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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 organic 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 ≥ 1.5 μ 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.

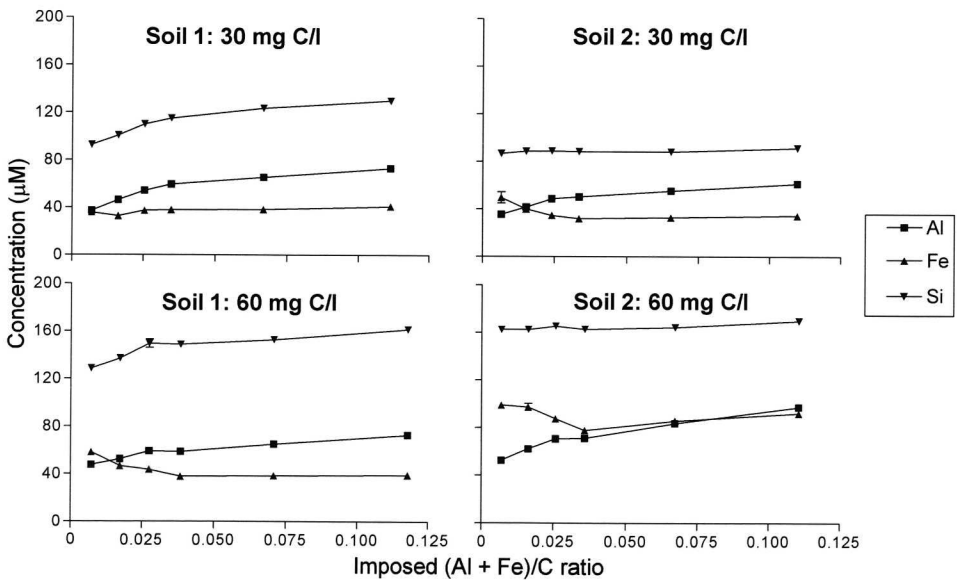


Fig. 1 Total metal concentrations in solution as a function of increasing imposed (Al + Fe)/C ratios, which consist of the theoretical molar metal concentration assuming all metal stayed in solution, divided by total molar DOC concentrations initially present. Error bars depict the standard error of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

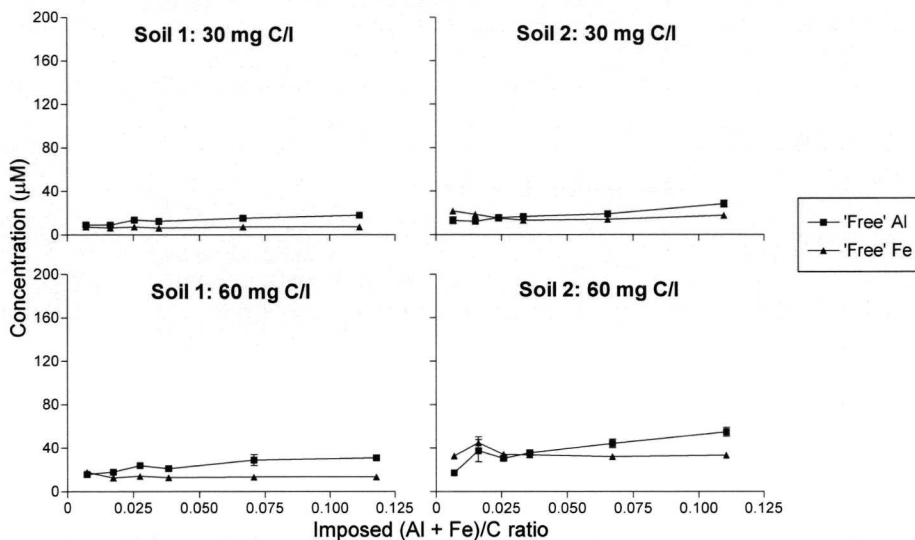


Fig. 2 'Free' metal concentrations in solution as a function of increasing imposed (Al + Fe)/C ratios (see the legend of Fig. 1 for explanation).

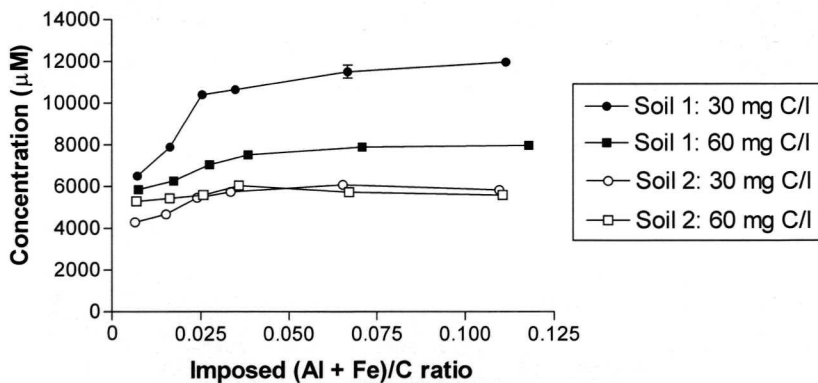


Fig. 3. DOC concentrations in solution as a function of increasing imposed (Al + Fe)/C ratios (see the legend of Fig. 1 for explanation).

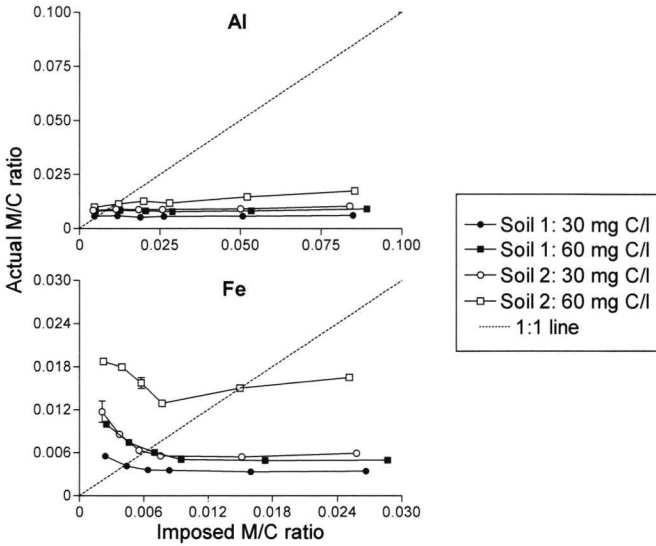


Fig. 4 Actual metal to organic carbon (M/C) ratios in solution as a function of the imposed (Al + Fe)/C ratios in solution (see the legend of Fig 1. for explanation) for the A(h)E soil material.

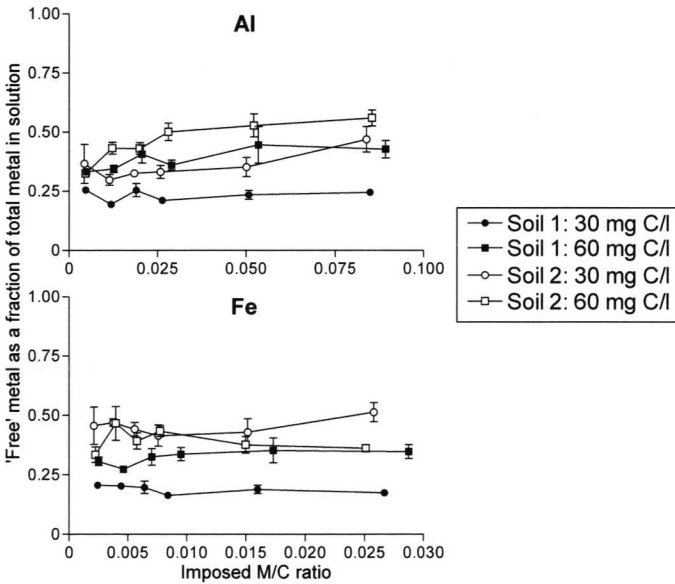


Fig. 5 The fraction of Al and Fe in solution that is present in the 'free' form, as a function of the imposed metal to organic carbon ratio (see the legend of Fig. 1 for explanation) for the A(h)E soil material.

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).

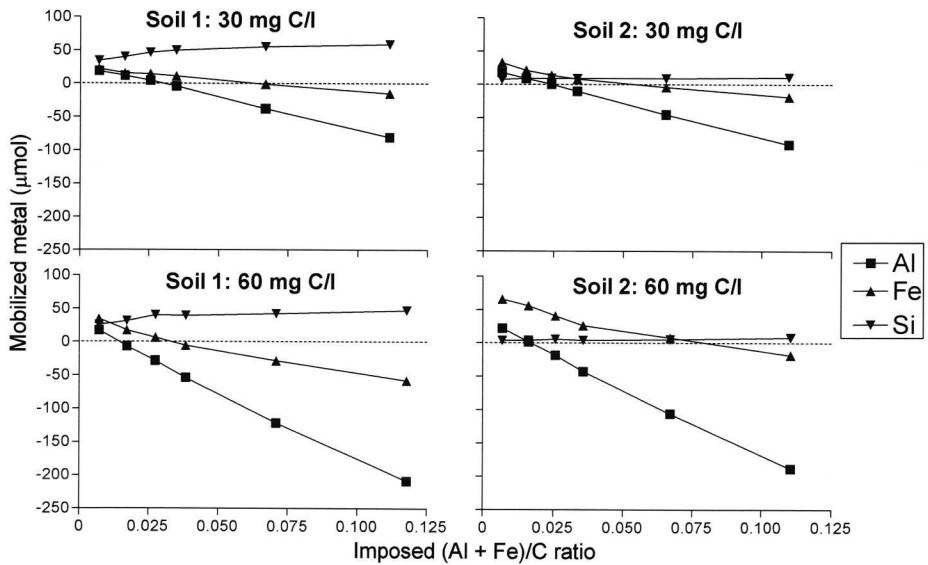


Fig. 6 The net cumulative number of µmoles of Al, Fe and Si mobilized or immobilized over the course of the experiments as a function of increasing imposed (Al + Fe)/C ratios (see the legend of Figure 1 for explanation), corrected for the addition of Al and Fe.

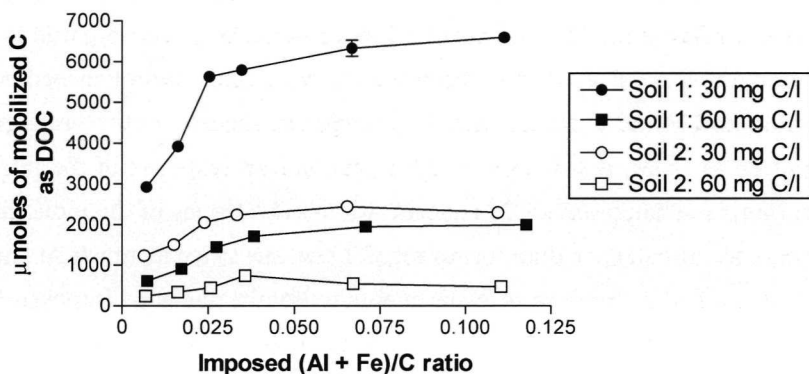


Fig. 7 The net cumulative number of μmoles of DOC mobilized or immobilized over the course of the experiments as a function of increasing imposed (Al + Fe)/C ratios (see the legend of Fig. 1 for explanation).

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

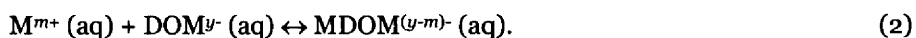
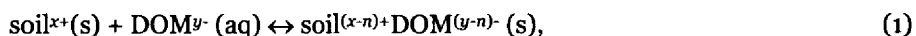
When comparing the two soils, the trends of (im)mobilization were remarkably similar except for greater initial mobilization of Fe in Soil 2, especially in Soil 2:

AE:60, which correlated positively with the larger BaCl_2 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 Al^{3+} and Fe^{3+} 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):

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

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.