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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-

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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_{so} values for $Al(OH)_3(s)$ were published (Gustafsson et al., 2001). When the solubility of Al is recalculated using these values, the results indicate that some precipitation of $Al(OH)_3(s)$ 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.

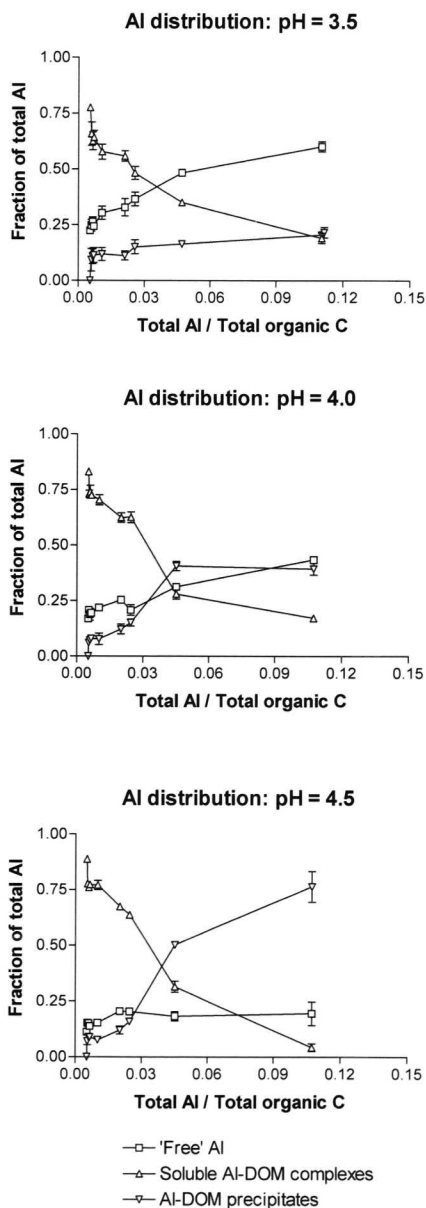


Fig. 1 Fractional distribution of Al over dissolved 'free' Al, soluble Al-DOM complexes and Al-DOM precipitates. Error bars depict standard error of the mean (S.E.M.)

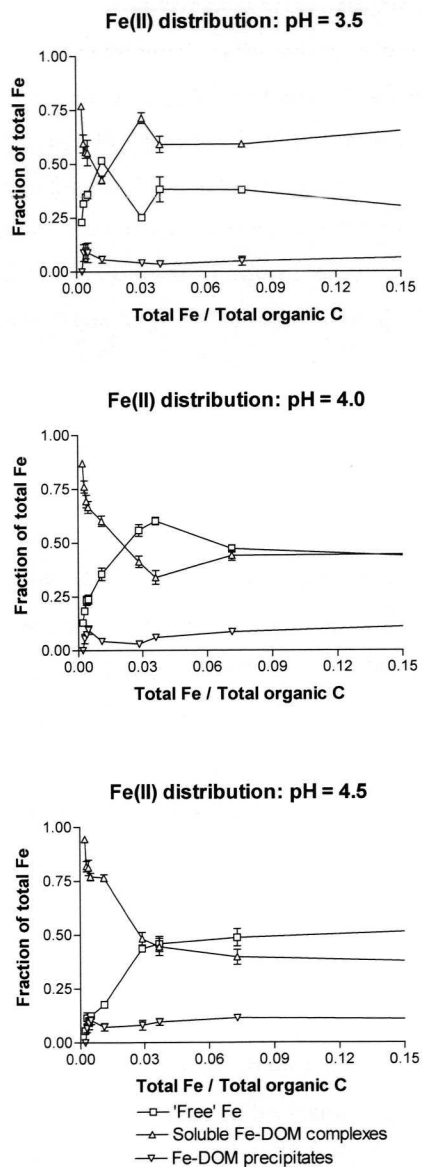


Fig. 2 Fractional distribution of Fe in the Fe(II) experiments over dissolved 'free' Fe, soluble Fe-DOM complexes and Fe-DOM precipitates at three pH values. Error bars depict standard error of the means (S.E.M.)

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.

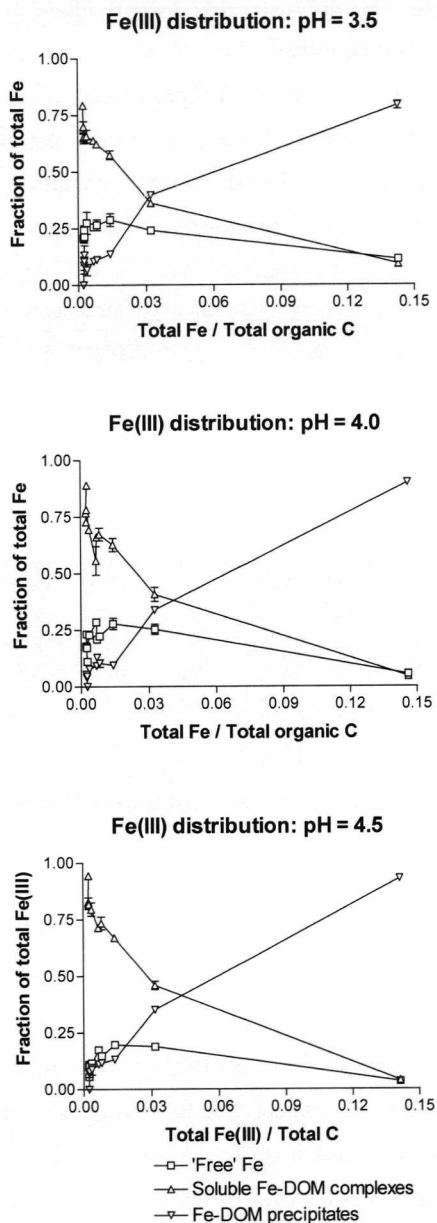


Fig. 3 Fractional distribution of Fe in the Fe(III) experiments over dissolved 'free' Fe, soluble Fe-DOM complexes and Fe-DOM precipitates at three pH values. Error bars depict standard error of the mean (S.E.M.)

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

Mobility of Fe(II), Fe(III) and Al mediated by dissolved organic matter

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.

