



# Speciation of aluminum in soils and stream waters: The importance of organic matter



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## ABSTRACT

Aluminum (Al) is the most common metal in the Earth's crust, and exists mainly in the form of silicates, oxides and hydroxides, or in complexes with natural organic matter (NOM) or inorganic ligands. Since speciation is a key factor for understanding the environmental impact of Al, it is important to determine the chemical forms of Al that predominate in different natural media and under varying geochemical conditions. This study investigated how complexation with NOM influenced the speciation of Al(III) in different environmental samples (isolated aquatic NOM, organic soils and stream waters) using X-ray absorption spectroscopy (XAS) and Infrared (IR) spectroscopy. The combined spectroscopic results showed that Al(III) formed mononuclear complexes with carboxylic functional groups in NOM that were sufficiently stable to suppress the hydrolysis and polymerization of Al(III). These organic Al complexes were favored at slightly acidic pH values between pH 3 and 6 and at decreasing Al concentrations. The XAS results of the organic soils and the stream water samples indicated a variation in the speciation from a predominance of organically complexed Al in the stream waters to a mixture of Al–NOM complexes and precipitated Al phases (Al hydroxides and/or Al silicates) in the organic soils. Although the presented XAS results were limited by relatively low signal-to-noise caused by the low K-edge energy of Al, the combined spectroscopic results provided new and useful information about Al in different environmental samples and showed that NOM and pH are important parameters controlling the speciation of Al.

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## 1. Introduction

Aluminum (Al) is one of the most abundant elements on Earth and occurs mainly in the form of sparingly soluble silicates, oxides and hydroxides, but can also be found in complexes with organic and inorganic ligands in environmental solutions (Ščančar and Milačič, 2006). These different forms, or species, of Al have different properties with respect to mobility, bioavailability and toxicity. Some of the Al species are of environmental concern; for example elevated concentrations of soluble forms of Al have been observed to have negative effects on the growth of plants (Rout et al., 2001) and acute toxic effects on fresh water fish (Polèo et al., 1997). Al can be released from naturally occurring oxides and hydroxides into the aqueous environment as a result of both acidification and elevated pH of soils and surface waters because of its amphoteric nature (Al solubility increases under acidic (pH < 5) or alkaline (pH > 8) conditions). Furthermore, Al is also widely used in society and this adds additional anthropogenic input to the environment. For example, a common method for removing particles and colloids (including organic matter) from drinking water sources is by precipitation using Al based salts (Edzwald, 1993). Thus, the risks with high Al

concentrations in the environment need to be addressed and an Environmental Quality Standard (EQS) value for Al in fresh water, drinking water, and wastewaters is greatly needed (Gardner et al., 2008).

Since speciation is a key factor influencing the adverse effects of Al, it is vital to determine its chemical forms in different natural media and under varying geochemical conditions. In this respect natural organic matter (NOM) is of importance as it is known to form strong complexes with Al (Tipping et al., 1995; Smith and Kramer, 1999; Ferro-Vázquez et al., 2014) and is abundant in most soils and surface waters. A number of different chemical equilibrium models have been developed and used to describe metal (including Al) interactions with NOM in soils and waters under varying conditions such as pH and metal concentration as well as concentration and chemical properties of the organic material (e.g., Kinniburgh et al., 1999; van Hees et al., 2001; Tipping et al., 2002; Weng et al., 2002; Sjöstedt et al., 2010; Tipping and Carter, 2011). However, these models are often based on macroscopic data alone and do not necessarily reflect the distribution of actual chemical species present in the system. This may limit the applicability of the models to capture the actual Al species of importance in environmental processes as well as to predict the effects of changing environmental conditions on metal speciation. Moreover, a proper description of Al(III)–NOM interactions is needed in order to understand the competition between Al and other metals (e.g., Pb, Cd, Cu) for binding sites in

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organic matter (Pinheiro et al., 2000; Chappaz and Curtis, 2013). Since most studies of Al interactions with NOM in soils and waters have utilized macroscopic techniques (e.g., Weng et al., 2002; Ferro-Vázquez et al., 2014) further research using molecular probes are motivated. Molecular-scale information on metal–NOM interactions can be obtained using different spectroscopic techniques, such as nuclear magnetic resonance (NMR), fluorescence and infrared (IR) spectroscopy (Ščančar and Milačič, 2006) as well as synchrotron-based X-ray absorption spectroscopy (XAS) (e.g., Skyllberg et al., 2006; Manceau and Matynia, 2010). XAS and IR, which are complementary techniques, have been shown to be very useful in this respect (Karlsson and Persson, 2012; Orsetti et al., 2013; Gustafsson et al., 2014; Hagvall et al., 2014) and in a few cases these techniques have been used to characterize Al in different environmental samples (e.g., Ildefonse et al., 1998; Doyle et al., 1999; Elkins and Nelson, 2002; Xu et al., 2010; Jones et al., 2011). To our knowledge, there are no previous XAS studies on Al(III)–NOM interactions but some infrared spectroscopic results from Al(III)–fulvic acid systems have been published (e.g., Patterson et al., 1992; Elkins and Nelson, 2002). These studies suggested that Al interacted with salicylic and phthalic-acid like sites of the fulvic acid. Furthermore, XAS (Hay and Myneni, 2010) and IR spectroscopy (Clausén et al., 2003, 2005) studies on systems containing Al(III) and well defined organic ligands like oxalate, citrate and salicylate have demonstrated the applicability to study the interactions between these species.

The limited number of XAS studies on Al in environmental samples is likely due to the technical difficulties caused by the low K-edge energy of Al (1.5596 keV) that results in strong scattering and absorption from air and light elements present in the samples. Special conditions such as helium atmosphere or vacuum are necessary, and typically only highly concentrated samples can be analyzed. This limits the possibilities to analyze the extended X-ray absorption fine structure (EXAFS) region of the XAS spectrum and as a result most studies on Al systems focus on the X-ray absorption near edge structure (XANES) region. Gallium (Ga; K-edge at 10.367 keV) on the other hand is readily accessible to both EXAFS and XANES and has been shown to be a suitable analog for Al due to the similar coordination chemistries in association with organic ligands and NOM (Clausén et al., 2003, 2005; Hagvall et al., 2014). Recent EXAFS results (Hagvall et al., 2014) showed that Ga(III) formed mononuclear chelate complexes with NOM that suppressed the hydrolysis and polymerization of Ga(III), and these results were also in general agreement with previous studies on Fe(III)–NOM interactions (Karlsson and Persson, 2010, 2012).

The present study was conducted to investigate the distribution of Al(III) between NOM complexes and inorganic forms in different environmental samples such as isolated aquatic NOM, organic soils and stream waters, and thereby to assess the influence of NOM on Al(III) speciation. The two main objectives of the study were to determine the extent of Al(III)–NOM complexation and to identify the functional groups participating in the Al(III)–NOM interactions. To accomplish this we have used the complementary XAS and IR spectroscopy techniques to probe the local Al(III) structures and changes of the functional group chemistry of NOM, respectively. The results have been compared to the previously studied Fe(III)– and Ga(III)–NOM systems.

## 2. Material and methods

### 2.1. Samples and sample preparation

The natural organic matters used in this study (Suwannee River Natural Organic Matter (SRN, 1R101N) and Suwannee River Fulvic Acid (SRFA, 1S101F)) were purchased from the International Humic Substance Society (IHSS) (for materials descriptions see the Supplementary data, Table S1). Both materials are collected from the Suwannee River, which is classified as a blackwater river, having a

dissolved organic carbon (DOC) concentration of 25–75 mg/L which lowers the pH below 4.0 (Averett et al., 1994).

The different organic materials were isolated by IHSS according to their protocols. The SRFA material was isolated using the XAD-8 resin adsorption method and contain only hydrophobic organic acids with molecular weights above 200 Da (Thurman and Malcolm, 1981). Reverse osmosis (Serkiz and Perdue, 1990) was used to isolate SRN, resulting in a material containing both hydrophobic and hydrophilic acids and other soluble organic molecules originally present in the water, with no size fractionation. Thus, the methods used to isolate the materials influence the final products and this can affect the metal complexation properties. The metal contents of these materials are relatively low (Table S1, Supplementary data) since they are delivered as desalted ( $H^+$ -saturated) freeze-dried powders.

Organic soils were collected at two different locations. A subalpine fen peat (FP) dominated by *Carex* spp. was sampled at Ifjord in northern Norway (70°5' N, 27°1' E), 5 km from the Atlantic Ocean. A second sample was obtained at Ravnholt skov (55°8' N, 11°3' E), near Allerød in Denmark, from a *Sphagnum* peat (SP) soil that was drained and planted with Norway spruce ca. 90 years ago. The soil samples were stored at 4 °C until freeze-dried (Edwards Modulyo 4K Freeze-dryer) and then homogenized by a tungsten carbide ball mill (Retsch, S2, Germany). One of the water samples was collected from Stor-kälsmyran (SK), a small-forested stream in northeastern Sweden (63°57' N, 20°38' E), and filtered through a 0.22 µm nitrocellulose membrane filter prior to ultrafiltration carried out on a Millipore Prep/Scale system (Prep/Scale Spiral Wound TFF-6 module) with cut-off of 1 kDa. The obtained material was freeze-dried and had a size distribution in the approximate range of 1 kDa–0.22 µm. The pH of the two soil samples and the ultrafiltered stream water was measured by equilibrating the freeze-dried materials with Milli-Q water at a soil:solution mass ratio of 1:10 for 6 days and then recording the values with a combination electrode (InLab®Micro, Mettler Toledo).

The other two stream waters were sampled at Risbäcken (S1) and Västrabäcken (S2) located in the boreal Krycklan catchment in northern Sweden (64°16' N, 19°46' E). Both of these streams flow mainly through a forested landscape (Björkvald et al., 2008). The stream waters were collected in thoroughly acid-washed polyethylene bottles that were filled under water to avoid air bubbles and pH was measured directly after sampling. The stream waters were pre-concentrated by an anion-exchange resin according to the procedure described in Sundman et al. (2013). Total organic carbon (TOC) and total Al in the water was analyzed before and after adsorption to the resin using a Shimadzu TOC-V<sub>CPH</sub> analyzer and ICP-OES (Varian Vista Ax), respectively. Data for the soil and stream water samples are presented in Table S2, Supplementary data.

IR samples were prepared by adding 92 mg SRN or 91 mg SRFA (dry weight) into volumetric flasks and dissolving the materials in Milli-Q water. Each solution was then divided into two samples and to one of these solution samples (SRN and SRFA)  $AlCl_3 \times 6H_2O$  (extra pure 99%, Scharlau, purchased from Sigma-Aldrich) dissolved in Milli-Q water (0.895 M, pH 1.47) was added reaching final Al concentrations of 27,316 µg g<sup>-1</sup> SRN and 32,679 µg g<sup>-1</sup> SRFA. The concentrations were expressed on a dry mass basis and corresponded to a molar ratio of 0.202 mol Al per mol of carboxylic functional groups (R–COOH). In all solution samples (SRN, Al-SRN, SRFA and Al-SRFA) the ionic strength was adjusted to 0.270 M by addition of 0.6 M NaCl and the final volumes were adjusted to 15 mL with Milli-Q water. The samples were equilibrated for 24–72 h on an end-over-end rotator. Prior to analysis the pH of each sample was measured using a pH combination electrode (InLab®Micro, Mettler Toledo) and a pH meter (SevenMulti modular meter system, Mettler Toledo).

The XANES SRN and SRFA samples (Table 1) were prepared by adding 18–28 mg of SRN and 18–27 mg of SRFA, based on dry weight, to 1.5 mL Eppendorf tubes.  $AlCl_3 \times 6H_2O$ , dissolved in Milli-Q water (0.895 M, pH 1.47) was added to the samples yielding final Al

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