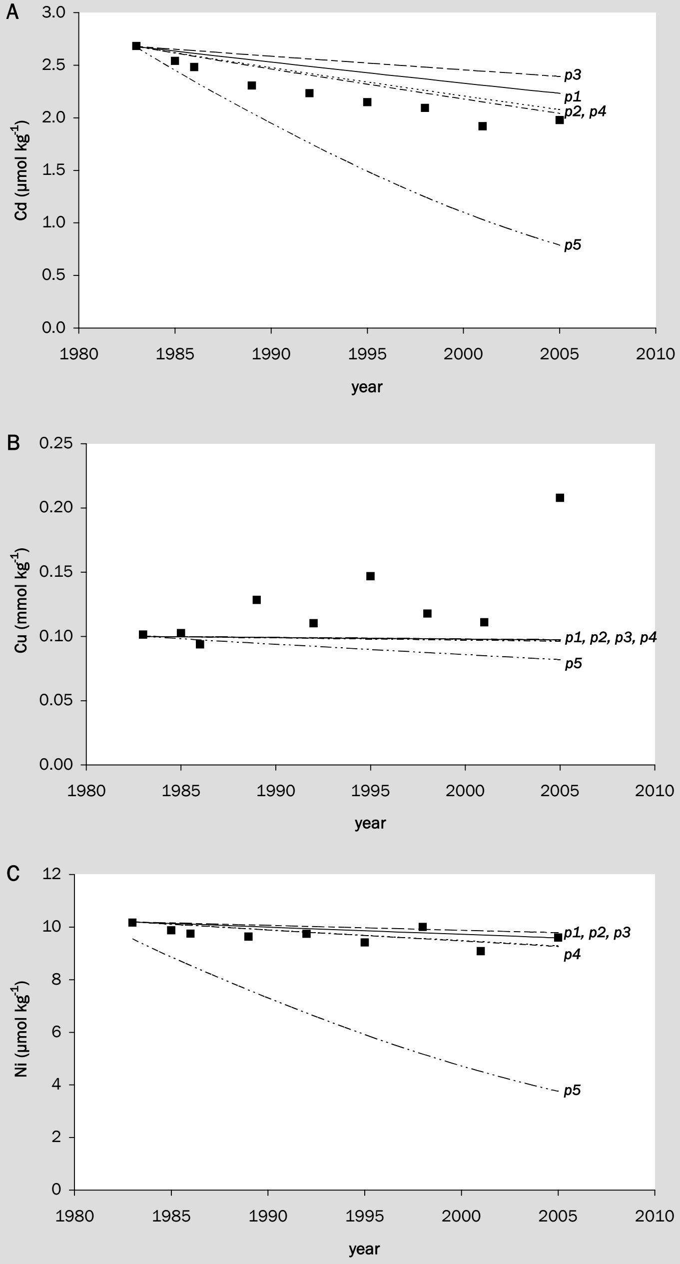

Figure 4.2: Continued on the next page.

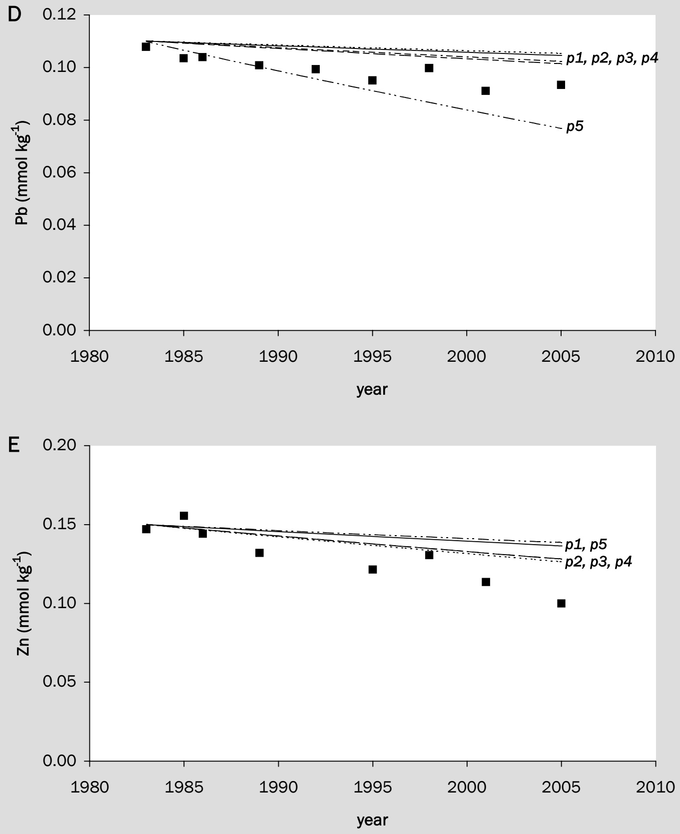

Figure 4.2: Metal content in the pH-6 plot as function of time. Field data are shown by the black squares and leaching predictions are indicated by the lines; straight line: prediction 1; dotted line: prediction 2; dashed line: prediction 3; dashed dotted line: prediction 4; dashed double dotted line: prediction 5. For soil properties used for the various predictions see Table 4.1. A: Cd; B: Cu; C: Ni; D: Pb; E: Zn.

tions of 10 mg C L^{-1} for the pH-4 plot and 20 mg C L^{-1} for the pH-6 plot at low ionic strength (0.003 M $NaNO_3$). Based on these contradicting findings it is still unclear what levels of DOC represent the field situation. Results from other studies indicate that DOC concentrations in sandy soil in agricultural use are somewhere in the range between 10 and 100 mg C L^{-1} (Kalbitz *et al.*, 2003; Vinther *et al.*, 2006).

Prediction 5 (Figure 4.1 and 4.2) shows that an increase in the DOC concentration from 10 to 100 mg C L^{-1} results in an increase in the metal leaching. This effect is quite large for Cd at both high and low pH; most of the Cd present will be leached at such a high DOC concentration. For Cu, the effect of an increased DOC concentration seems rather small; however compared to the other leaching predictions a DOC concentration of 100 mg C L^{-1} does result in a visible leaching of Cu. This effect was also found for Pb; both metals are strongly bound to soil organic matter.

With this multi-component modeling approach it is also possible to test the effect of competing cations in the soil system. In this context the competing effect of Al on metal leaching is tested. The effect of Al might have an effect on the leaching in the pH-4 plot Results of this prediction are given in the appendix assuming equilibrium with $Al(OH)_3$. The Al concentration does affect the leaching of some heavy metals; the effect of Al competition only becomes clear for the pH sensitive metals Cd, Ni and Zn. Furthermore, the effect of Al competition on metal leaching is only visible for the pH-4 plots and does not show any effect in the prediction of metal leaching for the pH-6 plot.

The leaching predictions show that notwithstanding certain uncertainties it is possible to predict long-term metal leaching quite successfully. The leaching of Pb is predicted quite well; very little Pb is predicted to be leached from the considered soil layer. This is in good agreement with the behavior of Pb in the field, showing a stable reactive content. In the case of the pH sensitive metals, Cd, Ni and Zn, leaching predictions at pH 4 are close to the measured leaching; however, at higher pH, the leaching for these metals is somewhat underpredicted. For Cu, the increased content was not calculated by the model prediction since the contamination from surrounding fields was not taken into account in the model prediction. However, these prediction indicate that Cu has a rather insignificant leaching behavior due to its very strong binding to the soil. This limited mobility of Cu was also found by Scokart *et al.* (1983) for metal polluted sandy and loamy soils around Zn-smelters. Besides this leaching behavior of Cu, the field data indicate that the deposition of metals from surrounding plots that are very high in copper considerably influence the total metal content in the plots; in this case the initial amount was tripled.

With the present knowledge of binding of metals to natural organic matter, the leaching of indigenous Cd, Cu, Ni, Pb and Zn can be predicted rather well by one-dimensional transport for field situation considering the necessary simplifications that are inherent in these calculations. This approach can be useful in determining potential risks of metal-polluted soils and can be used to develop sustainable remediation options. The impact of changes in soil properties as a result of land use changes on metal leaching can be estimated using this type of approach.

Acknowledgements

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> Leven is wat er met je gebeurt, terwijl je bezig bent
> met het maken van andere plannen
> - *John Lennon* -

CHAPTER 5

Modeling multi-component metal leaching from a Cu contaminated sandy soil

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Abstract

Predicting heavy metal leaching from soils is of importance for soil risk assessment studies. At present, advanced adsorption models are available to predict heavy metal behavior in soils. In the present study, the leaching of heavy metals from a Cu contaminated soil was studied and the multi-component leaching from this Cu contaminated soil was predicted with an advanced adsorption model, viz. the NICA-Donnan model. Significant Cu has been leached in 22 years after the contamination; more than 60% of the initial Cu content has been lost in both studied plots and was not influenced by the pH difference (pH 4 vs. 6). The leaching of other heavy metals is not influenced by the high Cu leaching. The used modeling approach has shown to be able to predict leaching of indigenous metals quite well, within a certain range of uncertainties. However, the considerable leaching of Cu from this Cu contaminated soil could not be predicted by the model under reasonable assumptions of soil properties. It must be concluded that after application of the Cu-salt, it will take several years before the Cu is distributed over all binding sites in the top soil layer. In the meanwhile, significant Cu has already been transported downward to deeper soil layers. Toxicological data should be handled with care, since these tests have been performed with highly mixed soils and cannot be compared with freshly contaminated soils. These results show the importance to consider 'bio-available' fractions in both toxicological testing as well as in soil research in order quantify risks of contaminations.

5.1 Introduction

Heavy metals are natural occurring elements in the environment; some are essential for organisms in their metabolic processes, others not. Increased levels of heavy metals occur in soils as a result of anthropogenic activities. For example, agricultural soils can have elevated metal contents as a result of manure and fertilizer application. But also atmospheric deposition from local sources (Zn smelters) can lead to increased heavy metal levels.

The leaching of heavy metals from agricultural soils plays important role in the loading of surface water with heavy metals. Sometimes this route can be even the dominant process for the loading of the surface water with heavy metals (Römkens *et al.*, 2003). From this perspective, thorough understanding of heavy metal behavior in field soils is important to identify effects of changing circumstances in soils on the heavy metal present in these soils. Changes in land use (Römkens and Salomons, 1998; Salomons, 1998) and climatic can affect soil properties and therefore also influence the sorptive behavior of the soil. However, it is still unclear in what way climate change influences sorptive properties of the soil in particular the soil organic matter content (Rustad *et al.*, 2001; Davidson and Janssens, 2006; Reich *et al.*, 2006; Rey *et al.*, 2007). Besides quantifying the effects of potential changes in soil properties, currently also the discussion on availability of pollutants for organisms arises between science and policy makers. The leaching behavior of heavy metals from soil is of general interest in for soil risk assessment and surface water quality aspects.

Ecotoxiclogical testing of heavy metals in soils is often forced to use spiked soil samples. The use of spiked soils has some advantages because the range of metal content can be determined by the added metals and also the effect of a single contamination can be tested. Whereas in the field often combinations of contaminations occurs and interpretation of toxic effects is complicated. On the other hand spiking of uncontaminated soils leads to many changes in the chemistry and biology of the soil and it is highly insecure that freshly contaminated soils can be compared with diffusely contaminated soils (Smit and Van Gestel, 1998). Field contaminated soils received their contamination on a longer time scale and are in a 'semi-equilibrium' with their contamination in contrast to laboratory spiked soils. Besides, the response of organisms that are brought to and reared in the laboratory can complicate the interpretation of these eco-toxicological tests

(Sauvé, 2006).

Prediction of heavy metal leaching from a sandy soil by application of an advanced adsorption model was already studied by Fest *et al.* (in preparation-b) for heavy metals present at background level. Prediction of metal leaching showed a good agreement with results from a long-term field experiment. In this study a distinct difference in leaching behavior was shown for various metals. Copper and Pb adsorb strongly onto organic matter and are therefore not very susceptible for leaching to deeper soil layers. Contrary, Cd, Ni and Zn are less strongly sorbed onto organic matter and are more susceptible for leaching especially at lower pH levels (pH ~4). Until now, long-term field data on the leaching of heavy metals from contaminated soils are lacking.

The distribution of heavy metals in soil profiles is besides the chemical solid/solution distribution also strongly dependent on the biological activity and the land management. For instance, earthworms are able to transport metals through the soil profile (Van Wijnhoven *et al.*, 2006). Also mechanical agricultural practices like ploughing affect the distribution of deposited heavy metals in the topsoil.

Soil organic matter is the major adsorption phase in sandy soils and characterization of the soil organic matter in terms of humic substances could improve adsorption modeling. Furthermore, the changes in soil organic matter composition could also give some information about the leached fraction of the humic substances and related metal leaching as well.

The aim of this study is two-fold: (i) to study Cu leaching from a Cu contaminated soil at two pH levels; (ii) to predict Cu leaching from a Cu contaminated soil with an advanced modeling approach.

5.2 Materials and Methods

Samples

In this study we used soil samples from the Wildekamp experimental field (Temminghoff *et al.*, 1994; Korthals *et al.*, 1996), situated in the surrounding of Wageningen. This experimental field consists of plots (6 × 11 m) with a randomized block design with 4 pH (pH-KCl: 4.0, 4.7, 5.4, and 6.1) levels and 4 Cu levels (addition of 0, 250, 500, and 750 kg $CuSO_4$ per ha). pH levels were established by application of calcium carbonate or sulphur and Cu levels were established by application of different amounts of $CuSO_4$ (Lexmond, 1980). The pH was readjusted back to their nominal value every 6 years. This experimental field is in use for crop production; maize, potato and oat are grown in rotation.

In a previous study we already used samples from this experimental field to predict metal leaching; only samples with metals at background level were used (Fest *et al.*, 2007b). For this study we sampled plots with elevated Cu contents (750 kg $CuSO_4$ ha^{-1}) at the two utmost pH levels (pH-KCl 4.0 and 6.1). According to their nominal value, the plot with the lowest pH will be further referred as pH-4 plot and the plot with the highest pH will be referred as pH-6 plot. Since the construction of the experimental field, samples from the plot have been taken on a regular basis. The sampling of the experimental field has resulted in a series of 9 samples since 1982. Samples have been dried at 40 °C, sieved (< 2 mm) and stored at room temperature until further analysis.

Soil characteristics

Determination of several soil characteristics has been preformed in the same batch (2005) for all used samples. pH and DOC concentration have been determined in a 0.01 M $CaCl_2$ extract (Van Erp *et al.*, 1998; Houba *et al.*, 2000). pH was measured with a combined glass electrode; DOC concentration was measured on a TOC analyzer (Skalar SK12). Reactive metal content was determined by 0.43 M HNO_3 extraction at a solid/solution ratio (SSR) of 0.1 kg L^{-1}). This method was used in previous studies as a measure for the reactive metal content (Boekhold *et al.*, 1993; Tipping *et al.*, 2003; Dijkstra *et al.*, 2004; Römkens *et al.*, 2004). Metal concentration in the HNO_3 extract were measured by ICP-AES (IRIS). Soil organic matter content of the soil samples was determined by loss-on-ignition (LOI) (Houba *et al.*, 1997).

Leaching calculations

Leaching calculations were performed in line with the paper on metal leaching from the non polluted plots (Fest *et al.*, 2007b). We calculated the amount of metals that has been leached from the sampled plots by using competitive adsorption modeling for heterogeneous sorbents combined with transport calculations. Both sorption and transport calculations were performed within the chemical equilibrium program ECOSAT (Keizer and Van Riemsdijk, 1998).

Distribution of metals between the solid and solution phase was calculated assuming that organic matter is the main sorptive phase in this sandy soil. The contribution of other sorbing surfaces is expected to be minor (< 10%) for these fields (Weng *et al.*, 2001a). Sorption onto organic matter (solid and dissolved) was described with the NICA-Donnan model (Kinniburgh *et al.*, 1999; Milne *et al.*, 2003). Similar as Weng *et al.* (2001a), the amount of organic matter is determined by LOI and using the measured CEC of the soil it is calculated that the binding capacity is approximately 31% of the generic humic acid. Total reactive metal content in the system is based on the 0.43 M HNO_3 extractable metal content. Since no exact data of metal deposition on the experimental field are available and since the average deposition is low, we assumed no significant deposition of heavy metals on this field since 1982.

Transport of metals in the water phase was calculated by one-dimensional flow with a constant flow and moisture content. The net precipitation flux for agricultural land on sandy soils under Dutch climatic conditions is about 350 mm yr^{-1} (Willems *et al.*, 2005). The volumetric water content was assumed to be 0.2 equal with a SSR of 6.75 kg L^{-1}. The transport calculations were performed for a period of 22 years, from 1983 to 2005 covering the total sampling period. Since salt concentration and composition varies throughout the year, an average of 0.01 M $CaCl_2$ was enforced in the system. Leaching calculations consider only the top soil layer (0-20 cm). After calculation of the total leaching for the 22 year period, the calculated metal content was averaged over the considered layer.

Organic matter composition

Organic matter composition was characterized in terms of a humic acid (HA), a fulvic acid (FA) and a hydrophilic (HY) fraction. After extraction of the solid organic matter from the soil samples, the fractions are determined quantitatively by a batch procedure (Van Zomeren and Comans, 2004). This method is based on the current recommend method by the International Humic Substance Society (IHSS) (Thurman and Malcolm, 1981; Swift, 1996). Samples from 1986 and 2005 were used at both pH levels to evaluate the effect of time on the composition of the organic matter.

5.3 Results and Discussion

Field experiment

Leaching behavior of the Cu is shown by the data points in Figure 5.1 and the leaching of the other studied metals is given in Appendix IV. Trends of the pH and organic matter content have already been discussed in the previous paper (Fest *et al.*, 2007b) and do considerably differ from the non Cu-polluted plots. Data on pH and organic matter are given for every sample in Appendix IV.
The reactive Cu content in the samples showed a considerable similar decrease since 1983 for both pH levels. This indicates that the leaching of Cu in these plots is not affected by the pH, since these plots differ in pH; the actual pH of these plots varies between 3.7 and 4.2 for the pH-4 plot and between 4.8 and 5.9 for the pH-6 plot. Both plots have lost more than 60% of their Cu-content since 1983, indicating a significant leaching of Cu from these plots. The highest leaching rates were found in the first years after application of Cu to these plots. After 1990 the leaching showed a more gradual trend.

To ensure that the decrease in reactive Cu content is the result of leaching and not of ageing of Cu, the total metal content (aqua regia) was also measured in some samples. The total Cu content in the samples showed the same decrease as the reactive Cu content. And therefore, it was concluded that ageing of Cu did not play a role in this study. Results of the aqua regia extraction are compared to the 0.43 M HNO_3 extraction in the supporting info.

Another factor that need to be considered in the perspective of the decreased reactive Cu content is the uptake of Cu and other metals by plants. From a similar experiment (Lexmond, 1980), Cu uptake by maize plants and accompanying yields are available. This study showed that although the Cu content in maize is higher for the pH-4 plot (25 mg Cu kg^{-1} for pH-4 plot vs. 5 mg Cu kg^{-1} for pH-6 plot), the total removed Cu is higher for the pH-6 plot because the yield of this plot is about 70 times higher than of the pH-4 plot (0.14 ton ha^{-1} for pH-4 plot vs. 9.73 ton ha^{-1} for pH-6 plot). The Cu concentration in the pH-4 plot reached the toxicity level indicating a significant loss in maize yield. From these results, the contribution of metal uptake by crops was estimated and compared to the reac-

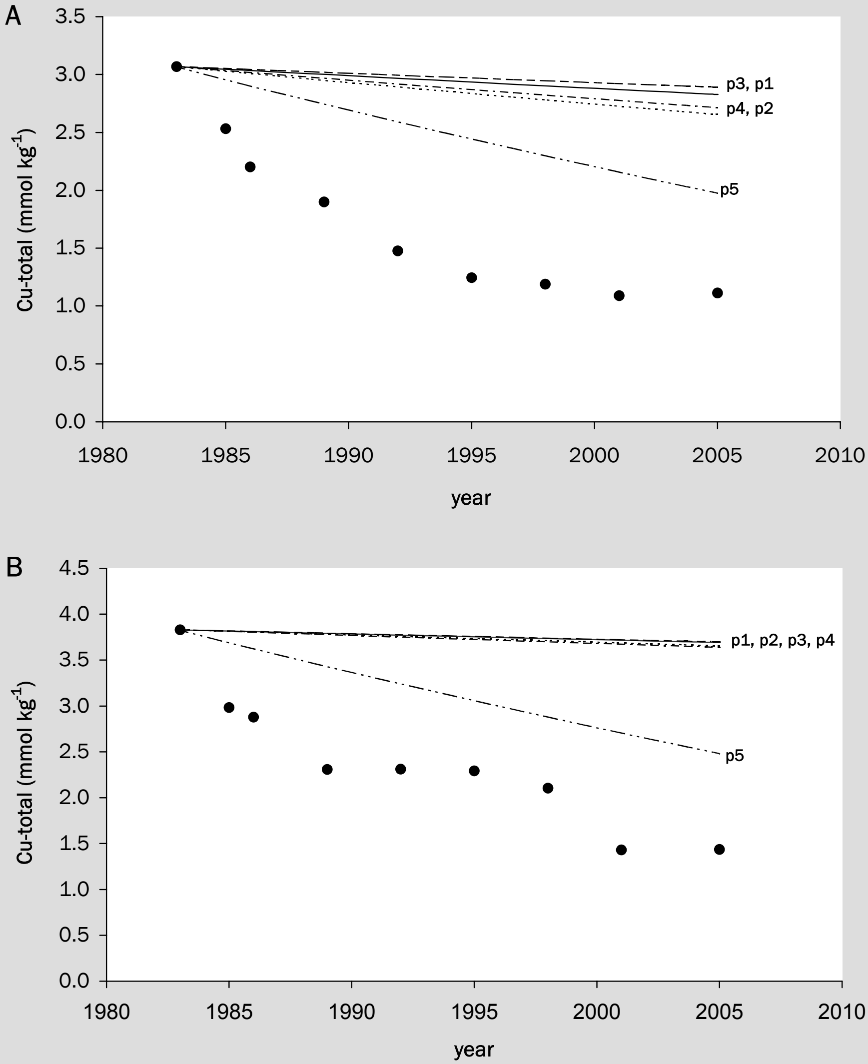

Figure 5.1: Copper content in the experimental plots as function of time. Field data are shown by the black circles and leaching predictions are indicated by the lines; straight line: prediction 1; dotted line: prediction 2; dashed line: prediction 3; dashed dotted line: prediction 4; dashed double dotted line: prediction 5. For explanation of the five options see text and for exact soil properties used in the various predictions see Table 5.1. A: pH-4 plot and B: pH-6 plot.

tive Cu content in the plots. Assuming that during the period 1983 and 2005 the same amount of Cu has been taken up by the crop and that the yield per field stayed also rather constant, the effect of Cu uptake by crops is not significant compared to the total loss of Cu from the plots (0.02% and 0.22% for respectively pH-4 and pH-6 plot). From these findings we concluded that the decrease in Cu content must be the result of leaching of Cu to deeper soil layers.

Reactive Ni content showed some elevation for both plots (20 and 40 µmol kg^{-1} for respectively the pH-4 and pH-6 plot) compared to the non Cu-polluted plots (~10 µmol kg^{-1}) described by Fest *et al.* (2007b). The Ni content has increased probably by the application of impure $CuSO_4$. The Ni content was immediately affected by the pH levels, because the pH-4 plot showed only half of the Ni content of the pH-6 plot. Reactive Ni content in the pH-4 is almost entirely leached in 2005 (97% lost); in the pH-6 plot more than half of the reactive Ni content was leached.

The other studied heavy metals (Cd, Pb and Zn) were not artificially elevated and show comparable leaching behavior as in the non Cu-polluted plots (Fest *et al.*, in preparation-b). Leaching data for Cd, Ni, Pb and Zn are given in the supporting info. The leaching of Cd and Zn was distinguished by the effect of pH, pH-4 plots showed higher leaching than the pH-6 plots (Cd: 68% vs 11% and Zn: 77% vs. 35% for pH-4 and pH-6 plots respectively). Lead does not show any significant leaching for both plots and is thus not measurably affected by pH.

Table 5.2 compares the relative decrease in metal content as a result of leaching for the non Cu-polluted and Cu–polluted plots. No significant effect of Cu pollution was found for the leaching of the other metals. Only a slight difference was found between Cd leaching in the pH-6 plot. The high Ni leaching in the Cu-polluted pH-6 plot was caused by the expected increase of Ni content as a result of Cu application on the field. Therefore, relative Ni leaching cannot be compared between the non Cu-polluted and Cu-polluted fields. Lead only showed a small leached amount or even an increase in Pb content, no effect of Cu on Pb is expected from these results.

Leaching predictions

Leaching predictions are shown for Cu under various assumptions in Figure 5.1. Assumptions made in the leaching predictions for some soil properties are given in Table 5.1. The first leaching calculation assumed the average pH over time in

Table 5.1: Soil properties used in the various leaching calculations shown in Figure 5.1.

	pH-4 plot			*pH-6 plot*		
prediction	pH	OM (%)	DOC (mg C L^{-1})	pH	OM (%)	DOC (mg C L^{-1})
1	4.0	4.0	12	5.5	3.8	14
2	3.7	4.0	12	4.8	3.8	14
3	4.2	4.0	12	5.9	3.8	14
4	4.0	2.5	12	5.5	3.0	14
5	4.0	4.0	144	5.5	3.8	170

the plot, the initial organic matter content and the DOC concentration measured in 0.002 M $CaNO_3$ extract (Fest *et al.*, 2007a). This first calculation showed a significant underprediction of the Cu leaching in both plots. The modeling prediction showed a rather strong binding of Cu on the soil organic matter, hardly influenced by the pH of the plot. Decreasing pH (prediction 2) and organic matter content (prediction 4) showed only a minor effect on the leaching of Cu from both plots. Only increasing the DOC concentration by a factor 10 showed an effect on the Cu leaching (prediction 5). This high DOC concentration was based on pore water extractions (Fest *et al.*, 2007a). It is still unclear in what range field DOC concentration can be expected. There are indications that DOC concentrations of 100 mg C L-1 are not uncommon in these soils (Römkens *et al.*, 2004), however other studies found DOC concentrations in these soils closer to 10 mg C L^{-1} (Temminghoff *et al.*, 1998; Weng *et al.*, 2002b).

As shown by the above described leaching predictions, organic matter is an important factor for Cu binding in these soils and therefore more insight was gained in the composition of the organic matter. The total organic matter content decreased since 1983 in the plots, because the organic fertilizer application was stopped after construction of the experimental field. The fractions of humic acid (HA), fulvic acid (FA) and hydrophilic acid (HY) have been quantified in the samples from 1986 and 2005. The amount of humic substances is about half of the total organic matter content, meaning that half of the organic matter content con-

Table 5.2: Relative loss of metal from the studied plots between 1983 and 2005; comparison of non Cu-polluted and Cu-polluted samples.

	relative decrease metal content (%)			
	pH-4 plot		*pH-6 plot*	
	- Cu	+ Cu	- Cu	+ Cu
Cd	70	68	26	11
Cu	-184	64	-105	63
Ni	96	97	6	57
Pb	3	0	13	-7
Zn	81	77	32	35

sists of insoluble organic matter. Humic acid is the major fraction of the humic substances and this fraction decreased with 1 g C kg^{-1} between 1986 and 2005. Less FA and HY were present in the organic matter compared to HA. The FA also showed a decrease of 1 g C kg^{-1} between 1986 and 2005 in contrast to HY fraction that stayed rather constant over time. The decrease in both HA and FA could be an indication that DOC concentrations were higher directly after the construction of the experimental field compared to concentrations found nowadays. Nevertheless, these findings are all based on dried and prepared samples and only direct field measurements can give insight in real amounts of DOC that can be found in these soils.

Prediction of leaching of other heavy metals (Cd, Ni, Pb and Zn) was satisfactory and did not significantly differ from the predictions in Fest *et al.* (2007b) and are not further discussed in this paper. Leaching prediction for these metals are given in Appendix IV.

Current adsorption modeling show that leaching of indigenous metals can be predicted rather well with the necessary simplifications inherent to these predictions. The considerable leaching of artificially added Cu could not be predicted with the model using reasonable assumptions for soil properties. The most likely explanation is that after the application of $CuSO_4$ salts at rather high quantities to the soil, it takes several years to distribute Cu over all available binding sites in the topsoil that is ploughed every year. During this period local Cu concentrations can be much higher than expected at equilibrium, resulting in increased leaching. This effect would be rather specific for Cu, because it is the only metal that has been added. Indirectly it can also affect other ions to some extent, because Cu competes with other metal ions for binding sites. However, leached amounts of indigenous metals do not show any effect of increased Cu contents. In addition, this great disturbance of the soil system could also have resulted in toxic effects on soil biota, which may have led to a larger DOC flux at the start of the experiment, and could be responsible for the strong decrease of Cu in the beginning of the experiment. However, such increased DOC level would also have led to increased leaching of the indigenous metals, which is not what is observed from the data.

At high Cu concentrations precipitation of Cu-minerals becomes a possibility is also a process that can influence Cu mobility in the soil. Such a process would only lead to lower leaching predictions. The high Cu leaching directly after contamination with copper salts suggest that also the toxic effects are in the beginning higher than would have been expected using the assumption of an immediate homogeneous distribution over all available binding sites. Similar processes can be operational in toxicological testing and derivation of critical limits should be considered carefully. The results from this field experiment indicate that significant time (years) can be needed in the field to obtain a distribution of the added pollutant over the available binding sites in the soil layer of interest, even when this layer is mixed regularly due to ploughing activities. Results of the present study emphasize the importance to consider 'bio-available' fractions in both toxicological testing as well as soil research in order quantify real risks of contaminations.

Acknowledgements

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> *Goed luisteren vereist inleving en*
> *het achterwege laten van vooroordelen*
> *- Conny Palmen -*

CHAPTER 6

Groundwater chemistry of Al under Dutch sandy soils: Effects of land use and depth

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Abstract

Aluminum has received great attention in the second half of the 20th century, mainly in the context of the acid rain problem mostly in forest soils. In this research the effect of land use and depth of the groundwater on Al, pH and DOC concentration in groundwater under Dutch sandy soils has been studied. Both pH and DOC concentration play a major role in the speciation of Al in solution. Furthermore, the equilibrium with mineral phases like gibbsite, amorphous $Al(OH)_3$ and imogolite, has been considered. Agricultural and natural land use were expected to have different effects on the pH and DOC concentration, which in turn could influence the total Al concentration and the speciation of Al in groundwater at different depth (phreatic, shallow and deep). An extensive dataset (n = 2181) from the national and some provincial monitoring networks on soil and groundwater quality was used. Land use type and groundwater depth did influence the pH, and Al and DOC concentration in groundwater samples. The Al concentration ranged from < 0.4 µmol L^{-1} at pH > 7 to 1941 µmol L^{-1} at pH < 4; highest Al concentrations were found for natural-phreatic groundwater. The DOC concentration decreased and the median pH increased with depth of the groundwater. Natural-phreatic groundwater showed lower pH than the agricultural-phreatic groundwater. Highest DOC concentrations were found for the agricultural-phreatic groundwater, induced by the application of organic fertilizers. Besides inorganic complexation, the NICA-Donnan model was used to calculate Al^{3+} concentrations for complexation with DOC. Below pH 4.5 groundwater samples were mainly in disequilibrium with a mineral phase. This disequilibrium is considered to be the result of kinetic constraints or equilibrium with organic matter. Log K values were derived by linear regression and were close to theoretical values for $Al(OH)_3$ minerals (e.g. gibbsite or amorphous $Al(OH)_3$), except for natural-phreatic groundwater for which lower log K values were found. Complexation of Al with DOC is shown to be an important factor for the Al concentrations, especially at high DOC concentrations as was found for agricultural-phreatic groundwater.

6.1 Introduction

Since the end of the 1970s, the chemistry of Al in the environment has received great attention. Elevated Al concentrations are an important result of acidification of forest soils (Cronan and Schofield, 1979; Ulrich *et al.*, 1980; Johnson *et al.*, 1981; David and Driscoll, 1984; Mulder *et al.*, 1989). Increased Al concentrations can be toxic to aquatic biota and terrestrial vegetation (David and Driscoll, 1984) and these increased Al concentrations could therefore also be a potential risk for drinking water production.

Dissolution of Al from the soil matrix plays an important role in the buffering of acid deposition on soils (Berggren *et al.*, 1998). In previous research the Al concentration in soil solutions and natural waters has been assumed to be controlled by the equilibrium with gibbsite or some other forms of $Al(OH)_3$ (Nordstrom and Ball, 1986; Gustafsson *et al.*, 2001). However, it has often been shown that Al in soil solutions is frequently in disequilibrium with $Al(OH)_3$ as well as with many other Al-minerals e.g. jurbanite ($AlSO_4OH$) (Haag *et al.*, 2001). Other research has shown that Al concentrations are controlled by complexation with soil organic matter (Cronan *et al.*, 1986; Mulder *et al.*, 1989; Walker *et al.*, 1990; Berggren and Mulder, 1995; Wesselink and Mulder, 1995). Wesselink *et al.* (1996) concluded that organic matter controls the Al activity in soils by complexation, but both organic matter complexation and kinetic controlled dissolution of inorganic Al will contribute to the Al mobilization in soils. For example, Swiss forest soil samples are close to saturation with respect to amorphous Al hydroxides at pH > 5.5, but these soils show that $Al(OH)_3$ is a poor predictor for the Al^{3+} activity in soil below pH 5.5. Instead, the Al^{3+} activity is controlled by complexation with organic matter below pH 5.5 (Graf Pannatier *et al.*, 2004). Van Hees (2001a) studied a large number of podzolic forest soils (Sweden) for their Al controlling mechanisms. The experimental results show that in the pH-range 4.0-6.2 no equilibrium with any mineral phase could explain the Al solubility in these soils and that for modeling purposes organic complexation models are best used for these soil samples.

Besides $Al(OH)_3$ minerals, other studied Al controlling phases are hydroxyl-Al interlayered 2:1 minerals (Dahlgren *et al.*, 1989), imogolite or the less ordered form proto-imogolite allophane (Farmer *et al.*, 1980), 1:1 aluminosilicate like poorly crystalline kaolinite (Zysett *et al.*, 1999) or feldspars (Mol *et al.*, 2003).

These potential controlling mineral phases show a 1:3-relation between pAl^{3+} and pH, except for the hydroxyl-Al interlayered 2:1 minerals. In contrast, when Al concentration is regulated by equilibrium with organic matter a more or less 1:2-relation is found between pAl^{3+} and pH (Berggren and Mulder, 1995; Wesselink *et al.*, 1996; Skyllberg, 1999). Similar to the disequilibrium between Al-hydroxide minerals and soil solutions, Al concentrations found in surface waters are not in equilibrium with mineral phases. Sullivan and Cosby (1998) found a relation between pH and pAl^{3+} close to 2:1 for lake waters. This is in contrast with the expected 3:1-relationship when the Al concentration is controlled by $Al(OH)_3$. Cronan *et al.* (1986) concluded that Al-speciation in natural waters is controlled by equilibrium with a solid humic phase, instead of Al dissolution being kinetically constrained.

The Al chemistry of soil solutions and natural waters is very important in the context of acidification of aquifers. Several studies have been conducted on the effect of acidification of specific aquifers (Moss and Edmunds, 1992; Hansen and Postma, 1995; Kjøller *et al.*, 2004) or the susceptibility of aquifers to acidification on national scales (Edmunds and Kinniburgh, 1986). The objective of this research was to study the effect of land use and depth of the sampled groundwater on Al speciation in groundwater under Dutch sandy soils. Here, depth is an indication for residence time, with a net discharge in the Netherlands of 250-300 mm $year^{-1}$. We used an extensive dataset of the Dutch groundwater and soil monitoring network (n = 2181), at a provincial and national scale. The speciation of Al was calculated taking DOC complexation into account. Furthermore, the relationship between pH and pAl^{3+} was studied for the different land use types and depths of the groundwater by regression analysis. Finally, with the log K values from the regression analysis the total Al concentration was calculated as a function of pH with and without taking DOC complexation into account.

6.2 Materials & Methods

Monitoring networks

The groundwater data originated from various Dutch monitoring networks. A dataset was compiled on samples from sandy soils with agricultural and natural land use types, since these two groups were the main land use types in the monitoring networks. Only samples with measurements of pH, DOC and Al were

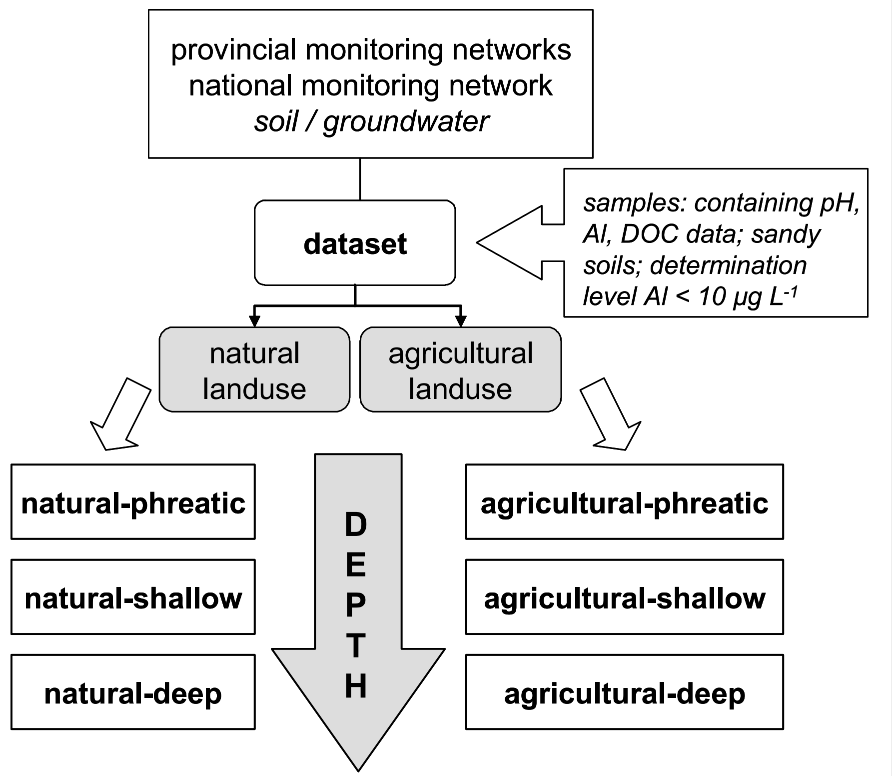

Figure 6.1: Schematization of the division of the total dataset in different groups based on land use and depth of the groundwater.

added to the dataset (*n* = 2181). First, the dataset was divided into two groups based on land use (agricultural and natural). Furthermore both groups were subdivided by the depth of the sampled groundwater, phreatic (groundwater immediately below groundwater table), shallow (< 10 m) and deep (> 10 m). A schematization of the division of the dataset is shown in Figure 6.1. The data on phreatic groundwater originated from the soil quality monitoring network Noord Brabant (Van der Grift *et al.*, 2004). The data on shallow and deep groundwater originated from national (Van Duijvenbooden *et al.*, 1985; Pebesma and De Kwaadsteniet, 1997) and provincial groundwater quality networks. Van der Grift *et al.* (2004) provide extended information on the monitoring networks and their results. A thorough description of the Dutch environmental monitoring systems is given by Mol *et al.* (2001).

The division between phreatic groundwater on one hand and shallow and deep groundwater on the other hand is based on the way the samples were taken. Phreatic groundwater was sampled for the first meter below the actual groundwater table in an open borehole. Shallow groundwater was sampled from permanent monitoring wells which have their well screen up to 10 m below surface, whereas deep groundwater was sampled from permanent monitoring wells which have their well screen between 10 m and 25 m below surface. All samples were filtered through 0.45 μm filter and analyzed for the elemental composition. Electrical conductivity and pH were immediately measured in the field. Samples were analyzed for HCO_3 by titration, for Cl and SO_4 by ion chromatography, for NO_3 and NH_4 by auto-analyzer (AA3), for Al, Ca, Cu, Fe, K, Na, Ni, Mg, P, Pb and Zn by ICP-MS and for DOC by total organic carbon (TOC-500). The groundwater dataset included the replication of sampling over several years. The detection limits varied because different laboratories were involved in the measurements. To exclude uncertainties in measured Al concentrations, all measurements below 10 μg L^{-1} were ruled out (568 of 2749 samples). Data on shallow and deep groundwater were collected from 1990 to 1999 and data on phreatic groundwater were collected from 2002 to 2005.

Data handling and modeling

After the division of the data in the six groups, basic statistics were calculated per group. Furthermore, the relation between the pAl^{3+} and pH was studied per group after calculation of the Al^{3+} concentration for every measurement. DOC complexation and competition with other cations was taken into account. The calculated concentrations of Al^{3+} were plotted versus pH. Linear regression was applied on the pAl^{3+} and pH data with SPSS (version 12.0.1), with a calculated and fixed slope. The linear regression was repeated for samples with $pH > 4.5$. Regression results were compared with solubility constants of various Al-(hydr) oxides. In addition, with the derived regression parameters the effect of DOC complexation on total dissolved Al was shown.

The speciation calculations for Al were performed with the chemical equilibrium program ECOSAT (Keizer and Van Riemsdijk, 1998) using the measured solution composition (Al, DOC, Ca, Cu, Fe, K, Mg, Mn, NH_4, Na, Ni, Pb, Zn, Cl, HCO_3, NO_3, PO_4, and SO_4). Complexation of cations with DOC was described with the NICA-Donnan model (Kinniburgh *et al.*, 1999). The NICA-Donnan model has been used with good results in previous studies to describe metal complexation with DOC, e.g. (Temminghoff *et al.*, 1997; Pinheiro *et al.*, 2000; Osté *et al.*, 2002; Weng *et al.*, 2002b; Ge *et al.*, 2005; Unsworth *et al.*, 2005). Weng *et al.* (2002c) showed for a pH range between 3 and 7 that the NICA-Donnan model can describe the Al complexation to HA reasonably well. For the studied pH range of the groundwater it was assumed that specific binding of hydrolyzed Al could be neglected.

The composition of DOC may vary for natural water, soil solution and groundwater. Since the exact composition of DOC was not known, assumptions had to be made about this composition. Assumptions in previous research vary from 100% FA (Christensen *et al.*, 1999) to 50% FA and 50% inert (Lofts and Tipping, 2000; Tye *et al.*, 2004; Guthrie *et al.*, 2005). A DOC composition of 65% FA and 35% inert that has been used in several previous studies was chosen (Bryan *et al.*, 2002; Weng *et al.*, 2002b; Tipping *et al.*, 2003; Ge *et al.*, 2005; Guthrie *et al.*, 2005). Low molecular weight organic acids (LMWOAs) could also play an important role in Al complexation, especially in organic and eluvial horizons of non-acidified podzolized soils. About 20-40% of Al can be complexed by these small LMWOAs. However, in this research, the LMWOAs are assumed to play a minor role since LMWOAs are not commonly present at greater depth (Holmström *et al.*, 2005).

The K-values used to calculate the solubility of gibbsite and amorphous $Al(OH)_3$ are shown in Table 6.1, as well as other reported solubility constants for Al minerals. Temperature has a significant effect on the K-values for these Al $(OH)_3$ forms: Gustafsson *et al.* (1998) found a value for log K for gibbsite of 9.40 at 281 K whereas Lindsay (1979) reported a value of log K for gibbsite of 8.04 at 298 K. Also for amorphous $Al(OH)_3$ the log K value increased when temperature decreased (9.66 at 298 K (Lindsay, 1979) and 10.78 at 281 K (Farmer, 1999)). The temperature of Dutch groundwater is 283 K on a yearly average therefore a log K value of 9.4 for gibbsite and 10.78 for amorphous $Al(OH)_3$ (281 K) were more suited for the studied groundwater data.

6.3 Results

In Table 6.2 median, 25 and 75 percentiles, minimum and maximum values are given for pH, Al concentration and DOC concentration. Results are shown for all

Table 6.1: Stability constants for Al-containing minerals used in this study and other constants found in literature at T = 298 K.

	equilibrium reaction	log K
	solubility constants used in this study (Figure 6.4)	
amorphous $Al(OH)_3$ 281K [a]	$Al(OH)_3$ (s) + 3 $H^+ \leftrightarrow Al^{3+}$ + 3 H_2O	10.78
gibbsite 281K [b]		9.40
	other reported solubility constants	
amorphous $Al(OH)_3$ [d]	$Al(OH)_3$ (s) + 3 $H^+ \leftrightarrow Al^{3+}$ + 3 H_2O	9.66
amorphous $Al(OH)_3$ [e]		10.80
gibbsite [d]		8.04
gibbsite (crystalline) [f]		7.74
gibbsite (synthetic) [e]		8.11
gibbsite (natural) [e]		8.77
gibbsite (microcrystalline) [e]		9.35
gibbsite [b]		8.29
imogolite [c]	0.5 $(OH)_3Al_2O_3SiOH$ (s) + 3 $H^+ \leftrightarrow Al^{3+}$ + 0.5 $H_4SiO_4^0$ + 1.5 H_2O	6.05
proto-imogolite sol [g]	0.5 $(HO)_3Al_2O_3SiOH$ (s) + 3 $H^+ \leftrightarrow Al^{3+}$ + 0.5 $H_4SiO_4^0$ + 1.5 H_2O	7.02
kaolinite [d]	$Al_2SiO_5(OH)$ + 6 $H^+ \leftrightarrow$ 2 Al^{3+} + 2 $H_4SiO_4^0$ + H_2O	5.45
kaolinite [h]		7.44

[a] (Farmer, 1999); [b] (Gustafsson *et al.*, 1998); [c] (Gustafsson *et al.*, 2001); [d] (Lindsay, 1979); [e] (Johnson *et al.*, 1981); [f] (Palmer and Wesolowski, 1992); [g] (Lumsdon and Farmer, 1995); [h] (Stumm and Morgan, 1996).

six land use-groundwater combinations. The median of the groundwater pH increased with depth for each land use type, indicating that pH of the groundwater is buffered by the soil. For shallow and deep groundwater no difference existed in median of the pH between the two land use types. However, the phreatic groundwater shows a clear difference in median of the pH (> 1 pH unit) between natural (4.25) and agricultural (5.46) land, which can be explained by the acidification of soils under natural vegetation and the adjustment of pH of agricultural sandy soils by liming. The range of the pH is larger for the deepest groundwater, rang-

Table 6.2: Statistics (number of data points, median, 25- and 75-percentile, minimum and maximum) of the observed concentrations (pH, total Al concentration and DOC concentration) per group.

		agri-phrea	nat-phrea	agri-shallow	nat-shallow	agri-deep	nat-deep
n		311	151	801	271	463	184
pH	median	5.46	4.25	5.70	5.60	6.10	5.89
	25percentile	4.90	4.15	5.03	4.85	5.64	5.50
	75percentile	5.97	4.48	6.39	6.50	6.74	6.62
	minimum	3.55	3.68	2.80	3.10	2.90	3.34
	maximum	6.96	6.56	7.90	7.96	8.05	8.50
Al-total (μmol L^{-1})	median	27	230	4.8	6.7	1.6	1.4
	25percentile	9.4	77	1.3	1.7	0.8	0.8
	75percentile	49	430	30	45	3.5	4.1
	minimum	0.4*	1.9*	0.4*	0.4*	0.4*	0.4*
	maximum	263	1941	295	546	641	587
DOC (mg L^{-1})	median	24.3	5.4	5.2	2.7	2.6	1.8
	25percentile	13.8	3.5	2.7	1.8	1.4	1.1
	75percentile	38.2	9.3	9.5	4.7	4.6	3.2
	minimum	2.5	0.8	0.0	0.0	0.0	0.0
	maximum	88.6	33.0	57.0	50.0	121.0	18.1

*detection limit of Al set at 10 μg L^{-1}
agri-phrea = agricultural-phreatic, nat-phrea = natural-phreatic, agri-shallow = agricultural-shallow, nat-shallow = natural-shallow, agri-deep = agricultural-deep, nat-deep = natural-deep.

ing from 2.9 to 8.5. This implies that acidification of deeper groundwater and high Al concentrations could be expected. Because of the direct relation between Al^{3+} and pH, the natural-phreatic groundwater with a low median pH showed a higher median for Al than the other groups. The median of the Al concentration seemed to decrease with the depth of the groundwater (phreatic > shallow > deep). In addition, for shallow and deep groundwater no significant difference was found for Al concentration between the land use types. The highest DOC concentration was found for the agricultural-phreatic groundwater, which is even

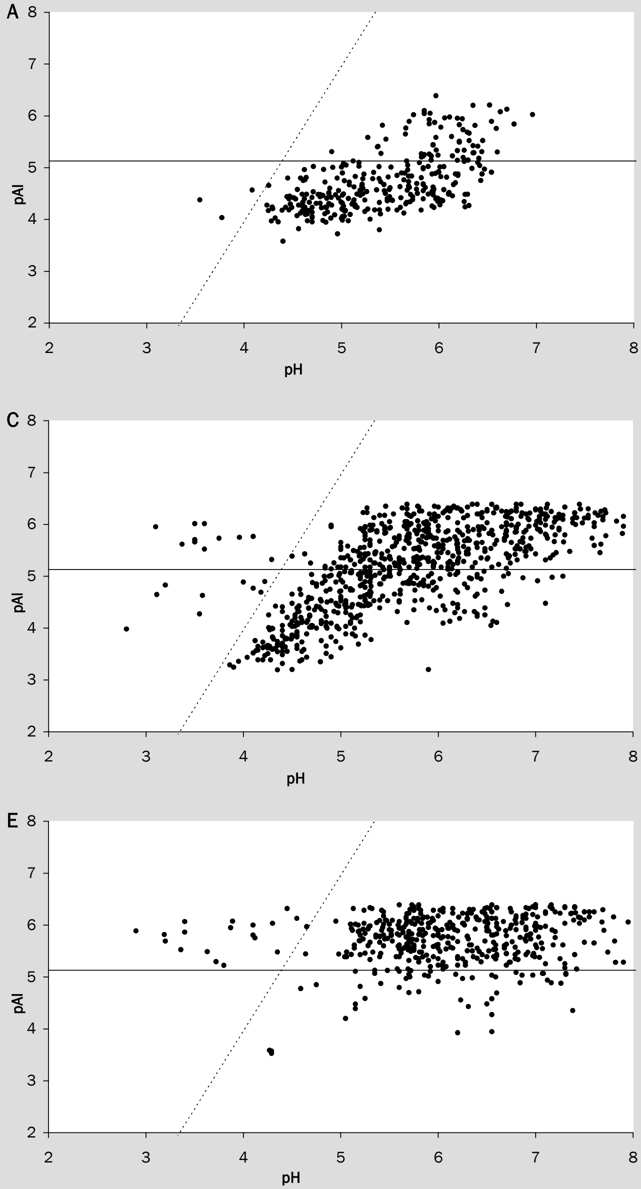

Figure 6.2 A, C, E: Relationship between total Al (pAl; mol L^{-1}) and pH (data points ●); A) agricultural-phreatic; C) agricultural-shallow; E) agricultural-deep; equilibrium line between pAl^{3+} and pH for gibbsite (dotted line) and the Dutch drinking water limit for Al (VROM, 2001; straight line) are plotted.

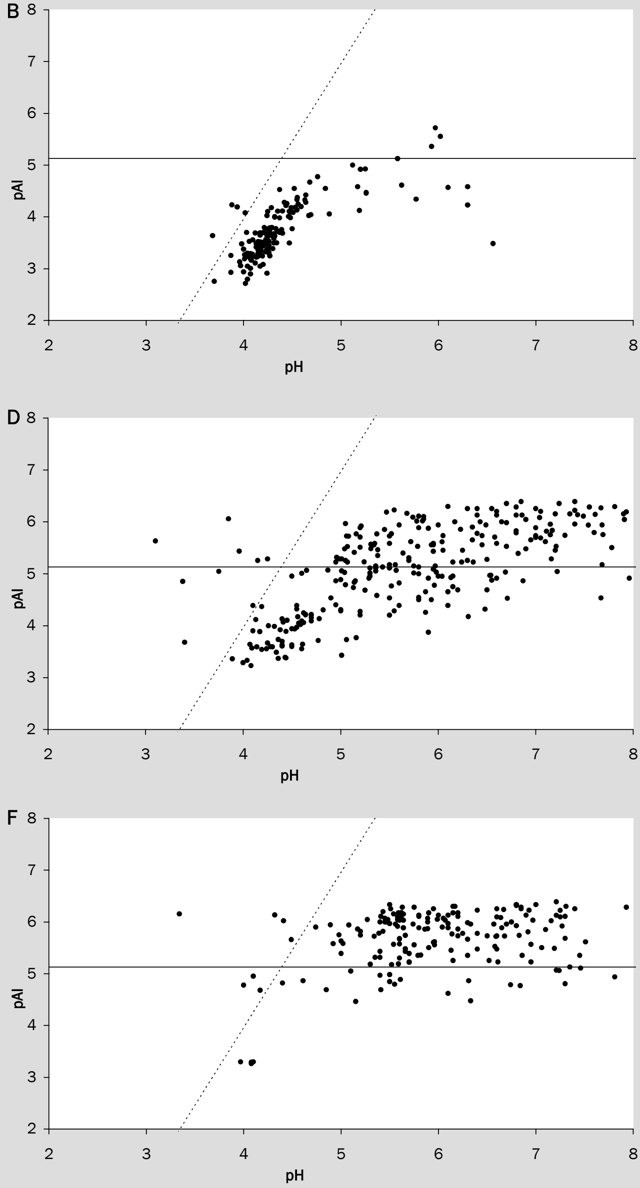

Figure 6.2 B, D, F: Relationship between total Al (pAl; mol L^{-1}) and pH (data points ●); B) natural-phreatic; D) natural-shallow; F) natural-deep; equilibrium line between pAl^{3+} and pH for gibbsite (dotted line) and the Dutch drinking water limit for Al (VROM, 2001; straight line) are plotted.

higher than the 75-percentiles of the other groups. For each groundwater depth, the median DOC concentration for agricultural land was higher than for natural land, even though the difference was rather small for the shallow and deep groundwater.

In Figure 6.2 the measured total Al concentrations are plotted versus the pH and also the Dutch drinking water limit (VROM, 2001) is shown in the graphs. Most groundwater groups showed a big cloud of data points for the measured pH range, except the natural-phreatic group. For this group, most measurements were in the range between pH 3.5 and 4.5, and measured Al concentration showed a correlation with the pH in this range. This relation is lacking for the other groups.

The Al concentration also depends on the DOC concentration and therefore the DOC concentrations are given in Figure 6.3 versus the pH for all six groundwater groups. No correlation between DOC and pH was found. For all groups the 95% upper limit was shown (sum of the mean and twice the standard deviation). Highest DOC concentrations (61.4 mg L^{-1}) were found for the agricultural-phreatic group. Lowest DOC concentration (6.8 mg L^{-1}) was found for the natural-deep group over the entire measured pH range. For the other groups the 95% upper limit was somewhat around 20 mg C L^{-1}.

The calculated pAl^{3+} by taking pH and DOC complexation into account, showed a good linear correlation with the pH (Figure 6.4) and for most groups it perfectly matched the 1:3 relationship between pAl^{3+} and pH (at pH > 4.5) that is shown for by the mineral equilibrium lines in Figure 6.4. Most calculated data were close to equilibrium for gibbsite. Below pH 4.5 several measurements deviated from the 1:3 relation (Figure 6.4A, C-F). The relation between pH and Al^{3+} was studied by linear regression on the data as plotted in Figure 6.4. The regression was performed with a variable slope and a fixed slope of 3 for all measurements per group (Table 6.3a). Linear regression for this total dataset resulted in slopes from 2.10 to 2.69 and log K values from 4.61 to 7.24. For natural-phreatic groundwater a log K value of 4.84 and slope of 2.10 were found, indicating that no mineral equilibrium with a mineral phase existed. Instead, Al concentrations in this group were assumed to be determined mainly by equilibrium with the organic phase. Other research (e.g. Berggren and Mulder, 1995; Wesselink *et al.*, 1996; Skyllberg, 1999) has shown that equilibrium with the organic phase resulted in a slope around 2, which is in agreement with the value found for the natural-

Table 6.3a: Results of regression between pH and pAl^{3+} for the different groundwater groups.

	linear regression			regression slope=3	
	log K	slope	R^2	log K	R^2
agricultural-phreatic	7.06 (0.35)	2.60 (0.06)	0.846	9.25 (0.04)	0.826
natural-phreatic	4.84 (0.22)	2.10 (0.05)	0.921	8.79 (0.05)	0.754
agricultural-shallow	7.21 (0.18)	2.69 (0.03)	0.904	9.01 (0.03)	0.892
natural-shallow	7.24 (0.27)	2.69 (0.05)	0.924	9.01 (0.05)	0.912
agricultural-deep	4.61 (0.25)	2.31 (0.04)	0.873	8.85 (0.04)	0.794
natural-deep	6.06 (0.31)	2.54 (0.05)	0.930	8.84 (0.05)	0.898

Linear regression and regression with a fixed slope of 3; $\log(Al^{3+}) = \log K - slope*pH$; standard deviation between parenthesis

Table 6.3b: Results of regression between pH and pAl^{3+} for the different groundwater groups for samples with $pH \geq 4.5$.

	linear regression			regression slope=3	
	log K	slope	R^2	log K	R^2
agricultural-phreatic	8.39 (0.38)	2.83 (0.07)	0.926	9.34 (0.04)	0.855
natural-phreatic	-	-	-	-	-
agricultural-shallow	9.18 (0.16)	3.00 (0.03)	0.973	9.15 (0.02)	0.947
natural-shallow	9.13 (0.26)	2.99 (0.04)	0.977	9.20 (0.04)	0.955
agricultural-deep	7.41 (0.20)	2.75 (0.03)	0.970	9.00 (0.02)	0.934
natural-deep	7.43 (0.30)	2.75 (0.05)	0.975	8.95 (0.04)	0.943

Linear regression and regression with a fixed slope of 3; $\log(Al^{3+}) = \log K - slope*pH$; standard deviation between parenthesis

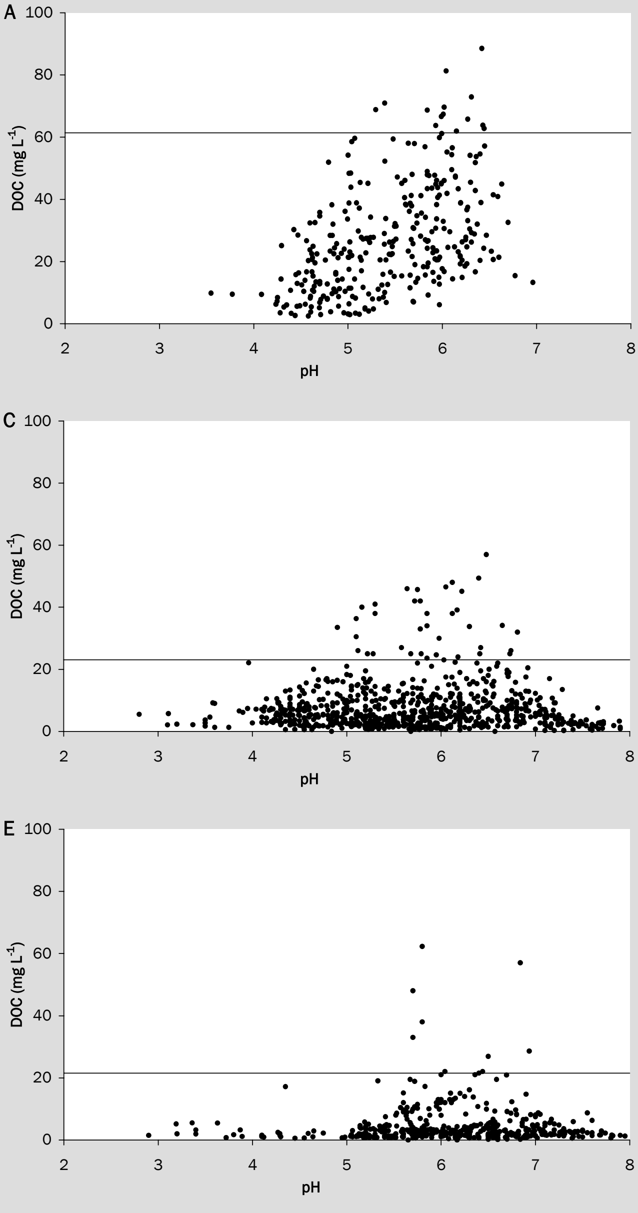

Figure 6.3 A, C, E: DOC (mg L^{-1}) concentration versus pH shown for each groundwater group; the straight line shows the 95% upper limit of the DOC concentration (mean + 2*st.dev.); A) agricultural-phreatic (61.4 mg CL^{-1}); C) agricultural-shallow (23.1 mg C L^{-1}); E) agricultural-deep (21.5 mg C L^{-1}).

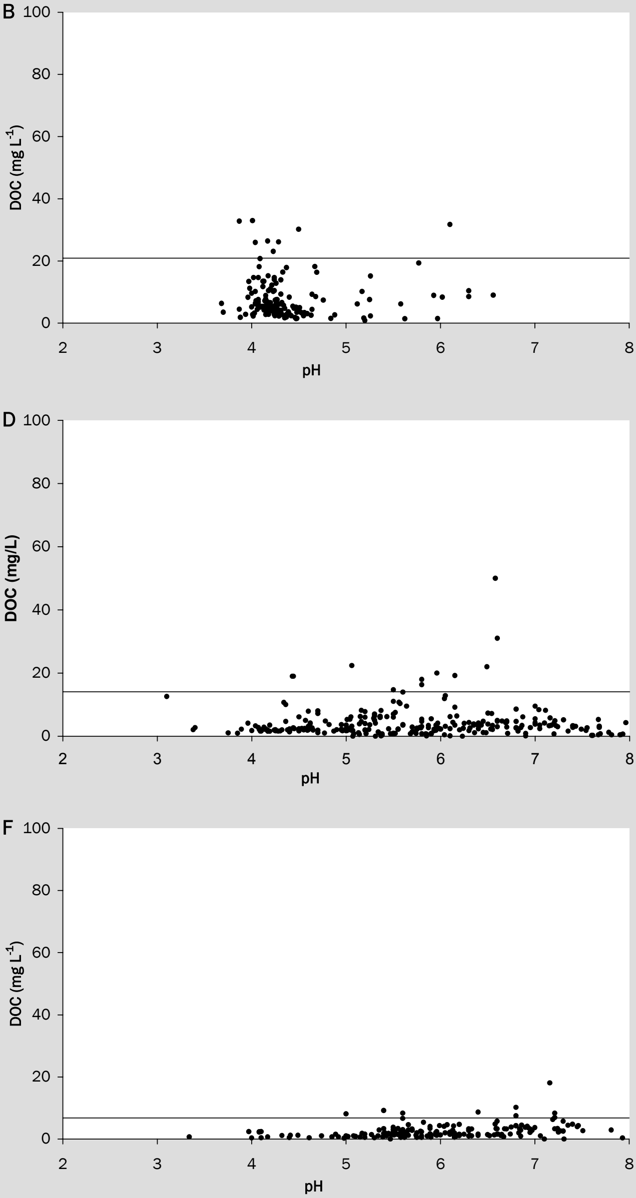

Figure 6.3 B, D, F: DOC (mg L^{-1}) concentration versus pH shown for each groundwater group; the straight line shows the 95% upper limit of the DOC concentration (mean + 2*st.dev.); B) natural-phreatic (20.9 mg C L^{-1}); D) natural-shallow (14.1 mg C L^{-1}); F) natural-deep (6.8 mg C L^{-1}).

phreatic group. For the agricultural-deep group also a low log K value and slope were found. Since this group showed a broad pH range (2.90-8.05), these regression results were dedicated to disequilibrium below pH 4.5. Since most groups show this disequilibrium with mineral phases below pH 4.5, leaving out the measurement below pH 4.5 lead to a better correlation (Table 6.3b). Regression analysis for pH > 4.5 was not performed for the natural-phreatic group, because the majority of the measurements lie below pH 4.5. The pAl^{3+}-pH relations found in Table 6.3b (fixed and variable slope) are plotted in Figure 6.4. Regression on the data above pH 4.5 (Table 6.3b) showed very good correlation (R^2 0.926 – 0.977) for field data sets. Calculated slopes were close to 3 suggesting equilibrium with a mineral $Al(OH)_3$ phase. Lowest slopes and log K values were found for the deepest groundwater. Land use type did not influence the log K and slope, except for the earlier mentioned natural-phreatic group. Derived log K values (fixed slope) were close to the theoretical equilibrium constant of gibbsite (9.40 at 281K, Table 6.1) with satisfying correlation coefficients.

In Figure 6.5 the effect of DOC complexation on total Al concentration is shown for the agricultural-phreatic group (high DOC) and natural-deep group (low DOC). Equilibrium concentrations are shown for the situation with and without DOC complexation. These equilibrium Al concentrations were calculated with derived log K values from Table 6.3b (slope = 3) and plotted as a function of the pH (Weng *et al.*, 2002c). The DOC concentration was set at the 95% upper limit that was shown in Figure 6.3. The upper curve represented the model calculation for mineral equilibrium in the absence of DOC. At pH between 4.5 and 8 the DOC complexation did have a significant effect on the calculated Al concentration for the agricultural-phreatic group, whereas this effect is much smaller for the natural-deep group with lower DOC concentrations. For the agricultural-phreatic group the difference between the Al concentration with and without DOC complexation is about a factor 10 on the Al concentration at pH 5.5.

6.4 Discussion

The largest differences for Al and DOC occur in the phreatic groups. In this most shallow groundwater, the effect of land use on the studied parameters is the largest. The land use effects disappeared during transport further down in the soil. The buffering capacity of the soil for pH and Al concentration seemed to be large enough and DOC mineralization also continued. However, the deep groundwater also showed low pH levels and related high Al concentrations. This indicated that acidification of groundwater does happen in Dutch sandy soils. Relating these high Al concentrations to the Dutch drinking water regulation (VROM, 2001) (0.2 mg Al L^{-1}), it was shown that this limit was exceeded in several samples (Figure 6.2). Phreatic groundwater showed Al concentrations that were for a large part above this drinking water limit. Although this effect diminished further downwards, the deepest groundwater also showed several measurements above or close to this limit. Serious attention should be paid to Al concentrations in groundwater from sandy soils, when this groundwater is to be used for drinking water.

The calculated 95% upper limit of DOC (Figure 6.3) was remarkably high for the agricultural-phreatic group, which was already indicated by the median of the DOC concentration (Table 6.2). Agricultural land use affected the phreatic groundwater resulting in high DOC concentrations. These high DOC concentrations could be explained by the application of organic fertilizers and these high concentrations were pronounced closest to the soil surface. In contrast, the natural-deep groundwater had the lowest DOC 95% upper limit of all groups. Increased residence time, shown here by the depth of the groundwater, resulted in decreased DOC concentration. During transport through the soil, DOC could have been mineralized or bound to mineral surfaces.

Calculated Al^{3+} showed a strong linear correlation with pH. The complexation of Al by DOC varied between 1% and 99 % depending on pH and total DOC concentration of the measurement. Highest complexation of Al was found for the phreatic and shallow groundwater for both agricultural and natural land use. This variation in amount of complexed Al emphasized the importance to take the complexation with DOC into account when studying the Al chemistry of groundwater samples.

Below pH 4.5 some samples were undersaturated for the three Al-phases considered in Figure 6.4. Previous research also showed a deviation from the 1:3 relationship between pAl^{3+} and pH at low pH (< 4.5). Adams (2000) explained that this deviation in soil solutions is the result of equilibrium with an organic phase instead of a mineral phase. However, it might be expected that groundwater (deep) is not in equilibrium with an organic phase because sandy aquifer sediments were mainly low in organic matter and that organic matter is often less

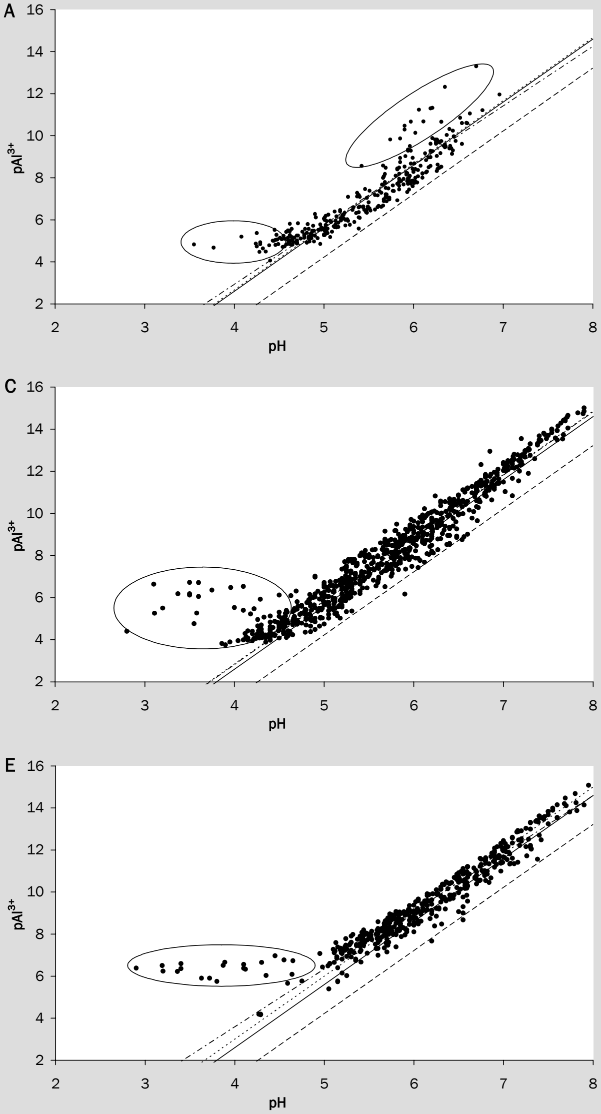

Figure 6.4 A, C, E: Relationship between calculated p(Al^{3+}) and pH; data points are shown by circles (●). Equilibrium lines are plotted for gibbsite 281 K (straight line), amorphous $Al(OH)_3$ 281 K (dashed line). Regression lines from Table 6.3b (except for natural-phreatic regression lines from Table 6.3a) are also shown (variable slope (dashed-dotted line) and slope = 3 (dotted line)); A) agricultural-phreatic; C) agricultural-shallow; E) agricultural-deep.

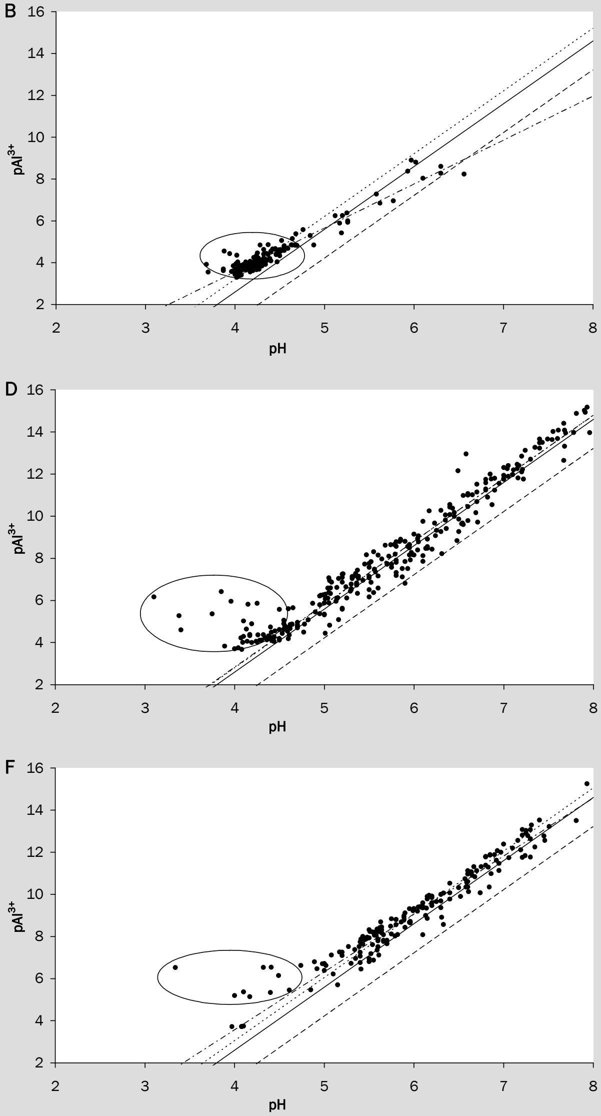

Figure 6.4 B, D, F: Relationship between calculated p(Al^{3+}) and pH; data points are shown by circles (●). Equilibrium lines are plotted for gibbsite 281 K (straight line), amorphous $Al(OH)_3$ 281 K (dashed line). Regression lines from Table 6.3b (except for natural-phreatic regression lines from Table 6.3a) are also shown (variable slope (dashed-dotted line) and slope = 3 (dotted line)); B) natural-phreatic; D) natural-shallow; F) natural-deep.

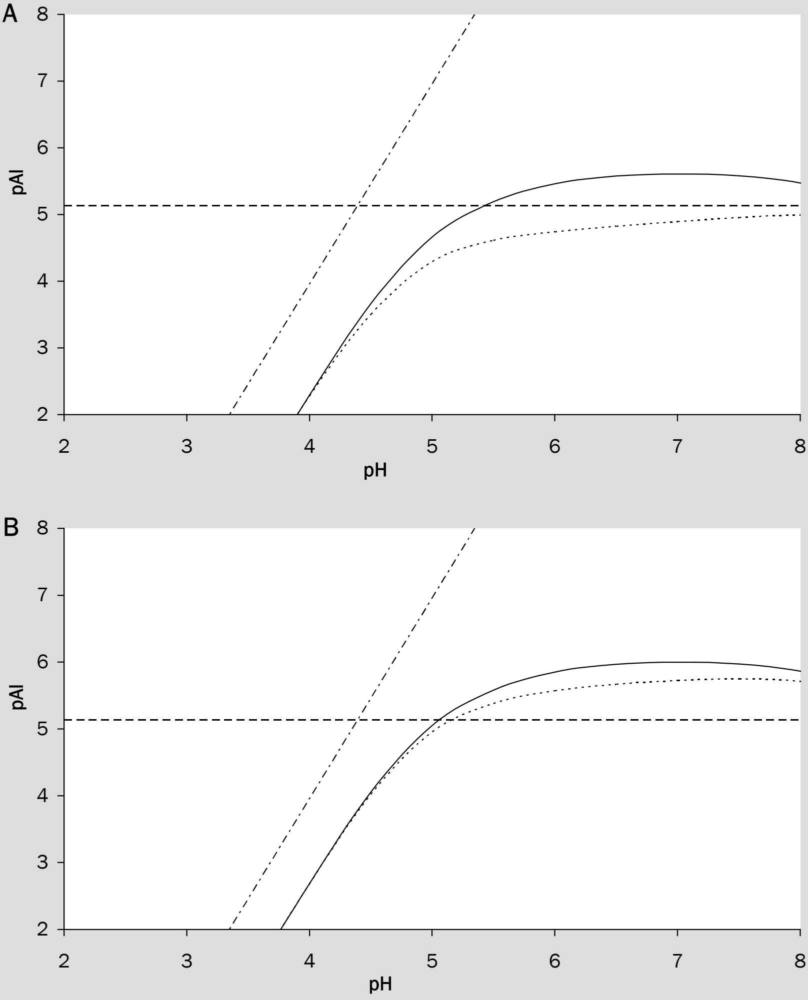

Figure 6.5: Effect of DOC complexation on total dissolved Al in equilibrium with an Al(OH)$_3$ mineral phase with a log K derived from regression of Table 6.3b (slope = 3). Results are shown for the two extremes, viz. A) agricultural-phreatic and B) natural-deep. Total Al in solution (pAl; mol L^{-1}) plotted versus pH with (dotted line) and without (straight line) of DOC complexation (used DOC concentrations see text and Figure 6.3); the Dutch drinking water limit for Al (VROM, 2001) (dashed line) is also plotted; the dashed dotted line represents the relation between pAl^{3+} and pH for gibbsite.

reactive (Hartog *et al.*, 2002). Studies on natural waters (Neal, 1988; Haag *et al.*, 2001) have shown that this deviation is the result of equilibrium with other mineral phases, e.g. $AlSO_4OH$, but minerals like imogolite (Farmer *et al.*, 1980) or kaolinite (Zysett *et al.*, 1999) could also determine the Al concentration in podzols. Nevertheless, the authors could not find a mineral phase which explained the Al^{3+} activity at low pH. Therefore, the conclusion was reached that the deviating pAl^{3+} was the result of kinetic constraints of dissolution of Al containing minerals. The agricultural-phreatic group also showed the same disequilibrium with the studied mineral phases at pH around 6.

The importance of taking DOC complexation into account follows also from Figure 6.5. Equilibrium Al concentration was calculated with log K values derived in Table 6.3b (fixed slope). Using this log K value implies that equilibrium exists with an Al(hydr)oxide with a log K value derived for a specific groundwater group. At higher pH (5-8) the calculated Al concentration without DOC can be almost more than a factor 10 lower than with DOC. The graphs also show that this calculated Al concentrations due to DOC were close to the drinking water limit. Since the DOC concentrations decrease with increasing groundwater depth, the influence of DOC complexation on total Al concentrations in groundwater is reduced with increasing groundwater depth.

6.5 Conclusion

Land use type and depth of the groundwater did affect the pH, Al concentration and DOC concentration in groundwater under Dutch sandy soils. The median pH increased gradually with the depth of the groundwater, because during transport the groundwater is buffered by the soil. The natural-phreatic groundwater showed a relatively low pH, which was also responsible for the very high Al concentrations in the groundwater. DOC concentrations showed increased Al levels for the agricultural-phreatic groundwater that resulted from the application of organic fertilizers on agricultural soils. The relationship between pAl^{3+} and pH showed that the majority of the groundwater samples under sandy soils were in equilibrium with a mineral $Al(OH)_3$ phase at $pH > 4.5$. Below pH 4.5 the groundwater samples were mainly in disequilibrium with a mineral phase as a result of kinetic constraints or equilibrium with the organic phase. Equilibrium calculation of the total Al concentration with derived log K values in the presence and absence of DOC showed the importance of DOC complexation. This complexation is mainly important for the agricultural-phreatic groundwater. Agricultural-phreatic groundwater showed the highest DOC concentrations, whereas the lower DOC concentration in deeper layers resulted in smaller effects on total Al concentration.

Acknowledgements

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> Je moet tegenslagen kennen
> om de overwinningen te kunnen vieren
> *- Erik Dekker in zijn afscheidsdocumentaire, NOS, 2006 -*

APPENDICES

Appendix I

Contents:

Table I.1: NICA-Donnan model parameters for generic fulvic acid (Milne *et al.*, 2003).

b (log $V_D = a + b \log I$)	-0.57			
	site 1		site 2	
Q_{max}	5.88		1.86	
p	0.59		0.70	
ion specific parameters	log K_1	n_1	log K_2	n_2
H	2.34	0.66	8.60	0.76
Al	-4.11	0.42	12.16	0.31
Ca	-2.13	0.85	-3.0	0.8
Cd	-0.97	0.68	0.50	0.50
Cu	0.26	0.53	8.26	0.36
Mg	-2.1	0.77	-2.4	0.59
Mn	-1.55	0.72	-1.1	0.56
Ni	-2.07	0.65	2.03	0.53
Pb	-1.16	0.60	6.92	0.69
Zn	-3.84	0.67	-0.73	0.61

Table I.2: NICA-Donnan model parameters for generic humic acid (Milne *et al.*, 2003).

b (log $V_D = a + b \log I$)	-0.49			
	site 1		site 2	
Q_{max}	3.15		2.55	
p	0.62		0.41	
ion specific parameters	log K_1	n_1	log K_2	n_2
H	2.93	0.81	8.00	0.63
Al	-1.05	0.40	8.89	0.30
Ca	-1.37	0.78	-0.43	0.75
Cd	-0.20	0.73	2.37	0.54
Cu	2.23	0.56	6.85	0.34
Mg	-0.6	0.77	0.6	0.59
Mn	-0.3	0.72	1.3	0.56
Ni	-0.26	0.64	1.0	0.55
Pb	1.25	0.60	4.84	0.69
Zn	0.11	0.67	2.39	0.27

Table I.3: DDL model parameters of HFO (Dzombak & Morel, 1990).

surface area: $6 \cdot 10^5$ m^2 kg^{-1}

S_1-OH site: 0.056 nm^{-2}

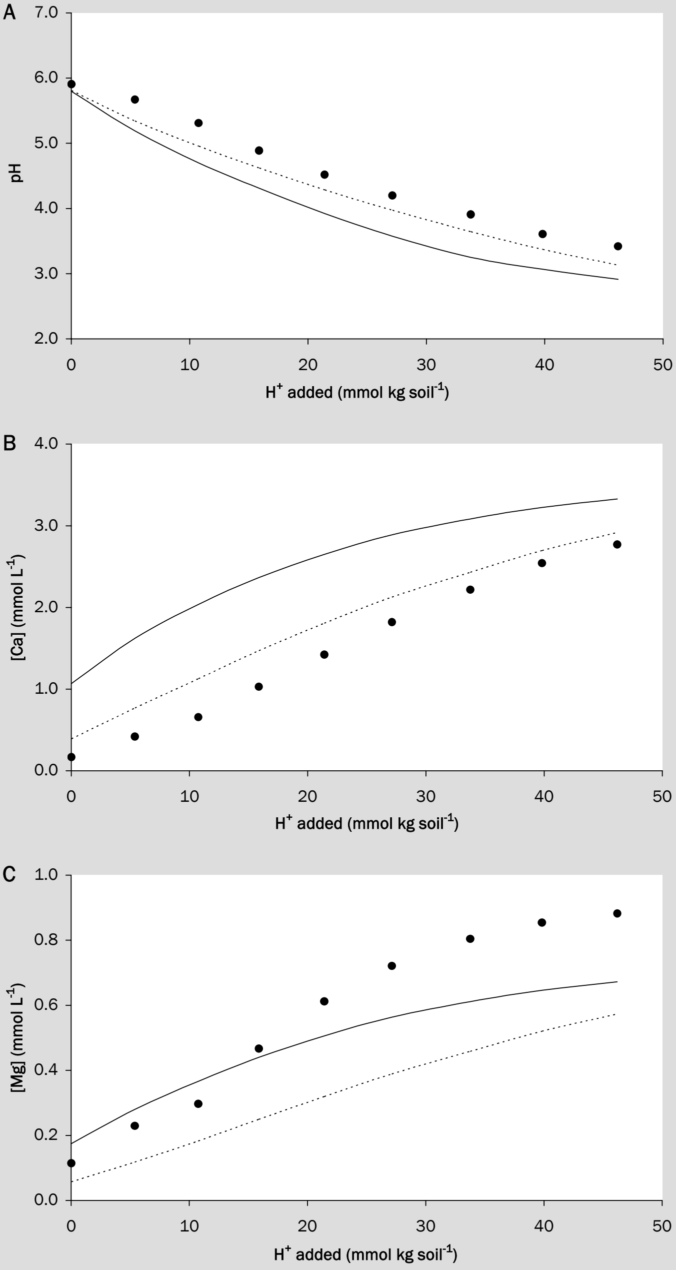
S_2-OH site: 2.255 nm^{-2}

surface species	log K_0	surface species	log K_0
S_1-OH	0	S_2-OH	0
S_1-OH_2^+	7.29	S_2-OH_2^+	7.29
S_1-O^-	-8.93	S_2-O^-	-8.93
S_1-$OHCa^{2+}$	4.97	S_2-$OHCa^{2+}$	-5.85
S_1-OCu^+	2.89	S_2-OCu^+	0.60
S_1-OCd^+	0.47	S_2-OCd^+	-2.90
S_1-OZn^+	0.99	S_2-OZn^+	-1.99
S_1-ONi^+	0.37	S_2-ONi^+	-2.50
S_1-OPb^+	1.65	S_2-OPb^+	0.30

Table I.4: CD-MUSIC model parameters of goethite (Weng *et al.* 2001a).

110 face	012 face
surface area: $4.5 \cdot 10^4$ m^2 kg^{-1}	surface area: $5 \cdot 10^3$ m^2 kg^{-1}
$FeOH^{-0.5}$ site: 3.0 nm^{-2}	$FeOH^{-0.5}$ site: 3.75 nm^{-2}
$Fe_3O^{-0.5}$ site: 3.0 nm^{-2}	$Fe_hO^{-0.5}$ site: 3.75 nm^{-2}

species parameters						
surface species	log K_0	site 1	site 2	0-plane	1-plane $C_1 = 1.02$ F m^{-2}	2-plane $C_2 = 5$ F m^{-2}
$FeOH^{-0.5}$	0	$1FeOH^{-0.5}$		0	0	0
$FeOH_2^{+0.5}$	9.2	$1FeOH^{-0.5}$		1	0	0
$FeOHK^{+0.5}$	-1.0	$1FeOH^{-0.5}$		0	0	1
$Fe_3O^{-0.5}$	0	$1Fe3O^{-0.5}$		0	0	0
$Fe_3OH^{+0.5}$	9.2	$1Fe3O^{-0.5}$		1	0	0
$Fe_3OK^{+0.5}$	-1.0	$1Fe3O^{-0.5}$		0	0	1
$Fe_hOH^{-0.5}$	0.0	$1Fe_hOH^{-0.5}$		0	0	0
$Fe_hOH_2^{+0.5}$	9.2	$1Fe_hOH^{-0.5}$		1	0	0
$Fe_hOHK^{+0.5}$	-1.0	$1Fe_hOH^{-0.5}$		0	0	1
$FeOHCa^{+1.5}$	3.55	$1FeOH^{-0.5}$		0.2	1.8	0
$FeOPO_3^{-2.5}$	20.8	$1FeOH^{-0.5}$		0.25	-2.25	0
$FeOHCu^{+1.5}$	8.62	$1FeOH^{-0.5}$		0.83	1.17	0
$FeOHCuOH^{+0.5}$	3.03	$1FeOH^{-0.5}$		0.83	0.17	0
$Fe_hOHCu^{+1.5}$	8.62	$1Fe_hOH^{-0.5}$		0.83	1.17	0
$Fe_hOHCuOH^{+0.5}$	3.03	$1Fe_hOH^{-0.5}$		0.83	0.17	0
$(FeOH)_2Cd^{+1}$	6.98	$2FeOH^{-0.5}$		0.71	1.29	0
$(FeOH)_2CdOH^0$	-2.94	$2FeOH^{-0.5}$		0.71	0.29	0
$(Fe_hOH)_2Cd^{+1}$	6.98	$2Fe_hOH^{-0.5}$		0.71	1.29	0
$(Fe_hOH)_2CdOH^0$	-0.32	$2Fe_hOH^{-0.5}$		0.71	0.29	0
$(FeOH)_2Pb^{+1}$	9.75	$2FeOH^{-0.5}$		1.15	0.85	0
$(Fe_hOH)_2Pb^{+1}$	9.75	$2Fe_hOH^{-0.5}$		1.15	0.85	0
$(FeOHFe_3O)Zn^{+1}$	8.01	$1FeOH^{-0.5}$	$1Fe3O^{-0.5}$	0.83	1.17	0
$(FeOHFe_3O)Zn^{+1}OH$	-1.0	$1FeOH^{-0.5}$	$1Fe3O^{-0.5}$	0.83	0.17	0
$(Fe_hOH)_2Zn^{+1}$	6.63	$2Fe_hOH^{-0.5}$		0.83	1.17	0
$(Fe_hOH)_2ZnOH^0$	-2.38	$2Fe_hOH^{-0.5}$		0.83	0.17	0



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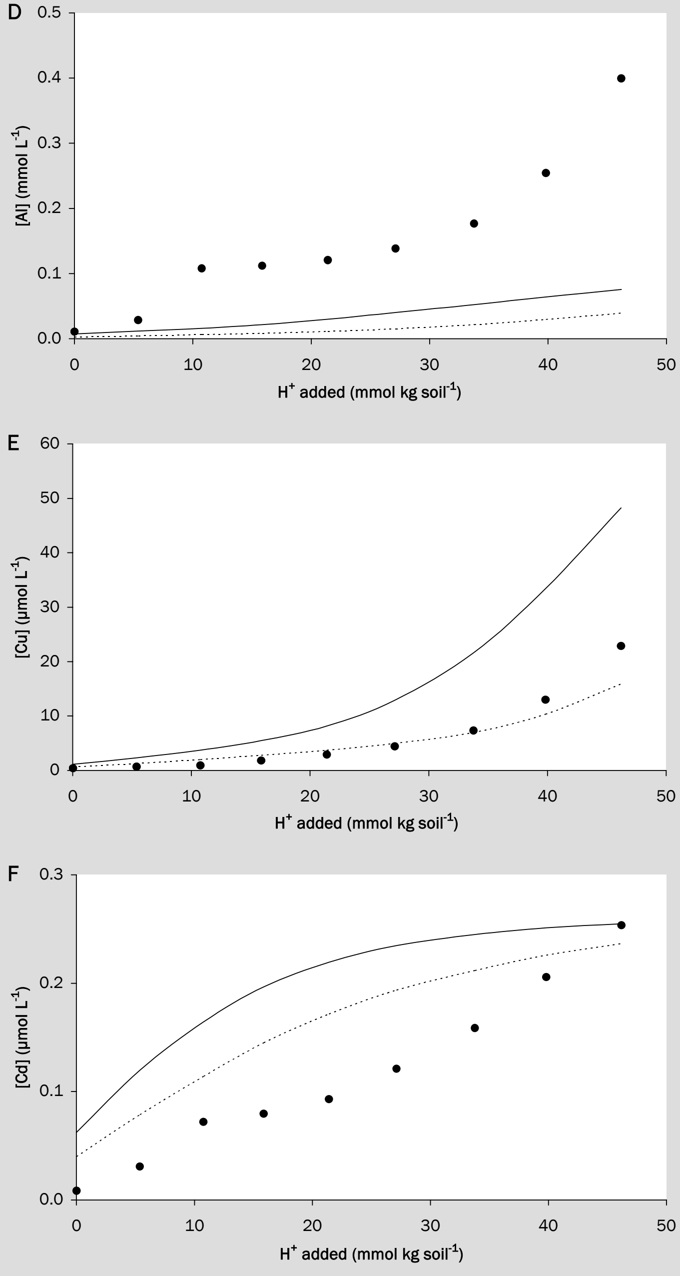

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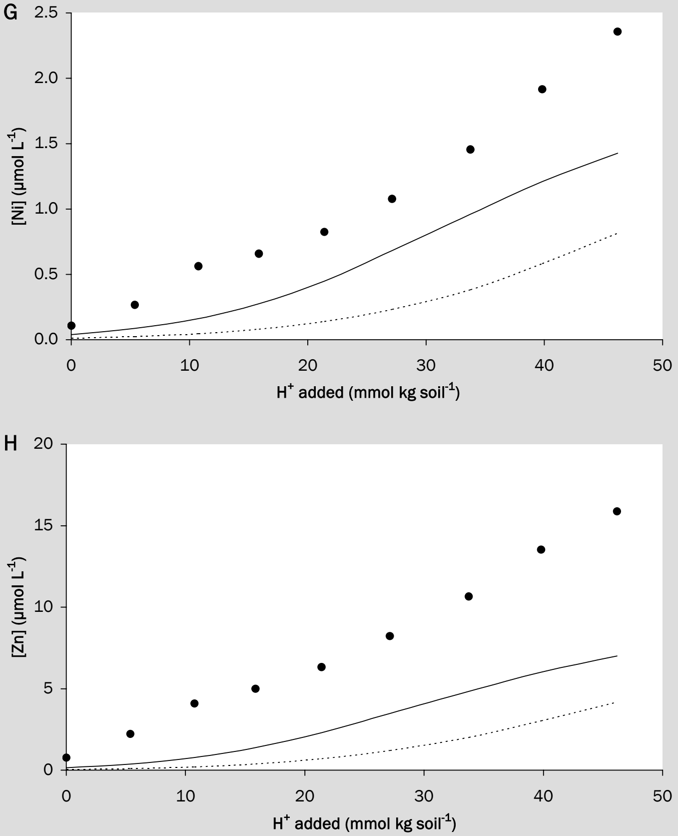


Figure I.1: pH and cumulative concentration of metals as function of protons added to the samples during the acidification experiment for sample H-II (high pH – high Cu) at reactive content of organic matter of 31 and 46%; (A) pH. (B) Ca, (C) Mg, (D) Al, (E) Cu, (F) Cd, (G) Ni, and (H) Zn. Experimental results H-II: ●; Model predictions: the black line represents reactive OM 31% and the black dotted line represents reactive OM 46%.

Appendix II

Contents:

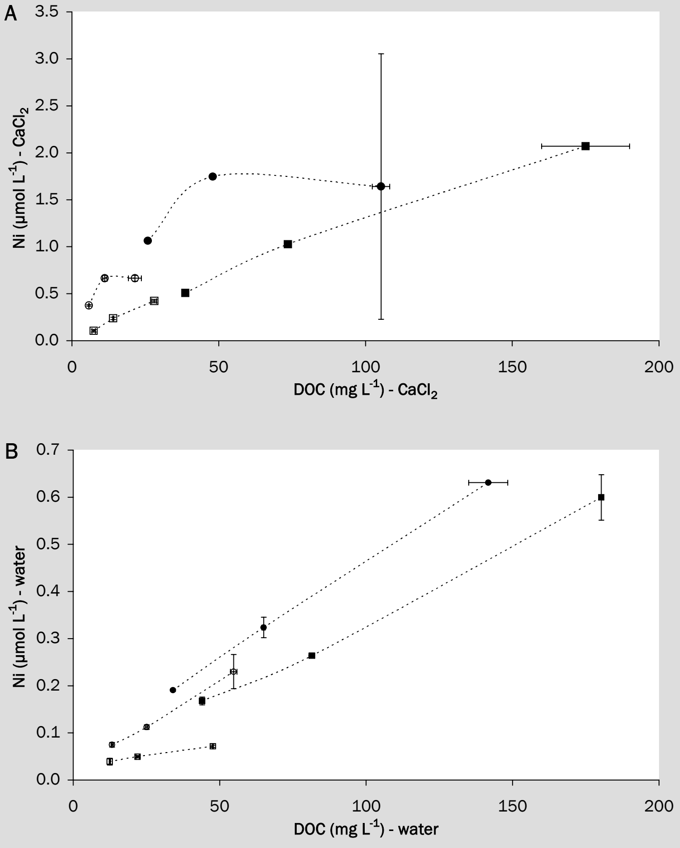
Table II.1: Free and total metal concentrations (log mol L^{-1}) in the DMT-soil column experiment; A) Cd, Cu and Ni, B) Pb and Zn.

Table II.1A

sample		Cd			Cu			Ni	
	free	*%free*	*total*	*free*	*%free*	*total*	*free*	*%free*	*total*
L-I$_{1986}$	-7.30	71.4	-7.15	-7.84	0.7	-5.67	-6.53	51.7	-6.24
L-II$_{1986}$	-7.18	75.1	-7.06	-5.05	30.6	-4.54	-6.03	69.0	-5.86
H-I$_{1986}$	-9.09	18.4	-8.35	-9.63	0.0	-6.25	-10.31	0.0	-6.97
H-II$_{1986}$	-8.07	39.8	-7.67	-6.72	1.3	-4.82	-6.59	29.0	-6.06
L-I$_{2005}$	-7.54	90.2	-7.49	-6.39	20.7	-5.71	-6.86	69.3	-6.70
L-II$_{2005}$	-7.68	90.4	-7.64	-5.39	58.8	-5.16	-6.75	82.2	-6.66
H-I$_{2005}$	-9.00	37.7	-8.57	-9.67	0.1	-6.43	-8.90	2.4	-7.28
H-II$_{2005}$	-8.71	44.3	-8.35	-8.39	0.2	-5.65	-7.70	13.6	-6.83

Table II.1B

sample		Pb			Zn	
	free	*%free*	*total*	*free*	*%free*	*total*
L-I$_{1986}$	-10.10	0.3	-7.51	-5.29	71.5	-5.15
L-II$_{1986}$	-8.82	3.6	-7.38	-5.24	75.7	-5.12
H-I$_{1986}$	-		-	-6.85	21.9	-6.19
H-II$_{1986}$	-11.30	0.2	-8.62	-5.87	43.5	-5.51
L-I$_{2005}$	-9.73	2.6	-8.14	-5.71	84.4	-5.63
L-II$_{2005}$	-8.93	1.8	-7.18	-5.62	88.3	-5.57
H-I$_{2005}$	-		-	-6.97	29.1	-6.43
H-II$_{2005}$	-		-	-6.81	27.7	-6.25



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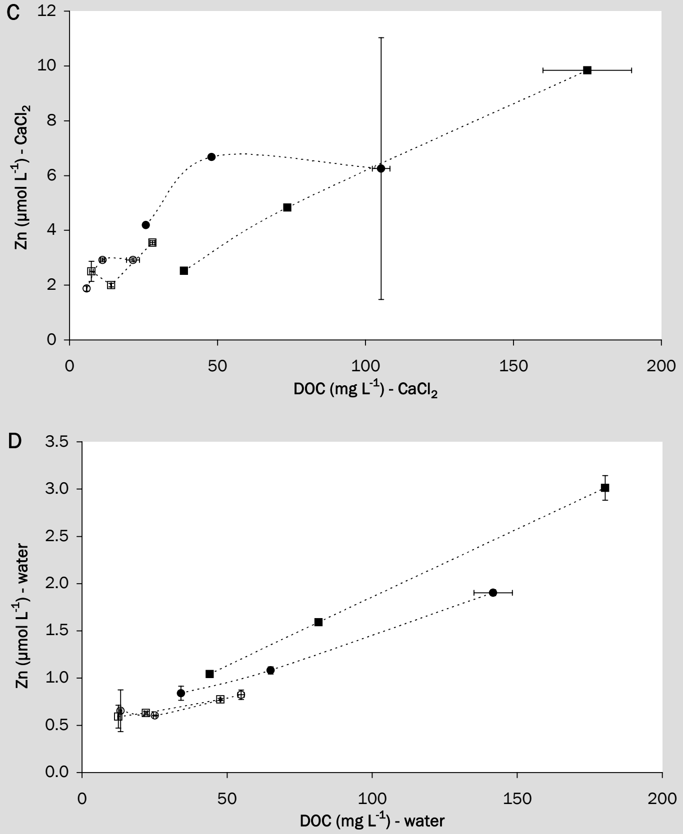

Figure II.1: Ni and Zn concentration in the 0.01 M $CaCl_2$ and water extract plotted as function of the total DOC concentration. DOC concentration because of the increasing solid/solution ratio (see Figure 3.1) A) Ni concentration in the 0.01 M $CaCl_2$ extract; B) Ni concentration in the water extract; C) Zn concentration in the 0.01 M $CaCl_2$ extract; D) Zn concentration in the water extract; (■ L-II$_{1986}$, □ L-II$_{2005}$, ●H-II$_{1986}$, ○ H-II$_{2005}$). Standard deviations are given by the error bars.

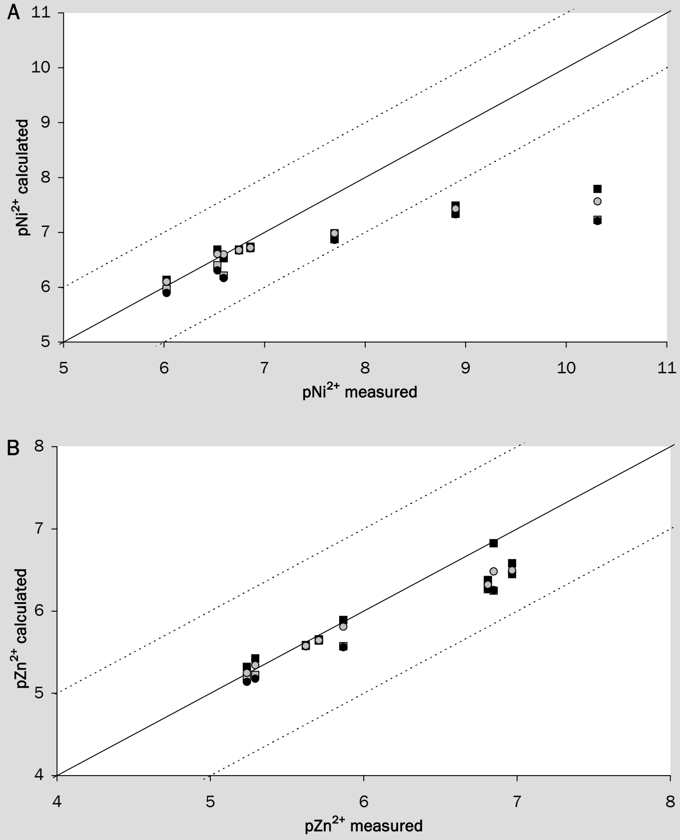

Figure II.2: Calculated free metal concentrations plotted versus the measured free metal concentrations. Symbols show different DOC compositions in speciation calculations (● HA-FA measured, ○ HA-FA-citric acid, ■ 50%HA-50%FA, □ 50%FA). The solid line shows the 1 to 1 relation, whereas the dotted lines represent the one log variation. A) Ni; B) Zn.

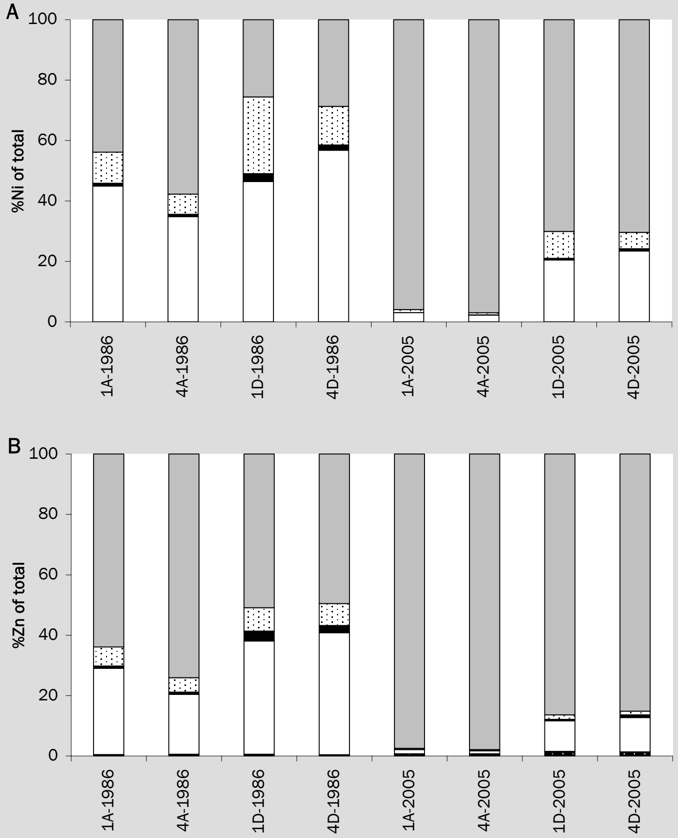

Figure II.3: Speciation of metals in the donor solution calculated with the measured DOC composition (HA-FA-hydrophilic acids) shown as percentage of total metal concentration in solution. Dark grey bar: free metal; white bar with black dots: metal bound to FA; black bar: metal bound to HA; white bar: metal bound to citric acid (representing hydrophilic acids); light grey bar: inorganic metal species; A) Ni; B) Zn.

Appendix III

Contents:

Table III.1: pH, organic matter content and reactive metal content of the experimental field between 1983 and 2005. pH measured in 0.01 M $CaCl_2$ extract, organic matter determined by loss-on-ignition and reactive metal content determined in 0.43 M HNO_3. Standard deviation is given between parentheses. Results are given for plot I (A) and plot II (B). Relative losses of metal between 1983 and 2005 are also given in the table.

Table II.1A: pH- plot (low pH-no Cu)

	pH	OM	DOC	reactive metal content				
				Cd	Ni	Cu	Pb	Zn
		(%)	(mg C L^{-1})	- - - - (μmol kg^{-1}) - - - -		- - - - - - - - (mmol kg^{-1}) - - - - - - - -		
1983	4.3 (0.0)	3.8	41.0 (1.9)	2.15 (0.09)	9.6 (0.4)	0.15 (0.01)	0.08 (0.00)	0.11 (0.00)
1985	4.2 (0.0)	3.8	45.4 (1.2)	1.93 (0.08)	9.5 (0.2)	0.27 (0.01)	0.08 (0.00)	0.08 (0.00)
1986	4.0 (0.0)	3.7	40.2 (0.3)	1.93 (0.01)	9.2 (0.2)	0.29 (0.00)	0.09 (0.00)	0.08 (0.00)
1989	4.0 (0.0)	3.6	34.2 (0.8)	1.84 (0.08)	7.7 (0.1)	0.34 (0.01)	0.09 (0.00)	0.06 (0.00)
1992	4.0 (0.0)	3.5	31.0 (0.0)	1.23 (0.03)	3.8 (0.8)	0.36 (0.01)	0.09 (0.00)	0.17 (0.00)
1995	3.8 (0.0)	3.3	25.0 (0.9)	1.01 (0.02)	1.6 (0.1)	0.32 (0.01)	0.08 (0.00)	0.03 (0.00)
1998	3.9 (0.0)	3.3	15.2 (0.5)	0.82 (0.02)	0.8 (0.1)	0.36 (0.01)	0.09 (0.00)	0.03 (0.00)
2001	4.0 (0.0)	3.0	15.1 (0.2)	0.71 (0.02)	0.2 (0.0)	0.38 (0.00)	0.09 (0.00)	0.02 (0.00)
2005	4.0 (0.0)	3.1	7.6 (0.1)	0.65 (0.02)	0.4 (0.0)	0.42 (0.01)	0.08 (0.00)	0.02 (0.00)
average	4.0							
relative loss				*70%*	*96%*	*-184%*	*3%*	*81%*

Table II.1B: pH-6 plot (high pH-no Cu)

	pH	OM	DOC	reactive metal content				
				Cd	Ni	Cu	Pb	Zn
		(%)	(mg C L^{-1})	- - - - (μmol kg^{-1}) - - - -		- - - - - - - - (mmol kg^{-1}) - - - - - - - -		
1983	6.2 (0.6)	3.7	30.6 (0.8)	2.68 (0.09)	10.2 (0.4)	0.10 (0.01)	0.11 (0.00)	0.15 (0.00)
1985	5.5 (0.0)	3.8	34.1 (0.1)	2.54 (0.04)	9.9 (0.1)	0.10 (0.00)	0.10 (0.00)	0.16 (0.00)
1986	5.3 (0.0)	3.7	25.3 (0.0)	2.48 (0.01)	9.8 (0.0)	0.09 (0.00)	0.10 (0.00)	0.14 (0.00)
1989	6.2 (0.3)	3.2	19.9 (1.5)	2.31 (0.00)	9.6 (0.0)	0.13 (0.00)	0.10 (0.00)	0.13 (0.00)
1992	5.3 (0.1)	3.1	17.9 (0.4)	2.23 (0.02)	9.7 (0.0)	0.11 (0.00)	0.10 (0.00)	0.16 (0.00)
1995	5.4 (0.0)	2.9	13.6 (0.2)	2.15 (0.05)	9.4 (0.1)	0.15 (0.00)	0.10 (0.00)	0.12 (0.00)
1998	5.1 (0.0)	2.8	10.7 (0.2)	2.09 (0.03)	10.0 (0.1)	0.12 (0.00)	0.10 (0.00)	0.13 (0.00)
2001	5.6 (0.0)	2.8	10.3 (0.5)	1.92 (0.01)	9.1 (0.1)	0.11 (0.00)	0.09 (0.00)	0.11 (0.00)
2005	5.5 (0.0)	2.7	5.8 (0.6)	1.98 (0.21)	9.6n (0.9)	0.21 (0.01)	0.09 (0.01)	0.10 (0.01)
average	5.6							
relative loss				*26%*	*6%*	*-105%*	*13%*	*32%*

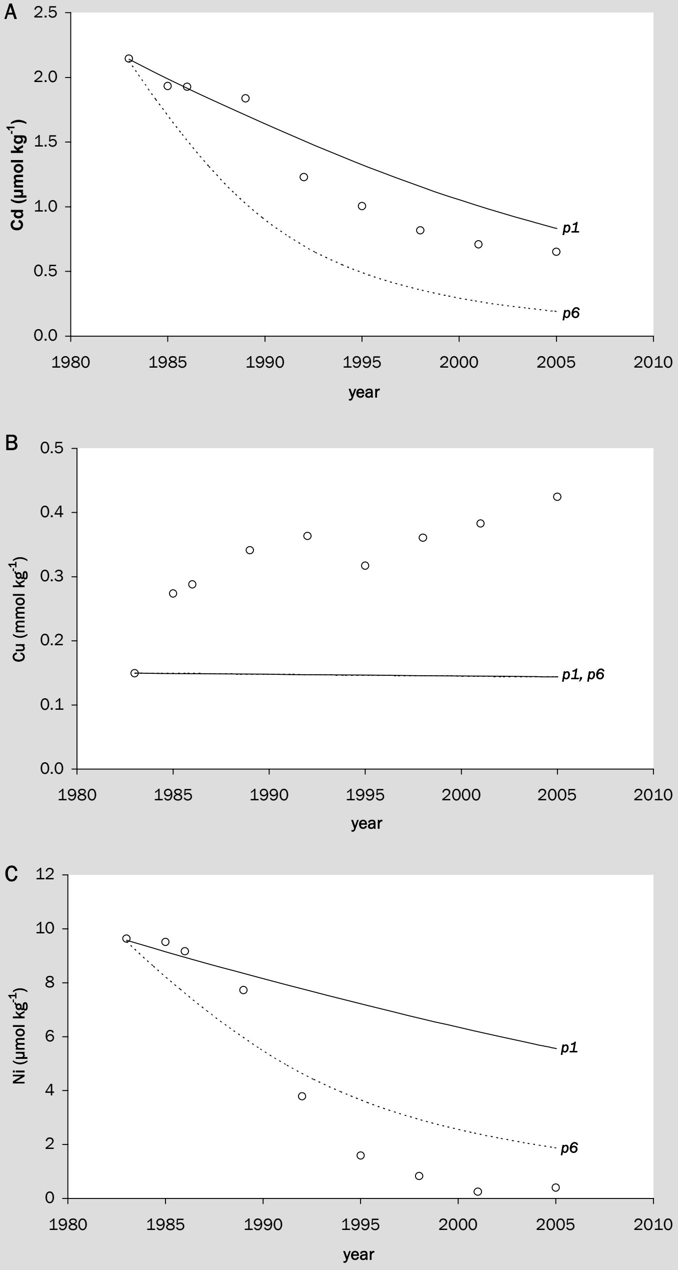

Figure III.1: Continued on the next page.

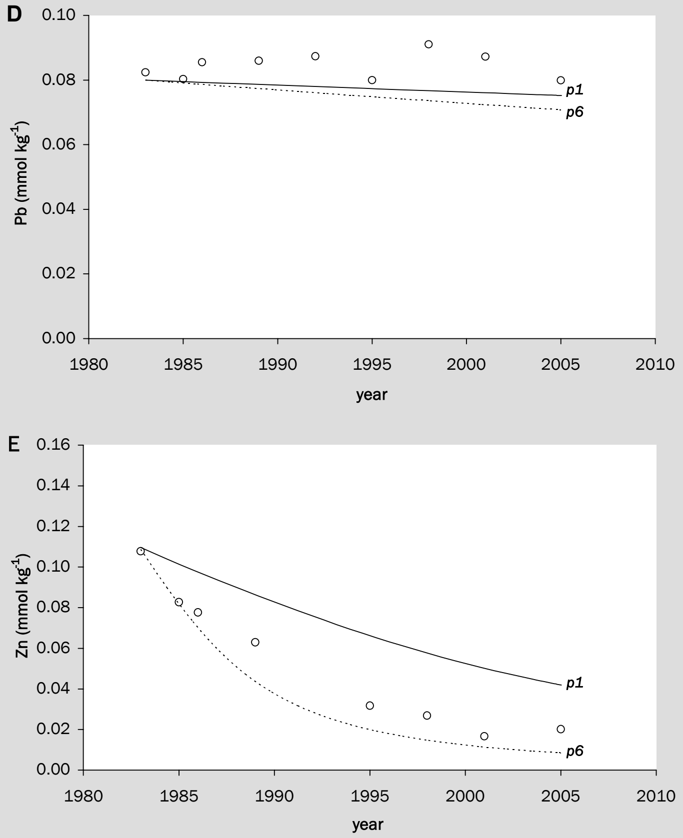

Figure III.1: Metal content in the pH-4 plot as function of time. Field data are shown by the open circles and leaching predictions are indicated by the lines; straight line: prediction 1; dotted line: prediction 6 (same as prediction 1 but with $Al(OH)_3$ mineral phase determining Al concentration). For soil properties used for prediction 1 see Table 4.1 in the main text.

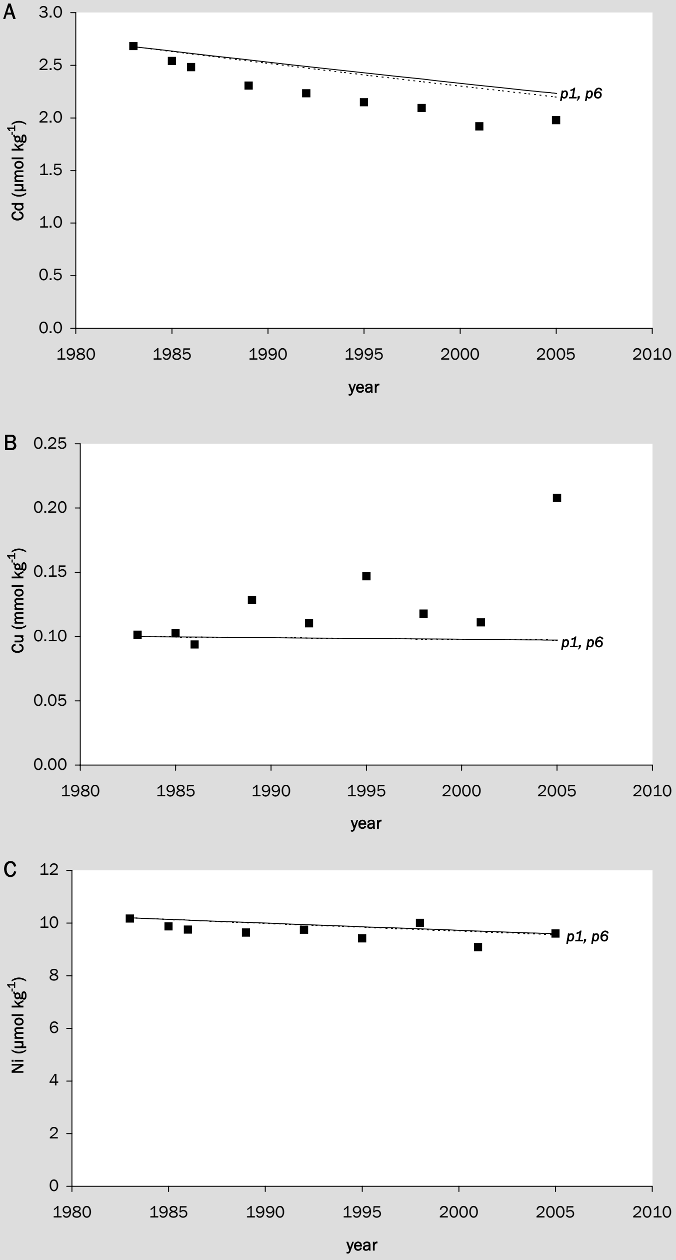

Figure III.2: Continued on the next page.

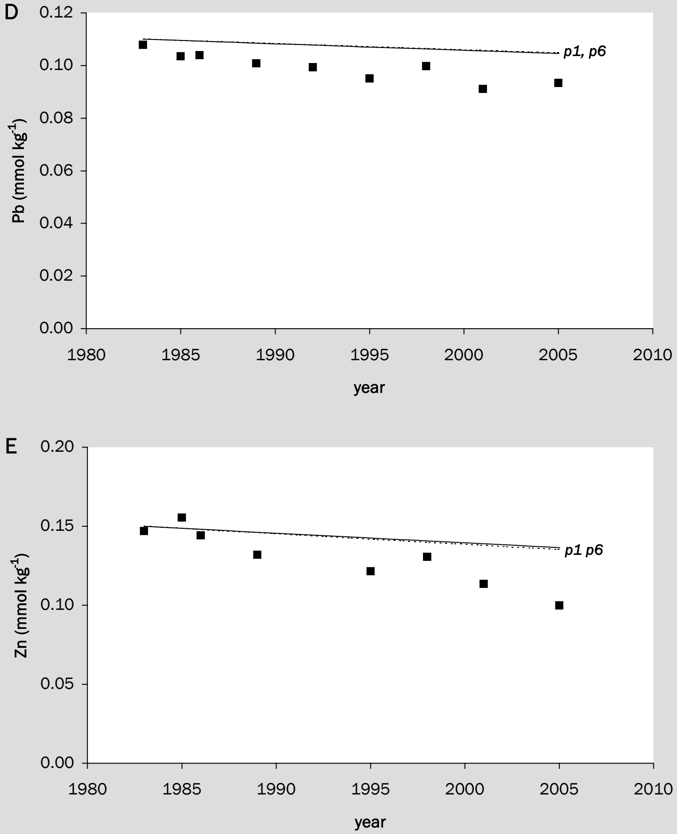

Figure III.2: Metal content in the pH-6 plot as function of time. Field data are shown by the black squares and leaching predictions are indicated by the lines; straight line: prediction 1; dotted line: prediction 6 (same as prediction 1 but with $Al(OH)_3$ mineral phase determining Al concentration). For soil properties used for prediction 1 see Table 4.1 in the main text.

Appendix IV

Contents:

Table IV.1: pH, organic matter content, DOC concentration and reactive metal content of the experimental field between 1983 and 2005. pH and DOC concentration measured in 0.01 M $CaCl_2$ extract, organic matter determined by loss-on-ignition and reactive metal content determined in 0.43 M HNO_3 extract. Standard deviation is given between parenthesis. Results are given for the pH-4 (A) and pH-6 (B) plot.

Table IV.1A: pH-4 plot (low pH – high Cu)

	pH	OM	DOC	reactive metal content				
				Cd	Ni	Cu	Pb	Zn
		(%)	(mg C L^{-1})	- - - - - (µmol kg^{-1}) - - - - -		- - - - - - - - (mmol kg^{-1}) - - - - - - - -		
1983	4.1 (0.0)	4.0	42.0 (0.1)	1.85 (0.06)	20.1 (0.8)	3.07 (0.10)	0.09 (0.00)	0.10 (0.00)
1985	4.2 (0.0)	3.8	40.7 (0.3)	1.78 (0.01)	14.9 (0.2)	2.53 (0.00)	0.09 (0.00)	0.08 (0.00)
1986	4.0 (0.0)	3.9	38.7 (0.2)	1.56 (0.08)	10.2 (0.8)	2.20 (0.03)	0.09 (0.00)	0.07 (0.01)
1989	3.9 (0.0)	3.6	34.0 (0.5)	1.24 (0.02)	4.6 (0.3)	1.90 (0.02)	0.09 (0.00)	0.05 (0.00)
1992	3.9 (0.0)	3.5	30.5 (0.2)	0.83 (0.02)	1.1 (0.1)	1.48 (0.02)	0.08 (0.00)	0.04 (0.01)
1995	3.7 (0.0)	3.4	25.6 (0.7)	0.77 (0.01)	0.9 (0.0)	1.25 (0.02)	0.08 (0.00)	0.03 (0.00)
1998	3.9 (0.0)	3.3	18.1 (0.4)	0.58 (0.00)	0.3 (0.0)	1.19 (0.02)	0.09 (0.00)	0.03 (0.00)
2001	4.0 (0.0)	3.3	15.2 (0.1)	0.59 (0.01)	0.4 (0.0)	1.09 (0.01)	0.09 (0.00)	0.02 (0.00)
2005	3.9 (0.0)	3.2	7.4 (0.6)	0.59 (0.01)	0.6 (0.1)	1.11 (0.02)	0.09 (0.00)	0.02 (0.01)

Table IV.1B: pH-6 plot (high pH – high Cu)

	pH	OM	DOC	reactive metal content				
				Cd	Ni	Cu	Pb	Zn
		(%)	(mg C L^{-1})	- - - - - (µmol kg^{-1}) - - - - -		- - - - - - - - (mmol kg^{-1}) - - - - - - - -		
1983	5.8 (0.0)	3.8	28.1 (0.8)	2.54 (0.06)	40.1 (1.1)	3.83 (0.02)	0.09 (0.00)	0.17 (0.01)
1985	5.4 (0.4)	3.7	29.4 (0.5)	2.56 (0.01)	35.6 (0.2)	2.98 (0.04)	0.10 (0.00)	0.18 (0.00)
1986	4.8 (0.0)	3.6	25.8 (0.2)	2.64 (0.08)	33.3 (0.1)	2.88 (0.02)	0.10 (0.00)	0.17 (0.00)
1989	5.9 (0.8)	3.4	17.8 (0.0)	2.40 (0.02)	26.7 (0.1)	2.31 (0.00)	0.10 (0.00)	0.15 (0.00)
1992	5.1 (0.0)	3.4	17.7 (0.7)	2.47 (0.02)	25.8 (0.3)	2.31 (0.01)	0.10 (0.00)	0.23 (0.00)
1995	5.4 (0.0)	3.1	13.4 (0.5)	2.46 (0.01)	23.6 (0.2)	2.29 (0.05)	0.10 (0.00)	0.16 (0.00)
1998	5.0 (0.0)	3.1	10.9 (0.5)	2.38 (0.00)	23.6 (0.8)	2.11 (0.07)	0.10 (0.00)	0.15 (0.01)
2001	5.1 (0.0)	3.0	10.5 (0.7)	2.00 (0.01)	16.3 (0.3)	1.43 (0.02)	0.09 (0.00)	0.10 (0.00)
2005	5.3 (0.0)	3.0	5.8 (0.0)	2.26 (0.01)	17.1 (1.5)	1.44 (0.09)	0.10 (0.01)	0.11 (0.01)

Table IV.2: Total Cu content (aqua regia), reactive Cu content (0.43 M HNO_3) and the ratio between the total and reactive Cu content. Results are given for samples from 1983, 1985, 1989, 1995, 2001 at both pH levels.

	pH-4 plot			pH-6 plot		
	total Cu	reactive Cu	ratio	total Cu	reactive Cu	ratio
	- - - - - - - mmol kg^{-1} - - - - - - -			- - - - - - - mmol kg^{-1} - - - - - - -		
1983	3.9	3.1	0.8	4.7	3.8	0.8
1985	3.1	2.5	0.8	4.2	3.0	0.7
1989	2.3	1.9	0.8	2.8	2.3	0.8
1995	1.7	1.2	0.7	2.8	2.3	0.8
2001	1.4	1.1	0.8	2.0	1.4	0.7

Table IV.3: Total HS content determined by SuperFAST (Van Zomeren and Comans, 2004) and LOI expressed as g OM and HS per kg and the amount HA, FA and hydrophilic acid (HY) expressed as g C per kg.

	SuperFAST				LOI
sample	HA	FA	HY	total	OM
	- - - - - - - - - - g C kg^{-1} - - - - - - - - - -			g HS kg^{-1}	g OM kg^{-1}
pH-4 plot 1986	7.1	1.4	2.1	20	39
pH-4 plot 2005	6.3	0.2	2.4	16	32
pH-6 plot 1986	6.9	1.1	1.4	17	36
pH-6 plot 2005	5.9	0.1	1.9	15	30

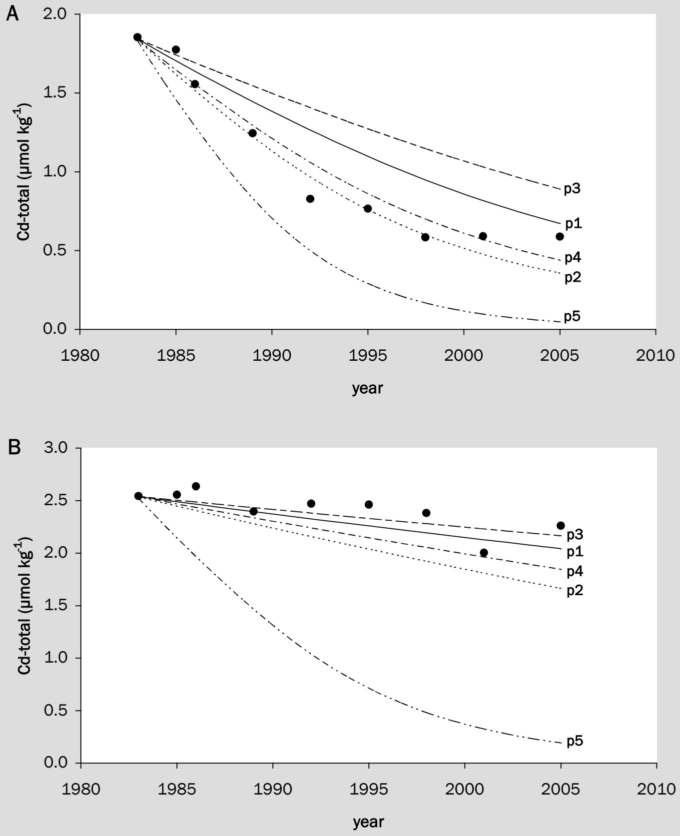

Figure IV.1: Cadmium content in the experimental plots as function of time. Field data are shown by the black circles and leaching predictions are indicated by the lines; straight line: prediction 1; dotted line: prediction 2; dashed line: prediction 3; dashed dotted line: prediction 4; dashed double dotted line: prediction 5. For soil properties used for the various predictions see Table 5.1. A: pH-4 plot and B: pH-6 plot.

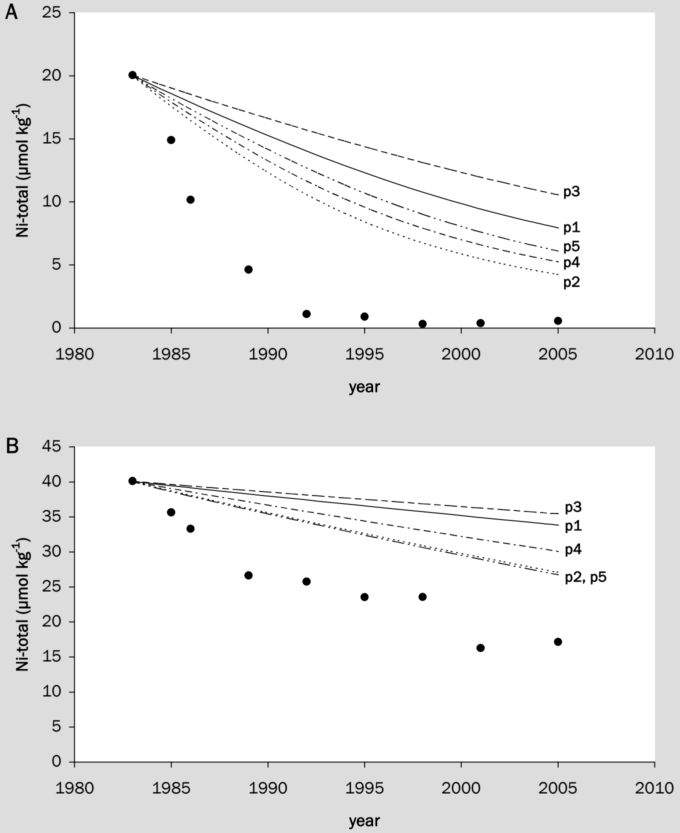

Figure IV.2: Nickel content in the experimental plots as function of time. Field data are shown by the black circles and leaching predictions are indicated by the lines; straight line: prediction 1; dotted line: prediction 2; dashed line: prediction 3; dashed dotted line: prediction 4; dashed double dotted line: prediction 5. For soil properties used for the various predictions see Table 5.1. A: pH-4 plot and B: pH-6 plot.

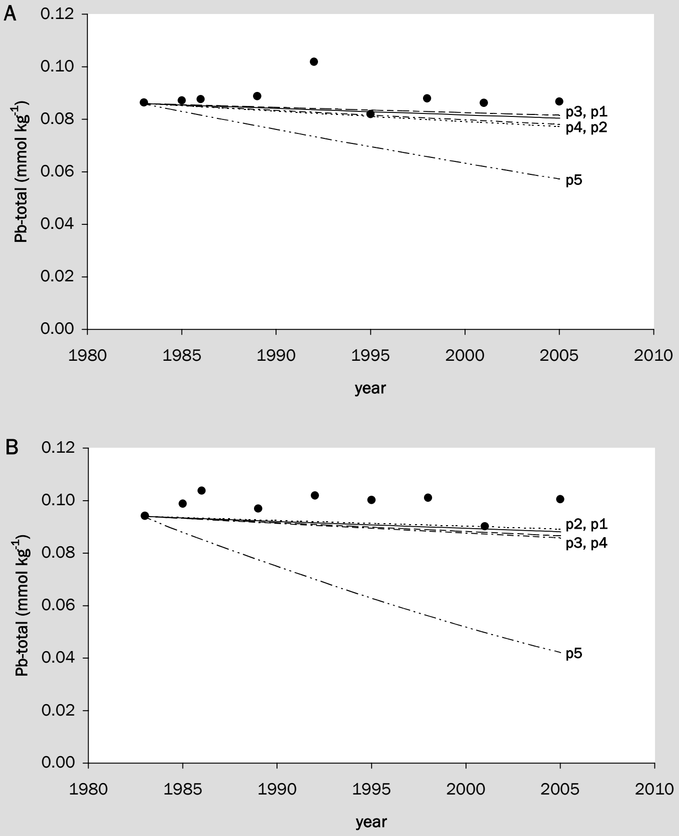

Figure IV.3: Lead content in the experimental plots as function of time. Field data are shown by the black circles and leaching predictions are indicated by the lines; straight line: prediction 1; dotted line: prediction 2; dashed line: prediction 3; dashed dotted line: prediction 4; dashed double dotted line: prediction 5. For soil properties used for the various predictions see Table 5.1. A: pH-4 plot and B: pH-6 plot.

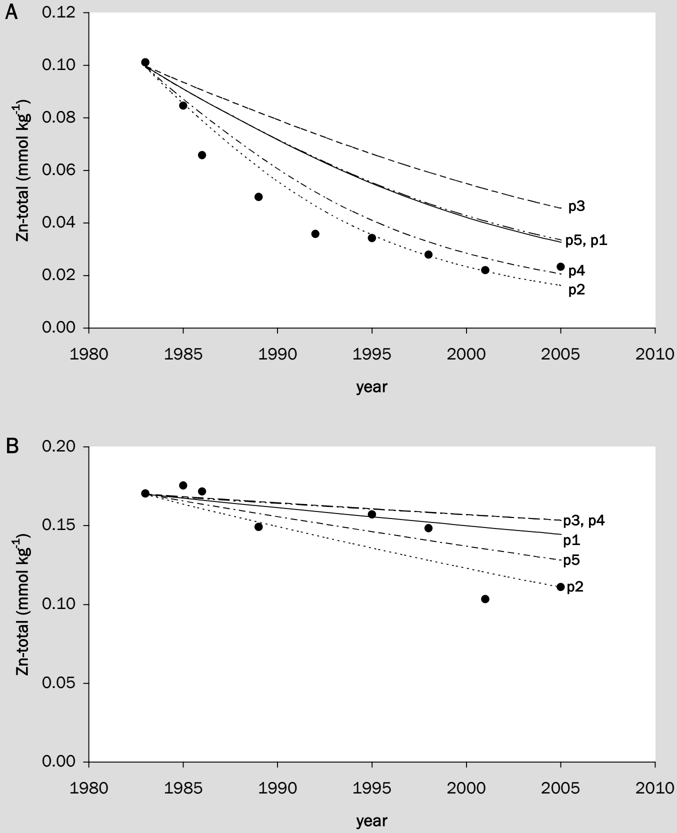

Figure IV.4: Lead content in the experimental plots as function of time. Field data are shown by the black circles and leaching predictions are indicated by the lines; straight line: prediction 1; dotted line: prediction 2; dashed line: prediction 3; dashed dotted line: prediction 4; dashed double dotted line: prediction 5. For soil properties used for the various predictions see Table 5.1. A: pH-4 plot and B: pH-6 plot.

> Als je geduldig bent
> Gebeurt het vanzelf
> Als je genieten wil
> Wil het dan niet te snel
>
> Het komt allemaal goed
> Wacht nou maar af wat de tijd met je doet
> Het is nu nog te vroeg
> Alles wat groot is, begon ooit klein
> Je hoeft niet meteen een vlinder te zijn
>
> *- John Ewbank - Marco Borsato - Vlinder -*

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> You have to take risks.
> We will only understand the miracle of life fully
> when we allow the unexpected to happen.
> - *Paulo Coelho* -

SUMMARY

Introduction

At present, advanced geochemical models have become available to describe solid/solution partitioning of cations with various reactive surfaces in soils. These models have been tested thoroughly in experimental setups; however application to field data is still rather scarce. Since large areas suffer from diffuse pollution with heavy metals, the understanding of the behavior of these contaminants is of great importance. For instance, more and more agricultural fields are transformed into natural areas and this transformation results in changing soil properties. These changes can have an effect on the accumulated heavy metals in these agricultural fields. Organic matter content (solid and dissolved) and pH play an important role in the solid/solution partitioning of heavy metals and other cations in sandy soils. In this thesis, these factors (pH and organic matter) are considered in the geochemical modeling of the solid/solution partitioning of metals in sandy soils. Furthermore, geochemical modeling can be helpful for soil risk assessment.

Proton buffering (chapter 2)

In view of groundwater protection it is of great importance to predict the effect of acid deposition on the solid/solution partitioning of accumulated heavy metals. Although acid deposition has decreased in many parts of the world, the soil still receives a significant amount of acid (in the Netherlands 3000 eq $(\text{ha yr})^{-1}$). In most geochemical modeling studies the pH is introduced as a constant soil property, however the soil is a complex dynamic system and deposited protons influence the sorbed metals. The buffering process and the (de)sorption of metals are described by a multi-surface modeling approach, in which the sorption onto different soil surfaces is described. The soil is considered as a combination of sorbing surfaces viz. organic matter, clay and Fe-oxides. The total proton and metal sorption is predicted by the sum of the sorption onto the single surfaces.

Acidification of soil samples was performed in a flow-trough reactor; soil samples were equilibrated with an acid solution by circulation of the solution through the sample. Acidification has been performed in successive steps of acid addition and after each acidification step the solution has been sampled. Prediction of the pH upon acidification with the multi-surface modeling approach was successful between pH 6 and 4; however below pH 4 the pH was predicted too low because buffering by dissolution of Al-containing minerals was not taken into account in the current modeling approach. Below pH 4 this buffering process started to play a major role in the buffering of these sandy soils samples, indicated by the increased Al concentration below pH 4. Desorption of major and trace metals during acidification was predicted within a factor five. Overall the combination of modeling proton buffering and metal leaching during acidification was done quite well with the multi-surface modeling approach. One of the major advantages of this modeling approach is that effects of acidification on the multi-metal behavior can be predicted by using general soil characteristics and generic model parameters.

Solid/solution partitioning of DOC (chapter 3)

The partitioning of organic matter between the solid phase and the soil solution is important in perspective of heavy metal behavior in sandy soils, since organic matter is the major sorptive phase for heavy metals in sandy soils. Metals sorbed onto dissolved organic matter (DOC) can be transported with the DOC through the soil and contribute to total leaching of metals from soils. Still, few studies incorporate the partitioning of organic matter between the solid phase and soil solution in the modeling of metal mobility in soils.

The effect of extraction solution (salt concentration), solid/solution ration (SSR), pH and storage on the extractability of DOC from sandy soils was studied to understand the behavior of DOC in sandy soils. Besides DOC quantity also the DOC quality was taken into account in this study by measuring the humic acid (HA), fulvic acid (FA) and a hydrophilic (HY) fraction in the soil solution. We performed a soil column experiment in which the soil column was connected to a DMT-cell. In the effluent of the soil column the free metal concentration was measured as well as the DOC composition.

As expected the extraction solution, SSR and pH affected the DOC concentration in the samples as well as the extracted amount of metals. The DOC concentrations were highest at high solid/solution ratios approaching field ratios and decreased further from water extracts to $CaCl_2$ extracts. In general, with increasing solid/solution ratio the metal-DOC ratio decreased, which indicated that the increased DOC at higher solid/solution ratios had a lower average metal binding capacity than DOC released at the lowest solid/solution ratio. Long stored samples (> 20 yr) showed higher DOC concentrations than short stored (< 1 yr) samples, indicating the effect of storage time on the DOC quantity. Extracted

DOC mainly comprises of FA and HY, whereas the contribution of HA is low. These results of the DOC composition are in contrast with the often used assumptions in modeling studies. Model calculation shows that also the HY fraction could be significant for metal binding in soil solution. Finally, this study shows that more research is needed to gain insight in the composition, concentration and behavior of DOC under field conditions in order to improve the prediction of metal leaching in the field.

Indigenous metal leaching in the field (chapter 4)

The current advanced adsorption models have shown the applicability to predict solid/solution partitioning of metals in soil systems. Up till now, these models have been mostly tested in under laboratory conditions or in the aquatic environment. Application of these advanced sorption models to long-term field situations is lacking. Leaching of heavy metals (Cd, Cu, Ni, Pb and Zn) from an experimental field (Wildekamp) has been studied at two pH levels. In the studied field plots these metals are present at background level.

The multi-component leaching of these metals has been predicted using an advanced sorption model (NICA-Donnan) assuming that soil organic matter is the dominant sorptive phase in the studied sandy soil for these metals. For the leaching prediction assumptions have been made to compose the model; the used soil properties (pH, organic matter content and DOC concentration) have been assumed to be constant throughout the time. However, since some of these properties vary in the field soils, the sensitivity for changes in these properties has been tested. The leaching predictions are simplified by assuming one-dimensional transport through the soil.

At low pH (~pH 4) the content of Cd, Ni and Zn decreased significantly during the studied period. In contrast, both the Cu and Pb content stayed rather constant within the studied period, indicating a strong sorption in the soil. At higher pH (~pH 6), the metal content decreased less compared to the decrease from the low pH plot. The pH dependence of the metal leaching is in these plots highest for the metal ions that do not form strong complexes with DOC, like Cd, Ni and Zn. Transport calculations show good predictions of the leaching of Cd, Ni, Pb and Zn after 22 years at both low and higher pH. The observed small increase in the Cu content was not predicted by this modeling approach. This increase of the Cu content was attributed to the contamination of the sampled plots by their neighboring plots, which have high Cu contents as a results of intentional addition of Cu.

All in all, the prediction of metal leaching indicate the this modeling approach has successfully been applied to metal leaching in a field situation. This approach is in potential very useful for scenario type calculations.

Metal leaching from a Cu contaminated field (chapter 5)

The modeling approach used in chapter four to predict leaching of metal from a sandy soil has in chapter five been applied to two field plots contaminated with Cu. From these two field plots contaminated with Cu, significant Cu has been leached in 22 years after the contamination; more than 60% of the initial Cu content has been lost from both studied plots and this is not influenced by the pH difference of the plots (pH 4 vs. 6). The high rate of Cu leaching does not influence the leaching of other metals (Cd, Ni, Pb and Zn).

The application of an advanced sorption model (NICA-Donnan) in leaching calculations has shown that the leaching of indigenous metal can be predicted quite well, within a certain range of uncertainties. However, the considerable leaching of Cu from the Cu contaminated soils could not be predicted by the model under reasonable assumptions of soil properties. From this it is concluded that after application of the Cu-salt, it will take several years before the Cu has been distributed over all binding sites in the top soil layer. In the mean time, significant amounts of Cu have already been transported downward to deeper soil layers.

Furthermore, toxicological data should be handled with care, because they often deal with freshly contaminated soils that may not yet be in equilibrium with all reactive binding sites of the soil. The results from this chapter emphasize the importance to consider 'bio-available' fractions in both toxicological testing as well as soil research in order quantify risk of contaminations.

Aluminum in groundwater (chapter 6)

Since the end of the 70's the element aluminum received great attention in relation to the acid rain problem. As a result of acidification elevated Al concentrations have been found in soil and surface water. These elevated Al concentrations can be toxic to aquatic biota and terrestrial vegetation and could therefore be a potential problem for drinking water production. To study the effect of land use type and groundwater depth (representing residence time) on the pH, DOC concentration and Al concentration data from provincial and national monitoring networks were examined. In order to study speciation of the Al in groundwater the complexation with DOC and the equilibrium with mineral phases like gibbsite and amorphous $Al(OH)_3$ have been taken into account. The type of land use (agriculture land use and nature vegetation) and groundwater depth (phreatic, shallow and deep) were expected to influence the pH and DOC concentration of the groundwater, which in turn can influence total Al concentration and its speciation.

Land use type and groundwater depth influenced pH, DOC concentration and Al concentration in the studied groundwater dataset. Highest Al concentrations have been found for natural-phreatic groundwater. The median DOC concentration decreased with the depth of the groundwater, in stead the median pH increased wit the depth of the groundwater. Phreatic groundwater below natural vegetation showed lower pH values than phreatic groundwater below agricultural land. Highest DOC concentrations have been found for agricultural-phreatic groundwater, these high DOC concentrations are induced by the application of organic fertilizers on agricultural fields.

The speciation of Al has been calculated for all the studied samples, taking into account the formation of inorganic species, mineral precipitation and complexation with DOC. The complexation with DOC has been described with the NICA-Donnan model. Groundwater samples below pH 4.5 were mainly in disequilibrium with mineral phases like gibbsite and amorphous $Al(OH)_3$. This disequilibrium is considered to be the result of kinetic constraints on the dissolution while equilibrium with Al bound to soil organic matter may still occur. Relation between pH and Al^{3+} for every combination of land use type and groundwater depth was derived by linear regression and derived relations were close to theoretical values for $Al(OH)_3$ minerals, except for natural-phreatic groundwater lower log*K* values have been found. Overall, complexation with DOC showed to be important for the speciation of Al especially at high DOC concentrations, like found for agricultural-phreatic groundwater.

Concluding remarks

The current available advanced geochemical models can be applied to a broad range of soil-metal studies as was shown by the results of this thesis. Application was tested in both laboratory and field situations. However, for each new application the assumptions and simplifications necessary for the application of these kind of model should be carefully considered. For example, large uncertainties exist on the concentration and variability of DOC in field situation. For metal transport, the DOC concentration could be a very important transport agent and reliable data are necessary to incorporate DOC in the modeling approach. Furthermore, this thesis indicates that from a toxicological point of view the 'bio-availability' is of great importance to consider in the risk evaluation of contaminants in soils and the applied advanced geochemical models can be very useful herein. Finally, the applied geochemical modeling in this thesis can be a powerful tool for scenario studies considering the bio-availability and mobility of heavy metals answering questions for water councils, landscape managers, nature conservation organizations and local and regional authorities.

> I loved the feeling of freedom in running, the fresh air,
> the feeling that the only person I'm competing with is me
> - *Wilma Rudolph* -

SAMENVATTING

‘voor leken’

Inleiding

Momenteel wordt steeds meer landbouwgrond uit productie genomen en veranderd in natuurgebieden. Tijdens deze omzetting kunnen veranderingen optreden in bodemeigenschappen. Zo kan de hoeveelheid organische stof toenemen, de bodem zuurder worden of de hoeveelheid voedingsstoffen afnemen. Om de effecten van de mogelijke verzuring te kunnen kwantificeren, is kennis van het gedrag van de zuurdeeltjes (= protonen) noodzakelijk. Veel landbouwgronden hebben verhoogde gehalten aan zware metalen, als gevolg van de jarenlange bemesting met dierlijke mest en kunstmest. In sommige gebieden kunnen ook andere bronnen oorzaak zijn van verhoogde gehalten zware metalen. De kennis van mobiliteit van zware metalen in de bodem is van belang bij de bescherming van de grondwaterwinning en voor de kwaliteit van het oppervlaktewater. Zandige, kalkarme bodems zijn erg gevoelig voor verzuring en daarmee gepaard gaande uitspoeling van de aanwezige zware metalen.

Recentelijk brachten enkele onderzoeken naar voren dat er nog steeds problemen zijn met zware metalen in de bodem, zoals blijkt uit de volgende krantenkoppen: "Cadmium in grondwater van Belgische grensgemeenten" (Spits, 25 januari 2007) en " Uranium gevonden in grondwater bij oude Brabantse stortplaatsen" (De Volkskrant, 23 januari 2007).

Dit proefschrift laat de toepassing zien van geochemische modellen bij het voorspellen van het gedrag van zware metalen in zandige bodems. Deze voorspellingen kunnen in de praktijk worden toegepast bij milieuonderzoeken en beleidsplannen. De geochemische modelberekeningen uit dit proefschrift zijn toe te passen op zowel landbodems als waterbodems. In het laatste geval kan de uitwisseling van zware metalen tussen waterbodem en de waterfase worden berekend. Dit kan nuttig zijn bij de bepaling van de kwaliteit waaraan oppervlaktewater moet voldoen in het kader van de Kaderrichtlijn Water. Voor landbodems kunnen scenarioberekeningen inzicht geven in effecten van landgebruiksveranderingen die plaatsvinden binnen diverse beleidsplannen, zoals Ruimte voor de Rivier en de Ecologische Hoofdstructuur.

Zware metalen in de bodem

Zware metalen en protonen komen voor als positief geladen deeltjes en kunnen daardoor hechten aan bodemdeeltjes met een negatief geladen oppervlak. Dit proces wordt adsorptie genoemd. Daarnaast kunnen de zware metalen ook hechten aan stoffen die opgelost zijn in het bodemvocht, zoals opgeloste organische stof (DOC) en negatief geladen stoffen (anionen). Ook kunnen de zware metalen voorkomen als individueel opgelost stofje in het bodemvocht (vrije vorm). De verdeling over deze verschillende vormen waarin metalen in de bodem voorkomen hangt af van de totale hoeveelheid zware metalen, de hoeveelheid oppervlakken waaraan de zware metalen kunnen adsorberen en de zuurgraad (pH) van de bodem. Om de verdeling van de zware metalen over al deze verschillende vormen te berekenen, wordt gebruik gemaakt van geochemische berekeningen. In dit proefschrift wordt de bodem benaderd als een combinatie van verschillende oppervlakken waaraan zware metalen kunnen adsorberen en waarbij deze geadsorbeerde metalen in evenwicht met metalen in het bodemvocht (multi-oppervlak model). In het bodemvocht bestaat ook weer een evenwicht tussen de vrij voorkomende zware metalen en zware metalen die een complex vormen met de in het bodemvocht opgeloste stoffen.

Het buffergedrag van de bodem

Verzuring van de bodem wordt veroorzaakt door processen die van nature in de bodem spelen, maar kan ook worden veroorzaakt door deeltjes die vanuit de lucht op de bodem komen. Vanuit het oogpunt van grondwaterbescherming is het belangrijk om het effect van deze zure neerslag op geaccumuleerde zware metalen in de bodem te voorspellen. Hoewel zure neerslag is afgenomen in grote delen van de wereld, wordt de bodem toch nog aan een behoorlijke hoeveelheid zuur blootgesteld (ongeveer 3000 eq per ha per jaar in Nederland). In de meeste studies met geochemische modellen is de pH meegenomen als een constante parameter. De bodem is echter een complex en dynamisch waarbij de zure neerslag (protonen) de geadsorbeerde metalen beïnvloedt. Het gedrag van protonen (buffergedrag) en de zware metalen is beschreven met behulp van een multi-oppervlak model, waarbij de binding aan diverse soorten oppervlakken is beschreven.

In een experiment zijn grondmonsters verzuurd. De grondmonsters worden in een reactor op evenwicht gebracht met een zure oplossing door middel van circulatie van de oplossing door het monster. De verzuring van de grondmonsters is uitgevoerd in opeenvolgende stappen van zuurtoediening en na elke stap is de oplossing bemonsterd. De voorspelling van de pH als gevolg van verzuring met het multi-oppervlak model was succesvol tussen pH 6 en 4. Echter beneden pH 4 wordt de pH te laag voorspeld omdat het oplossen van aluminium-mineralen bij deze pH niet is opgenomen in de huidige modelaanpak. Beneden pH 4 begint dit bufferproces een belangrijke rol te spelen in het buffergedrag van de bestudeerde zandgronden. Dit wordt aangetoond door het vrijkomen van aluminium (Al) beneden pH 4. De combinatie van het modelleren van de protonbuffering en metaaluitspoeling met het multi-oppervlak model heeft geleid tot redelijk goede resultaten. Een van de grote voordelen van deze modelaanpak is dat het effect van verzuring op het totale metaalgedrag kan worden voorspeld met behulp van algemene bodemeigenschappen en generieke modelparameters.

Verdeling van DOC tussen vaste en vloeistof fase

Naast pH is ook de verdeling van organische stof over de bodemdeeltjes en het bodemvocht een bepalende factor voor de mobiliteit van zware metalen in de zandige bodems. Dit komt omdat organische stof het belangrijkste adsorptie-oppervlak is voor zware metalen in zandige bodems. Metalen die gebonden zijn aan opgeloste organische stof (DOC) kunnen worden getransporteerd met het DOC door de bodem en daarmee bijdragen aan de totale uitspoeling van metalen in de bodem.

In dit hoofdstuk is het effect van de extractie-oplossing (zoutconcentratie), de grond/vloeistofverhouding, de pH en de bewaartermijn op de extraheerbaarheid van DOC afkomstig van zandige bodems bestudeerd om het gedrag van DOC in zandige bodems enigszins te kunnen begrijpen. Naast de hoeveelheid extraheerbaar DOC is ook de samenstelling van het DOC onderzocht. Hierbij is het DOC onderverdeeld in humuszuur (HA), fulvozuur (FA) en een hydrofiele fractie (HY). Om de samenstelling van het DOC te bestuderen is een kolomexperiment uitgevoerd waarbij de kolom is aangesloten op een DMT ('Donnan Membrane Technique') cel. Met deze techniek is het mogelijk om de hoeveelheid vrij metaal te meten in het bodemvocht.

Zoals verwacht hebben de extractie-oplossing, de grond/vloeistofverhouding en de pH invloed op zowel de DOC-concentratie in de monsters als de geëxtraheerde hoeveelheid metalen. De DOC-concentratie is het hoogst bij grond/vloeistofverhoudingen die in de buurt liggen van verhoudingen in veldsituaties. In het algemeen neemt de verhouding tussen metaal en DOC af bij een toenemende grond/vloeistofverhouding. Dit duidt op een lagere adsorptiecapaciteit van het DOC bij de hoogste grond-vloeistofverhouding. De lang opgeslagen monsters (> 20 jaar) vertonen hogere DOC-concentraties dan kort opgeslagen monsters (< 1 jaar). Hieruit blijkt het effect van de bewaartermijn op de hoeveelheid DOC in de grondmonsters. Het geëxtraheerde DOC bestaat voornamelijk uit FA en HY waarbij het aandeel HA zeer minimaal is. Deze resultaten zijn tegengesteld aan aannames die vaak in andere modelstudies gedaan worden over de samenstelling van het DOC. Modelberekeningen tonen aan dat ook de HY-fractie een significante rol kan spelen in de binding van metaalionen in oplossing. Dit proefschrift laat zien dat meer onderzoek nodig is om inzicht te krijgen in de samenstelling, concentratie en gedrag van DOC onder veldomstandigheden om de voorspelling van metaalgedrag in veldsituaties te verbeteren.

Uitspoeling van metalen in veldsituaties

De adsorptiemodellen in het multi-oppervlakmodel hebben hun toepasbaarheid laten zien bij de voorspelling van de verdeling van metalen over de vaste fase en oplossing in bodems. Tot op heden zijn deze modellen voornamelijk getest onder laboratoriumomstandigheden of in waterige systemen. De toepassing van deze geavanceerde modellen op lange termijn veldexperimenten ontbreekt. De uitspoeling van zware metalen (Cd, Cu, Ni, Pb en Zn) uit een onderzoeksveld is bestudeerd bij twee pH's. De metalen in dit onderzoeksveld zijn aanwezig bij een natuurlijk achtergrondgehalte.

Bij de berekening van de uitspoeling van de metalen is aangenomen dat organische stof het meest dominante adsorptie-oppervlak is in de bestudeerde zandgrond waarbij het multi-oppervlakmodel enkel bestaat uit het adsorptiemodel voor organische stof (NICA-Donnan). Bij de modelvoorspellingen is aangenomen is dat de gebruikte bodemeigenschappen (pH, gehalte organische stof en DOC concentratie) constant blijven gedurende de bestudeerde periode (22 jaar). Omdat deze bodemeigenschappen wel degelijk veranderen in de tijd, is getest hoe gevoelig de metaaluitspoeling is voor veranderingen van deze eigenschappen. De transportberekeningen zijn vereenvoudigd door aan te nemen dat de waterstroming door de bodem eendimensionaal is, namelijk verticaal.

Bij lage pH (~pH 4) daalt het gehalte Cd, Ni en Zn in de bodem aanzienlijk in de bestudeerde periode. Dit in tegenstelling tot het gehalte Cu en Pb, dat redelijk constant blijft gedurende de bestudeerde periode. Dit duidt op een sterke adsorptie aan de bodem. Bij hogere pH (~pH 6) neemt het metaalgehalte minder sterk af dan bij lagere pH (pH 4-veld). De pH-afhankelijkheid van metaaluitspoeling in deze veldjes is het grootst voor de metalen die minder sterke verbindingen vormen met DOC zoals Cd, Ni en Zn. De transportberekeningen laten zien dat de uitspoeling van Cd, Ni, Pb en Zn na 22 jaar goed wordt voorspeld zowel voor een veld met een lage pH als met een hoge pH veld.

Geconcludeerd kan worden dat de voorspelling van metaaluitspoeling met behulp van het NICA-Donnan model succesvol is toegepast voor metaaluitspoeling onder veldomstandigheden in zandige bodems.

Metaaluitspoeling uit een met koper verontreinigd veld

De in hoofdstuk 4 gehanteerde modelaanpak is in hoofdstuk vijf toegepast op twee veldjes die met koper (Cu) verontreinigd zijn. Na 22 jaar is de hoeveelheid Cu in deze veldjes sterk afgenomen, het koper is samen met het infiltrerende regenwater dieper de bodem in verplaatst. Meer dan 60 % van de initiële hoeveelheid Cu is verdwenen uit de bovenste 20 cm van de bodem en deze uitspoeling lijkt niet te worden beïnvloed door de pH.

De toepassing van een geavanceerd adsorptiemodel (NICA-Donnan) in uitspoelingsberekeningen laat zien dat de uitspoeling van metalen op achtergrondniveau zeer behoorlijk berekend wordt binnen een bepaalde marge van onzekerheden (zie hoofdstuk 4). De resultaten van uitspoelingsberekeningen voor de met Cu verontreinigde veldjes wijken sterk af van de daadwerkelijk gemeten uitspoeling. Bij de uitspoelingsberekeningen zijn realistische modelgegevens als uitgangspunt genomen. Hieruit wordt geconcludeerd dat na verontreiniging van de bodem met Cu, in dit specifieke geval, het een aantal jaren duurt voordat het Cu zich over alle aanwezige bindingsplaatsen in de bovenste laag van de bodem heeft verdeeld . Ondertussen is al een aanzienlijke hoeveelheid Cu uitgespoeld en naar diepere lagen getransporteerd.

Aluminium in grondwater

Sinds de jaren 70 van de vorige eeuw heeft het element aluminium (Al) veel aandacht gekregen in relatie tot het "zure regenprobleem". Als gevolg van verzuring worden verhoogde concentraties aan Al gevonden in de bodem en het oppervlaktewater. Zulke verhoogde Al-concentraties kunnen toxisch zijn voor organismen in het water en vegetatie op het land en daarmee een probleem vormen voor de drinkwaterproductie. Gegevens van provinciale en landelijke meetnetten zijn onderzocht om het effect van bodemgebruik en diepte van het grondwater (verblijftijd) op pH, DOC-concentratie en Al-concentratie te bestuderen.

Het grondwater is verdeeld in drie dieptes: freatisch (nabij grondwaterspiegel), ondiep (< 10 m) en diep (> 10 m) grondwater. Om de verschijningsvormen van Al te bestuderen in het grondwater wordt de binding van Al met DOC en het evenwicht met mineralen, zoals gibbsiet en amorf $Al(OH)_3$, beschouwd. De verwachting is dat het type bodemgebruik (agrarisch bodemgebruik of natuurlijke vegetatie) en de diepte van het grondwater (freatisch, ondiep of diep) de pH van en DOC-concentratie in het grondwater beïnvloeden, hetgeen uiteindelijk leidt tot een effect op de Al-concentratie en de verschijningsvormen van Al.

Analyse van en berekeningen met de grondwatergegevens laten zien dat de pH, DOC-concentratie en Al-concentratie worden beïnvloed door het type bodemgebruik en de diepte van het grondwater. De hoogste Al-concentraties worden aangetroffen in het natuurlijk-freatisch grondwater. De gemiddelde DOC-concentratie neemt af met de diepte van het grondwater, daarentegen neemt de gemiddelde pH toe met de diepte van het grondwater. Freatisch grondwater onder natuurlijke vegetatie laat lagere pH-waarden zien dan freatisch grondwater onder agrarisch land. De hoogste DOC-concentraties worden aangetroffen in agrarisch-freatisch grondwater; deze hoge DOC-concentraties worden veroorzaakt door de toediening van organische meststoffen op landbouwgronden.

De verschijningsvormen van Al zijn berekend voor alle grondwatermonsters uit de dataset, waarbij de vorming van anorganische verbindingen, neerslag van mineralen en binding aan DOC wordt meegnomen. De binding aan DOC is beschreven met het NICA-Donnan model. De grondwatermonsters beneden pH 4.5 zijn over het algemeen niet in evenwicht met mineralen zoals gibbsiet en amorf $Al(OH)_3$. Het wordt aangenomen dat deze niet-evenwichtssituatie wordt veroorzaakt door kinetische beperkingen van oplosbare mineralen. De relatie tussen pH en vrij Al (Al^{3+}) is afgeleid met behulp van lineaire regressie voor elke combinatie tussen bodemgebruik en grondwaterdiepte. De afgeleide relaties liggen dichtbij de theoretische waarden voor $Al(OH)_3$-mineralen met uitzondering van natuurlijk-freatisch grondwater dat een lagere oplosbaaheidsconstante (log$K$) kent. De conclusie is dat binding aan DOC belangrijk blijkt te zijn voor de verschijningsvormen van Al in het grondwater vooral bij hoge DOC concentraties, zoals die worden gevonden voor agrarisch-freatisch grondwater.

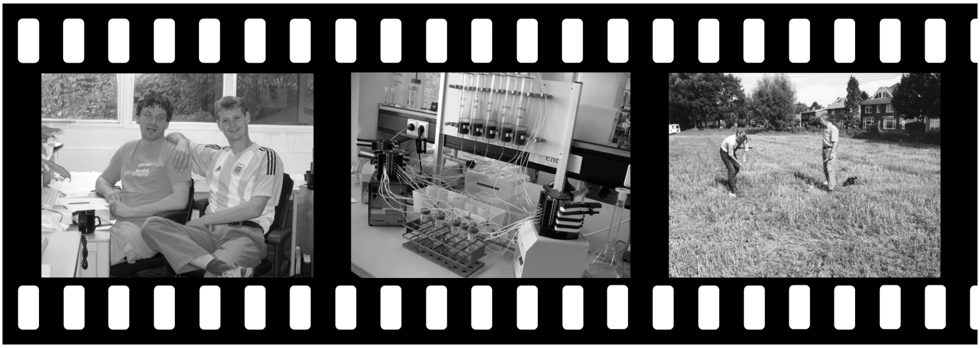
Afsluitende opmerkingen

Het multi-oppervlakmodel kan worden toegepast in een brede scala aan studies over het gedrag van metalen in de bodem, zoals wordt aangetoond in dit proefschrift. De toepassing van geochemische modellen is getest in zowel laboratorium-experimenten als veldsituaties. Echter, voor elke nieuwe toepassing moeten de aannames en simplificaties, die noodzakelijk zijn voor de toepassing van zulke modellen grondig worden bekeken. Zo bestaan bijvoorbeeld grote onzekerheden omtrent de concentratie en variatie van DOC in veldsituaties. Voor het transport van metalen is de DOC-concentratie een zeer belangrijke parameter en betrouwbare gegevens zijn noodzakelijk om DOC mee te nemen in de modelaanpak. De in dit proefschrift toegepaste geochemische modellering kan een krachtig instrument zijn voor scenario-studies over de mobiliteit van metalen en resultaten van zulke scenariostudies zouden vragen van waterschappen, landschapsbeheerders, natuurbeschermingsorganisaties en overheden met betrekking tot de mobiliteit van zware metalen kunnen beantwoorden.

> Als je honderd mensen niet kunt helpen,
> help er dan eentje
> - *Moeder Theresa* -

DANKWOORD

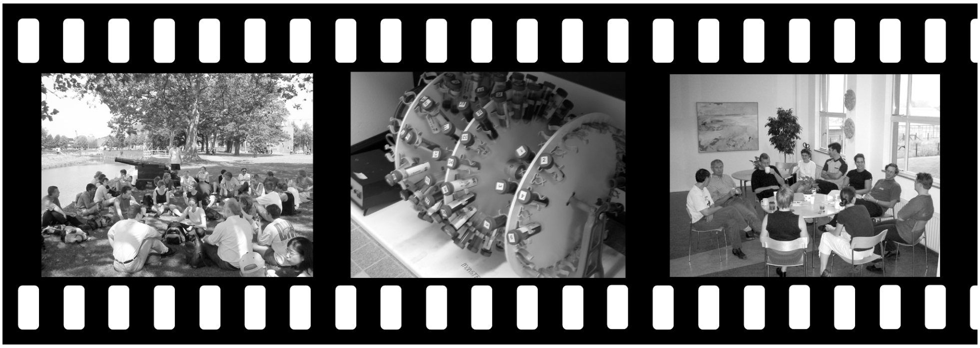
In februari 2002 begon ik aan dit promotieonderzoek en op dat moment leken die vier jaren erg lang en de promotie nog ver weg. Uiteindelijk is het vijf en een half jaartje geworden, ook omdat ik tijdens dit promotieonderzoek grotendeels parttime heb gewerkt. Daardoor was er voldoende tijd om lekker te sporten en leuke dingen te doen. En nu, nu is het klaar, het onderzoek is afgerond en alle resultaten zijn opgeschreven. Een promotieonderzoek verloopt zelden zonder diepe dalen en hoge bergen, zo ook voor mij. Menigmaal heb ik me afgevraagd, waarom doe ik dit? En wat heb ik hieraan? Terugkijkend ben ik erg blij dat ik heb doorgezet en trots op de voltooiing van mijn proefschrift. Al lijkt het vaak een solistische bezigheid, er zijn veel mensen die op diverse manieren hebben bijgedragen aan het promotieproces. Hiervoor wil graag mijn dank uitspreken.



Als eerste zijn daar vanzelfsprekend mijn promotor en copromotor. Willem en Erwin, hartelijk dank voor de begeleiding en het faciliteren van mijn promotieonderzoek. Tijdens mijn studie had ik al in dezelfde setting onderzoek gedaan en ik begon dus op een vertrouwd nest. Gedurende mijn AIO-schap heb ik van jullie beide veel geleerd, niet alleen op het inhoudelijke vlak, maar over alle zaken die om wetenschappelijk onderzoek heen spelen. Willem, de gesprekken over de resultaten gaven mij altijd veel inspiratie en een nieuwe impuls aan het onderzoek. De snelheid waarmee jij manuscripten leest en becommentarieert is bijzonder. Ik was ook vaak verrast door de tijdstippen waarop jij mailtjes verstuurt. Erwin, jij was meer voor de dagelijkse gang van zaken. Met kleine en grote vragen kon ik altijd binnenlopen en zeker als ik weer wat nieuwe resultaten had. Ook bood je een luisterend oor als het even niet mee zat in de privé-sfeer; Erwin, ik heb deze gesprekken zeer gewaardeerd. Heren, nogmaals bedankt!

Naast de begeleiding vanuit de universiteit kon ik ook rekenen op steun vanuit TNO. Jasper en Bas, hartelijk dank voor jullie kritische noten bij de manuscripten die ik produceerde. En natuurlijk ook dank voor het aanleveren van de grondwaterdata, een zeer waardevolle database, waarover we een mooi artikel hebben geschreven.

Rob, jammer genoeg kwam de samenwerking met jou pas tegen het einde van mijn onderzoek tot stand. Desalniettemin bewaar ik goede herinnering aan jouw enthousiasme als we samen onderzoeksresultaten bespraken en heb je in ieder geval bijgedragen aan het derde hoofdstuk van dit proefschrift. We houden contact.



Bij de praktische uitvoering van het onderzoek heb ik hulp gehad van diverse personen en die wil ik dan ook hartelijk danken. Alle medewerkers van het Chemisch Biologisch Laboratorium Bodem hartelijk dank voor alle analyses die jullie hebben uitgevoerd. Ook de VEP, hartelijk dank voor jullie hulp, al deed ik geen experimenten met planten, er moesten soms wel grondmonsters genomen worden. Last but, not least, wil ik ook het management en ondersteunend team bedanken voor alle bureaucratische rompslomp die bij het onderzoek komt kijken.

Het begeleiden van studenten was niet in het minst leerzaam voor mijzelf. Ik hoop echter dat jullie er zelf ook wat van hebben opgestoken. Judith Sterken en Christian Kwakernaak, jullie durfden het aan een afstudeervak te doen binnen mijn project en ik hoop dat jullie er met plezier aan terugdenken. Judith, jouw werk heeft geleid tot een publicatie in ES&T en Christian jouw werk kun je terug vinden in zowel hoofdstuk 3, 4 en 5. Heel veel dank voor jullie inzet.

Een speciale plaats in dit lijstje met bedankjes wordt ingeruimd voor mijn collega's uit de kelder, met wie ik een groot deel van mijn aio-schap heb doorgebracht, de generatie 2002.

Als eerste wil ik Gijs bedanken voor de vier jaren dat we samen een kamer hebben gedeeld. We hebben veel gelachen, maar ook geklaagd over van alles en nog wat en vele persoonlijke gesprekken gevoerd. Toen we begonnen had ik het idee dat onze onderzoeken op elkaar zouden aansluiten, maar al snel bleken we ieder een totaal andere richting op te gaan, desalniettemin waren die vier jaren onvergetelijk. Ik hoop dat we contact blijven houden.

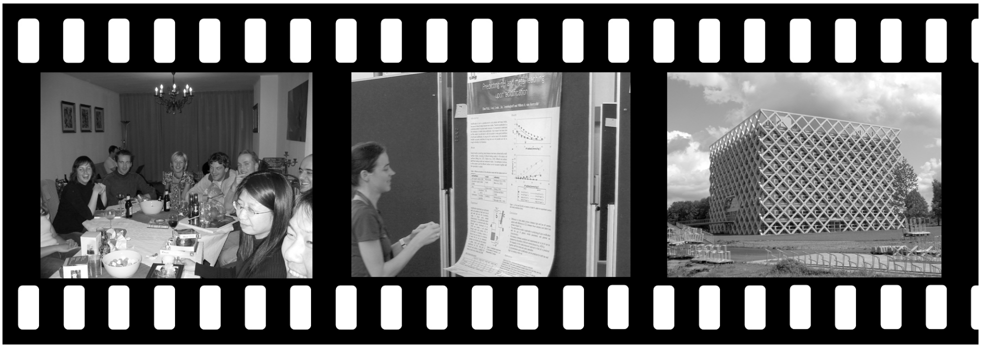
Bert, op de valreep zijn we toch nog kamergenoten geworden. Een paar maanden samen op een kamer in het nieuwe Atlas gebouw, het was erg gezellig. Ik denk dat het voor ons beide een goede basis was om het werk bij de WUR af te ronden. Begin april vertrokken wij beiden uit kamer B0.23, jij al met Dr-titel, ik nog niet. Ik hoop dat onze vriendschap blijft bestaan.

Erwin, bedankt voor vier en een half jaar gezelligheid in de kelder, je altijd vrolijke blik vanuit die kamer aan het einde van de gang en je onverwachte bezoekjes en fietstochtjes met Robin en Ivan. Ook bedankt voor de hulp bij het formuleren van de stellingen, met een biertje in de kroeg. Dat biertje in de kroeg dat houden we erin, maar dan zonder stellingen. Het lijkt me zeker leuk om eens samen te gaan hardlopen al vrees ik dat jij met die lange benen veel harder gaat.

Monika, bedankt voor alle gezellige babbeltjes tussen het werk door, niet alleen over werk, maar ook de persoonlijke gesprekken heb ik zeer gewaardeerd. Daarnaast konden we het ook de hele koffiepauze hebben over kleren, lekker vrouwenpraat. Knap hoor, hoe jij in je eentje vanuit Polen naar Nederland bent gekomen en je plaats hebt gevonden.

Generatie 2002, ik wens jullie allemaal veel succes in jullie verdere carrière; ik concludeer dat onze generatie niet veel èchte wetenschappers heeft opgeleverd.

Debby, Walter, Odair, Laura, Renske, Petra, Gerwin, Jan-Willem, Xiaopeng, Nicole, Ram, Maria, Franciska, Dorien, Gerard, Piet, Anke, Thomas, Annemieke, Louise, Simone, Eduaro, Romulo, Aliou and Gerson allemaal bedankt voor de gezelligheid tijdens en buiten de werkzaamheden.



De sectie Bodemkwaliteit was voor mij een prettige werkomgeving, met de nodige sociale activiteiten, zoals de borrels, de uitstapjes en het zeilweekend. Iedereen die ik nog niet persoonlijk heb genoemd allemaal bedankt voor de fijne werkomgeving de afgelopen jaren.

Een speciale band is tijdens mijn werk bij Bodemkwaliteit ontstaan met Thom en Ali. Wat begon als op het huis passen tijdens een vakantie, omdat ik toevallig om de hoek woon, is uitgegroeid tot een fijne vriendschap. Jullie hartelijkheid en gastvrijheid samen met de kookkunsten van Thom waardeer ik zeer. Bedankt!

Een speciaal woord van dank gaat uit naar mijn paranimfen Charlotte en Jacqueline. Ik ben zeer verheugd dat jullie vandaag met mij op het podium willen staan.

Charlotte, we zijn al bevriend sinds de brugklas en ook al heeft onze vriendschap wel eens een deukje opgelopen, alle gebeurtenissen van de afgelopen jaren heeft onze band verstrekt.

Jacqueline, tijdens onze studie BWA werd als snel duidelijk dat wij meer van de chemie waren dan van de veldbodemkunde. Ik denk dat dat ook de basis is van onze vriendschap, hoewel we eigenlijk niet zo heel vaak inhoudelijk over het werk praten. Ik hoop nog lang van onze vriendschappen te kunnen genieten, in goede en slechte tijden.

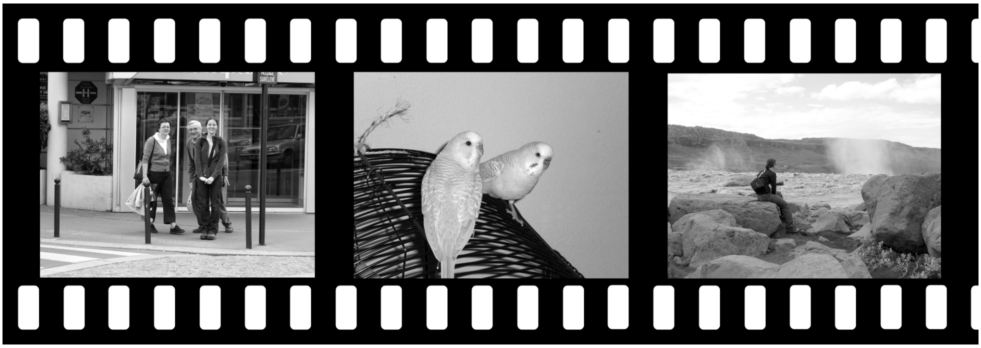
Bijna twee jaar geleden begon ik als spinning-instructrice bij sportcentrum de Plataan in Wageningen en ik kon toen niet vermoeden hoeveel energie deze uit de hand gelopen hobby oplevert. De wekelijkse lessen waren tijdens mijn promotieonderzoek een welkome afwisseling in de dagelijkse bezigheden van voornamelijk nadenken en schrijven. Ik wil daarom Wiljan en Doreth heel erg bedanken voor de kans die ik heb gekregen om mijn hobby in een professionele omgeving uit te voeren en alle steun die jullie gaven als het even tegenzat. En natuurlijk niet te vergeten Anja, Arne, Barbara, Bram, Bonnie, Casper, Carolien, Daniéla, Erik, Evert, Fieke, Floor, Francis, Frans, Hetty, Irma, Khedija, Linda, Marc, Marco, Margaret, Maria, Marjan, Marjon, Nicole, Nina, Peter, Petra, Rien, Sarina en Valentijn bedankt voor jullie steun, enthousiasme en fijne werksfeer.

Ondertussen ben ik al weer een paar maanden werkzaam bij Witteveen+Bos en ook aan mijn collega's daar wil ik graag een woord van dank uitspreken. Allereerst wil ik Willem bedanken voor de kans die ik heb gekregen om na mij aioschap aan de slag te gaan in advieswereld en mijn opgedane kennis tijdens de afgelopen periode in de praktijk te kunnen brengen. Willem, ik hoop dat we nog veel mooi projecten van de grond gaan krijgen. Martijn, jij ook bedankt voor je vertrouwen en je enthousiasme voor mijn promotieonderzoek, ook wij gaan samen nog veel leuke projecten doen. En tenslotte, alle andere collega's bij Witteveen+Bos, ook al ben ik nog maar kort werkzaam bij jullie, bedankt voor jullie steun en enthousiasme zodat ik me door de laatste loodjes van het promotieonderzoek kon worstelen.

Familie, vrienden en iedereen die ik hier nog vergeten ben te noemen, zonder jullie steun was het me nooit gelukt om deze onderneming tot een succesvol einde te brengen. Naast werk, is ontspanning heel erg belangrijk en daar hebben jullie een belangrijke bijdrage aan geleverd.

Tot slot, Pap en Mam veel dank ook aan jullie voor de onvoorwaardelijke steun bij het promoveren. Ik realiseer met dat jullie vaak geen idee hadden van wat ik uitspookte, maar dat vonden jullie geen probleem. Hopelijk breekt nu een rustigere periode aan en kan ik wat vaker naar het Brabantse land komen. Niet gebruikelijk, maar in mijn dankwoord ook een plaatsje voor mijn twee lieve huisdiertjes Joep en Pino; bedankt voor jullie vrolijke noot in huis.

Ellen



> Keep smiling, keep shining
> Knowing you can always count on me, for sure
> That's what friends are for
> For good times and bad times
> I'll be on your side forever more
> That's what friends are for
>
> *- Burt Bacharach & Carole Bayer Sager -*

CURRICULUM VITAE

Petronella Maria Johanna (roepnaam Ellen) Fest werd geboren op 22 januari 1977 in Boxmeer. In juni 1995 behaalde zij haar VWO diploma aan het Elzendaalcollege te Boxmeer. In september van datzelfde jaar begon zij met de studie Bodem, Water en Atmosfeer aan Wageningen Universiteit. Tijdens de studie in Wageningen koos zij voor de richting bodem en in het bijzonder de chemie van de bodem. De liefde voor de chemie in de bodem blijkt uit haar afstudeeronderzoeken en gelopen stage. Het eerste afstudeeronderzoek richtte zich op de effecten van humus- en fulvozuren op de mobiliteit van koper in de bodem. Dit afstudeeronderzoek heeft geleid tot een eerste wetenschappelijke publicatie. Haar tweede afstudeeronderzoek betrof een literatuurstudie naar de binding van polycyclisch aromatische koolwaterstoffen (PAKs) in veengronden. Beide afstudeeronderzoeken heeft zij uitgevoerd bij de sectie Bodemkwaliteit. Een deel van haar stage heeft ze uitgevoerd bij Fugro Milieuconsult, alwaar zij ervaring opdeed in 'het verkennend bodemonderzoek' en de mogelijkheden onderzocht naar de toepassing van betoninjectie in de bodem om verontreinigingen te mobiliseren. Het andere deel van haar stage heeft zij uitgevoerd bij het RIVM en daar heeft zij gewerkt aan het eindrapport van de eerste meetronde van het landelijk meetnet bodemkwaliteit. In september 2001 studeerde zij af aan Wageningen Universiteit met als specialisatie bodemhygiëne en –verontreiniging. Na haar afstuderen heeft zij nog enkele maanden bij het RIVM gewerkt. Van februari 2002 tot april 2007 was zij aangesteld als assistent in opleiding (AIO) bij de sectie Bodemkwaliteit van Wageningen Universiteit. Tijdens deze periode deed zij onderzoek naar de protonbuffering van en metaaluitspoeling uit zandgronden. De resultaten van dit onderzoek zijn vastgelegd in dit proefschrift. Vanaf april 2007 is zij werkzaam bij Witteveen+Bos te Deventer als projectmedewerker bij de afdeling bodem. Daarnaast is zij sinds september 2005 werkzaam als spinning-instructrice bij sportcentrum de Plataan in Wageningen.

> De liefde heeft geduld,
> en haat het bitter spreken
> De liefde ziet en zwijgt,
> de liefde dekt gebreken

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Abstracts

Fest, E.P.M.J., Temminghoff, E.J.M., Griffioen, J., Van der Grift, B. and Van Riemsdijk, W.H., 2004. Buffering behaviour of sandy soils in relation to metal sorption. In: Proceedings of the Soil & Water Symposium 2004, 2 - 3 June 2004, Zeist, p. 29-30.

Fest, E.P.M.J., Temminghoff, E.J.M., Griffioen, J. and Van Riemsdijk, W.H. 2006. The role of organic matter in proton buffering in metal leaching in sandy soils. In: Proceedings of the Soil & Water Symposium 2006, 14 - 15 June 2006, Zeist, p. 23.

Fest, E.P.M.J., Temminghoff, E.J.M., Griffioen, J. and Van Riemsdijk, W.H. 2006. The role of organic matter in proton buffering in metal leaching in sandy soils. In: Frimmel, F and Abbt-Braun, G (eds). Humic substances – Linking structure to functions Proceedings of the 13th Meeting of the International Humic Substances Society, 30 July – 4 August 2006, Karlsruhe, Germany, Volume II, p. 809-812.

Submitted papers

Fest, E.P.M.J., Temminghoff, E.J.M., Comans, R.N.J. and Van Riemsdijk, W.H. Solid/solution partitioning of DOC and heavy metals in soils: effects of extracting solution, solid/solution ratio, pH and storage time.

Fest, E.P.M.J., Temminghoff, E.J.M. and Van Riemsdijk, W.H. Metal leaching from a sandy soil: results from a long term field experiment and model predictions.

> Je hebt iemand nodig, stil en oprecht
> die als het er op aankomt, voor je bidt en vecht
> Pas als die iemand met je lacht en grient,
> dan pas kan je zeggen..."Ik heb een vriend"
>
> *- Toon Hermans -*

EDUCATION CERTIFICATE

SENSE

Netherlands Research School for the
Socio-Economic and Natural Sciences of the Environment

CERTIFICATE

The Netherlands Research School for the
Socio-Economic and Natural Sciences of the Environment
(SENSE), declares that

Petronella Maria Johanna Fest

Born on: 22 January 1977 at: Boxmeer The Netherlands

has successfully fulfilled all requirements of the
Educational Programme of SENSE.

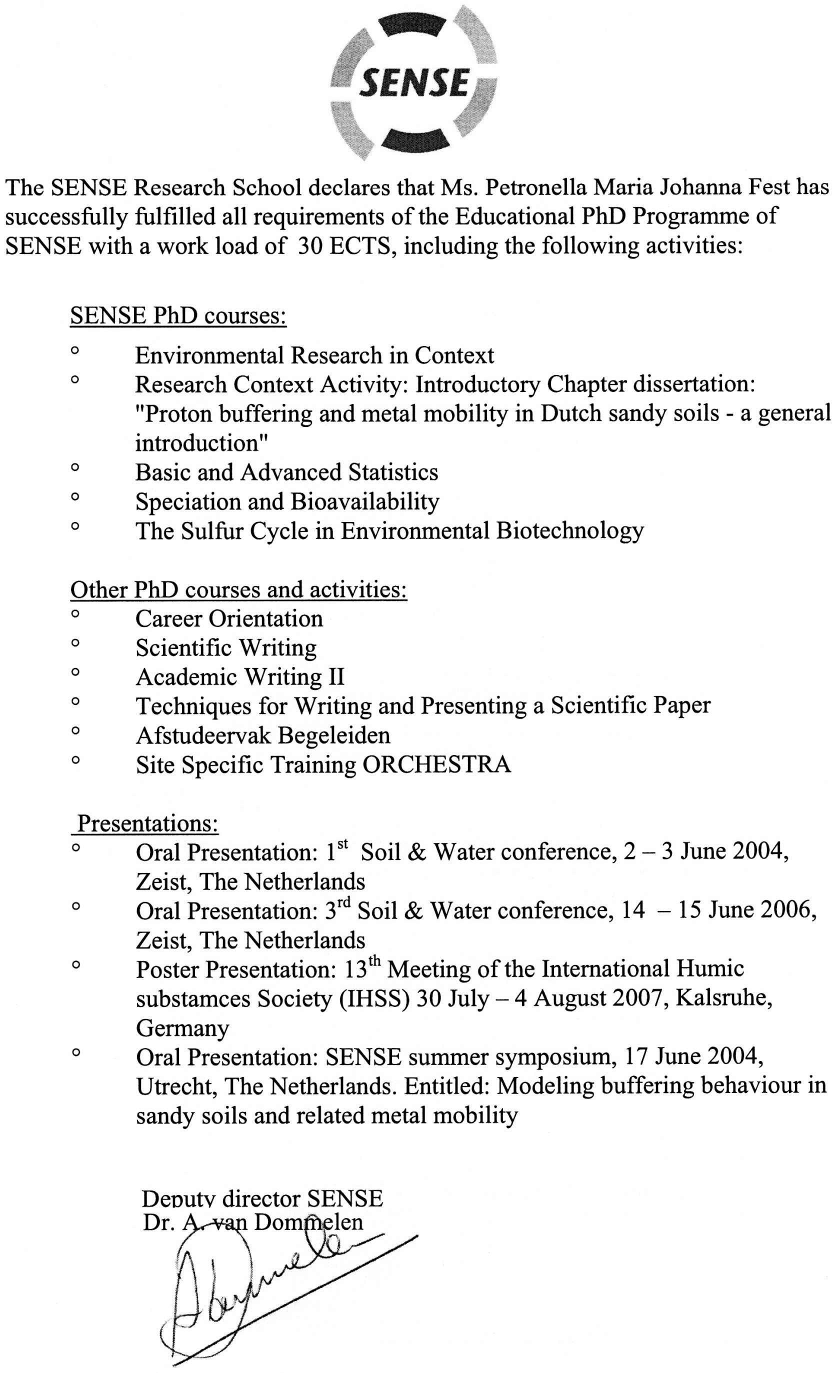
Place: Wageningen Date: 18 September 2007

the Chairman of the
SENSE board

Prof. dr. R. Leemans

the SENSE Director
of Education

Dr. C. Kroeze



SENSE

The SENSE Research School declares that Ms. Petronella Maria Johanna Fest has successfully fulfilled all requirements of the Educational PhD Programme of SENSE with a work load of 30 ECTS, including the following activities:

<u>SENSE PhD courses:</u>

- Environmental Research in Context
- Research Context Activity: Introductory Chapter dissertation: "Proton buffering and metal mobility in Dutch sandy soils - a general introduction"
- Basic and Advanced Statistics
- Speciation and Bioavailability
- The Sulfur Cycle in Environmental Biotechnology

<u>Other PhD courses and activities:</u>

- Career Orientation
- Scientific Writing
- Academic Writing II
- Techniques for Writing and Presenting a Scientific Paper
- Afstudeervak Begeleiden
- Site Specific Training ORCHESTRA

<u>Presentations:</u>

- Oral Presentation: 1st Soil & Water conference, 2 – 3 June 2004, Zeist, The Netherlands
- Oral Presentation: 3rd Soil & Water conference, 14 – 15 June 2006, Zeist, The Netherlands
- Poster Presentation: 13th Meeting of the International Humic substamces Society (IHSS) 30 July – 4 August 2007, Kalsruhe, Germany
- Oral Presentation: SENSE summer symposium, 17 June 2004, Utrecht, The Netherlands. Entitled: Modeling buffering behaviour in sandy soils and related metal mobility

Deputy director SENSE
Dr. A. van Dommelen

Ik loop hier alleen
In een te stille stad
Ik heb eigenlijk nooit last
Van heimwee gehad
Maar de mensen ze slapen
De wereld gaat dicht
En dan denk ik aan Brabant
Want daar brandt nog licht

Ik mis hier de warmte
Van een dorpscafé
De aanspraak van mensen
Met een zachte G

Ik mis zelfs het zeiken
Op alles om niets
Was men maar op Brabant
Zo trots als een Fries

- Guus Meeuwis - Brabant -