

The mobility of aluminium, iron and organic matter in acidic sandy soils

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door Boris Jansen

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Promotor

Prof. Dr. J.M. Verstraten

Overige leden promotiecommissie

Prof. Dr. H.A.J. Govers

Prof. Dr. J. Mulder

Prof. Dr. J. Sevink

Dr. Ir. W. Bouten

Dr. Ir. E.J.M. Temminghoff

Dr. K. Kaiser

Faculteit der Natuurwetenschappen, Wiskunde en Informatica

Jansen, B.

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Contents

| | |
|--|-----|
| Voorwoord----- | 5 |
| 1. Introduction----- | 7 |
| Part I: Measuring and modeling the interactions between metals and dissolved organic matter in acidic soil solutions | |
| 2. Comparison of diffusive gradients in thin films and equilibrium dialysis for the determination of Al, Fe(III) and Zn complexed with dissolved organic matter ----- | 19 |
| 3. Influence of pH and metal/carbon ratios on soluble organic complexation of Fe(II), Fe(III) and Al in soil solutions determined by diffusive gradients in thin films ----- | 37 |
| 4. Organic complexation of Al and Fe in acidic soil solutions: A comparison of DGT analyses with Model V and VI predictions ----- | 57 |
| Part II: The implications of interactions of Al, Fe and organic matter for their mobility in acidic sandy soils | |
| 5. Mobility of Fe(II), Fe(III) and Al in acidic forest soils mediated by dissolved organic matter: influence of solution pH and metal/organic carbon ratios ----- | 79 |
| 6. Mobilization of organic matter, Al and Fe in eluvial podzol horizons as affected by complexation and interactions with solid soil material ----- | 101 |
| 7. Mechanisms controlling the mobility of dissolved organic matter, Al and Fe in podzol B horizons ----- | 123 |
| 8. Synthesis----- | 151 |
| Summary ----- | 159 |
| Samenvatting----- | 167 |
| References ----- | 175 |
| Appendix ----- | 185 |
| Curriculum Vitae ----- | 187 |

Voorwoord

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1

Introduction

1.1 General Introduction

1.1.1 Background

‘Soils sustain life’ as the Soil Science Society of America so eloquently puts it in their promotional campaigns. The development of soils and the transport of substances through soils are of great human interest because they are key factors in important issues ranging from developing efficient agricultural practices, through predicting and preventing the spread of pollutants, to sustaining the environment.

Organic matter plays a key role in many processes that take place in soils. Due to its predominantly acidic nature, organic matter causes soil acidification that is enhanced by the ability of organic matter to increase rates of mineral weathering, resulting in the release of the Lewis acids Al and Fe (McBride, 1994). Furthermore, organic matter can bind to other substances, thereby influencing the mobility and transport in soils of a variety of components ranging from organic pollutants such as PAH’s and pesticides to (trace) metals and nutrients (e.g. Fang et al., 1998; Martinez and McBride, 1999; Mitra and Dickhut, 1999). In addition to influencing the mobility of components, the association of substances with organic matter can lower their bioavailable fraction and alleviate their toxicity to plants and soil organisms (e.g. Lucassen et al., 2000; Ma et al., 2001). Finally, because of its involvement in both mineral weathering and the transport of substances, organic matter in soils can be of great influence on pedogenesis (McBride, 1994).

Organic matter in soils consists of complex, organic molecules mainly formed by the decomposition of plant, animal and microbial material (Zech and Guggenberger, 1996). By definition the most mobile fraction of organic matter in soils is the part that is present in the form of dissolved organic matter (DOM) (Zsolnay, 1996). DOM is usually operationally defined as all non-living organic molecules in solution able to pass through a 0.45 µm filter (Herbert and Bertsch,

1995). As a consequence DOM includes truly dissolved molecules as well as smaller colloids. Solid organic matter (SOM) consists of all non-living organic material larger than 0.45 μm , as well as DOM that has precipitated out of solution or is adsorbed on soil particles. An alternative to the division into DOM and SOM is the subdivision of organic matter into humine, humic acids (HA) and fulvic acids (FA). HA and FA are operationally defined fractions of organic matter that have several, slightly different definitions. According to one of the more common definitions by the International Humic Substances Society, together HA and FA in soils represent the fraction of organic matter that is removed by extraction with 0.1 M NaOH under an atmosphere of N_2 , while humine is the fraction that is insoluble in a NaOH solution at room temperature. Subsequently, HA is the fraction of dissolved organic matter in the 0.1 M NaOH solution that precipitates out of this solution when the pH is lowered to 1.0, while FA consist of the humic substances that remain in solution (Swift, 1996). As a consequence, analogous to DOM, FA represents the most mobile fraction of organic matter. However, because FA is obtained after invasive chemical extractions of SOM, it is probably less realistic with respect to the actual organic matter found in acidic sandy soil solutions.

1.1.2 Interactions between Al, Fe and organic matter

While organic matter in soils can bind to many different substances, it is especially reactive towards the complexation of cations in general and in particular multicharged species like Al^{3+} and Fe^{3+} (Tipping, 2002). In general, there are two types of binding mechanisms through which metal cations can associate with organic matter. All cations interact with negatively charged (dissociated) functional groups on the organic molecules through non-specific electrostatic interactions. In addition, Al and Fe can form specific bonds with one or more specific functional groups on the organic molecule through co-ordination bonding. (Tipping, 2002). When polyvalent cations bind to two or more chelates simultaneously through co-ordination bonding, this can lead to the formation of very stable ring structures (Pohlman and McColl, 1988; Tam, 1987). In addition to

(hydrated) metal cations themselves, charged hydration products of Fe and Al such as FeOH^{2+} and AlOH^{2+} bind to organic matter through similar mechanisms (Ares and Ziechman, 1988). In general, binding of metals capable of co-ordination bonding occurs first at those sites that form the strongest complexes. As the stronger sites become saturated, weaker binding through electrostatic interactions becomes increasingly important (Stevenson, 1994).

Functional groups on organic matter that bear nitrogen, sulfur or oxygen can all be involved in the co-ordination bonding of Al and Fe. However, due to the much greater abundance of oxygen bearing groups in comparison to functional groups containing sulfur and nitrogen, oxygen bearing groups in general and carboxylic and phenolic hydroxyl groups in particular are regarded as the dominant groups involved in the association of Al and Fe with organic matter (e.g. Erich and Trusty, 1997; Jordan et al., 1997; Shen, 1999).

The binding of Al and Fe to organic matter is influenced by several soil chemical variables including the pH, the solution ion strength, the redox potential and the ratio of metal to organic carbon present (M/C ratio) (e.g. Stevenson, 1994; Tipping, 2002). The pH determines the degree of dissociation of the acidic functional groups on the organic molecules and the inorganic speciation of the metals that can potentially bind to organic matter. Protonation of acidic functional groups on organic molecules leads to a reduction in charge of the molecule, which lowers metal binding through electrostatic interactions. In case of DOM it may also induce precipitation when insufficient charge remains to keep the molecule in question in solution. In addition, a lower pH increases proton competition for acidic functional groups involved in co-ordination bonding. At higher pH values, the formation of hydroxy complexes of the metal cations in addition to forming soluble inorganic complexes, may induce precipitation of the metal in question and thereby a reduction of the pool of metal species capable of binding to organic matter. Finally, the pH affects the sterical configuration of organic molecules and thereby the accessibility of the functional groups involved in co-ordination bonding.

The solution ion strength influences metal binding in three main ways. Firstly, the activity coefficients of charged inorganic species depend on the ionic

composition of the solution. While activity coefficients of all metal cations are decreased by increasing ionic solution strength, the effect increases with increasing valency thus discriminating between metals of different valencies (e.g. Fe^{2+} and Fe^{3+}). Secondly, ionic solution strength influences the sterical configuration of DOM molecules. Thirdly, ionic solution strength affects binding through electrostatic interactions because of counterion condensation in the diffuse double layer of the DOM molecules. However, the ionic strength of soil solutions is often low and therefore the effect of ionic strength may be limited in the range that occurs under natural conditions.

The redox potential is of special importance for Fe, because it determines the speciation of total Fe in solution over Fe(II) and Fe(III). This affects the valency of the Fe cations, the inorganic speciation in solution and the total solubility of Fe.

The M/C ratio finally, has an impact on the binding of Al and Fe to organic matter because it determines the abundance of metal binding sites relative to the amount of metal present. At higher M/C ratios, it will be increasingly difficult for Al and Fe to find still unoccupied binding sites and there will be an increasing electrostatic repulsion by residual positive charge left on Al and Fe cations that are already bound to organic matter.

The binding of Al and Fe to organic matter affects the fate of the two metals and organic matter itself in two important ways. In the first place binding of Al and Fe to organic matter influences the mobility of all three through soils. In addition, it lowers the bioavailability of Al and Fe to plants and microorganism, especially when larger dissolved organic colloids (> 10.000 kDa) or SOM are involved (e.g. Chen and Wang, 2001; Ma et al., 2001). At high dissolved metal concentrations, this can alleviate Al and Fe toxicity (e.g. Lucassen et al., 2000; Ma et al., 2001).

1.1.3 The effect of the binding of Al and Fe to organic matter on their mobility

The binding of Al and Fe to organic matter can influence the mobility of both metals and organic matter in several ways. Obvious immobilization occurs when Al and Fe bind to SOM or when the binding of Al and Fe to DOM leads to the formation of insoluble organic Al/Fe complexes. Immobilization also occurs when

charged dissolved organic Al/Fe complexes bind to solid soil components. When negative charge remains on the DOM molecule after binding of Al or Fe, the dissolved organic Al/Fe complex can be adsorbed on positively charged sites on the solid soil matrix, such as amorphous sesquioxides at pH values below their point of zero charge (PZC). Dissolved organic Al/Fe complexes can also bind to negatively charged sites on the solid soil matrix through cation bridging when not all of the positive charge on the binding cation is compensated (e.g. Guggenberger and Zech, 1993). On the other hand, the association of Al and Fe with DOM can mobilize both metals by preventing binding to SOM and shifting equilibria with secondary mineral phases such as gibbsite, imogolite or ferrihydrite.

It is clear that changes in soil chemical variables that influence the binding of Al and Fe to DOM also affect their respective mobilities. In addition, the composition of the solid soil matrix, e.g. the content of SOM and solid phases of Al and Fe, will affect the mobility of Al, Fe and organic matter. However, the quantitative influence of changes in specific soil chemical variables in combination with different solid phase compositions on the influence exerted on the mobility of Al, Fe and organic matter in soils remains unresolved.

1.1.4 Podzolization

The fact that many aspects of the influence of the association of Al, Fe and organic matter on their respective mobility in soils remain unresolved, is illustrated by the lack of consensus on the mechanisms involved in the process of podzolization. Podzols are characterized by a bleached eluvial E horizon from which organic matter, Al and Fe have been removed, overlying one or more illuvial B horizons in which organic matter, Al and in most cases Fe have been deposited (FAO, 1988). Podzols occur in all climatic zones, from the tropics to the boreal zone. Podzols and podzolization have been the subject of research for many decades. As indicated in one of the important standard works on podzolization by Petersen (Petersen, 1976), the first reported research of podzols and the process of podzolization took place as early as the late nineteenth century. In the early fifties of the twentieth century, Bloomfield was amongst the first to suggest that DOM may play an important role in the translocation of Al and Fe in podzols (e.g.

Bloomfield, 1953; Bloomfield, 1954). This suggestion was also made by Petersen (1976) and Mokma and Buurman (1982). Many now believe that interactions with organic matter are a key process regulating the mobilization of Al and Fe from eluvial podzol horizons. Much more debate exists about the mechanisms governing the immobilization of Al, Fe and organic matter itself in illuvial horizons. In short the following main podzolization theories currently exist.

The classical fulvate theory (e.g. De Coninck, 1980; Mokma and Buurman, 1982; Petersen, 1976) proposes that initially, FA dissolves primary and secondary minerals and amorphous materials in the E horizon. The Al and Fe thereby released react with FA to form dissolved organic Al/Fe complexes. While moving downwards through the soil profile, the organic molecules become saturated as more and more Al and Fe bind to them, leading to precipitation in the B horizons as the negative charge on the organic molecules is sufficiently compensated by the positive charge on the hydrated Al and Fe cations. Subsequent re-dissolution of precipitated Al and Fe from the upper B horizon by complexation to still unsaturated DOM leads to a deepening of the podzol profile and the differentiation of a generic B horizon into a Bh horizon enriched in organic matter, overlying a Bs horizon enriched in sesquioxides.

In an alternative podzolization theory, DOM does not play an active role at all in the process of podzolization: neither in mobilizing Al and Fe in the eluvial horizons nor in immobilizing them in the illuvial horizons (Anderson et al., 1982; Farmer and Lumsdon, 2001). According to this theory, positively charged inorganic (proto)imogolite sols carry Al, Si and intrusions of Fe from the eluvial to the illuvial horizons. The adsorption of DOM on solid phase Al and Fe in the top of the B horizon as well as dissolution of Al-SOM complexes and allophanic precipitates at the Bh-Bs interface followed by precipitation in the form of immogolite, causes the development of Bh and Bs horizons and deepens the podzol profile. In this theory, dissolved organic Al/Fe complexes only play a role in recycling Al and Fe that was moved to the O horizons by biological processes, back to the B horizons.

Gustafsson et al. (2001) also propose immobilization of Al in B horizons in the form of inorganic precipitates at the higher pH values (> 4.2) that are generally

found in B horizons. However, they suggest that precipitation is induced by the equilibrium of dissolved Al with $\text{Al}(\text{OH})_3(\text{s})$ and explicitly rule out that imogolite plays a significant role. At pH values below 4.2, such as found in the O and possibly E horizons, they propose equilibria with SOM to control the solubility of Al in podzols. Also, in contrast with the previous theory but analogous to the classic fulvate theory, they believe that DOM can act as a carrier that transports Al and Fe to the B horizons.

Another contemporary podzolization theory was formulated by Lundström et al. (2000b) after a study of several Scandinavian podzols. They observed that 40% of dissolved Al was complexed to low molecular weight (LMW) organic acids in the O and E horizons, decreasing to 20% in the B horizons. Furthermore, in contrast with the classical fulvate theory, they found no indications of saturation of DOM molecules with Al and Fe in the illuvial horizons. As a consequence, they propose that complexation of Al and Fe to LMW organic acids plays a main role in the mobilization of Al, Fe and organic matter from podzol E horizons. Subsequently, microbial degradation of the LMW organic acid carrier deeper in the soil followed by precipitation of inorganic Al and Fe complexes in the form of simple metal hydroxides or imogolite is responsible for the immobilization of Al and Fe in the B horizons. In addition, some dissolved organic Al/Fe complexes are adsorbed on solid phase Al and Fe, after which the organic 'tail' of the complexes is removed by microbial degradation. Dissolved high molecular weight (HMW) organic acids that are more resistant to microbial degradation than LMW organic acids, in turn are adsorbed on solid phase Al and Fe.

Several researchers have tried to reconcile some of the different theories by assuming that a combination of the mentioned processes is involved in podzolization (e.g. Mossin et al., 2002; Van Breemen and Buurman, 2002). Mossin et al. noted that imogolite seems to occur less in podzols and become less important for the process of podzolization, as one moves down from north to south Scandinavia. At the same time organic precipitation induced by high M/C ratios in solution appears to gain in importance. A similar trend with respect to the occurrence of imogolite in Canada was reported by Kodama and Wang (1989). Mossin et al. conclude that different mechanisms dominate in different locations,

controlled by climate. Possibly the differences are linked to the relatively rich parent materials found under boreal climates resulting in a relatively high production of LMW organic acids in the litter layer, while intrazonal podzols are always formed on very poor parent materials and have slower organic matter turnover (Van Breemen and Buurman, 2002). Still, much scientific debate about the topic of podzolization remains, especially concerning the role of DOM versus inorganic sols as a carrier for Al and Fe. This is exemplified by a recent re-interpretation of the results of Gustafsson et al. by Farmer and Lumsdon (2002).

1.2 Objectives

The main objective of this study was to investigate the influence of the interactions of Al, Fe and organic matter on their mobility in acidic sandy soils in the Netherlands. More specifically the goal was to answer the following three research questions:

1. To what extent do Al and Fe interact with DOM in acidic sandy soil solutions to form soluble and insoluble organic complexes, and how are these interactions affected by changes within realistic ranges of the solution pH and M/C ratios?
2. How are the solubility of Al, Fe and DOM and their interactions in acidic sandy soil solutions influenced by the presence of SOM and amorphous Al and Fe phases in different eluvial and illuvial soil horizons?
3. What new insights do the answers to the two previous questions give us into the mechanisms that govern the mobility of Al, Fe and DOM in acidic sandy soils in general and podzols in particular?

The goals were attained through a combination of laboratory experiments and mathematical modeling.

1.3 Outline

This thesis consists of two parts. The first part (Chapters 2-4) focuses on the analysis of the interactions of Al, Fe and DOM in solution, while the second part (Chapters 5-7) deals with the influence of solid soil material on the association of Al and Fe with organic matter and the implications for their respective mobilities. The chapters of this thesis are papers that all have been or will be published independently in international, peer-reviewed journals. As a consequence some duplication occurs.

In Chapter 2 the relatively new analytical chemical method of Diffusive Gradients in Thin films (DGT) (Zhang and Davison, 1995) was tested for its applicability to distinguish between ‘free’ Al and Fe(III) and soluble Al/Fe-DOM complexes in soil solutions. The ‘free’ fraction here is defined as consisting of the hydrated metal cations as well as their soluble inorganic complexes. The results obtained by DGT were compared to those obtained by the better established, but more time consuming method of equilibrium dialysis. As a further performance test, the ‘environmentally important’ trace metal Zn was considered. In Chapter 3, DGT was applied to investigate the influence of changes in pH and metal/organic carbon ratios on the soluble complexation of Al, Fe(II) and Fe(III) to DOM. Subsequently, in Chapter 4 the resulting dataset was modeled using the speciation code Model V and its recent successor Model VI (Tipping, 1994; Tipping, 1998). Both are deterministic speciation models specifically designed to model the interactions between metals and organic matter. Together with an inorganic speciation model, they form the comprehensive solution speciation models WHAM-W 1.0 and WHAM-W 6.0, respectively. The comparison between the model calculation and DGT results allowed for testing of the internal consistency of DGT with both models and gave further insights into the interactions between Al, Fe and DOM in solution.

Chapter 5 deals with the expected implications of interactions between Al, Fe and DOM in soil solutions for their mobility in acidic sandy soils. As a consequence it focuses not only on the overall degree of organic complexation, but specifically on which fraction of the resulting dissolved organic metal complexes

remains in solution and which fraction precipitates out of solution in the form of insoluble organic metal complexes. The question of (im)mobilization of Al, Fe and DOM in soils was further explored in Chapters 6 and 7. While Chapter 6 focuses primarily on eluvial podzol AE horizons, Chapter 7 deals specifically with the complex issue of immobilization of Al, Fe and DOM in podzol B horizons.

In Chapter 8, a general synthesis of the knowledge gained from the research performed in the framework of this thesis is presented. Specifically, it points out which new insights with respect to the mobility of Al, Fe and DOM were obtained and what implications they have for our understanding of the process of podzolization. Finally, it indicates what further research is still required.

Part I: Measuring and modeling the interactions
between metals and dissolved organic matter in
acidic soil solutions

2

Comparison of diffusive gradients in thin films and equilibrium dialysis for the determination of Al, Fe(III) and Zn complexed with dissolved organic matter*

Abstract

The distinction between 'free' metals and organically complexed metals in aqueous solutions is important for research involving the mobility or bioavailability of metals in the environment. In this study the applicability of equilibrium dialysis (Molecular Weight Cut-Off = 1000 Da) and Diffusive Gradients in Thin films (DGT) to determine 'free' Al, Fe(III), and Zn in four forest soil solutions was compared. The 'free' metals as measured by both methods, consist of hydrated metal cations and soluble inorganic metal complexes. In addition, dialysis measures any organic complexes < 1000 Da and DGT measures a portion of smaller labile organic complexes. The four soil solutions were prepared by water extraction of an organic soil horizon (H) from a Fimic Anthrosol, and contained either 20 or 75 mg C/l dissolved organic matter at pH = 4.0 and pH = 7.0. To test the performance of both methods and optimize experimental volume and time, experiments using metal nitrate solutions were carried out. In the solutions at pH = 4.0, no significant differences in average 'free' metal contents were found for Al, Fe(III) or Zn. This makes DGT a viable alternative for equilibrium dialysis for the study of the complexation of all three metals in acidic soils. At pH = 7.0, again no significant difference between both methods were found for Al and Fe(III), but the DGT results for Zn were significantly higher. This was likely caused by labile organic complexes that were only detected by DGT.

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2.1 Introduction

The interaction of metals with naturally occurring dissolved organic matter (DOM) plays an important role in determining the fate of those metals in soils. Not only does association with DOM influence the mobility of metals through the soil system (Fox, 1995; Sauvé et al., 2000), it also affects their bioavailability and toxicity (Lores et al., 1999; Simpson et al., 1997; Tam and McColl, 1990). In addition, metal-DOM interactions can affect the mobility of DOM itself in soils (Ares and Ziechman, 1988; Fox, 1995; Kaiser, 1998). Polyvalent metal cations are especially important, because of their capability of strong and specific binding to organic molecules (Stevenson, 1994; Tam and McColl, 1990; Tam and McColl, 1991).

In order to study metal-DOM interactions, several experimental methods have been developed to distinguish between organically complexed metals and 'free' metals (Saar and Weber, 1982; Simpson et al., 1997; Stevenson, 1994). These 'free' metals usually consist of a combination of hydrated metal cations and soluble inorganic metal complexes and are usually considered to represent the bioavailable metal fraction. A major pitfall with most of the existing experimental methods, such as voltammetry and the use of ion-selective electrodes, is that they are only applicable to a limited number of metals that do not include important metals like Al and Fe (Saar and Weber, 1982; Stevenson, 1994). Furthermore, the shifting of binding equilibria during the analysis of 'free' metals and the inability to use undisturbed samples are often a concern (Saar and Weber, 1982). One of the few techniques that do not suffer from these problems is equilibrium dialysis. This technique is based on the separation of the smaller hydrated metal cations and soluble inorganic complexes from the larger metal-DOM complexes by means of a dialysis membrane (Truitt and Weber, 1981) and has been used successfully in several studies of the binding of metals to DOM in natural systems (Hintelmann et al., 1997; Lores and Pennock, 1998; Lores et al., 1999; Truitt and Weber, 1981; Van Loon et al., 1992). However, there is a dilemma when using equilibrium dialysis. If a membrane with a relatively large pore-size (> 1000 Da) is used, the time before equilibrium is reached is relatively short but the

separation will be inaccurate. When a smaller pore size is used, the separation will be more complete but the time needed to reach equilibrium increases substantially, because the diffusive permeability of dialysis membranes is proportional to the square of the pore size (Kokubo and Sakai, 1998).

Recently, a new separation technique called Diffusive Gradients in Thin films (DGT) was developed (Zhang and Davison, 1995). DGT uses a chelating resin to immobilize metal cations and labile (in)organic complexes. 'Free' metal concentrations are calculated from the mass of metals collected on the resin (Zhang and Davison, 1995). The resin is covered with an ion-permeable hydrogel of defined area and thickness that allows free metals to pass at known rates. The diffusion rate of larger organic complexes through the commonly used APA hydrogel is slow enough to prevent significant diffusion, but smaller organic complexes will be able to penetrate the hydrogel to some extent (16% at 2400 Da) (Zhang and Davison, 1999). Therefore, in addition to hydrated metal cations and soluble (labile) inorganic complexes, DGT will measure a small portion of the smaller labile organic complexes.

Like equilibrium dialysis, DGT promises applicability to a wide range of metals and the ability to use undisturbed samples. Because metal concentrations are calculated from known diffusion rates through the hydrogel, the time needed for a given analysis can be very short (Zhang and Davison, 1995). DGT has already been used successfully to determine free concentrations of several metals in surface waters and specific trace metals, such as Cu, Zn and Cd, in soil solutions (Zhang and Davison, 1995; Zhang et al., 1998). However, problems may arise at the lower pH values ($\text{pH} < 5$) common in many soils because of competition with protons for the exchange resin, especially when weakly binding metals are concerned (Zhang and Davison, 1995). Furthermore, the performance of DGT has not been tested thoroughly for many metals commonly encountered in soil solutions, such as Al that is a dominant metal cation in acidic soils.

In this study, the applicability of DGT to the determination of free metal concentrations in soil solutions was tested by comparison with results obtained by the established method of equilibrium dialysis. The soil under consideration is an acidic sandy forest soil in the temperate zone. In this type of soil the polyvalent

metals Fe(III) and Al are important, amongst others because of their relative abundance, their potential toxicity to soil organisms and their role in pedogenesis (McBride, 1994). Therefore, the detection of these two metals by DGT was tested. Because small, but significant amounts of the polyvalent and environmentally important metal Zn were found in the soil under study, this metal was also considered. Two water extracts at pH = 4.0 of the H horizon of the forest soil were used. These extracts contained either 20 mg C/l or 75 mg C/l, spanning the range of DOM concentrations usually found in sandy forest soils in the temperate zone. In addition, the same extracts brought to a pH of 7.0 were used for reference purposes, since no problems with DGT were expected at this pH value (Zhang and Davison, 1995).

2.2 Materials and methods

All chemicals used in the experiments were of analytical grade. To prevent metal contamination, all glassware was acid washed prior to the experiments. For the determination of metal content, a Perkin Elmer Optima 3000XL ICP-OES and a Varian Vista CCD simultaneous ICP-AES were used. The pH of samples analyzed on the ICP was adjusted to 1.0 by addition of a concentrated HNO₃ solution, to dissociate any metal complexes present. DOM content was measured as Dissolved Organic Carbon (DOC) by colorimetric determination on a Skalar continuous flow auto-analyzer.

2.2.1 Preparation of DOM solutions

Soil material was collected from the H horizon (pH_{H₂O} = 3.8) of a Fimic Anthrosol at the Buunderkamp location at the Veluwe, the Netherlands, and sieved without prior drying over 2 mm using a polyethylene sieve to avoid metal contamination. Two water extracts were prepared by adding 150 g and 400 g, respectively of the homogenized material per liter of doubly deionized water, shaking the resulting suspension for 16 hours, centrifuging at 3000 rpm and filtering the supernatant using a 0.45 µm membrane filter. The extract prepared from 400 g of material per liter water was subsequently concentrated by a factor

of 1.2 by evaporation at 65 °C using a Rotavab vacuum evaporation device, because using a higher material to water ratio to obtain a higher DOM content proved impractical. The two DOM solutions were each divided over two aliquots, one of which was adjusted to pH = 4.0 and the other to pH = 7.0 by adding small quantities of a 1.0 M KOH solution. Samples were taken and analyzed to determine the initial metal and DOC contents of the four resulting solutions.

To all solutions 0.01 M NaN₃ was added to prevent microbial degradation of DOM (De Maagd et al., 1998). The pH was readjusted to compensate for the resulting rise in pH. To prevent osmosis during the dialysis experiments, the ionic strength of all solutions was adjusted by adding KNO₃ to obtain a concentration of 0.01 M.

2.2.2 Equilibrium dialysis experiments

For the dialysis experiments, Spectra/Por Biotech CE dialysis membrane tubing with a Molecular Weight Cut-Off (MWCO) of 1000 Da was used. Glass containers were filled with the sample solution, referred to as the outside solution. In this outside solution a dialysis tube filled with doubly deionized water, referred to as the inside solution, was immersed. To minimize disturbance of metal-DOM binding equilibria in the sample as a result of metals migrating into the inside solution, the volumic ratio of outside to inside solution was set at 25:1 (Truitt and Weber, 1981). KNO₃ and NaN₃ were added to the inside solutions to match the concentrations in the outside solutions and the pH of the inside solutions was adjusted by adding small amounts of either 1.0 M KOH or 1.0 M HNO₃. During the experiments, the closed containers were continuously shaken at a constant room temperature of 20 °C. At the beginning of the experiments, samples were taken from both the inside and outside solutions to determine initial DOC and total metal contents. After equilibrium had been reached, again samples were taken from both the inside and outside solutions and analyzed to allow calculation of the 'free' metal contents and DOM that possibly passed the membrane.

Two types of equilibrium dialysis experiments were performed. First, pilot experiments were carried out to determine the time needed to reach equilibrium over the membrane. Second, the main experiments using each of the four DOM

solutions were conducted, to determine the 'free' metal contents for comparison to those found with DGT. For the pilot experiments, aqueous solutions of the nitrate salts of the metals of interest were used. These solutions had the same metal concentrations as found in the DOM solutions. Since all metals are assumed to be in the 'free' metal form in the absence of DOM, equilibrium is reached when the concentrations in the inside and outside solutions are equal. The pilot experiments were started at the same time but were ended after different regularly spaced time periods to test for equilibrium. In addition, a pilot experiment using the 20 mg C/l DOM solution at pH = 4.0 was performed to test the attainment of equilibrium in the presence of DOM. This solution was spiked with 185 μM $\text{Al}(\text{NO}_3)_3$ to assure significant complexation.

Based on the results of the pilot experiments, the experimental time in the main experiments was set at 400 hours. An outside solution volume of 300 mL, the smallest practical volume, was used. The main experiments were carried out in five-fold. At the same time, experiments containing the same DOM solutions without dialysis membranes were conducted, to test for fluctuations in metal and DOM contents in the course of the experiment due to other causes than the dialysis process.

2.2.3 DGT experiments

Standard DGT units for metals were obtained from DGT Research Ltd, UK, and assembled according to the procedures described elsewhere (Zhang and Davison, 1995; Zhang et al., 1995). The units contained a Chelex 100 chelating resin in the Na^+ form, covered with an APA hydrogel (Zhang and Davison, 1999) and a 0.45 μm membrane filter. In the experiments, DGT units were suspended vertically halfway down glass containers filled with the initial sample solution. During the experiments, the closed containers were constantly shaken at a room temperature of 20 °C. At the beginning of the DGT experiments, samples from the sample solution were taken and metal and DOC contents were determined. At the end of the experiments, the metal content of the outside solution was determined to check for significant removal of metals from solution. In addition, the DGT units

were opened and metals were removed from the chelating resin using a 1.0 M HNO₃ solution, and subsequently analyzed (Zhang and Davison, 1995). The metal concentrations in the hydrogels were also measured to determine if the gel had retained significant amounts of metal.

First, pilot experiments were conducted to test the performance of DGT and determine the deployment time and sample volume needed, as DGT was primarily developed for use in large volumes (Zhang and Davison, 1995). Good performance of DGT in determining Fe, Zn, and Cd has been reported in several publications (Zhang and Davison, 1995; Zhang et al., 1998; Zhang et al., 1995). However, only limited data has been published about Al (Zhang and Davison, 1999). Therefore, more extensive tests using 10 μM Al(NO₃)₃ solutions were performed. The pilot experiments were performed in a similar manner to those for equilibrium dialysis, with the exception that in addition to the metals of interest Cd(NO₃)₂ was added as a performance reference.

Second, the main experiments using each of the four DOM solutions were conducted. Again the main experiments were carried out in five-fold. Based on the pilot experiments, a sample volume of 0.5 l and an experimental time of 16 hours were used in the main experiments.

2.2.4 Calculation and comparison of the free metal fractions

The performance of DGT was assessed by calculating the recovery, defined as the calculated 'free' metal concentrations divided by the total metal concentrations as measured in the bulk solutions. A recovery of 100% indicates all metal is present as 'free' metal.

For both the dialysis and DGT experiments the 'free' metal fraction in the main experiments was calculated as the mass of 'free' metal divided by the total metal mass present in solution. This total metal mass was calculated from the initial metal concentrations in the outside solutions.

For the equilibrium dialysis experiments, the 'free' metal mass was calculated from the metal concentrations measured in the inside solutions at the end of the experiments. For the DGT experiments the 'free' metal mass was calculated from

the amount of metal captured on the exchange resin, using the DGT formulas (Zhang and Davison, 1995).

$$M = Ce(V_{\text{HNO}_3} + V_{\text{gel}})/fe \quad (1)$$

$$C = M\Delta g/(DtA) \quad (2)$$

M represents the metal mass captured on the chelating resin and is calculated from the metal concentration in the elution sample (Ce), the volume of the elution fluid (V_{HNO_3}) and the chelating resin (V_{gel}), and an elution factor (fe) of 0.8 needed to compensate for incomplete metal removal from the resin (Zhang and Davison, 1995). From M, the 'free' metal concentration is calculated by taking into account the thickness of the diffusion gel layer (Δg), the diffusion coefficient of the metals in the hydrogel (D), the deployment time (t) and the area of exposure to the sample solution (A). The diffusion coefficients in the APA hydrogel are similar to those in water, but vary slightly depending on the cross-linker used during the manufacturing of the hydrogel (Li and Gregory, 1974; Zhang and Davison, 1999). Accurate diffusion coefficients were supplied by the manufacturer. For the metals of interest at 20°C these are: Al: $4.14 \times 10^{-6} \text{ cm}^2/\text{s}$; Fe: $5.32 \times 10^{-6} \text{ cm}^2/\text{s}$, Zn: $5.29 \times 10^{-6} \text{ cm}^2/\text{s}$ and Cd: $5.30 \times 10^{-6} \text{ cm}^2/\text{s}$ (used in the DGT performance tests).

The variance and means of the duplicate experiments for both DGT and dialysis were calculated and compared by use of F- and t-tests with $\alpha = 0.05$. If a significant difference in means was found an additional non-parametric test (Mann-Whitney test) was performed.

2.3 Results and discussion

The initial composition of the DOM solutions is provided in Table 1. Colorimetric tests confirmed that all Fe in the four DOM solutions was present as Fe(III).

2.3.1 Equilibrium dialysis experiments

The rate at which equilibrium was reached varied for the three metals and was slowest for Al and Fe(III). This difference in rate was most likely caused by slower passage of small soluble organic metal complexes, just small enough to penetrate the membrane. In addition, trivalent cations are surrounded by bulkier water shells and anion layers than divalent ions such as Zn^{2+} . This slows down their passage through the membrane. The approach to equilibrium for the pilot experiment using the Al-spiked 20 mg C/l solution at pH = 4.0 is presented in Fig. 1. The remaining differences between inside and outside solutions after equilibrium signify complexed metal, which is the highest for Al due to the spiking with Al. As a result of the much higher Al concentrations, we had problems detecting Zn on the ICP in this particular experiment, especially at the points before equilibrium. Therefore, Zn is not included in Fig. 1. Instead Mg^{2+} , which was present at higher concentrations, is included as a reference for the behavior of divalent cations. At the lower Al concentrations in the other pilot experiments we experienced no problems with the detection of Zn.

Table 1

Characterization of the outside (bulk) soil solutions and the inside dialysis solutions

| pH | DOC ($\mu\text{mol C/l}$) | | Total Al($\mu\text{mol/l}$) | | Total Fe(III) ($\mu\text{mol/l}$) | | Total Zn ($\mu\text{mol/l}$) | |
|-----|-----------------------------|---------------------|-------------------------------|---------------------|-------------------------------------|---------------------|--------------------------------|---------------------|
| | Bulk | Inside ^a | Bulk | Inside ^a | Bulk | Inside ^a | Bulk | Inside ^a |
| 4.1 | 1680 | 276 | 8.3 | 0.80 | 3.4 | 0.90 | 1.25 | 1.00 |
| 4.0 | 5920 | 1245 | 23.4 | 2.95 | 9.8 | 1.70 | 1.15 | 0.85 |
| 7.1 | 1770 | 198 | 8.0 | 0.30 | 3.6 | 0.15 | 1.10 | 0.10 |
| 7.0 | 6040 | 694 | 22.4 | 0.90 | 9.7 | 0.35 | 1.10 | 0.10 |

^aAverage of the five duplicate experiments, for explanation see text.

The final composition of the inside solutions in the main dialysis experiments is provided in Table 1. The amount of DOC that penetrated the membranes ranged from an average of 11.3 % for the experiments at pH = 7.0 to 18.6 % for the

experiments at pH = 4.0. The difference can be explained by the fact that the average size of DOM configurations decreases with decreasing pH, due to curling of the molecules (Conte and Piccolo, 1999). The metal composition of the outside solutions in the main dialysis experiments did not change significantly with respect to metal concentrations, when compared to solutions without a dialysis membrane. This indicates the volume ratio of inside to outside solutions was sufficient to prevent alteration of the association equilibrium between metals and DOM. A small decline in DOC concentrations in the outside solutions was found (< 6.0%), but this did not differ significantly from the decline in solutions without a dialysis membrane except for the 20 mg C/l, pH = 4.0 solution. The decline in DOC concentrations was probably caused by microbial degradation, in spite of the addition of NaN_3 .

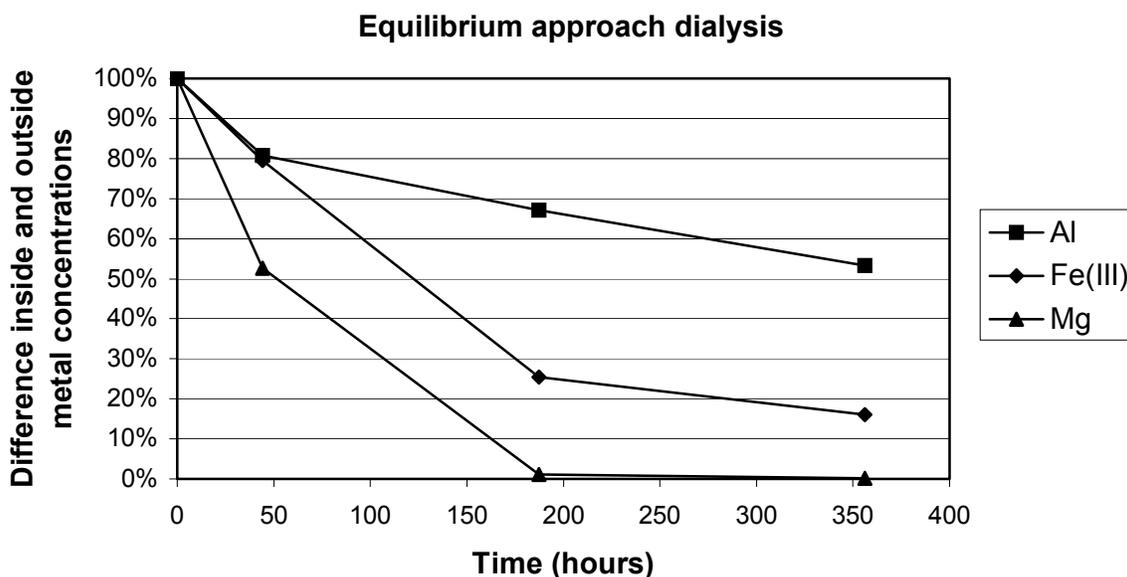


Fig. 1. Approach to equilibrium for dialysis pilot experiment with 20 mg C/l and spiked with 185 μM $\text{Al}(\text{NO}_3)_3$. A difference between metal concentrations of inside and outside solutions at equilibrium represents metal bound by DOM.

2.3.2 DGT experiments

In the pilot experiments the recoveries of Cd, commonly used to test DGT units, were 94% (RSD = 2.0%) at pH = 4.0 and 99% (RSD = 7.0%) at pH = 7.0, indicating that the units were functioning properly. The recoveries in the pilot experiments for Al were 99.7% (RSD = 3.6%) at pH = 4.0 and 80.2% (RSD = 18.6%) at pH = 7.0. This indicates DGT detection of Al at pH = 4.0 worked well. The lower recovery, as well as higher variability for Al at pH = 7.0 can be explained by precipitation of $\text{Al}(\text{OH})_{3(s)}$. Calculations using the speciation code PHREEQC (Parkhurst, 1995) show that as much as 80% of Al may precipitate at pH = 7.0 in a solution without organic ligands. Such precipitation is usually slow and equilibrium will not have been reached in the course of the experiment. Because DOM complexation will dramatically shift the equilibrium away from precipitation by lowering 'free' metal contents, and significant complexation of Al was found in the main experiments, no precipitation of Al was expected in the main experiments.

In the main DGT experiments, the composition of the outside solution did not change significantly with respect to metal content during the experiments. This indicates the metal-DOM ratio in the bulk solution was not altered. The mass percentages of metals found in the gel layer covering the ion exchange resin in all cases were lower than 6.0 % of the total metal mass in solution.

2.3.3 Equilibrium dialysis versus DGT

The percentages of 'free' metal as determined by both equilibrium dialysis and DGT are presented in Table 2 and Figs. 2 through 4. A total of eight experimental situations is presented: situations 1 and 3 represent the results of the equilibrium dialysis experiments at pH = 4.0, for respectively the 20 mg C/l and the 75 mg C/l DOM solutions. Situations 2 and 4 represent the same for DGT. Situations 5 and 7 represent the results for dialysis at pH = 7.0, for respectively the 20 mg C/l and the 75 mg C/l DOM solutions. Situations 6 and 8 represent the same for DGT. For each situation the results of all duplicate experiments are presented. Due to experimental problems (acid contamination), for situation 1 and 7 less than five measurements were available. In addition, systematic outliers were removed from

the Fe(III) and Al data of situation 5 and from the Zn data of situation 6. To allow comparison of the different metals, all figures were scaled to 100 % of 'free' metal.

Table 2

Average 'free' metal percentages and standard deviations of equilibrium dialysis and DGT analyses of the four soil extracts.

| | 20 mg C/l | | 75 mg C/l | | 20 mg C/l | | 75 mg C/l | |
|-----------------------------|-----------|------|-----------|------|-----------|------|-----------|------|
| | pH = 4.0 | | pH = 4.0 | | pH = 7.0 | | pH = 7.0 | |
| | dialysis | DGT | dialysis | DGT | dialysis | DGT | dialysis | DGT |
| Average 'free' ^a | | | | | | | | |
| Al (%) | 10.1 | 13.9 | 12.8 | 11.8 | 2.4 | 3.3 | 4.4 | 3.5 |
| SD (%) | 1.3 | 2.3 | 1.8 | 1.0 | 1.0 | 1.9 | 3.2 | 1.3 |
| Average 'free' ^a | | | | | | | | |
| Fe (%) | 24.3 | 15.6 | 18.3 | 15.1 | 2.4 | 3.5 | 3.8 | 3.0 |
| SD (%) | 1.5 | 3.4 | 1.7 | 5.1 | 1.0 | 2.8 | 2.7 | 1.3 |
| Average 'free' ^a | | | | | | | | |
| Zn (%) | 86.3 | 76.6 | 79.7 | 70.0 | 8.8 | 32.0 | 11.1 | 31.5 |
| SD (%) | 2.9 | 7.9 | 6.2 | 8.7 | 1.1 | 5.1 | 2.0 | 1.5 |

^a'Free' metal consists of hydrated metal cations and soluble inorganic complexes

For all metals the results showed a decrease of the 'free' metal fraction with increasing pH. This is consistent with observations from other studies and can be explained by a higher degree of dissociation of acidic groups at the DOM molecules, involved in metal binding (Martell et al., 1988; Tam and McColl, 1990). Furthermore, the results showed a larger degree of organic complexation of Al and Fe(III) on one hand and a smaller degree of organic complexation of Zn on the other, the difference being most pronounced at low pH values. This is in agreement with the fact that Zn is a weaker binding metal than Al and Fe(III) (Stevenson, 1994). Generally no significant difference in variance between dialysis and DGT was found (Table 2). However, a larger number of measurements may be necessary to draw proper conclusions on the precision of both methods.

Overall the variance of the Al and Fe(III) results were the lowest for both methods, due to their higher concentrations compared to Zn.

The results for Al and Fe(III) from the equilibrium dialysis and DGT experiments (Figs. 2 and 3) were similar for all four DOM solutions. Statistical tests confirmed that there was no significant difference in variance or mean for any situation, except for Fe(III) in the solution at pH = 4.0, containing 20 mg C/l. Here the mean 'free' metal percentage found in the equilibrium dialysis experiments was slightly higher than that obtained by DGT. The absence of differences between 'free' Al measurements at pH = 7.0 indicate that it was indeed precipitation of $\text{Al(OH)}_3(\text{s})$ that caused the underestimation by DGT in the pilot experiments without DOM and that DOM complexation indeed prevented such precipitation.

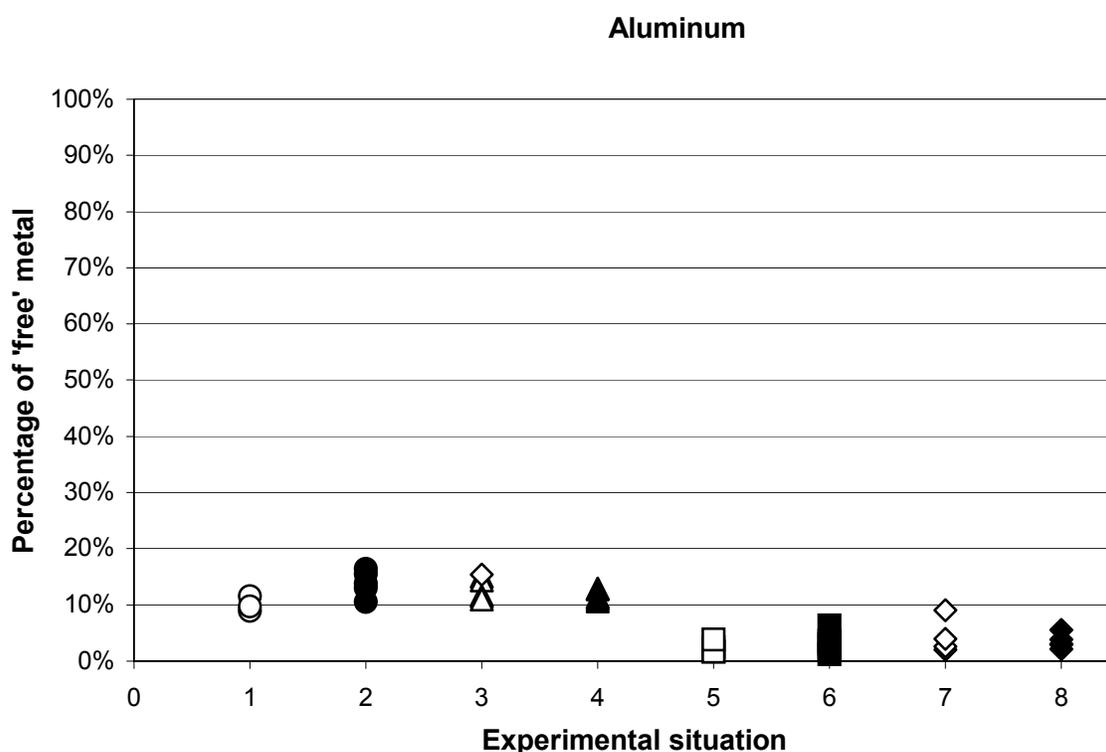


Fig. 2. Percentage of 'free' Al determined by equilibrium dialysis (open symbols) and DGT (closed symbols) for the four DOM solutions, with respect to the initial solution composition. (1 + 2: pH = 4.0, 20 mg C/l; 3 + 4: pH = 4.0, 75 mg C/l; 5 + 6: pH = 7.0, 20 mg C/l; 7 + 8: pH = 7.0, 75 mg C/l).

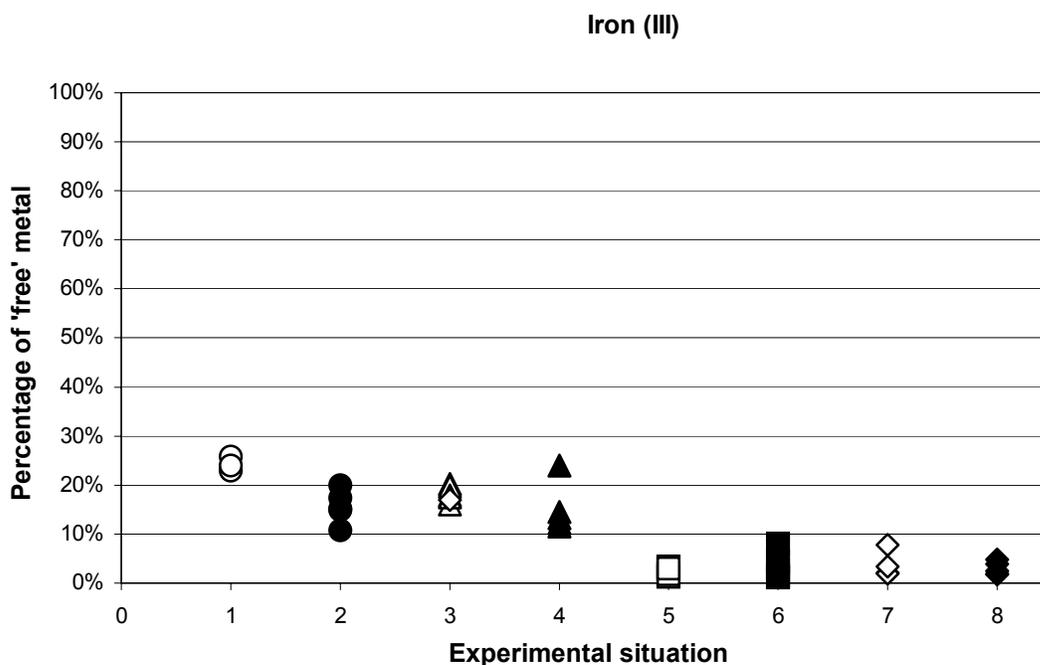


Fig. 3. Percentage of 'free' Fe(III) determined by equilibrium dialysis (open symbols) and DGT (closed symbols) for the four DOM solutions, with respect to the initial solution composition. (1 + 2: pH = 4.0, 20 mg C/l; 3 + 4: pH = 4.0, 75 mg C/l; 5 + 6: pH = 7.0, 20 mg C/l; 7 + 8: pH = 7.0, 75 mg C/l).

Both Al and Fe(III) are believed to form strong, non-labile complexes with DOM. If this is the case, DGT will not detect any organic Al or Fe(III) complexes even if they are small enough to significantly penetrate the hydrogel. However, dialysis will measure any metal-DOM complexes < 1000 Da. Consequently, the differences between dialysis and DGT for Fe(III) at low pH and low DOC concentrations were most likely caused by a slight overestimation by equilibrium dialysis resulting from smaller metal-DOM complexes penetrating the dialysis membrane. As explained earlier, such penetration was found to be most pronounced at pH = 4.0. Research by Tam (Tam, 1987) shows that Al has a preference for association with larger DOM molecules. This explains why contrary to Fe(III), equilibrium dialysis did not overestimate the amount of 'free' Al present in the low DOC solution at pH = 4.0.

At pH = 7.0, calculations using the speciation code PHREEQC indicate that in solutions without DOM, over 90% of both Al and Fe(III) will be present as inorganic complexes. However, in the presence of DOM the actual amount of

inorganic complexes will be much lower because DOM in solution will quite effectively compete with inorganic ligands for the binding of Al and Fe(III). Due to their size, all dissolved inorganic complexes will be part of the ‘free’ metal as detected by dialysis. However, DGT will only measure labile inorganic complexes. Since only little ‘free’ Al and Fe(III) was found by both methods at pH = 7.0 and no significant difference was observed between DGT and equilibrium dialysis, either little inorganic complexation of Al and Fe(III) occurred in the presence of DOM, or all such complexes were labile.

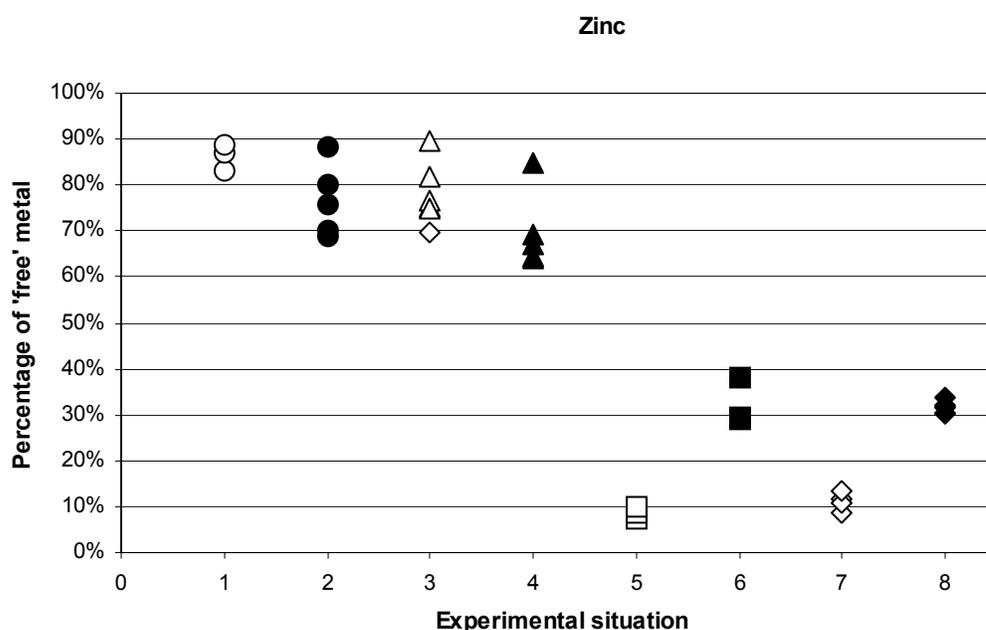


Fig. 4. Percentage of ‘free’ Zn determined by equilibrium dialysis (open symbols) and DGT (closed symbols) for the four DOM solutions, with respect to the initial solution composition. (1 + 2: pH = 4.0, 20 mg C/l; 3 + 4: pH = 4.0, 75 mg C/l; 5 + 6: pH = 7.0, 20 mg C/l; 7 + 8: pH = 7.0, 75 mg C/l).

For Zn (Fig. 4), there was no significant difference between the equilibrium dialysis and DGT results at pH = 4.0, but the variance of the results was relatively large for both methods. This is the result of the very low Zn concentrations present in the initial solutions. As expected, at low pH most of the weaker binding Zn was found to be present in the ‘free’ metal form by both DGT and dialysis.

At pH = 7.0, the average ‘free’ metal percentages from the DGT experiments were higher than those from the equilibrium dialysis experiments. Because Zn is a weaker binding metal than Al and Fe(III), larger portions of the Zn-DOM

complexes will be labile. Therefore, small labile Zn-DOM complexes, still too large to pass the dialysis membrane, will have been measured by DGT and may explain the higher results as compared to equilibrium dialysis. Other studies by Loes and Pennock (Loes and Pennock, 1998), and Wells et al. (Wells et al., 1998) using DOM solutions from a leaf compost and seawater at pH values of 5.5 and 7.0 respectively, reported 'free' Zn percentages ranging from 30 to 55 %. These values in are in the range of those found by us using DGT and would indicate a possible underestimation by dialysis. However, comparison with the data from other studies is difficult because the results strongly depend the detection method and experimental conditions that were used. Further research of the preference of Zn for a certain DOM size fraction and the lability of the complexes formed, is needed to clarify the differences between DGT and dialysis at pH = 7.0.

2.4 Conclusions

No significant differences were found between DGT and equilibrium dialysis (MWCO = 1000 Da) for the detection of Al, Fe(III) and Zn in both the 20 mg C/l and 75 mg C/l soil solutions at pH = 4.0. This shows that DGT is a viable alternative for equilibrium dialysis for the determination of 'free', and therefore bioavailable, Al, Fe(III) and Zn in soil solutions from acidic sandy forest soils. The fact that at pH = 7.0 again no significant differences between equilibrium dialysis and DGT were found for Al and Fe(III), further vindicates both methods for the detection of these two metals. Even though such high pH values do not occur in acidic sandy forest soils, the results are relevant for studies of other soil types.

For Zn the 'free' metal fractions as determined by DGT at pH = 7.0 were significantly higher than those measured by equilibrium dialysis. Due to the weaker binding of Zn, more labile organic complexes are formed than with Al and Fe(III). The observed difference is possibly caused by the detection of such labile complexes larger than 1000 Da by DGT.

In general the results indicate that in the case of strongly binding trivalent metals such as Al and Fe(III), the species measured by DGT and equilibrium

dialysis with a small MWCO are approximately the same under the circumstances tested. For weaker binding divalent (or monovalent) metals such as Zn, the measured species differ because of the detection by DGT of small labile complexes. The choice for either method would then depend on the species one is interested in.

3

Influence of pH and metal/carbon ratios on soluble organic complexation of Fe(II), Fe(III) and Al in soil solutions determined by diffusive gradients in thin films*

Abstract

Soluble complexation of Al, Fe(II) and Fe(III) with dissolved organic matter (DOM) greatly influences the bioavailability and mobility of the metals as well as the DOM itself in acidic forest soils. A scarcity of analytical tools to distinguish between 'free' Al, Fe(II) and Fe(III) and soluble organic complexes in acidic soil solutions, has limited research in this area. We further tested Diffusive Gradients in Thin films (DGT) for this purpose and used it to assess the influence of pH, redox potential and metal/organic carbon (M/C) ratios on soluble organic complexation of Al, Fe(II) and Fe(III). We used water extracts of an organic soil (H) horizon from a Fimic Anthroisol at pH = 3.5, 4.0 and 4.5 to which we sequentially added the three metals. DGT worked well for all but Fe(II) at pH = 3.5 where a correction for proton competition was needed. For all three metals, the 'free' fraction increased with increasing M/C ratios. The order of soluble complexation strength was Fe(III) > Al > Fe(II). At low M/C ratios the 'free' fraction was highest at the lowest pH value due to less deprotonated functional groups, at high M/C ratios increased (organic) precipitation at higher pH reversed this effect. Both reduction of Fe(III) and oxidation of Fe(II) were found. Selective precipitation of Fe(III) complexes led to predominantly soluble Fe(II)-DOM complexes at higher M/C. Therefore, in studies of the mobility and bioavailability of Fe and Al in acidic forest soils, both M/C ratios and Fe(II)/Fe(III) speciation in solution must be determined.

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3.1 Introduction

Dissolved Al and Fe play an important role in many biogeochemical processes that take place in acidic forest soils. For instance, Al and Fe play a crucial role in the acidification and pedogenesis of many soils in the temperate region (McBride, 1994). Furthermore, both Al and Fe can be toxic to soil organisms at higher concentrations, but Fe is an essential element at lower concentrations (Hue et al., 1986; Lucassen et al., 2000).

The presence of dissolved organic matter (DOM) in soil solutions has a large influence on the bioavailability and mobility of Fe and Al in acidic forest soils. Because of their polyvalence, Fe(II), Fe(III) and Al can form very stable complexes with DOM by binding to multiple functional groups on one DOM molecule through coordination bonding, thereby creating stable ring structures (Pohlman and McColl, 1988; Tam and McColl, 1991). The creation of such strong complexes is believed to remove the metals in question from the bioavailable pool and therefore reduce their availability and potential toxicity to soil organisms (Stumm and Morgan, 1996). If *insoluble* metal-DOM complexes are formed, the mobility of the metals in question, as well as the DOM to which they are complexed, obviously decreases. However, if *soluble* complexes are created the influence on the mobility of the metals in question and the DOM to which they are complexed, is not as apparent. On the one hand, the mobility of DOM could increase because the metals in question occupy functional groups that are also involved in the adsorption of DOM to solid soil components (Kaiser et al., 1997). This would also increase the mobility of the metals themselves because their binding to DOM prevents immobilization by precipitation as inorganic metal complexes. On the other hand, the mobility of both metals and DOM through soils could decrease if the soluble metal-DOM complexes bind to solid soil components through cation bridging (Guggenberger and Zech, 1993).

Important soil chemical variables that can influence complexation of Fe and Al to DOM are the pH value and redox potential of soil solutions, and the molar ratio of metal to organic carbon (M/C) in soil solutions (Stevenson, 1994). The soil solution pH determines the number of acidic functional groups on a given DOM

molecule that is deprotonated and available for binding metals (Stevenson, 1994). In addition, the pH value influences the inorganic speciation of Fe and Al, while both the pH and the redox potential determine whether Fe is predominantly present as Fe(II) or Fe(III). The M/C ratio could influence the complexation of Fe and Al to DOM in a number of ways. DOM molecules can contain different groups of metal binding sites, each with their own metal binding affinity (Esteves da Silva et al., 1997; Scott Smitt and Kramer, 1999). At higher M/C ratios the sites with the highest affinity will be filled up and metal binding shifts to sites with lower binding affinities, thereby altering the complexation behavior (Esteves da Silva et al., 1997; Scott Smitt and Kramer, 1999). In addition, given specific pH, redox potential (and ionic solution strength) conditions, the M/C ratio is expected to determine the relative importance of the formation of soluble metal-DOM complexes as compared to the formation of insoluble complexes.

Because of the influence of the complexation of Fe(II), Fe(III) and Al with DOM in forest soil solutions on their mobility and bioavailability in these soils, further investigation of the influence of pH, redox potential and M/C ratio on metal complexation with DOM is necessary. The investigation of strong soluble complexation is of special importance because of the before mentioned potentially ambivalent influence on both DOM and metal mobility in soils. Therefore, in order to understand the mechanisms that govern the mobility and bioavailability of Fe and Al in acidic forest soils, an understanding of the speciation of Fe(II), Fe(III) and Al over free metals and soluble inorganic complexes on the one hand and soluble Fe- and Al-DOM complexes on the other hand is necessary.

Many studies of the solubility of Al and to a lesser extent Fe in acidic sandy soils have been performed in the past (Riise et al., 2000; Van der Salm et al., 2000; Zysset et al., 1999). However, until recently direct measurement of the speciation in solution of Al and Fe over 'free' metal and metal-DOM complexes was difficult. Analytical tools commonly used for metal speciation measurements in solution, such as ion-specific electrodes and anodic stripping voltammetry (ASV), do not exist for Fe and Al or are difficult to use and limited in their applicability (Alfaro-De la Torre et al., 2000; Stevenson, 1994). As an alternative, thermodynamic speciation models could be employed (Alfaro-De la Torre et al.,

2000). However, reliable equilibrium constants for Fe and Al that are needed for such models are scarce (Alfaro-De la Torre et al., 2000).

Recently, the analytical technique of Diffusive Gradients in Thin films (DGT) was developed to distinguish between (hydrated) metal cations and small labile dissolved complexes on the one hand and metal-DOM complexes on the other, primarily in surface waters (Davison and Zhang, 1994). DGT uses a chelating resin to immobilize metal cations and labile (in)organic complexes. Their bulk solution concentrations are subsequently calculated from the mass of metals collected on the resin (Zhang and Davison, 1995). The resin is covered with an ion-permeable hydrogel of defined area and thickness that allows metal cations and small (in)organic complexes to pass at known rates. The diffusion rate of relatively large organic complexes through the commonly used APA hydrogel is slow enough to prevent significant diffusion, but small organic complexes will be able to penetrate the hydrogel to some extent (16% at 2400 Da) (Zhang and Davison, 1999). Therefore, in addition to hydrated metal cations and soluble (labile) inorganic complexes, DGT measures a small portion of the smaller labile organic complexes. In the present study the metal fraction as detected by DGT is called the 'free' metal fraction.

So far the application of DGT has mainly been limited to trace metals such as Cu, Cd and Zn (Denney et al., 1999; Hooda et al., 1999). Furthermore, few tests have been performed at the low pH values commonly found in soil solutions from sandy forest soils in temperate regions (pH = 3.0 - 5.0), where problems due to proton competition at the chelating resin could arise (Zhang and Davison, 1995). Therefore, in a previous study we successfully tested the applicability of DGT for the determination of 'free' Fe and Al in sandy forest soil solutions by comparison to the results obtained by the time consuming method of equilibrium dialysis (Jansen et al., 2001).

The purpose of the present study was to further test DGT and use it to assess the influence of pH and M/C ratios on the speciation of Al, Fe(II) and Fe(III) in acidic forest soil solutions over 'free' metal and soluble metal-DOM complexes. The use of both Fe(II) and Fe(III) allowed us to draw inferences on the influence of the redox potential on the behavior of the redox labile Fe. We used water

extracts of the H horizon of a sandy forest soil, brought to pH = 3.5, 4.0 and 4.5, to represent conditions of soil solutions from acidic sandy forest soils in the temperate zone (Kaiser and Zech, 1998). To these water extracts we added increasing amounts of solutions containing Al, Fe(II) or Fe(III) in nine sequential steps. The added amounts of metal created the M/C ranges in which we expected to find significant soluble complexation of the three metal species. These ranges all fell within the M/C range as observed in lysimeter data from a two-year field monitoring project in the soil from which the H horizon samples for the water extracts were taken (Tietema et al., 1993).

3.3.2 Materials and methods

All chemicals used in the experiments were of analytical grade. To prevent metal contamination, all glassware was acid washed prior to the experiments.

3.2.1 Preparation of the DOM solutions

Soil material was collected from the H horizon ($\text{pH}_{\text{H}_2\text{O}} = 3.8$) of a Fimic Anthrosol (FAO, 1988) at the Buunderkamp location at the Veluwe, the Netherlands, and sieved without prior drying over 2 mm using a polyethylene sieve to avoid metal contamination. Water extracts were prepared by adding 350 g of the homogenized soil material per liter of nano-pure (18.3 M Ω) water, shaking the resulting suspension for 16 hours, centrifuging at 12,000 rpm and filtering the supernatant through a 0.45 μm membrane filter. The DOM solution that was thus obtained, was divided over three aliquots. The pH values of the three aliquots were adjusted to pH = 3.5, pH = 4.0 and pH = 4.5 respectively, by adding small quantities of a 1.0 M HNO₃ solution or a 1.0 M KOH solution.

To all DOM solutions NaN₃ was added to obtain an overall electrolyte concentration of 0.01 M and to prevent microbial degradation of DOM (De Maagd et al., 1998). The pH was readjusted to compensate for the resulting rise in pH. While preventing microbial degradation, the addition of NaN₃ also ensured that the ionic solution strength was high enough to prevent problems with the DGT measurements that may occur at lower ionic solution strengths ($I < 10^{-4}$ M)

(Alfaro-De la Torre et al., 2000). Furthermore, the addition of NaN_3 served to buffer changes in ionic strength that were introduced by the addition of metals during the experiments. This is important because the ionic solution strength is believed to influence metal-DOM complexation (Stevenson, 1994). The initial compositions of the three DOM solutions are presented in Table 1.

Table 1
Initial composition of the DOM solutions at the three different pH values

| pH | DOC (mmol Cl) | Fe(II) (μM) | Fe(III) (μM) | Al (μM) | Ca (μM) | Mg (μM) |
|------|---------------|--------------------------|---------------------------|----------------------|----------------------|----------------------|
| 3.50 | 3.66 | 3.95 | 5.97 | 22.1 | 24.9 | 19.7 |
| 4.00 | 3.62 | 2.70 | 7.40 | 22.4 | 23.9 | 18.9 |
| 4.50 | 3.70 | 2.83 | 7.11 | 21.9 | 24.1 | 19.3 |

3.2.2 Metal addition experiments

For each of the DOM solutions at the three different pH values, three experimental situations were created, representing either Al, Fe(II) or Fe(III) to be added. For each of these three metal species, the addition experiments were carried out in triplicate. Each of the 27 resulting situations was represented by a closeable glass container, filled with 1.0 l of DOM solution. Over the course of the experiments, the containers were kept in an isothermic room at a constant temperature of 20°C. Fe(II), Fe(III) or Al was added to these containers in the form of small amounts of aqueous metal nitrate solutions (metal chloride for Fe(II)), to obtain the theoretical M/C ratios represented in Table 2. We expected the M/C range in which significant soluble concentration occurs to be different for the three species, because of differences in their respective binding strengths (McBride, 1994). Therefore, different concentrations of the different metals were used. To limit dilution, the concentrations of the metal solutions used to add the metals were such that no more than 2 ml needed to be added to a specific container during a specific addition step. After each addition, the pH, redox potential and electric conductivity were determined. If necessary the pH was readjusted to its original value by addition of small volumes of a concentrated KOH solution. After this, the solutions were shaken for 24 hours to obtain

equilibrium with regard to soluble metal-DOM complexation (Yates and Von Wandruszka, 1999). Subsequently, samples were taken, centrifuged at 24,000 rpm and filtrated over 0.45 μm . In the resulting filtrates total metal contents and DOC contents were measured. For the solutions to which Fe(II) or Fe(III) was added, the Fe(II)/Fe(III) ratio was also determined to check for oxidation or reduction of Fe. In all containers ‘free’ metal contents were analyzed by deploying DGT units directly in solution. These same measurements were also performed in samples of the three DOM solutions before the first addition of metals, to determine the initial composition of the DOM solutions.

Table 2

M/C molar ratios in the metal addition experiments under the assumption that no precipitation occurs

| | Addition step | | | | | | | | | |
|----------------------|---------------|-------|-------|-------|-------|-------|-------|------|------|------|
| | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Fe(II) ^a | 0.234 | 0.314 | 0.407 | 0.495 | 1.13 | 2.93 | 3.72 | 7.37 | 18.4 | 117 |
| Fe(III) ^a | 0.234 | 0.243 | 0.254 | 0.264 | 0.371 | 0.675 | 0.809 | 1.40 | 3.21 | 14.3 |
| Al ^a | 0.526 | 0.564 | 0.619 | 0.672 | 1.03 | 2.04 | 2.48 | 4.56 | 10.9 | 69.0 |

^a M/C ratios $\times 100$.

3.2.3 Total metal and DOC analyses

For the detection of total metal contents, a Perkin Elmer Optima 3000XL ICP-OES was used. To dissociate any metal complexes present, before ICP analyses the pH of the samples to be analyzed was adjusted to 1.0 by adding a concentrated HNO₃ solution. The ratio of Fe(II)/Fe(III) in solution was determined by measuring total Fe(II) in solution by colorimetric detection after complexation with 1,10-phenantroline (Begheijn, 1979). In the same sample Fe(II) was determined again, but now after reduction of all Fe(III) in solution of the sample to Fe(II) using hydroquinone (Begheijn, 1979). The total Fe that was thus determined was scaled to the total Fe results obtained by ICP and the separate Fe(II) and Fe(III) results were adjusted accordingly. DOM content was measured as Dissolved Organic Carbon (DOC) by colorimetric determination on a Skalar continuous flow auto-analyzer.

3.2.4 'Free'-metal analyses by DGT

Standard DGT units for metals were obtained from DGT Research Ltd, UK, and assembled according to the procedures described elsewhere (Zhang and Davison, 1995). The units contained a Chelex 100 chelating resin in the Na⁺ form, covered with an APA hydrogel (Zhang and Davison, 1999) and a 0.45 µm membrane filter in order to prevent DOM penetration. Per analysis an assembled DGT unit was suspended in the sample solution, by means of a synthetic wire. The sample solution containing the unit was subsequently shaken for at least 18 hours, after which the DGT unit was removed and disassembled. The Chelex 100 disk was then eluted for at least 24 hours using 1.0 ml of a 1.0 M HNO₃ solution, after which metal contents were determined on the ICP. From these ICP results, 'free' metal contents were calculated.

Before the DGT units were deployed, performance tests were carried out. As recommended by the manufacturer we used Cd(NO₃)₂ for general performance tests. Water solutions containing 10 µM Cd(NO₃)₂ and 0.01 M KNO₃ as a background electrolyte were used for this purpose. The performance of DGT was assessed by calculating the recovery, defined as the calculated 'free' metal concentrations divided by the total metal concentrations as measured in the bulk solutions. A recovery of 100% indicates all metal is present as 'free' metal.

In our previous study, we extensively tested the applicability of DGT for the detection of Fe(III) and Al in acidic forest soil solutions (Jansen et al., 2001). However, we did not test Fe(II) in that study. The lower valence of Fe(II) in the cationic form as compared to Fe(III) will result in a weaker binding of Fe(II) to the chelating resin than Fe(III). Even though no problems with Fe(III) were found, proton competition for binding to the chelating resin could interfere with DGT detection of Fe(II) at lower pH values. In order to test for such adverse effects, extra DGT performance tests were carried out. For this purpose, three identical solutions of 10 µM FeCl₂ in water brought at pH = 3.5, and three identical solutions brought at pH = 4.0 were prepared. In these solutions, the recovery of 'free' Fe(II) was determined using DGT in the same way as with the regular DGT performance experiments.

3.2.5 Calculation of free metal and metal-DOM complexes

The ‘free’ metal mass from the DGT analyses was calculated from the amount of metal determined by ICP in the elution samples of the chelating resin, using the DGT formulas (Zhang and Davison, 1995):

$$M = C_e(V_{\text{HNO}_3} + V_{\text{gel}})/f_e \quad (1)$$

$$C = M\Delta g/(DtA) \quad (2)$$

M represents the metal mass captured on the chelating resin and is calculated from the metal concentration in the elution sample (C_e), the volume of the elution fluid (V_{HNO_3}) and the chelating resin ($V_{\text{gel}} = 1.6 \times 10^{-4}$ l), and an elution factor (f_e) of 0.8 needed to compensate for incomplete metal removal from the resin (Zhang and Davison, 1995). From M, the ‘free’ metal concentration is calculated by taking into account the thickness of the diffusion gel layer ($\Delta g = 0.094$ cm), the diffusion coefficient of the metals in the hydrogel (D), the deployment time ($t = 5.76 \times 10^4$ s) and the area of exposure to the sample solution ($A = 3.14$ cm²). The diffusion coefficients in the APA hydrogel are similar to those in water, but vary slightly depending on the cross-linker used during the manufacturing of the hydrogel (Li and Gregory, 1974; Zhang and Davison, 1999). Accurate diffusion coefficients were supplied by the manufacturer. For the metals of interest at 20°C these are: Al: 4.14×10^{-6} cm²/s; Fe: 5.32×10^{-6} cm²/s and Cd: 5.30×10^{-6} cm²/s (used in the DGT performance tests).

We determined the extent of soluble metal-DOM complexation of the three different metal species in the addition experiments from the ‘free’ metal fraction in solution. This ‘free’ metal fraction was calculated by dividing the ‘free’ metal mass in solution by the total metal mass in solution, consisting of ‘free’ metal + soluble complexed metal. We then plotted the ‘free’ metal fraction as a function of the M/C ratio for the three metal species at the three pH values and compared the results. The M/C ratios were expressed in two ways. M/C_{total} represents total metal in solution versus total initial DOC content. In this ratio disappearance of organic carbon from solution due to precipitation is not compensated for.

Therefore, the relationship between the 'free' metal fraction and the M/C_{total} ratio is the same as the relationship between the 'free' metal fraction and total metal in solution and allows for comparison with other studies. M/C_{soluble} represents total metal in solution versus DOC remaining in solution after each addition step, thereby compensating for removal of organic C from solution by precipitation. M/C_{soluble} , represents the total metal and DOC values as they would be measured for instance in lysimeter data in the field.

3.3 Results and discussion

3.3.1 DGT performance tests

The average recovery for the performance tests using $\text{Cd}(\text{NO}_3)_2$ solutions was 94% (RSD = 2.0%). This is within the $\pm 10\%$ criterion set by the manufacturer, indicating the units were functioning properly.

Calculations using the speciation code PHREEQC (Parkhurst, 1995) show that at pH = 3.5 and pH = 4.0 all Fe(II) will remain dissolved. Therefore, in the absence of DOM all Fe(II) must be in the 'free' form. This means that in the Fe(II) performance tests, a recovery lower than 100% signifies proton competition. The average recovery in the Fe(II) performance tests at pH = 3.5 was 68% (RSD = 2.4%), while the average recovery at pH = 4.0 was 94% (RSD = 5.6%). The lower recovery at pH = 3.5 indicates an underestimation by DGT due to proton competition, while at pH = 4.0 the recovery was within the acceptable range of $\pm 10\%$. Because the variance of the DGT results at pH = 3.5 was low, a correction factor of 1.40 was used in the calculations of the 'free' Fe(II) fraction at pH = 3.5 to compensate for the underestimation. At the higher pH values (≥ 4.0) no correction was necessary.

3.3.2 Metal addition experiments

The 'free' metal fractions as determined after the different addition steps in the metal addition experiments, are provided in Table 3. Due to the high Fe(II) and Al concentrations in solution after the ninth and last addition step, the chelating resins in the DGT units were saturated and therefore did not function properly.

Consequently, the results of this last addition step for Fe(II) and Al were discarded. For addition step 8 for the Al experiments at pH = 3.5 and the Fe(II) experiments at both pH = 4.0 and pH = 4.5, four additional DGT measurements were performed because of an initially high variance in the results. The same was done for addition step 9 at pH = 4.5 for Fe(III). Due to experimental error, the DGT results of the last three steps of the second container in the Fe(II) experiments were discarded.

Table 3

'Free' metal as fraction of total metal in solution after each addition step

| | pH | Step | | | | | | | | | |
|------------------------------|-----|------|------|------|------|------|------|------|------|------|----------------|
| | | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 ^a |
| Al (III) | | | | | | | | | | | |
| 'Free' Al ^b | 3.5 | 0.22 | 0.27 | 0.30 | 0.28 | 0.34 | 0.37 | 0.43 | 0.58 | 0.76 | |
| SD (%) | | 0.2 | 4.9 | 4.4 | 1.2 | 5.4 | 6.2 | 5.2 | 1.4 | 5.7 | |
| 'Free' Al ^b | 4.0 | 0.17 | 0.22 | 0.20 | 0.21 | 0.24 | 0.29 | 0.25 | 0.53 | 0.72 | |
| SD (%) | | 0.8 | 2.6 | 5.0 | 1.6 | 1.8 | 1.3 | 4.0 | 4.4 | 1.6 | |
| 'Free' Al ^b | 4.5 | 0.11 | 0.16 | 0.17 | 0.15 | 0.17 | 0.23 | 0.24 | 0.37 | 0.83 | |
| SD (%) | | 0.7 | 2.1 | 0.8 | 1.6 | 2.5 | 0.7 | 2.2 | 7.3 | 5.3 | |
| Fe(II) | | | | | | | | | | | |
| Total 'free' Fe ^b | 3.5 | 0.19 | 0.28 | 0.31 | 0.30 | 0.43 | 0.26 | 0.30 | 0.30 | 0.25 | |
| SD (%) | | 1.1 | 2.7 | 1.1 | 4.8 | 1.6 | 8.1 | 5.6 | 0.6 | 5.5 | |
| Total 'free' Fe ^b | 4.0 | 0.12 | 0.19 | 0.25 | 0.26 | 0.37 | 0.57 | 0.64 | 0.52 | 0.49 | |
| SD (%) | | 1.1 | 2.8 | 4.4 | 4.2 | 4.9 | 4.8 | 4.1 | 3.8 | 10.0 | |
| Total 'free' Fe ^b | 4.5 | 0.06 | 0.12 | 0.11 | 0.14 | 0.25 | 0.48 | 0.51 | 0.55 | 0.59 | |
| SD (%) | | 0.2 | 4.5 | 3.9 | 0.4 | 10.9 | 3.4 | 6.9 | 7.2 | 18.8 | |
| Fe(III) | | | | | | | | | | | |
| Total 'free' Fe ^b | 3.5 | 0.19 | 0.23 | 0.27 | 0.24 | 0.29 | 0.29 | 0.30 | 0.33 | 0.40 | 0.56 |
| SD (%) | | 1.1 | 3.4 | 2.2 | 0.9 | 7.9 | 1.2 | 3.9 | 5.1 | 2.0 | 7.1 |
| Total 'free' Fe ^b | 4.0 | 0.12 | 0.19 | 0.24 | 0.18 | 0.25 | 0.32 | 0.24 | 0.31 | 0.38 | 0.55 |
| SD (%) | | 1.1 | 2.9 | 0.8 | 0.4 | 1.3 | 2.4 | 2.8 | 4.9 | 6.6 | 1.8 |
| Total 'free' Fe ^b | 4.5 | 0.06 | 0.11 | 0.11 | 0.11 | 0.13 | 0.20 | 0.17 | 0.23 | 0.29 | 0.43 |
| SD (%) | | 0.2 | 2.6 | 3.7 | 0.7 | 2.3 | 2.1 | 3.3 | 2.5 | 2.9 | 7.0 |

^a Due to saturation of Chelex disks no fractions were determined for step 9 for Fe(II) and Al(III).

^b 'Free' metal comprises soluble inorganic complexes and hydrated metal cations.

3.3.2.1 Soluble Al-DOM complexation at different pH values

In Fig. 1, the 'free' Al fraction in solution is plotted against M/C_{soluble} . Initially, when DOM molecules and binding sites were available in excess, the 'free' Al fraction in solution was small and at all three pH values, the majority of soluble Al was complexed by DOM. At pH = 3.5 the fraction of initial 'free' Al was the highest, while at pH = 4.5 the fraction of initial 'free' Al was the lowest. These differences are caused by the fact that at lower pH values, less acidic functional groups on the DOM molecules were deprotonated and available for metal binding, as was expected (Stevenson, 1994). The difference between the 'free' Al fractions in the initial DOM solutions at the three pH values was a constant factor of 1.5. As the amount of added metal and thereby the M/C_{soluble} increased during the experiments, the fractions of 'free' Al increased as well, again according to expectations (Stevenson, 1994).

As can be seen in Fig. 1, at higher M/C_{soluble} ratios, increasing differences in the M/C_{soluble} values (position on the x-axis) occurred between the three pH values. Also, where at lower M/C_{soluble} ratios the fraction of soluble complexed Al was highest for pH = 4.5, the differences between the three pH values decreased with increasing M/C_{soluble} and even *reversed* order at the highest M/C_{soluble} ratio. Most likely at higher M/C_{soluble} ratios the deprotonated functional groups were more and more filled up with Al and additional Al was forced to bind to functional groups that were still protonated, deprotonating them in the process. This would have decreased the differences between the three pH values. The change in soluble complexing behavior at higher M/C_{soluble} ratios was further caused by the increasing contribution of insoluble complexation of Al and DOM at higher M/C ratios. Precipitation of insoluble Al-DOM complexes occurred to a higher degree at higher pH values. This left less DOM in solution to form soluble complexes with Al, and counteracted the effects of higher availability of deprotonated acidic functional groups at higher pH values. Also, the DOM that remained in solution may have been less susceptible or even wholly unsusceptible to Al complexation as some studies indicate that a fraction of DOM in soil solutions does not complex at all with metals (Vilg -Ritter et al., 1999). When the rest of the DOM

precipitates, the relative impact of such a soluble, non-complexing DOM fraction would increase, lowering soluble complexation at the higher pH values even more.

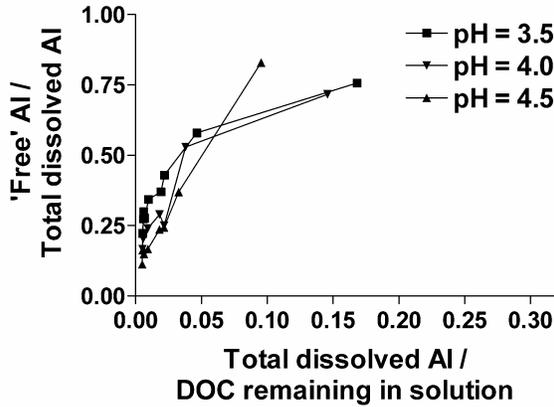


Fig.1. Fraction of 'free' Al versus the ratio of total soluble Al/total organic carbon in solution (M/C_{soluble}). For S.D. see Table 3.

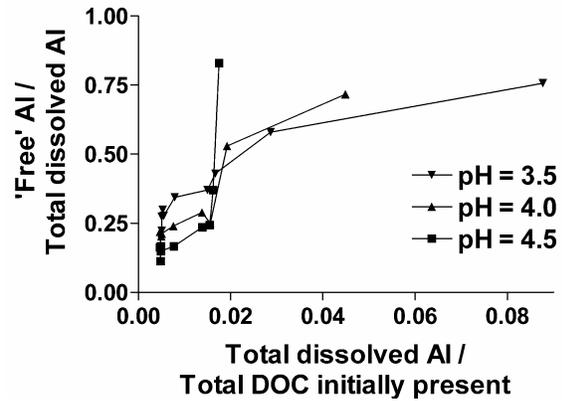


Fig. 2: Fraction of 'free' Al versus the ratio of total soluble Al/total organic carbon that was initially present in solution (M/C_{total}). For S.D. see Table 3.

The influence of organic precipitation on soluble complexation of Al with DOM at higher M/C ratios, can be seen even better in Fig. 2 where the relationship between the 'free' Al fraction and the M/C_{total} ratio is presented. In this figure the reversal of the pH effect with increasing metal contents is very clear. Overall the results for Al show that even over the small pH interval of 3.5 – 4.5, the pH value has a profound effect on soluble complexation of Al in acidic forest soil solutions. Furthermore, it underlines the importance of determining the M/C_{soluble} ratio in the field, since this determines the nature of the pH effect on soluble complexation.

Comparison of our results with those from other studies is difficult, due to differences in detection methods, pH ranges, origin and concentration of DOM and Al concentration ranges used. However, general trends can be compared. Powell and Hawke (1995) found increases in 'free' Al with increasing pH at low Al concentrations in acidic forest soil solutions from New Zealand, as did Browne and Driscoll (1993) who used Suwannee river Fulvic Acid. In both cases Al concentrations were too low to observe the reversal effect, but the results agree with our findings at lower $M/C_{\text{(soluble and total)}}$ ratios. Gerke (1994) calculated stability constants of Al-DOM complexes in soil solutions at pH = 4.0 and 4.5.

When comparing the trend in the values of these constant, there are some signs of the pH-reversal effect at higher M/C_{total} ratios that was also found by us.

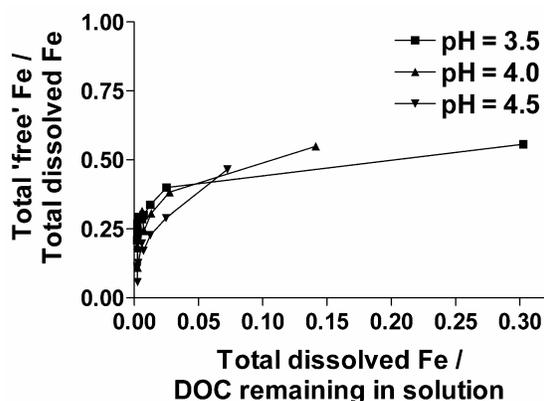


Fig. 3. Fraction of total 'free' Fe in the Fe(III) addition experiments versus the ratio of total soluble Fe / total organic carbon in solution (M/C_{soluble}). For S.D. see Table 3.

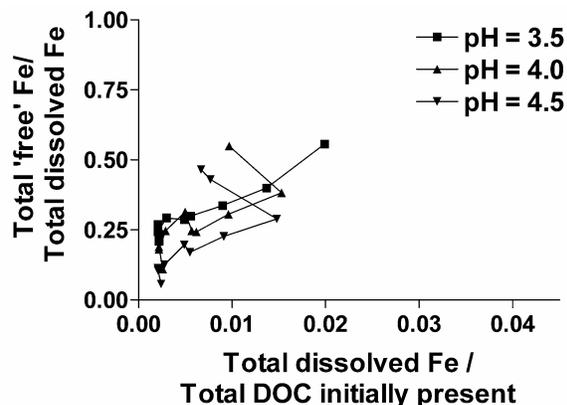


Fig. 4: Fraction of total 'free' Fe in the Fe(III) addition experiments versus the ratio of total soluble Fe / total organic carbon that was initially present in solution (M/C_{total}). For S.D. see Table 3.

3.3.2.2 Soluble Fe(III)-DOM complexation at different pH values

In Fig. 3, the 'free' Fe(III) fraction is plotted against M/C_{soluble} . The overall complexation behavior of Fe(III) was similar to that of Al. Again initially the fraction of bound metal was the lowest at $\text{pH} = 3.5$ (81%) and increased with increasing pH as expected (Stevenson, 1994). Also the 'free' metal fraction increased with increasing M/C_{soluble} in the course of the experiments and a reversal of order between the three pH values was again observed. The fact that the initial as well as the final 'free' Fe(III) fraction was lower than for Al at the same M/C_{soluble} ratio, indicates that Fe(III) has a stronger tendency for soluble complexation with DOM than Al. This is further emphasized by the fact that even at high M/C_{soluble} ratios approximately 50% of the soluble Fe(III) was bound to DOM and that such high M/C_{soluble} ratios were reached even though we added four times as little Fe(III) compared to Al. This also means that metal-DOM precipitation had a greater influence on soluble complexation behavior of Fe(III) than of Al. It is even more strikingly shown in Fig. 4, where 'free' Fe(III) is plotted against M/C_{total} . For both $\text{pH} = 4.0$ and $\text{pH} = 4.5$, the graphs show a sharp bend after the eighth addition step and the total metal concentration in solution

decreased as more metal was added. Apparently more and more 'free' Fe(III) species were complexed to a 'single' DOM molecule, until the addition of one single 'free' Fe(III) species caused the DOM molecule with all the other Fe(III) species already bound to it to precipitate from the solution.

In absence of DOM the solubility of Fe(III) is lower than in the presence of DOM, due to solution equilibria with highly insoluble inorganic Fe(III) salts. For example, calculations using PHREEQC (Parkhurst, 1995) show that even at pH values as low as 4.0 and [Fe(III)] as low as 100 μM , 52% of the Fe(III) in solution will precipitate as amorphous $\text{Fe}(\text{OH})_3$ in the absence of DOM. This means that on the one hand the presence of DOM enhances the solubility of Fe(III), but on the other hand concentrations of Fe(III) that are too high, counteract this effect by causing precipitation of both Fe(III) and DOM, resulting in an optimum dissolved Fe(III) concentration at a certain $\text{M}/\text{C}_{\text{total}}$ ratio.

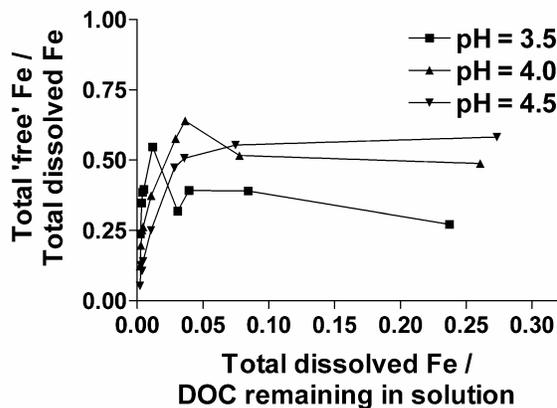


Fig. 5. Fraction of total 'free' Fe in the Fe(II) addition experiments versus the ratio of total soluble Fe/Total organic carbon in solution ($\text{M}/\text{C}_{\text{soluble}}$). For S.D. see Table 3.

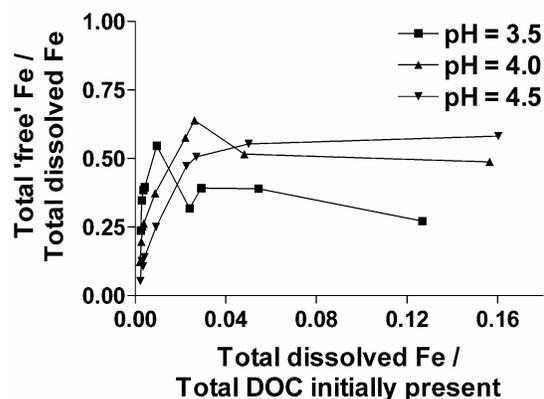


Fig. 6. Fraction of total 'free' Fe in the Fe(II) addition experiments versus the ratio of total soluble Fe/total organic carbon that was initially present in solution ($\text{M}/\text{C}_{\text{total}}$). For S.D. see Table 3.

In addition to pH effects, with Fe(III) possible reduction to Fe(II) must be taken into account. Several studies found that DOM is able to catalyze both reduction of Fe(III) in solution to Fe(II) and oxidation of Fe(II) to Fe(III) (Clarke and Danielsson, 1995; Stumm and Morgan, 1970). In addition, NO_3^- and O_2 present in solution could cause oxidation of Fe(II). All Fe(III) in the addition solution remained Fe(III) throughout the experiments, indicating that any Fe(II)

found during the experiments was the result of reduction of the Fe(III) after addition, plus the Fe(II) that was initially present in solution. Initially 60%, 73% and 72% of Fe in solution was present as Fe(III) at pH = 3.5, pH = 4.0 and pH = 4.5 respectively. These amounts fluctuated slightly over the course of the experiment, but remained relatively constant ($\pm 10\%$). After the sixth addition step and the onset of (significant) precipitation, a slight decline in Fe(III) content relative to Fe(II) content was observed for the experiments at pH = 4.0 and pH = 4.5. This decline was the strongest at pH = 4.5, where the most precipitation occurred. Since the Fe(II)/Fe(III) ratio that was determined applies to total Fe *in solution*, the higher percentage of Fe(II) at higher pH values was most likely caused by preferential precipitation of Fe(III)-DOM complexes. Judging from this and the observed strong binding and precipitation behavior, we believe the Fe bound in the soluble Fe-DOM complexes was initially predominantly Fe(III) but that the relative contribution of soluble Fe(II)-DOM complexes increased with increasing M/C ratios, due to the preferential precipitation of Fe(III)-DOM complexes. This shows that DOM indeed quite effectively reduced Fe(III) to Fe(II) in spite of the presence of O₂ and NO₃⁻ (Clarke and Danielsson, 1995; Stumm and Morgan, 1970).

Some other studies also report data of 'free' versus organically complexed Fe (Riise et al., 2000; Van Hees and Lundström, 2000). However, these are usually field studies where M/C_{soluble} and pH were not varied independently and no distinction between Fe(II) and Fe(III) was made. In a laboratory study, Hermann and Gerke used pyrophosphate extractions to differentiate between 'free' Fe and Fe-DOM complexes. They used low M/C ratios and found increasing soluble complexation of Fe(III) with DOM at higher pH values, with 'free' Fe(III) percentages roughly equal to the ones found by us (Hermann and Gerke, 1992). Furthermore, similar to our results they found soluble Fe(III)-DOM complexes to be dominant over soluble Fe(II)-DOM complexes at pH > 3.5 (Hermann and Gerke, 1992). In another study, Gerke (1997) also found significant soluble complexation of Fe(III) with DOM that increased with increasing pH.

3.3.2.3 Soluble Fe(II)-DOM complexation at different pH values

As explained earlier a correction factor of 1.40 was used in calculations of the results at pH = 3.5. However, since this correction factor only applies to the detection of Fe(II), it was only used to correct the fraction of Fe that was in the form of Fe(II) at a given addition step. Unfortunately, the results from the Fe(II)/Fe(III) partitioning analyses do not differentiate between 'free' Fe and soluble Fe-DOM complexes. Because of the preferential binding of Fe(III) to DOM, the fraction of Fe(II) in soluble Fe-DOM complexes and 'free' Fe that is in the Fe(II) form might not be the same. This would make the correction inaccurate. Therefore, in spite of the correction, the results for Fe(II) at pH = 3.5 must be interpreted with caution.

Fig. 5 represents the results of the 'free' Fe(II) fraction plotted against M/C_{soluble} . The initial 'free' Fe(II) fraction before addition of metals was of course the same as for the experiments in which Fe(III) was added. When compared to Fe(III) and Al, at first the rise of the 'free' Fe(II) fraction is steeper and starts to level off later. This is an indication of a lower binding affinity of Fe(II) for DOM than Fe(III) and Al, as would be expected from its lower valency. After 4 or 5 addition steps, depending on pH, the curves level off and even drop somewhat for pH = 3.5 and 4.0. Finally, for both pH = 4.0 and pH = 4.5 the final 'free' fraction approaches that of Fe(III). Again the reversal of order of soluble complexation at different pH values at higher M/C_{soluble} ratios was observed

Fig. 6 presents the 'free' Fe(II) fraction plotted against M/C_{total} . In contrast to the results for Al and especially Fe(III), the graph is essentially the same as the M/C_{soluble} graph. Since eight times more Fe(II) was added in the Fe(II) addition experiments than Fe(III) in the Fe(III) addition experiments, it is clear that precipitation had much less influence on the complexation behavior and the solubility of Fe(II) than on Fe(III). It also indicates that the Fe bound in soluble complexes was predominantly Fe(II), since Fe(III)-DOM complexes would have precipitated at higher Fe concentrations. The fact that at the higher M/C_{soluble} ratios the 'free' metal fractions in both the Fe(II) and Fe(III) experiments were approximately the same at pH = 4.0 and 4.5, supports our earlier observation that

the contribution of Fe(II)-DOM complexes in the Fe(III) addition experiments increases with increasing M/C ratios.

Our observations are confirmed by the results from the Fe(II)/Fe(III) speciation during the Fe(II) addition experiments. Tests showed that the Fe in the Fe(II) addition solutions remained in the Fe(II) form. Therefore, any Fe(III) that was found during the experiments was the result of oxidation of Fe(II) plus the initial Fe(III) that was present in the DOM solutions. The absolute Fe(II) concentrations showed a steady increase over the course of the experiments. The Fe(III) concentrations also showed an initial increase, indicating oxidation of Fe(II) to Fe(III). However, after the seventh addition of Fe(II) at pH = 3.5 and the sixth additions at pH = 4.0 and pH = 4.5, the absolute Fe(III) concentrations started to decrease, indicating preferential binding of Fe(III) and subsequent precipitation of Fe(III)-DOM complexes. This is further supported by an increase of the percentage of total Fe(II) in solution after the fourth addition step. Where initially 40%, 27% and 28% of total dissolved Fe was Fe(II) for respectively pH = 3.5, 4.0 and 4.5, these figures changed to 82%, 74% and 72% respectively after the eighth addition step. Overall these results indicate that where DOM-mediated reduction of Fe(III) occurred in the Fe(III) addition experiments, the opposite took place in the Fe(II) experiments.

3.3.3 Competition between Al and Fe

Although only one metal was added at a time in the metal addition experiments, initially all three species, Al, Fe(II) and Fe(III), were present in the DOM solutions used in the experiments (table 1). During the addition experiments of Al, the changes in 'free' metal concentrations of Fe(II) and Fe(III) with increasing M/C ratios were also determined and vice versa. Since no distinction between 'free' Fe(II) and 'free' Fe(III) can be made using the DGT method, these were considered together as total 'free' Fe. When looking at the total amount of Al or Fe in solution in experiments where the other metal was added, in all cases we observed a moderate decline (approx. 20%) of the total mass in solution of the metal that was not added. Most likely this metal co-precipitated with insoluble metal-DOM complexes of the metal that was added.

For Fe in the experiments where Al was added, the total 'free' Fe percentage showed no significant increase for pH = 3.5, but we observed significant increases for pH = 4.0 and pH = 4.5 from respectively 12% and 6% to 33% and 78% total 'free' Fe. For Al in the experiments where Fe(II) was added, a moderate increase in 'free' Al was observed at all three pH values starting with 22%, 17% and 11% at respectively pH = 3.5, pH = 4.0 and pH = 4.5 to reach final percentages of 44%, 53% and 36%. Finally, for Al in the experiments where Fe(III) was added, strong increases in the 'free' Al percentages were observed, from 22%, 17% and 11% 'free' Al to 77%, 80% and 83% for respectively pH = 3.5, pH = 4.0 and pH = 4.5. These observations show that there is a competition between the three species for at least some of the same binding sites at DOM molecules. Also they indicate the following order of binding strength for soluble complexation with DOM: Fe(III) > Al > Fe(II), which is in agreement with the tendency for soluble complexation we found in the metal addition experiments of the metals themselves. Few other studies have compared the relative tendency for soluble complexation between Fe(III) and Al. Stevenson states that the binding affinity of both for DOM is roughly the same (Stevenson, 1994). However, another study found that Fe(III) has a higher affinity for complexation with DOM than Al, which agrees with our results (Gerke, 1997).

3.4 Conclusions

The development of DGT has lead to powerful tool that can be successfully applied to measure 'free' Al, Fe(II) and Fe(III) in acidic sandy soil solutions and allow inferences on the soluble metal-DOM complexing behavior of the three species to be drawn. However, DGT underestimates 'free' Fe(II) at pH < 4.0 due to proton competition for Fe(II) binding on the chelating resin.

As expected, at lower M/C_{soluble} ratios Al, Fe(II) and Fe(III) in solution were predominantly present as soluble metal-DOM complexes while at higher M/C_{soluble} ratios the 'free' metal fraction increased. In agreement with other studies, at lower M/C_{soluble} ratios for all three metal species the 'free' metal fraction is the lowest at the highest pH value. However, at higher M/C_{soluble} ratios

this order reverses and there the 'free' metal fraction is the lowest at the lowest pH value. These results imply that even over such a small pH range of 3.5 – 4.5, soil solution pH greatly influences soluble complexation of Al, Fe(II) and Fe(III) to DOM and the M/C ratio in solution determines the type of influence. This means that when studying the influence of pH on the presence of Al, Fe(II) and Fe(III) in acidic soil solutions, it is crucial to take into account the M/C ratios in solution.

The differences between the soluble complexation behavior of Fe(II) and Fe(III) show that the redox potential of the soil solution has a profound influence on the soluble complexation of Fe. Due to the preferential binding of Fe(III) and limited solubility of Fe(III)-DOM complexes, both mobility and bioavailability of Fe(III) are expected to be lower than that of Fe(II). Furthermore, due to this preferential binding and precipitation, soluble Fe-DOM complexes at lower M/C_{soluble} ratios will have an important Fe(III) content while at higher M/C_{soluble} ratios the importance of Fe(II) complexes increases. Therefore, in studies of Fe in acidic soil solutions it is essential to determine the solution speciation between Fe(II) and Fe(III).

The observed pH and valency effects, can have far reaching implications for the mobility and bioavailability of Al, Fe(II) and Fe(III) in soils. However, to get a complete picture of the complexation behavior of Al, Fe(II) and Fe(III) in acidic forest soils, a combination of the insight gained in the present study with detailed studies of the effects and types of insoluble complexation with DOM is necessary. In addition, direct complexation of metals or charged metal-DOM complexes to solid soil components must be taken into account to fully understand and predict the implications of metal-DOM complexation on mobility and bioavailability of Al and Fe in acidic forest soils.

4

Organic complexation of Al and Fe in acidic soil solutions: A comparison of DGT analyses with Model V and VI predictions*

Abstract

The last decade has seen important development of analytical and modeling tools to investigate the interactions in solution between metals and dissolved organic matter. We evaluated the internal consistency of the analytical method of diffusive gradients in thin films (DGT) and the speciation models Model V and Model VI for investigating organic complexation of Al and Fe in acidic sandy soil solutions. For this purpose we used our dataset obtained by DGT of the speciation of Al and Fe(III) between dissolved inorganic metal and soluble metal-DOM complexes in acidic soil solutions at pH = 3.5, 4.0 and 4.5 and different imposed metal/organic carbon (M/C) ratios in solution. We modeled this dataset with Model V and VI, using the default parameter values but optimizing the fraction of DOM that is inert with respect to metal binding (24%). The calculated speciation of Al by both Model V and VI was generally in good agreement with the DGT results. However, at low Al/C ratios the Al fraction measured by DGT was higher than the dissolved inorganic fraction calculated by the models, most likely due to the detection of small (<1000 Da), labile Al-DOM complexes by DGT. This discrepancy did not occur with Fe(III) probably because its complexes with DOM are not labile enough to be detected by DGT. The dissolved, inorganic Fe fractions calculated by Model V were in good agreement with the DGT results, especially considering the fact that extra uncertainty was introduced by the analytically determined Fe(II)/Fe(III) speciation in solution. Model VI calculated the trends in Fe binding well, but generally estimated a higher dissolved, inorganic Fe fraction than Model V and DGT. The Fe(III) binding constant in Model VI was recently modified to reflect stronger binding to DOM. Since both Model V and VI predicted the inorganic Fe in solution to consist mainly of Fe(II), we propose a similar critical evaluation of the Fe(II) binding constant in Model VI.

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4.1 Introduction

The complexation of Al and Fe with dissolved organic matter (DOM) in soil solutions is of great scientific interest because of its influence on the mobility of both metals through the soil column, which in turn affects such processes as pedogenesis and acidification (McBride, 1994). In addition, organic complexation of Al may alleviate toxicity for plants and soil organisms (Ma et al., 2001).

Interactions of Al and Fe with DOM are of special relevance for acidic, sandy soils where relatively high metal concentrations have been reported (Aran et al., 2001; Buurman, 1984; Petersen, 1976). The impetus for further research on Al- and Fe-DOM interactions in this type of system is given amongst others by the continued scientific debate about the mechanisms involved in podzolization. For instance, there is no consensus about the mechanisms responsible for the transport and accumulation at depth of Al, Fe and DOM in sandy soils (Farmer and Lumsdon, 2001; Gustafsson et al., 2001; Lundström et al., 2000; Mossin et al., 2002).

Because of the importance of metal-DOM interactions, a number of new analytical chemical techniques has been developed over the last decade (Tipping, 2002). Contemporary methods used for this purpose include equilibrium dialysis (Jansen et al., 2001), the quickly reaction Al method (Clarke and Danielsson, 1995) and the donnan-membrane technique (Temminghoff et al., 2000). Disadvantages of these methods include the amount of time needed per analysis in the donnan-membrane technique and equilibrium dialysis (≥ 48 hours), and the impossibility to apply the quickly reacting Al method and to speciate Fe simultaneously. A promising alternative is the analytical method diffusive gradients in thin films (DGT), which can be used for simultaneous speciation of Al and Fe overnight (Jansen et al., 2001). DGT is based on the principle of diffusion of hydrated metal cations, as well as dissolved inorganic complexes and small, labile, organic complexes through a diffusion gel of known thickness, followed by immobilization on an chelating resin. The resin is subsequently removed and the metals are extracted by acid and detected (Zhang and Davison, 1995).

In addition to the development of analytical tools, considerable progress has been made with respect to the mathematical modeling of metal speciation in soils and water (Tipping, 2002). This has resulted amongst others in the development of Model V, which was recently succeeded by Model VI (Tipping, 1994; Tipping, 1998). Models V and VI are deterministic models, capable of predicting metal binding to organic matter taking into account multidentate binding, as well as site heterogeneity (Tipping, 1994; Tipping, 1998).

Both DGT and Models V and VI have been successfully used in several studies of the interactions of Al, Fe and DOM in acidic soil solutions (De Wit et al., 2001; Jansen et al., 2002; Jansen et al., 2003b; Lofts et al., 2001). However, so far little work has been done to compare analytical Al and Fe speciation data obtained using DGT with predictions by Model V and VI. Such an approach would allow for testing of the internal consistency of both methods and be helpful to further investigate their strengths and weaknesses. Ultimately this may lead to more insight in the interactions of Al, Fe and DOM.

The goal of this study was to evaluate the internal consistency of a combination of DGT and the speciation models Model V and VI for investigating organic complexation of Al and Fe in acidic sandy soil solutions and to gain more insight into the mechanisms involved in such complexation. We accomplished this by comparing Model V and VI calculations of the dissolved, inorganic Al and Fe fractions with DGT data obtained using soil extracts from the Oh horizon of a podzolic soil.

4.2 Materials and methods

4.2.1. Metal-DOM addition experiments

The dataset used in this study was obtained in a previous study and is described in detail elsewhere (Jansen et al., 2002). In short, we used a water extraction of the Oh horizon of a Fimic Anthrosol (FAO, 1988) to obtain a DOM solution. We divided this over three aliquots that we brought to pH = 3.5, pH = 4.0 and pH = 4.5, respectively. To each of these we added increasing amounts of $\text{Al}(\text{NO}_3)_3$ or $\text{Fe}(\text{NO}_3)_3$ stock solutions to obtain different metal to carbon (M/C)

ratios, adjusting the pH after each addition to keep it constant during the experiments. In order to prevent microbial degradation of the DOM and to maintain a constant background ionic strength during the experiments, we added sodium azide (NaN_3) to obtain a final concentration of 0.01 M. The resulting relatively high ionic strength also prevented potential problems with DGT that have been reported to occur at very low solution ionic strengths (Alfaro-De la Torre et al., 2000). After each metal addition and subsequent pH adjustment, the solutions were shaken for 24 hours to allow for equilibrium to be reached (Yates and Von Wandruszka, 1999) after which they were sampled. In the samples, total concentrations of Ca^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Al^{3+} , Zn^{2+} , Cu^{2+} , P and S were determined on a Perkin-Elmer Optima 3000XL ICP-OES. In addition, total concentrations of DOC were determined on a Skalar continuous flow automated analyzer and the Fe(II)/Fe(III) speciation was determined using 1,10-phenantroline in a colorimetric procedure (Begheijn, 1979). After sampling, DGT units were deployed in solution for 16 hours and the DGT concentrations of Al and total Fe (FeT) were determined. The experiments were conducted in triplicate.

4.2.2 DGT

DGT can be used for speciation of dissolved metals in both water and soils at the μM level or below (Zhang and Davison, 1995; Zhang et al., 1998). Metal concentrations (C) as estimated by DGT, are calculated using equations 1 and 2:

$$M = C_e(V_{\text{HNO}_3} + V_{\text{gel}})/fe \quad (1)$$

$$C = M\Delta g/(DtA) \quad (2)$$

M, the metal mass captured on the chelating resin, is calculated from the metal concentration in the elution sample (C_e), the volume of the elution fluid (V_{HNO_3}) and the volume of the chelating resin (V_{gel}). In addition, an elution factor (fe) of 0.8 is needed to compensate for incomplete metal removal from the resin (Zhang and Davison, 1995). From M, the DGT metal concentration is calculated by taking into account the thickness of the diffusion gel layer (Δg), the diffusion coefficient

of the metals in the hydrogel (D), the deployment time (t) and the area of exposure to the sample solution (A).

In principle, a variety of hydrogels can be used in DGT analyses. We used the common APA hydrogel supplied by the manufacturer of DGT (DGT Research Ltd, UK). The diffusion coefficients in the APA hydrogel are similar to those in water, but vary slightly depending on the cross-linker used during the manufacturing of the hydrogel (Li and Gregory, 1974; Zhang and Davison, 1999). Accurate diffusion coefficients were supplied by the manufacturer.

The diffusion rate of larger organic complexes through the APA hydrogel is slow enough to appreciably limit diffusion, but small metal-DOM complexes are able to penetrate the hydrogel (Zhang and Davison, 1999). Small organic complexes that are labile enough for the metal ion to be liberated from the organic ligand and bind to the chelating resin, will be included in the DGT metal fraction. Therefore, in addition to hydrated metal cations and soluble (labile) inorganic metal complexes, DGT in combination with the APA hydrogel measures a portion of the smaller labile organic complexes. However, because DGT concentrations are calculated based on free metal diffusion coefficients, the concentrations of labile complexes measured by DGT will increasingly be underestimated with increasing molecular size and thus decreasing diffusion rates through the APA hydrogel (Zhang and Davison, 2000). Previously, we compared the results obtained with DGT in acidic forest soil solutions to those obtained with equilibrium dialysis using a membrane with a 1000 Da molecular weight cut-off (Jansen et al., 2001). We found no significant differences between the two methods in the measured dissolved inorganic Al and Fe(III) concentrations, indicating that the detection of Al/Fe-DOM complexes as dissolved inorganic metal by DGT, if happening at all, is limited to those complexes smaller than approximately 1000 Da. Nevertheless, the incomplete distinction between actual dissolved inorganic metals and small metal-DOM complexes represents a drawback of the DGT method for this application. Recently, a more restricted hydrogel was developed to resolve this problem (Zhang and Davison, 1999). However, even with this gel the separation cannot be perfect because complexes smaller than 1 nM are still able to diffuse through the gel at high enough rates to

reach the chelating resin and be detected as dissolved inorganic metal if labile enough (Zhang and Davison, 1999). Another disadvantage of DGT for laboratory studies is the relatively large minimum volume of sample solution needed (approximately 500 ml) as the bulk dissolved inorganic metal concentrations must remain large compared to the amount of metals immobilized on the chelating resin.

4.2.3 Model V and VI

Model V and VI are described and compared in detail elsewhere (Tipping, 1994; Tipping, 1998). Therefore, we only give a short highlight of the main features. Model V and VI are discrete site/electrostatic models of the interactions of protons, metals and their first hydrolysis products with fulvic and humic acids. Both models have been incorporated in a water and soil version called WHAM-W and WHAM-S respectively (Tipping, 2002). The water version consists of Model V or VI, combined with a full inorganic speciation model. In addition, the soil version includes a surface complexation model (Tipping, 2002). Since our experiments were carried out in solution, we used the WHAM-W versions of Model V and VI to model our data.

Both Model V and VI contain a maximum of six adjustable parameters. In our model applications we used published default parameter values, previously obtained by model fitting to several datasets (Tipping, 1998). In a recent study, Tipping et al. (Tipping et al., 2002) showed that new Al and Fe(III) data in freshwaters can be modeled adequately using Model VI and default model parameters, only optimizing the percentage of dissolved organic carbon (DOC) that actively partakes in metal binding.

There is a number of differences between Model V and VI. In both models proton dissociation is represented by 8 groups of different acid strengths. In Model V, the strength of binding of a metal to the different acidic groups is positively correlated to that for protons, whereas this is no longer the case in Model VI. Another difference is that Model VI takes into account a small number of high affinity sites, normally expected to be filled up in natural samples but thought to be important for the binding of trace metals (Tipping, 1998). Finally,

Model VI allows for a percentage of the binding sites to be involved in tridentate binding, in addition to permitting monodentate and bidentate binding. Model V allows for monodentate and bidentate binding only (Tipping, 1998). As a result of the differences, the metal binding constants are defined in a different way in Model VI than in Model V.

The main advantage of Models V and VI in addition to being two of the very few comprehensive metal-organic matter binding models, is the fact that they are discrete site models and it is reasonable to assume that the parameters in the model represent real physical entities (Tipping, 2002).

4.2.4 Modeling and data analysis

As input for the models we used the measured total concentrations in solution, both initially and after each metal addition, of Ca^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Al^{3+} , Zn^{2+} and Cu^{2+} . For Cl^- , PO_4^{3-} , Na^+ and NH_4^+ we used the initial concentrations in all cases, since the concentrations of these solutes were not determined during the experiments, as significant changes in their concentrations over the course of the experiments were not expected. Because N_3^- is not included as an input species in Model V and VI, we replaced it with an equal concentration of NO_3^- as we expected similar binding behavior to metals and organic matter for these two monovalent nitrogen anions. Similar to Na^+ we used the initial concentrations for N_3^- for all data points. The concentration of K^+ was not determined over the course of the experiments. However, since K^+ will only bind weakly to DOM as compared to Al and Fe and was presumably present in much lower concentrations than Na^+ , we did not include K^+ in our model calculations as we did not expect a significant influence of its presence on the speciation of Al and Fe. The concentrations of SO_4^{2-} were based on the concentrations of total S as determined by ICP-OES. Probably this resulted in a slight overestimation, as some of the total S is represented by dissolved organic sulphur. However, sensitivity analyses showed that even a decrease of the SO_4^{2-} input concentrations by two orders of magnitude does not have a significant effect on the model output. All DOM was assumed to be present in the form of Fulvic Acid (FA). This variable, which has to be given in g/l of FA, was calculated using the DOC concentrations over the

course of the experiments and assuming 50% of the weight of FA to represent organic carbon (Tipping, 2002). In both Model V and VI we used the default parameter values provided with the model, except for the binding constant for Fe(III) to FA in Model VI where we used the optimized value derived in a recent study by Tipping et al. (2002) ($\log K_{MA} = 2.6$).

We calculated the DGT Al and Fe fraction by dividing the measured DGT metal mass in solution by the total molar metal mass in solution. Similarly, we calculated the modeled dissolved inorganic Al and Fe fraction from the inorganic metal concentrations calculated by Model V and Model VI. Since DGT cannot distinguish between Fe(II) and Fe(III), we only determined the DGT total Fe (FeT) fraction. However, we did use the measured total Fe(II) and Fe(III) concentrations as input variables in Model V and VI and calculated the dissolved inorganic FeT fraction as the sum of the modeled dissolved inorganic Fe(II) and Fe(III) fractions. This allowed the models to take into account differences in binding strength between Fe(II) and Fe(III).

We compared the DGT metal fractions with the dissolved inorganic metal fractions calculated by both models using both correlation and linear regression analyses of the entire dataset for Al and Fe. As the number of observations was greater than 30 in all cases, we assumed that the observations were normally distributed and therefore used parametric statistical tests. We used a confidence interval of 0.05.

Previous modeling studies using Model V and VI (Lofts et al., 2001; Tipping et al., 2002) suggest that a considerable fraction of the DOC in surface waters and soil solutions consists of inert material with respect to metal binding. Therefore, we optimized the model data by changing the percentage of inert DOC to obtain a maximum r^2 value for both the correlations and regression.

4.3 Results and discussion

In Table 1 we presented the total concentrations of DOC, Al, Fe(II) and Fe(III) in solution over the course of the experiments. For further details we refer to Jansen et al. (2002).

Table 1

Average total concentrations of Al, Fe(II), Fe(III) and DOC over the course of the Al and Fe addition experiments (metals in $\mu\text{mol/l}$, DOC in $\mu\text{mol C/l}$)

| pH | | Step | | | | | | | | |
|-----|---------|------|------|------|------|------|------|-------|-------|----------------|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 ^a |
| Al | | | | | | | | | | |
| 3.5 | Al | 20.1 | 21.6 | 23.3 | 35.1 | 69.6 | 80.9 | 145.8 | 325.3 | |
| | DOC | 3340 | 3549 | 3403 | 3356 | 3419 | 3508 | 3042 | 2357 | |
| 4.0 | Al | 19.7 | 21.5 | 23.1 | 35.7 | 67.7 | 79.9 | 103.0 | 251.3 | |
| | DOC | 3729 | 3711 | 3602 | 3651 | 3500 | 3565 | 2620 | 1723 | |
| 4.5 | Al | 19.7 | 21.2 | 23.1 | 36.0 | 68.2 | 79.5 | 86.6 | 98.1 | |
| | DOC | 3656 | 3699 | 3666 | 3612 | 3530 | 3574 | 2543 | 997 | |
| Fe | | | | | | | | | | |
| 3.5 | Fe(II) | 4.2 | 4.8 | 4.5 | 5.5 | 9.6 | 11.7 | 16.6 | 32.6 | 0.0 |
| | Fe(III) | 4.8 | 4.0 | 4.4 | 6.3 | 10.0 | 14.1 | 22.7 | 30.6 | 98.7 |
| | DOC | 3486 | 3618 | 3547 | 3571 | 3581 | 3597 | 3552 | 2880 | 378 |
| 4.0 | Fe(II) | 3.6 | 3.5 | 3.3 | 3.7 | 14.8 | 7.7 | 14.9 | 39.1 | 0.0 |
| | Fe(III) | 4.8 | 5.3 | 5.9 | 8.9 | 7.9 | 19.1 | 32.3 | 39.9 | 50.8 |
| | DOC | 3448 | 3632 | 3594 | 3461 | 3422 | 3484 | 3465 | 2873 | 380 |
| 4.5 | Fe(II) | 2.6 | 2.1 | 2.6 | 3.3 | 8.9 | 5.6 | 17.2 | 42.0 | 0.0 |
| | Fe(III) | 5.6 | 6.5 | 6.3 | 9.1 | 13.3 | 20.8 | 28.1 | 35.5 | 36.6 |
| | DOC | 3528 | 3744 | 3720 | 3641 | 3528 | 3490 | 3532 | 3135 | 505 |

^a Not performed due to problems with DGT (Jansen et al., 2002).

4.3.1 Modeling 'free' Al

In Fig. 1 we plotted DGT Al as a fraction of total Al in solution against the Al/DOC ratio in solution. In addition, the non-optimized and optimized model results obtained by Model V and VI are provided. The best fit of the data for Al alone was obtained by assuming 21% of the DOM to be inert. However, when the Fe data was considered simultaneously, an overall optimization for both metals was obtained assuming 24% of the DOM to be inert. This value is of the same order of magnitude as the 30% inert DOM reported by Tipping et al. in their study of Al and Fe(III) binding to DOM in freshwaters (Tipping et al., 2002). The regression lines corresponding with the non-optimized and optimized model V

and model VI runs are presented in Fig. 2. The r^2 values for both the linear regression and correlation are provided in Table 2.

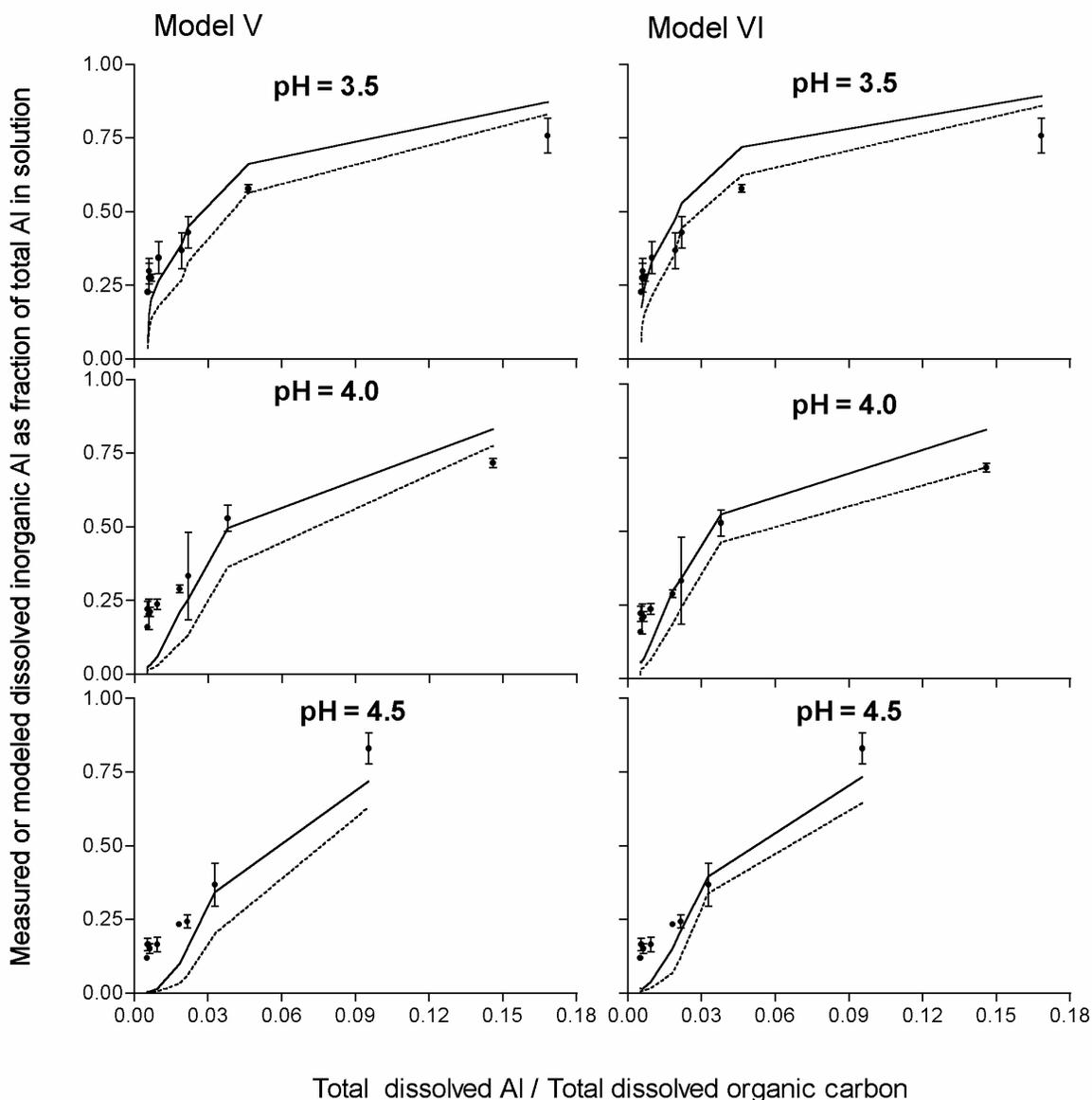


Fig. 1. Comparison of the optimized (solid line) and non-optimized (dotted line) dissolved inorganic Al fraction calculated by Model V and VI with the fraction measured by DGT (dots). The non-optimized simulations were based on the assumption that all DOC is active FA. The optimized predictions were obtained when assuming that 24% of the DOM is inert with respect to metal binding. The fractions were calculated on a mol/mol basis.

It is clear from Fig. 1 that both Model V and VI are able to fit the DGT data reasonably well. Overall the predicted values by Model VI are somewhat higher than those by Model V, but the differences are only small. Recall that one of the main differences between Model V and VI is the presence of a small number of

sites with high binding affinity. The affinity of Al^{3+} for these sites is modified in the model by the distribution term ΔLK_2 , which is only small for Al (Tipping, 1998). Therefore, the similarities between the two models are in line with expectations.

Table 2

r^2 values for the linear regression and correlation between the DGT data and the Model V and VI results for Al and Fe.

| | Model V Al | Model VI Al | Model V Fe | Model VI Fe |
|---------------------------------|------------|-------------|------------|-------------|
| r^2 correlation non-optimized | 0.9088 | 0.9267 | 0.8059 | 0.8650 |
| r^2 correlation optimized | 0.9288 | 0.9127 | 0.8258 | 0.8764 |
| r^2 regression non-optimized | 0.9034 | 0.9157 | 0.7987 | 0.8631 |
| r^2 regression optimized | 0.9247 | 0.9089 | 0.8207 | 0.8744 |

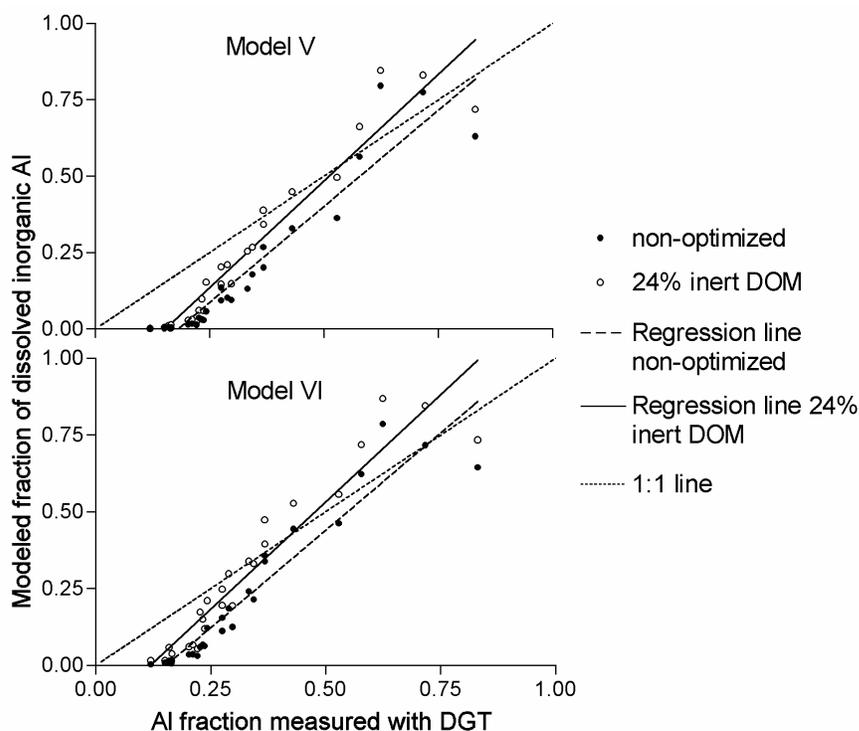


Fig. 2. Regression lines plotting the dissolved inorganic Al fraction calculated by Model V and Model VI against the Al fraction measured with DGT, using the non-optimized and the optimized models.

Even though the r^2 values in Table 2 are indicative of a strong correlation between the Model predictions and DGT measurements, the regression lines

shown in Fig. 2 clearly deviate from the ideal 1:1 line, in slope as well as in absolute values. This is caused by a systematically lower predicted 'free' Al fraction at lower Al/C ratios than found by DGT. A plausible explanation for the discrepancy is an overestimation by DGT caused by the earlier mentioned penetration of small Al-DOM complexes through the diffusion gel and their subsequent detection as 'free' Al. Such complexes would have to be very small (< 1000 Da) (Jansen et al., 2001). Therefore, even if their functional group density is higher than on larger molecules, due to their limited size it is not unreasonable to expect their absolute number of functional groups to be relatively small. Consequently, they would be amongst the first to become saturated with Al and precipitate out of solution. As a consequence, at higher Al/C ratios in solution where precipitation of Al-DOM complexes starts to play a role, the overestimation of 'free' Al by DGT if caused by detection of very small Al-DOM complexes should diminish. The Al/C ratio that marks the onset of precipitation of Al-DOM complexes is approximately 0.03 (Nierop et al., 2002), which corresponds well with the point where the overestimation of DGT vanishes (Fig. 1). Another explanation for the overestimation of 'free' Al by DGT could be a shift in the complexation equilibrium towards decomplexation of Al from soluble complexes as a result of Al being removed from solution and immobilized in the DGT units. However, due to the relatively large solution volume used (750 ml) and the relatively short deployment time of the DGT units, this is unlikely.

4.3.2 Modeling 'free' Fe

DGT Fe as a fraction of total Fe in solution, as well as the model results obtained by non-optimized and optimized Model V and VI runs are presented in Fig. 3. For reasons of clarity separate graphs of the first few points were also plotted in Fig. 4. The best fit of the data for Fe alone could be obtained by assuming 30% of the DOM to be inert. However, again when both the Fe and Al data were considered an overall optimal fit for both metals was obtained by assuming 24% of the DOM to be inert. The regression lines corresponding with the non-optimized and optimized runs with model V and VI are presented in

Fig. 5. The r^2 values for both the linear regression and correlation are again provided in Table 2.

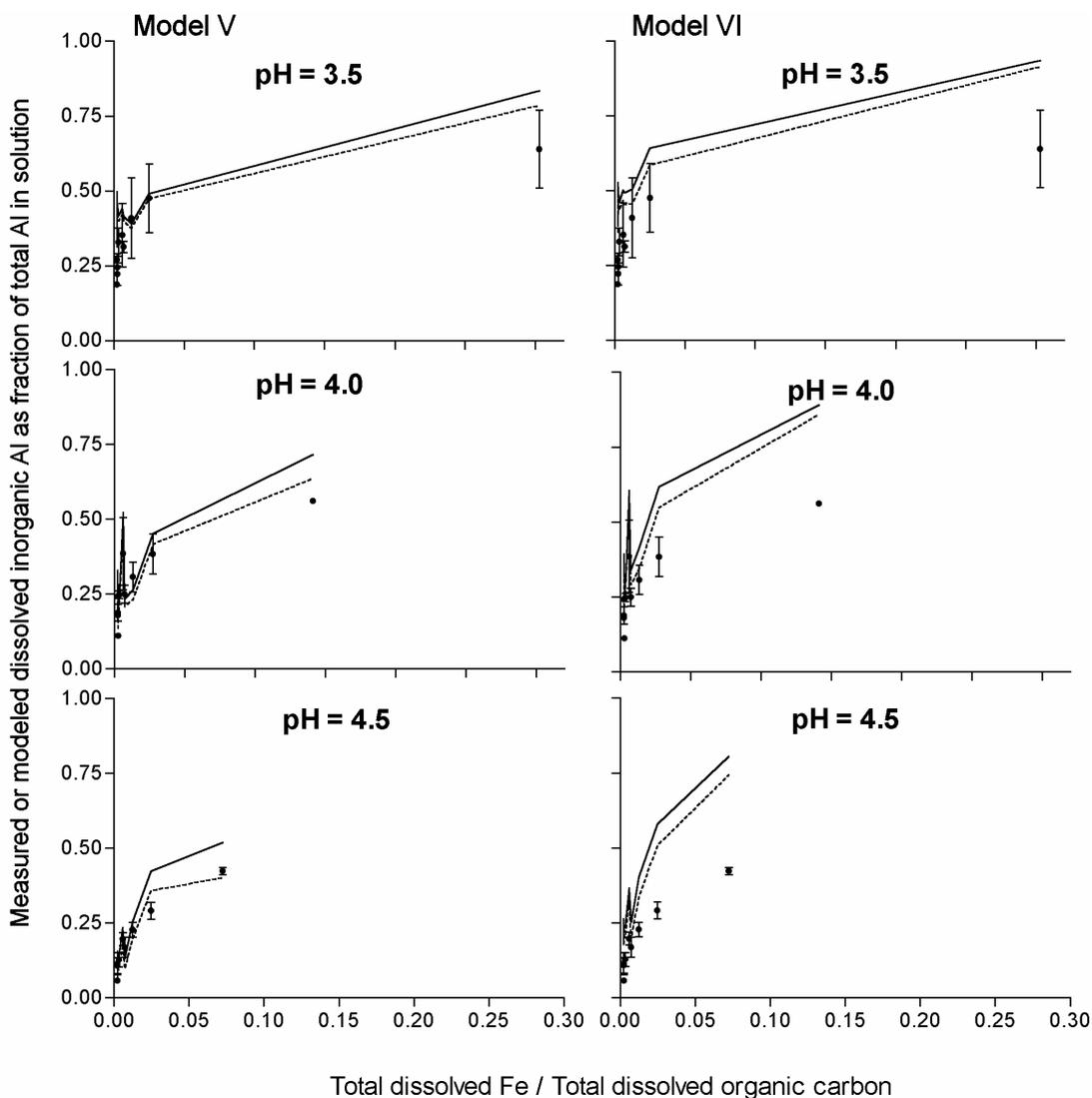


Fig. 3. Comparison of the optimized (solid line) and non-optimized (dotted line) dissolved inorganic Fe fraction calculated by Model V and VI with the fraction measured by DGT (dots). The non-optimized simulations were based on the assumption that all DOC is active FA. The optimized predictions were obtained when assuming that 24% of the DOM is inert with respect to metal binding. The fractions were calculated on a mol/mol basis.

The r^2 values for the regression and correlation using Model V and VI are lower for FeT than for Al. Yet they are remarkably high when one considers the fact that the modeled dissolved inorganic FeT fractions were based upon the sum of Fe(II) and Fe(III) binding. This introduces more uncertainty in the modeling results, as

two binding constants with their inherent uncertainty need to be used instead of one in the case of Al. In addition, the experimental speciation of Fe into total Fe(II) and Fe(III) concentrations, which are used as input for the model, introduces extra uncertainty in the model calculations. Both Model V and VI predict the majority of the Fe bound in DOM complexes to be present in the form of Fe(III) while Fe(II) dominates in the dissolved inorganic Fe fraction. This is in good agreement with the fact that in a previous study we found extensive complexation with DOM in experiments where Fe(III) was added, but only moderate complexation in experiments where Fe(II) was added (Jansen et al., 2002).

Table 3

Predicted 'free' Fe(II) and Fe(III) as fraction of total Fe(II) or Fe(III) in solution by Model V and VI for the optimal fit (24% inert DOM).

| Step: | Model V | | | | | | Model VI | | | | | |
|-------|----------|---------|----------|---------|----------|---------|----------|---------|----------|---------|----------|---------|
| | pH = 3.5 | | pH = 4.0 | | pH = 4.5 | | pH = 3.5 | | pH = 4.0 | | pH = 4.5 | |
| | Fe(II) | Fe(III) |
| 0 | 0.86 | 0.000 | 0.64 | 0.000 | 0.36 | 0.000 | 0.92 | 0.04 | 0.85 | 0.03 | 0.73 | 0.02 |
| 1 | 0.91 | 0.001 | 0.77 | 0.000 | 0.50 | 0.000 | 0.94 | 0.04 | 0.93 | 0.03 | 0.91 | 0.03 |
| 2 | 0.91 | 0.001 | 0.74 | 0.000 | 0.48 | 0.000 | 0.94 | 0.03 | 0.92 | 0.03 | 0.90 | 0.02 |
| 3 | 0.91 | 0.001 | 0.76 | 0.000 | 0.49 | 0.000 | 0.94 | 0.03 | 0.92 | 0.03 | 0.91 | 0.03 |
| 4 | 0.91 | 0.001 | 0.77 | 0.000 | 0.49 | 0.000 | 0.94 | 0.05 | 0.93 | 0.05 | 0.92 | 0.05 |
| 5 | 0.90 | 0.001 | 0.80 | 0.000 | 0.59 | 0.000 | 0.94 | 0.08 | 0.93 | 0.06 | 0.92 | 0.06 |
| 6 | 0.92 | 0.001 | 0.81 | 0.001 | 0.61 | 0.000 | 0.95 | 0.12 | 0.94 | 0.11 | 0.93 | 0.11 |
| 7 | 0.92 | 0.002 | 0.83 | 0.001 | 0.67 | 0.001 | 0.96 | 0.18 | 0.95 | 0.17 | 0.94 | 0.19 |
| 8 | 0.95 | 0.005 | 0.91 | 0.006 | 0.78 | 0.002 | 0.97 | 0.30 | 0.96 | 0.28 | 0.96 | 0.30 |
| 9 | 0.00 | 0.835 | 0.00 | 0.716 | 0.00 | 0.519 | 0.00 | 0.93 | 0.00 | 0.92 | 0.00 | 0.91 |

The calculated regression lines are presented in Fig. 5. For both Model V and VI the slopes of the regression lines are very close to that of the 1:1 line. This suggests that contrary to Al there is no systematic difference between the DGT Fe fraction and the modeled dissolved inorganic Fe fraction in a specific Fe/C range. Fe(III) binds much stronger to DOM than Al, as evidenced amongst others by the very limited influence of proton competition on the binding to DOM even at pH values as low as 3.5 (Jansen et al., 2002). In all likelihood, contrary to Al,

complexes of Fe^{3+} with DOM are not labile enough for significant dissociation to occur in the DGT diffusion gel layer.

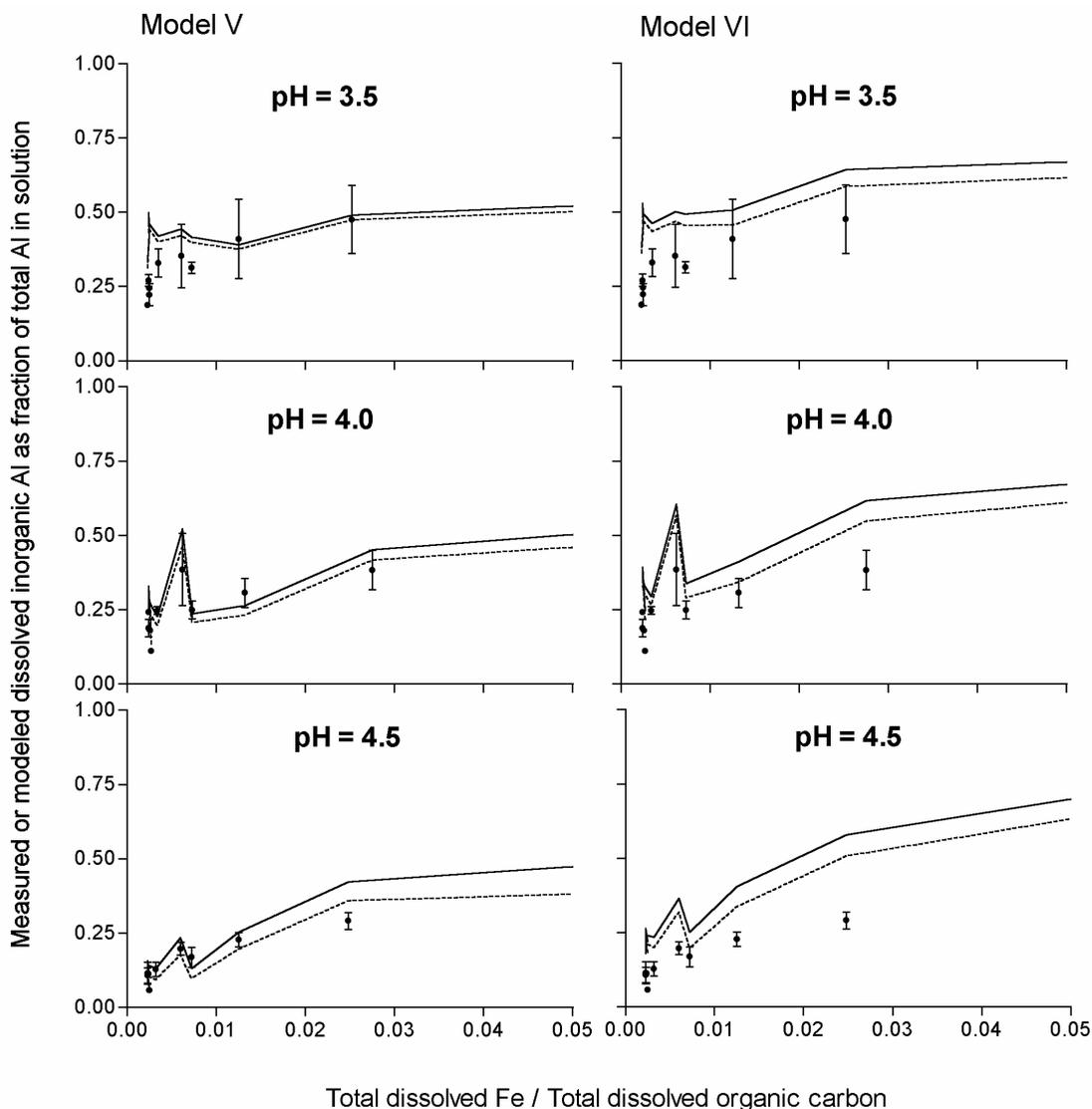


Fig. 4. A detailed representation of a comparison of the optimized (solid line) and non-optimized (dotted line) dissolved inorganic Fe fraction calculated by Model V and VI with the fraction measured by DGT (dots). The non-optimized simulations were based on the assumption that all DOC is active FA. The optimized predictions were obtained when assuming that 24% of the DOM is inert with respect to metal binding. The fractions were calculated on a mol/mol basis.

In their study of the binding of Al and Fe(III) to DOM, Tipping et al. (Tipping et al., 2002) conclude that in the pH range of 4 – 9, Fe(III) will predominantly be bound as FeOH^{2+} . Model V and VI allow for binding of the first hydrolysis products of metals, using the same metal-DOM binding constants as for the free

metal cations (Tipping, 1998; Tipping et al., 1995). Therefore, Model V and VI will predict the same degree of complexation for Fe(III), regardless of whether it be bound in the form of Fe^{3+} or FeOH^{2+} . However, due to the lower net charge per molecule, we expect FeOH^{2+} to form complexes with DOM that are more labile than those of Fe^{3+} . Accordingly, if Fe(III) were predominantly bound to DOM in the form of FeOH^{2+} , analogous to Al one would expect a higher measured Fe fraction by DGT at lower Fe/C ratios than predicted by the models. Consequently, the lack of a systematic difference at a particular range of Fe/C ratios between the DGT Fe fraction and dissolved inorganic Fe fraction calculated by Model V and VI, leads us to believe that whereas Fe(III) not bound to DOM may have been predominantly present in solution in the form of FeOH^{2+} , Fe(III) bound to DOM occurred mostly in the form of Fe^{3+} .

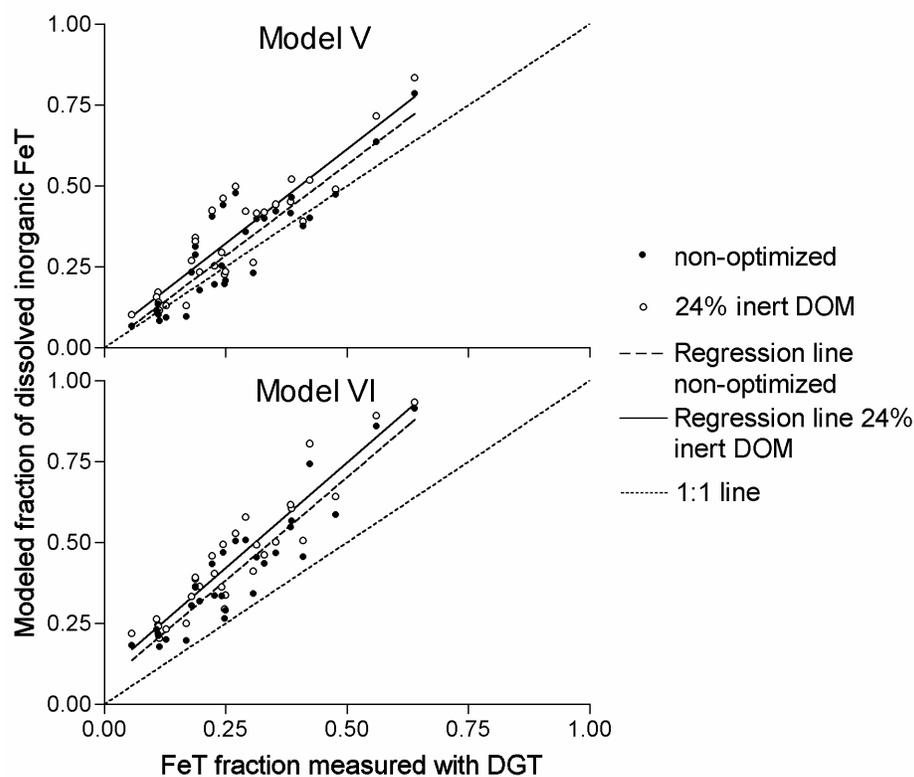


Fig. 5. Regression lines plotting the dissolved inorganic Fe fraction calculated by Model V and Model VI against the Fe fraction measured with DGT, using the non-optimized and the optimized models.

In addition, the lack of a systematic differences between DGT and Model V and VI at a particular range of Fe/C ratios, further strengthens our believe that the differences between the DGT Al fraction and calculated 'free' Al by Model V and VI at lower Al/C ratios was not caused by modeling uncertainty or a shift in the complexation equilibrium due to the removal of Al from solution by the DGT units. If that were the case, one would expect similar differences between the measured and modeled Fe fraction at lower Fe/C ratios.

While the slopes of the regression lines for both the Model V and VI predictions were very close the 1:1 line (Fig. 5), in the entire range of Fe/C ratios examined in the experiments, the dissolved inorganic FeT fraction computed by Model VI was significantly greater than the fraction measured by DGT. Surprisingly, we observed no such discrepancy between the Model V calculations and the DGT results.

As stated earlier, due to the differences in calculating metal binding to DOM, Model V and VI use different binding constants for metal binding to DOM. Because both Model V and VI calculations suggest that the majority of Fe(III) is bound to DOM (Table 3), the difference between the calculated 'free' FeT fractions are for a large part the result of differences in the binding constants of Fe²⁺ between the two models. In addition, even with the modified Fe(III) binding constant according to Tipping et al. (2002) the modeled binding of Fe(III) to DOM by Model VI was lower than that by Model V. This further increased the differences in the results between both models. Contrary to Fe(III) the default binding constant of Fe(II) in Model VI has not yet undergone a critical evaluation. More extensive experiments using DGT may be useful for this purpose.

Despite the systematic discrepancy between the dissolved inorganic FeT fraction calculated by Model VI and the FeT fraction calculated by Model V and measured by DGT, it is promising that the trends in the organic FeT speciation are predicted so well. An example of the close correspondence of trends predicted by both models and DGT measurements, is the peak in the measured and modeled FeT fraction after the third metal addition in the cases of pH = 4.0 and 4.5 (Fig. 4). At the point of the peak, there was a higher fraction of total Fe in solution (both inorganic Fe and Fe-DOM complexes) present as Fe(II) than in the

preceding and following points (Jansen et al., 2002). The causes for this temporary shift in the total Fe(II)/Fe(III) ratio in solution are unclear. A possible cause is contamination of the Fe(III) stock solution used for the addition of Fe in this particular point with Fe(II). The same stock solution was used for all three replicates, explaining the occurrence of the peak in all replicates. Subsequent metal additions were done using a different stock solution. The addition of higher concentrations of a fresh, non-contaminated Fe(III) stock solution, explains the disappearance of the peak in the following points. Since Fe(II) binds more weakly to DOM than Fe(III), it is not surprising to find a higher 'free' FeT fraction in the point where the peak occurred (Jansen et al., 2002). Because DGT only measures FeT, the fact that the trend of the peak in the dissolved inorganic FeT was calculated well by both Model V and VI, indicates that it was not experimental error in the Fe(II)/Fe(III) determinations that caused it.

The fact that a combination of DGT with Model V and VI can predict the trends so well, seems to make it well suited to further examine Fe(II)/Fe(III) - DOM interactions in soil solutions. It would be even better if Model V or VI were capable of calculating redox equilibria, as this would make analytical determination of the Fe(II)/Fe(III) speciation unnecessary.

In a recent study Gimpel et al. (2003) compared DGT analyses of Fe in lakewater with predictions by Model V, using default model parameters and assuming 20% of the DOM to be inert to metal binding. Generally, they found reasonable agreement between the model calculations and the DGT results, but could not exactly reproduce them. They suggest that the binding constant for Fe³⁺ to FA in Model V may be too high. This is in apparent contradiction with the good agreement between DGT results and Model V predictions found by us while using the default binding constant for Fe³⁺. However, instead of the acidic soil solutions considered here, Gimpel et al. (2003) studied lake water that in all but one case was at circumneutral pH. Furthermore, they did not analytically determine the speciation between Fe(II) and Fe(III) but assumed either all Fe to be present as Fe(II) or Fe(III). This makes direct comparison of our results difficult. Possibly, the discrepancy is caused by the increased influence of inorganic Fe(III) species and their binding to DOM at higher pH and lower DOC concentrations.

4.4 Conclusions

In this paper dissolved inorganic Al and Fe fraction in solutions from an acidic sandy soil, as calculated with Model V and VI, were compared with analytical observations obtained with DGT. Both approaches have their merits and drawbacks and we found that a comparison helped shed light on the strengths and weaknesses of either approach for the study of the speciation of Al and Fe in acidic soil solutions.

This study suggest that the Al fraction measured by DGT with the conventional APA hydrogel is somewhat higher than the true dissolved inorganic Al fraction due to the detection of small (<1000 Da) labile Al-DOM complexes. This effect will be strongest in systems where Al concentrations are low and concentrations of DOM are high, so that a relatively large fraction of Al is organically bound. Binding of Fe(III) to DOM is considerably stronger than that of Al and it appears that Fe(III)-DOM complexes are not labile enough to be detected by DGT. Consequently, DGT seems to give good estimates of dissolved, inorganic Fe in solution, even at low Fe(III) concentrations and high DOM concentrations.

While in general the trends of metal binding to DOM as measured by DGT and calculated by Model V and VI agree surprisingly well, the systematically higher calculated dissolved inorganic Fe(II) fraction by Model VI warrants further investigation.

Finally, a welcome improvement of Model VI would be the inclusion of the redox equilibrium between Fe(II) and Fe(III), which would make it unnecessary to determine the redox speciation of Fe analytically if the redox potential and specific redox couples are known.

Part II: The implications of interactions of Al, Fe and organic matter for their mobility in acidic sandy soils

5

Mobility of Fe(II), Fe(III) and Al in acidic forest soils mediated by dissolved organic matter: influence of solution pH and metal/organic carbon ratios*

Abstract

The mobility of Al and Fe in acidic sandy forest soils is greatly influenced by interactions with dissolved organic matter (DOM). We determined the distribution of Al, Fe(II) and Fe(III) over dissolved 'free' metal, dissolved metal-DOM complexes and metal-DOM precipitates as influenced by solution pH, redox potential and metal/organic carbon (M/C) ratios. For this we used water extracts of the Oh horizon of a Fimic Anthrosol brought at pH = 3.5, 4.0 and 4.5, and added increasing amounts of Fe(II), Fe(III) and Al. For all three metals, soluble metal-DOM complexes were dominant at low M/C ratios (< 0.03). At higher M/C ratios, a strong pH effect was observed for Al: at pH = 3.5 dissolved 'free' Al was the dominant species, while at pH = 4.5 insoluble Al-DOM complexes dominated. For both Fe-species the pH effect was much less pronounced. For Fe(III) at higher M/C ratios, insoluble complexes were the dominant species at all pH values. For Fe(II) very little precipitation was observed and while free metal in solution gained in importance at higher M/C ratios, soluble complexes remained equally important. The differences between Fe(II) and Fe(III) signify the influence of the redox potential of the soil solution. We propose that in horizons where negatively charged sorption sites dominate, cation bridging causes soluble metal DOM-complexation to lead to immobilization of DOM and bound metals, while in horizons where positively charged sites dominate soluble metal-DOM complexation prevents immobilization by adsorption. Combined with our results and the pH and M/C gradients found in acidic forest soils, this would mean mobilization of Al, Fe and DOM in O, A and E horizons and immobilization in B horizons, as is generally observed in podzols.

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5.1. Introduction

Dissolved Organic Matter (DOM) in soil solutions plays a crucial role in substance transport through acidic forest soils in the temperate zone. It can act as a carrier for a variety of components, ranging from nutrients and trace elements to toxics such as pesticides (Kalbitz et al., 2000 and references cited therein). Furthermore, DOM plays an important role in the soils carbon cycle (Kaiser and Guggenberger, 2000). Fe and Al are also vital in many biogeochemical processes that take place in acidic forest soils. Fe is an essential element for soil organisms (McBride, 1994), while both Fe and Al are toxic to soil organisms when present in too high a concentration (Hue et al., 1986; Lucassen et al., 2000). Together, Fe, Al and DOM play a fundamental part in acidification and pedogenesis in acidic forest soils (McBride, 1994; Petersen, 1976).

Polyvalent metals like Fe and Al are hard Lewis acids, capable of strong and specific bonding to hard Lewis base functional groups on DOM molecules (Martell et al., 1988; Stevenson, 1994). The most important such functional groups are carboxylic acid and phenolic OH groups (Pohlman and McColl, 1988; Tam and McColl, 1991) though other groups may also play a role (Martinez and McBride, 1999). In addition, polyvalent metals can bind with more than one functional group at the same time thereby forming very stable ring structures (Pohlman and McColl, 1988; Tam and McColl, 1991).

Binding of Al and Fe to DOM influences the mobility of Al, Fe and DOM in several ways. When insoluble complexes are formed, both DOM and metals are obviously immobilized (Kalbitz et al., 2000). When soluble metal-DOM complexes are formed, the influence on the mobility is less clear. On the one hand Al and Fe can occupy the same functional groups on DOM molecules that are also involved in sorption of DOM to solid soil components (Kaiser et al., 1997). When this results in a reduced negative charge on the DOM molecules, it could increase the mobility of DOM through the soil system by partially preventing sorption, especially since a large portion of DOM sorption is believed to be irreversible (Gu et al., 1994). This would also increase the mobility of Fe and Al themselves because binding to DOM alters precipitation equilibria with sparingly soluble

inorganic Al and Fe salts and competes with immobilization of Al and Fe by adsorption to solid soil components (Stevenson, 1994). On the other hand, because of their polyvalence, binding of Al and Fe to DOM can create positively charged complexes when not all of the charge on the metal cations is compensated. This can immobilize both metals and DOM molecules by cation bridging between DOM and negatively charged solid soil components (Dahlgren and Marrett, 1991; Guggenberger and Zech, 1993).

Complexation of Al and Fe with DOM in acidic forest soils is influenced by several soil solution variables, including the solution pH value, the redox potential that determines the Fe(II)/Fe(III) speciation, and the molar ratio of metals to organic carbon (M/C) (Stevenson, 1994). Furthermore, competition effects between different metal cations for binding on DOM can have a significant influence on the complexation with DOM (Pinheiro et al., 2000). Because of the influence of complexation of DOM with Al and Fe on the behavior of all three in acidic sandy forest soils, it is necessary to understand the influence of these soil solution variables on such complexation. While many studies have looked at the binding of Al and to a lesser extent of Fe with DOM, there is still much uncertainty. For instance, there is no consensus on the relative ability of Al compared to Fe to induce DOM precipitation under acidic conditions (De Coninck, 1980; Kaiser, 1998; Petersen, 1976; Schnitzer, 1978). When looking at soluble complexation, direct measurement of the speciation in solution of Al and Fe over 'free' metals and metal-DOM complexes is difficult and the results depend on the analytical method used (Alfaro-De la Torre et al., 2000; Jansen et al., 2001). Furthermore, for both soluble and insoluble complexation, only a few studies have taken the oxidation of Fe(II) into Fe(III) and vice versa into account.

In previous work we examined the influence of pH, redox potential and M/C ratio on soluble complexation of DOM with Al and Fe (Jansen et al., 2002). As both soluble and insoluble complexation occur simultaneously in soils, to understand and predict the implications of complexation of Al and Fe with DOM for their mobility in acidic forest soils, a combined study of soluble and insoluble complexation of Al and Fe with DOM was necessary.

Therefore, the objective of the present study was to determine the distribution of Al, Fe(II), and Fe(III) over 'free' metals, dissolved metal-DOM complexes and insoluble metal-DOM complexes as influenced by pH and M/C ratios. Furthermore, the objective was to assess the implications of this distribution on the mobility of Al, Fe(II), Fe(III) and DOM in acidic sandy forest soils. The use of both Fe(II) and Fe(III) allowed inferences on the influence of the redox potential on the behavior of Fe to be drawn.

We used forest soil water extracts brought at pH = 3.5, 4.0 and 4.5, to represent soil solutions from acidic sandy forest soils in the temperate zone (Kaiser and Zech, 1998). To these water extracts we added increasing amounts of solutions containing Al, Fe(II) or Fe(III), to create the M/C ranges in which we expected to find significant complexation. These ranges all fell within the M/C range as observed in lysimeter data from a two-year field monitoring project in the soil from which the samples for the water extracts were taken (Tietema et al., 1993).

5.2 Materials and methods

All chemicals used in the experiments were of analytical grade. All glassware was acid and water rinsed prior to use, to avoid metal contamination. The soil material used to create the water extracts, was collected from the Oh horizon ($\text{pH}_{\text{H}_2\text{O}} = 3.8$) of a Fimic Anthrosol (FAO, 1988) from Buunderkamp in the Netherlands. We used water extraction because this is generally regarded as one of the better ways to obtain a DOM composition representative of the soil solution (Herbert and Bertsch, 1995). The Oh horizon was chosen because the DOM in this soil type is believed to originate from the upper (O) horizons (Kalbitz et al., 2000).

5.2.1 Preparation of the DOM solutions

We sieved the collected Oh material without prior drying over 2 mm, using a polyethylene sieve to avoid metal contamination. DOM solutions were then prepared by water extraction of the sieved material in a 1:3 w/w ratio to nano-

pure (18.3 Ω M) water. The resulting suspension was shaken for 16 hours, centrifuged at 12,000 rpm for 30 minutes and filtrated over 0.45 μ m using a membrane filter. The DOM solution that was thus obtained, was divided over three aliquots. The pH values of the three aliquots were adjusted to pH = 3.5, pH = 4.0 and pH = 4.5 respectively, by adding small quantities of a 1.0 M HNO₃ solution or a 1.0 M KOH solution. The initial composition of the DOM solutions is presented in Table 1.

Table 1

Initial composition of the DOM solutions at the three different pH values^a

| | DOC (μ mol C/l) | Fe(II) (μ M) | Fe(III) (μ M) | Al (μ M) | Ca (μ M) | Mg (μ M) |
|----------|-------------------------|----------------------|-----------------------|------------------|------------------|------------------|
| pH = 3.5 | 3660 | 3.95 | 5.97 | 22.1 | 24.9 | 19.7 |
| pH = 4.0 | 3620 | 2.70 | 7.40 | 22.4 | 23.9 | 18.9 |
| pH = 4.5 | 3700 | 2.83 | 7.11 | 21.9 | 24.1 | 19.3 |

^a Only metal cations present in concentrations $\geq 1.5 \mu$ M are shown.

To all DOM solutions NaN₃ was added to obtain an overall electrolyte concentration of 0.01 M. This served to prevent microbial degradation of DOM during the experiments (De Maagd et al., 1998) and to maintain the overall ionic solution strength in the metal addition experiments, since ionic strength influences the binding of metals to DOM (Stevenson, 1994). Furthermore, the addition of NaN₃ prevented problems with measurements of free metals at very low ionic solution strengths using the method of Diffusive Gradients in Thin films (DGT) that is explained more in detail in section 2.3 (Alfaro-De la Torre et al., 2000).

5.2.2 Experimental setup

We subdivided the DOM solutions at pH = 3.5, pH = 4.0 and pH = 4.5 into nine 1l solutions for each pH value, representing the three metals Al, Fe(II) and Fe(III) to be added in triplicate. The solutions were kept in closed glass containers in an isothermic room at 20°C during the experiments. In nine sequential steps

Al, Fe(II) and Fe(III) were added from stock solutions of $\text{Al}(\text{NO}_3)_3$, FeCl_2 and $\text{Fe}(\text{NO}_3)_3$ to obtain the M/C ratios presented in Table 2. The M/C ratios here and in the rest of this article represent total metal present divided by total organic carbon present in both solution and precipitates. The average concentration ranges of the three metals in the addition experiments were: Al: 22 – 2900 $\mu\text{mol/l}$; Fe(II): 9.0 – 3100 $\mu\text{mol/l}$ and Fe(III): 9.0 – 360 $\mu\text{mol/l}$. These concentrations reflect theoretical concentrations based on the amount of metal added plus the metal initially present in the DOM solutions and assuming no precipitation takes place. To limit dilution of the DOM solutions, the metal stock solutions had such concentrations that no more than 2 ml needed to be added in a given addition step.

Table 2

Theoretical metal/organic carbon molar ratios in the metal addition experiments.

| | Addition step | | | | | | | | | |
|------------------------|---------------|-------|-------|-------|-------|-------|-------|------|------|------|
| | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Fe(II) ^{a,b} | 0.234 | 0.314 | 0.407 | 0.495 | 1.13 | 2.93 | 3.72 | 7.37 | 18.4 | 117 |
| Fe(III) ^{a,b} | 0.234 | 0.243 | 0.254 | 0.264 | 0.371 | 0.675 | 0.809 | 1.40 | 3.21 | 14.3 |
| Al ^a | 0.526 | 0.564 | 0.619 | 0.672 | 1.03 | 2.04 | 2.48 | 4.56 | 10.9 | 69.0 |

^a M/C ratios $\times 100$.

^b Based on total Fe concentrations initially present.

After each addition step the solutions were shaken for 24 hours to reach equilibrium with regards to organic complexation (Yates and Von Wandruszka, 1999). Subsequently, the solutions were shaken vigorously to obtain a homogenous suspension of solution and precipitates, after which samples were taken. These were centrifuged at 20,000 rpm and filtrated over 0.45 μm to separate the precipitates from the solutions. In the filtrated samples we determined dissolved organic carbon (DOC) and total dissolved metal contents as well as the Fe(II)/Fe(III) speciation. After sampling, DGT units were deployed into the DOM solutions that were again shaken for 16 hours, after which the units were collected and ‘free’ metals were determined.

5.2.3 Analyses

DOC contents were determined by colorimetric determination on a Skalar continuous flow autoanalyzer. Total metal contents were determined on a Perkin Elmer Optima 3000XL ICP-OES. Prior to analysis the ICP-OES samples were acidified to pH = 1.0 with concentrated HNO₃, to dissociate the metal complexes that were present. Speciation between Fe(II) and Fe(III) was done by colorimetric determination of Fe(II) after reaction with orthophenantroline (Begheijn, 1979). After reduction of the Fe(III) present in the sample with hydroquinone (Begheijn, 1979), total Fe was again determined colorimetrically and Fe(III) was calculated by difference. In all cases corrections for the intrinsic absorbance of DOM were applied. Due to the higher precision of ICP-OES measurements at low concentration levels, total Fe was scaled to the values obtained by ICP-OES and the measured absolute amounts of Fe(II) and Fe(III) were adjusted accordingly.

The 'free' metal contents were determined by Diffusive Gradients in Thin films (DGT). In previous studies we successfully tested the applicability of DGT for the determination of 'free' Al, Fe(II) and Fe(III) in acidic forest soil solutions (Jansen et al., 2001; Jansen et al., 2002). The DGT units were obtained from DGT Research Ltd, UK. The units consisted of a Na⁺ saturated Chelex 100 disc, covered with an APA hydrogel layer of 0.8 mm and a 0.45 μm membrane filter. The APA hydrogel allows hydrated metal cations and small inorganic metal complexes to pass unhindered (Zhang and Davison, 1999). Subsequently, the Chelex disc immobilizes the cations and any labile metal complexes that have passed the gel (Zhang and Davison, 1999). After deployment the DGT unit was opened and the metals were eluted from the Chelex disc by immersing it in 1.0 ml concentrated HNO₃ for 24 hours. We subsequently measured the metal content in the eluent by ICP-OES. Larger metal-DOM complexes (>2400 Da) will not pass through the APA-hydrogel at an appreciable rate and are therefore not determined (Zhang and Davison, 1999). In addition, of the small metal-DOM complexes that do penetrate the hydrogel, non-labile complexes are not immobilized on the Chelex disc. Consequently, 'free' metals as determined by DGT consist of hydrated metal

cations and soluble inorganic complexes as well as a small portion of the smaller labile metal-DOM complexes (Zhang and Davison, 1999).

5.2.5 Calculation of the metal fractions

For each of the nine additions the total molar masses of the metals of interest were calculated from the initial metal contents in the DOM solutions, the amount of metal added in the addition step and the change in volume due to metal addition and sampling. The three fractions (dissolved ‘free’ metal, dissolved metal-DOM complexes and insoluble metal complexes) were calculated as a molar fraction of the total molar mass.

The fraction of insoluble metal complexes was defined as the difference between the dissolved molar metal mass as determined in the samples after centrifugation and filtration, and the total molar metal mass. Because the container walls were made of smooth glass, we expected no significant contribution of adsorption to the container walls to the immobilization of DOM, metals or metal-DOM complexes.

The ‘free’ metal mass was calculated from the amount of metal determined by ICP-OES in the DGT elution samples, using the DGT formulas (Zhang and Davison, 1995):

$$M = C_e(V_{\text{HNO}_3} + V_{\text{gel}})/f_e \quad (1)$$

$$C = M\Delta g/(DtA) \quad (2)$$

M represents the metal mass captured on the chelating resin and is calculated from the metal concentration in the elution sample (C_e), the volume of the elution fluid ($V_{\text{HNO}_3} = 1.0$ ml) and the chelating resin ($V_{\text{gel}} = 1.6 \times 10^{-4}$ l), and an elution factor ($f_e = 0.8$) needed to compensate for incomplete metal removal from the resin (Zhang and Davison, 1995). From M, the ‘free’ metal concentration is calculated by taking into account the thickness of the diffusion gel layer ($\Delta g = 0.094$ cm), the diffusion coefficient of the metals in the hydrogel (D), the deployment time (t) and the area of exposure to the sample solution ($A = 3.14$

cm²). The diffusion coefficients in the APA hydrogel are similar to those in water, but vary slightly depending on the cross-linker used during the manufacturing of the hydrogel (Li and Gregory, 1974; Zhang and Davison, 1999). Accurate diffusion coefficients were supplied by the manufacturer. At 20°C these are: Al: 4.14×10^{-6} cm²/s and Fe: 5.32×10^{-6} cm²/s.

The fraction of dissolved metal-DOM complexes was calculated from the difference between total dissolved metal and dissolved 'free' metal.

5.3 Results and discussion

Due to the high Fe(II) and Al concentrations in solution after the ninth and last addition step, the chelating resins in the DGT units were saturated and therefore did not function properly. Consequently, the results of this last addition step for Fe(II) and Al were discarded. For addition step 8 for the Al experiments at pH = 3.5 and the Fe(II) experiments at both pH = 4.0 and pH = 4.5, four additional DGT measurements were performed because of an initial variance in the results that was unacceptably high. The same was done for Fe(III) for addition step 9 at pH = 4.5. Due to experimental error, the DGT results of the last three steps of the second container in the Fe(II) experiments at pH = 3.5 were discarded. For the determination of 'free' Fe(II) at pH = 3.5, a correction factor of 1.40 was used to compensate for proton competition for binding at the Chelex discs in the DGT units (Jansen et al., 2002).

5.3.1 Fractional distribution of Al

The distribution of Al over 'free' Al, soluble Al-DOM complexes and Al-DOM precipitates at pH = 3.5, 4.0 and 4.5 and different Al/C ratios is depicted in Fig. 1. At all three pH values, initially soluble Al-DOM complexes were the dominant fraction and Al-DOM precipitates were the least important of the three fractions. The initial 'free' Al fraction was highest at pH = 3.5 and lowest at pH = 4.5 due to a higher availability of deprotonated acidic functional groups (Jansen et al., 2002). The order of importance of the three fractions and the change in distribution with increasing Al/C ratios remained the same for all three pH values

until an Al/C ratio of approximately 0.03 was reached. After this point profound differences in the fractional distribution between the three pH values occurred due to the difference in degree of precipitation. Where the precipitated fraction remained the least important fraction at pH = 3.5 until the second highest Al/C ratio, it quickly became the dominant fraction at pH = 4.5. At the same time the fraction of soluble Al-DOM complexes decreased with increasing Al/C ratios for all three pH values. While the decrease was the strongest at pH = 4.5 where the most insoluble complexes were formed, the differences in soluble complexation at the three pH values were not as large as for the precipitated Al fraction. This discrepancy was compensated by an increased importance of the 'free' Al fraction, which indeed quickly became dominant at pH = 3.5 while remaining less important at pH = 4.5. Calculations using the chemical speciation code PHREEQC (Parkhurst, 1995) showed that no precipitation of inorganic Al salts occurred during our experiments*. This means overall Al complexation by DOM (both soluble and insoluble) at the higher Al/C values increased with increasing pH. This can be explained by a higher availability of deprotonated functional groups at higher pH values. It is interesting to note that while overall complexation increased, soluble complexation alone *decreases* with increasing pH at higher Al/C ratios (Jansen et al., 2002).

5.3.2. Fractional distribution of Fe(II) and Fe(III)

Even though the Fe when added was either completely in the Fe(II) form or completely in the Fe(III) form, significant oxidation of Fe(II) and reduction of Fe(III) occurred in solution. This resulted in the Fe(II)/Fe(III) distribution presented in Table 3. However, this distribution represents the speciation of *total* Fe in solution, including both dissolved 'free' Fe and soluble complexes. Consequently, it does not reflect the Fe(II)/Fe(III) distribution in either soluble complexes or precipitates. In fact, other studies show that at pH < 7.0 the association of Fe(II) with DOM is fast compared to oxidation of Fe(II) to Fe(III)

* Recently, more restrained K_{sp} values for $\text{Al}(\text{OH})_3$ (s) were published (Gustafsson et al., 2001). When the solubility of Al is recalculated using these values, the results indicate that some precipitation of $\text{Al}(\text{OH})_3$ (s) may have occurred in the experiments at pH = 4.5.

by O₂ (Hering and Morel, 1990). At the same time we expect the displacement of Fe(II) from Fe(II)-DOM complexes by Fe(III) to be slow due to the strong and specific binding of polyvalent metals to organic matter (McBride, 1994). Therefore, even though significant oxidation occurred, the Fe bound in soluble Fe-DOM complexes in the Fe(II) experiments was most likely for a large part Fe(II). Reduction of Fe(III) in the Fe(III) experiments was in all likelihood DOM-mediated (Clarke and Danielsson, 1995; Stumm and Morgan, 1970). Therefore, even in the Fe(III) experiments at least part of the soluble complexes contained Fe(II). Because of the higher charge of Fe(III) compared to Fe(II), less Fe(III) than Fe(II) is needed to completely compensate the negative charge on DOM molecules. Furthermore, Fe(III) has a higher binding affinity for DOM in soluble complexes than Fe(II) (Jansen et al., 2002). Therefore, the precipitation in both Fe(II) and Fe(III) experiments is expected to have been predominantly in the Fe(III) form. These observations suggest that at higher M/C ratios in both the Fe(II) and Fe(III) experiments increasing parts of the Fe-DOM complexes remaining in solution contained Fe(II) (Jansen et al., 2002).

5.3.2.1 Fe(II) experiments

Fig. 2 shows the distribution of Fe over 'free', soluble complexed and precipitated Fe with increasing Fe/C ratios in the Fe(II) experiments at pH = 3.5, 4.0 and 4.5. To allow comparison with the other metals, the x-axis was scaled to a maximum of Fe/C = 0.15. As a consequence, the points for the ninth addition step are not shown. As with Al, initially the soluble complexed fraction was dominant and was the highest at pH = 4.5, due to a higher availability of deprotonated acidic functional groups. However, contrary to Al at all three pH values precipitation played only a minor role and soluble complexes remained very important or even the dominant fraction, even at the highest Fe/C ratios. Although precipitation was minimal, a general trend of (slightly) more precipitation at higher pH was again observed. Due to a relatively high uncertainty of the last point at pH = 4.5 we were unable to determine the trend of 'free' Fe between point seven and eight. At pH = 3.5 and pH = 4.0 the 'free' fraction showed a decline with increasing pH. This may be caused by increased

binding of Fe at undissociated functional groups at higher Fe/C ratios where the Fe(II)/H⁺ ratios were also higher and Fe(II) could more effectively compete with protons for binding to acidic functional groups.

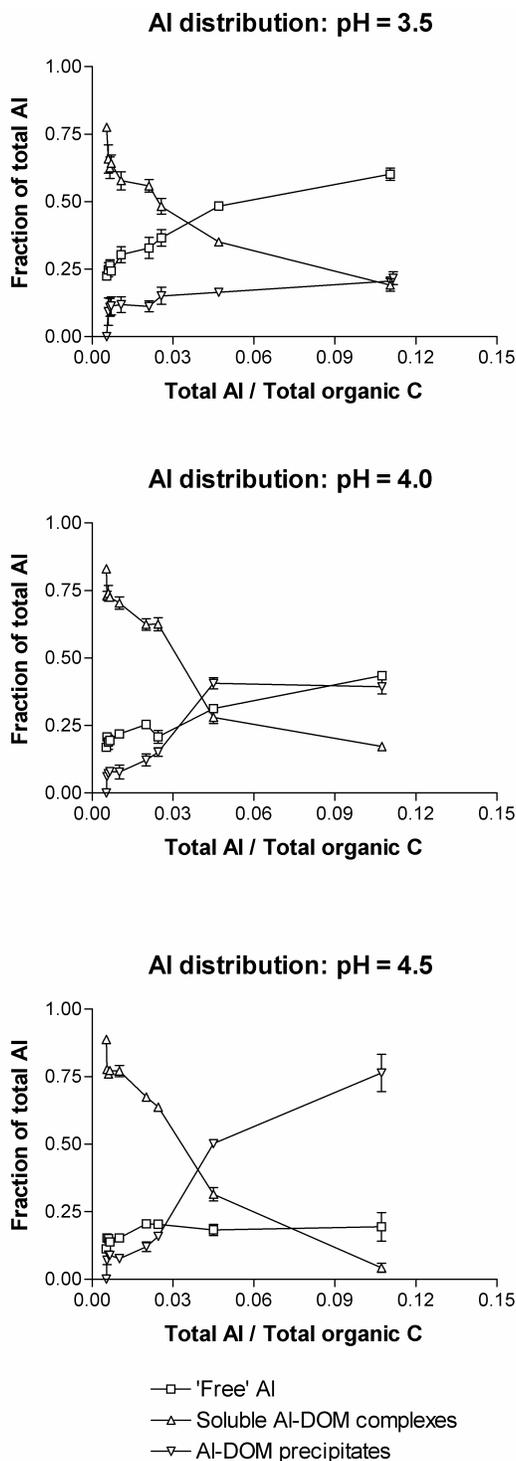


Fig. 1 Fractional distribution of Al over dissolved 'free' Al, soluble Al-DOM complexes and Al-DOM precipitates. Error bars depict standard error of the mean (S.E.M.)

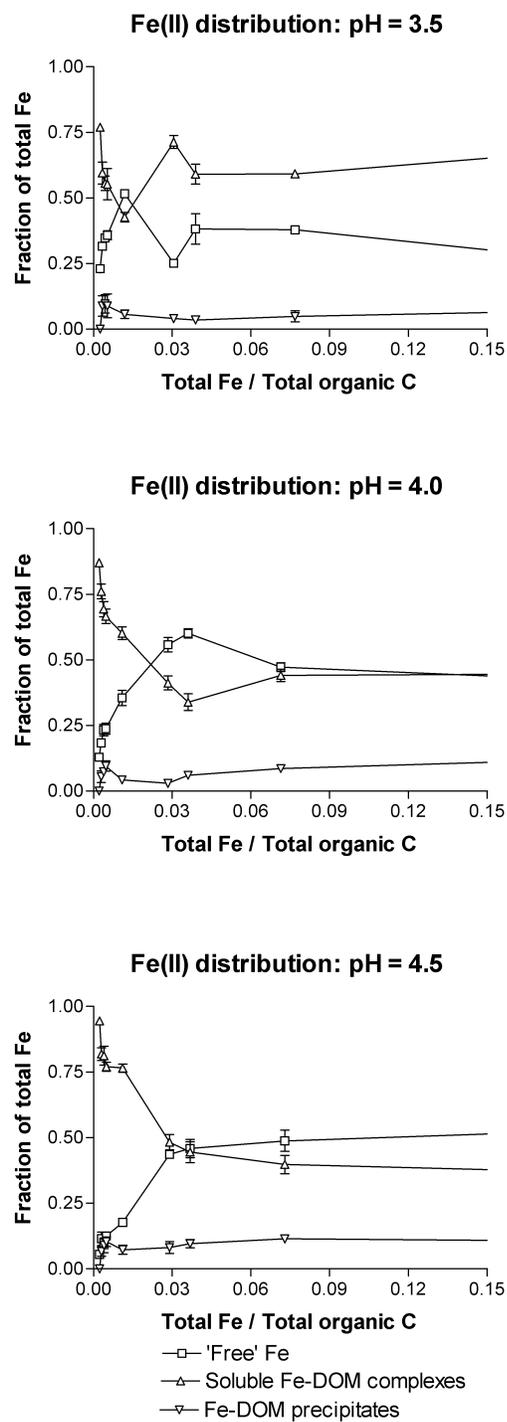


Fig. 2 Fractional distribution of Fe in the Fe(II) experiments over dissolved 'free' Fe, soluble Fe-DOM complexes and Fe-DOM precipitates at three pH values. Error bars depict standard error of the means (S.E.M.)

5.3.2.2 Fe(III) experiments

The earlier mentioned preferential precipitation of Fe(III)-DOM complexes versus Fe(II) complexes is clear from Fig. 3, where the fractional distribution of Fe over 'free' Fe, soluble complexes and precipitates in the Fe(III) experiments is presented. Initially soluble Fe(III)-DOM complexes dominated, but the importance of the precipitated fraction increased rapidly with increasing Fe/C ratios and it soon became the dominant fraction at higher Fe/C ratios, even at pH = 3.5. Thereby, the results of the Fe(III) experiments were very different from the Fe(II) experiments where precipitation played only a minor role and soluble complexes were the most abundant. The results of the Fe(III) experiments at all three pH values resemble those for Al at pH = 4.5, with the difference that the precipitated fraction at all three pH values rose even steeper with increasing Fe/C values and ended higher. The type of differences between the three pH values at lower Fe/C ratios were the same as for Al: soluble complexes were the dominant fraction and were the highest at the lowest pH value. However, the differences between the three pH values at higher Fe/C ratios were much smaller than for Al, due to the importance of precipitation at all pH values tested. Also, in contrast to the Al results, the 'free' Fe(III) fraction after an initial increase showed a decline with increasing Fe/C ratios and remained low for all three pH values. Even though the differences were much smaller, as with Al the trend of an increase in overall (soluble + insoluble) complexation with increasing pH at higher M/C ratios was observed. Again similar to the results for Al, this is the *opposite* of the behavior of soluble complexation alone of Fe(III) (Jansen et al., 2002). However, contrary to Al at pH = 4.0 and pH = 4.5 calculations using PHREEQC (Parkhurst, 1995) showed that precipitation of poorly soluble Fe(OH)₃ contributed to the overall precipitation and was partly responsible for the very low 'free' Fe(III) fraction at these pH values. Furthermore, the fraction of soluble Fe-DOM complexes started to decline earlier than for Al.

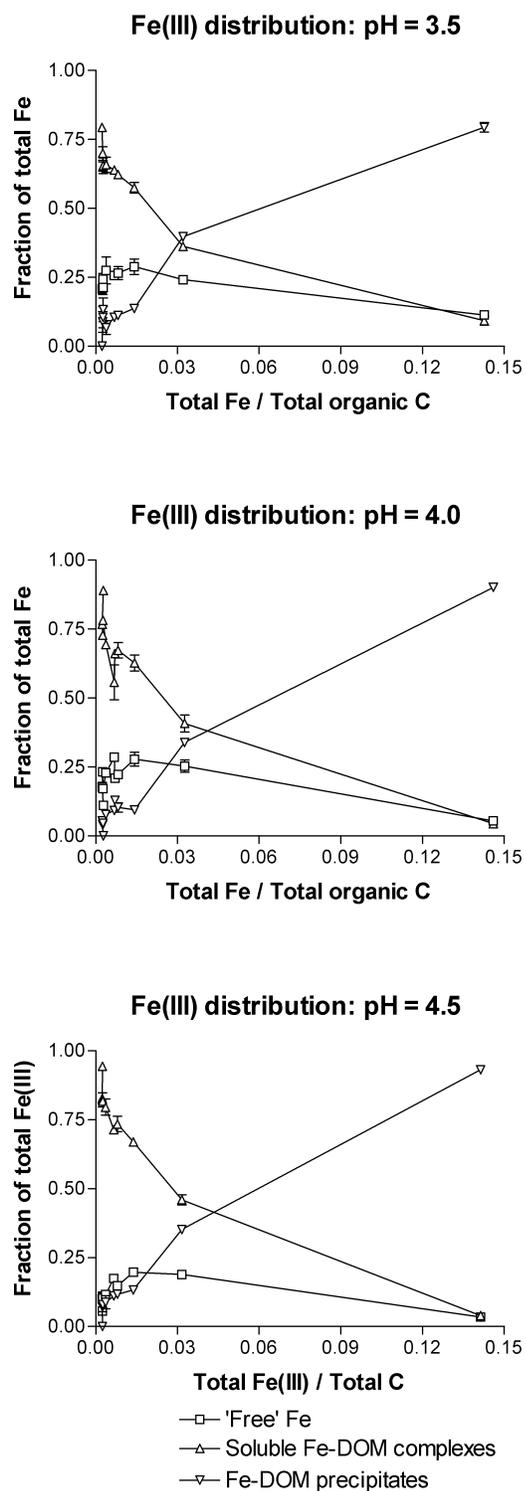


Fig. 3 Fractional distribution of Fe in the Fe(III) experiments over dissolved 'free' Fe, soluble Fe-DOM complexes and Fe-DOM precipitates at three pH values. Error bars depict standard error of the mean (S.E.M.)

5.3.3 Implications for the mobility of Al, Fe and DOM in acidic forest soils

5.3.3.1. Metal and DOM mobility

As explained earlier, insoluble complexation of Al and Fe with DOM will immobilize both DOM and metals. However, soluble complexation could either mobilize or immobilize Al, Fe and DOM, depending on whether sorption is prevented or cation bridging is stimulated.

Table 3
Speciation of total Fe in solution over Fe(II) and Fe(III) fractions in the experiments

| Step | Experiments where Fe(II) was added | | | | | | Experiments where Fe(III) was added | | | | | |
|------|------------------------------------|---------|----------|---------|----------|---------|-------------------------------------|---------|----------|---------|----------|---------|
| | pH = 3.5 | | pH = 4.0 | | pH = 4.5 | | pH = 3.5 | | pH = 4.0 | | pH = 4.5 | |
| | Fe(II) | Fe(III) | Fe(II) | Fe(III) | Fe(II) | Fe(III) | Fe(II) | Fe(III) | Fe(II) | Fe(III) | Fe(II) | Fe(III) |
| 0 | 0.40 | 0.60 | 0.27 | 0.73 | 0.28 | 0.72 | 0.40 | 0.60 | 0.27 | 0.73 | 0.28 | 0.72 |
| 1 | 0.48 | 0.52 | 0.37 | 0.63 | 0.45 | 0.55 | 0.47 | 0.53 | 0.43 | 0.57 | 0.32 | 0.68 |
| 2 | 0.51 | 0.49 | 0.34 | 0.66 | 0.28 | 0.72 | 0.55 | 0.45 | 0.40 | 0.60 | 0.24 | 0.76 |
| 3 | 0.68 | 0.32 | 0.61 | 0.39 | 0.49 | 0.51 | 0.51 | 0.49 | 0.36 | 0.64 | 0.29 | 0.71 |
| 4 | 0.60 | 0.40 | 0.32 | 0.68 | 0.36 | 0.64 | 0.46 | 0.54 | 0.29 | 0.71 | 0.27 | 0.73 |
| 5 | 0.54 | 0.46 | 0.36 | 0.64 | 0.25 | 0.75 | 0.49 | 0.51 | 0.65 | 0.35 | 0.40 | 0.60 |
| 6 | 0.64 | 0.36 | 0.38 | 0.62 | 0.40 | 0.60 | 0.45 | 0.55 | 0.29 | 0.71 | 0.21 | 0.79 |
| 7 | 0.61 | 0.39 | 0.42 | 0.58 | 0.36 | 0.64 | 0.42 | 0.58 | 0.32 | 0.68 | 0.38 | 0.62 |
| 8 | 0.82 | 0.18 | 0.78 | 0.22 | 0.74 | 0.26 | 0.52 | 0.48 | 0.50 | 0.50 | 0.54 | 0.46 |
| 9 | 1.00 | 0.00 | 0.80 | 0.20 | 0.78 | 0.22 | 0.00 | 1.00 | 0.00 | 1.00 | 0.00 | 1.00 |

Direct sorption of DOM to solid soil components involves binding to positively charged sites on solid soil components. These are usually Fe- and Al(oxo)hydroxic sites on clay minerals and especially amorphous sesquioxides (Kaiser and Wilcke, 1996; Kaiser and Zech, 2000; Kalbitz et al., 2000). Consequently, in soil horizons where direct sorption is dominant (e.g. horizons high in these sesquioxides and low in particulate organic matter), insoluble complexation would lead to immobilization while soluble complexation would cause mobilization. Therefore, based upon our results we expect the following scenario in these horizons. At lower M/C ratios an increase in pH mobilizes all three metal species. At higher M/C ratios an increase in pH immobilizes Al and DOM in Al-DOM complexes and to a much lesser extent Fe(II), Fe(III) and DOM in Fe-DOM complexes. An increase in M/C ratio results in immobilization of Al, Fe(III) and DOM. For Fe(II) this will only be true at lower M/C ratios. Due to the much higher fractions of soluble Fe-DOM complexes in the Fe(II) than in the Fe(III) experiments, a change

in redox potential increasing the relative contribution of Fe(II) leads to a strong rise in DOM mobility that increases with increasing M/C. Furthermore, the results from our study of soluble Fe-DOM complexation show that at higher Fe concentrations more Fe(II) could be maintained in soluble complexes and thus be mobilized (Jansen et al., 2002). This scenario does not take into account other interactions with solid soil components such as dissolution equilibria with mineral phases. Complexation of metals with DOM could lead to undersaturation with respect to mineral phases already present and thereby influence both pH and M/C ratios. This in turn would influence the complexation of metals and DOM and consequently metal and DOM mobility. Experiments in the presence of solid soil components are necessary to quantify this influence.

Cation bridging involves binding to negatively charged functional groups on solid soil components (Dahlgren and Marrett, 1991; Guggenberger and Zech, 1993). These are most abundant on particulate organic matter and on permanent negative charge sites (McBride, 1994). In soil horizons where cation bridging is dominant over direct sorption of DOM (e.g. horizons high in particulate organic matter and low in amorphous sesquioxides), both soluble and insoluble complexation would lead to immobilization of DOM and the metals bound to it. When this is applied to our results, we propose the following scenario in these horizons. An increase in pH at any M/C ratio results in immobilization of Al and DOM in Al-DOM complexes. The same is true for Fe(III). For Fe(II) it is only the case at lower M/C ratios, while at higher M/C ratios the opposite occurs. An increase in M/C ratio results in a slight increase in mobilization of Al and DOM from Al-DOM complexes, due to the sharp drop in soluble complexation. For Fe(III) the same effect will only take place at low M/C while at higher M/C immobilization will occur. The immobilization of Fe(II) increases strongly with increasing M/C at lower M/C ratios but remains almost constant at higher M/C ratios. A change in redox potential increasing the relative contribution of Fe(II) will therefore result in increased mobilization of Fe and DOM in the entire M/C range. However, the difference in behavior between Fe(II) and Fe(III) will be relatively constant with changing Fe/C ratios. Another process that must be considered in soil horizons where negatively charged sorption sites dominate is

direct sorption of Al and Fe to these sites. Complexation of these metals with DOM will shift sorption equilibria towards desorption. This in turn will increase the M/C ratio and consequently influence the complexation with DOM.

The implications of changes in pH and M/C ratios for DOM and metal mobility as just discussed are summarized in Table 4. One should keep in mind that these scenarios do not take immobilization by hydrophilic/hydrophobic interactions or Van der Waals forces into account. However, both these mechanisms are weak compared to cation exchange or direct sorption through coordination bonding (Tipping, 1990)

5.3.3.2 Podzolization

A specific case where the (im)mobilization of Al, Fe and DOM as influenced by pH and M/C ratios plays a fundamental role in acidic sandy soils, is the process of podzolization. Podzols are characterized by a thick ectorganic layer, overlying a bleached eluvial E horizon poor in Al, Fe and organic matter and a dark illuvial B horizon enriched in Al, Fe and organic matter. The processes responsible for the formation of podzols have been studied extensively (Anderson et al., 1982; Browne, 1995; Lundström et al., 2000a; Mokma and Buurman, 1982; Petersen, 1976). While there are still conflicting theories about the exact mechanisms involved, there is general consensus that podzols are formed by complexation of Al and Fe by DOM in the top (O, A, E) horizons and subsequent immobilization of these complexes in the lower (B) horizons (Lundström et al., 2000a). Even though interactions with solid soil components and microbial decay are believed to be important factors in podzolization (Lundström et al., 2000a) and were not considered in the present study, it is interesting to compare the observed relationships between Al and Fe mobility and changes in pH, M/C ratios and redox potential with data obtained from the field.

In many studies podzols in the temperate regions have been characterized (Mokma and Buurman, 1982; Petersen, 1976; Riise et al., 2000). In general in the O and A horizons a pH in the range of 3.0-5.0 is found, remaining constant or even decreasing with depth in these horizons (Petersen, 1976; Riise et al., 2000). This is followed by a steady increase of the pH with depth to 4.5 - 6.5 in the

underlying E and B horizons (Petersen, 1976; Riise et al., 2000). At the same time the lowest M/C ratios are found in O, A and E horizon, while a sharp increase in M/C ratios is found in the underlying B horizons. For instance the average values found by (Petersen, 1976) in ten Danish podzols are: Al/C = 0.007 - 0.040 and Fe/C = 0.02 - 0.09 in the O through E horizons, while Al/C = 0.20 - 0.80 and Fe/C = 0.26 - 1.40 in the B horizons.

Table 4

Summary of the expected implications of DOM interactions on Fe and Al mobility in acidic sandy forest soils in the temperate zone

| | Mobility in horizons where negatively charged sites dominate | Mobility in horizons where positively charged sites dominate |
|--|--|--|
| <i>Al</i> | | |
| Increase in pH at low M/C ^a | - | + |
| Increase in pH at high M/C ^a | - | - |
| Increase in M/C at low M/C ^a | + | - |
| Increase in M/C at high M/C ^a | + | - |
| <i>Fe(II)</i> | | |
| Increase in pH at low M/C ^a | - | + |
| Increase in pH at high M/C ^a | + | o/- |
| Increase in M/C at low M/C ^a | + | - |
| Increase in M/C at high M/C ^a | o | o/+ |
| <i>Fe(III)</i> | | |
| Increase in pH at low M/C ^a | o | + |
| Increase in pH at high M/C ^a | o | o/- |
| Increase in M/C at low M/C ^a | + | - |
| Increase in M/C at high M/C ^a | - | - |

^a The ranges of M/C values that are considered 'low' or 'high' M/C ratio's depend on the metal in question and the pH value (see Fig.1 - 3); roughly: low M/C < 0.03; high M/C > 0.03

According to our results, this combination of pH and M/C ratios would result in mobilization of Al, Fe(II) and Fe(III) in the O horizon where negatively charged sites on solid soil material dominate. In the underlying E horizon where negatively charged sites will be less abundant, further mobilization of Al, Fe(II) and Fe(III) would occur as long as the M/C ratio stays relatively low. In both Bh and Bs horizons, Al and Fe(III) would be immobilized by precipitation, but Fe(II) would remain mobile. These results are consistent with observations from podzols, including the lack of immobilization of Fe(II) that is reported in waterlogged podzols where Fe is in the reduced form (Lundström et al., 2000a; Petersen, 1976).

A comparison of Al and Fe leads to the following conclusions. In the top horizons where pH is low, Al would be more mobile than Fe(III). In the lower horizons, mobility would be similar. In a previous study we found that at pH = 4.5, in competition with Fe(III), Al is dominant in the precipitate at lower M/C ratios, while Fe(III) is dominant at high M/C ratios [Nierop, 2001 #171]. Because the pH is higher in the lower horizons, this suggests more and earlier immobilization of Fe(III) than of Al.

There is still no consensus on the mechanism of immobilization of Al and Fe in podzol B horizons (Lundström et al., 2000a). Some believe it is mainly precipitation of metal-DOM complexes (Mokma and Buurman, 1982; Petersen, 1976), while other studies indicate the formation of imogolite type material (Anderson et al., 1982; Farmer et al., 1980) or microbial degradation of organic ligands and subsequent precipitation of inorganic metal complexes (Lundström et al., 2000b) are the dominant mechanisms. Our results as applied to field data support the theory of immobilization by organic and for Fe(III) by some inorganic precipitation induced by changing pH and most importantly changing M/C ratios. However, while the use of NaN_3 made immobilization by microbial degradation unlikely in our experiments, the formation of (some) imogolite type material cannot be ruled out. Furthermore, as stated in the previous section, other interactions with solid soil components could influence the scenario sketched above.

5.4 Conclusions

All variables tested in the present study were found to influence the distribution of Al, Fe(II) and Fe(III) over 'free' metals, dissolved metal-DOM complexes and metal-DOM precipitates. At low M/C ratios soluble complexes were dominant for all three metals. Increases in M/C ratio within the range of 0 – 0.15 dramatically changed the distribution for all three metals. This led to extensive precipitation for Fe(III) in general and Al at pH = 4.0 and 4.5. On the other hand, for Fe(II) and Al at pH = 3.5 soluble complexes and 'free' metals remained the dominant fractions. A decrease in pH at low M/C ratios generally

increased the importance of 'free' metal at the expense of soluble complexation. At higher M/C ratios even within the limited range of $3.5 \leq \text{pH} \leq 4.5$, a change in pH profoundly affected the fractional distribution of Al and thereby regulated the effect of changing M/C ratios on this distribution. For Fe(II) and Fe(III) the effect of pH at higher M/C ratios was much smaller.

We propose that soluble complexation immobilizes metals in soil horizons rich in particulate organic matter where cation bridging is dominant, but mobilizes metals in horizons rich in sesquioxides and clay minerals where direct sorption of DOM is dominant. Combined with the pH and M/C ratio gradients found in podzols, this would mean mobilization of Al, Fe(II), Fe(III) and DOM in O, A and E horizons and immobilization in B horizons. This is consistent with observations from podzols.

The fact that the relationships we found are consistent with observations from the field illustrates the importance of complexation of Fe and Al with DOM in regulating the mobility of Fe, Al and DOM in acidic forest soils. Still to fully understand these processes, future experiments using solid soil components of different composition as found in Podzols are necessary to further test the scenarios presented here.

6

Mobilization of organic matter, Al and Fe in podzol eluvial horizons as affected by formation of metal-organic complexes and interactions with solid soil material *

Abstract

Interactions with dissolved organic matter (DOM) are generally believed to play a crucial role in the translocation of Al and Fe in acid sandy soils. Binding of Al and Fe to DOM affects their mobility in soils by altering sorption equilibria of charged sites on solid soil material, inducing precipitation of organo-metallic complexes and preventing the formation of inorganic Al and Fe phases. The relative importance of the different processes, especially with respect to the translocation of Al, Fe and organic matter in podzols, remains unresolved. We determined the effect of the presence of solid soil material from the eluvial (A(h)E) horizons of a Fimic Anthrosol and a Haplic Podzol on the metal-to-organic carbon (M/C) ratio in solution and the formation of dissolved organic Al and Fe complexes. Furthermore, we assessed the resulting influence on the mobilization of Al, Fe and DOM. Even under considerable metal loading, the M/C ratios and 'free' metal fractions in solution remained low and relatively constant, due to an apparent buffering by the solid phase and the formation of organo-metal complexes in solution. The M/C ratios remained so low that significant precipitation of organo-metal complexes due to saturation with metals was not found. The apparent buffering by the solid phase can be explained by a strong release of organic matter from solid soil material and adsorption of non-complexed Al and Fe on solid organic matter upon metal addition. Adsorption of organo-metal complexes most likely played only a minor role. The observations confirm the expected mobilization of Al, Fe and DOM in eluvial horizons and seem to indicate that even under fluctuating input of Al, Fe and DOM the soil solution will have a constant composition with respect to M/C ratios and percentage of Al and Fe present in dissolved organo-metal complexes.

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6.1 Introduction

The multi-charged metals Al and Fe play a fundamental role in acidification and pedogenesis in acid sandy soils (McBride, 1994). The mobility of Al and Fe in acid sandy soils is greatly influenced by their binding to dissolved organic matter (DOM). Al, Fe and DOM are immobilized when insoluble organo-Al and Fe complexes are formed or when Al, Fe or DOM are adsorbed on charged sites on solid soil components. On the other hand, when soluble organo-metal complexes are formed, this can lead to mobilization of Fe and Al because it prevents the formation of sparingly soluble inorganic Fe and Al phases (Stevenson, 1994). However, the mobility of soluble organo-metal complexes themselves is affected by sorption on solid soil material. In horizons where (potentially) negatively charged sorption sites dominate (e.g. acidic groups of solid organic matter in AE horizons), dissolved organo-metal complexes may be immobilized through cation bridging, especially because Al and Fe can replace protons in protonated groups (McBride, 1994). On the other hand, in soil horizons where positively charged sorption sites dominate (e.g. amphoteric sites on sesquioxides at lower pH), sorption of dissolved organo-metal complexes may be lower than sorption of DOM without metal bound to it. The reason is a shift of the binding equilibrium of DOM to positively charged sorption sites due to the binding to dissolved Al or Fe cations. A complicating factor when assessing the mobility of Al, Fe and organic matter in soils is that the different processes that affect their mobility, influence each other. For instance, adsorption of Al, Fe or DOM on solid soil material affects the metal:organic carbon (M/C) ratios in solution, which in turn determines whether predominantly soluble or insoluble organo-metal complexes are formed (Nierop et al., 2002).

Many studies have investigated the interaction of Al and to a lesser extent of Fe with DOM and the influence thereof on their mobility (e.g. De Wit et al., 1999; Riise et al., 2000; Van der Salm et al., 2000; Zysset et al., 1999). Yet no consensus exists concerning the exact mechanisms involved in the mobilization and immobilization of Al, Fe and organic matter in acid sandy soils. For instance, the mechanisms involved in the transport of Al, Fe and organic matter during the

process of podzolization remain unresolved. Many researchers believe that the formation and subsequent transportation of organo-Al and Fe complexes plays a dominant role in the mobilization of Al, Fe and organic matter from eluvial podzol horizons, (e.g. De Coninck, 1980; Mokma and Buurman, 1982; Petersen, 1976). However, this is contested by other researchers who propose that dissolved organo-Al and Fe complexes do not play a significant role in the process of podzolization (Anderson et al., 1982; Farmer et al., 1980).

In previous studies, we examined the influence of changes in M/C ratios, pH and the redox state of Fe on their interaction with DOM in soil solutions without solid soil materials present (Jansen et al., 2002; Jansen et al., 2003b; Nierop et al., 2002). We found that, at lower M/C ratios and lower pH values, the majority of Al and Fe was present in soluble organo-metal complexes. However, at higher pH and M/C ratios, most of the Al and Fe(III) was present as insoluble organo-metal complexes. These results suggest mobilization of Al, Fe and organic matter at the pH values and M/C ratios prevailing in eluvial horizons. However, the potential influence of the presence of solid soil material on solution composition and the mobility of soluble organo-metal complexes, is still unknown.

The purpose of the present study was to investigate the effect of the presence of solid soil material from eluvial, organic-rich AE horizons of two podzol(ic) soils on the solution chemistry with respect to interactions of Al and Fe with DOM. Further, we also assessed the impact of interactions of Al, Fe and DOM with solid soil material on the mobilization of Al, Fe and organic matter in these acid sandy soils. To accomplish this, we equilibrated DOM solutions with soil material collected from the eluvial horizons of the same soil in batch experiments at different pH and at different DOM concentrations and under different imposed M/C ratios.

6.2 Materials and methods

All chemicals used in the experiments were of analytical grade and all glassware was rinsed with acid and nano-pure (18.3 M Ω) water prior to use. All experiments were carried out in quadruplicate.

6.2.1 Description of soil materials

Two acid sandy soils from The Netherlands were used in the experiments. Soil 1: A young, incipient podzolic soil under oak (Fimic Anthrosol) (FAO, 1988), and Soil 2: an older podzol under heath with a well developed, buried profile (Haplic Podzol) (FAO, 1988). The choice of these two soils was based on the relative amounts of solid organic material *versus* amorphous Fe and Al (hydr)oxides present in the different horizons, resulting in different ratios of the number of negatively to positively charged binding sites in each horizon. The eluvial horizons, the A(h)E horizon of Soil 1 and the AE horizon of Soil 2, were used in the experiments. The soil samples were initially characterized as follows (Table 1). Water extractable and exchangeable cations were determined by water (1:1 w/v) and 0.125 M BaCl₂ (1:25 w/v) extractions. Amorphous and organically-bound Al and Fe were estimated by ammonium oxalate/oxalic acid extraction (pH 3.0, 1:50 w/v, in the dark) and 0.1 M sodium pyrophosphate/NaOH extraction (pH = 9.5, 1:75 w/v). Organic carbon was also determined in the latter extract. Total Al and Fe were determined by digestion with HF/HNO₃/HCl (Dixon and Weed, 1989, and references cited therein). The total carbon content was determined using an Elementar Vario EL CNS analyser.

Table 1
Initial composition of the soil samples used in the experiments

| | AhE (Soil 1) | AE (Soil 2) | | AhE (Soil 1) | AE (Soil 2) | |
|---|--------------|-------------|---|--------------|-------------|---|
| Al _{BaCl₂} μmol/kg | 3310 | 2770 | Fe _{BaCl₂} μmol/kg | 14.0 | 29.0 | Al _{BaCl₂} μmol/kg |
| Al _p μmol/kg | 9780 | 11080 | Fe _p μmol/kg | 9590 | 7900 | Al _p μmol/kg |
| Al _o μmol/kg | 9670 | 9340 | Fe _o μmol/kg | 9260 | 7040 | Al _o μmol/kg |
| Al _t mmol/kg | 381 | 310 | Fe _t mmol/kg | 51 | 29 | Al _t mmol/kg |
| C _p mmol/kg | 625 | 440 | Si _o μmol/kg | 260 | 300 | C _p mmol/kg |

M_{BaCl₂} = water extractable + exchangeable metal; M_p = pyrophosphate extractable metal; M_o = ammonium oxalate extractable metal; M_t = total metal from destruction with HF/HNO₃/HCl; C_t = total organic carbon (CNS analysis); C_p = pyrophosphate extractable organic carbon.

6.2.2 Preparation of DOM solutions

The DOM solutions used in the experiments were obtained by water extraction of the Oh horizons of both soils because the composition of the DOM thus obtained resembles that of DOM entering the upper mineral soil horizons (Kalbitz et al., 2000).

We sieved the collected Oh material at 2 mm without prior drying, using a polyethylene sieve to avoid metal contamination. DOM solutions were then prepared by extraction of the sieved material with nano-pure (18.3 M Ω) water (soil:water ratio 1:3 w/w). The resulting suspension was shaken for 16 hours, centrifuged at 23,000 g for 30 minutes and filtered at 0.45 μ m using a membrane filter. The DOM solution obtained for each horizon had a dissolved organic carbon (DOC) concentration of approximately 30 mg C/l. The two solutions were divided into two aliquots, one of which was subsequently evaporated using a Rotavab vacuum evaporator to create a DOC concentration of approximately 60 mg C/l. The pH of the 30 mg C/l solution was adjusted to 4.0 and that of the 60 mg C/l to 3.5 by adding small quantities of 1 M HNO₃ or 1 M KOH. The initial composition of the four resulting DOM solutions is presented in Table 2.

Table 2
Initial composition of the DOM solutions:^a

| | DOC (μ mol C/l) | Fe (μ M) | Al (μ M) | Ca (μ M) | Mg (μ M) | Si (μ M) |
|------------------|-------------------------|------------------|------------------|------------------|------------------|------------------|
| Soil 1; low DOC | 2600 | 6.5 | 12.5 | 15.5 | 11.0 | 46.5 |
| Soil 1; high DOC | 5030 | 12.5 | 24.5 | 31.0 | 22.5 | 95.0 |
| Soil 2; low DOC | 2640 | 5.5 | 11.5 | 10.0 | 10.0 | 76.0 |
| Soil 2; high DOC | 4970 | 11.0 | 23.0 | 22.0 | 21.5 | 157.5 |

^a Only polyvalent, positively charged species present in concentrations $\geq 1.5 \mu$ M and Si are shown.

To all four DOM solutions, NaN₃ was added to prevent microbial degradation of DOM during the experiments (De Maagd et al., 1998) and to maintain a constant overall ionic solution strength of 0.01 M in the metal addition experiments, since ionic strength influences the binding of metals to DOM (Stevenson, 1994). Furthermore, the addition of NaN₃ prevented problems with measurements of ‘free’ metals at very low ionic solution strengths using diffusive gradients in thin films (DGT) (Alfaro-De la Torre et al., 2000). The addition of

NaN_3 led to a slight increase in pH due to the formation of HN_3 (g). The increase in pH was corrected by adding minute amounts of concentrated HNO_3 .

6.2.3 Experimental setup

Samples of the eluvial soil material from both soils were placed in closed glass containers in a constant temperature room at 20°C without prior drying. The two DOM extracts from the same soil at the two different DOC concentrations were added to the same soil in separate batches, resulting in two different initial states per soil. The solid-to-solution ratio was 1:5 with a liquid volume of 750 ml taking into account the moisture content of the soil samples. The 60 mg C/l, pH 3.5 solution was chosen as a realistic DOC concentration and pH for this type of horizon (Mokma and Buurman, 1982; Petersen, 1976). The 30 mg C/l, pH 4.0 solution was chosen to assess the influence of a change in pH and DOC content. This resulted in four different initial situations: Soil 1: AhE:30; Soil 1: AhE:60; Soil 2: AE:30 and Soil 2: AE:60. The initial soil/solution mixtures were shaken for 120 hours to equilibrate. Subsequently, the mixtures were shaken vigorously to obtain a homogeneous suspension from which 35 ml samples were taken for analysis. These were centrifuged at 40,000 g and filtered at $0.45\ \mu\text{m}$ to separate solids from solution. DOC, total Al, Fe and Si contents were determined in the filtered samples. After sampling, DGT units were deployed in the soil-solution mixtures that were again shaken for 16 hours, after which the units were collected and 'free' Al and Fe were determined from the Al and Fe adsorbed on the chelating resin contained within the units.

After the initial step, Al and Fe(III) were added to the different soil-solution mixtures as small amounts (< 1.0 ml) of solutions of their nitrate salts in a 3:1 Al to Fe(III) ratio in 5 sequential steps to impose M/C ratios ranging from 0.0050 to 0.075 for Al and 0.0025 to 0.025 for Fe. The maximum absolute metal concentrations added are high (0.375 mmol Al and 0.125 mmol Fe in the experiments with an initial DOC concentration of 60 mg C/l). This was necessary to investigate the impact of changes in the imposed M/C ratios. In addition, high metal concentrations might, for instance, be reached after evaporation during a

period of drought. If the addition of metal resulted in a change in the pH value of the solution, this was corrected by adding minute amounts of a concentrated KOH solution. After each addition, the soil-solution mixture was shaken for 24 hours before being sampled and analysed in a manner similar to the initial suspensions. In total, the duration of the experiments was 384 hours. The experiments were performed in two sets, with experimental situations randomly assigned to either set.

In addition to the experiments with soil samples and DOM solutions, batch experiments of the same soil samples with nano-pure (18.3 M Ω) water and added NaN₃ were performed as blanks. They were treated and sampled the same way as the initial soil-solution mixtures in the experiments with DOM, although the pH values were not constrained.

6.2.4 Analyses

DOC contents were determined by colorimetric determination on a Skalar continuous flow autoanalyser. Metals were determined on a Perkin Elmer Optima 3000XL ICP-OES. Prior to analysis, the ICP-OES samples taken during the experiments were acidified to pH 1.0 with concentrated HNO₃, to dissociate the metal complexes present. The Al and Fe content of the different extractions performed for characterization of the soil samples were also determined on the ICP-OES, except for the pyrophosphate extractable metals, which were determined on a Perkin Elmer 5000 flame AAS due to interference of the matrix with ICP-OES measurements. The AAS measurements had a detection limit that was two orders of magnitude poorer than by ICP measurement.

The 'free' metal contents determined by DGT. 'Free' metals consist of hydrated metal cations and soluble inorganic complexes, as well as a very small portion of the smaller labile metal-DOM complexes (Zhang and Davison, 1999). In previous studies, we successfully tested the applicability of DGT for the determination of 'free' Al, and Fe in acidic forest soil solutions of similar composition to those used in the current study (Jansen et al., 2001; Jansen et al., 2002). The DGT units were obtained from DGT Research Ltd, UK, and consist of a Na⁺ saturated Chelex 100

disc, covered with an APA hydrogel layer of 0.8 mm and a 0.45- μm membrane filter.

6.3 Results

6.3.1 Chemical soil properties

Table 1 shows that the total organic carbon (C_t) and total Fe contents of Soil 1 are approximately twice those in Soil 2. The total and amorphous Al contents in Soil 1 are only slightly larger. Because Al, Fe and organic matter are removed from eluvial podzol horizons during podzolization and both soils were formed in the same parent material, these results support the observation that Soil 2 is a more developed podzol than Soil 1. However, when considering the oxalate extractable metal fraction (M_o), the resulting M_o/C_t ratios in both Soil 1 and 2 are well below the threshold value of 0.02 that can be used to distinguish AE from B podzol horizons, a value lower than 0.02 indicating an (A)E horizon (Mokma and Buurman, 1982). From the pyrophosphate and oxalate extractable Al and Fe, it would appear that there are more organic amorphous Al and Fe phases than total amorphous Al and Fe phases present, which cannot be true. The slight overestimation of the pyrophosphate extractable Al and Fe is presumably caused by measurement error and the fact that pyrophosphate extraction is known to extract some inorganic amorphous Al and Fe phases as well (Dixon and Weed, 1989).

Table 3

Average composition of four blanks in which the soil samples used in the experiments were shaken for 5 days with nanopure water containing 0.01 M NaN_3 .

| | pH | total Al μM | total Fe μM | total Si μM | 'free' Al μM | 'free' Fe μM | DOC $\mu\text{mol C/l}$ |
|------------|------|---------------------------|---------------------------|---------------------------|----------------------------|----------------------------|----------------------------|
| AhE Soil 1 | 3.85 | 21.3 | 17.5 | 46.5 | 4.0 | 1.4 | 2800 |
| AE Soil 2 | 4.55 | 24.5 | 15.0 | 34.2 | 2.4 | 1.0 | 1900 |

In Table 3 the solution composition of the blanks is provided. The higher final pH value and lower DOM concentration of the AE horizon of Soil 2 compared to the AhE horizon of soil 1 correspond well with the lower C_t content of Soil 2

(Table 1). The differences in Al and Fe concentrations in solution coincide with the differences in pyrophosphate extractable Al and Fe (Table 1).

6.3.2 Changes in soil solution composition over the course of the experiments

Fig. 1, 2 and 3 display the concentrations of total Al, Fe and Si, 'free' Al and 'free' Fe, and DOC, respectively, over the course of the experiments. In Table 4, the theoretical concentrations of Al and Fe after each metal addition are given, these representing the hypothetical metal concentration in solution if no precipitation or interaction with the solid soil components had occurred. Fig. 1 shows that the total Al concentrations increased only slightly in spite of the addition of increasing amounts of Al, whereas the Fe concentrations show a small decline. The Si concentrations increased slightly in Soil 1 but remained constant in Soil 2. The DOC concentrations increased in all cases, the greatest increase being in Soil 1. The 'free' Al and Fe concentrations remained low and relatively constant throughout all experiments.

In Fig. 4, we plotted the actual M/C ratio in solution versus the M/C ratio that was imposed by the addition of Al and Fe for both soils and both DOC concentrations. In all cases, the Al/C ratios in solution were very well buffered against addition of Al over the entire range of added metal. The same is true for Fe after an initial decrease in Fe/C ratios during the first few additions of Fe. Even after addition of substantial amounts of metal, in all cases, for both Al and Fe, the M/C ratios remained well below 0.03. At this level, the onset of precipitation of M-DOM complexes is expected at both pH values used in the experiments, the precipitation being greater at the higher pH value (Nierop et al., 2002).

In Figure 5, 'free' Al and Fe are plotted as a molar fraction of the total amount of Al and Fe in solution over the course of the experiments. In all but one case, the majority of Al and Fe in solution was present at all times in the form of soluble organo-metal complexes.

Table 4

Theoretical average Al and Fe concentrations in solution over the course of the experiments, assuming all metal to have stayed in solution and corrected for sampling.

| | Initial step ^a (μM) | Addition 1 (μM) | Addition 2 (μM) | Addition 3 (μM) | Addition 4 (μM) | Addition 5 (μM) |
|-------------------|---|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|
| Soil 1:AhE:60b Al | 17.4 | 86.0 | 91.1 | 97.9 | 174.8 | 224.3 |
| Soil 1:AhE:60 Fe | 34.5 | 70.9 | 59.4 | 56.4 | 76.1 | 90.8 |
| Soil 1:AhE:30 Al | 18.7 | 55.5 | 64.8 | 72.8 | 120.1 | 146.7 |
| Soil 1:AhE:30 Fe | 22.2 | 41.9 | 38.8 | 43.5 | 57.7 | 65.0 |
| Soil 2:AE:60 Al | 22.2 | 90.6 | 100.3 | 109.1 | 185.8 | 237.2 |
| Soil 2:AE:60 Fe | 66.0 | 111.5 | 110.1 | 100.4 | 115.5 | 136.3 |
| Soil 2:AE:30 Al | 18.3 | 54.6 | 60.5 | 66.9 | 111.6 | 137.5 |
| Soil 2:AE:30 Fe | 33.1 | 55.8 | 46.1 | 40.9 | 52.2 | 59.7 |

^a Equilibrium between solution and solid soil material before the first addition of metal.

^b Soil type and initial DOC concentration in mg C/L. See text for explanation.

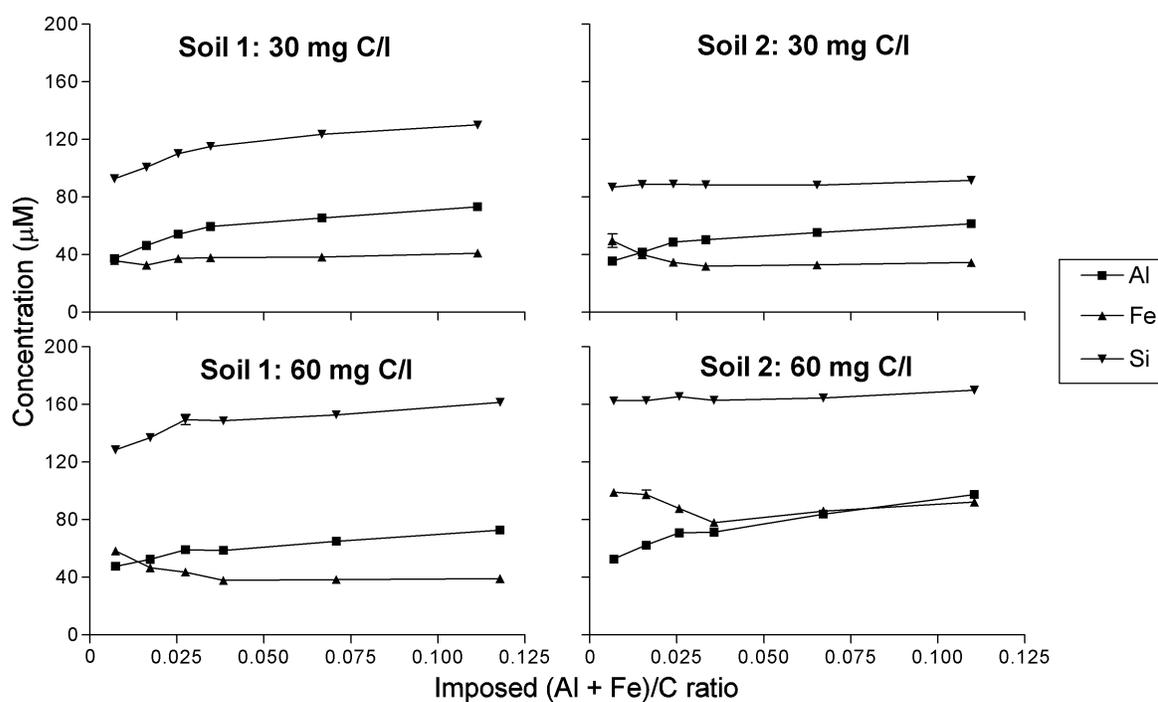


Fig. 1 Total metal concentrations in solution as a function of increasing imposed (Al + Fe)/C ratios, which consist of the theoretical molar metal concentration assuming all metal stayed in solution, divided by total molar DOC concentrations initially present. Error bars depict the standard error of the mean.

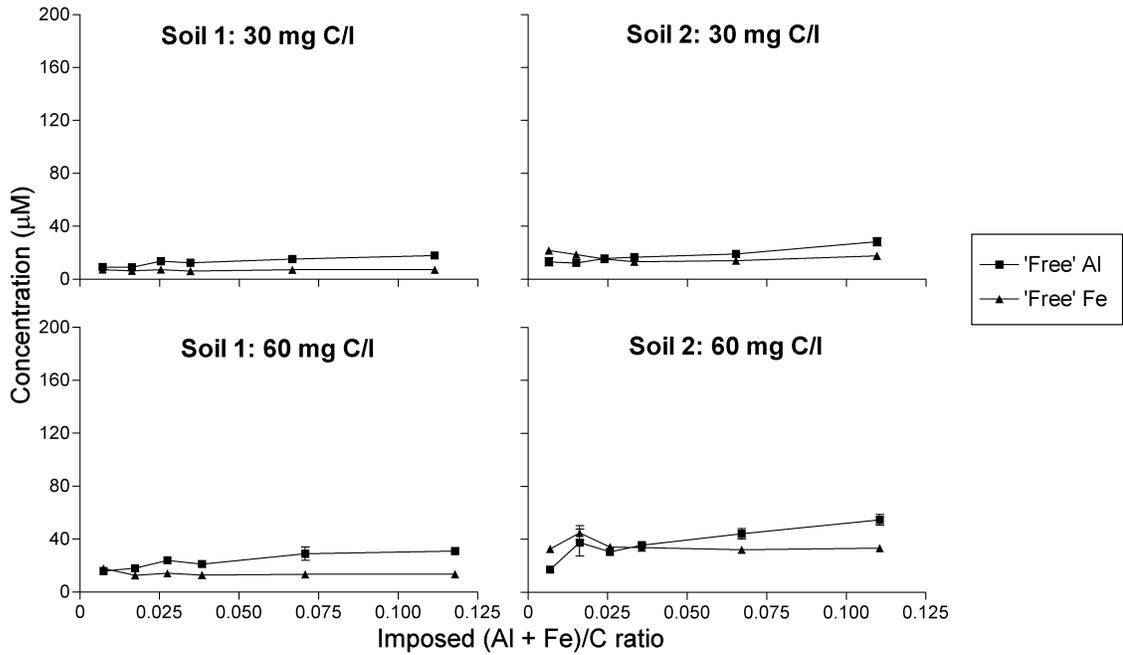


Fig. 2 'Free' metal concentrations in solution as a function of increasing imposed (Al + Fe)/C ratios (see the legend of Fig. 1 for explanation).

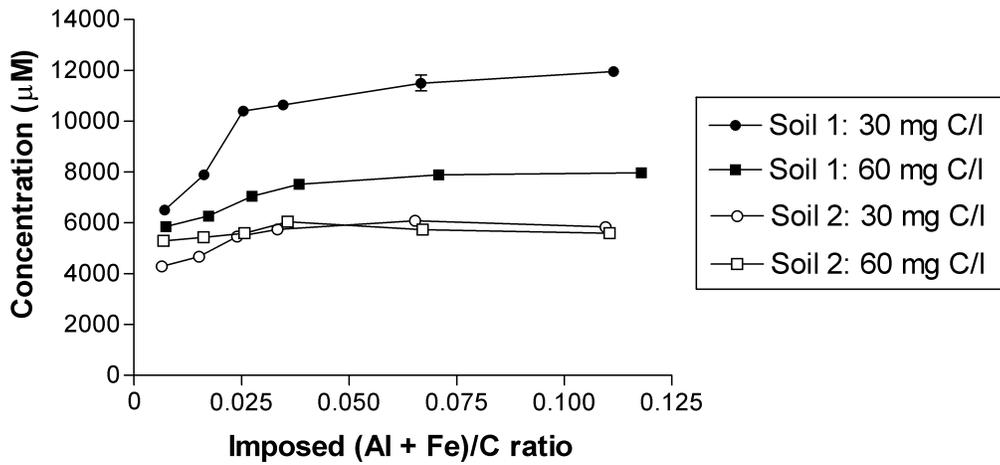


Fig. 3. DOC concentrations in solution as a function of increasing imposed (Al + Fe)/C ratios (see the legend of Fig. 1 for explanation).

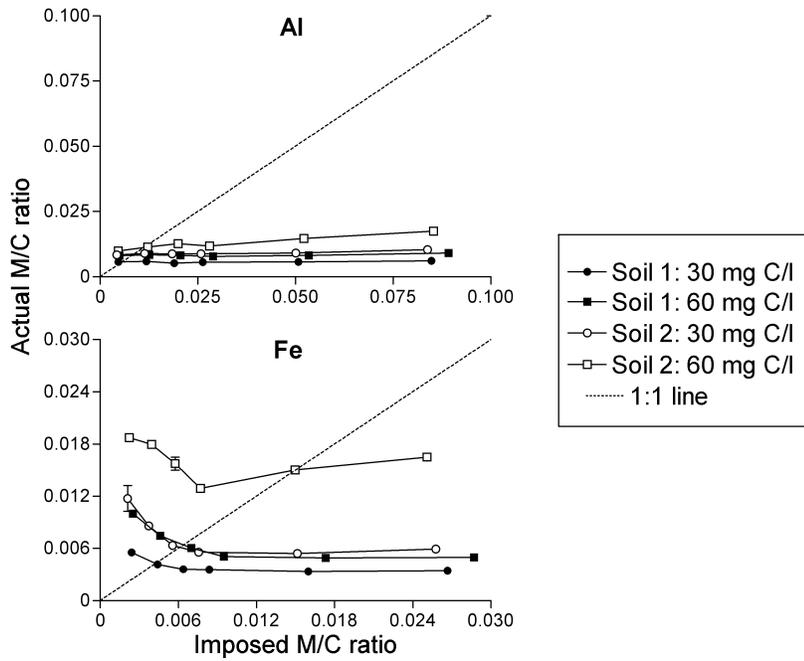


Fig. 4 Actual metal to organic carbon (M/C) ratios in solution as a function of the imposed (Al + Fe)/C ratios in solution (see the legend of Fig. 1. for explanation) for the A(h)E soil material.

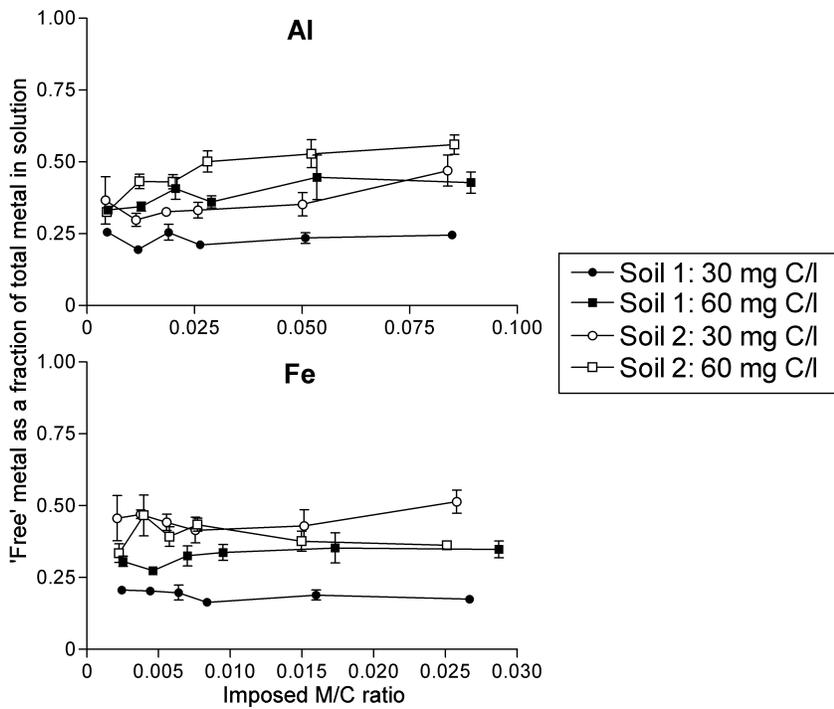


Fig. 5 The fraction of Al and Fe in solution that is present in the 'free' form, as a function of the imposed metal to organic carbon ratio (see the legend of Fig. 1 for explanation) for the A(h)E soil material.

6.3.3 Mobility of Al, Fe, Si and organic matter

In Fig. 6 and 7, we examined the net cumulative amount of Al, Fe, Si and organic matter that was mobilized or immobilized as a function of the imposed total M/C ratio. This approach is similar to the initial mass isotherm approach (Nodvin et al., 1986). For Al and Fe, the amounts were corrected for the addition of Al and Fe. A positive value means net mobilization, as more Al, Fe, Si or DOM is present in solution than the sum of initially dissolved amounts plus the amount added. A negative value signifies the opposite.

Initially, there was a significant net mobilization of Fe and Al in all cases. As the amount of added Al and Fe increased, net immobilization of Al and Fe took place, which resulted in the relatively constant concentrations of Al and Fe present in solution (Fig. 1). The slope of the (im)mobilization line during the last few additions for Al (Fig. 6) is approximately three times steeper than for Fe, which is explained by the fact that Al and Fe were added in a 3:1 ratio. The ratio of the slopes of both lines is smaller during the first few additions, which coincides with a decline of the Fe concentrations, whereas the Al concentrations initially show a small increase (Fig. 1). The mobilization and initial solution concentrations of both Al and Fe were larger in the experiments than in the blanks, indicating an active role of DOM in mobilizing Al and Fe from these two soil horizons. However, the pH values of the blanks were not adjusted (Table 2) so that the pH differed slightly from the pH values in the experiments.

6.3.3.1 Si

Because of the alleged influence of mobile (proto)imogolite or imogolite-like sols in the transport of Al and Fe in podzols (Anderson et al., 1982), we took a closer look at possible mobilization of Si. Fig. 3 shows that in the experiments with Soil 1, there was some mobilization of Si, without a clear difference between Soil 1: AhE:30 and Soil 1: AhE:60. In the case of Soil 2, there was no significant mobilization of Si. The Si concentrations shown in Fig. 1 were mostly caused by Si already present in the initial DOM solutions (Table 3).

6.3.3.2 Organic matter

Fig. 7 shows that in all cases there was a strong initial mobilization of organic matter that increased with increasing addition of Al and Fe. Organic matter mobilization was largest in the experiments with the lowest initial DOM concentration. The stronger mobilization surpassed the amount necessary to compensate for the higher initial DOM concentrations in the 60 mg C/l experiments, resulting in larger final concentrations in the 30 mg C/l experiments from the same soil (Fig. 3). A likely explanation is the higher pH in the 30 mg C/l experiments. When comparing the two soils, the mobilization was the strongest in Soil 1, which had the largest solid organic carbon content (see Table 1). These differences in initial mobilized amount of DOM between Soil 1 and 2 were also observed in the blanks (Table 2).

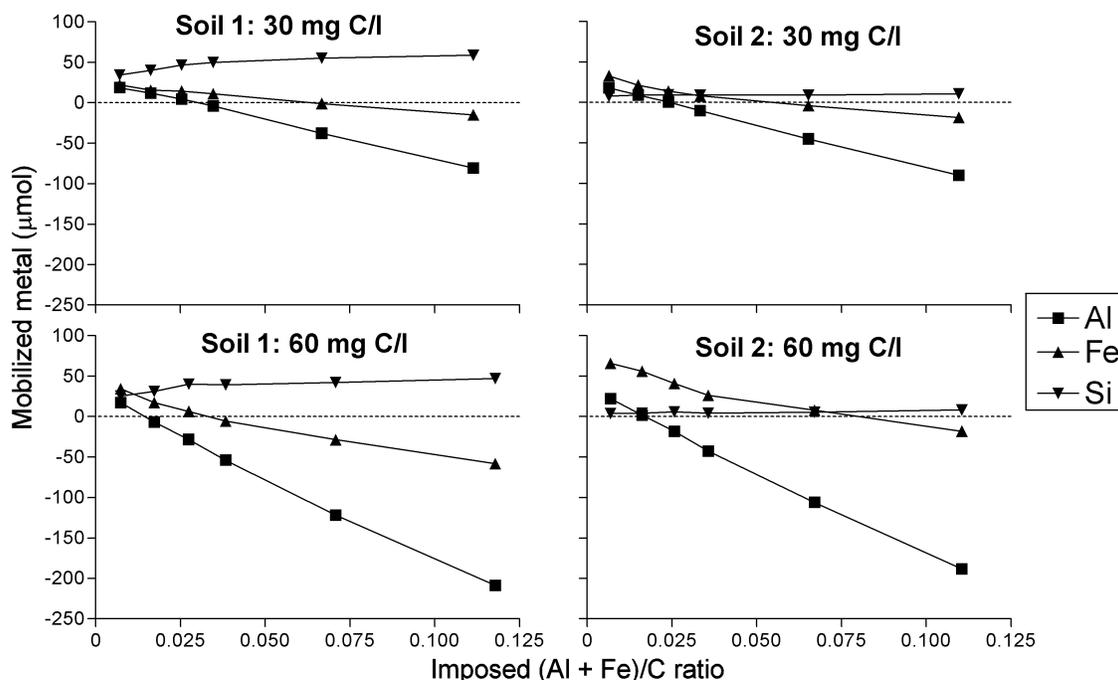


Fig. 6 The net cumulative number of μmol of Al, Fe and Si mobilized or immobilized over the course of the experiments as a function of increasing imposed (Al + Fe)/C ratios (see the legend of Figure 1 for explanation), corrected for the addition of Al and Fe.

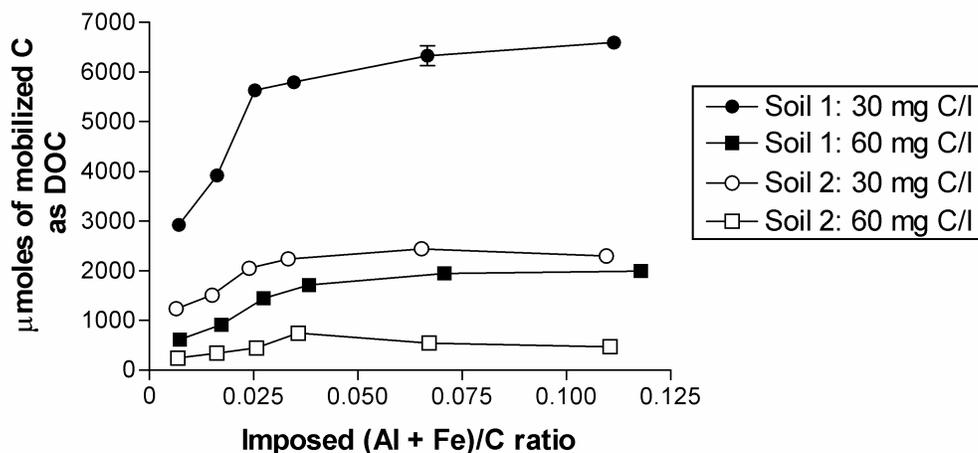


Fig. 7 The net cumulative number of μmoles of DOC mobilized or immobilized over the course of the experiments as a function of increasing imposed (Al + Fe)/C ratios (see the legend of Fig. 1 for explanation).

6.4 Discussion

6.4.1 Trends in M/C ratios and 'free' metal concentrations in solution

Both the M/C ratios in solution and the 'free' metal concentration were the lowest for Soil 1: AhE:30 and the highest for Soil 2: AE:60. A combination of a C_t content and little DOM, such as Soil 1: AhE:30, caused high adsorption of Al and Fe to solid phase organic matter, resulting in the lowest M/C ratio and the smallest 'free' metal fraction in solution. The initial decrease in Fe/C ratios with increasing metal additions was most likely caused by preferential adsorption to organic matter of Fe over Al. This is supported by the results from a previous study using DOM similar to that of Soil 1, where we observed preferential binding of Fe over Al to DOM in the pH range used in the present study (Jansen et al., 2002). However, one should keep in mind that in our previous study, only interactions of Al and Fe with DOM were investigated and that interactions with solid phase organic matter are not necessarily the same.

6.4.2 Trends in (im)mobilization of organic matter, Al and Fe

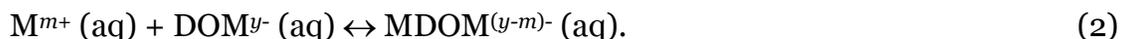
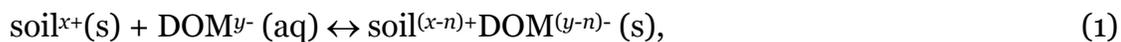
When comparing the two soils, the trends of (im)mobilization were remarkably similar except for greater initial mobilization of Fe in Soil 2, especially in Soil 2:

AE:60, which correlated positively with the larger BaCl₂ extractable Fe content of Soil 2 (Table 1). The initial amount of mobilized Fe was approximately 1.5 or 2.0 times larger for Soil 1: AhE:60 and Soil 2: AE:60, respectively, as compared to Soil 1: AhE:30 and Soil 2: AE:30. For Al, there was no clear correlation between initial mobilization and initial DOC content. A possible explanation is the preferential binding of Fe to DOM, resulting in a more pronounced response of the total Fe concentrations to changes in DOM concentrations. The slopes of the plots for 60 mg C/l were always steeper than for 30 mg C/l because twice as much Al and Fe needed to be added in the former experiments to obtain the same imposed M/C ratios. When this correction was taken into account, there was no significant difference in slopes.

6.4.3 mobilization of organic matter

The strong initial mobilization of organic matter depended on the initial DOM concentrations and the C_t content of the soil materials, and was most likely caused by dissolution of organic matter similar to that commonly observed in water extractions of organic-rich soil horizons. This is supported by the significant mobilization of organic matter that was also observed in the blanks (Table 2). The further mobilization of organic matter upon addition of Al and Fe may seem a bit surprising. Most likely the following processes played a role. First, bonding of Al³⁺ and Fe³⁺ to solid phase organic matter may have made the organic molecules more polar, thereby increasing the solubility in water of organic molecules that were too hydrophobic to dissolve in the initial step before metal addition. Second, 'free' Al and Fe may have competed with organo-metal complexes bound to solid phase organic matter through cation bridging. Third, sorption equilibria for organic matter adsorbed on solid phase Al and Fe may have shifted towards dissolution of organic matter because of binding to 'free' Al and Fe in solution. This latter mechanism can be described as follows. In a system without dissolved Al or Fe, negatively charged DOM can be adsorbed at positively charged sites on the solid matrix (reaction 1) and consequently be removed from solution. However, when dissolved Al or Fe are present, the negatively charged DOM can also react with dissolved Al or Fe (reaction 2) and remain in solution. As a

consequence, the equilibrium of reaction 1 will shift to the left, resulting in more organic matter staying in solution, either in the form of 'free' DOM or in soluble Al or Fe-DOM complexes:



In the first equation, x represents the charge on the adsorption site on the solid phase, y represents the charge on the dissolved organic molecule and n represents the number of binding places involved in the adsorption of the organic molecule. In the second equation, M represents an Al or Fe cation, m represents the charge on the Al or Fe cation and y again represents the charge on the dissolved organic molecule. Third, reduced concentrations of uncomplexed DOM upon metal binding, may have increased the dissolution of organic matter not attached to minerals.

6.4.4 Mobilization of Al and Fe

The initial mobilization of Al and Fe can be explained by desorption from negatively charged binding sites on solid phase organic matter, which is supported by the relation with BaCl_2 extractable amounts of Al and Fe (Table 1). Desorption may have been induced by transfer of Al and Fe from solid phase organic matter to DOM that, on average, has a lower molecular weight and is more hydrophilic (Herbert and Bertsch, 1995). While other factors influence the solubility of organic matter as well, in general a higher hydrophilicity is indicative of a higher charged functional group content and therefore higher reactivity towards metal binding. The initial removal of metals seemed indeed partly influenced by the presence of DOM, as evidenced by the dependence of the initial Fe desorption on the initial DOM concentration in solution. However, this effect cannot be separated from the difference in imposed pH. For Al, there was no clear correlation between initial mobilization and DOM concentrations. Possibly this is caused by some Al that was desorbed in the form of organic Al complexes as

mentioned before. Also, competition for binding sites on DOM with the more strongly binding Fe, especially at the lower pH value in the 60 mg C/l experiments, might have played a role (Jansen et al., 2002). The immobilization of Al and Fe, as more metal was added, was probably caused by direct adsorption on solid phase organic matter. However, the total DOC concentrations in solution slowly increased as more metal was added. Furthermore, significant amounts of Al and Fe remained bound to the mobilized DOM, as shown by the low 'free' metal fractions in solution throughout the experiments. Apparently, as available binding sites on DOM became rare, increased adsorption on the large pool of available solid phase organic matter occurred. The drop in Fe/C ratios in solution as compared to constant Al/C ratios in solution throughout the experiments, again indicates preferential adsorption of Fe over Al on solid phase organic matter. Increasing amounts of bound Al, expressed as the equivalent ratio of the moles of organically bound Al divided by the moles of carboxylic groups in batch addition experiments with organic horizons from sandy soils were also reported by others (De Wit et al., 1999; De Wit et al., 2001). Furthermore, in agreement with the Al concentrations increasing over the course of the experiments (Fig. 1), they found increasing solubility of Al at increasing additions of Al.

Recently, a number of articles has been published in which a simple model was proposed to describe the total Al concentration in solutions of forest O, A and B horizons in the presence of organic ligands. At $\text{pH}_{\text{H}_2\text{O}} < 4.2$, the solubility of Al is controlled by complexation on solid organic matter, whereas at $\text{pH}_{\text{H}_2\text{O}} > 4.2$ the Al^{3+} concentration can be described by the dissolution equilibrium with $\text{Al}(\text{OH})_3(\text{s})$ (Berggren and Mulder, 1995; Gustafsson et al., 2001; Simonsson and Berggren, 1998; Wesselink et al., 1996). Considering the $\text{pH}_{\text{H}_2\text{O}}$ of the two soil horizons tested (Table 1), this would mean that the solubility of Al in both would be controlled by the former mechanism. Indeed, the strong immobilization of Al upon metal addition we observed indicates that adsorption on solid phase organic matter plays an important role in regulating Al concentrations in the two soils under study. To test for this, we considered the relationship proposed by Wesselink et al. (1996) to describe the solubility of Al in systems where control by organic

matter is expected. This relationship can be expressed by the following equation (Wesselink et al., 1996):

$$\log Al_t = \log (A_{org}/C_{org}) - xpH + \log K_{H-Al}, \quad (3)$$

where Al_t is the total Al concentration in solution, A_{org} is Al bound to solid phase organic matter, C_{org} is the amount of solid organic carbon present, K_{H-Al} is the complexation constant for Al with solid phase organic matter and x is a parameter representing the reaction stoichiometry. Wesselink et al. (1996) fitted the parameters x and $\log K_{H-Al}$ on an extensive dataset from mineral soils in the Netherlands, Sweden and Germany and obtained the following optimal parameters: $x = 1.08$ and $\log K_{H-Al} = 1.63$.

We attempted to model our total Al data by using equation (3) and the optimised parameters from Wesselink et al. (1996). We assumed all Al immobilized per time step had become organically-bound Al and we combined all our observations in a single dataset. This led to poor fits, regardless of whether pyrophosphate extractable or oxalate extractable Al was used or pyrophosphate extractable or total carbon. The main problem was that the measured Al concentrations increased more rapidly over the course of the experiments than predicted by the model. However, the pH was kept constant in our experiments and the initial amounts of solid phase Al were high compared to the subsequently immobilized amounts. Since these are the two main input variables in equation (3), the range of variation in the input was too constrained to allow thorough testing of the applicability of the proposed model in the two soil horizons under study.

6.4.6 The influence of cation bridging

In addition to the proposed mobilization, at the initial metal additions, of soluble organic Al complexes bound through cation bridging, towards the end of the experiments there were again indications of organo-metal complexes binding to solid phase organic matter through cation bridging (Guggenberger and Zech, 1993). The indication is a slight increase in the 'free' Al and Fe fraction in

combination with a slight decrease in mobilized DOM, which is especially visible in Soil 2: AE:60 (Fig. 6). The shift from desorption to adsorption of cation bridged organo-metal complexes can be assigned to the increasing amounts of adsorbed Al and Fe on solid phase organic matter, and the increasing concentrations of DOM in solution. It is not surprising that the effect was most pronounced in Soil 2: AE:60 because here the amount of mobilized DOM was the smallest, the metal additions the largest and the C_t content also the smallest.

In contrast to our results, other studies of DOM dynamics in forest soils (Kalbitz et al., 2000; Lofts et al., 2001) found an immediate decrease of mobilized DOM with added metals in solid phase organic matter-rich sandy topsoil horizons. Such immobilization is usually also attributed to cation bridging. However, in most cases the amounts of extractable Al and Fe were higher and the amounts of total carbon lower than in our experiments (Lofts et al., 2001). In line with the trends observed in our experiments when going from Soil 1: AhE:60 to Soil 2: AE:30, we expect a more significant role of immobilization of DOM through cation bridging at increasing metal additions, in soils with less solid phase organic matter and more extractable Al and Fe than Soil 2. Still, one should keep in mind that some of the differences between literature reports and the present study might also have been caused by differences in the experimental set-up.

6.4.7 The influence of imogolite sols

The low amounts of Si mobilized in Soil 1, the absence of Si mobilization in Soil 2 and the lack of correlation between Si and Al/Fe (im)mobilization, leads us to believe that Si does not play a significant role in the mobilization of Al and Fe from the eluvial horizons in these soils.

6.4.8 Summary of the mechanisms governing the mobility of Al, Fe and organic matter

We propose the following mechanisms to explain the observed (im)mobilization of Al, Fe and organic matter in the eluvial podzol horizons under study.

- 1) Organic matter was mobilized by detachment from solid soil material. As Al and Fe were added, extra organic matter was mobilized due to competition of 'free' Al and Fe with organo-metal complexes adsorbed on solid phase organic matter through cation bridging, and desorption of organic matter from solid phase Al and Fe complexes upon addition of further Al and Fe.
- 2) Both Al and Fe were initially mobilized by formation of soluble complexes with DOM. The more Al and Fe was added, the larger the portion of the metals that was immobilized by adsorption on solid phase organic matter.
- 3) Towards the end of the experiment, there were indications at higher imposed M/C ratios of immobilization of soluble organic Al/Fe complexes through cation bridging.
- 4) Formation of (proto)imogolite or imogolite-like sols did not play a significant role in the mobilization of Al or Fe.

6.5 Conclusions

The observed low M/C ratios and the high percentage of Al and Fe that was present in the form of (mobile) dissolved organo-Al and Fe complexes agrees well with the results from previous research in the absence of solid soil material. Furthermore, both the M/C ratios in solution and the portion of metals in soluble organic complexes remained remarkably constant upon Al or Fe addition. This means that the eluvial horizons of both soils can buffer short-term changes in DOM, Al and Fe concentrations. Furthermore, our results indicate an important role of soluble organic complexes of Al and Fe in both mobilizing DOM and maintaining relatively high concentrations of Al and Fe in solution, while immobilization of dissolved organo-metal complexes through cation bridging played only a limited role.

This study confirms the expected DOM-facilitated mobilization of Al and Fe from eluvial horizons. It also shows that even under fluctuating input of DOM, Al and Fe from the overlying horizons, the soil solution leaving the eluvial horizons will most likely have a steady composition with respect to the M/C ratio and

percentage of organically-complexed metals. In the long run, the steady removal of organic matter, Al and Fe is expected to change the soil solution composition as the soil horizon becomes depleted of organic matter and metals. These results have important implications when assessing the influence of environmental changes on the mobility of Al, Fe and DOM in sandy soils and the process of podzolization. However, our study was performed using batch experiments in which the contact time was long enough to assume equilibrium. In the field, this may not always be the case as water flow in sandy soils can be fast, especially along preferential flow paths. Kinetic studies using soil columns and field manipulation experiments may be helpful in shedding further light on the mobility of Al, Fe and DOM in eluvial podzol horizons.

7

Mechanisms controlling the mobility of dissolved organic matter, Al and Fe in podzol B horizons*

Abstract

The processes governing the (im)mobilization of Al, Fe and DOM in podzols are still subject to debate. In this study we investigated the mechanisms of (im)mobilization of Al, Fe and organic matter in the upper and lower B horizons of a younger and a more developed podzol from the Netherlands. We equilibrated batches of soil material from the different horizons with dissolved organic matter (DOM) solutions obtained from the Oh horizon of the same profile. We determined the amount of (im)mobilized Al, Fe and DOM after addition of Al and Fe at pH = 4.0 and 4.5 and an initial DOC concentration of 10 mg C/l or 30 mg C/l respectively. We observed some mobilization of organic matter in the younger soil, while organic matter was immobilized in the more developed one. In the upper B horizon of the younger soil, after initial mobilization, Al and Fe were immobilized by direct adsorption on solid organic matter. In the other B horizons at pH = 4.5 adsorption in the form of Al/Fe-DOM complexes and both organic and inorganic precipitation led to immobilization of Al and Fe immediately or after the first few metal additions. Fe was immobilized more strongly than Al and for Fe inorganic precipitation seems to have played a role in all cases. Inorganic precipitation only controlled Al concentrations in the lower B horizons of both soils. The results confirm the important role of organic matter in the transport of Al and Fe to initially create a B horizon and subsequently deepening and differentiating it into a Bh and Bs horizon. Except for solubility control by inorganic precipitation of Al, all results are in agreement with the classical fulvate theory. The discrepancy can be explained by our use of recent, more constrained K_{so} values of $Al(OH)_3(s)$.

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7.1 Introduction

Podzols are characterized by a bleached eluvial E horizon from which organic matter, Al and Fe have been removed, overlying one or more illuvial B horizons in which organic matter, Al and in most cases Fe have been deposited (FAO, 1988). Podzols and podzolization have been the subject of research for many decades, yet no consensus exists concerning the exact mechanisms involved in the mobilization and immobilization of Al, Fe and organic matter. As a consequence, several podzolization theories currently exist. The classical fulvate theory (De Coninck, 1980; Mokma & Buurman, 1982; Petersen, 1976) proposes that initially, Fulvic Acid (FA) dissolves primary and secondary minerals in the E horizon. The Al and Fe thereby released react with FA to form soluble dissolved organic Al and Fe complexes. While moving downwards through the soil profile, the organic molecules become saturated as more and more Al and Fe bind to them leading to precipitation in the B horizons as the negative charge on the DOM molecules is sufficiently compensated by the positive charge on the binding Al and Fe cations.

In an alternative podzolization theory, DOM does not play an active role at all in the process of podzolization: neither in mobilizing Al and Fe in the eluvial horizons nor in immobilizing them in the illuvial horizons (Anderson et al., 1982; Farmer & Lumsdon, 2001). According to this theory, positively charged inorganic (proto)imogolite sols carry Al, Si and intrusions of Fe from the eluvial to the illuvial horizons. The adsorption of DOM on solid phase Al and Fe in the top of the B horizon as well as dissolution of Al-solid organic matter (SOM) complexes and allophanic precipitates at the Bh-Bs interface followed by precipitation in the form of immogolite, causes the development of Bh and Bs horizons and deepens the podzol profile. In this theory, Al/Fe-DOM complexes only play a role in recycling Al and Fe that was moved to the O horizons by biological processes, back to the B horizons.

Gustafsson et al. (2001) also propose immobilization of Al in B horizons in the form of inorganic precipitates at the higher pH values (> 4.2) that are generally found in B horizons. However, they suggest that precipitation is induced by the equilibrium of dissolved Al with $\text{Al}(\text{OH})_3(\text{s})$ and explicitly rule out that imogolite

plays a significant role. At pH values below 4.2 such as found in the O and E horizons, they propose equilibria with SOM to control the solubility of Al. Also, in contrast with the previous theory but analogous to the classical fulvate theory, they believe that DOM acts as a carrier that transports Al and Fe to the B horizons.

Another contemporary podzolization theory was formulated by Lundström et al. (2000) after a study of several Scandinavian podzols. They observed that 40% of dissolved Al was complexed with low molecular weight (LMW) organic acids in the O and E horizons, decreasing to 20% in the B horizons. Furthermore, in contrast with the classical fulvate theory, they found no indications of saturation of DOM molecules with Al and Fe in the illuvial horizons. As a consequence, they propose that complexation of Al and Fe to LMW organic acids plays a main role in the mobilization of Al, Fe from podzol E horizons. Subsequently, microbial degradation of the LMW organic acid carrier deeper in the soil followed by precipitation of inorganic Al and Fe complexes in the form of simple metal hydroxides or imogolite is responsible for the immobilization of Al and Fe in the B horizons. In addition, some dissolved organic Al/Fe complexes are adsorbed on solid phase Al and Fe, after which the organic 'tail' of the dissolved organic Al/Fe complexes is removed by microbial degradation. Dissolved high molecular weight organic acids that are more resistant to microbial degradation than LMW organic acids, in turn are adsorbed on solid phase Al and Fe.

Most likely several different mechanisms are involved in the process of podzolization and the dominant mechanism varies in different soils, possibly linked to the variation in climate under which the soil is formed (Mossin et al., 2002; Van Breemen & Buurman, 2002). Still much scientific debate about the topic of podzolization remains.

In order to gain more insight into the interactions of Al, Fe with organic matter and the influence thereof on the process of podzolization, first in previous studies we examined the influence of changes in metal to organic carbon (M/C) ratios, pH and the valency of Fe on the extent of soluble and insoluble complexation with DOM in the soil solution from a podzolic soil (Jansen et al., 2002; Jansen et al., 2003b; Nierop et al., 2002). Because of their multiple charge,

Al and Fe are able to form strong, specific bonds with multiple functional groups of the same organic molecule (Pohlman and McColl, 1988; Tam and McColl, 1991). Without the presence of solid soil components, the complexation of Al and Fe with DOM affects their potential mobility in two ways. On the one hand, binding of Al and Fe to DOM can lead to the formation of insoluble organic Al/Fe complexes. On the other hand binding of Al and Fe to DOM lowers their respective 'free' metal concentrations and thereby prevents precipitation as insoluble inorganic Al and Fe phases.

When solid soil components are present, the solution composition and consequently the interactions of Al and Fe with DOM are influenced by ad- or desorption of Al, Fe and DOM to those solid soil components. Furthermore, the speciation in solution over 'free' metals and soluble organic metal complexes influences the mobility of both metals and organic matter. While the formation of may mobilize both metals by preventing adsorption on solid phase organic matter, soluble organic Al/Fe complexes may themselves be immobilized by forming ternary complexes with either solid phase organic matter through cation bridging, or with Al and Fe secondary solid phases through acidic functional groups on the DOM molecules (Schmitt et al., 2002). Therefore, to better understand the implications of interactions of Al and Fe with DOM on their mobility in podzols, an investigation of the mobility of Al and Fe in the presence of solid soil material is necessary. Consequently, in a recent study we investigated the mobility of Al, Fe and DOM in batch metal addition experiments using solid soil material from eluvial podzol horizons (Jansen et al., 2003c). We observed that due to interactions with the solid phase, the metal to organic carbon (M/C) ratios in solution remained low enough to prevent insoluble organic complexation even when significant amounts of Al and Fe were added. Furthermore, we found strong indications of a significant role of DOM in the mobilization of Al and Fe (Jansen et al., 2003c).

The purpose of the present study was to investigate the influence of solid soil material from illuvial (B) horizons of two soils from the Veluwe in the Netherlands on the solution chemistry with respect to interactions of Al and Fe with DOM and the mobility of Al, Fe and organic matter. To accomplish this, we

chose a younger podzolic soil and an older podzol with B horizons that differed in contents of SOM and solid secondary (amorphous) Al and Fe phases. We equilibrated the soil horizons with DOM solutions of different pH and imposed a range of M/C ratios by addition of Al and Fe. After each addition we determined the fraction of Al and Fe bound to organic matter in solution and assessed the net cumulative amount of (im)mobilized metal and organic matter.

7.2 Materials and methods

All chemicals used in the experiments were of analytical grade and all glassware was acid and nano-pure (18.3 M Ω) water rinsed prior to use, to avoid contamination. All experiments were carried out in quadruplicate.

7.2.1 Description of soil materials

Two acidic sandy soils in the Netherlands were used in the experiments. Soil 1: A young, incipient Podzol under oak (Fimic Anthrosol) (FAO, 1988) and Soil 2: an older Podzol under heath with a well developed, buried profile (Haplic Podzol) (FAO, 1988). The choice of these two soils was based on the relative amounts of solid organic material versus amorphous iron and aluminum (hydr)oxides present. From both soils two illuvial horizons, the Bhs and BC horizons of Soil 1 and the 2Bhs1b and 2Bsb horizons of Soil 2 were used in the experiments. The soil samples were initially characterized as follows. Water extractable and exchangeable cations were determined by water (1:1 w/v) and 0.125 M BaCl₂ (1:25 w/v) extractions. Labile amorphous organically bound Al was determined by 0.5 M CuCl₂ extraction (Juo and Kamprath, 1979). Total amorphous and total organically bound amorphous Al and Fe were estimated by ammonium oxalate/oxalic acid extraction (pH = 3.0, 1:50 w/v, in the dark) and 0.1 M sodium pyrophosphate/NaOH extraction (pH = 9.5, 1:75 w/v). In the latter extract organic carbon was also determined. Total Al and Fe were determined by destruction using HF/HNO₃/HCl (Dixon and Weed, 1989 and references cited therein). The total carbon content, was determined using an Elementar Vario EL

CNS analyzer. Finally, the samples were analyzed for the presence of imogolite using IR spectroscopy after an acid dispersion procedure (Farmer et al., 1980).

7.2.2 Preparation of DOM solutions

The DOM solutions used in the experiments were obtained by water extraction of the Oh horizons of both soils. We sieved the collected Oh material without prior drying over 2 mm, using a polyethylene sieve to avoid metal contamination. DOM solutions were then prepared by extraction of the sieved material in a 1:3 w/w ratio to nano-pure (18.3 M Ω) water. The resulting suspensions were shaken for 16 hours, centrifuged at 23,000g for 30 minutes and filtrated over a 0.45 μ m membrane filter. The DOM solutions that were thus obtained from each of the two Oh horizons, had a dissolved organic carbon (DOC) concentration of approximately 30 mg C/l. Both were divided over two aliquots and one of each was subsequently diluted to create a DOC concentration of approximately 10 mg C/l. The pH of the 30 mg C/l solutions was adjusted to pH = 4.0 and that of the 10 mg C/l solutions to pH = 4.5 by adding small quantities of 1.0 M KOH. The initial composition of the resulting four DOM solutions is presented in Table 1.

Table 1
Initial composition of the DOM solutions:^a

| | DOC | Fe | Al | Ca | Mg | Si |
|-------------------|---------------|---------|---------|---------|---------|---------|
| | μ mol C/l | μ M |
| Soil 1; 30 mg C/l | 2600 | 6.5 | 12.5 | 15.5 | 11.0 | 46.5 |
| Soil 1; 10 mg C/l | 900 | 2.1 | 4.3 | 5.4 | 3.7 | 16.4 |
| Soil 2; 30 mg C/l | 2640 | 5.5 | 11.5 | 10.0 | 10.0 | 76.0 |
| Soil 2; 10 mg C/l | 967 | 2.1 | 4.4 | 3.9 | 3.5 | 28.5 |

^a Only polyvalent, positively charged species present in concentrations ≥ 1.5 μ M and Si are shown.

To all DOM solutions sodium azide (NaN₃) was added to obtain an overall electrolyte concentration of 0.01 M. This served to prevent microbial degradation of DOM during the experiments (De Maagd et al., 1998) and to maintain the overall ionic solution strength in the metal addition experiments, since ionic strength influences the binding of metals to DOM (Stevenson, 1994). Furthermore, the addition of NaN₃ prevented problems with measurements of

free metals at very low ionic solution strengths using Diffusive Gradients in Thin films (DGT) (Alfaro-De la Torre et al., 2000). The addition of NaN_3 resulted in a slight rise in pH due to the formation of HN_3 . This was compensated by the addition of minute amounts of a concentrated HNO_3 solution.

7.2.3 Experimental setup

Samples of the illuvial soil horizons from both soils were placed in closed glass containers in an isothermic room at 20°C without prior drying. To the samples of each soil, the two DOM extracts from the same soil profile at the two different DOC concentrations were added in separate batches, resulting in two different initial situations per soil. The solid to solution ratio was 1:5 with a liquid volume of 750 ml taking into account the moisture content of the soil samples. The 10 mg C/l, pH = 4.5 solution was chosen as a realistic DOC concentration and pH for the type of horizon used in our experiments (Mokma and Buurman, 1982; Petersen, 1976). The 30 mg C/l, pH = 4.0 solution was chosen to assess the influence of a change in pH and DOC content. In addition, it allowed us to compare the B horizons with eluvial soil material (Jansen et al., 2003c). In total, eight different situations were created, that were coded according to soil number, soil horizon and initial DOM concentration, thus ranging from: Soil 1:Bhs:10 to Soil 2:Bsb:30*.

The initial soil/solution mixtures were shaken for 120 hours to equilibrate. Subsequently, the mixtures were shaken vigorously to obtain a homogeneous suspension from which samples were taken for analysis. These samples were centrifuged at 40,000g and filtrated over 0.45 μm to separate solid materials from solution. In the filtrated samples, dissolved organic carbon (DOC) and total Al, Fe and Si contents were determined. After sampling, DGT units were deployed in the soil/solution mixtures that were again shaken for 16 hours, after which the units were collected and 'free' Al and Fe in solution were determined from the Al and Fe adsorbed on the chelating gel in the DGT units.

After the initial step, Al and Fe(III) were added to the different soil/solution mixtures in the form of small amounts (< 1.0 ml) of solutions of their nitrate salts

* For reasons of clarity, the prefix '2' was omitted from the label of the two horizons of Soil 2.

in a 3:1 Al to Fe(III) ratio in 5 sequential steps to impose a range of M/C ratios (see Table 4). When the addition of metals resulted in a change in pH, this was corrected by addition of minute amounts of a concentrated KOH solution. After each addition of metals the soil/solution mixture was shaken for 24 hours before being sampled and analyzed in a manner similar to the initial suspensions. In total the duration of the experiments was 384 hours. The experiments were performed in two sets, with experimental situations randomly assigned to either set.

In addition to the experiments with soil samples and DOM solutions, batch experiments of the same soil samples with nanopure (18.3 M Ω) water and again a background of 0.01 M NaN₃ were performed as blanks. They were treated and sampled the same way as the initial soil/solution mixtures in the experiments with DOM, however the pH values were not constrained.

7.2.4 Analyses

DOC contents were determined by colorimetric determination on a Skalar continuous flow autoanalyzer. Metals were determined on a Perkin Elmer Optima 3000XL ICP-OES. Prior to analysis, the samples to be determined on ICP were acidified to pH = 1.0 with concentrated HNO₃, to dissociate the metal complexes that were present. The Al and Fe content of the different extractions performed for characterization of the soil samples were also determined on the ICP, except for the pyrophosphate extractable metals that were determined on a Perkin Elmer 5000 flame AAS due to interference of the medium with ICP measurements. The AAS data had a detection limit that was two orders of magnitude higher than by ICP measurement.

The 'free' metal contents were determined by Diffusive Gradients in Thin films (DGT). 'Free' metals as determined by DGT consist of hydrated metal cations and soluble inorganic complexes as well as a very small portion of the smaller labile metal-DOM complexes (Zhang and Davison, 1999). In previous studies we successfully tested the applicability of DGT for the determination of 'free' Al, and Fe in acidic forest soil solutions of similar composition (Jansen et al., 2001;

Jansen et al., 2002). The DGT units were obtained from DGT Research Ltd, UK. The units consisted of a Na⁺ saturated Chelex 100 disc, covered with an APA hydrogel layer of 0.8 mm and a 0.45 µm membrane filter.

7.3 Results

7.3.1 Chemical soil properties

In Table 2 the composition of the soil material used in this study with respect to the different pools of Al, Fe, Si and organic carbon is presented. We found no evidence of the presence of imogolite in the IR spectra (results not shown).

The total carbon to oxalate extractable Al and Fe (C_t/M_o) molar ratios as well as the total carbon to pyrophosphate extractable Al and Fe (C_t/M_p) ratios were in all cases lower than 50, which is a threshold value that can be used to distinguish between eluvial and illuvial podzol horizons (Mokma and Buurman, 1982) This confirms the illuvial character of the soil material used in this study. In addition, the C_t/M_p ratios as well as the C_t/M_o ratios decreased in the order: Soil 1:Bhs > Soil 1:BC > Soil 2:Bhs1b > Soil 2:Bsb. These ratios are an indication of the relative amount of negatively charged sorption sites on SOM as compared to positively charged sorption sites on amorphous Al and Fe phases. The trend confirms the observation that Soil 2 is a more developed podzol (Mokma and Buurman, 1982), as was also noticed for the A(h)E horizons (Jansen et al., 2003c).

Other indications that Soil 1 and 2 are in different stages of podzolization are the differences in the amount of amorphous Al and Fe phases present. In Soil 1 in both horizons organically amorphous Al and Fe phases were strongly dominant over the inorganic amorphous species, while in Soil 2 this was only the case for the Bhs1b horizon. The smallest pyrophosphate extractable carbon to pyrophosphate extractable Al (C_p/Al_p) ratio and the smallest $C_p/(Al_p + Fe_p)$ ratio in the soils under consideration were found in Soil 1:BC and Soil 2:Bsb respectively, which are the two lowest B horizons of either soil. Since these ratios represent the ratio of reactive carbon to reactive Al and Fe, they are in accordance with the lower B horizons in both soils having a Bs signature, as opposed to the

upper B horizons in both soil having a Bh signature (Mokma and Buurman, 1982).

Table 2

Initial composition of the soil samples used in the experiments.

| | Al _{BaCl₂} mmol/ kg | Al _{CuCl₂} mmol/ kg | Al _p mmol/ kg | Al _o mmol/ kg | Al _t mmol/ kg | Si _o mmol/ kg | C _t mmol/ kg |
|---------------|---|---|--------------------------------|--------------------------------|--|--|---------------------------------|
| Bhs Soil 1 | 3.40 | 6.05 | 8.60 | 12.25 | 461.5 | 0.85 | 525.9 |
| BC Soil 1 | 3.00 | 13.75 | 31.20 | 39.30 | 516.5 | 3.65 | 530.8 |
| 2Bhs1b Soil 2 | 5.15 | 34.45 | 139.45 | 146.40 | 462.5 | 2.25 | 1751.8 |
| 2Bsb Soil 2 | 1.20 | 14.25 | 52.80 | 80.45 | 468.5 | 13.15 | 462.0 |
| | Fe _{BaCl₂} mmol/ kg | Fe _p mmol/ kg | Fe _o mmol/ kg | Fe _t mmol/ kg | C _t /(Al _o + Fe _o) | (Al _o -Al _p)/Si | C _p /Al _p |
| Bhs Soil 1 | 0.030 | 9.15 | 10.65 | 65.70 | 23.0 | 4.4 | 25 |
| BC Soil 1 | 0.015 | 6.80 | 7.75 | 70.10 | 11.5 | 2.2 | 6.7 |
| 2Bhs1b Soil 2 | d.l. ^a | 66.95 | 67.50 | 102.20 | 8.0 | 3.1 | 9.0 |
| 2Bsb Soil 2 | 0.005 | 9.75 | 14.05 | 52.55 | 5.0 | 2.1 | 5.9 |

M_{BaCl₂} = water extractable + exchangeable metal; Al_{CuCl₂} = copper chloride extractable aluminum; M_p = pyrophosphate extractable metal; M_o = ammonium oxalate extractable metal; M_t = total metal from destruction with HF/HNO₃/HCl; C_t = total organic carbon (CNS analysis); C_p = pyrophosphate extractable organic carbon.

^ad.l. = below the detection limit (< 0.004 mmol/kg for Fe)

Table 3

Average composition of four blanks in which the soil samples used in the experiments were shaken for 5 days with nanopure water containing 0.01 M NaN₃.

| | pH | total Al μM | total Fe μM | total Si μM | 'free' Al μM | 'free' Fe μM | DOC μmol C/l |
|--------------|------|----------------|-------------------|----------------|-------------------|-------------------|-----------------|
| Soil 1:Bhs | 4.27 | 26.6 | 19.6 | 23.1 | 5.1 | 2.0 | 1445 |
| Soil 1:BC | 4.53 | 30.6 | 3.3 | 19.6 | 11.3 | d.l. ^a | 738 |
| Soil 2:Bhs1b | 4.42 | 18.0 | d.l. ^a | 22.0 | n.d. ^b | n.d. ^b | 234 |
| Soil 2:Bsb | 4.54 | 13.9 | d.l. ^a | 18.2 | n.d. ^b | n.d. ^b | 170 |

^ad.l. = below the detection limit (< 0.1 μM for Fe). ^bn.d. = not determined

In Table 3 the average solution composition of the blanks is provided. The suspensions of soil material from both horizons of Soil 2 contained very fine material that got between the ring and the base of the DGT unit and caused leakages during the experiments and contamination upon opening of the units. Unfortunately, this lead to unacceptably high variance in the 'free' metal results of both the blanks and the actual experiments. As a consequence, the 'free' Al and Fe

concentrations from Soil 2 are not given. Still they have to be very low if total amounts of Al and Fe are taken into account.

Table 4

Theoretical Al and Fe concentrations in solution over the course of the experiments, assuming all metal to have stayed in solution and corrected for sampling.

| | | Addition 1 ^a (μM) | Addition 2 (μM) | Addition 3 (μM) | Addition 4 (μM) | Addition 5 (μM) |
|---------------------|----|--|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Soil 1 | | | | | | |
| Bhs:10 ^b | Al | 45.6 | 53.9 | 62.5 | 82.0 | 93.7 |
| Bhs:10 | Fe | 39.3 | 45.0 | 53.3 | 61.3 | 64.4 |
| Bhs:30 | Al | 75.4 | 83.4 | 87.5 | 135.1 | 162.1 |
| Bhs:30 | Fe | 66.5 | 73.2 | 77.1 | 91.8 | 102.9 |
| BC:10 | Al | 49.9 | 55.8 | 59.3 | 75.0 | 83.9 |
| BC:10 | Fe | 14.9 | 16.1 | 16.7 | 22.4 | 22.6 |
| BC:30 | Al | 122.0 | 156.0 | 167.8 | 214.7 | 258.7 |
| BC:30 | Fe | 33.0 | 41.1 | 47.1 | 63.4 | 76.7 |
| Soil 2 | | | | | | |
| Bhs1b:10 | Al | 35.7 | 36.1 | 35.9 | 45.2 | 57.6 |
| Bhs1b:10 | Fe | 7.6 | 7.0 | 7.7 | 11.3 | 14.4 |
| Bhs1b:30 | Al | 187.2 | 309.1 | 315.8 | 354.1 | 411.5 |
| Bhs1b:30 | Fe | 18.2 | 24.8 | 28.7 | 44.2 | 53.6 |
| Bsb:10 | Al | 34.3 | 43.4 | 44.7 | 55.8 | 64.9 |
| Bsb:10 | Fe | 3.9 | 3.0 | 3.8 | 8.4 | 11.2 |
| Bsb:30 | Al | 153.6 | 240.2 | 274.6 | 321.6 | 385.8 |
| Bsb:30 | Fe | 9.0 | 10.7 | 12.7 | 28.1 | 38.9 |

^aInitial differences due to different concentrations in solution after equilibrium between solution and solid soil material before the first addition of metal.

^bSoil type and initial DOC concentration in mg C/l. See text for explanation.

7.3.2 Changes in soil solution composition over the course of the experiments

The initial equilibration of the DOM solutions (Table 1) with the solid soil material and subsequent addition of Al and Fe lead to the theoretical range of concentrations in solution described in Table 4. The concentrations in this table are corrected for experimental error and volume changes due to sampling and represent the hypothetical concentrations that would have been present if no precipitation or interactions with the solid phase had taken place. The actual concentrations of Al, Fe, Si and DOM in solution over the course of the experiments are depicted in Fig. 1-3. The maximum concentrations of Fe and Al in solution during the experiments are given in Table 5. The maximum

concentrations of Fe decrease when going from Soil 1: Bhs to Soil 2: Bsb and are positively correlated with the C_t/M_o ratios for both the initial DOC concentrations of 10 mg C/l and 30 mg C/l. For Al there was no correlation at the initial DOC concentration of 10 mg C/l and there was a negative correlation at the initial DOC concentration of 30 mg C/l.

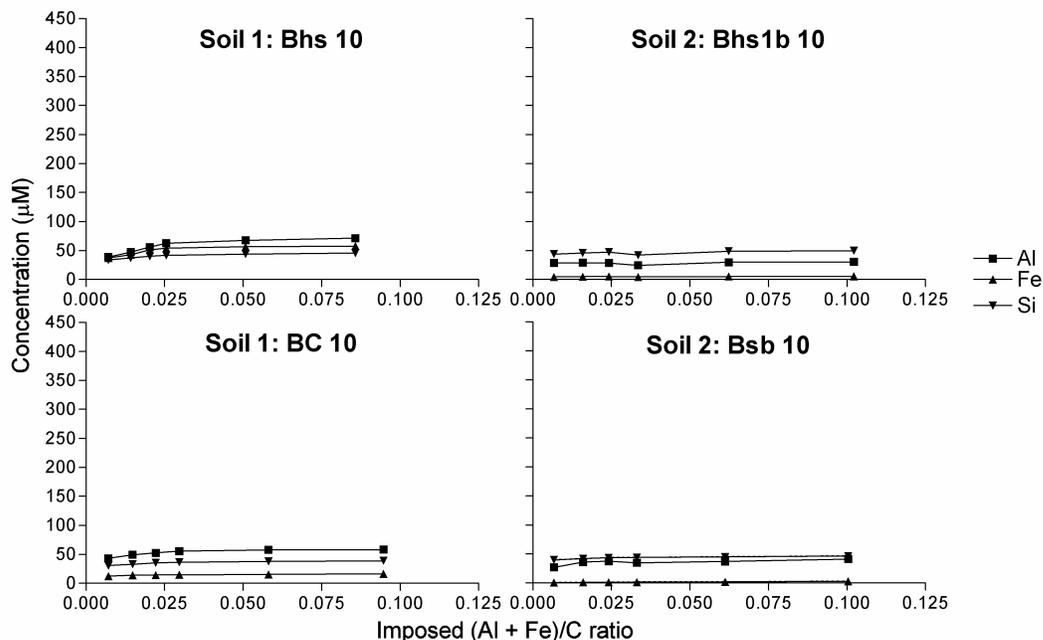
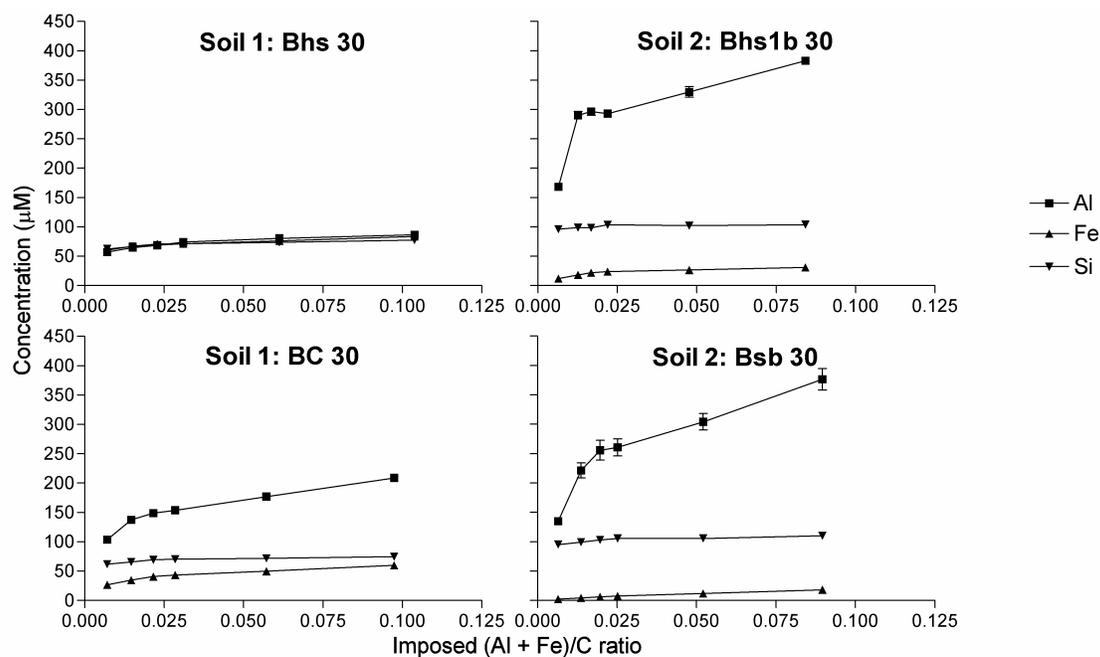


Fig. 1 and 2 Total metal and silica concentrations in solution in the experiments with pH = 4.5 and an initial DOC concentration of 10 mg C/l (top) and pH = 4.0 and an initial DOC concentration of 30 mg C/l (bottom), as a function of increasing imposed M/C ratios, which consist of the theoretical molar metal concentration assuming all metal stayed in solution, divided by total molar DOC concentrations initially present. Error bars depict standard error of the mean.



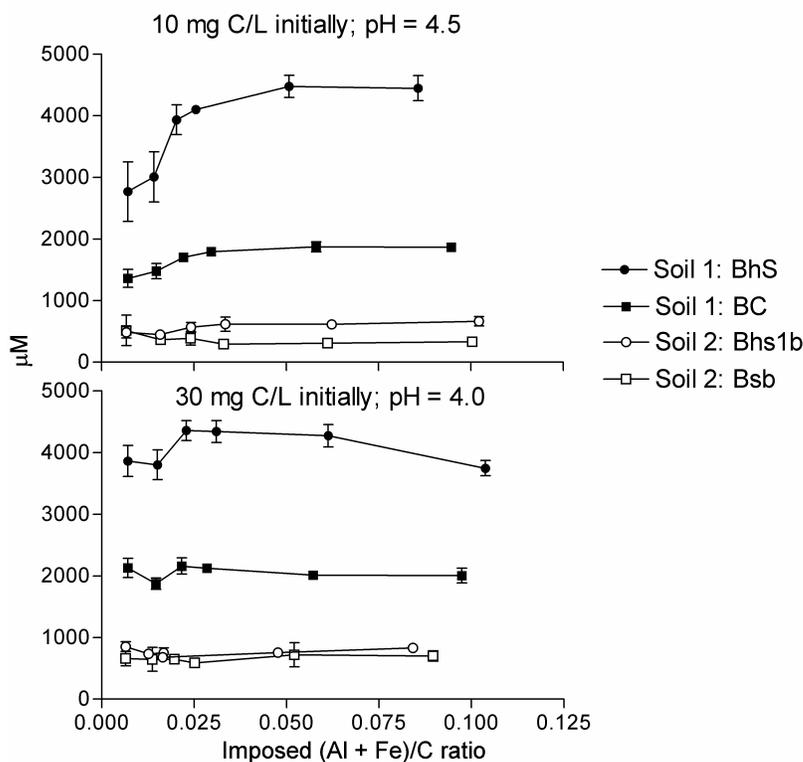


Fig. 3 DOM concentrations in solution determined as DOC, as a function of increasing imposed M/C ratios (see the legend of Figure 1 for explanation). Error bars depict standard error of the mean.

In Fig. 4, we plotted the actual M/C ratio in solution versus the M/C ratio that was imposed by the addition of Al and Fe in the different experiments. It is interesting to note that the M/C ratios appear to be reasonably well buffered against metal addition at 10 mg C/l and pH = 4.5. We observed similar buffering against metal addition in our previous study using A(h)E horizons (Jansen et al., 2003c). In all cases but Soil 1:Bhs, the M/C ratio in solution was larger than 0.03, which is the threshold value for the onset of precipitation of our dissolved organic Al/Fe complexes at both pH values used in the experiments (Nierop et al., 2002).

In Fig. 5, ‘free’ Al and Fe were plotted as a molar fraction of the total amount of Al and Fe present in solution over the course of the experiments. Due to the earlier described problems with DGT for Soil 2, only the results for Soil 1 are presented. The ‘free’ Al fraction in Soil 1:BC:30 is larger than in Soil 1:BC:10 while for Fe the situation is exactly opposite. At the same time, in Soil 1:BC:30 the Al concentration was much larger than the Fe concentration, while in Soil 1:BC:10

the difference in concentrations between Al and Fe was much smaller (Fig. 2). Therefore, the high 'free' Fe fraction in Soil 1:BC:30 was most likely caused by increased competition of Al for binding on DOM.

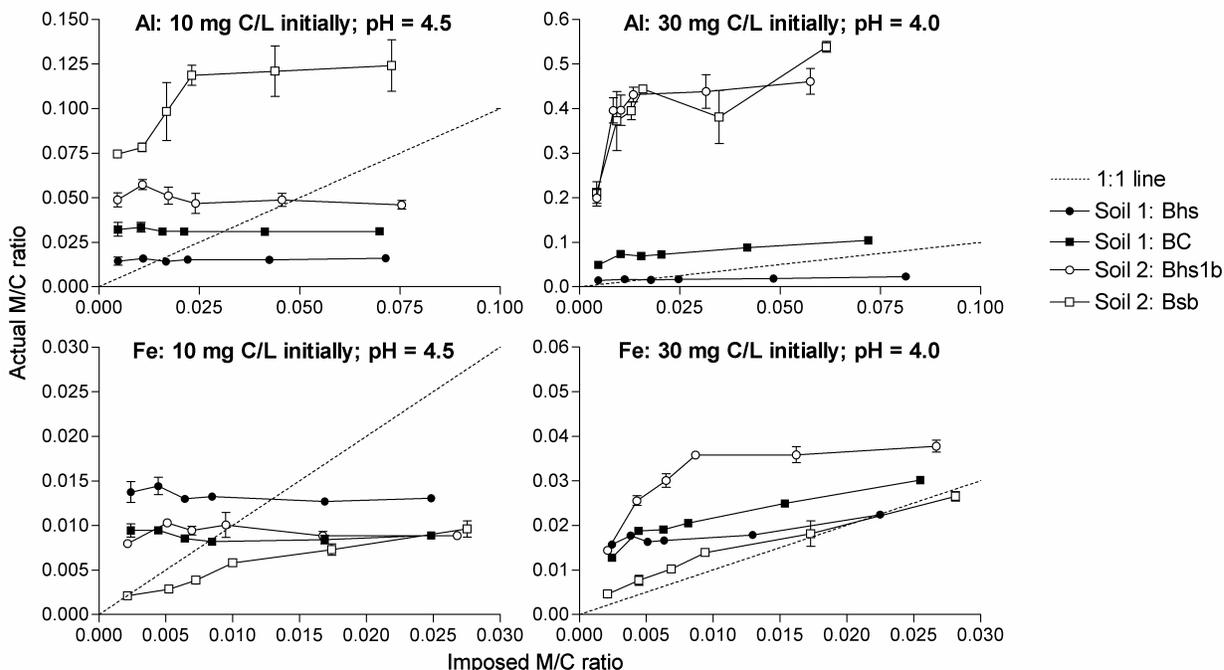


Fig. 4 Actual metal to organic carbon (M/C) ratios in solution as a function of the imposed M/C ratios in solution (see the legend of Figure 1 for explanation) for the soil material of Soil 1 and 2. Error bars depict standard error of the mean.

7.3.3 Mobility of organic matter

In Fig. 6-8, we used an approach similar to the initial mass isotherm (Nodvin et al., 1986) to investigate the net cumulative amount of organic matter, Al, Fe and Si mobilized or immobilized as a function of the imposed total M/C ratios. For Al and Fe, the amounts were corrected for the addition of the metals. A positive value means net mobilization, as more organic matter, Al, Fe or Si is present in solution than the sum of the initially dissolved amounts plus the amount added. A negative value signifies net immobilization.

The extent of (im)mobilization of DOM depended on both the type of soil material and the initial DOM concentrations present in solution (Fig. 6). In Soil 1:Bhs, organic matter was initially mobilized and further mobilization occurred throughout the experiments, while in Soil 2:Bhs1b and Soil 2:Bsb organic matter

was initially immobilized and remained net immobilized throughout the experiments regardless of the initial DOC concentrations. In contrast, in Soil 1:BC the behavior did depend on the initial DOC concentrations: in Soil 1:BC:10 net mobilization of organic matter both initially and over the course of the experiments occurred, while in Soil 1:BC:30 the opposite was observed. The trend of decreasing mobilization to increasing immobilization in the different soil samples correlated positively with the C_t/M_o ratios. In the cases where net immobilization of DOM occurred, we visually observed flocculation followed by discoloring of the experimental solutions.

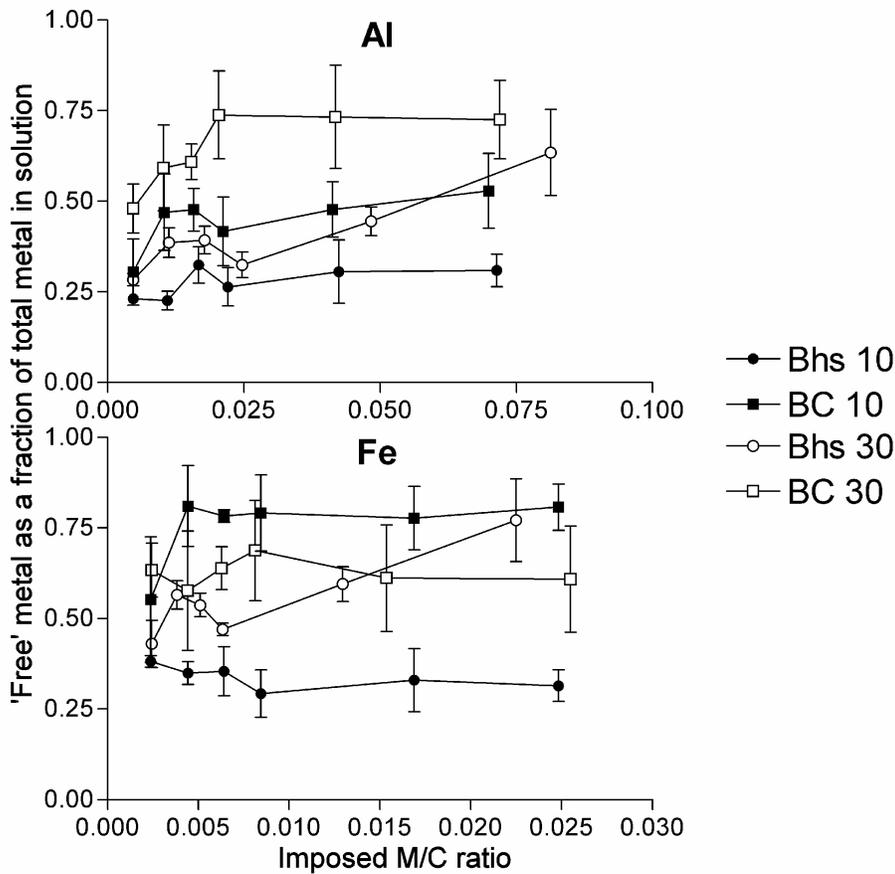


Fig. 5 the fraction of Al and Fe in solution that is present in the 'free' form, as a function of the imposed metal to organic carbon ratio (see legend of Figure 1 for explanation), for the soil material of Soil 1. Error bars depict standard error of the mean.

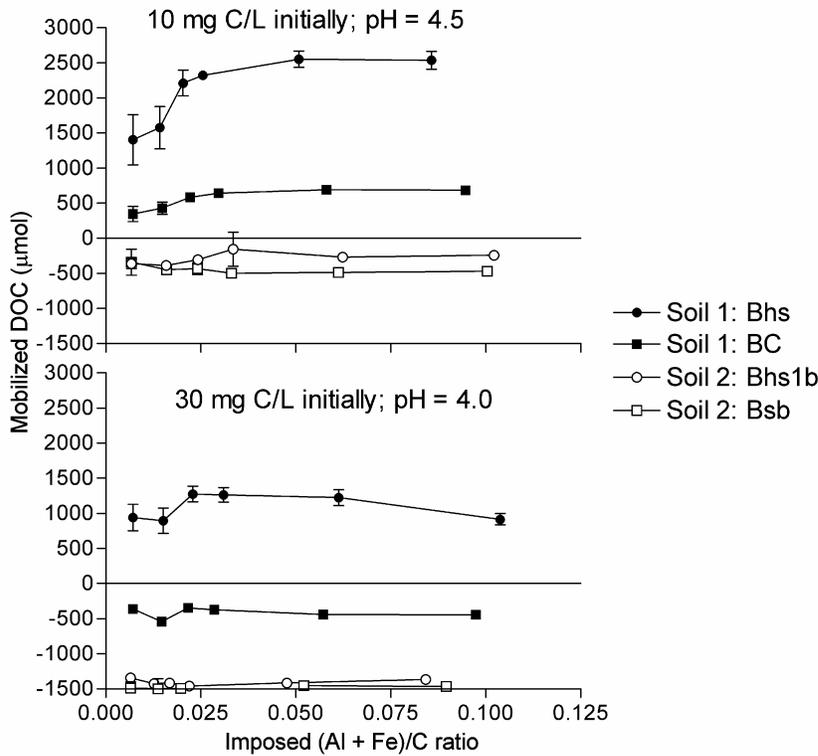


Fig. 6 The net cumulative number of μmoles of DOC mobilized or immobilized over the course of the experiments as a function of increasing imposed M/C ratios (see the legend of Figure 1 for explanation). Error bars depict standard error of the mean.

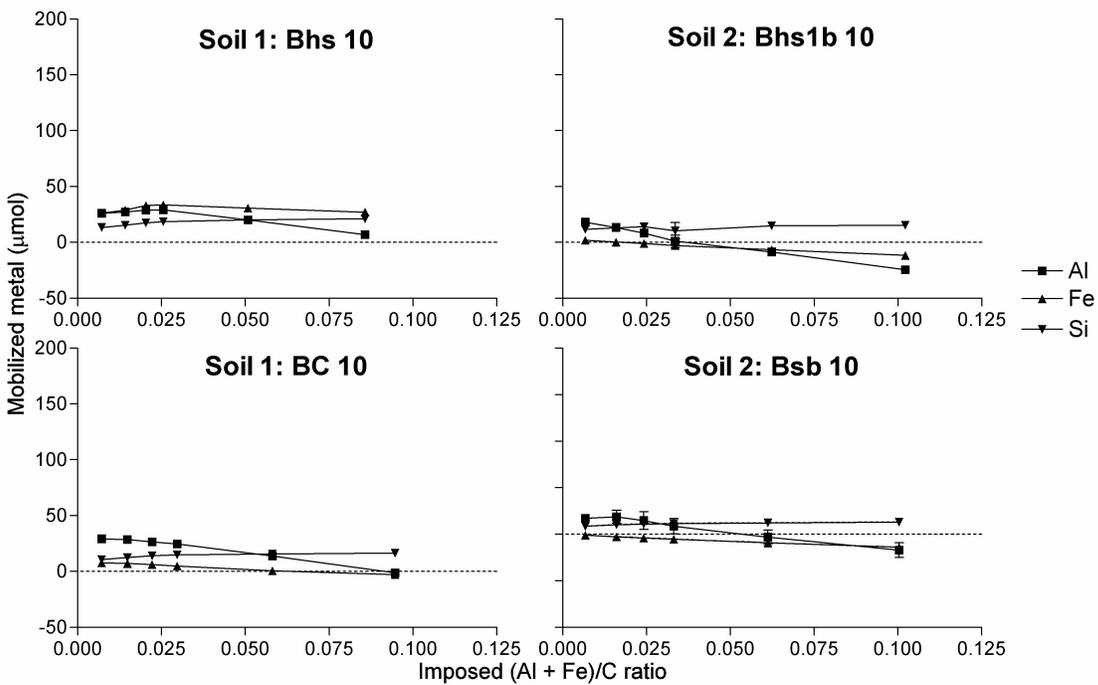


Fig. 7 The net cumulative number of μmoles of Al, Fe and Si mobilized or immobilized over the course of the experiments as a function of increasing imposed M/C ratios (see the legend of Figure 1 for explanation), corrected for the addition of Al and Fe. Error bars depict standard error of the mean.

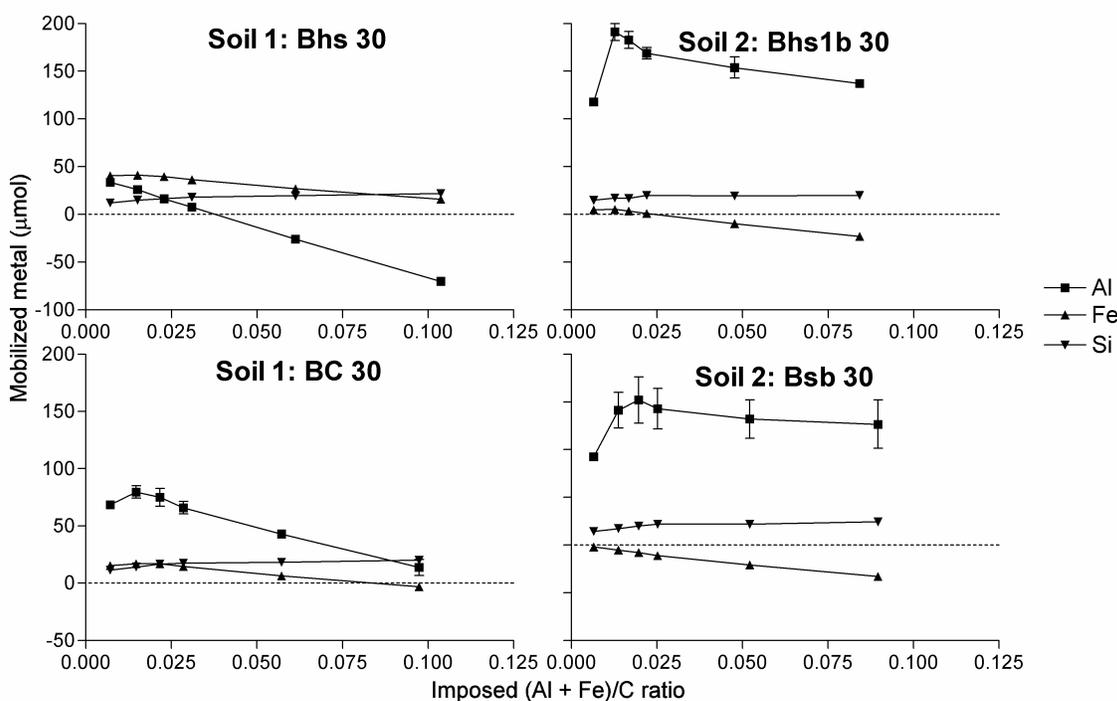


Fig. 8 The net cumulative number of μmoles of Al, Fe and Si mobilized or immobilized over the course of the experiments as a function of increasing imposed M/C ratios (see the legend of Figure 1 for explanation), corrected for the addition of Al and Fe. Error bars depict standard error of the mean.

7.3.4 Mobility of Al, Fe and Si

In all experiments Al was initially mobilized (Fig. 7 and 8), but after at most three additions each subsequent addition resulted in more Al being removed from solution than was added in that specific addition. In the experiments with 10 mg C/l initially present, the initial amount of mobilized Al was lower in Soil 2 than in Soil 1. Because of this lower initial amount of mobilized Al there was already net immobilization of Al after the fourth addition of Al in Soil 2:Bhs1b:10 and Soil 2:2Bsb. In Soil 1 there was only net immobilization of Al after the last addition for Soil 1:BC:10. The immobilization of Al was positively correlated with the total amount of amorphous Al present (Al_0), being the strongest in Soil 2:Bhs1b (Table 2).

In the experiments with an initial DOC concentration of 30 mg C/l, the initial amount of mobilized Al was much higher than in the 10 mg C/l experiments. Furthermore, in all soils but Soil 1:Bhs there was a significant mobilization of Al after the second addition and in Soil 2:Bsb even after the third addition of Al. As a

result we only observed a net immobilization of Al in Soil 1:Bhs:30. Contrary to the 10 mg C/l experiments, the initial and maximum amounts of mobilized Al increased when going from Soil 1 to Soil 2 and thereby were positively correlated with the Al_o contents.

For Fe the differences between the (im)mobilization in the 10 mg C/l and 30 mg C/l experiments were much smaller than for Al. In all cases there was a trend of more Fe being removed from solution than added in any given addition except for Soil 1:Bhs:10. Initial amounts of mobilized Fe were much lower than for Al. In all experiments with Soil 2 except Soil 2:Bhs1b:30 there was even immediate immobilization during the equilibration of the solid soil material with the DOM solutions before metal additions. We observed no correlation between the amount of immobilized Fe and Fe_o contents, however the amount of immobilized Fe was positively correlated with the C_t/M_o ratios.

As is shown in Fig. 6 and 7, in all experiments we observed a slight mobilization of Si over the course of the experiments. There were no significant differences between the different horizons used in the experiments or the different initial DOM solutions.

7.4 Discussion

In the following paragraphs, we will propose a set of mechanisms that explain the (im)mobilization of organic matter, Al and Fe. An overview of the different mechanisms is given in Table 6.

7.4.1 (Im)mobilization of organic matter

The conditions of the experiments with an initial DOM concentration of 30 mg C/l were identical to those of our previous study of A(h)E horizons of the same two soil profiles (Jansen et al., 2003c), which allows for proper comparison of the results. Soil 1:Bhs had the highest C_t/M_o ratio and was relatively rich in SOM (Table 2). Similar to the A(h)E horizons in our previous study that were also rich in SOM, a significant influence of SOM on the behavior of DOM was expected. Indeed in Soil 1:Bhs:30, the trend of mobilization of organic matter upon metal

addition was similar to that in the A(h)E horizons (Jansen et al., 2003c). The observed mobilization in the A(h)E horizon was attributed to initial detachment of organic matter from the solid phase, followed by further mobilization upon metal addition due to desorption of organic matter from (amorphous) solid phase Al and Fe. In addition, probably competition of 'free' Al and Fe with adsorbed organic Al and Fe complexes took place (Jansen et al., 2003c). The absolute amount of mobilized organic matter in Soil 1:Bhs:30 was approximately six times smaller than in the AhE horizon of soil 1, which corresponds to the total organic carbon content that was also approximately six times smaller in Soil 1:Bhs:30 (Jansen et al., 2003c). Contrary to the AhE horizon of soil 1, organic matter was removed from solution after the last few additions in Soil 1:Bhs:30. Such removal was also observed in the AE horizon of Soil 2, which is less rich in organic matter and has a smaller C_t/M_o ratio than the AhE of Soil 1 (Jansen et al., 2003c). The immobilization was attributed to increasing influences of cation bridging at higher M/C ratios in solution (Jansen et al., 2003c). Most likely this was also the case in Soil 1:Bhs:30. Further support is the fact that no immobilization of organic matter was observed in Soil 1:Bhs:10 where initial DOM concentrations were smaller. Again, this is in line with the trend observed in the AE horizons when comparing experiments with high and low initial DOC concentrations (Jansen et al., 2003c).

In the subsequent horizons (Soil 1:BC and Soil 2:Bhs1b + Soil 2:Bsb) with decreasing C_t/M_o ratios we found an increasing influence of dissolved and solid phase Al and Fe in regulating the mobility of organic matter. In Soil 1:BC:10 there was still some mobilization of organic matter analogous to Soil 1:Bhs and most likely again caused by the same mobilization mechanisms (Table 6). However, the fact that the final concentration of DOM in solution in Soil 1:BC:10 was approximately half that of Soil 1:Bhs:10 (Fig. 3) indicates an increasing importance of immobilization mechanisms for organic matter here. The absolute amounts of SOM (C_t , see Table 2) were similar in both Soil 1:Bhs and Soil 1:BC, while the amount of amorphous Al and Fe phases ($Al_o + Fe_o$, Table 2) was twice as high. We therefore propose that the diminished mobilization of organic matter in Soil 1:BC:10 as compared to Soil 1:Bhs:10 was caused by adsorption of DOM on

amorphous Al and Fe phases. The M/C ratios in Soil 1:BC:10 were larger than 0.03 (Fig. 4), the threshold value for precipitation of M-DOM complexes (Nierop et al., 2002). However, because they were only slightly larger, they were too low for a dominant role of this immobilization mechanism (Jansen et al., 2003b)

In Soil 1:BC:30 and all instances of Soil 2, the M/C ratios in solution were high enough above the threshold value of 0.03 to expect a significant influence of the precipitation of organic Al and Fe complexes (Jansen et al., 2003b). In fact, the only cases where net immobilization of organic matter occurred were also the only cases where the M/C ratio in solution was high enough to cause significant precipitation of organic Al and Fe complexes. Combined with our visual observation of flocculation, these analytical data offer further support for an important role of precipitation of organic metal complexes as an immobilization mechanism for organic matter in these situations.

In a recent study, Mossin et al. (2002) also identified precipitation of Al/Fe-DOM complexes as a prime mechanism of immobilization of both organic matter and metals in Danish podzol B horizons. However, others believe that adsorption of organic matter on amorphous phases of Al and Fe is the main immobilization process (e.g. Jardine et al., 1989; Kaiser et al., 2000). It is difficult to distinguish between sorption and precipitation as controlling mechanisms of organic matter immobilization in our experiments, especially when considering the possibility of the observed flocculation being in fact inorganic Al and Fe precipitates on which DOM subsequently adsorbed (Farmer and Lumsdon, 2001). However, the lower pH in the 30 mg C/l experiments makes such inorganic precipitation unlikely, as will be discussed in more detail in the paragraph dealing with the immobilization of Al and Fe. Still precipitation of organic matter occurred in the 30 mg C/l experiments and the precipitates therefore most likely were predominantly organic metal complexes. Also the degree of immobilization was the highest in Soil 2:Bsb, whereas the maximum content of amorphous Al and Fe phases occurred in Soil 2:Bhs1b (Table 2). Therefore, if adsorption were the only immobilization mechanism of organic matter, one would have expected the immobilization maximum to occur in Soil 2:Bhs1b, which was not the case.

If precipitation determined the organic matter concentrations in solution, one would expect three times as much immobilization of organic matter from the 30 mg C/l solutions as compared to the 10 mg C/l solutions. This was indeed the case for Soil 2:Bsb but in Soil 2:Bhs1b the final concentration of organic matter in solution was approximately the same regardless of the initial DOM concentration (Fig. 3). A probable cause for the lack of difference in DOM concentrations between Soil 2:Bhs1b:10 and Soil 2:Bhs1b:30 is desorption of organic matter in Soil 2:Bhs1b:10, which had by far the largest reactive carbon content as evidenced by the high C_p content (Table 2). Such desorption could have been caused by a shift in the sorption equilibrium of organic matter following a lowering of the DOM concentrations due to precipitation of dissolved organic metal complexes. This would also explain the rise in the (im)mobilization curve of organic matter after the second addition of metals in Soil 2:Bhs1b:10. At this smaller initial DOM concentration the low initial DOM concentration would most favor desorption (Fig. 8). In summary, precipitation of M-DOM complexes determined organic matter mobility together with some adsorption/desorption of organic matter on amorphous Al and Fe phases.

Even in Soil 2:Bhs1b where the highest degree of organic matter immobilization occurred and the M/C ratios in solution were high enough to have caused all DOM to precipitate out of solution, 24-30% of the DOM present remained in solution after the last addition of metals, regardless of the initial DOC concentration. This is consistent with 30% of DOM being inert for binding to Al and Fe(III), as was observed in freshwater by Tipping et al. (2002). Similar inert DOM percentages were found by Vilg -Ritter et al. (1999). It is also in agreement with modeling results of the interactions of the binding of Al and Fe to DOM from soil solutions of Soil 1 using Model V and VI (Jansen et al., 2003a). However, in our precipitation study of DOM in Soil 1 we used the same dataset as in the modeling study but found that when looking at the change in DOC concentrations over the course of the experiments, only approximately 10% of DOM remained in solution (Nierop et al., 2002). The discrepancy seems to indicate that DOM precipitation mechanisms other than charge compensation by metal binding also play a role in the immobilization of organic matter.

Table 6

Overview of the proposed (im)mobilization mechanisms for organic matter, Al and Fe.

| | Mobilized by | Immobilized by |
|-----------------------|---|---|
| Organic matter | <ul style="list-style-type: none"> dissolution of SOM ^(a,b,c) | <ul style="list-style-type: none"> adsorption through cation bridging to SOM in horizons where net mobilization took place ^(a,b,c) |
| | <ul style="list-style-type: none"> desorption from (amorphous) solid phase Al and Fe ^(a,b,c) | <ul style="list-style-type: none"> adsorption on (amorphous) solid phase Al and Fe ^(d,e,f,g,h) |
| | <ul style="list-style-type: none"> competition of 'free' Al and Fe with organic matter bound as organic metal complexes ^(a,b,c) | <ul style="list-style-type: none"> precipitation as insoluble organic Al and Fe complexes ^(d,e,f,g,h) |
| Al and Fe | <ul style="list-style-type: none"> initially by soluble complexation with organic matter ^(a,b) | <ul style="list-style-type: none"> direct adsorption on SOM ^(a,b) |
| | <ul style="list-style-type: none"> dissolution of amorphous Al(OH)₃(s) ^(d,f,h) | <ul style="list-style-type: none"> precipitation as insoluble organic Al and Fe ^(c,d,e,f,g,h) complexes |
| | <ul style="list-style-type: none"> desorption of organic Al and Fe complexes ^(a,b,c,d,e,f,g,h) | <ul style="list-style-type: none"> precipitation as inorganic Al^(c,g) and Fe ^(c,d,e,f,g,h) complexes adsorption of Al/Fe-DOM complexes ^(a,b,c,d,e,f,g,h) |

^aSoil 1:Bhs:10; ^bSoil 1:Bhs:30; ^cSoil 1:BC:10; ^dSoil 1:BC:30;^eSoil 2:Bhs1b:10; ^fSoil 2:Bhs1b:30; ^gSoil 2:Bsb:10; ^hSoil 2:Bsb:30 (for explanation see text).

7.4.2 (Im)mobilization of Al and Fe

Similar to organic matter, the mobility of Al and Fe in Soil 1:Bhs at both initial DOC concentrations resembled the mobilization in the A(h)E horizons (Jansen et al., 2003c). Consequently, as for organic matter we conclude that the same mechanisms regulate the mobility of Al and Fe here as in the A(h)E horizons (Table 6). These mechanisms include an initial mobilization of Al and Fe by complexation with DOM in solution, followed by net immobilization through adsorption of both free metal cations and dissolved organic metal complexes on solid phase organic matter as more Al and Fe are added. As indicated by the results for organic matter, some Al and Fe was bound in the form of organic Al and Fe complexes, through cation bridging (Jansen et al., 2003c). Organic control of the Al mobility in organic rich mineral horizons is in agreement with the reports of several other researchers (e.g. Berggren and Mulder, 1995; Lofts et al., 2001).

In Soil 1:BC and Soil 2:Bhs1b + Soil 2:Bsb several mechanisms seem to be acting together to regulate the mobility of Al and Fe. In the situations where the initial DOC concentration was 10 mg C/l, according to Gustafsson et al. (2001) both the pH (> 4.2) and the Al_p/C_p ratios (> 0.1) were high enough to expect the solution concentrations of Al to be regulated by the equilibrium with $Al(OH)_3(s)$ (Table 2). However, in the experiments with an initial DOC concentration of 30 mg C/l, the pH was too low (< 4.2) to expect such regulation (Gustafsson et al., 2001). A problem when calculating maximum Al concentrations in equilibrium with $Al(OH)_3(s)$ is the choice of the equilibrium constant K_{so} , as a wide range of values for this constant is reported (e.g. Appelo and Postma, 1994; Gustafsson et al., 2001; Lofts et al., 2001; Parkhurst, 1995). We used two recently published pK_{so} values at 298K of 8.61 (Gustafsson et al., 2001) and 8.82 (Lofts et al., 2001) from studies in soil systems similar to ours. These pK_{so} values resulted in a calculated maximum concentration of Al at pH = 4.5 and 293K of respectively 36.5 μM and 59.2 μM using the extended Debye-Hückel approximation to correct for activities (Appelo and Postma, 1994). The maximum Al concentrations in Soil 1:BC:10 and Soil 2:Bsb:10 are close to the limiting value of 59.2 μM (Table 5), which would corroborate the expected control of the Al concentrations by $Al(OH)_3(s)$ in these two horizons. The maximum Al concentration in Soil 2:Bhs1b:10 is much smaller and it thereby seems to be undersaturated with respect to $Al(OH)_3(s)$. In the experiments with an initial DOC concentration of 30 mg C/l and pH = 4.0, the calculated maximum Al concentrations are 1150 μM ($pK_{so} = 8.61$) and 1890 μM ($pK_{so} = 8.82$) respectively and all soils appear undersaturated with respect to $Al(OH)_3(s)$. In fact the significant mobilization of Al initially and after the first two additions of Al in Soil 1:BC:30, Soil 2:Bhs1b:30 and Soil 2:Bsb:30 are indicative of dissolution instead of precipitation of $Al(OH)_3(s)$ at this lower than usual pH value for B horizons. Dahlgren et al. (1989) found dissolution rates of amorphous $Al(OH)_3(s)$ that are fast enough (equilibrium within 0.3 hours) to have occurred within the time frame of our experiments (24 hours equilibration time after each metal addition). The observed undersaturation with respect to $Al(OH)_3(s)$ in Soil 2:Bhs1b, and all

situations at 30 mg C/l as well as the observed immobilization of Al immediately (Soil 2:Bhs1b:10, Fig. 5) or after the first or second metal addition (Soil 2:Bhs1b:30, Soil 1:BC:30 and Soil 2:Bsb:30, Fig. 6) indicate that other mechanisms must be acting to regulate Al mobility as well.

There are two main other mechanisms to consider for the immobilization of Al and Fe: sorption/desorption reactions (either directly on SOM or in the form of M-DOM complexes on amorphous solid phases of Al and Fe), and precipitation of insoluble organic metal complexes (e.g. Mossin et al., 2002; Powell and Hawke, 1995; Wesselink et al., 1996). As was explained earlier, there was a significant immobilization of organic matter that in view of the high M/C ratios in solution was at least partly due to precipitation of organic metal complexes especially in the experiments at pH = 4.0. Both Al and Fe could have caused this precipitation, but from previous research we know that Fe(III) forms stronger complexes with DOM than Al and the degree of precipitation of Fe(III) is approximately equal at pH = 4.5 and pH = 4.0 (Jansen et al., 2002; Nierop et al., 2002). While Al is able to precipitate DOM to a similar degree as Fe(III) at pH = 4.5, it induces much less precipitation at pH = 4.0. (Jansen et al., 2003b; Nierop et al., 2002). Furthermore, Fe(III) has a very low solubility when in equilibrium with Fe(OH)₃ (s) at both pH values, while this is not the case for the equilibrium between Al and Al(OH)₃(s). As a consequence, we believe that Fe was mainly immobilized by precipitation, both organically and inorganically. Corroborating evidence for this hypothesis is the observation that in all horizons except Soil 1:Bhs, the addition of Fe quickly lead to net immobilization of Fe that was negatively correlated with C_t/M_o ratios and independent of pH and initial DOC concentrations (Fig. 5 and 6). If sorption/desorption processes were dominating, one would have expected a maximum immobilization of Fe in Soil 2:Bhs1b with the largest content of both solid phase Al, Fe and solid phase organic matter (Table 2).

Contrary to Fe, in Soil 2:Bhs1b:10 the immobilization of Al was stronger than in both Soil 1:BC:10 and Soil 2:Bsb:10. The same was true for the immobilization after the first addition in Soil 2:Bhs1b:30 as compared to Soil 1:BC:30 and Soil 2:Bsb:30. This positive correlation of Al immobilization with the content of amorphous Al and Fe phases and the absence of such a correlation for Fe, is an

indication that sorption processes are more important in the (im)mobilization of Al than of Fe. A further support for the involvement of sorption as an (im)mobilization mechanism of Al is the much larger BaCl_2 extractable amount of Al as compared to Fe (Table 2). We proposed desorption of M-DOM complexes to explain slight DOM mobilization after the first metal addition in Soil 2:Bhsb1:10. Desorption of M-DOM complexes seems contradictory to concurrent adsorption of Al. An explanation could be desorption of organic Al complexes together with a concurrent adsorption of 'free' Al on the significant amounts of SOM present here.

Another immobilization mechanism of Al that warrants investigation is that of precipitation in the form of (proto)imogolite (Anderson et al., 1982; Farmer and Lumsdon, 2001). Formation of imogolite can be expected when the ratio of $(\text{Al}_o - \text{Al}_p)/\text{Si}_o$ is around 2.0 (Dixon and Weed, 1989). In the soils used this is true for Soil 1:BC and Soil 2:Bsb (Table 2), the same horizons in which we propose inorganic precipitation of Al to be an important immobilization mechanism. However, we based the assumption of inorganic Al precipitation on the apparent saturation with respect to $\text{Al}(\text{OH})_3(\text{s})$. More importantly, we found no imogolite in our IR analyses of the soil horizons used in this study and we observed no correlation between Si, pH and Al concentrations or even a clear trend in Si (im)mobilization in any of the horizons. Consequently, we conclude that the formation or dissolution of (proto)imogolite does not play a significant role in controlling the Al mobility in the soils investigated in this study.

Finally, microbial degradation of DOM in M-DOM might play a role in the transport of Al and Fe in podzols complexes as proposed by Lundström et al. (Lundström et al., 2000). It is impossible to assess the contribution of microbial degradation of DOM to the immobilization of Al and Fe in the soils under study here because of the addition of NaN_3 that inhibited microbial activity. However, the fact that we found significant immobilization Al and Fe in spite of the absence of microbial activity indicates that at least microbial degradation of DOM is not the only immobilization mechanism governing Al and Fe mobility in the soils under investigation here.

7.4.3 Implications for podzolization

The implications of the results for the process of podzolization in general are as follows. Organic matter is mobilized from the B horizons of the younger, less developed Podzolic soil (Soil 1) in which the C_t/M_o ratio is relatively high so that added metal is adsorbed on SOM and M/C ratios in solution remain low enough to prevent immobilization of organic matter due to precipitation. At the same time the adsorption of Al and Fe on SOM causes influxing Al and Fe to be immobilized. Over time as the soil develops further, the process of mobilization of DOM and immobilization of Al and Fe will lead to a decrease in the C_t/M_o ratios. At the resulting lower C_t/M_o ratios, organic matter will no longer be mobilized, but will be immobilized by a combination of precipitation in the form of Al/Fe-DOM complexes and adsorption on amorphous solid phase Al and Fe as evidenced by the results from Soil 2. At the same time Al and Fe will also be immobilized through precipitation of both Al/Fe-DOM complexes and in the form of $Al(OH)_3(s)$ and $Fe(OH)_3(s)$ (ferrihydrite). For Al inorganic precipitation will only take place in Bs horizons, while inorganic precipitation of Fe also occurs in Bh horizons. In addition to precipitation, sorption processes will play a role for Al, especially in B horizons relatively rich in organic matter. Sorption processes seem less important for the immobilization of Fe, which will occur to both a higher degree and at lower metal concentrations than for Al.

The proposed mechanisms are in agreement with the classical fulvate theory, with the exception of the fact that we considered generic DOM while the classical fulvate theory considers only fulvic acid, and with exception of the inorganic precipitation in the lower B horizons. The latter is not surprising as we used recent, more constrained pK_{so} values to calculate inorganic precipitation of Al. When using older, less constrained values (e.g. Appelo and Postma, 1994) one would find undersaturation with respect to $Al(OH)_3(s)$ in all cases.

Because of the differences we encountered in immobilization mechanisms between the upper (Bhs) and lower (Bs/BC) B horizons in both soils, we compared their composition with those of the soils used in some other studies in the same geographic region as the Netherlands at the Bh(s)/Bs(C) interface. The C_p/Al_p ratios in the lowest Bh(s) horizons of 10 Dutch podzols investigated by

Mokma and Buurman (1982) range from 22 to 7.4, while those of the upper Bs(C) horizons range from 13.8 to 4.7. Our results fall in these same ranges (see Table 2). However, the C_p/Al_p ratios in 9 soils from more Nordic podzols from Sweden, Norway and Finland were similar (24.0-6.0 for the Bh(s) horizons and 10.0-3.0 for the Bs(C) horizons (Mokma and Buurman, 1982). Some researchers suggest that several podzolization processes are active at the same time and that different mechanisms dominate in different soils, possibly formed under different climates (Mossin et al., 2002; Van Breemen and Buurman, 2002). Mossin et al. (2002) for instance reported a lessened occurrence and importance of imogolite in podzols when moving from north to south through Scandinavia. Kodama and Wang (1989) reported the same trend when moving from north to south in Canada. At the same time in accordance with the classical fulvate theory, Mossin et al. (2002) found organic precipitation to be a major immobilization mechanism in the Danish soils they investigated.

The fact that the podzolization mechanism we found in the present study are largely in agreement with the classical fulvate theory suggested by other researchers in our geographic region, are a support for the applicability of this theory in this region with the addition of a role for inorganic precipitates. However, the lack of significant differences in C_p/M_p ratios in Bh and Bs horizons from our geographical region and a more Nordic geographical region in the data of Mokma and Buurman (1982) also indicates that the C_p/M_p ratio apparently is not an adequate marker of possible differences between podzols and podzolization in different geographical regions.

7.5 Conclusions

When considering the results of the present study for the more realistic experimental situations with respect to the field situation (i.e. 10 mg C/l; pH = 4.5), we found evidence of adsorption and both organic and inorganic precipitation as major immobilization mechanisms for Al and Fe in the podzol B horizons under study. We also observed some mobilization of Al and Fe upon addition of fresh DOM. The lower B horizons (Soil 1:BC and Soil 2:Bsb) were the

only ones that showed indications of inorganic precipitation controlling Al concentrations, whereas the upper B horizons seemed to be undersaturated with respect to inorganic Al phases. These observations, together with the observed (im)mobilization behavior of organic matter confirm the important role of organic matter in the transport of Al and Fe to initially create a B horizon and subsequently deepening and differentiating it into a Bh and Bs horizon. Our results agree most with the classical fulvate theory as do most other studies from the geographical region of the Netherlands, although possible differences between the behavior of generic DOM and FA were not investigated. The only difference is the inorganic precipitation controlling Al solubilities, which can be explained by the use of recent, more constrained K_{so} values for the equilibrium with $Al(OH)_3(s)$. Alternative podzolization theories are based mainly on studies of more Nordic podzols. The fact that our results agree with others from our geographical region but contrast with those from different regions, supports the idea posed among others by Mossin et al., (2002) that different podzolization mechanisms dominate podzolization in different regions. However, future research using a large number of different soil samples from podzols from different climatic regions is necessary to test hypotheses of climatic differentiation of podzolization mechanisms. In addition, one should keep in mind that the present study was conducted using batch experiments in which equilibrium was assumed. Flow rates through sandy soils can be high, in particular along preferential flow paths and equilibrium might not always be reached. Future research using soil columns or field manipulation experiments may be helpful to investigate this aspect.

Synthesis

In this synthesis the practical and scientific implications of the research presented in this thesis will be discussed. An indication will be given of what new insights were gained and what parts of the puzzle remain to be solved.

8.1 Studying interactions of Al, Fe and DOM

To shed light on the processes that control the mobility of Al, Fe and organic matter in acidic sandy soils, it is necessary to determine the speciation of Al and Fe over 'free' metal in solution, dissolved organic Al/Fe complexes and (in)organic Al/Fe precipitates. Here 'free' metal is defined as the hydrated metal cation and dissolved inorganic metal complexes. Especially the distinction between 'free' metal and dissolved organic Al/Fe complexes has been difficult in the past. The relatively new analytical tool of DGT as well as the speciation models WHAM-W 1.0 and WHAM-W 6.0 based on respectively Model V and Model VI were critically examined for this purpose.

DGT was originally designed to determine the labile fraction of trace metals in surface waters around neutral pH. In order to apply DGT for the speciation of Al and Fe over 'free' metal and dissolved organic Al/Fe complexes in acidic soil solutions, the following potential problems needed to be considered:

- a) Disturbance of Al and Fe complexation equilibria in solution, due to removal of a portion of the 'free' metal from solution by the DGT units in the limited sample volume used in the laboratory as compared to the volume of surface waters.
- b) Underestimation of the 'free' Al and Fe fraction due to increased proton competition for binding on the chelating resin in the DGT unit at low pH values.
- c) Detection as 'free' metal of dissolved organic Al/Fe complexes small enough to penetrate the hydrogel in the DGT unit relatively unhindered, and labile enough to be detected.

Problem a) and b) could be conquered relatively easily. A minimum experimental volume of 500 ml proved sufficient to avoid significant disturbance of solution equilibria when DGT is deployed overnight (Chapter 2). Overnight deployment was long enough to allow for reproducible detection of Al and Fe in the μM concentration range that was encountered in our soil solutions. Proton competition did not significantly influence the detection of 'free' Al and Fe(III) in the pH ranges used in our experiments, ($\text{pH} \geq 3.5$). The detection of 'free' Fe(II) at $\text{pH} \leq 4.0$ was slightly lowered due to proton competition. However, the 'free' Fe(II) fraction was lowered by a constant percentage (40% at $\text{pH} = 3.5$) which could be corrected for (Chapter 3). Problem c) proved to be slightly more difficult to conquer. Our comparison of DGT with equilibrium dialysis showed that detection of smaller dissolved organic Al/Fe complexes as 'free' metal when using the common APA hydrogel is limited to those complexes smaller than 1000 Da. DOM ranges in molecular weight from 500 to over 100000 Da (Herbert and Bertsch, 1995), which means that small dissolved organic Al/Fe complexes could in theory be detected as 'free' metal, leading to incomplete separation. The comparison with WHAM 1.0 and WHAM 6.0 indicated that at lower M/C ratios the metal fraction as detected by DGT indeed seems to be slightly larger than the 'free' Al fraction due to detection of small, labile dissolved organic Al complexes. In contrast small dissolved organic Fe(III) complexes appeared not to be labile enough to be detected as 'free' metal (Chapter 4) and the metal fraction determined by DGT seems to correspond well with the 'free' Fe(III) fraction. Of course theoretically it could also be the case that the DGT measurements were accurate and WHAM 1.0 and 6.0 underestimated 'free' Al. However, there are no reasons to assume the models would underestimate 'free' Al while there are reasonable grounds to expect a (slight) overestimation by DGT.

While the abovementioned potential problems could be solved reasonably well, an unexpected practical problem arose during the experiments. It turned out that DGT was relatively sensitive to experimental error, as became evident amongst others during the experiments involving soil suspensions containing very fine particulates that upon opening of the DGT units caused contamination of the

chelating gel even after careful rinsing (Chapter 7). A critical evaluation of the practical design of the DGT units will be very helpful if DGT is to be used more frequently in studies involving soil suspensions with fine particulates.

WHAM-W 1.0 and WHAM-W 6.0 were specifically designed to model the complexation of metals to DOM. We were able to calculate the 'free' Al and Fe fraction determined by DGT adequately using the default parameters and optimizing for an inert DOM fraction except for 'free' Fe(III) as calculated by WHAM-W 6.0 (Chapter 4). In addition, the optimized inert DOM fraction (24 %) was in the same order of magnitude as those found in other studies (Gimpel et al., 2003; Tipping et al., 2002) and in our experiments in the presence of B horizon solid soil material (Chapter 7). However, in a precipitation study using the same dataset as the modeling study, only approximately 10 % of DOM was found to remain in solution according to the DOC concentrations (Nierop et al., 2002). This discrepancy may be explained by precipitation/adsorption of DOM in the presence of solid material due to other mechanisms than charge compensation through metal binding. Overall, our successful application of WHAM-W 1.0 and WHAM-W 6.0 to new datasets further vindicates both models and the underlying concepts used to describe the binding of Al and Fe to DOM. In addition, the successful use in most cases of default parameters for the binding of Al and Fe to DOM strengthens the belief that they represent actual physical entities. At the same time the apparent overestimation of 'free' Fe(III) and especially 'free' Fe(II) by WHAM-W 6.0 reveals one of the weaknesses of the model. Partially due to the difficulties encountered until recently in analytically speciating between 'free' Fe(II) and 'free' Fe(III) on one hand and dissolved organic Fe(II)/Fe(III) complexes on the other, the number of datasets in literature describing the binding of Fe(II) and Fe(III) to DOM is very limited (Tipping et al., 2002). This makes it difficult to parameterize speciation models such as WHAM-W 6.0 and may have led to an inaccurate default binding parameter for Fe(II) in the model.

In summary, in spite of some imperfections, both DGT and WHAM-W 1.0 and 6.0 proved to be very useful tools to study the binding of Al and Fe to DOM in acidic soil solutions and a combination of measuring and modeling proved to be a powerful way to critically evaluate both tools. There is of course always the very

small possibility that both methods produce similar but erroneous data. However, this is unlikely since neither WHAM 1.0 nor WHAM 6.0 were originally parameterized using DGT data (Tipping, 1994; Tipping, 1998). Future research using a combination of DGT and WHAM-W 1.0 and 6.0 will be an effective approach to further test and develop either method. This will for instance help in the testing of more restricted hydrogels that further limit the detection of small dissolved organic Al complexes by DGT and the derivation of more accurate binding constants for Fe to DOM for WHAM-W 6.0 as well as the inclusion of redox speciation in the model.

Future challenges consist of combining results from DGT in solution as well as DGT probes directly deployed in soils, with calculations from the soil version of WHAM.

8.2 Podzolization

With respect to the translocation of Al, Fe and organic matter in general and the process of podzolization in particular, the results presented in this thesis indicate the following underlying mechanisms (Chapter 5, 6 and 7):

1. In (A)E horizons, the majority of Al and Fe in solution is present as mobile organic Al/Fe complexes and the pH (≤ 4.0) and M/C ratios (< 0.03) are low enough to prevent significant (in)organic precipitation of Al and Fe. Instead, the Al and Fe concentrations in solution are mainly controlled by adsorption on SOM, which in combination with the release of organic matter keeps the M/C ratios in solution low even when significant amounts of Al and Fe are added. Together, this leads to a steady mobilization of Al, Fe (and organic matter) under control of SOM and DOM.
2. In Bh horizons, Al is immobilized by precipitation of the dissolved organic Al complexes as they become saturated with metal at the pH (4.5) and M/C ratios (> 0.03) that prevail here. In addition, dissolved organic Al complexes are adsorbed on (amorphous) Al and Fe phases.

3. In Bs/BC horizons, Al is removed from solution by precipitation of dissolved organic Al complexes at the pH value (>4.0) and M/C ratios (>0.03) that prevail in solution. In addition, precipitation as $\text{Al}(\text{OH})_3(\text{s})$ is a significant immobilization mechanism in BC horizons. Furthermore, some adsorption of dissolved organic Al complexes occurs.
4. In all B horizons, Fe is immobilized by a combination of organic and inorganic precipitation. Adsorption of dissolved organic Fe complexes also occurs, but this is a less important immobilization mechanism for Fe than for Al. Also the immobilization of Fe is more extensive and occurs at lower metal concentrations than that of Al. The immobilized Fe consists predominantly of Fe(III). The binding of Fe(II) to DOM is much weaker than Fe(III) and no significant organic or inorganic precipitation of Fe(II) will occur, as is supported by the lack of Fe immobilization in reduced, water-logged podzol B horizons (Lundström et al., 2000a).

As pointed out in Chapters 6 and 7, the proposed mechanisms are based on a number of experimental assumptions, an important one being that in the soils under study the negative charge on the solid soil phase is related to its total carbon content (C_t) and the positive charge is related to its amorphous Al and Fe content. To seek further support for this assumption, recently we attempted to determine the cation exchange capacity (CEC), anion exchange capacity (AEC) and point of zero charge (PZC) of the horizons that were used in the experiments, of both soils used for our studies (see the Appendix). For this titrations with H^+ and OH^- , and titrations using K^+ and Cl^- were used (Martinez and McBride, 1989). Preliminary results indicate the CECs as determined by both methods are in good agreement and exhibit a positive correlation with the total carbon content. This supports our assumption concerning the distribution of negative charge in the soils under consideration. Unfortunately, due to the fast and extensive acid neutralizing capacity of some soil horizons, we were unable to determine the AEC at low pH values (<4.0 - 4.5).

The mechanisms we propose are in agreement with the classical fulvate theory in combination with the inorganic precipitation of Al (in some cases) as proposed

by Gustafsson et al. (2001). The exception is that the classical fulvate theory only considers FA, while we looked at DOM as the organic ligand.

A strong support that DOM acts as a transporter of Al and Fe during their downwards movement through the soils are the direct measurements of the high percentage of Al and Fe in solution that was present in the form of dissolved organic Al/Fe complexes in the presence of solid soil material. This was made possible by the use of DGT. The fact that no imogolite was found in any of the soil material used in the experiments, nor any correlation between 'free' Al, pH and Si concentrations, makes it unlikely that the imogolite theory holds true in the soils studied in the framework of this thesis.

8.3 Final remarks

The research presented in this thesis has increased our understanding of the translocation of Al and Fe in acidic sandy soils in the Netherlands and the tools that can be used to study it. Still as all researchers know, research is never really finished and many questions remain to be answered. For instance, what is the role of specific fractions of DOM in the process of podzolization? Do LMW organic acids or other DOM fractions indeed play a dominant role in the (im)mobilization of DOM? Kaiser and Zech (1997) for example found a higher mobility of hydrophilic than of hydrophobic DOM fractions in acidic sandy soils. This question is also related to the origin of the SOM found in B horizons. What percentage of it originates from DOM transported by the flow of soil water and which part is local root input? Furthermore, what are the differences between well drained and water logged podzols? For Fe, there is still uncertainty about the quantitative influence of DOM on the redox equilibrium between Fe(II) and Fe(III). We found both significant oxidation and reduction of Fe in soil solutions in the presence of DOM (Chapter 3 and 5) but more research is needed to further investigate the mechanisms involved. Another question is the role of microbial degradation in the process of podzolization. Because microbial decay was inhibited in all experiments and still immobilization of Al, Fe and DOM was found, microbial degradation as proposed by Lundström et al. (2000b) is clearly

not the only immobilization mechanism. However, the influence of microbial degradation, especially of LMW organic acids, cannot be completely ruled out either and warrants further investigation. Finally, in the light of the recently proposed climatic differentiation between the mechanisms that govern podzolization as described in Chapter 8, a detailed comparative study of podzols from different climatic regions is necessary in order to test the hypothesis of different podzolization mechanisms prevailing in different climatic regions and fully resolve the conundrum of the different, conflicting podzolization theories.

Summary

Organic matter in soils plays a key role in important processes such as soil acidification, mineral weathering and pedogenesis. Furthermore, by binding to other substances such as (trace) metals, organic pollutants and nutrients, organic matter influences their mobility and bioavailability. Organic matter can be subdivided in solid organic matter (SOM) and dissolved organic matter (DOM). SOM comprises both particulate organic matter and organic matter associated with mineral phases, whereas DOM represents all organic matter in solution smaller than $0.45\ \mu\text{m}$. An alternative division is that in humine, humic acids (HA) and fulvic acids (FA) where according to the most common definition humine is the fraction insoluble in $0.1\ \text{M NaOH}$ at room temperature, HA is the fraction that is extracted by NaOH but precipitates out of solution at $\text{pH} = 1.0$ and FA is the fraction that remains in solution at $\text{pH} = 1.0$. Organic matter is especially reactive towards the multicharged metals Al^{3+} , Fe^{2+} and Fe^{3+} and their charged hydration products, due to its capability of strong coordination bonding mainly with acidic functional groups on the organic molecules. When dissolved Al and Fe bind to organic matter, this has a large influence on the mobility of both metals and organic matter itself in soils. Obvious immobilization occurs when dissolved Al and Fe bind to SOM or when binding to DOM leads to the formation of insoluble organic Al/Fe complexes. Immobilization also occurs when charged, dissolved organic Al/Fe complexes are adsorbed on the solid soil matrix. On the other hand, the association of Al and Fe with DOM may mobilize both metals by preventing binding to SOM and shifting equilibria with secondary mineral phases such as gibbsite and ferrihydrite. The binding of Al and Fe to organic matter is influenced by several soil chemical variables, including the pH, the redox potential and the ratio of metal to dissolved organic carbon present (M/C ratio). Changes in these variables influence both the extent of complexation with organic matter as well as the type of complexes formed (soluble or insoluble) in the case of binding with DOM. As a consequence, changes in pH, redox potential and M/C ratio also influence the mobility of Al, Fe and organic matter in soils. However, the quantitative influence of such changes on the mobility of Al, Fe and organic

remains unclear. This is exemplified by lack of consensus on the mechanisms involved in the process of podzolization, where Al and Fe are removed from a bleached, eluvial E horizon overlying one or more illuvial B horizons in which Al and in most cases Fe are deposited. Several theories exist to explain this phenomenon. The classical fulvate theory proposes that FA mobilizes Al and Fe by weathering of minerals and subsequently binding Al and Fe in dissolved organic metal complexes. Upon downwards movement through the soil, the organic molecules become saturated with Al and Fe and precipitate out of solution when their negative charge is sufficiently compensated. The imogolite theory reserves no role for organic matter in the transport of Al and Fe, but instead proposes that (proto) immogolite sols are responsible for the downwards translocation of Al and intrusions of Fe. Immobilization occurs due to precipitation of immogolite and adsorption of DOM on solid phase Al and Fe. Other theories propose that the formation of soluble organic Al and Fe complexes is responsible for their mobilization, but propose alternatives for the immobilization by precipitation of dissolved organic Al/Fe complexes. These alternatives include adsorption of dissolved organic Al/Fe complexes or inorganic precipitation e.g. in the form of $\text{Al}(\text{OH})_3(\text{s})$, directly or after microbial degradation of the organic molecules. Some researchers propose that different podzolization mechanisms dominate under different climates.

The main objective of this study was to investigate the influence of the interactions of Al, Fe and organic matter on their mobility in acidic sandy soils in the Netherlands. This thesis consists of two parts. The first part (Chapters 2-4) focuses on the analysis of the interactions of Al, Fe and organic matter in solution, while the second part (Chapters 5-7) deals with the influence of solid soil material on the association of Al and Fe with organic matter and the implications for their respective mobilities. Two podzol(ic) soils were chosen to be used for the research performed in the framework of this thesis. These were Soil 1: a young incipient podzol (Fimic Anthrosol) and Soil 2: an older more developed podzol (Haplic Podzol), both from the Veluwe in the Netherlands.

In Chapter 2 the relatively new analytical chemical method of Diffusive Gradients in Thin films (DGT) containing the standard APA hydrogel and

Na⁺-saturated chelating resin, was tested for its applicability to distinguish between 'free' Al and Fe(III) and dissolved organic Al/Fe complexes in soil solutions. The 'free' fraction here is defined as consisting of both the hydrated metal cations as well as their dissolved inorganic complexes. The results obtained by DGT were compared to those obtained by the better established, but more time consuming method of equilibrium dialysis with a Molecular Weight Cut-Off (MWCO) of 1000 Da. In addition the 'environmentally important' trace metal Zn was considered as an additional performance test. Four DOM solutions were tested that were obtained by water extraction of Oh material from Soil 1 and brought at pH = 4.0 or 7.0 and DOM concentrations of 20 or 75 mg C/l by addition of acid or base and concentration or dilution. For Al and Fe(III) there were no significant differences between the 'free' metal fraction as determined by DGT or equilibrium dialysis in any of the experimental solutions, when DGT was deployed in a minimum sample volume of 500 ml for 16 hours or more. Since equilibrium dialysis took over two weeks, this indicates that DGT can be used as a fast alternative for the determination of Al and Fe(III) in acidic sandy soil solutions. With DGT we found higher 'free' Zn concentrations than with equilibrium dialysis at pH = 7.0. Most likely, this was caused by labile organic Zn complexes that were only detected by DGT.

In Chapter 3, the performance of DGT was further tested for the determination of Al, Fe(II) and Fe(III) at the lowest experimental pH of 3.5. The detection of 'free' Al and Fe(III) was good. 'Free' Fe(II) concentrations as determined by DGT at pH = 3.5 were consistently 40% too low, which could be corrected for. No correction was needed at higher pH values (≥ 4.0). Subsequently, DGT was applied to investigate the influence of changes in pH and M/C ratios on the soluble complexation of Al, Fe(II) and Fe(III) to DOM. Again water extracts of the Oh horizon of Soil 1 were used, which were brought at pH = 3.5, 4.0 or 4.5 at a constant DOM concentration of 30 mg C/l. To these solutions Al, Fe(II) and Fe(III) were added to create a range of M/C ratios in solution. At all three pH values, Fe(III) showed the highest degree of complexation with DOM, while Fe(II) showed the lowest. At low M/C ratios, the 'free' metal fraction for all three metal

species was the highest at the lowest pH value. This can be explained by the smaller amount of deprotonated acidic functional groups involved in metal binding on the DOM molecules. However, due to increased precipitation of organic-metal complexes, at higher M/C ratios for Al and Fe(III) the pH effect reversed. As a consequence, more ‘free’ metal was present at higher pH values because less reactive DOM remained available in solution to bind metals. Over the course of the experiments we observed both reduction of Fe in the experiments where Fe(III) was added, as well as oxidation of Fe in the experiments where Fe(II) was added. Overall the results confirm and quantify the important influence of pH, M/C ratios as well as the redox potential on the interactions of Al and Fe with dissolved organic matter.

In Chapter 4 we used the metal binding dataset that was obtained in Chapter 3 to compare the ‘free’ metal fractions as determined by DGT with calculations by the speciation codes Model V and its recent successor Model VI. Both are deterministic speciation models specifically designed to model the interactions between metals and organic matter. Together with an inorganic speciation model, they form the comprehensive solution speciation models WHAM-W 1.0 and WHAM-W 6.0, respectively. The comparison allowed for testing of the internal consistency of DGT with both models and gave further insights into the interactions between Al, Fe and DOM in solution. We applied both Model V and VI using the default parameter values but optimizing for the fraction of DOM that is inert with respect to metal binding (24%). The inert fraction agrees well with results from other studies. The calculated speciation of Al by both Model V and VI was generally in good agreement with the DGT results. However, at low Al/C ratios the Al fraction measured by DGT was systematically higher than the modelled ‘free’ Al fraction due to penetration of small dissolved organic Al complexes through the diffusion gel. Such a difference did not occur with Fe because apparently its complexes with DOM are not labile enough to be detected by DGT. The Model V calculations were in good agreement with the DGT results, especially considering the fact that extra uncertainty was introduced by the analytically determined Fe(II)/Fe(III) speciation in solution. Model VI calculated the trends in Fe binding well, but generally overestimated the ‘free’ Fe fraction.

Both Model V and VI predicted Fe to be bound to DOM predominantly in the form of Fe(III) while 'free' Fe in solution was dominated by Fe(II). Consequently, the overestimation of 'free' Fe by Model VI was mainly due to a calculated 'free' Fe(II) fraction that was too high. The Fe(III) binding constant in Model VI was recently modified to reflect stronger binding to DOM. We propose a similar critical evaluation of the Fe(II) binding constant.

In Chapter 5 the focus was shifted to the implications of the interactions between Al, Fe and DOM in soil solutions for their mobility in acidic sandy soils. For this purpose we examined the speciation of Al, Fe(II) and Fe(III) over 'free' dissolved metal, dissolved organic metal complexes and insoluble organic metal complexes. We used again the Oh horizon extracts of Soil 1 at pH = 3.5, 4.0 and 4.5 and a DOM concentration of 30 mg C/l. For all three metals, dissolved organic complexes were dominant at low M/C ratios (< 0.03). At higher M/C ratios, a strong pH effect was observed for Al: at pH = 3.5 dissolved 'free' Al was the dominant species, while at pH = 4.5 insoluble Al-DOM complexes dominated. For both Fe-species the pH effect was much less pronounced. For Fe(III) at higher M/C ratios, insoluble complexes were the dominant species at all pH values. For Fe(II) very little precipitation was observed and while free metal in solution gained in importance at higher M/C ratios, soluble complexes remained equally important. The differences between Fe(II) and Fe(III) signify the influence of the redox potential of the soil solution. Considering the higher pH and M/C ratios commonly found in illuvial podzol horizons as compared to eluvial horizons, our results predict mobilization of Al, Fe and DOM in O, A and E horizons by the formation of dissolved organic Al/Fe complexes as long as these complexes are not immobilized to a great extent through cation bridging. Subsequently, in illuvial horizons Al, Fe and organic matter would mainly be immobilized due to precipitation of organic Al and Fe(III) complexes.

In Chapter 6 and 7 we tested the hypotheses from Chapter 5 by performing experiments in the presence of solid soil material from eluvial (Chapter 6) and illuvial (Chapter 7) podzol horizons of Soil 1 and Soil 2. Again we used water extractions of the Oh horizon to create DOM solutions from both Soils. These were subsequently brought at pH = 3.5 and 60 mg C/l; pH = 4.0 and 30 mg C/l;

and pH = 4.5 and 10 mg C/l. The first solution was used in the study of the eluvial horizons and the last solution in the study of the illuvial horizons because they are realistic pH values and DOM concentrations for either horizon. The middle solution was used in both studies for reasons of comparison. The solutions from Soil 1 were equilibrated with solid soil material from its AhE, Bhs and BC horizons while the solutions from Soil 2 were equilibrated with solid soil material from its AE, Bhs1b and Bsb horizons. To the different experimental situations so created, increasing amounts of Al and Fe were added in a 3:1 molar ratio to impose a range of M/C ratios. The pH values were kept constant during the experiments. After each addition, the solution composition with respect to M/C ratio, DOC content and total and 'free' Al and Fe content was determined and the net amount of (im)mobilized metal and organic carbon was assessed.

In the eluvial horizons, even under considerable metal loading, the M/C ratios and 'free' metal fractions in solution remained low and relatively constant due to an apparent buffering by the solid phase and the formation of organic-metal complexes in solution. The M/C ratios remained so low that significant precipitation of organic-metal complexes due to saturation with metals was not found. The apparent buffering by the solid phase can be explained by a strong release of organic matter from solid soil material and adsorption of non-complexed Al and Fe on solid organic matter upon metal addition. Adsorption of organic-metal complexes most likely played only a minor role. The observations confirm the expected mobilization of Al, Fe and DOM in eluvial horizons and seem to indicate that even under fluctuating input of Al, Fe and DOM the soil solution will have a steady composition with respect to M/C ratios and percentage of Al and Fe present in dissolved organic metal complexes.

In the illuvial horizons, we observed some mobilization of organic matter in Soil 1, while organic matter was immobilized in Soil 2. In the Bhs horizon of Soil 1, after initial mobilization, Al and Fe were immobilized by direct adsorption on solid organic matter with increasing M/C ratios. In the BC horizon of Soil 1 and both B horizons of Soil 2 at pH = 4.5 organic and inorganic precipitation as well as adsorption of dissolved organic metal complexes on amorphous Al and Fe phases, led to immobilization of Al and Fe. This immobilization occurred

immediately or after the first few metal additions. Fe was immobilized more strongly than Al and inorganic precipitation seems to have played a role in all cases. Inorganic precipitation only controlled Al concentrations in the lower B horizons of both soils. The results confirm the important role of organic matter in the transport of Al and Fe to initially create a B horizon and subsequently deepening and differentiating it into a Bh and Bs horizon. The results of Chapter 6 and 7 agree well with the expectations from Chapter 5, with the exception of inorganic precipitation of $\text{Al}(\text{OH})_3(\text{s})$ as an immobilization mechanism. Also adsorption of dissolved organic Al/Fe complexes, in particular through cation bridging seems to play a less pronounced role than expected.

In the synthesis in Chapter 8 the insights gained in the different chapters were combined. The research presented in this thesis has increased our knowledge of interactions of Al and Fe with dissolved organic matter, the analytical tools that can be used to study them and the impact they have on the mobility of Al, Fe and organic matter in acidic sandy soils. Concerning the experimental analysis of the interactions of Al and Fe with dissolved organic matter, it was concluded that in spite of some imperfections, both DGT and WHAM-W 1.0 and 6.0 are very useful tools to study the binding of Al and Fe to DOM in acidic soil solutions. Future research using a combination of DGT and WHAM-W 1.0 and 6.0 will be an effective approach to further test and develop either method. The mobility of Al, Fe and organic matter in the studied acidic sandy soils, was mainly governed by the mechanisms as put forth in the classical fulvate theory. An exception is the solubility control in some instances by inorganic precipitation of Al. The discrepancy can be explained by our use of recent, more constrained K_{so} values of $\text{Al}(\text{OH})_3(\text{s})$ that were not available when the classical fulvate theory was formulated. Furthermore, the classical fulvate theory considers FA, while we considered generic DOM.

Samenvatting

Organische stof in bodems speelt een sleutelrol in belangrijke processen zoals bodemverzuring, de verwerking van mineralen en pedogenese. Verder beïnvloedt organische stof de mobiliteit en biobeschikbaarheid van andere stoffen, zoals organische vervuilingen, (sporen)metalen en nutriënten, door aan deze stoffen te binden. Organische stof kan worden onderverdeeld in vaste organische stof (SOM) en opgeloste organische stof (DOM). DOM vertegenwoordigt per definitie alle organische stof in oplossing die kleiner is dan $0.45 \mu\text{m}$. Onder SOM wordt naast deeltjes groter dan $0.45 \mu\text{m}$ ook organische stof die geadsorbeerd is aan mineralen verstaan. Een alternatieve indeling van organische stof is de onderverdeling in humine, humuszuren (HA) en fulvozuren (FA). Volgens de meest gangbare definitie is humine de fractie organische stof die bij kamertemperatuur onoplosbaar is in 0.1 M NaOH . HA is de fractie die wel in NaOH oplost maar neerslaat bij $\text{pH} = 1.0$, terwijl FA de fractie is die ook bij $\text{pH} = 1.0$ in oplossing blijft. Omdat organische stof in staat is tot het vormen van sterke coördinatieve bindingen via zijn zure functionele groepen, reageert het sterk met de meervoudig geladen metaalkationen Al^{3+} , Fe^{2+} en Fe^{3+} en hun geladen gehydrateerde species. Wanneer Al en Fe in bodems op deze manier aan organische stof binden, heeft dit grote invloed op de mobiliteit van zowel de metalen als de organische stof zelf. Als opgelost Al en Fe aan SOM binden of als de binding van opgeloste Al en Fe leidt tot het neerslaan van de gevormde organometaalcomplexen, heeft dit uiteraard immobilisatie als gevolg. Anderzijds kan de binding van Al en Fe aan DOM leiden tot mobilisatie van Al en Fe, indien opgeloste organometaalcomplexen gevormd worden. Dit voorkomt namelijk dat Al en Fe aan SOM binden, waardoor het oplosevenwicht van Al en Fe met secundaire minerale fasen zoals gibbsiet en ferrihydriet verschuift. De binding van Al en Fe aan organische stof wordt beïnvloed door een aantal bodemchemische variabelen, waaronder de pH, de redoxpotentiaal en de verhouding metaal tot opgeloste organische koolstof in het systeem (M/C verhouding). Veranderingen in de waarde van deze variabelen beïnvloeden zowel de mate waarin Al en Fe met organische stof complexeren, als het type complex

dat gevormd wordt (opgelost of neergeslagen). Dientengevolge leiden veranderingen in de pH, redoxpotentiaal en M/C verhouding tot veranderingen in de mobiliteit van Al, Fe en organische stof in bodems. De invloed van veranderingen in deze variabelen op de mobiliteit van Al, Fe en organische stof is echter nog onvoldoende gekwantificeerd. Dit blijkt onder andere uit feit dat er geen wetenschappelijke overeenstemming is over welke mechanismen verantwoordelijk zijn voor het proces van podzolering. Hierbij worden Al en Fe in een uitspoelingshorizont (E) in de bodem gemobiliseerd, waarna Al en in de meeste gevallen ook Fe in de onderliggende inspoelingshorizonten (B) worden afgezet. Er bestaan verschillende theorieën om dit bodemvormingsproces te verklaren. De klassieke fulvaattheorie stelt dat Al en Fe gemobiliseerd worden doordat FA mineralen verweert en de vrijgekomen Al en Fe vervolgens bindt in de vorm van opgeloste organometaalcomplexen. Naarmate deze opgeloste complexen dieper in de bodem doordringen, bindt er meer en meer Al en Fe aan, waardoor op een gegeven moment de negatieve lading op de moleculen voldoende gecompenseerd wordt om ze te doen neerslaan. De imogoliettheorie daarentegen stelt dat organisch materiaal helemaal geen rol speelt in het transport van Al en Fe in podzolen, maar neemt aan dat (proto)imogoliet sols met daarin insluitingen van Fe hiervoor verantwoordelijk zijn. Immobilisatie van Al en Fe vindt vervolgens plaats door neerslag van imogoliet, terwijl inspoeling van organische stof te wijten is aan adsorptie van DOM aan Al en Fe in de vaste fase. Weer andere theorieën nemen aan dat de vorming van opgeloste organische Al en Fe complexen weliswaar verantwoordelijk zijn voor de mobilisatie van deze metalen, maar stellen dat de immobilisatie op een andere manier plaatsvindt dan door neerslag van organische Al/Fe complexen. Dit kan bijvoorbeeld adsorptie van opgeloste organische Al/Fe complexen zijn, of neerslag van anorganische complexen zoals $\text{Al}(\text{OH})_3(\text{s})$, meteen of na microbiële afbraak van de organische moleculen. Sommige wetenschappers menen dat bij verschillende klimaten, verschillende podzoleringsmechanismen overheersen.

Het hoofddoel van deze studie was de invloed van de interacties van Al en Fe met organische stof op hun mobiliteit in zure zandige bodems in Nederland te onderzoeken. Dit proefschrift bestaat uit twee delen. Het eerste deel (Hoofdstuk

2-4) richt zich op het analyseren van de interacties van Al en Fe met organische stof in oplossing. Het tweede deel (Hoofdstuk 5-7) behandelt de invloed van vast bodemmateriaal op de associatie van Al en Fe met organische stof en de implicaties hiervan voor hun respectievelijke mobiliteit. Voor het onderzoek zijn twee podzol(ige) bodems uit de Veluwe in Nederland gekozen: Bodem 1, een jonge beginnende podzol (Fimic Anthrosol) en Bodem 2, een oude meer ontwikkelde podzol (Haplic Podzol).

In Hoofdstuk 2 is de relatief nieuwe analytisch chemische methode Diffusive Gradients in Thin films (DGT) in combinatie met de gangbare APA hydrogel en Na⁺-verzadigde chelatiehars getest op zijn toepasbaarheid om ‘vrij’ Al en Fe van opgeloste organische Al/Fe complexen in bodemoplossingen te onderscheiden. Hierbij wordt de ‘vrije’ fractie gedefinieerd als de gehydrateerde metaalkationen plus hun opgeloste anorganische complexen. De met DGT verkregen resultaten werden vergeleken met resultaten van analyses met de meer gevestigde, maar ook meer tijdrovende techniek van evenwichtsdi dialyse met een Molecular Weight Cut-Off (MWCO) van 1000 Da. Naast Al en Fe, is als extra test ook het belangrijke ‘milieumetaal’ Zn meegenomen. Als testoplossingen zijn vier waterextracten van de Oh horizont van Bodem 1 gebruikt. Deze zijn door toevoegen van zuur of loog en door concentratie of verdunning, op een pH van 4.0 of 7.0 en DOM concentraties van 20 of 75 mg C/l gebracht. Voor Al en Fe(III) vonden we in geen van de testoplossingen een significant verschil tussen de ‘vrije’ metaalfraction zoals bepaald door DGT en door evenwichtsdi dialyse, mits DGT 16 uur of langer werd toegepast in een volume van minimaal 500 ml. Aangezien de analyse met evenwichtsdi dialyse ruim 2 weken duurde, geeft dit aan dat DGT in vergelijking met evenwichtsdi dialyse een snel alternatief is om ‘vrij’ Al en Fe(III) in zure bodemoplossingen te meten. Bij pH = 7.0 werden met DGT echter hogere ‘vrije’ Zn concentraties gevonden dan met evenwichtsdi dialyse. Waarschijnlijk is dit het gevolg van de detectie van opgeloste labiele organische Zn verbindingen die niet met dialyse gemeten werden.

In Hoofdstuk 3 hebben we de toepasbaarheid van DGT verder getest voor de detectie van ‘vrij’ Al, Fe(II) en Fe(III) bij de laagst voorkomende pH van 3.5. Vrij Al en Fe(III) kon probleemloos worden gemeten bij deze lage pH. De gemeten

‘vrije’ Fe(II) gehalten waren echter systematisch 40% te laag, waarvoor een correctie nodig was. Bij hogere pH waarden (≥ 4.0) werd ‘vrij’ Fe(II) wel correct gemeten. Vervolgens hebben we DGT toegepast om de invloed van veranderingen in de pH en M/C verhoudingen op de complexering van Al, Fe(II) en Fe(III) met DOM in oplossing te onderzoeken. Hiervoor zijn opnieuw waterextracten van de Oh horizont van Bodem 1 gebruikt, die vervolgens bij een constante DOM concentratie van 30 mg C/l, op pH = 3.5, 4.0 of 4.5 werden gebracht. Aan deze oplossingen hebben we Al, Fe(II) en Fe(III) toegevoegd om een range van M/C verhoudingen in oplossing te creëren. Bij alle drie de pH waardes vertoonde Fe(III) de hoogste mate van binding aan DOM, terwijl Fe(II) het minst bond. Bij lage M/C verhoudingen was de ‘vrije’ metaal fractie voor alle drie de metaalspecies het hoogst bij de laagste pH waarde. Een verklaring hiervoor is de kleinere hoeveelheid gedeprotoneerde zure, metaalbindende functionele groepen bij lagere pH. Bij hogere M/C verhoudingen sloegen in het geval van Al en Fe(III) steeds meer organo-metaalcomplexen neer, waarbij de meeste neerslag bij de hoogste pH werd gevormd. Omdat hierdoor minder DOM in oplossing over bleef om metalen te binden, was het pH effect op de complexering in oplossing bij hogere M/C verhoudingen precies omgekeerd. Ook bevond zich hierdoor bij hogere pH meer metaal in de ‘vrij’ metaal fractie. Tijdens de experimenten waarbij Fe(III) werd toegevoegd trad reductie van Fe op, terwijl in de experimenten waar Fe(II) werd toegevoegd, sprake was van oxidatie. Alles bij elkaar bevestigen en kwantificeren deze experimenten de belangrijke invloed van de drie bodemchemische variabelen: pH, M/C verhouding en redoxpotentiaal op de interacties van Al en Fe met DOM.

In Hoofdstuk 4 hebben we de metaalbindingsdataset die we in Hoofdstuk 3 hebben verzamelt gebruikt om de ‘vrije’ metaalfracties zoals met DGT gemeten te vergelijken met berekeningen met de speciatie modellen Model V en Model VI. Beide zijn deterministische modellen die specifiek zijn ontworpen om de interacties tussen metalen en organische stof te modelleren. Samen met een anorganisch speciatie model vormen ze de volgende twee speciatie modellen voor de opgeloste fase: WHAM-W 1.0 en WHAM-W 6.0. Vergelijking van de modellen

met DGT stelde ons in staat de interne consistentie van beide methoden te testen. We hebben Model V en VI toegepast met de standaard parameter set, maar hebben wel de fractie DOM die inert is voor metaalbinding geoptimaliseerd (24%). Deze waarde komt overeen met de waarde die in andere studies gevonden is. De door Model V en VI berekende speciatie van Al kwam over het algemeen goed overeen met de DGT resultaten. Bij lager Al/C verhoudingen, waren de DGT resultaten echter systematisch hoger dan de modelberekeningen. Dit komt waarschijnlijk door de bijdrage van kleine, labiele, opgeloste organische Al complexen die snel genoeg door de DGT diffusiegel diffunderen om door DGT mee gemeten te worden. Een dergelijk verschil deed zich niet voor bij Fe, waarschijnlijk omdat kleine opgeloste organische Fe complexen die door de diffusiegel heen kwamen niet labiel genoeg waren om door DGT gemeten te worden. De berekeningen voor Fe door Model V kwamen dan ook verrassend goed overeen met de DGT resultaten, zeker als men bedenkt dat er extra onzekerheid geïntroduceerd werd door de gemeten Fe(II)/Fe(III) speciatie in oplossing als invoer voor het model te gebruiken. Model VI berekende wel de trends van de binding van Fe aan DOM goed, maar overschatte de 'vrije' Fe fractie systematisch. Omdat zowel Model V als Model VI aangaven dat veruit het meeste Fe(III) ten alle tijden aan DOM gebonden zat, werd de overschatting door Model VI waarschijnlijk veroorzaakt door een te hoog geschatte 'vrije' Fe(II) fractie. De bindingsconstante voor Fe(III) in Model VI is onlangs aangepast zodat Fe(III) sterker aan DOM bindt. We stellen echter voor om ook de bindingsconstante voor Fe(II) in Model VI kritisch te evalueren.

In Hoofdstuk 5 ligt de nadruk op de implicaties van de interacties van Al en Fe met DOM in bodemoplossingen op hun mobiliteit in zure zandige bodems. Hiervoor is de verdeling van Al, Fe(II) en Fe(III) over 'vrij' opgelost metaal, opgeloste organo-metaalcomplexen en neergeslagen organo-metaalcomplexen beschouwd. Er is hierbij opnieuw gebruik gemaakt van waterextracten van de Oh horizont van Bodem 1 bij pH = 3.5, 4.0 en 4.5 en een DOM concentratie van 30 mg C/l. Voor alle drie de metalen waren opgeloste organometaalcomplexen dominant bij lagere M/C verhoudingen (< 0.03). Bij hogere M/C verhoudingen was er voor Al een sterk pH effect zichtbaar, waarbij bij pH = 3.5 de 'vrije' Al

fractie dominant was terwijl bij pH = 4.5 de meerderheid van het Al als onoplosbare organische Al complexen aanwezig was. Voor zowel Fe(II) als Fe(III) was het pH effect veel minder duidelijk. Bij hogere M/C verhoudingen was Fe(III) altijd hoofdzakelijk aanwezig in de vorm van onoplosbare organische Fe complexen, ongeacht de pH. Bij Fe(II) vormden zich daarentegen nauwelijks onoplosbare complexen, en hoewel de 'vrije' fractie toenam met stijgende M/C verhoudingen, bleef ook een groot deel als opgeloste organische Fe(II) complexen aanwezig. Deze verschillen tussen Fe(II) en Fe(III) geven aan hoe belangrijk de redoxpotentiaal van de bodemoplossing is voor de mobiliteit van Fe. In uitspoelingshorizonten worden doorgaans hogere pH waarden en M/C verhoudingen gevonden dan in inspoelingshorizonten. Deze verschillen voorspellen dat Al, Fe en DOM gemobiliseerd worden in O, A en E horizonten, doordat daar opgeloste organische Al en Fe complexen worden gevormd, mits de complexen niet teveel door kationbruggen worden vastgelegd. Vervolgens slaan Al, Fe en organische stof neer in inspoelingshorizonten, vooral in de vorm van onoplosbare organische Al en Fe(III) complexen.

In Hoofdstuk 6 en 7 hebben we de voorspellingen uit Hoofdstuk 5 getest door experimenten uit te voeren in aanwezigheid van vast bodemmateriaal uit podzol uitspoelings- (Hoofdstuk 6) en inspoelingshorizonten (Hoofdstuk 7) uit Bodem 1 en Bodem 2. Hierbij hebben we wederom waterextracties van de Oh horizonten gebruikt om DOM oplossingen te maken. Deze oplossingen werden vervolgens respectievelijk op pH = 3.5 en 60 mg C/l; pH = 4.0 en 30 mg C/l; en pH = 4.5 en 10 mg C/l gebracht. De eerste oplossing is gebruikt in de experimenten met de uitspoelingshorizonten en de laatste in de experimenten met de inspoelingshorizonten, omdat ze realistische pH waarden en DOM concentraties voor de respectievelijke horizonten vertegenwoordigen. De middelste oplossing is in beide studies gebruikt, om een vergelijking tussen inspoelings- en uitspoelingshorizonten mogelijk te maken. De oplossingen verkregen uit Bodem 1 zijn vervolgens in evenwicht gebracht met bodemmateriaal van de AhE, Bhs en BC horizonten uit deze bodem, terwijl de oplossingen van Bodem 2 aan de AE, Bhs2b en Bsb horizonten uit Bodem 2 zijn toegevoegd. In de aldus verkregen set experimentele uitgangssituaties hebben we een range van M/C verhoudingen

gecreëerd door stijgende hoeveelheden Al en Fe toe te voegen in een onderlinge molverhouding van 3:1. Hierbij werden de pH waarden constant gehouden. Na elke toevoeging van metalen werd de M/C verhouding, het DOC gehalte en de totale en 'vrije' Al en Fe gehalten in oplossing bepaald, evenals de netto hoeveelheid ge(im)mobiliseerde Al, Fe en organische koolstof.

In de uitspoelingshorizonten bleven de M/C verhoudingen en 'vrije' metaalfracties in oplossing laag en relatief constant, zelfs nadat relatief grote hoeveelheden Al en Fe waren toegevoegd. Dit werd veroorzaakt door een kennelijke buffering door de vaste fase en de vorming van opgeloste organometaalcomplexen. De M/C verhoudingen bleven zo laag dat neerslag van organometaalcomplexen ten gevolge van verzadiging met metalen uitbleef. De buffering door de vaste fase kan worden verklaard door het in oplossing gaan van grote hoeveelheden organisch materiaal onder gelijktijdige adsorptie van nog niet gecomplexeerd Al en Fe. Adsorptie van organometaalcomplexen speelde waarschijnlijk slechts een beperkte rol. De resultaten bevestigen de verwachte mobilisatie van Al, Fe en DOM in uitspoelingshorizonten en geven aan dat zelfs als de input van Al, Fe en DOM fluctueert, de M/C verhouding en het percentage Al en Fe dat aanwezig is in opgeloste organometaalcomplexen min of meer constant blijft.

In de inspoelingshorizonten vonden we een beperkte mate van mobilisatie van organische stof in Bodem 1 en immobilisatie van organische stof in Bodem 2. In de Bhs horizont van Bodem 1 werden Al en Fe eerst gemobiliseerd, maar naarmate er meer metaal werd toegevoegd veranderde dit in een netto immobilisatie door directe adsorptie op vaste organische stof. In de BC horizont van Bodem 1 en de beide B horizonten van Bodem 2 leidde bij pH = 4.5 een combinatie van neerslag van zowel organische als anorganische Al en Fe complexen en adsorptie van opgeloste organometaalcomplexen, tot immobilisatie van beide metalen. Deze immobilisatie begon meteen of na de eerste paar metaal toevoegingen. Hierbij werd Fe in sterkere mate geïmmobiliseerd dan Al en lijkt neerslag van anorganische Fe complexen in alle gevallen een rol te hebben gespeeld in de immobilisatie van Fe. Voor Al speelde neerslag van anorganische complexen alleen een rol in de onderste B horizont van beide bodems. Deze

resultaten bevestigen dat organische stof een belangrijke rol speelt in het transport van Al en Fe om een inspoelings B horizont te vormen die vervolgens verdiept en splits in een Bh en Bs horizont. De resultaten van Hoofdstuk 6 en 7 bevestigen hiermee de verwachtingen uit Hoofdstuk 5, met als uitzondering de rol van neerslag van anorganische Al complexen in de immobilisatie van Al. Daarnaast lijkt de adsorptie van opgeloste organometaalcomplexen, met name middels kationbruggen, een minder belangrijke rol te spelen dan verwacht.

In Hoofdstuk 8 zijn de inzichten uit voorgaande hoofdstukken samengevoegd. Het onderzoek dat in dit proefschrift gepresenteerd wordt heeft onze inzichten met betrekking tot de interacties van Al en Fe met opgeloste organische stof en de invloed hiervan op de mobiliteit van Al, Fe en organische stof in zure zandige bodems vergroot. Verder heeft het een licht geworpen op recente analytische methoden om de interacties van Al en Fe met opgeloste organische stof te onderzoeken. Met betrekking tot de experimentele analyse, is de conclusie dat zowel DGT als WHAM-W 1.0 en 6.0 ondanks een paar onvolkomenheden, zeer goede methoden zijn om de binding van Al en Fe aan DOM in zure zandige bodems te bestuderen. Onderzoek waarbij gebruik gemaakt wordt van een combinatie van DGT en WHAM-W 1.0 en 6.0 lijkt een effectieve manier om beide methoden nog verder te ontwikkelen. De mobiliteit van Al, Fe en organische stof in de bestudeerde zure zandige bodems werd hoofdzakelijk gestuurd door de mechanismen zoals omschreven in de klassieke fulvaattheorie. Een uitzondering hierop vormt het feit dat de oplosbaarheid van Al soms werd bepaald door neerslag van anorganische Al complexen. Deze afwijking van de theorie kan worden verklaard door ons gebruik van recente K_{so} waarden voor $Al(OH)_3(s)$, die hoger zijn dan de waarden die beschikbaar waren toen de klassieke fulvaattheorie opgesteld werd. Daarnaast beschouwt de klassieke fulvaattheorie FA, terwijl wij steeds generiek DOM gebruikt hebben.

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Appendix: description and characterization of the soils studied within the framework of this thesis

't Harde: Haplic Podzol

Table 1

Description of the location

| | |
|-------------------|---|
| Location | ASK Oldebroek, Oldebroeksche Heide, Community of Oldebroek, province of Gelderland, The Netherlands |
| Coordinates | 52° 24' N, 5° 55' E |
| Elevation (m) | 25 |
| Slope | Class 1 – almost flat (2%) |
| Groundwater class | VII |
| Plant species | Calluna vulgaris, Molinia caerulea, Deschampsia flexuosa, Pinus sylvestris, Betula pendula, Empetrum nigrum, Juniperus communis |
| Parent material | Coversand; fluvioglacial deposit |
| Climate | Temperate, humid, mean annual precipitation 800 mm |

Table 2

Description of the soil profile

| Depth (cm): | Horizon: | Description: | Color (Munsell scale; field moist): |
|-------------|----------|---|-------------------------------------|
| +4 - +3.5 | L | Relatively fresh litter; abrupt and wavy boundary to F | |
| +3.5 - +0.5 | F | Dark brown fermentation layer; abrupt and wavy boundary to H | |
| +0.5 - 0 | H | Black humus layer; slight admixture of bleached sand grains; abundant roots; abrupt and wavy boundary to AE | 10 YR 1/1 |
| 0 - 8 | AE | Bleached eluvial layer; frequent roots; abrupt and smooth boundary to Bhs1 | 10 YR 3/1 |
| 8 - 14 | Bhs1 | Illuvial layer; few roots; clear and smooth boundary to Bhs2/BC | 7.5 YR 2.5/2 |
| 14 - 45 | Bhs2/BC | Illuvial layer; few roots; clear and wavy boundary to 2Bhs1b | 10 YR 3/6 |
| 45 - 52 | 2Bhs1b | Buried illuvial layer; few roots; abrupt and smooth boundary to 2Bhs2b | 10 YR 2/1 |
| 52 - 75 | 2Bhs2b | Buried illuvial layer; few roots; clear and wavy boundary to 2Bsb | 10 YR 2/1 |
| 75 - 85 | 2Bsb | Buried illuvial layer; few roots; clear and wavy boundary to 2BCb | 7.5 YR 2.5/2 |
| 85+ | 2BCb | Buried illuvial layer; few roots | 10 YR 4/4 |

Buunderkamp: Fimic Anthrosol

Table 3

Description of the location

| | |
|-------------------|---|
| Location | Boswachterij Oostereng, Community of Ede, province of Gelderland, The Netherlands |
| Coordinates | 52° 02' N, 5° 48' E |
| Elevation (m) | 27 |
| Slope | Class 1 – almost flat (2%) |
| Groundwater class | VII |
| Plant species | Quercus robur |
| Parent material | Coversand; Preglacial, fluvial deposit of the river Rhine |
| Climate | Temperate, humid, mean annual precipitation 800 mm |

Table 4

Description of the soil profile

| Depth (cm): | Horizon: | Description: | Color (Munsell scale; field moist): |
|-------------|----------|---|-------------------------------------|
| +4.5 - +3 | L | Relatively fresh litter; abrupt and wavy boundary to F | |
| +3 - +1 | F | Dark brown fermentation layer; abrupt and wavy boundary to H | |
| +1 - 0 | H | Black humus layer; slight admixture of bleached sand grains; abundant roots; abrupt and wavy boundary to AhE | 10 YR 1/1 |
| 0 - 2 | AhE | Bleached eluvial layer; coarse angular sand, abundant gravel; frequent roots; abrupt and wavy boundary to Bhs | 10 YR 3/1 |
| 2 - 7 | Bhs | Illuvial layer; coarse angular sand, abundant gravel; few roots; clear and wavy boundary to BC | 10 YR 3/3 |
| 7 - 18 | BC | Illuvial layer; coarse angular sand; few roots; abrupt and wavy boundary to 2Aanb | 10 YR 3/4 |
| 18 - 55 | 2Aanb | Buried disturbed layer; coversand; abundant roots; clear and wavy boundary to 2Bsb | |
| 55 - 67 | 2Bsb | Buried illuvial layer; coversand; few roots; clear and wavy boundary to 3BCb | |
| 67 - 82 | 3BCb | Buried illuvial layer; coarse angular sand; few roots; gradual and wavy boundary to 3Cb | |
| 82+ | 3Cb | Coarse angular sand; few roots | |

Curriculum Vitae

Boris Jansen werd geboren op 22 juni 1974 in Eemnes. Dat hij al vroeg interesse voor bodems had, blijkt uit het Roosvicee boekje dat hij op driejarige leeftijd kreeg en waarin hij een avontuur met onder de grond wonende aardkabouters beleefde. Daarnaast werd hij waarschijnlijk geïnspireerd door de enorme hoeveelheid zand in de woestijn van Saoedi-Arabië waar hij, toen hij vijf was, tweeënehalf jaar met zijn ouders naar toe ging. Ook zijn middelbare schoolopleiding aan het Alberdink Thijm College in Hilversum werd onderbroken voor een bezoek aan het buitenland. Ditmaal betrof het de Verenigde Staten waar hij de 10th en 11th grade volbracht aan de Dublin Highschool in Dublin, Ohio. Weer terug in Nederland haalde Boris in 1993 zijn VWO diploma met het hoogste cijfergemiddelde van zijn jaar en begon met de studie Milieuwetenschappen / Scheikunde aan de Vrije Universiteit in Amsterdam. Alvorens deze studie in 1998 met goed gevolg af te ronden, keerde hij acht maanden terug naar de VS om aan het Energy and Environmental Research Center in Grand Forks, North Dakota een onderzoeksstage uit te voeren. Hierin onderzocht hij de toepasbaarheid van een nieuwe extractiemethode voor pesticiden uit vervuilde bodems. Na afloop van zijn studie werkte Boris eerst een tijdje bij Cap Gemini. Hij besloot echter al snel dat zijn liefde voor de wetenschap te groot was om onbeantwoord te laten en solliciteerde in 1999 met succes naar een promotieplaats bij Fysische Geografie aan de Universiteit van Amsterdam. Dit bleek een juiste beslissing te zijn, want vier jaar met veel plezier werken had het proefschrift dat nu voor u ligt als tastbaar resultaat.