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The mobility of aluminium, iron and organic matter in acidic

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Introduction

1.1 General Introduction

1.1.1 Background

'Soils sustain life' as the Soil Science Society of America so eloquently puts it in their promotional campaigns. The development of soils and the transport of substances through soils are of great human interest because they are key factors in important issues ranging from developing efficient agricultural practices, through predicting and preventing the spread of pollutants, to sustaining the environment.

Organic matter plays a key role in many processes that take place in soils. Due to its predominantly acidic nature, organic matter causes soil acidification that is enhanced by the ability of organic matter to increase rates of mineral weathering, resulting in the release of the Lewis acids Al and Fe (McBride, 1994). Furthermore, organic matter can bind to other substances, thereby influencing the mobility and transport in soils of a variety of components ranging from organic pollutants such as PAH's and pesticides to (trace) metals and nutrients (e.g. Fang et al., 1998; Martinez and McBride, 1999; Mitra and Dickhut, 1999). In addition to influencing the mobility of components, the association of substances with organic matter can lower their bioavailable fraction and alleviate their toxicity to plants and soil organisms (e.g. Lucassen et al., 2000; Ma et al., 2001). Finally, because of its involvement in both mineral weathering and the transport of substances, organic matter in soils can be of great influence on pedogenesis (McBride, 1994).

Organic matter in soils consists of complex, organic molecules mainly formed by the decomposition of plant, animal and microbial material (Zech and Guggenberger, 1996). By definition the most mobile fraction of organic matter in soils is the part that is present in the form of dissolved organic matter (DOM) (Zsolnay, 1996). DOM is usually operationally defined as all non-living organic molecules in solution able to pass through a 0.45 µm filter (Herbert and Bertsch,

1995). As a consequence DOM includes truly dissolved molecules as well as smaller colloids. Solid organic matter (SOM) consists of all non-living organic material larger than $0.45 \mu\text{m}$, as well as DOM that has precipitated out of solution or is adsorbed on soil particles. An alternative to the division into DOM and SOM is the subdivision of organic matter into humine, humic acids (HA) and fulvic acids (FA). HA and FA are operationally defined fractions of organic matter that have several, slightly different definitions. According to one of the more common definitions by the International Humic Substances Society, together HA and FA in soils represent the fraction of organic matter that is removed by extraction with 0.1 M NaOH under an atmosphere of N_2 , while humine is the fraction that is insoluble in a NaOH solution at room temperature. Subsequently, HA is the fraction of dissolved organic matter in the 0.1 M NaOH solution that precipitates out of this solution when the pH is lowered to 1.0, while FA consist of the humic substances that remain in solution (Swift, 1996). As a consequence, analogous to DOM, FA represents the most mobile fraction of organic matter. However, because FA is obtained after invasive chemical extractions of SOM, it is probably less realistic with respect to the actual organic matter found in acidic sandy soil solutions.

1.1.2 Interactions between Al, Fe and organic matter

While organic matter in soils can bind to many different substances, it is especially reactive towards the complexation of cations in general and in particular multicharged species like Al^{3+} and Fe^{3+} (Tipping, 2002). In general, there are two types of binding mechanisms through which metal cations can associate with organic matter. All cations interact with negatively charged (dissociated) functional groups on the organic molecules through non-specific electrostatic interactions. In addition, Al and Fe can form specific bonds with one or more specific functional groups on the organic molecule through co-ordination bonding. (Tipping, 2002). When polyvalent cations bind to two or more chelates simultaneously through co-ordination bonding, this can lead to the formation of very stable ring structures (Pohlman and McColl, 1988; Tam, 1987). In addition to

(hydrated) metal cations themselves, charged hydration products of Fe and Al such as FeOH^{2+} and AlOH^{2+} bind to organic matter through similar mechanisms (Ares and Ziechman, 1988). In general, binding of metals capable of co-ordination bonding occurs first at those sites that form the strongest complexes. As the stronger sites become saturated, weaker binding through electrostatic interactions becomes increasingly important (Stevenson, 1994).

Functional groups on organic matter that bear nitrogen, sulfur or oxygen can all be involved in the co-ordination bonding of Al and Fe. However, due to the much greater abundance of oxygen bearing groups in comparison to functional groups containing sulfur and nitrogen, oxygen bearing groups in general and carboxylic and phenolic hydroxyl groups in particular are regarded as the dominant groups involved in the association of Al and Fe with organic matter (e.g. Erich and Trusty, 1997; Jordan et al., 1997; Shen, 1999).

The binding of Al and Fe to organic matter is influenced by several soil chemical variables including the pH, the solution ion strength, the redox potential and the ratio of metal to organic carbon present (M/C ratio) (e.g. Stevenson, 1994; Tipping, 2002). The pH determines the degree of dissociation of the acidic functional groups on the organic molecules and the inorganic speciation of the metals that can potentially bind to organic matter. Protonation of acidic functional groups on organic molecules leads to a reduction in charge of the molecule, which lowers metal binding through electrostatic interactions. In case of DOM it may also induce precipitation when insufficient charge remains to keep the molecule in question in solution. In addition, a lower pH increases proton competition for acidic functional groups involved in co-ordination bonding. At higher pH values, the formation of hydroxy complexes of the metal cations in addition to forming soluble inorganic complexes, may induce precipitation of the metal in question and thereby a reduction of the pool of metal species capable of binding to organic matter. Finally, the pH affects the sterical configuration of organic molecules and thereby the accessibility of the functional groups involved in co-ordination bonding.

The solution ion strength influences metal binding in three main ways. Firstly, the activity coefficients of charged inorganic species depend on the ionic

composition of the solution. While activity coefficients of all metal cations are decreased by increasing ionic solution strength, the effect increases with increasing valency thus discriminating between metals of different valencies (e.g. Fe^{2+} and Fe^{3+}). Secondly, ionic solution strength influences the sterical configuration of DOM molecules. Thirdly, ionic solution strength affects binding through electrostatic interactions because of counterion condensation in the diffuse double layer of the DOM molecules. However, the ionic strength of soil solutions is often low and therefore the effect of ionic strength may be limited in the range that occurs under natural conditions.

The redox potential is of special importance for Fe, because it determines the speciation of total Fe in solution over Fe(II) and Fe(III). This affects the valency of the Fe cations, the inorganic speciation in solution and the total solubility of Fe.

The M/C ratio finally, has an impact on the binding of Al and Fe to organic matter because it determines the abundance of metal binding sites relative to the amount of metal present. At higher M/C ratios, it will be increasingly difficult for Al and Fe to find still unoccupied binding sites and there will be an increasing electrostatic repulsion by residual positive charge left on Al and Fe cations that are already bound to organic matter.

The binding of Al and Fe to organic matter affects the fate of the two metals and organic matter itself in two important ways. In the first place binding of Al and Fe to organic matter influences the mobility of all three through soils. In addition, it lowers the bioavailability of Al and Fe to plants and microorganism, especially when larger dissolved organic colloids (> 10.000 kDa) or SOM are involved (e.g. Chen and Wang, 2001; Ma et al., 2001). At high dissolved metal concentrations, this can alleviate Al and Fe toxicity (e.g. Lucassen et al., 2000; Ma et al., 2001).

1.1.3 The effect of the binding of Al and Fe to organic matter on their mobility

The binding of Al and Fe to organic matter can influence the mobility of both metals and organic matter in several ways. Obvious immobilization occurs when Al and Fe bind to SOM or when the binding of Al and Fe to DOM leads to the formation of insoluble organic Al/Fe complexes. Immobilization also occurs when

charged dissolved organic Al/Fe complexes bind to solid soil components. When negative charge remains on the DOM molecule after binding of Al or Fe, the dissolved organic Al/Fe complex can be adsorbed on positively charged sites on the solid soil matrix, such as amorphous sesquioxides at pH values below their point of zero charge (PZC). Dissolved organic Al/Fe complexes can also bind to negatively charged sites on the solid soil matrix through cation bridging when not all of the positive charge on the binding cation is compensated (e.g. Guggenberger and Zech, 1993). On the other hand, the association of Al and Fe with DOM can mobilize both metals by preventing binding to SOM and shifting equilibria with secondary mineral phases such as gibbsite, imogolite or ferrihydrite.

It is clear that changes in soil chemical variables that influence the binding of Al and Fe to DOM also affect their respective mobilities. In addition, the composition of the solid soil matrix, e.g. the content of SOM and solid phases of Al and Fe, will affect the mobility of Al, Fe and organic matter. However, the quantitative influence of changes in specific soil chemical variables in combination with different solid phase compositions on the influence exerted on the mobility of Al, Fe and organic matter in soils remains unresolved.

1.1.4 Podzolization

The fact that many aspects of the influence of the association of Al, Fe and organic matter on their respective mobility in soils remain unresolved, is illustrated by the lack of consensus on the mechanisms involved in the process of podzolization. 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 occur in all climatic zones, from the tropics to the boreal zone. Podzols and podzolization have been the subject of research for many decades. As indicated in one of the important standard works on podzolization by Petersen (Petersen, 1976), the first reported research of podzols and the process of podzolization took place as early as the late nineteenth century. In the early fifties of the twentieth century, Bloomfield was amongst the first to suggest that DOM may play an important role in the translocation of Al and Fe in podzols (e.g.

Bloomfield, 1953; Bloomfield, 1954). This suggestion was also made by Petersen (1976) and Mokma and Buurman (1982). Many now believe that interactions with organic matter are a key process regulating the mobilization of Al and Fe from eluvial podzol horizons. Much more debate exists about the mechanisms governing the immobilization of Al, Fe and organic matter itself in illuvial horizons. In short the following main podzolization theories currently exist.

The classical fulvate theory (e.g. De Coninck, 1980; Mokma and Buurman, 1982; Petersen, 1976) proposes that initially, FA dissolves primary and secondary minerals and amorphous materials in the E horizon. The Al and Fe thereby released react with FA to form dissolved organic Al/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 organic molecules is sufficiently compensated by the positive charge on the hydrated Al and Fe cations. Subsequent re-dissolution of precipitated Al and Fe from the upper B horizon by complexation to still unsaturated DOM leads to a deepening of the podzol profile and the differentiation of a generic B horizon into a Bh horizon enriched in organic matter, overlying a Bs horizon enriched in sesquioxides.

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 and 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-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, dissolved organic Al/Fe 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 $\text{Al}(\text{OH})_3(\text{s})$ and explicitly rule out that imogolite plays a significant role. At pH values below 4.2, such as found in the O and possibly E horizons, they propose equilibria with SOM to control the solubility of Al in podzols. Also, in contrast with the previous theory but analogous to the classic fulvate theory, they believe that DOM can act as a carrier that transports Al and Fe to the B horizons.

Another contemporary podzolization theory was formulated by Lundström et al. (2000b) after a study of several Scandinavian podzols. They observed that 40% of dissolved Al was complexed to 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 and organic matter 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 complexes is removed by microbial degradation. Dissolved high molecular weight (HMW) organic acids that are more resistant to microbial degradation than LMW organic acids, in turn are adsorbed on solid phase Al and Fe.

Several researchers have tried to reconcile some of the different theories by assuming that a combination of the mentioned processes is involved in podzolization (e.g. Mossin et al., 2002; Van Breemen and Buurman, 2002). Mossin et al. noted that imogolite seems to occur less in podzols and become less important for the process of podzolization, as one moves down from north to south Scandinavia. At the same time organic precipitation induced by high M/C ratios in solution appears to gain in importance. A similar trend with respect to the occurrence of imogolite in Canada was reported by Kodama and Wang (1989). Mossin et al. conclude that different mechanisms dominate in different locations,

controlled by climate. Possibly the differences are linked to the relatively rich parent materials found under boreal climates resulting in a relatively high production of LMW organic acids in the litter layer, while intrazonal podzols are always formed on very poor parent materials and have slower organic matter turnover (Van Breemen and Buurman, 2002). Still, much scientific debate about the topic of podzolization remains, especially concerning the role of DOM versus inorganic sols as a carrier for Al and Fe. This is exemplified by a recent re-interpretation of the results of Gustafsson et al. by Farmer and Lumsdon (2002).

1.2 Objectives

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. More specifically the goal was to answer the following three research questions:

1. To what extent do Al and Fe interact with DOM in acidic sandy soil solutions to form soluble and insoluble organic complexes, and how are these interactions affected by changes within realistic ranges of the solution pH and M/C ratios?
2. How are the solubility of Al, Fe and DOM and their interactions in acidic sandy soil solutions influenced by the presence of SOM and amorphous Al and Fe phases in different eluvial and illuvial soil horizons?
3. What new insights do the answers to the two previous questions give us into the mechanisms that govern the mobility of Al, Fe and DOM in acidic sandy soils in general and podzols in particular?

The goals were attained through a combination of laboratory experiments and mathematical modeling.

1.3 Outline

This thesis consists of two parts. The first part (Chapters 2-4) focuses on the analysis of the interactions of Al, Fe and DOM 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. The chapters of this thesis are papers that all have been or will be published independently in international, peer-reviewed journals. As a consequence some duplication occurs.

In Chapter 2 the relatively new analytical chemical method of Diffusive Gradients in Thin films (DGT) (Zhang and Davison, 1995) was tested for its applicability to distinguish between 'free' Al and Fe(III) and soluble Al/Fe-DOM complexes in soil solutions. The 'free' fraction here is defined as consisting of the hydrated metal cations as well as their soluble inorganic complexes. The results obtained by DGT were compared to those obtained by the better established, but more time consuming method of equilibrium dialysis. As a further performance test, the 'environmentally important' trace metal Zn was considered. In Chapter 3, DGT was applied to investigate the influence of changes in pH and metal/organic carbon ratios on the soluble complexation of Al, Fe(II) and Fe(III) to DOM. Subsequently, in Chapter 4 the resulting dataset was modeled using the speciation code Model V and its recent successor Model VI (Tipping, 1994; Tipping, 1998). 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 between the model calculation and DGT results 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.

Chapter 5 deals with the expected implications of interactions between Al, Fe and DOM in soil solutions for their mobility in acidic sandy soils. As a consequence it focuses not only on the overall degree of organic complexation, but specifically on which fraction of the resulting dissolved organic metal complexes

remains in solution and which fraction precipitates out of solution in the form of insoluble organic metal complexes. The question of (im)mobilization of Al, Fe and DOM in soils was further explored in Chapters 6 and 7. While Chapter 6 focuses primarily on eluvial podzol AE horizons, Chapter 7 deals specifically with the complex issue of immobilization of Al, Fe and DOM in podzol B horizons.

In Chapter 8, a general synthesis of the knowledge gained from the research performed in the framework of this thesis is presented. Specifically, it points out which new insights with respect to the mobility of Al, Fe and DOM were obtained and what implications they have for our understanding of the process of podzolization. Finally, it indicates what further research is still required.