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

Abstract

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

* Submitted to European Journal of Soil Science by B. Jansen, K.G.J. Nierop and J.M. Verstraten.

7.1 Introduction

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

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

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

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

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

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

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

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

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

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

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

7.2 Materials and methods

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

7.2.1 Description of soil materials

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

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

7.2.2 Preparation of DOM solutions

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

Table 1
Initial composition of the DOM solutions:^a.

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

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

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

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

7.2.3 Experimental setup

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

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

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

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

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

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

7.2.4 Analyses

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

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

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

7.3 Results

7.3.1 Chemical soil properties

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

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

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

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

Table 2

Initial composition of the soil samples used in the experiments.

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

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

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

Table 3

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

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

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

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

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

Table 4

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

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

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

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

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

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

concentrations of Fe decrease when going from Soil 1: Bhs to Soil 2: Bsb and are positively correlated with the C_t/M_0 ratios for both the initial DOC concentrations of 10 mg C/l and 30 mg C/l. For Al there was no correlation at the initial DOC concentration of 10 mg C/l and there was a negative correlation at the initial DOC concentration of 30 mg C/l.

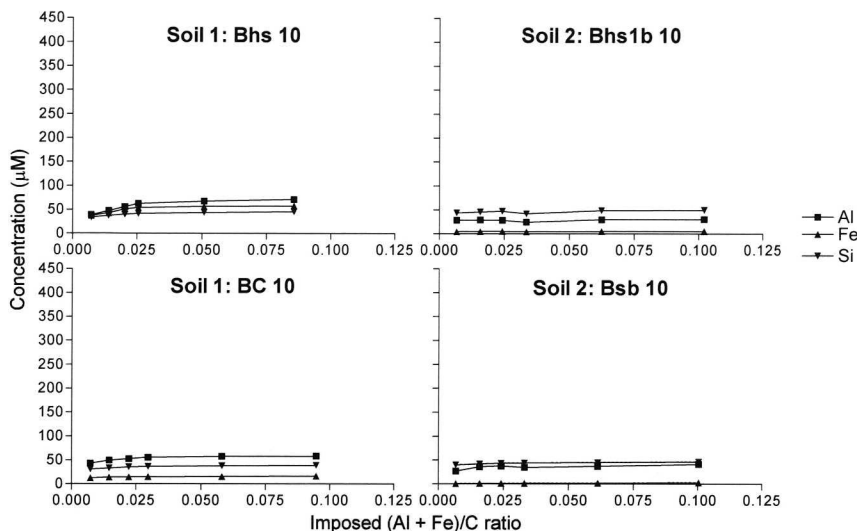
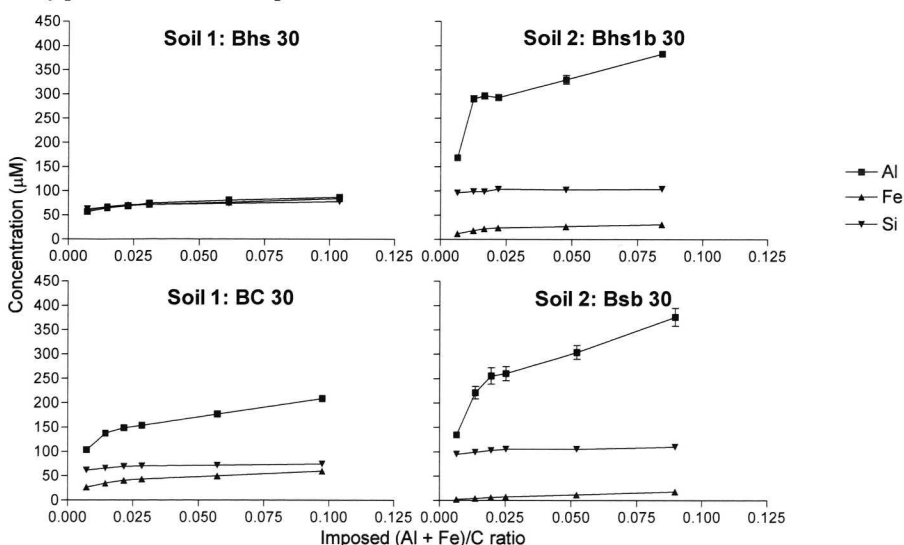


Fig. 1 and 2 Total metal and silica concentrations in solution in the experiments with pH = 4.5 and an initial DOC concentration of 10 mg C/l (top) and pH = 4.0 and an initial DOC concentration of 30 mg C/l (bottom), as a function of increasing imposed M/C ratios, which consist of the theoretical molar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



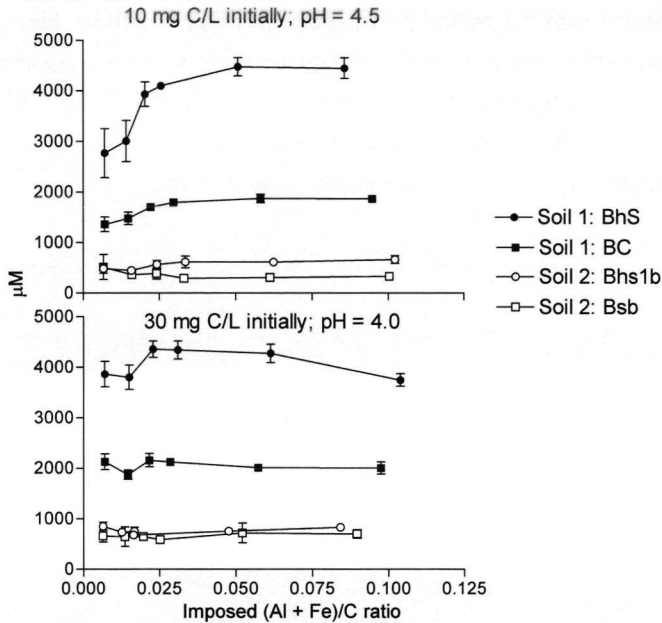


Fig. 3 DOM concentrations in solution determined as DOC, as a function of increasing imposed M/C ratios (see the legend of Figure 1 for explanation). Error bars depict standard error of the mean.

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

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

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

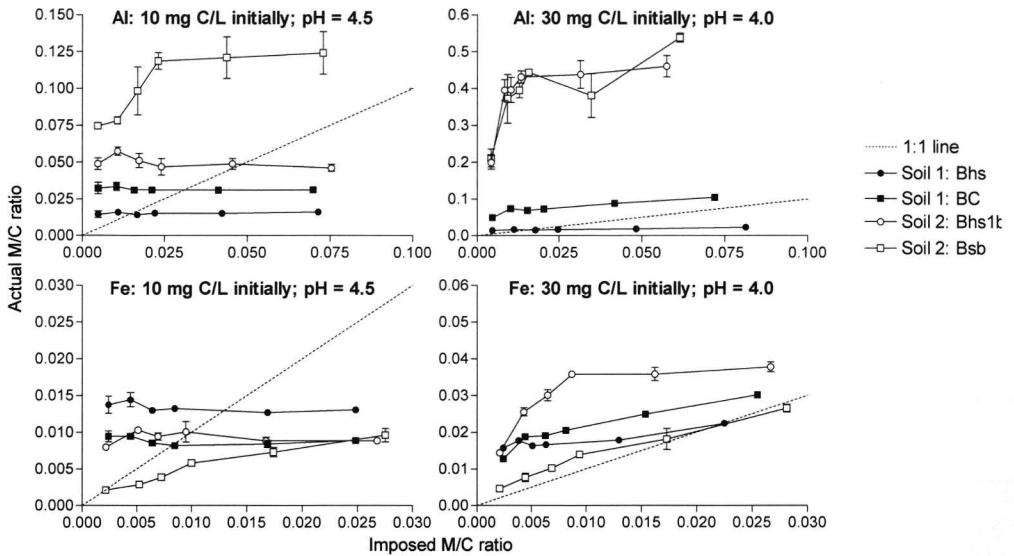


Fig. 4 Actual metal to organic carbon (M/C) ratios in solution as a function of the imposed M/C ratios in solution (see the legend of Figure 1 for explanation) for the soil material of Soil 1 and 2. Error bars depict standard error of the mean.

7.3.3 Mobility of organic matter

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

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

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

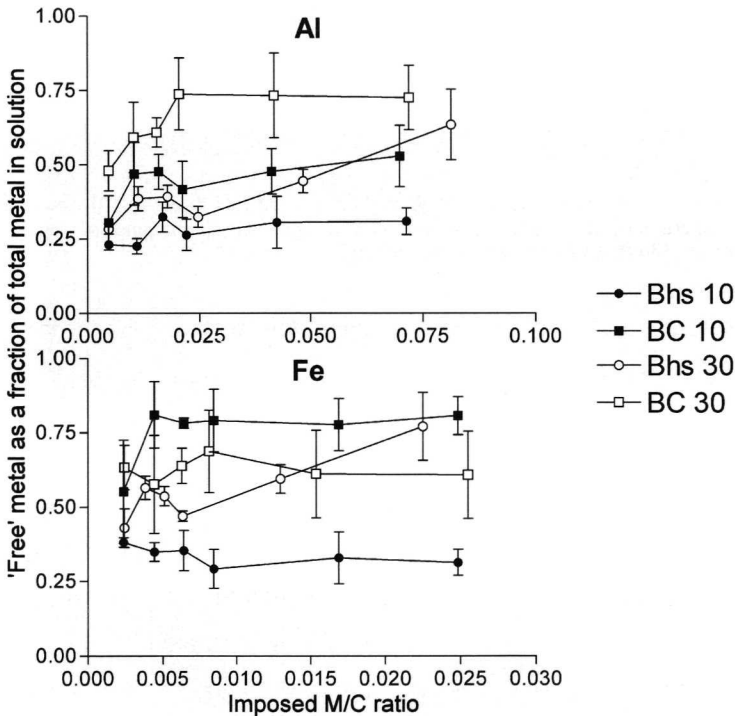


Fig. 5 the fraction of Al and Fe in solution that is present in the 'free' form, as a function of the imposed metal to organic carbon ratio (see legend of Figure 1 for explanation), for the soil material of Soil 1. Error bars depict standard error of the mean.

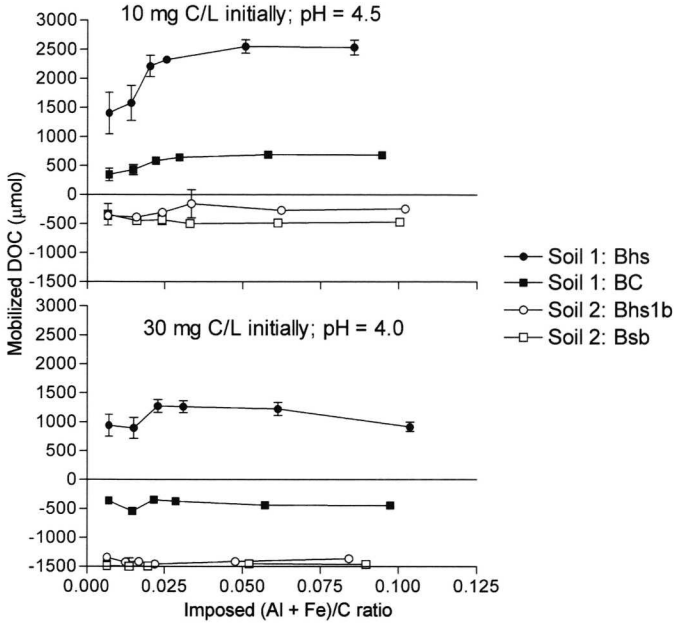


Fig. 6 The net cumulative number of μmoles of DOC mobilized or immobilized over the course of the experiments as a function of increasing imposed M/C ratios (see the legend of Figure 1 for explanation). Error bars depict standard error of the mean.

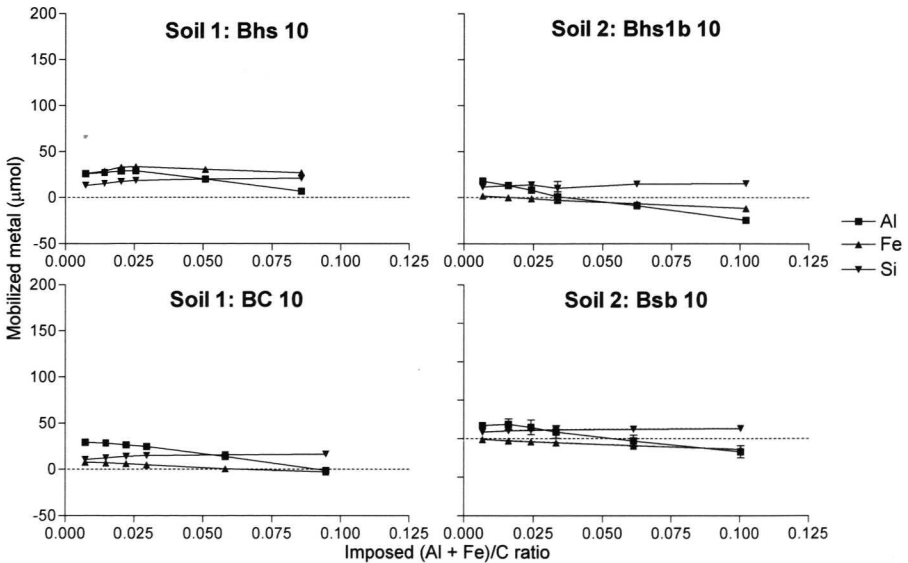


Fig. 7 The net cumulative number of μmoles of Al, Fe and Si mobilized or immobilized over the course of the experiments as a function of increasing imposed M/C ratios (see the legend of Figure 1 for explanation), corrected for the addition of Al and Fe. Error bars depict standard error of the mean.

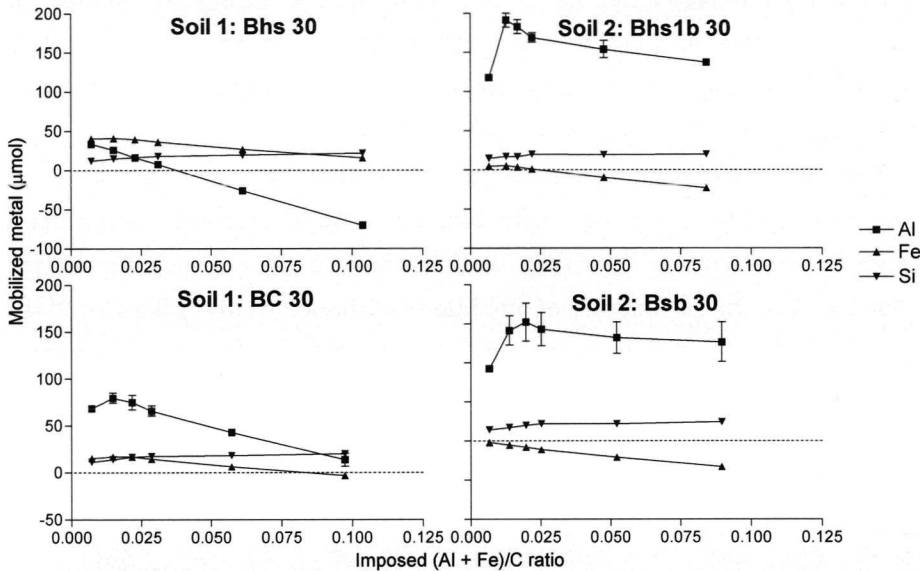


Fig. 8 The net cumulative number of μmol of Al, Fe and Si mobilized or immobilized over the course of the experiments as a function of increasing imposed M/C ratios (see the legend of Figure 1 for explanation), corrected for the addition of Al and Fe. Error bars depict standard error of the mean.

7.3.4 Mobility of Al, Fe and Si

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

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

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

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

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

7.4 Discussion

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

7.4.1 (Im)mobilization of organic matter

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

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

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

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

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

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

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

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

Table 6

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

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

^aSoil 1:Bhs:10; ^bSoil 1:Bhs:30; ^cSoil 1:BC:10; ^dSoil 1:BC:30;

^eSoil 2:Bhs1b:10; ^fSoil 2:Bhs1b:30; ^gSoil 2:Bsb:10; ^hSoil 2:Bsb:30 (for explanation see text).

7.4.2 (Im)mobilization of Al and Fe

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

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

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

There are two main other mechanisms to consider for the immobilization of Al and Fe: sorption/desorption reactions (either directly on SOM or in the form of M-DOM complexes on amorphous solid phases of Al and Fe), and precipitation of insoluble organic metal complexes (e.g. Mossin et al., 2002; Powell and Hawke, 1995; Wesselink et al., 1996). As was explained earlier, there was a significant immobilization of organic matter that in view of the high M/C ratios in solution was at least partly due to precipitation of organic metal complexes especially in the experiments at pH = 4.0. Both Al and Fe could have caused this precipitation, but from previous research we know that Fe(III) forms stronger complexes with DOM than Al and the degree of precipitation of Fe(III) is approximately equal at pH = 4.5 and pH = 4.0 (Jansen et al., 2002; Nierop et al., 2002). While Al is able to precipitate DOM to a similar degree as Fe(III) at pH = 4.5, it induces much less precipitation at pH = 4.0. (Jansen et al., 2003b; Nierop et al., 2002). Furthermore, Fe(III) has a very low solubility when in equilibrium with Fe(OH)_3 (s) at both pH values, while this is not the case for the equilibrium between Al and Al(OH)_3 (s). As a consequence, we believe that Fe was mainly immobilized by precipitation, both organically and inorganically. Corroborating evidence for this hypothesis is the observation that in all horizons except Soil 1:Bhs, the addition of Fe quickly lead to net immobilization of Fe that was negatively correlated with C_t/M_o ratios and independent of pH and initial DOC concentrations (Fig. 5 and 6). If sorption/desorption processes were dominating, one would have expected a maximum immobilization of Fe in Soil 2:Bhs1b with the largest content of both solid phase Al, Fe and solid phase organic matter (Table 2).

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

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

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

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

7.4.3 Implications for podzolization

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

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

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

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

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

7.5 Conclusions

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

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