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The mobility of aluminium, iron and organic matter in acidic

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Publication date
2003

Citation for published version (APA):
Jansen, B. (2003). *The mobility of aluminium, iron and organic matter in acidic*. [Thesis, fully internal, Universiteit van Amsterdam]. IBED, Universiteit van Amsterdam.

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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 Anthrosol 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.

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 (pH_{H_2O} = 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 MΩ) 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 HNO_3 solution or a 1.0 M KOH solution.

To all DOM solutions NaN_3 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 NaN_3 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 × 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 HNO_3 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 HNO_3 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 $Cd(NO_3)_2$ for general performance tests. Water solutions containing 10 µM $Cd(NO_3)_2$ and 0.01 M KNO_3 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 $FeCl_2$ 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):

$$M = Ce(V_{HNO3} + Vgel)/fe \tag{1}$$
$$C = M\Delta g/(DtA) \tag{2}$$

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_{HNO3}) and the chelating resin (Vgel = 1.6×10^{-4} l), 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 = 0.094 cm), the diffusion coefficient of the metals in the hydrogel (D), the deployment time (t = 5.76×10^4 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 $Cd(NO_3)_2$ solutions was 94% (RSD = 2.0%). This is within the ±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 ±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 (Vilgé-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.
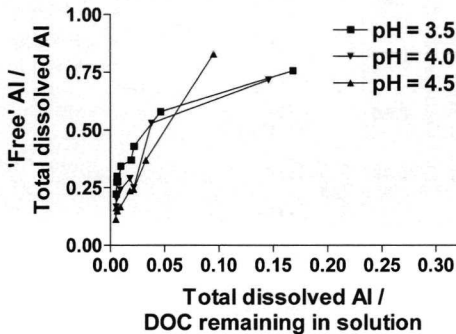

Fig.1. Fraction of 'free'Al versus the ratio of total soluble Al/total organic carbon in solution (M/C$_{soluble}$). For S.D. see Table 3.
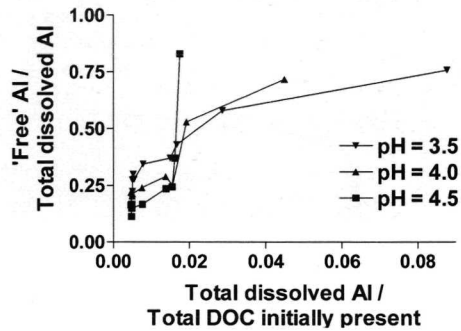
Fig. 2: Fraction of 'free'Al versus the ratio of total soluble Al/total organic carbon that was initially present in solution (M/C$_{total}$). For S.D. see Table 3.

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$_{(soluble\ and\ total)}$ 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.
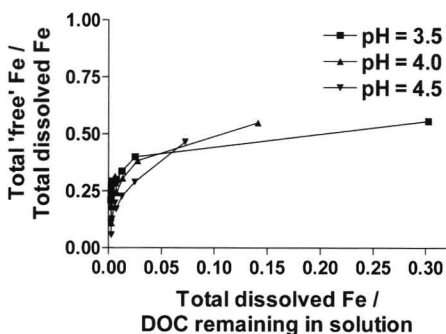

Fig. 3. Fraction of total 'free'Fe in the Fe(III) addition experiments versus the ratio of total soluble Fe / total organic carbon in solution $(M/C_{soluble})$. For S.D. see Table 3.
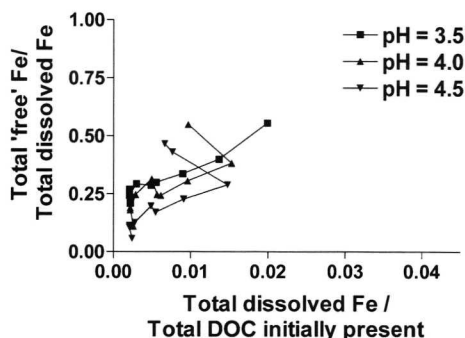
Fig. 4: Fraction of total 'free'Fe in the Fe(III) addition experiments versus the ratio of total soluble Fe / total organic carbon that was initially present in solution (M/C_{total}). For S.D. see Table 3.

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 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 pH = 4.0 and pH = 4.5, the graphs show a sharp bend after the eighth addition step and the total metal concentration in solution

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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 $Fe(OH)_3$ 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 M/C_{total} ratio.
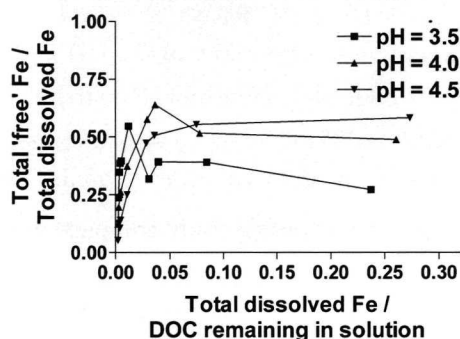

Fig. 5. Fraction of total 'free'Fe in the Fe(II) addition experiments versus the ratio of total soluble Fe/Total organic carbon in solution ($M/C_{soluble}$). For S.D. see Table 3.
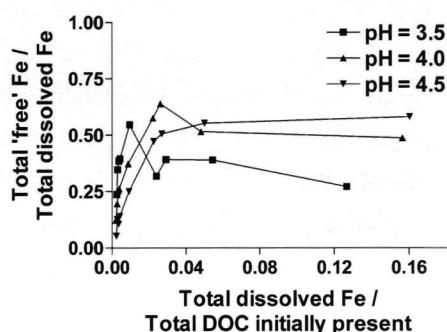
Fig. 6. Fraction of total 'free'Fe in the Fe(II) addition experiments versus the ratio of total soluble Fe/total organic carbon that was initially present in solution (M/C_{total}). For S.D. see Table 3.

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 (± 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 occured. 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 O_2 and NO_3^- (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 calcultations 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.