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### The mobility of aluminium, iron and organic matter in acidic

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## Summary

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

