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The mobility of aluminium, iron and organic matter in acidic

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Synthesis

In this synthesis the practical and scientific implications of the research presented in this thesis will be discussed. An indication will be given of what new insights were gained and what parts of the puzzle remain to be solved.

8.1 Studying interactions of Al, Fe and DOM

To shed light on the processes that control the mobility of Al, Fe and organic matter in acidic sandy soils, it is necessary to determine the speciation of Al and Fe over 'free' metal in solution, dissolved organic Al/Fe complexes and (in)organic Al/Fe precipitates. Here 'free' metal is defined as the hydrated metal cation and dissolved inorganic metal complexes. Especially the distinction between 'free' metal and dissolved organic Al/Fe complexes has been difficult in the past. The relatively new analytical tool of DGT as well as the speciation models WHAM-W 1.0 and WHAM-W 6.0 based on respectively Model V and Model VI were critically examined for this purpose.

DGT was originally designed to determine the labile fraction of trace metals in surface waters around neutral pH. In order to apply DGT for the speciation of Al and Fe over 'free' metal and dissolved organic Al/Fe complexes in acidic soil solutions, the following potential problems needed to be considered:

- a) Disturbance of Al and Fe complexation equilibria in solution, due to removal of a portion of the 'free' metal from solution by the DGT units in the limited sample volume used in the laboratory as compared to the volume of surface waters.
- b) Underestimation of the 'free' Al and Fe fraction due to increased proton competition for binding on the chelating resin in the DGT unit at low pH values.
- c) Detection as 'free' metal of dissolved organic Al/Fe complexes small enough to penetrate the hydrogel in the DGT unit relatively unhindered, and labile enough to be detected.

Problem a) and b) could be conquered relatively easily. A minimum experimental volume of 500 ml proved sufficient to avoid significant disturbance of solution equilibria when DGT is deployed overnight (Chapter 2). Overnight deployment was long enough to allow for reproducible detection of Al and Fe in the μM concentration range that was encountered in our soil solutions. Proton competition did not significantly influence the detection of 'free' Al and Fe(III) in the pH ranges used in our experiments, ($\text{pH} \geq 3.5$). The detection of 'free' Fe(II) at $\text{pH} \leq 4.0$ was slightly lowered due to proton competition. However, the 'free' Fe(II) fraction was lowered by a constant percentage (40% at $\text{pH} = 3.5$) which could be corrected for (Chapter 3). Problem c) proved to be slightly more difficult to conquer. Our comparison of DGT with equilibrium dialysis showed that detection of smaller dissolved organic Al/Fe complexes as 'free' metal when using the common APA hydrogel is limited to those complexes smaller than 1000 Da. DOM ranges in molecular weight from 500 to over 100000 Da (Herbert and Bertsch, 1995), which means that small dissolved organic Al/Fe complexes could in theory be detected as 'free' metal, leading to incomplete separation. The comparison with WHAM 1.0 and WHAM 6.0 indicated that at lower M/C ratios the metal fraction as detected by DGT indeed seems to be slightly larger than the 'free' Al fraction due to detection of small, labile dissolved organic Al complexes. In contrast small dissolved organic Fe(III) complexes appeared not to be labile enough to be detected as 'free' metal (Chapter 4) and the metal fraction determined by DGT seems to correspond well with the 'free' Fe(III) fraction. Of course theoretically it could also be the case that the DGT measurements were accurate and WHAM 1.0 and 6.0 underestimated 'free' Al. However, there are no reasons to assume the models would underestimate 'free' Al while there are reasonable grounds to expect a (slight) overestimation by DGT.

While the abovementioned potential problems could be solved reasonably well, an unexpected practical problem arose during the experiments. It turned out that DGT was relatively sensitive to experimental error, as became evident amongst others during the experiments involving soil suspensions containing very fine particulates that upon opening of the DGT units caused contamination of the

chelating gel even after careful rinsing (Chapter 7). A critical evaluation of the practical design of the DGT units will be very helpful if DGT is to be used more frequently in studies involving soil suspensions with fine particulates.

WHAM-W 1.0 and WHAM-W 6.0 were specifically designed to model the complexation of metals to DOM. We were able to calculate the 'free' Al and Fe fraction determined by DGT adequately using the default parameters and optimizing for an inert DOM fraction except for 'free' Fe(III) as calculated by WHAM-W 6.0 (Chapter 4). In addition, the optimized inert DOM fraction (24 %) was in the same order of magnitude as those found in other studies (Gimpel et al., 2003; Tipping et al., 2002) and in our experiments in the presence of B horizon solid soil material (Chapter 7). However, in a precipitation study using the same dataset as the modeling study, only approximately 10 % of DOM was found to remain in solution according to the DOC concentrations (Nierop et al., 2002). This discrepancy may be explained by precipitation/adsorption of DOM in the presence of solid material due to other mechanisms than charge compensation through metal binding. Overall, our successful application of WHAM-W 1.0 and WHAM-W 6.0 to new datasets further vindicates both models and the underlying concepts used to describe the binding of Al and Fe to DOM. In addition, the successful use in most cases of default parameters for the binding of Al and Fe to DOM strengthens the belief that they represent actual physical entities. At the same time the apparent overestimation of 'free' Fe(III) and especially 'free' Fe(II) by WHAM-W 6.0 reveals one of the weaknesses of the model. Partially due to the difficulties encountered until recently in analytically speciating between 'free' Fe(II) and 'free' Fe(III) on one hand and dissolved organic Fe(II)/Fe(III) complexes on the other, the number of datasets in literature describing the binding of Fe(II) and Fe(III) to DOM is very limited (Tipping et al., 2002). This makes it difficult to parameterize speciation models such as WHAM-W 6.0 and may have led to an inaccurate default binding parameter for Fe(II) in the model.

In summary, in spite of some imperfections, both DGT and WHAM-W 1.0 and 6.0 proved to be very useful tools to study the binding of Al and Fe to DOM in acidic soil solutions and a combination of measuring and modeling proved to be a powerful way to critically evaluate both tools. There is of course always the very

small possibility that both methods produce similar but erroneous data. However, this is unlikely since neither WHAM 1.0 nor WHAM 6.0 were originally parameterized using DGT data (Tipping, 1994; Tipping, 1998). 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. This will for instance help in the testing of more restricted hydrogels that further limit the detection of small dissolved organic Al complexes by DGT and the derivation of more accurate binding constants for Fe to DOM for WHAM-W 6.0 as well as the inclusion of redox speciation in the model.

Future challenges consist of combining results from DGT in solution as well as DGT probes directly deployed in soils, with calculations from the soil version of WHAM.

8.2 Podzolization

With respect to the translocation of Al, Fe and organic matter in general and the process of podzolization in particular, the results presented in this thesis indicate the following underlying mechanisms (Chapter 5, 6 and 7):

1. In (A)E horizons, the majority of Al and Fe in solution is present as mobile organic Al/Fe complexes and the pH (≤ 4.0) and M/C ratios (< 0.03) are low enough to prevent significant (in)organic precipitation of Al and Fe. Instead, the Al and Fe concentrations in solution are mainly controlled by adsorption on SOM, which in combination with the release of organic matter keeps the M/C ratios in solution low even when significant amounts of Al and Fe are added. Together, this leads to a steady mobilization of Al, Fe (and organic matter) under control of SOM and DOM.
2. In Bh horizons, Al is immobilized by precipitation of the dissolved organic Al complexes as they become saturated with metal at the pH (4.5) and M/C ratios (> 0.03) that prevail here. In addition, dissolved organic Al complexes are adsorbed on (amorphous) Al and Fe phases.

3. In Bs/BC horizons, Al is removed from solution by precipitation of dissolved organic Al complexes at the pH value (>4.0) and M/C ratios (>0.03) that prevail in solution. In addition, precipitation as $\text{Al}(\text{OH})_3(\text{s})$ is a significant immobilization mechanism in BC horizons. Furthermore, some adsorption of dissolved organic Al complexes occurs.
4. In all B horizons, Fe is immobilized by a combination of organic and inorganic precipitation. Adsorption of dissolved organic Fe complexes also occurs, but this is a less important immobilization mechanism for Fe than for Al. Also the immobilization of Fe is more extensive and occurs at lower metal concentrations than that of Al. The immobilized Fe consists predominantly of Fe(III). The binding of Fe(II) to DOM is much weaker than Fe(III) and no significant organic or inorganic precipitation of Fe(II) will occur, as is supported by the lack of Fe immobilization in reduced, water-logged podzol B horizons (Lundström et al., 2000a).

As pointed out in Chapters 6 and 7, the proposed mechanisms are based on a number of experimental assumptions, an important one being that in the soils under study the negative charge on the solid soil phase is related to its total carbon content (C_t) and the positive charge is related to its amorphous Al and Fe content. To seek further support for this assumption, recently we attempted to determine the cation exchange capacity (CEC), anion exchange capacity (AEC) and point of zero charge (PZC) of the horizons that were used in the experiments, of both soils used for our studies (see the Appendix). For this titrations with H^+ and OH^- , and titrations using K^+ and Cl^- were used (Martinez and McBride, 1989). Preliminary results indicate the CECs as determined by both methods are in good agreement and exhibit a positive correlation with the total carbon content. This supports our assumption concerning the distribution of negative charge in the soils under consideration. Unfortunately, due to the fast and extensive acid neutralizing capacity of some soil horizons, we were unable to determine the AEC at low pH values (<4.0-4.5).

The mechanisms we propose are in agreement with the classical fulvate theory in combination with the inorganic precipitation of Al (in some cases) as proposed

by Gustafsson et al. (2001). The exception is that the classical fulvate theory only considers FA, while we looked at DOM as the organic ligand.

A strong support that DOM acts as a transporter of Al and Fe during their downwards movement through the soils are the direct measurements of the high percentage of Al and Fe in solution that was present in the form of dissolved organic Al/Fe complexes in the presence of solid soil material. This was made possible by the use of DGT. The fact that no imogolite was found in any of the soil material used in the experiments, nor any correlation between 'free' Al, pH and Si concentrations, makes it unlikely that the imogolite theory holds true in the soils studied in the framework of this thesis.

8.3 Final remarks

The research presented in this thesis has increased our understanding of the translocation of Al and Fe in acidic sandy soils in the Netherlands and the tools that can be used to study it. Still as all researchers know, research is never really finished and many questions remain to be answered. For instance, what is the role of specific fractions of DOM in the process of podzolization? Do LMW organic acids or other DOM fractions indeed play a dominant role in the (im)mobilization of DOM? Kaiser and Zech (1997) for example found a higher mobility of hydrophilic than of hydrophobic DOM fractions in acidic sandy soils. This question is also related to the origin of the SOM found in B horizons. What percentage of it originates from DOM transported by the flow of soil water and which part is local root input? Furthermore, what are the differences between well drained and water logged podzols? For Fe, there is still uncertainty about the quantitative influence of DOM on the redox equilibrium between Fe(II) and Fe(III). We found both significant oxidation and reduction of Fe in soil solutions in the presence of DOM (Chapter 3 and 5) but more research is needed to further investigate the mechanisms involved. Another question is the role of microbial degradation in the process of podzolization. Because microbial decay was inhibited in all experiments and still immobilization of Al, Fe and DOM was found, microbial degradation as proposed by Lundström et al. (2000b) is clearly

not the only immobilization mechanism. However, the influence of microbial degradation, especially of LMW organic acids, cannot be completely ruled out either and warrants further investigation. Finally, in the light of the recently proposed climatic differentiation between the mechanisms that govern podzolization as described in Chapter 8, a detailed comparative study of podzols from different climatic regions is necessary in order to test the hypothesis of different podzolization mechanisms prevailing in different climatic regions and fully resolve the conundrum of the different, conflicting podzolization theories.

