Characterization of aluminum in environmental systems using X-ray absorption and vibrational spectroscopy

-The importance of organic matter

Kristoffer Hagvall
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Electronic version available at http://umu.diva-portal.org/
Printed by: Service Center, KBC
Umeå, Sweden 2015
To the Ones I Love...
Table of Contents

Table of Contents i
Abstract iii
Abbreviations v
List of papers vii
Populärvetenskaplig sammanfattning på svenska ix
1. Introduction 1
   1.1. Natural Organic Matter 2
   1.2. Speciation of Al(III) 4
2. Outline of This Thesis 6
3. Experimental Techniques and Data Analysis 9
   3.1. X-ray Absorption Spectroscopy 9
      3.1.1. XANES 9
      3.1.2. EXAFS 10
      3.1.3. Wavelet transform 10
   3.2. Attenuated Total Reflectance Fourier Transform Infrared spectroscopy 11
      3.2.1. New device for Simultaneous Infrared and Potentiometric Titrations (SIPT) 12
      3.2.2. MCR-ALS 14
4. Materials and Methods 19
   4.1. Chemicals, samples, and pH measurements 19
      4.1.1. Natural organic matter 19
      4.1.2. Gibbsite 22
   4.2. Collection and analysis of XAS data 23
      4.2.1. XANES data treatment 24
      4.2.2. EXAFS data treatment 24
   4.3. Collection and analysis of Infrared Spectroscopy data 24
      4.3.1. Batch experiments 25
      4.3.2. SIPT 25
      4.3.3. MCR-ALS 25
   4.4. Collection and analysis of dissolution data 26
   4.5. Chemical equilibrium modeling 26
5. Results and Discussion 29
   5.1. Complexation of Al(III) by NOM 29
      5.1.1. Identification of functional groups for Ga(III)/Al(III)-NOM complexation 29
      5.1.2. Qualitative analysis of EXAFS spectra of the Ga(III)-NOM system 33
      5.1.3. Quantitative EXAFS analysis of the Ga(III)-NOM system 34
      5.1.4. Qualitative analysis of XANES spectra and their first derivatives of the Al(III)-NOM system 38
   5.2. Al(III) speciation in organic soils and stream waters 41
      5.2.1. Qualitative analysis of XANES spectra and their first derivatives 42
5.2.2. XAS: Shell-by-shell EXAFS fitting results

5.3. Interactions between NOM and gibbsite and the effect on mineral dissolution
   5.3.1. Dissolution of gibbsite in presence of NOM
   5.3.2. IR results from the gibbsite-NOM system
   5.3.3. Ga(III)-NOM complexes at the surface of gibbsite

5.4. A new approach to the characterization of NOM
   5.4.1. MCR analysis of the IR data series
   5.4.2. Chemical equilibrium modeling of the SRFA system

6. Summary
   6.1. Implications
      6.1.1. The importance of NOM for metal speciation and mineral dissolution
      6.1.2. Using Ga(III) as a probe for other metals
      6.1.3. A new method for the characterization of NOM
   6.2. The bigger picture

7. Acknowledgements

8. References
Abstract

The fate and behavior of many metals in the environment are highly dependent on interactions with natural organic matter (NOM), which is abundant in most soils and surface waters. The complexation with NOM can influence the speciation of the metals by affecting their hydrolysis and solubility. This in turn will also have an effect on the mobility and potential toxicity of the metals. For aluminum (Al) these interactions are of high environmental importance since Al have been shown to have negative effects on plant growth, water living organisms, and fish.

This thesis will focus on the interactions between Al(III) and NOM in different environments and under varying geochemical conditions. To study this, infrared (IR) spectroscopy and X-ray absorption spectroscopy (XAS) have primarily been used. Due to the difficulties in analyzing Al using XAS, gallium(III), shown to be a suitable analogue for Al(III), was used as a probe to get complementary information from the Ga(III)-NOM system. The combined results from these studies showed that Ga(III) and Al(III) formed strong chelate complexes with carboxylic groups in NOM and that these complexes were strong enough to suppress the hydrolysis and polymerization of the metals. Furthermore, Al in organic soil and stream water samples was also studied using XAS and the results showed a variation in the speciation from a predominance of organically complexed Al(III) in the stream waters to a mixture of Al(III)-NOM complexes and precipitated Al phases (Al-hydroxides and/or Al-silicates) in the organic soils. To further study mineral-NOM interactions the effects of NOM on the dissolution of gibbsite (γ-Al(OH)₃(s); a common mineral in the environment) were investigated. The results showed that NOM can promote mineral dissolution and presence of inner-sphere Al(III)-NOM species on the gibbsite surface, detected by IR spectroscopy, could indicate a ligand induced dissolution. To further investigate the structure of the complex formed at the surface of the mineral, an EXAFS study was conducted on the ternary Ga(III)-NOM-gibbsite system. The results indicated either formation of inner-sphere complexes with Ga(III) acting like a bridge between NOM and the gibbsite surface, or the presence of two separate species; Ga(III)-NOM complexes in solution and a precipitated Ga(OH)₃(s) phase.

As a sidetrack to the Al(III)-NOM studies, a new way of characterizing NOM was developed using simultaneous infrared and potentiometric titrations, multivariate data analysis, and chemical equilibrium modeling. An acid/base model for a fulvic acid was constructed, based on spectroscopic information about functional groups and their pKₐ values, and indicated that the fulvic acid is to be regarded as a tetra carboxylic acid consisting of at least four fractions of carboxylic acids. This demonstrates new possibilities to
study the acid/base and metal complexing properties of NOM, in which the presence of carboxylic acid groups predominate, and to design equilibrium models more reliable than presented before.
Abbreviations

ALS          Alternating Least Squares
ATR         Attenuated Total Reflectance
CN           Coordination Number
DOC          Dissolved Organic Carbon
EXAFS        Extended X-Ray Absorption Fine Structure
FA           Fulvic Acid
FT           Fourier Transform
HA           Humic Acid
ICP-OES      Inductively Coupled Plasma Optical Emission Spectroscopy
IHSS         International Humic Substances Society
IRE          Internal Reflection Element
IR           Infrared
LCF          Linear Combination Fit
LMW          Low Molecular Weight
MCR          Multivariate Curve Resolution
NOM          Natural Organic Matter
R            Bond distance
R-COOH       Carboxylic functional groups
SIPT         Simultaneous Infrared and Potentiometric Titrations
SRFA         Suwannee River Fulvic Acid
SRN          Suwannee River Natural Organic Matter
SSRL  Stanford Synchrotron Radiation Lightsource
U      Total residual sum of squares
WT     Wavelet Transform
XANES  X-ray Absorption Near Edge Structure
XAS    X-ray Absorption Spectroscopy
List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals I-V.

I. Spectroscopic characterization of the coordination chemistry and hydrolysis of gallium(III) in the presence of aquatic organic matter

Hagvall K., Persson P., Karlsson T.


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

Hagvall K., Persson P., Karlsson T.

Manuscript submitted to Chemical Geology.

III. Effects of natural organic matter on gibbsite dissolution

Hagvall K., Persson P., Karlsson T.

Manuscript

IV. Adsorption of gallium(III)-organic matter complexes on gibbsite particles

Karlsson T., Hagvall K., Persson P.

Manuscript prepared for submission to Environmental Science and Technology.

V. Combining IR spectroscopy with potentiometric titrations to characterize an aquatic fulvic acid with respect to pK_a-values and carboxylic site concentration

Hagvall K., Sjöberg S., Persson P., Karlsson T.

Manuscript
Author’s contributions

For paper I, the work conducted at Stanford Synchrotron Lightsource (SSRL), i.e. collection of X-ray absorption spectroscopy (XAS) spectra, was shared between K. Hagvall, A. Sundman, T. Karlsson and P. Persson.

Paper I: K. Hagvall co-designed and conducted the experiments, collected the majority of the XAS spectra, did the majority of the data reduction/evaluation and was the main author.

Paper II: K. Hagvall co-designed and conducted the experiments, collected all of the XAS spectra, did the majority of the data reduction/evaluation and was the main author.

Paper III: K. Hagvall designed and conducted the experiments, did the majority of the data reduction/evaluation and was the main author.

Paper IV: K. Hagvall co-designed and conducted the experiments, collected all of the XAS spectra, did some data reduction/evaluation, assisted in the writing of the article.

Paper V: K. Hagvall designed the project, prepared and measured all of the IR spectroscopy samples, did substantial data reduction/evaluation, assisted with input data for the thermodynamic calculations and was the main author.
Populärvetenskaplig sammanfattning på svenska

När organiskt material från djur och växter bryts ned bildas en blandning av organiska molekyler som benämns Naturligt Organiskt Material (NOM). Detta material består av allt från små molekyler till stora makromolekyler och har en mängd olika funktionella grupper i sin struktur. Dessa grupper har en stor betydelse när det kommer till hur NOM interagerar med andra ämnen i naturen däribland metaller. Aluminium (Al) är en av de metaller som förekommer i störst utsträckning i jordskorpan. Som en följd av detta så är Al närvarande i många naturligt förekommande kemiska processer. Då inbindningen till NOM kan förändra metallers speciation, alltså i vilken form de förekommer, är det av stor vikt att studera hur Al(III) interagerar med organiskt material i olika miljöer och under olika förhållanden.

Fokus i denna avhandling har varit att karakterisera Al i naturligt förekommande system. Det har framför allt gjorts med hjälp av röntgenabsorptionspektroskopi (XAS) och infrarödspektroskopi (IR) och har syftat till att öka förståelsen för hur Al interagerar med NOM på molekynivå samt öka kunnaskap om i vilka former Al förekommer i jordar och vattendrag. I litteraturen finns det relativt få artiklar där XAS och IRSpektroskopi har använts i detta syfte och anledningen till detta kan delvis vara den heterogena sammansättningen av NOM samt de kemiska och spektroskopiska egenskaperna hos Al.

Denna avhandling har fyra delar där NOM står i centrum i samtliga. Den första delen berör interaktion mellan Al(III) och NOM och här studerades även Gallium (Ga(III)) som ett komplement och en analog för Al(III) p.g.a. den betydligt starkare XAS-signalen hos Ga. Resultaten från denna del visade på bildandet av kelatkomplex, d.v.s. ringstrukturer med 5 eller 6 ingående atomer, mellan NOM och Ga(III)/Al(III) och att det framför allt är karboxylsyror i NOM som binder dessa metaller i det pH- och koncentrationsintervall som undersöks. De komplex som bildas mellan NOM och Ga(III)/Al(III) är starka nog att förskjuta hydrolysen av Ga(III)/Al(III) till högre pH. Detta påverkar metallernas löslichkeit och då också koncentrationen av potentiellt toxiska lösta former av t.ex. Al i mark och vatten. I avhandlingens andra del undersökt speciationen av Al(III) i jordar och vattendrag. Denna studie visade tydligt att både organiskt bundet Al(III) samt Al-mineraler kunde påvisas i dessa prover. Resultaten från de tidigare studierna motiverade en fortsatt studie där påverkan av NOM på mineralytor undersöckes (del tre i avhandlingen). Resultaten indikerade en upplösning av gibbsit (ett naturligt förekommande Al-hydroxid-mineral) men själva mekanismen bakom denna upplösning kunde inte fastställas. Det

Sammanfattningsvis visar denna avhandling på hur viktiga interaktioner mellan metaller och NOM är för kemiska processer i naturen. Resultaten kan bidra med viktiga ledtrådar inför framtida studier av liknande system. Till exempel så är fortsatta studier på hur och i vilken utsträckning NOM påverkar upplösning av mineraler i jordar och vattendrag av stor vikt och det är processer som till stora delar är relativt okända. De sammanslagna resultaten från studierna i denna avhandling bidrar med en liten del till den stadigt ökande kunskapen kring betydelsen av interaktionen mellan metaller och NOM för olika processer i miljön.
“It always seems impossible until it’s done.”

_Nelson Mandela_
1. Introduction

All around us, in the environment and in our daily life, we come in contact with Aluminum (Al). As one of the earth’s most abundant elements (Greenwood and Earnshaw, 1997), Al can be found in nature as sparingly soluble silicates, oxides and hydroxides, but can also be found in complexes with organic and inorganic ligands in environmental solutions. Because of its strong affinity to oxygen, Al is seldom observed in its elemental state. Aluminosilicate minerals known as feldspars are the most common minerals in the earth’s crust. Furthermore, Al can be found in other minerals, such as beryl, cryolite, spinel, turquoise and garnet and the gemstones ruby and sapphire, are Al₂O₃ that obtain their colors from iron (red) or chromium (blue) impurities. Although Al is highly abundant in the environment, it is almost solely produced from the ore bauxite; a weathering product of Al and silica bedrock (Guilbert and Parc, 1986).

Although Al is considered a non-toxic metal for humans, the speciation (meaning the specific form of Al) has effects on the bioavailability and mobility of the metal, and its toxicity, e.g., toward fish. The history of Al toxicity in acidic freshwater began in Norway in the 1920s (Dahl, 1927), where a decline in the trout and salmon populations was found to be concomitant with a decrease in pH. More than 40 years later, Dannevig (1959) hypothesized a link between acidic lakes and reduced precipitation of Al(III), but it took another 20 years before Al was recognized as a toxic element in acidic waters (Scofield, 1977; Dickson, 1979). Today, vast numbers of studies have demonstrated the effects of Al on biota; for example, Al has negative effects on plant growth (Rout et al., 2001) and acute toxic effects on fresh water fish (Polèo et al., 1997). The hydrolysis of Al(III) is a factor that affects the chemistry of Al(III) to a great extent; specifically, its speciation. Hence, pH plays an important role in the speciation of Al(III), and its solubility is significantly increased under acidic (pH<5) or alkaline (pH>8) conditions. As the acidification of many soils, lakes, and streams increases in the environment, the Al toxicity becomes more pronounced (Scofield, 1977; Dickson, 1979). The complexity of the problem becomes even greater because of the wide usage of Al in society, adding additional anthropogenic sources of Al to the environment, an example is the addition of aluminium based salts to drinking water for the removal of particles and colloids (e.g., organic matter) through precipitation (Edzwald, 1993).

Previous studies have shown that interactions with natural organic matter (NOM) strongly alter the hydrolysis and polymerization of metals (e.g., Karlsson et al., 2006; Karlsson and Persson, 2012; Sundman et al., 2014). Strong complexes between Fe(III) and NOM originate from the formation of
5- or 6-membered rings (so-called chelate structures) that are highly stable due to resonance stabilization (Elkins and Nelson, 2002; Karlsson and Persson, 2012). The existence of a chelate structure for Fe(III) implies that the same complex could exist for Al(III) and would be sufficiently strong to suppress the hydrolysis and polymerization of Al(III). Hence, to elucidate the behavior of Al(III) in the environment, studies on how Al(III) interacts with natural occurring ligands are necessary; for example, with NOM, which is known to form strong complexes with Al(III) (Smith and Kramer, 1999) and is abundant in most soils and surface waters.

1.1. Natural Organic Matter

Natural organic matter is abundant in most natural systems and contributes greatly to the accessible terrestrial and aquatic carbon in the environment. This matter is formed via the degradation of organic materials from plants and animals, such as proteins, carbohydrates, lignins, lipids, and fats (e.g., Ogner and Schnitzer, 1971; Rouhi, 2000; Fig. 1), and consists of a mixture of low molecular weight substances and large macromolecules. Although the exact structure of NOM remains unknown (Wang and Mulligan, 2006), its chemical properties have been widely studied (e.g., Gjessing et al., 1998; Abbt-Braun and Frimmel, 1999; Croué 2004). An important property is the high capacity of NOM to complex metal ions via coordination to a variety of functional groups (e.g., amide, amine, carbonyl, carboxyl, hydroxyl, phenol and sulfhydryl groups) present in this material (Stevenson, 1982; Ritchie and Perdue, 2003; Essington, 2004). In general, organic material contains mostly carboxylic sites followed by phenol groups and only small amounts of other sites. The great diversity in functional groups implies that NOM can bind a wide range of substances or surfaces via the different groups under different chemical and environmental conditions. Another important property of NOM is its negative charge, which leads to a high affinity for mineral surfaces and cations in the environment (Essington, 2004). Previous studies have shown that Al(III) is strongly complexed by NOM (Elkins and Nelson, 2002), and the importance of NOM for maintaining Al(III) in a more bioavailable state has been addressed.
In general, NOM is divided into three main fractions: humic acid (HA), fulvic acid (FA), and humin (Thurman and Malcolm 1981; Rice, 2001). The general isolation procedure for NOM is shown in Fig. 2. HA and FA are soluble in water under certain pH conditions, but humin is insoluble in water, regardless of the pH, and consists of lipids, aromatics, and carbohydrate carbons. Approximately 50% of the organic matter in soils are contained in the humin fraction (Rice, 2001). The hydrophilic fraction (HA and FA) has more aliphatic components than the humin fraction. The difference between HA and FA is operationally defined by their solubility at different pH regions; HA is soluble at pH values down to pH 2, and FA is soluble in the entire pH range (Wang and Mulligan, 2006). FA typically contains compounds with molecular weights in the range of 300 to 2000 Da (Essington, 2004) and HA components generally have a molecular mass above 2000 Da (Essington, 2004). Furthermore, low molecular weight (LMW) organic acids, e.g., oxalic, citric, and acetic acids (e.g., van Hees et al., 2000; Strobel 2001), can be present in NOM and can potentially be of great importance in the complexation between NOM and metals. The solubility of organic matter is greatly affected by pH, which precipitates more easily in an
acidic environment. The metal concentration also affects the solubility of NOM in the environment; as the concentration increases, NOM have shown indications of aggregate formation, which subsequently precipitate. Studies have been conducted on the molecular weight of dissolved organic carbon (DOM) upon the addition (Jones et al., 1993; Nierop et al., 2002; Murray and Parsons, 2004) and removal (Pullin et al., 2007) of Al(III) and Fe(III), indicating a potential bridge between trivalent metals and DOM and the aggregation of DOM into larger components. This phenomenon is widely utilized for cleaning drinking water, in which Al-based salts (Edzwald, 1993) are added to the water as a flocculent, effectively removing organic material from the water by precipitation.

![Figure 2](image_url)

**Figure 2.** General picture showing the isolation of different fractions of humus material.

### 1.2. Speciation of Al(III)

A literature search on speciation of metals and complexation with NOM yields a number of different papers. The most common approach to study this speciation is to develop chemical equilibrium models that describe how metals interact with NOM in soil and water under various geochemical conditions (e.g., pH, metal concentration, NOM concentration, and chemical properties of the organic material) (e.g., van Hees et al., 2001; Tipping et al., 2002; Sjöstedt et al., 2010; Tipping and Carter, 2011). However, in most of these studies, the models are constructed without any detailed molecular-scale information regarding the local structure and bonding environment of the metals, which introduces uncertainty in the description of the speciation of the metal.
Various spectroscopic techniques such as synchrotron-based X-ray absorption spectroscopy (XAS) and infrared (IR) spectroscopy, can be used to obtain this type of molecular-scale information, which would make the model obtained more accurate (e.g., Ildefonse et al., 1998; Doyle et al., 1999; Elkins and Nelson, 2002; Skyllberg et al., 2006; Xu et al., 2010; Jones et al., 2011; Karlsson and Persson, 2012; Sundman et al., 2014). Studies of Al(III) in environmental samples using these techniques have been conducted (e.g., Ildefonse et al., 1998; Doyle et al., 1999; Elkins and Nelson, 2002; Xu et al., 2010; Jones et al., 2011) but few studies on Al(III)-NOM interactions. Some studies on the Al(III)-FA system using IR and fluorescence spectroscopy have been published (e.g., Patterson et al., 1992; Elkins and Nelson, 2002) but nothing has been published on the Al(III)-NOM system using XAS. However, a number of studies using XAS (Hay and Myneni, 2010) and IR spectroscopy (Clausén et al., 2003, 2005) have been conducted on the interaction between Al(III) and small organic acids, demonstrating that these techniques are powerful tools for studying and characterizing Al(III)-ligand systems.

The limited number of XAS studies of environmental systems might be attributable to difficulties in analyzing Al using XAS. Aluminum has a low K-edge energy (1.5596 keV) that results in strong background absorption and therefore only highly concentrated samples can be analyzed. Because most natural systems do not contain high enough Al concentrations, the possibilities of analyzing the extended X-ray absorption fine structure (EXAFS) region of the XAS spectrum is limited. Hence, most studies on these types of samples utilize the X-ray absorption near edge structure (XANES) region which does not provide as much information concerning the metal’s surroundings. However, information regarding the molecular structure of Al(III) complexes are of great importance and could be utilized to improve thermodynamic speciation models and increase our understanding of the effects Al(III) on the environment.
2. Outline of This Thesis

The focus of this thesis is to increase our understanding of the interactions between Al(III) and natural organic matter on a molecular level, as well as providing new molecular-scale information regarding the fate and behavior of Al(III) in different environments. Few studies have been conducted on the speciation of Al(III) in natural systems using XAS and IR spectroscopy. One reason could be the complexity of NOM; organic matter has a highly variable structure, molecular weights and chemical properties. Because of this complexity, the materials are not well-characterized; hence, the interpretation of results is difficult. Thus, to obtain useful information from these systems spectroscopic data of high quality is important, but this is a problem for Al because its XAS signals are very weak due to the low K-edge energy of the Al atom. Due to these problems, gallium (Ga(III)) (which has a stronger XAS signal) was used as a probe to get complementary information from the Ga(III)-NOM system (Paper I). These data were subsequently used in the analysis of the XANES data for two different Al(III)-NOM systems (Paper II). These results were then combined with those from Paper I and utilized to interpret Al XAS data for soil and surface waters samples (Paper II). Because Al(III) mainly exists in nature in the form of minerals, either as Al(oxy)hydroxides, Al-silicates or complexed with other elements, naturally the next step was to study mineral-NOM complexes, as well as the effects of NOM on Al-based minerals. The mineral gibbsite was used and the effect of NOM adsorption on the mineral surface was studied using two different NOM fractions (Paper III). The ability to dissolve the mineral was measured using inductively coupled plasma optical emission spectroscopy (ICP-OES), and to further investigate the NOM complex formed at the surface of the mineral, a modified simultaneous infrared and potentiometric titration (SIPT) apparatus was used (Paper III). To further study the adsorption of NOM to mineral surfaces, Ga(III) was used once again as a probe to study the adsorption of Ga(III)-NOM complexes to gibbsite using EXAFS and IR spectroscopy (Paper IV). During the investigation of these different systems, the importance of NOM characterization for the interpretation of the results became clear. Therefore, a method using SIPT combined with multivariate data analysis and chemical equilibrium modelling was suggested to be a new and interesting approach to characterize organic material (Paper V).
“What we see depends mainly on what we look for.”

Sir John Lubbock
3. Experimental Techniques and Data Analysis

A combination of XAS, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and several different macroscopic analyses were used for the studies presented in this thesis. ATR-FTIR and XAS are spectroscopic techniques that provide good molecular-level information for processes at different interfaces and in the bulk. The former offers information of the nature of the ligand in metal-ligand complexes in which functional groups can be studied. Moreover, XAS provides information regarding the metals by analyzing the surroundings of a metal in a sample. This molecular-level information was combined with the results from macroscopic techniques, such as ICP-OES and potentiometric titrations, to clarify to the research questions addressed in this study.

3.1. X-ray Absorption Spectroscopy

X-ray Absorption Spectroscopy (XAS) is an element-specific technique that can be used to analyze the local surroundings of X-ray absorbing atoms. The X-ray radiation used in XAS is a monochromatic beam that usually arises from a synchrotron radiation source. Every atom has core electrons that in turn have a specific binding energy, and the analysis is performed by scanning over this energy (ca. 30 eV before the binding energy up to 800 eV after). When the energy of the incident X-ray beam matches the binding energy of the electron, the energy is absorbed, showing a drastic increase in the absorption (called the absorption edge) in the X-ray absorption spectrum (Fig. 3). When the energies above the edge are scanned, a photoelectron can be released and backscattered from the neighboring atoms. When this happens the backscattered wave interferes in-phase or out-of-phase with the original photoelectron wave, resulting in an increase or decrease in the electron density of the absorbing atom. An increased density means a higher absorption and this affects the absorption spectrum. The analysis of an absorption spectrum allows the extraction of structural information about the absorbing atom and its surroundings and can be performed on solids, liquids, and gaseous samples. Because of its potential for analyzing both amorphous and crystalline samples, XAS is a highly versatile technique, unlike such techniques as X-ray diffraction.

3.1.1. XANES

For certain elements, electronic transitions to energy levels that are unfilled or partly filled within the atom will give rise to a pre-edge. This pre-edge and edge (defined as approximately 50 eV above the edge) is the X-ray
absorption near edge structure (XANES) region (Fig. 3), and can give information about the elements oxidation state and coordination geometry. The most common way to analyze the information present in this region is to visually compare the structures around the edge as well as the structures in the first derivative of the edge. Furthermore, a linear combination fit (LCF) can be performed, using different reference spectra, to obtain an estimate of the composition of different species present in the sample or a detailed analysis of the pre-edge region can be conducted as outlined by Wilke et al. (2001). All of these approaches to analyze the XANES data are very dependent on the references used for analysis.

3.1.2. EXAFS

The region after the edge is called the extended X-ray absorption fine structure (EXAFS) region (ca. 50-800 eV after the edge, Fig. 3). The oscillating structure of the region is due to the backscattered photoelectrons from neighboring atoms and depends on the distance between the atoms, numbers, and identity of the backscattering atoms. Therefore, the EXAFS region provides information about the identity of the neighboring atoms, the coordination number (CN), and the distances (given in Ångström (Å) 10^-10 m) at which they occur.

![Figure 3](image)

*Figure 3.* A XAS spectra showing the XANES and EXAFS regions as well as the position of the pre-edge.

3.1.3. Wavelet transform

Wavelet transform (WT) analysis was performed using the Igor Pro script developed by Funke et al. (2005). The WT is a complementary tool for the Fourier transform (FT) that resolves backscattering atoms based on their
distance from the absorbing atom. The advantage of WT is that it measures the separation distance to the absorbing atoms similar to FT, but offers a second dimension and resolves the \( k \)-space enabling the separation of light and heavy atoms present at the same distance (Funke et al., 2005). Therefore, WT can provide a general picture of the nature of the backscattering atoms, which gives valuable hints for the further analysis of the data. The use of WT in environmental studies has recently increased and can be used, for example, to qualitatively differentiate between C and metal backscattering atoms (Karlsson et al., 2008; Karlsson and Persson, 2010, 2012; Sundman et al., 2013). The results from a WT analysis are usually presented in a contour plot in which the different backscattering atoms give rise to a ridge at a specific position. The position of the ridge is usually compared with standard WTs. Heavier compounds give rise to a ridge at a higher \( k \) (a higher value on the x-axis in the contour plot) than lighter compounds and the backscattering atoms can be identified thereby. Fig. 4 shows an elementary example of WT construction and interpretation.

![Figure 4](image)

**Figure 4.** Figure explaining the construction of a WT contour plot of a Ga-hydroxide sample. I) Is the FT spectrum. II) Showing the WT (\( \eta=10, \sigma=1 \)) of the Ga-hydroxide, III) High resolution WT, and IV) showing the \( k^3 \)-weighted EXAFS spectrum. The WT, \( R(\text{Å}) \) is plotted as a function of \( k(\text{Å}^{-1}) \).

### 3.2. Attenuated Total Reflectance Fourier Transform Infrared spectroscopy

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy is a widely used technique for the collection of IR spectra of dense and highly absorbing materials, such as solids and liquids. The sample is placed on an ATR crystal called an internal reflection element (IRE), which consists of an inert infrared-transparent material with a high
refractive index. The IR radiation is directed to hit the IRE such that it undergoes total internal reflection at the crystal-sample interface. Total internal reflection occurs when the incidence angle $\theta$ is greater than the critical angle $\theta_c$:

$$\theta_c = \sin^{-1} \frac{n_{21}}{n_{12}} = \frac{n_2}{n_1}$$

Where $n_1$ and $n_2$ are the refractive indices of the IRE and the sample, respectively. When the conditions for total internal reflection are fulfilled, the incident light penetrates the sample as an evanescent wave that exponentially decreases in intensity with distance. The wave is transported into the sample and is absorbed (or attenuated) at certain vibrational frequencies characteristic of the substrate composing the sample. Because of the short penetration depth (a few microns for infrared light, depending on the wavelength of the radiation, the angle of incidence, and the refractive indices of the IRE and sample), ATR-IR is especially convenient for investigating highly absorbing samples.

The results from a normal ATR-IR measurement are presented as an interferogram containing information in the wavelength-domain. This interferogram can be converted mathematically to a spectrum in the frequency (wavenumber) domain using a Fourier transform. Instruments that offer Fourier transform of the interferogram have the advantages of high light throughput, good resolution, and the capability of averaging a large number of scans.

3.2.1. New device for Simultaneous Infrared and Potentiometric Titrations (SIPT)

The majority of the work performed on aqueous solutions or mineral suspensions using ATR-FTIR in this thesis was conducted by combining ATR-FTIR spectroscopy with pH measurement using a method called simultaneous infrared and potentiometric titration (SIPT; Loring et al., 2009). The main advantage of this method is that it allows in situ monitoring of molecular-scale changes in solution or at the water-mineral interface as a function of pH.

The original apparatus described by Loring et al. (2009) consists of two separate vessels connected with tubing and a peristaltic pump. The titration vessel is located outside the spectrometer and the IR measurement is performed in a second vessel inside the spectrometer. The fact that the experiment takes place in two separate vessels has drawbacks specifically because of the tubing. Although it is stated that the potentiometric titration and the ATR-FTIR measurement occur simultaneously in this flow-through apparatus, the movement of the titrated solution through the tubing causes a
delay of the spectroscopic measurement. In addition to the delay between the titration and the spectroscopic measurement, the tubing necessitates a large sample volume, which increases the risk for clogging and errors due to contamination (e.g., by carbon dioxide) and incoming light.

The apparatus described above has been widely used but modifications were made to address some of these problems. The modifications allowed all the tubing to be removed by placing the titration vessel directly on the ATR accessory in the vacuum chamber. A single-reflection, 45º, ZnSe ATR crystal (FastIR, Harrick Scientific) was fitted in the bottom of the titration vessel. The lid of the IR instrument, holding the vacuum of the sample chamber, was made concave so the titration vessel could be positioned for IR measurements under vacuum, as well as being open to arbitrary pressure on top (see Fig. 5).

![Diagram](image)

**Figure 5.** Schematic illustration of the apparatus used for the infrared titration experiments. 1. Inlet from an automatic titrator (702 SM Titrino, Metrohm); 2. Automatic stirrer; 3. Combination electrode coupled to the titrator; 4. Lid of the sample chamber; 5. O-rings keeping the pressure; 6. ATR crystal.

The removal of the tubing enabled reaction mechanisms and short-lived species to be more accurately studied. Furthermore, the use of a single vessel
reduced the amount of solution required so that measurement could be carried out with a small sample volume. The vessel could also be equipped with an additional wall enclosing the container with an inlet and outlet for water. The temperature of the vessel could be controlled by the circulation of water at a set temperature in the enclosed space between the outer wall and the vessel.

The ATR crystal could be covered with a thin film, an overlayer, of a mineral when titrations of mineral suspensions are performed. This effect was achieved by evaporating a dilute suspension of the mineral onto the crystal, which concentrated and immobilized the mineral particles in the area probed by the infrared evanescent wave. A resultant increase in the signal strength and the sensitivity of the measurements was achieved (Hug and Sulzberger, 1994). Creating an overlayer by this method has been widely used to study the adsorption and desorption of various ligands at water-mineral interfaces (Hug and Sulzberger, 1994; Dobson and McQuillan, 1999; Mendive et al., 2005; Hug and Bahnemann, 2006; Lindegren et al., 2009; Noren et al., 2009; Young and McQuillan, 2009).

3.2.2. MCR-ALS

Multivariate curve resolution is a chemometric technique that deconstructs data sets that have limited or absent reference information and system knowledge into pure response profiles (e.g., spectra, pH profiles, time profiles, elution profiles) of a fixed number of species. The technique was first introduced by Lawton and Sylvestre in the early 1970s (Lawton and Sylvestre, 1971; Sylvestre et al., 1974) and has recently been applied to non-evolutionary multicomponent systems (e.g., spectroscopic images or environmental monitoring data tables). Two requirements are necessary to apply MCR analysis to a data set; the first is that the data set must be presented as a two-way (or multiset structure) data set and the second is that the data set can be reasonably explained by a bilinear model using a fixed number of components.

The bilinear model can be explained with the equation $D = CS^T$, where $D$ is a dataset (e.g., a set of spectra, $t_R$, in the spectra range $\lambda$), and $C$ and $S^T$ are the matrices of the component concentration profiles and the related pure spectra for each of the components used to explain the system, respectively (Fig. 6).
If the MCR basic bilinear model is solved by a constrained alternating least squares algorithm (ALS), the technique is known as MCR-ALS. Constraints on the ALS are used to improve the interpretability of the profiles in C and $S^T$ using known chemical properties of these components (e.g., non-negatively, unimodality, or known interrelationships between the individual components such as kinetic or mass-balance constraints) or that have a mathematical origin (e.g., local rank and selective windows, and trilinear structure) (de Juan and Tauler, 2003; 2006). The possibility of introducing constraints is the main advantage for MCR-ALS, however experience as to when and how to apply constraints is of great importance to the results.

MCR-ALS analysis is implemented as an analytical technique in MATLAB® and it has a few graphical interfaces for easier control of the analysis and possibilities for constraints. The most popular interface, which was used for the MCR-ALS analysis in this thesis, is the MCR-ALS toolbox designed by Jaumot et al. (2005).
“The method of scientific investigation is nothing but the expression of the necessary mode of working of the human mind.”

Thomas Henry Huxley in “Our Knowledge of the Causes of the Phenomena of Organic Nature”, 1863
4. Materials and Methods

4.1. Chemicals, samples, and pH measurements

Unless otherwise indicated, all chemicals used in papers I-V were of p.a. quality. Milli-Q water was used in all experiments and sample preparation, as well as the execution of the IR experiments, were conducted in a 25°C thermostatic lab. A Mettler Toledo InLab® Micro pH combination electrode (3 M KCl) and a pH controller from Mettler Toledo (SevenMulti modular meter system) were used for the pH measurements in all five papers. The electrodes were 2-point calibrated at pH 3 and 7 using commercial buffers. In general, the samples prepared for the various papers were pure NOM or NOM with added Ga(III)/Al(III). In paper III, samples of gibbsite mineral suspensions were prepared with and without NOM. Finally, in paper IV, samples containing NOM, Ga, and gibbsite were prepared.

4.1.1. Natural organic matter

NOM was either purchased or collected directly from the source. Suwannee River NOM (SRN; 1R101N and 2R101N) and Suwannee river fulvic acid (SRFA; 1S101F) were purchased from the International Humic Substances Society (IHSS). NOM from IHSS was used to be able to critically compare the obtained results with results from other studies. SRN and SRFA are standards offered by IHSS and have been widely used in studies worldwide. Both materials were isolated from the Suwannee River, which is classified as a blackwater river and runs through the Okefenokee Swamp in southern Georgia and then flows southwest to the Gulf of Mexico. The river has a relatively high amount of dissolved organic carbon (DOC) with concentrations of 25 to 75 mg/L and consequently a relatively low pH (below 4). Furthermore, the DOC found in the river is believed to originate mainly from decomposing vegetation. Additional information about the Suwannee River can be found in Averett et al. (1994).

The isolation of the two different NOM materials from the Suwannee River was performed via reverse osmosis and the XAD-8 resin adsorption method for SRN and SRFA, respectively, according to IHSS protocols. To isolate SRN, the river water was first filtered, to eliminate large particles such as leaves, and then subjected to reverse osmosis. The collected material was milled and freeze-dried resulting in a material containing both hydrophobic and hydrophilic acids, as well as other soluble organic solutes, in a wide molecular size range from small organic acids, such as oxalate and citrate, to macromolecules (Serkiz and Perdue, 1990; Sun et al., 1995). SRFA isolation involved a multi-step procedure starting with the acidification of the river water, which then was passed repeatedly over a XAD-8 resin. The
material was then eluted with NaOH and re-acidified with HCl. To eliminate excess Na$^+$, the material was passed over a hydrogen-saturated cation-exchange resin, then milled and freeze-dried (Aiken, 1985). This isolation method introduced some fractionation in the material obtained. The XAD-8 resin adsorbs mostly hydrophobic compounds and as the material is eluted from the XAD-8 resin a size fractionation causes molecules smaller than ca. 200 Da (the molecules that are first eluted from the resin) not to be collected. Therefore, the SRFA material contains mostly hydrophobic molecules (Thurman and Malcolm, 1981) and has a molecular size distribution of ca. 200 to 3000 Da. This means that SRFA is a fraction of the SRN and can be regarded as a more homogeneous material compared to SRN (Fig. 7). The isolation method could influence the ability of the isolated materials to form complexes with metals. More information on the various materials can be found in Table 1.

**Figure 7.** Diagram of the isolation method, illustrating the types of humus material included in the different fractions (SRN and SRFA).
Table 1.
Elemental composition (% w/w) and content of carboxyl and phenolic functional groups in the Suwannee River NOM (SRN: 1R101N) and fulvic acid (SRFA: 1S101F), as provided by the IHSS\textsuperscript{a-e} and others \textsuperscript{f-g}.

<table>
<thead>
<tr>
<th>Organic material</th>
<th>Element/compound</th>
<th>% (w/w)</th>
<th>meq g\textsuperscript{-1} C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRN</td>
<td>H\textsubscript{2}O</td>
<td>8.15\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ash</td>
<td>7.0\textsuperscript{b}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>52.47\textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>0.103\textsuperscript{d}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Carboxyl</td>
<td>9.85\textsuperscript{d}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phenolic</td>
<td>3.94\textsuperscript{e}</td>
<td></td>
</tr>
<tr>
<td>SRFA</td>
<td>H\textsubscript{2}O</td>
<td>8.8\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ash</td>
<td>0.46\textsuperscript{b}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>52.44\textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>0.0084\textsuperscript{g}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>0.00025\textsuperscript{g}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>0.0047\textsuperscript{g}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>0.00006\textsuperscript{g}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Carboxyl</td>
<td>11.44\textsuperscript{d}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phenolic</td>
<td>2.91\textsuperscript{e}</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} H\textsubscript{2}O in the air-equilibrated sample.
\textsuperscript{b} Inorganic residue in the dry sample.
\textsuperscript{c} Element composition in the dry ash-free sample.
\textsuperscript{d} The charge density (meq g\textsuperscript{-1} C) at pH 8.0.
\textsuperscript{e} Two times the charge density (meq g\textsuperscript{-1} C) between pH 8.0 and pH 10.0.
\textsuperscript{f} Fe content in the dry sample, corresponding to 1026 \textmu g Fe g\textsuperscript{-1} (Karlsson and Persson, 2012).
\textsuperscript{g} Content in the dry sample according to Fujii et al. (2014).

For paper III additional organic materials were analyzed. Two different organic soils were collected at two different locations. The first was a subalpine fen peat (FP) dominated by \textit{Carex spp.} and was collected at Ifjord in northern Norway (70°5' N, 27°1' E), 5 km from the Atlantic Ocean, and the second was a \textit{Sphagnum} peat (SP), drained and planted with Norway spruce (>90 years old at present), collected in Denmark at Ravnhold skov (55°8' N, 11°3' E) near Allerod. Both soils were freeze-dried and homogenized by a tungsten carbide ball mill. Another material was collected from a small-forested stream in northeastern Sweden called Stor-kålsmyran (SK, 63°57' N, 20°38' E). The water from the stream was first filtered through a 0.22 \textmu m nitrocellulose membrane filter prior to ultrafiltration on a Millipore Prep/Scale system (Prep/Scale Spiral Wound TFF-6 module) with a molecular weight cut-off of ca. 1 kDa. The material obtained was freeze-dried and had a size distribution in an approximate range of 1 kDa-0.22 \textmu m.
Furthermore, water from two streams (Risbäcken (S1) and Västrabäcken (S2)) was pre-concentrated by an anion-exchange resin according to the procedure described in Sundman et al. (2013). The two streams are located in the boreal Krycklan catchment in northern Sweden (64°, 16’N, 19°, 46’E) and both streams flow mainly through a forested landscape (Björkvald et al., 2008). Water sampling was performed using acid-washed polyethylene bottles, and to avoid the exposure to air, the bottles were filled under water. Directly after sampling, the pH was measured, and the samples were divided into smaller acid-washed polyethylene bottles for easier handling, after which the anion-exchange resin was added. The resin was then collected and stored as a wet paste prior to analysis (for more information on the experimental procedures, see paper II). Total organic carbon (TOC) and the total Al in the water was analyzed before and after adsorption to the resin using a Shimadzu TOC-VCPH analyzer and ICP-OES (Varian Vista Ax), respectively. More information on the various materials can be found in Table 2.

Table 2.
Chemical composition of the soil and stream water samples and results for the Al and TOC measurements of the stream waters adsorbed to ion-exchange resins.

<table>
<thead>
<tr>
<th>Sample (pH)</th>
<th>[Org-C] (g kg⁻¹)</th>
<th>[TOC]² (mg L⁻¹)</th>
<th>Adsorbed TOC (%)</th>
<th>[Al] (µg g⁻¹)</th>
<th>[Al] (µM)</th>
<th>Adsorbed Al (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FP (5.2)</td>
<td>410</td>
<td>-</td>
<td>-</td>
<td>3840e</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SP (3.1)</td>
<td>510</td>
<td>-</td>
<td>-</td>
<td>1016e</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SK (4.4⁴ b)</td>
<td>481</td>
<td>38.6c</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S1 (5.4ᵃ)</td>
<td>-</td>
<td>13.7c,d</td>
<td>57.8</td>
<td>-</td>
<td>14.3c,d</td>
<td>23.1</td>
</tr>
<tr>
<td>S2 (5.2ᵃ)</td>
<td>-</td>
<td>11.7c,d</td>
<td>56.7</td>
<td>-</td>
<td>12.7c,d</td>
<td>14.5</td>
</tr>
</tbody>
</table>

ᵃ pH of the stream water.
ᵇ pH of the freeze-dried ultra-filtrated material dissolved in Milli-Q water was 3.1.
ᶜ Concentration in the stream water.
ᵈ Analyzed concentration before adsorption to the resin.
ᵉ Extraction with 0.5 M CuCl₂ according to Skyllberg and Borggaard (1998), assumed to extract mainly organically complexed Al.

4.1.2. Gibbsite

The gibbsite used in the different articles in this thesis was synthesized in-house following the protocol of Gastuche and Herbillon, (1962). Amorphous Al(OH)₃(S) precipitation was achieved by titrating a 1 M AlCl₃ solution with 4 M NaOH to a pH of 4.6. The precipitate was oven dried for 2 h at 40 °C and transferred to a pre-cleaned dialysis tube. Dialysis was performed in a large Milli-Q water bath at a temperature of 50 °C for 5 weeks. The water was changed daily for the first two weeks and every second day thereafter.
Complementary techniques were used to verify and characterize the gibbsite. X-ray diffraction was used to identify the crystal structure and the specific surface area was determined using the BET N₂ adsorption method (Brunauer et al., 1938). Furthermore, earlier studies have shown that the maximum proton adsorption value of gibbsite is in the range 2-4.5 μmol/m² (Kavanagh et al., 1975; Rosenqvist et al., 2002). A SEM picture of the gibbsite can be seen in Fig. 8. Two different batches of gibbsite were used in this thesis, one with a specific surface area of 28.52 m² g⁻¹ (used in paper IV and in the IR section of paper III) and another with a specific surface area of 15.23 m² g⁻¹ (used for the dissolution experiment in paper III). Diluted stock suspensions with concentrations of ca. 5 g gibbsite L⁻¹ were prepared from the batch suspension. The ionic strength of all mineral stock suspensions was set to 0.1 M with NaCl except for the suspension used to overlayer the ATR crystal, which was left uncorrected.

![Figure 8. SEM of dried gibbsite particles.](image)

4.2. Collection and analysis of XAS data

Data for the XAS analysis were collected on four different occasions at the Stanford Synchrotron Radiation Lightsource (SSRL) (Stanford, USA), in July 2011 and May 2012 (data used in paper I), at SOLEIL, the French national synchrotron facility (Paris, France) in March, 2012 (data used in paper II), and at MAX-Lab (Lund, Sweden) in May, 2014 (data used in paper IV). The beamlines used for the experiments were beamline 4-1 at SSRL, LUCIA at SOLEIL, and i811 at MAX-Lab. The rings at SSRL and SOLEIL were operated in top-up mode, which means that the ring energy was continuously stable, but the ring at MAX-Lab was shut down twice a day for refilling. All spectra were collected in fluorescence mode (I_f/I_0 versus energy).
4.2.1. XANES data treatment

The Al XANES data for paper II was analyzed with the ATHENA software (Ravel & Newville, 2005). The pre-edge and background was subtracted and because of problems with low XAS signals, the data were smoothed using interpolative smoothing. After normalization and energy calibration, all spectra for each sample were merged into an average file. The edge data and its first derivative were visually analyzed and compared to spectra of reference samples to find trends and hints to the compositions of the samples. The XANES data were further analyzed by LCF using a number of standard compounds identified by the visual analysis. The LCF is accomplished by optimizing a linear combination of a pre-decided number of standards using their individual spectra. The spectra obtained from the linear combination of the standards were compared to the sample spectra and the procedure was repeated to minimize the errors between them. A maximum of three standards were included in the final fit, with a weight between 0 and 1, and the total sum of the standards was constrained to 100%.

4.2.2. EXAFS data treatment

The EXAFS data in papers I, II, and IV were analyzed using the program SIXPack (Webb, 2005). For each sample, one or several spectra were collected and an average file was created. A first-order polynomial pre-edge function together with the background was subtracted from the averaged spectra and the spectra were normalized. The spectra were then $k^3$-weighted to enhance the higher k-values and Fourier transformed using a Bessel window function. The sample spectra were quantitatively evaluated in R-space (paper I), back-filtered k-space (q-space, paper II), or k-space (paper IV) using a non-linear least-squares refinement procedure with theoretical phase and amplitude functions calculated by the ab initio code FEFF7 (Zabinsky et al., 1995). The amplitude of the EXAFS spectra are proportional to the coordination numbers (CN) of the different scattering paths used for fitting as well as the $S_0^2$ value; therefore, when fitting EXAFS data, the $S_0^2$ value must be determined prior to analysis. Reference systems with known CN:s were used to optimize the $S_0^2$ value, which was subsequently used as a fixed parameter in the fitting procedure.

4.3. Collection and analysis of Infrared Spectroscopy data

All the IR measurements were conducted using a Bruker Vertex 80v FTIR spectrometer equipped with a RT-LADTGS (room temperature deuterated triglycine sulphate substituted with L-alanine) detector and a single-reflection, 45º, ZnSe ATR crystal (FastIR, Harrick Scientific).
4.3.1. **Batch experiments**

For the batch experiment in paper I, the samples were added directly onto the ZnSe crystal and analyzed at room temperature. The sample chamber was kept under vacuum during the analysis while a vacuum-tight lid protected the sample. The absorption of the empty cell was collected as the background and to eliminate the strong water background, a spectrum of the ionic medium was recorded and subtracted from each sample spectra. The resultant spectra showed the spectral features of the different NOM systems with or without added metal. All the data treatment (as well as control of the spectrometer) was accomplished by the OPUS software (Bruker).

4.3.2. **SIPT**

The SIPT experiments in paper II, III, IV, and V were conducted with the modified SIPT system described in section 3.2.1. The sample solution or the mineral suspension was added directly into the reaction vessel and the solution/suspension was continuously stirred with an electric stirrer during the experiment. In the titrations of the NOM and Al(III)-NOM systems (paper II and V), spectra of the empty cell and the ionic medium were collected and subtracted from each sample spectra. For the gibbsite experiments in paper III, the spectrum of the ionic medium was subtracted together with the spectrum from the overlayer on the ATR crystal. The overlayer was created by adding 0.7 mL of a dilute suspension of gibbsite onto the crystal, which was then evaporated in an oven for approximately 3 hours at 60 °C. The pH titrations were performed using an automatic titrator (702 SM Titrino, Metrohm). Data treatment, as well as spectrometer control, was accomplished with the OPUS software (Bruker).

4.3.3. **MCR-ALS**

Prior to the MCR-ALS analysis, the IR data were background subtracted using the script developed by Felten et al. (2015). The script allows for truncation of the data and the background was subtracted over the selected wavenumber region. The MCR-ALS analysis was carried out using MATLAB® and the freeware MCR-ALS toolbox described in Jaumot et al. (2005). The determination of the number of components used in the analyses was carried out with the help of singular value decomposition (SVD) and estimation of the initial concentration profiles was accomplished by means of evolving factor analysis (EFA). Non-negativity (concentrations and spectra) and unimodality (concentrations) were used as constraints in the MCR-ALS analysis.
4.4. Collection and analysis of dissolution data

The dissolution experiment was conducted by taking samples from gibbsite solutions with and without added NOM at different NOM concentrations and pH values. The samples were collected during two weeks and analyzed using a Perkin Elmer OPTIMA 2000 DV (ICP-OES) equipped with a CCD detector. A Peak Performance, Single-Element Aluminum standard (2% HNO₃, 1000 ± 3 µg/mL) from CPI was analyzed and a standard calibration curve was constructed. The average background signal was subtracted from each sample and then the calculated concentrations for the samples without added NOM were subtracted from the samples with added NOM, giving a value for the dissolution of gibbsite in the presence of NOM. The program WinLAB (Perkin Elmer Inc.) was used to control the instrument, and the data analysis was performed in Excel (MS Office).

4.5. Chemical equilibrium modeling

The equilibrium modeling in paper V was conducted using the computer code WinSGW (Karlsson and Lindgren, 2006), based on the SOLGASWATER algorithm (Eriksson, 1979). In WinSGW a model is constructed and this model is then fitted to experimental data by changing parameters data (e.g., formation constants and/or total concentrations) to minimize the total residual sum of squares (U). In paper V this is done by first knowing the measured pH, the total proton concentration in each point, and the total carboxylate concentration. To calculate U the program uses the equation presented below (eq 1):

\[ U = (\left[H^+\right]_{\text{tot(calc)}} - \left[H^+\right]_{\text{tot(exp)}})^2 \]  

\[ \left[H^+\right]_{\text{tot(exp)}} \text{ is calculated from the amounts of base (or acid) added in the titrations and is equal to zero if no acid or base is added.} \]

\[ \left[H^+\right]_{\text{tot(calc)}} \text{ is given by equation 2.} \]

\[ \left[H^+\right]_{\text{tot(calc)}} = \left[H^+\right] - [OH^-] - \Sigma[R_i\text{COO}^-]_{\text{tot}} - \Sigma[R_j\text{O}^-]_{\text{tot}} \]  

Here \( \Sigma[R_i\text{COO}^-]_{\text{tot}} \) is the total concentration of generated carboxylate groups and \( \Sigma[R_j\text{O}^-]_{\text{tot}} \) is the total concentration of deprotonated hydroxyl groups. Experimental \( \left[H^+\right]_{\text{tot(exp)}} \) data as a function of pH were recalculated to yield \( Z(pH) \) curves. \( Z \) is the average number of COO- groups generated within the pH range 2-8 and is defined as:

\[ Z = (\left[H^+\right]_{\text{tot(exp)}} + \left[H^+\right] - [OH^-]) / \Sigma[R\text{COO}^-]_{\text{tot}} \]
“I think that only daring speculation can lead us further and not accumulation of facts.”

*Albert Einstein in letter to Michele Besso, 8 October 1952*
5. Results and Discussion

In this section the results from the five different papers will be summarized and discussed. The first part will summarize the first two papers (paper I and II) where Al(III)-NOM interactions are investigated with the use of Ga(III) as a probe. The speciation in the Al(III)-NOM system is determined and how it is effected by NOM concentration and pH. In the next section the obtained information from the Al(III)-NOM system is utilized to study natural samples where Al(III) and NOM is present (paper II). Paper III and IV is summarized in section 3 where the effects of NOM on gibbsite surfaces as well as Ga(III)-NOM complexes absorbed to gibsite are studied. The final section summarizes paper V where a new way of characterizing NOM is described.

5.1. Complexation of Al(III) by NOM

When studying Al(III)-NOM interactions, the technical difficulties caused by the low K-edge energy of Al (1.5596 keV), that results in strong background absorption, must be overcome. This limits the possibilities for analysis of the EXAFS region of the XAS spectrum and therefore most studies on Al systems are conducted using the XANES region instead. Gallium, on the other hand, has a high K-edge energy (10.367 keV) and hence are readily accessible to both EXAFS and XANES. Furthermore, Ga(III) has been shown to be a suitable analogue for Al(III) because of its comparable coordination chemistry in association with organic ligands (Clausén et al., 2003, 2005). Thus, it should be possible to use Ga(III) as a probe for Al(III) to obtain complementary information about Al(III)-NOM interactions. To acquire more information about these systems, IR spectroscopy was used to study the functional groups in NOM that are involved in the complexation of Al(III) and Ga(III). This knowledge was then utilized in the analysis of the XAS data of the Al(III)/Ga(III)-NOM systems.

5.1.1. Identification of functional groups for Ga(III)/Al(III)-NOM complexation

IR studies of the SRN and SRFA materials were conducted for both Al(III) and Ga(III). All systems (Al(III)/Ga(III)-SRN and Al(III)/Ga(III)-SRFA) behaved similarly and therefore only data for the SRN material are presented in Fig. 9. The figure illustrates the differences between the SRN system with and without Al(III) or Ga(III) added at different pH values. The displayed spectral region in Fig. 9 is dominated by bands originating from carbohydrates as well as carboxylic functional groups, which agrees with previous studies (Persson and Axe, 2005; Karlsson and Persson, 2012).
Figure 9. Infrared spectra illustrating the pH effects on the SRN (dashed line) and I) the Ga(III)-SRN (solid line) system, and II) the Al(III)-SRN (solid line) system in the pH range 3-7. The vertical dashed lines indicate the carbonyl vibrational mode at ca. 1720 cm$^{-1}$, the asymmetric ($\nu_{C-O\text{as}}$) carboxylate stretching frequencies at ca. 1620 cm$^{-1}$, and the symmetric ($\nu_{C-O\text{s}}$) carboxylate stretching frequencies at ca. 1400 cm$^{-1}$. Spectra are offset for clarity.

As the pH is altered, the most pronounced changes in the spectra of the NOM (SRN/SRFA) originated from the protonation/deprotonation reactions of the carboxylic groups (Karlsson and Persson, 2012). These changes were indicated by the increase of the symmetric ($\nu_{C-O\text{s}}$) and asymmetric ($\nu_{C-O\text{as}}$) carboxylate stretching frequencies at ca. 1400 and 1600 cm$^{-1}$, respectively, as the pH increased. Furthermore, the carbonyl mode of the carboxylic acid decreased concomitantly (Fig. 9). As Al(III) or Ga(III) were added to the system, two main observations were made. The first was the loss of carbonyl intensity relative to the asymmetric carboxyl band at low pH. The second observation was a shift of the asymmetric carboxyl band to a higher frequency compared to the NOM system without added metal at a similar pH. The combined results for both the Al(III) and Ga(III) systems indicated that the metals outcompeted some of the carboxylic protons of the NOM material, and thus become coordinated directly to the carboxylate groups in a monodendate fashion. Furthermore, the IR results indicated that the
Al(III)/Ga(III)-NOM complexes seemed predominant in the pH range of 3 to 6. This can be compared to the behavior of complexes between Al(III)/Ga(III) and carboxylic ligands such as oxalate (Fig. 10). This further supported the results that indicated that carboxylate groups are an important functional group in the complexation between NOM and Al(III)/Ga(III) under the current experimental conditions. It should be mentioned that other functional groups could be involved in the complexation between metals and NOM, e.g., phenols. However, in the IR results presented in this study, no major involvement from other functional groups could be detected; note that there are 2.5 and 3.9 times more carboxyl groups than phenols in SRN and SRFA, respectively (see Table 1).

![Figure 10](image-url)

**Figure 10.** Speciation diagram of the Al(III)-oxalate system with an Al(III) concentration of 40 mM and an oxalate concentration of 160 mM. Calculations were performed in WinSGW (Karlsson and Lindgren, 2006) using constants from Sjöberg and Öhman (1985). Figure modified from paper II.

It is noteworthy that it is possible that the strong bending mode of water at ca. 1640 cm\(^{-1}\) interferes with the isolation of the asymmetric carboxylate stretching band which could cause the observed shift as Al(III)/Ga(III) is added to NOM. To eliminate this problem, a replicate of the experiment performed for Ga(III)-SRN was conducted with D\(_2\)O as the solvent. Using D\(_2\)O instead of water eliminates this problem because no overlap of the bending mode of D\(_2\)O and the asymmetric carboxylate stretching band is present. The experiment clearly showed that the shift was indeed caused by Ga(III) interactions with the carboxylate groups in SRN (for figures and in depth discussion, see paper I).

A further important observation was made in the IR data for the Ga(III)-NOM system, for which it was possible to estimate the fraction of carboxylate
groups that were involved in the interaction with Ga(III). This estimation was performed by first isolating the spectra of the fully deprotonated NOM by subtracting the spectra at pH 2 (mostly protonated NOM) from the spectra at pH 8 (mostly deprotonated NOM). Then, by assuming that the area under the carboxylate peak is representative of the amount of Ga(III)-NOM complexes present at different pH, an estimation of the fraction of carboxylate groups that are active for metal complexation can be made by calculating the ratios between this obtained area and the total area of the carboxyl bands in the fully deprotonated spectra (Fig. 11.). The results indicated that not all of the carboxylate sites are active for metal complexation. For SRN the maximum number of coordinated sites observed was approximately 20 %, at a total Ga(III) to R-COOH molar ratio of 0.202, and an even lower number for SRFA of approximately 10 %. Thus, the 1:1 ratio between Ga(III) and the coordinated carboxylate groups together with the knowledge that metal ions coordinate to NOM as chelate structures involving several functional groups (Manceau and Matynia, 2010; Karlsson and Persson, 2012), indicates that at a 0.202 Ga(III) to R-COOH molar ratio, a substantial amount of Ga(III) is not coordinated to carboxyl groups. The observed difference in the amount of active sites of the two organic materials could be due to the isolation methods (Thurman and Malcolm, 1981; Serkiz and Perdue, 1990). In the isolation of SRFA, small organic acids (<200 Da) are removed but are present in SRN. Hence, the larger amount of active sites in the SRN material could be due to the presence of these small organic acids. For more details regarding these results see paper I.

![Figure 11](image.png)

**Figure 11.** Figure showing the fraction of active sites for metal complexation in SRN (diamonds) and SRFA (triangles), at a concentration 0.202 mol Ga(III)/mol R-COOH groups in the NOM. The figure was modified from paper I.

By comparing the two systems (Ga(III)-NOM and Al(III)-NOM) it is clear that they behaved similarly and the trends in spectral changes due to pH
were nearly identical. This further indicated that Ga(III) can be used as a probe for Al(III) to study interactions with NOM and XAS studies of the Ga(III)-NOM system can thus reveal useful information about the interpretation of the XAS results from the Al(III)-NOM system.

5.1.2. Qualitative analysis of EXAFS spectra of the Ga(III)-NOM system

The XAS study on the Ga(III)-NOM system was conducted by analyzing 25 individual samples. To obtain an overview of the distribution of species in the samples, a WT analysis was performed. Reference samples were used for comparison with the Ga(III)-NOM samples. The concentration range of the Ga(III)-NOM samples was 0.0003-0.202 mol Ga(III) per mol R-COOH in the NOM and the pH ranged from 3 to 7.

The results from the WT analysis gave similar results for both SRN and SRFA. The first-shell contribution had a backscattering maximum at approximately 6 Å⁻¹ similar to the Ga-O scattering of the reference samples containing Ga(OH)₃(s) (an amorphous aqueous paste) and Ga(C₂O₄)₃³⁻ (an aqueous solution) (Fig. 12). For the higher coordination shells the samples with the highest concentration of Ga(III) at pH 5-7 showed a distinct feature at ca. 7.7-8 Å⁻¹ and 2.7 Å. The same feature was found in Ga(OH)₃(s) originating from Ga-Ga backscattering. This feature disappeared as the pH decreased and was believed to be a consequence of a substantial amount of free Ga(III) present in these samples (Fig. 12). If the Ga(III) concentration was lowered, the signal from free Ga(III) also disappeared and strong features at 2.0-2.5 Å and 3-3.8 Å at lower energies (2-6 Å⁻¹) arose. These features were in fair agreement with features caused by single and multiple backscattering from C/O in the second and third coordination shells of Ga(C₂O₄)₃³⁻ and suggested the presence of mononuclear organic Ga(III) complexes in these samples (Fig. 12).
Figure 12. WT showing the second and third coordination shells \((\eta = 10, \sigma = 1)\) of the reference samples and the Ga(III)-SRN system at different pH and molar ratios. Plotted as a function of \(k (\text{Å}^{-1})\) on the x-axis, in the range 2-15, and \(R (\text{Å})\) on the y-axis in the range 2.0-4.0

5.1.3. Quantitative EXAFS analysis of the Ga(III)-NOM system

The results from the WT analysis gave hints on how to perform the quantitative EXAFS analysis. Selected results from the EXAFS data fitting of the Ga(III)-SRN system are presented in Table 3 and visualized in Fig. 13 (for complete results, see paper 1). The modeling of the EXAFS data revealed that Ga(III) formed a mononuclear chelate complex with NOM and these complexes dominated the speciation at concentrations of 0.04 mol Ga/mol R-COOH and below over the entire pH range. To make it easy to visualize, the Ga(III)-oxalate structure \((\text{Ga(C}_2\text{O}_4)_3^{3-})\) was adopted as a model for the visualization of the mononuclear Ga(III)-NOM complexes (Fig. 14). This structure was supported by the IR results showing that Ga(III) coordinates to carboxylate groups and that the Ga-C, Ga-O-C, and Ga-C-O distances obtained agreed with the distances for Ga(C_2O_4)_3^{3-} (Clausén et al., 2003). Furthermore, at a concentration of 0.005 mol Ga/mol R-COOH, the CN of the Ga-C scattering path is approximately 6-7 (Table 3) which is in accordance with Ga(C_2O_4)_3^{3-} that has a structure with three 5-membered chelate rings. Formation of chelate structures have previously been
described by Clausén et al. (2003, 2005) for Ga(III) complexed with malonate and citrate, and recent studies have shown that Fe(III) and Cu(II) can form 5- or 6-membered chelate ring structures in similar NOM systems (Karlsson et al., 2006; Karlsson and Persson, 2010; Manceau and Matynia, 2010; Karlsson and Persson, 2012). By comparing the results for the Ga(III)-NOM system with an aqueous Ga(III) system without NOM, it is clear that the complexes formed between NOM and Ga(III) are strong enough to suppress the hydrolysis and polymerization of Ga(III) (Fig. 15). This effect has also been demonstrated in previous studies of NOM interactions with other metals, e.g., Fe(III) (Mikutta, 2011; Karlsson and Persson, 2012). Furthermore, the high stability of the metal-NOM complexes has also been indicated by Fe isotope studies of organic-rich waters (Ilina et al., 2013).

Figure 13. Fourier transform of the EXAFS spectra (solid line, not corrected for phase shift) together with fit results (dotted line) of SRN. Spectra of the Ga(III)-oxalate were taken from Clausén et al. (2003). The vertical dashed lines indicate approximate positions for the main atomic neighbors (C, O, and Ga) and multiple scattering (C-O and O-C) contributions in Ga(C₂O₄)₃³⁻ and Ga(OH)₃(5). Spectra are offset for clarity.
At the lowest Ga(III) concentrations (0.0003-0.0012 mol Ga/mol R-COOH) the structure of the Ga(III)-NOM complexes started to diverge from the suggested Ga(III)-oxalate like structure. This was indicated by more pronounced second and third shell contributions in the samples (Table 3, Fig. 13). The modelling of the EXAFS data showed an increase in the CN for the Ga-C scattering path from approximately 6-7 (at 0.005 mol Ga/mol R-COOH) to 7.2-10.9 (Table 3), which suggested a shift of the dominant species and instead of the supposed oxalate-like Ga(III) carboxylic complexes, either a different dominant complex or a mixture of complexes was present in these samples. High CN:s for second-shell C atoms (10-12) are found in metal complexes with artificial chelating agents (e.g., EDTA, NOTA) and these complexes are very stable (Anderegg, 1977; Anderegg et al., 2005). Thus, there is a possibility that Ga(III) associated with NOM (at these low concentrations) could form cage like-structures similar to Ga(III)-EDTA (Wadas et al., 2010).

For the samples with the highest concentrations (0.202 mol Ga/mol R-COOH), the EXAFS results showed a mixture of mononuclear organic Ga(III) complexes, Ga(III) (hydr)oxide, and free Ga(III) (defined here as the hydrated Ga³⁺ ion and its soluble hydrolysis products). Thus, the contribution from organic complexes was weaker than at lower Ga(III) concentrations (Table 3), which is in line with the IR results indicating that only a limited number of carboxylic sites are available for metal complexation. As the concentration of Ga(III) increased, the CN for the Ga-C
scattering path decreased (see Table 3). Hence, at the highest Ga(III) concentration, the number of available sites for complexation (estimated to be approximately 10-20 % of the carboxylic sites) are too few to form chelate complexes with all the added Ga(III). For a deeper discussion of the results, see paper I.

Table 3.
Fits to Fourier-transformed EXAFS data for Ga(OH)$_3(s)$ and the Ga(III)-SRN samples. Only the scattering paths, coordination numbers (CN), and bond distances (R) are given in this table, for a more detailed table of the fitting results see paper I.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Path</th>
<th>CN</th>
<th>R(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga(OH)$_3(s)$</td>
<td>Ga-O</td>
<td>6.0 ± 0.8</td>
<td>1.96 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Ga-Ga</td>
<td>2.0</td>
<td>2.99 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>Ga-Ga</td>
<td>2.0</td>
<td>3.10 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>Ga-Ga</td>
<td>4.0</td>
<td>3.52 ± 0.04</td>
</tr>
<tr>
<td>Ga(III)-SRN pH 3, molar ratio 0.202</td>
<td>Ga-O</td>
<td>5.6 ± 0.5</td>
<td>1.96 ± 0.01</td>
</tr>
<tr>
<td>Ga(III)-SRN pH 5, molar ratio 0.202</td>
<td>Ga-O</td>
<td>5.3 ± 0.7</td>
<td>1.95 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Ga-C</td>
<td>2.2 ± 1.1</td>
<td>2.70 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>Ga-C-O</td>
<td>4.4 ± 2.2</td>
<td>4.08 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>Ga-Ga</td>
<td>0.4 ± 0.3</td>
<td>3.06 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>Ga-Ga</td>
<td>3.2 ± 2.3</td>
<td>3.56 ± 0.05</td>
</tr>
<tr>
<td>Ga(III)-SRN pH 7, molar ratio 0.202</td>
<td>Ga-O</td>
<td>5.3 ± 0.7</td>
<td>1.94 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Ga-C</td>
<td>1.6 ± 0.8</td>
<td>2.76 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>Ga-C-O</td>
<td>3.2 ± 1.6</td>
<td>4.06 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>Ga-Ga</td>
<td>1.0 ± 0.3</td>
<td>3.06 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>Ga-Ga</td>
<td>3.1 ± 1.5</td>
<td>3.56 ± 0.04</td>
</tr>
<tr>
<td>Ga(III)-SRN pH 5, molar ratio 0.040</td>
<td>Ga-O</td>
<td>5.5 ± 0.3</td>
<td>1.96 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Ga-C</td>
<td>3.8 ± 0.5</td>
<td>2.76 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Ga-O-C</td>
<td>7.6 ± 1.0</td>
<td>3.02 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>Ga-C-O</td>
<td>7.6 ± 1.0</td>
<td>4.09 ± 0.02</td>
</tr>
<tr>
<td>Ga(III)-SRN pH 5, molar ratio 0.005</td>
<td>Ga-O</td>
<td>5.3 ± 0.4</td>
<td>1.97 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Ga-C</td>
<td>6.9 ± 1.1</td>
<td>2.76 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Ga-O-C</td>
<td>13.8 ± 2.2</td>
<td>3.06 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>Ga-C-O</td>
<td>13.8 ± 2.2</td>
<td>4.09 ± 0.02</td>
</tr>
<tr>
<td>Ga(III)-SRN pH 5, molar ratio 0.0003</td>
<td>Ga-O</td>
<td>5.6 ± 1.1</td>
<td>1.97 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Ga-C</td>
<td>10.9 ± 2.1</td>
<td>2.76 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>Ga-O-C</td>
<td>21.8 ± 4.2</td>
<td>3.07 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>Ga-C-O</td>
<td>21.8 ± 4.2</td>
<td>4.11 ± 0.04</td>
</tr>
</tbody>
</table>
Figure 15. Distribution diagram of Ga(III) species at two different concentrations representing the highest (44.8 mM; 0.202 mol Ga(III)/mol R-COOH) and lowest (0.27 mM; 0.0003 mol Ga(III)/mol R-COOH) Ga(III) concentration analyzed using XAS. The calculations were performed in WinSGW using constants from Baes and Mesmer (1976), Bénézeth et al. (1997), and Clausén et al. (2002). The solid phase considered is amorphous Ga(OH)$_3$(s). Figure modified from paper I.

5.1.4. Qualitative analysis of XANES spectra and their first derivatives of the Al(III)-NOM system

The knowledge obtained from studying the Ga(III)-NOM system was used when analyzing the XANES data of the Al(III)-NOM system in paper II, motivating the choice of references for further analysis. Al(III)-oxalate and Al(III)-citrate were used as references for the Al(III)-NOM complexes and amorphous Al(OH)$_3$(s), gibbsite, and free Al(III) (defined here as the hydrated Al(III) ion and its soluble hydrolysis products and represented by AlCl$_3$(aq)) as references for the Al(III) (hydr)oxide and free Al(III) fractions (Fig. 16). The analysis was mainly conducted by visually comparing the edge data and its first derivative of the reference systems with the Al(III)-NOM samples. A complementary LCF analysis was also performed, however the limited set of references made these results uncertain and therefore the visual comparison was emphasized in the XANES analysis (for LCF results and further details see paper II).
Figure 16. Normalized Al K-edge XANES spectra (I), and first derivatives (II) for the reference samples used for the visual comparison with the Al(III)-NOM samples. The vertical dashed lines are for comparison of features between spectra. Spectra are offset for clarity. Figure modified from paper II.

The XANES spectra and the corresponding first derivatives of the SRN and SRFA show similar trends and because of this similarity, only the SRN system is shown in the figures. At the highest Al(III) concentration in the SRN samples the system was dominated by free Al(III) at low pH values, but at higher pH values, mononuclear organic Al(III) complexes were the dominant species (Figs. 16 and 17). At pH 7, the first derivative showed a clear feature at 1570 eV indicating the presence of amorphous Al-hydroxide, but this feature disappeared as the pH decreased (Fig. 17). These observations agree with the results found for the Ga(III)-NOM system further supporting the assumption that the Ga(III)-NOM complex is a valid analogue for Al(III)-NOM interactions. Furthermore, a sharp first derivative peak at 1565 eV was found in most SRN samples over the entire pH and concentration range (Figs. 17 and Fig. 18). This feature was also present in the Al(III)-citrate and Al(III)-oxalate samples indicating the presence of Al(III)-organic complexes. This feature is not as clear in the SRFA samples,
which could be due to a lower contribution from mononuclear organic Al(III) complexes. Furthermore, a trend towards increasing amounts of organic Al(III) complexes with decreasing Al(III) concentrations was evident. A shift of the main peak in the first derivative of these samples supports this statement (Fig. 18).

**Figure 17.** Normalized Al K-edge XANES spectra of the SRN samples at a concentration of 0.202 mol Al(III)/mol R-COOH and three different pH values. The figures show the Al-K edge spectra (I), and first derivatives (II). The vertical dashed lines are for the comparison of features between spectra. The line at ca. 1567 eV marks the maximum of the main peak in the first derivative for free Al(III). Spectra are offset for clarity. Figure modified from paper II.
Figure 18. Normalized Al K-edge XANES spectra of the SRN samples at pH 5 and different concentrations 0.04-0.4 mol Al(III)/mol R-COOH. The figure shows the Al-K edge spectra (I), and first derivatives (II). The vertical dashed lines are for comparison of features between spectra. The line at ca. 1567 eV marks the maximum of the main peak in the first derivative for free Al(III). Spectra are offset for clarity. Figure modified from paper II.

5.2. Al(III) speciation in organic soils and stream waters

To further investigate the speciation of Al(III) in natural systems, two organic soils and three stream water samples (Table 2) were analyzed using XAS. To evaluate this data, knowledge from the two reference systems previously described (Ga(III)-NOM and Al(III)-NOM) was utilized and the results were presented in paper II. Moreover, for three of these samples (two organic soils (FP and SP) and the ultra-filtrated stream water (SK)) the EXAFS spectra were of sufficient quality to perform a shell-by-shell fit analysis, which was partly constrained by the XANES and LCF results.
5.2.1. Qualitative analysis of XANES spectra and their first derivatives

The soils and stream water samples were subjected to the same analysis as the Al(III)-NOM reference system and showed similarities to both the organic mononuclear reference compounds (Al(III)-citrate and Al(III)-oxalate) and the hydroxides (amorphous Al-hydroxide and gibbsite) (Figs. 16 and 19). The primary edge maxima for all these samples showed a position similar to that of the organic references. Furthermore, the stream water samples (SK, S1 and S2) showed no contributions from polymeric hydroxide species in the edge data nor in the first derivative (Figs. 16 and 19). Samples S1 and S2 showed contributions from organic complexes in the first derivative because of the presence of a feature near 1565 eV that was also present in the organic references (Figs. 16 and 19). Furthermore, there was no feature near 1570 eV that would indicate contribution from an Al-hydroxide phase. It should be mentioned that the adsorption of Al(III) species on the anion-exchange resin for S1 and S2 was low (15-23 %), thus only a relatively small part of the total Al in these stream waters was included in the XAS analyses. In contrast to the stream water samples, the soil samples (FP and SP) showed features in the edge data, as well as in the first derivative, indicating the presence of both an Al-hydroxide phase and organic Al(III) complexes. It should be mentioned that clay minerals, such as kaolinite (Al₂Si₂O₅(OH)₄(s)), have very similar XANES spectra as those of gibbsite and amorphous Al-hydroxide (Ildefonse et al., 1998), which means that the presence of the Al-hydroxide phases observed could instead be a contribution from the clay minerals.
Figure 19. Normalized Al K-edge XANES spectra of Västrabäcken (S2), Risbäcken (S1) and Stor-kälsmyran (SK), and the two soil samples, fen peat (FP) and sphagnum peat (SP). The figure shows the Al-K edge spectra (I), and first derivatives (II). The vertical dashed lines are for comparison of features between spectra. Spectra are offset for clarity. Figure modified from paper II.

5.2.2. XAS: Shell-by-shell EXAFS fitting results

The XANES results for the soils (FP and SP) suggested a mixture of Al-hydroxides and organic Al(III) complexes, while for the ultra-filtrated stream water (SK), only Al(III)-organic complexes were indicated. As mentioned above, contributions from clay minerals cannot be ruled out and their presence was considered in the EXAFS analysis by the use of an Al-Si scattering path. In the first coordination shell, all of the samples showed Al-O coordination numbers and distances that corresponded to 6-coordinated Al(III) (Table 4). The higher shells displayed substantial differences among the samples (Fig. 20). The FP sample was satisfactorily fitted with an Al-C path at 2.65 Å together with Al-Al and Al-O paths at distances in agreement with the amorphous Al-hydroxide and gibbsite references (Table 4). On the
other hand, the SP sample was best-fitted using scattering paths from an Al-silicate model. The Al-Si distance agreed with the Al-Si distances in kyanite (3.083 and 3.097 Å; Yang et al., 1997) and kaolinite (3.143 and 3.256 Å; Ildefonse et al., 1998). Furthermore, in contrast to the XANES result, the EXAFS fit result for the SK sample exhibited a substantial contribution from both organic Al(III) complexes and Al-hydroxide phases (Table 4).

Table 4.
Fits to EXAFS data in back-filtered k-space for gibbsite, amorphous Al-hydroxide (am. Al(OH)$_3$(S)), the fen peat (FP) and sphagnum peat (SP) soils and the ultrafiltrated stream water from Stor-kälsmyran (SK). Coordination number (CN) and bond distance (R).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Path</th>
<th>CN</th>
<th>R (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gibbsite$^a$</td>
<td>Al-O</td>
<td>6.0</td>
<td>1.88 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Al-Al</td>
<td>3.0</td>
<td>2.89 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Al-O</td>
<td>6.0</td>
<td>3.57 ± 0.02</td>
</tr>
<tr>
<td>Amorphous Al(OH)$_3$(S)</td>
<td>Al-O</td>
<td>5.8 ± 0.6</td>
<td>1.89 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>Al-Al</td>
<td>2.7 ± 0.2</td>
<td>2.89 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Al-O</td>
<td>2.9 ± 0.7</td>
<td>3.56 ± 0.03</td>
</tr>
<tr>
<td>FP</td>
<td>Al-O</td>
<td>5.7</td>
<td>1.88</td>
</tr>
<tr>
<td></td>
<td>Al-C</td>
<td>1.1 ± 0.8</td>
<td>2.65 ± 0.07</td>
</tr>
<tr>
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<td>Al-Al</td>
<td>1.0 ± 0.3</td>
<td>2.90 ± 0.02</td>
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<tr>
<td></td>
<td>Al-O</td>
<td>3.3 ± 0.9</td>
<td>3.64 ± 0.03</td>
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<td>Al-O</td>
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<td>Al-Al</td>
<td>1.4 ± 1.1</td>
<td>2.85 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>Al-Si</td>
<td>2.8 ± 1.3</td>
<td>3.06 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>Al-O</td>
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<td>3.60 ± 0.02</td>
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<td>SK</td>
<td>Al-O</td>
<td>6.1</td>
<td>1.90</td>
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<td>Al-C</td>
<td>0.7 ± 0.9</td>
<td>2.53 ± 0.12</td>
</tr>
<tr>
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<td>Al-Al</td>
<td>0.7 ± 0.4</td>
<td>2.97 ± 0.04</td>
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<tr>
<td></td>
<td>Al-O</td>
<td>6.4 ± 1.2</td>
<td>3.64 ± 0.02</td>
</tr>
</tbody>
</table>

$^a$ CNs in all shells were fixed according to the crystalline structure (Saalfeld and Wedde, 1974).
5.3. Interactions between NOM and gibbsite and the effect on mineral dissolution

After characterizing the Al(III)-NOM system and gaining knowledge of the speciation of Al(III) in some soils and stream waters, the next step was to take a more detailed look at the interactions between minerals and NOM. This is highly relevant since NOM is present in most environments and mineral particles in soil and surface waters all possess at least a partial surface coating of NOM (Mayer and Xing, 2001). Furthermore, as described in paper II, both Al minerals and organic Al(III) complexes were indicated in the organic soils and stream water samples. To further investigate these interactions, two different studies were conducted. In the first one the interactions between NOM and gibbsite, and the possibility of mineral dissolution in the presence of NOM, were investigated using IR spectroscopy and dissolution experiments (paper III). In the second study Ga(III)-NOM complexes at the surface of gibbsite particles were studied using EXAFS and IR spectroscopy (paper IV) to get an approximate picture of how this
complex looks like. This is of great importance since earlier studies have shown that metal-organic complexes at mineral surfaces could have an impact on the ligand-promoted dissolution of minerals (Simanova et al., 2011). Gallium(III) was used as an analogue for Al(III) since Al(III)-NOM complexes cannot be analyzed at the surface of Al based minerals with EXAFS, the signal from the Al(III)-NOM complex will simply drown in the signal from the gibbsite. Furthermore, as described earlier, Ga has a good XAS signal, which makes the results easier to interpret.

5.3.1. Dissolution of gibbsite in presence of NOM

The first step was to study the possibility for dissolution of gibbsite in the presence of two different organic materials, SRN and SRFA. The dissolution was investigated under varying pH and NOM concentrations under a 14 day period. In order to isolate the dissolution induced by the presence of the NOM, references (without added NOM) at the same pH were also analyzed. The mineral suspensions (with and without NOM) were continuously stirred for two weeks and solution samples were taken at certain intervals. These samples were then analyzed using ICP-OES and the concentration of the references was subtracted from samples with added NOM at the same pH. The obtained Al concentrations were addressed to originate from the dissolution of the gibbsite in the presence of NOM (for more information see paper III). The reference systems at higher pH (pH 5 and 6) indicated a low dissolution similar to that of Al(oxyhydr)-oxides (Baes and Mesmer, 1976; Bethke, 2002). However, at pH 4 the dissolution was drastically increased indicating a proton-promoted dissolution.

In the presence of high concentrations of NOM and at low pH values, the dissolution of gibbsite was increased (Fig. 21). These results were in contrast to previous studies where the presence of SRFA was indicated to inhibit the dissolution of boehmite and corundum, especially at low pH (Johnson et al., 2005; Yoon et al., 2005) and that increased NOM concentrations at pH above 4 further inhibited the dissolution (Yoon et al., 2005). One explanation for the difference in results could be that fact that different Al-(hydr)oxides were studied. Another reason could originate from the analysis approach itself. In the present study the dissolution was continuously measured under a 14-day period, enough time to reach steady-state conditions (Fig. 21). Yoon et al. (2005) looked at the system a bit more statically, where the dissolution was measured once after 48 hours giving results which might represent a transient condition and not steady-state. As the NOM concentration was lowered, no dissolution of the gibbsite could be indicated and at the lowest concentration the dissolution was inhibited by the presence of NOM. This could indicate that the presence of NOM, to a
certain extent, can inhibit the proton-induced dissolution of the gibbsite surface by acting as a shield.

The two different materials tested in paper III gave similar results, but some important differences were observed. In the SRN system the Al(III) concentration was maintained at steady-state after initial release (Fig. 21), while SRFA induced a larger and faster initial release of Al(III) into solution but thereafter the concentration of dissolved Al(III) gradually decreased. The reason for this could be the higher amount of active carboxylic sites available for metal binding in SRN compared to SRFA (see paper I). With a higher amount of these strong binding sites more Al can be retained in solution, the re-precipitation and/or re-adsorption of Al(III) is then suppressed (paper I and II; Karlsson and Persson, 2012) and the dissolution would be more stable over time.

![Figure 21. Dissolution of gibbsite in presence of SRN at I) different concentrations at pH 5; 5.0 µmol/m² (black diamonds), 2.0 µmol/m² (grey squares), and 1.2 µmol/m² (light grey triangles) and, II) different pH and a concentration of 2.0 µmol/m²; pH 4 (black diamonds), pH 5 (grey squares), and pH 6 (light grey triangles). The figures are modified from paper III.](image-url)

Two different mechanisms are hypothesized as the possibility for the observed dissolution. The first is that NOM forms inner-sphere complexes with the gibbsite mineral and hence is able to dissolve the mineral through ligand induced dissolution by de-stabilizing the surface Al-O bonds. The second one is a proton induced dissolution where an anionic ligand (NOM in this case) is adsorbed to a mineral surface and thereby the overall surface charge is decreased. This, in turn, will enhance the surface protonation at a given pH. However, based on the dissolution data alone, we cannot determine which mechanism that caused the enhanced dissolution. Anyhow, our data clearly showed that there are enough SRN present in solution to form stable aqueous complexes with Al(III) preventing re-precipitation.
and/or re-adsorption. The dissolution of the mineral was significant, but still only a few percent of the reported proton active site concentration, 2-4.5 μmol/m² for gibbsite (Kavanagh et al., 1975; Rosenqvist et al., 2002), was affected by the dissolution and most of the gibbsite surfaces were intact after the NOM-promoted dissolution. To further investigate how NOM adsorbs to gibbsite surfaces, the system was analyzed by simultaneous infrared and potentiometric titration (SIPT).

5.3.2. IR results from the gibbsite-NOM system

The IR results for SRN adsorbed to gibbsite, as a function of pH, at three different concentrations showed clear indications of carboxylic groups interacting with the surface of the gibbsite (Fig. 22). The spectra for SRN (adsorbed to gibbsite) displayed the same characteristic features of protonation/deprotonation of SRN carboxyl groups as described in Karlsson and Persson (2012) and paper I (Fig. 22). This was seen as a decrease in the intensities of the symmetric and asymmetric carboxylate stretching band at 1400 and 1570 cm⁻¹, respectively, due to protonation as the pH was decreased (Fig. 22). Consequently, the appearance of a new peak at ca. 1720 cm⁻¹ was also indicated and assigned to the C=O-H vibrational modes. The relative intensity between the band at ca. 1720 and at ca. 1570 cm⁻¹ showed that the protonation state of SRN is dependent on the total SRN concentration, and that deprotonated forms of SRN were relatively stabilized at the low concentration. Furthermore, a shift was observed in the asymmetric carboxylate stretching band at ca. 1570 cm⁻¹ to a higher wavenumber at lower pH values (Fig. 22). Previous studies (paper I and II) have shown that a shift of the asymmetric carboxylate stretching band to wavenumbers above 1600 cm⁻¹ indicates an interaction between Me(III) and the carboxylate.
Figure 22. IR spectra of SRN adsorbed to gibbsite at total SRN concentrations of I) 1.2 \( \mu \text{mol/m}^2 \), II) 2.0 \( \mu \text{mol/m}^2 \), III) 5.0 \( \mu \text{mol/m}^2 \) at pH ranges from 2.3-2.5 to 5.4-5.8 and pH step-sizes of ca. 0.15-0.2 pH units. Spectra are offset for clarity. The figure is reprinted from paper III.

Thus, combining the IR results in paper III with previous results from other studies of Me(III)-NOM systems (Karlsson and Persson, 2012; paper I and II), suggested an involvement of inner-sphere coordination between Al(III) and SRN/SRFA carboxyl groups. To get further information on whether or not the observed inner-sphere complex have anything to do with the observed dissolution of the mineral in the presence of NOM, further analysis of the IR data was conducted. Spectra at pH 5 from each concentration of SRN were selected and compared. This showed a clear trend in the shift of the asymmetric carboxylate stretch going from ca. 1590 cm\(^{-1}\) at 1.2 \( \mu \text{mol/m}^2 \) of SRN to ca. 1615 cm\(^{-1}\) at 5.0 \( \mu \text{mol/m}^2 \) (Fig. 23) as well as a significant intensity loss of the symmetric carboxylate stretch at ca. 1400 cm\(^{-1}\) with increasing SRN concentration. This was in agreement with an increasing Al(III)-SRN inner-sphere coordination via carboxyl groups as the SRN concentration was increased, further corroborated by the resemblance between the spectrum at 5.0 \( \mu \text{mol/m}^2 \) and the Al(III)-SRN reference complex (Fig. 23), showing a correlation between the amount of inner-sphere interactions at the water-gibbsite interface and increased dissolution.

The actual structure and configuration of the indicated inner-sphere complex cannot be determined by the results from this study and could either consist of SRN bonded to Al(III) surface sites or Al(III) that are dissolved from the gibbsite surfaces but remaining at the interface as adsorbed Al(III)-SRN complexes. The likely scenario is that both species coexist and that the presence of these species increases the dissolution of the
mineral. These results are in contrast to previous results shown by Yoon et al. (2005) who only observed outer-sphere NOM at the surface of boehmite.

Figure 23. IR spectra of SRN adsorbed on gibbsite at pH 5 and SRN concentrations of 1.2, 2.0, and 5.0 µmol/m². Included is also a spectrum of an Al(III)-SRN complex prepared at pH 3 and concentration 0.202 mol Al(III)/mol R-COOH in SRN. Figure modified from paper III.

5.3.3. Ga(III)-NOM complexes at the surface of gibbsite

The results from paper III indicated that dissolution promoted by NOM was correlated to increasing amount of Al(III)-NOM inner-sphere interactions at the water-gibbsite interface. However, the exact structure and configuration of the formed inner-sphere complexes could not be determined and therefore a complementary study was conducted in order to identify and characterize the formed surface complexes in the ternary Ga(III)-NOM-gibbsite system. The characterization was done using EXAFS and the results gave clues to a possible mechanism behind the observed dissolution in paper III.

The EXAFS data were first analyzed using the WT method. In the reference where Ga(III) was added to the gibbsite surface, a clear feature with a maximum at high $k$ (ca. 8-9 Å⁻¹ and R 2.7 Å) was observed and probably originates from both Ga-Al interactions and MS contributions from the well-ordered gibbsite structure (Fig. 24). The Ga(III)-SRN reference showed features at low $k$ (ca. 3-4 Å⁻¹) at distances of ca. 2.2 and 3.4 Å (Fig. 24) and these features were assigned to the single scattering from second shell C atoms and mainly multiple scattering from C/O atoms, respectively (in accordance with results in paper I). The WT of the Ga(III)-SRN-gibbsite
sample showed features in accordance with the Ga(III)-SRN reference, although the multiple scattering contribution from C/O atoms was weaker, and in addition a feature at \( k \approx 8 \, \text{Å}^{-1} \) and \( R \approx 2.5 \, \text{Å} \) indicating presence of heavier backscattering atoms (i.e., Al or Ga) and/or MS contributions as in the Ga/gibbsite and Ga(OH)\(_3\)(s) references (Fig. 24). Thus, the WT results for the Ga(III)-SRN-gibbsite samples suggest that Ga(III) complexed by SRN either interacts directly with Al atoms of the gibbsite surface or that there is mixture of Ga(III)-SRN complexes in solution and a precipitated Ga(OH)\(_3\)(s) phase or possibly a combination of both. Based on the WT results alone we cannot distinguish between these possibilities.
Figure 24. Left: Fourier Transforms (solid line), not corrected for phase shift, together with fit results (dashed line) of a) amorphous Ga(OH)$_3$(s) (Persson et al., 2006), b) Ga(III) adsorbed onto gibbsite at 2.0 µmol m$^{-2}$ (pH 3.0), c) Ga(III)-SRN adsorbed onto gibbsite at 0.09 µmol m$^{-2}$ (pH 5.9), d) Ga(III)-SRN adsorbed onto gibbsite at 0.18 µmol m$^{-2}$ (pH 5.9), e) SRN with 11,714 µg Ga(III) g$^{-1}$ (pH 5.5). The vertical dashed lines indicate the positions for the main atomic neighbors in the Ga/gibbsite sample. Spectra are offset for clarity. Right: WT showing the second and third coordination shells ($\eta = 10$, $\sigma = 1$) of the reference samples and the Ga(III)-SRN/gibbsite system at different concentrations. Plotted as a function of $k$ (Å$^{-1}$) on the x-axis, in the range 2-15, and R (Å) on the y-axis in the range 2.0-4.0. The areas that are white/brown indicate a strong contribution from back-scattering atoms and the ones that are blue/green indicate no or weak contribution. MS indicate multiple scattering contributions.

The results from the WT analysis were used in the fitting of the EXAFS data, and models with single-scattering Ga-O, Ga-C, and either Ga-Al or Ga-Ga together with a multiple Ga-O-C scattering path were possible to fit to the Ga(III)-SRN/gibbsite samples (Fig. 24). The model with a Ga-Al path gave better fitting results compared to the model with Ga-Ga and therefore the results for this model is presented herein. However, it should be noted that
in the EXAFS fitting of data it can be difficult to separate between Al and Ga contributions in the second shell. This means that the results presented in Fig. 24 is one possible way to describe this data and we cannot with certainty say that this model is more valid than a model with Ga-Ga interactions. The fitting results showed contributions from Al and C and multiple scattering contributions from C/O atoms in the second and third coordination shells (Fig. 24; for more in-depth discussion of the results, see paper IV). This suggested that Ga(III) is coordinated to both NOM and gibbsite functional groups and do not form a precipitated Ga(OH)$_3$ phase. Furthermore, an IR investigation revealed differences in the adsorption behavior of NOM to the gibbsite surface in the presence and absence of Ga(III). These results could indicate that the organically complexed Ga(III) coordinate directly to the surface, as suggested as one possibility by the EXAFS results, or that Ga(III) effects the structure and/or the chemical properties of the adsorbed NOM at the surface of gibbsite. Thus, the collective spectroscopic results showed that there is a possibility that Ga(III)-NOM adsorbs inner-spherically onto gibbsite by forming ternary type A surface complexes where Ga(III) acts as a bridge between NOM and the surface. However, as noted above, this is one of two possible ways to explain our EXAFS results. The other model with Ga-Ga interactions in the second coordination shell suggest presence of two different Ga species; Ga(III)-NOM complexes in solution and a precipitated Ga(OH)$_3$ phase.

5.4. A new approach to the characterization of NOM

As the investigations of how metals form complexes with NOM proceeded, the importance of detailed characterization of NOM became obvious. To fully understand the speciation of metals in environmental samples, relevant models for NOM needs to be developed. A number of different models have been established and the most common method to characterize the acid/base properties of NOM is by modeling potentiometric titration data utilizing chemical equilibrium models like the modified Henderson-Hasselbalch model (Katchalsky and Spitnik, 1947; Ritchie and Perdue, 2003; 2008), NICA-Donnan model (presented in details in Kinniburgh et al., 1996; Kinniburgh et al., 1998; Kinniburgh et al., 1999), Model VI (Tipping, 1998), or Stockholm Humic Model (Gustafsson, 2001).

One problem with adjusting the model, used to characterize NOM, based merely on potentiometric titration data is that inherent properties of the material itself are not used to develop the model. To partly overcome this problem, a second analytical method (e.g., spectroscopy) can be introduced to characterize the material and give additional information that can be used in the development of the model. The obtained model will then be specific for each material giving results that would be more relevant. Combining IR
with multivariate data analysis, such as MCR-ALS, can be one way to obtain additional information for the development of a model.

5.4.1. MCR analysis of the IR data series

The SRFA material was analyzed using the modified SIPT set-up, described in section 3.2.1., in the pH range 2-8. The most obvious changes in the IR spectra with increasing pH were a gradual shift towards lower wavenumber in the asymmetric carboxylate peak at ca. 1600 cm\(^{-1}\) and a decrease in amplitude of the protonated carboxylate peak at ca. 1720 cm\(^{-1}\) (Fig. 25, I). This indicated that the carboxylic acids are affected by the pH change which is in agreement with previous IR studies on organic materials (Persson and Axe, 2005; Karlsson and Persson, 2012; paper I) and give valuable clues for the construction of an acid/base model of the SRFA material. The IR results were then subjected to a MCR-ALS analysis. This analysis showed that a four component model, with their own unique component spectra (Fig. 25, II), was needed to describe the data. The component distribution diagram is displayed in Fig. 25, III.
Figure 25. I) The complete dataset from the simultaneous IR and potentiometric titration from pH 2 (darker spectra) to pH 8 (lighter spectra). II) Component spectra from the MCR-ALS analysis. The vertical dashed line marks the position of the asymmetric stretching mode for the carboxylate. Spectra are offset for clarity. III) Distribution diagram for the components in the MCR-ALS analysis with the estimated pK$_a$-values. The figure is reproduced from paper V.

Three different criteria were used to evaluate the result from the MCR-ALS analysis; (1) the fit quality based on the percentage of variance explained, (2) the appearance and changes of the component spectra, and (3) the predicted component distribution as a function of pH. The results from the MCR-ALS showed a 99.82% model fit and the component distribution diagram was in agreement with what could be expected. The component spectra follows a gradual trend from a protonated carboxylic acid to something looking like a fully deprotonated one (for more in-depth discussions, see paper V). From the distribution diagram the pK$_a$-values for the components can be estimated and the three pK$_a$ values found for the four-component system were 3.66, 5.66, and 7.07. However, a fourth pK$_a$ value had to be introduced into the model to be able to explain the high carboxylate concentration (approximate 10 mM) at pH$_0 = 2$. This pK$_a$ value had to be optimized from the titration curve and could not be obtained from the IR analysis (as the previous three) because lowering pH below 2 would
seriously corrode the ZnSe ATR crystal. Hence, the deprotonated form of this acidic group likely constituted a subgroup of Component 1.

5.4.2. Chemical equilibrium modeling of the SRFA system

The chemical equilibrium modeling started with the determination of the total number of carboxylic functional groups (Σ[RCOOH]_{tot}) in SRFA. The obtained value of 39.2 mM (equal to 12.4 meq g⁻¹ C) is slightly higher than the value previously reported by Ritchie and Perdue (2003) at 11.44 meq g⁻¹ C. This difference could be due to the short equilibration times used between each base addition by Ritchie and Perdue (2003), where a full titration from pH 3 to 11 were done in 25-35 minutes (allowing a drift of ca. 0.009 pH units/min), compared to ca. 5 days for a titration from pH 2 to 8 (allowing a pH drift of 0.0003 per minute) in paper V. Important to mention is that a reversibility experiment was conducted to make certain that the observed titration curve could be assigned solely to the protonation/deprotonation of carboxylic acids and not to any other irreversible process(es) (Fig. 26).

![Figure 26](image)

**Figure 26.** Z-plot of the two replicate titrations and the reversed titration showing reproducibility and reversibility. Figure modified from paper V.

Different models were tested using the three obtained pKₐ-values from the MCR-ALS analysis and optimizing the fourth pKₐ-value. The best fit was obtained by treating each total concentration of carboxylic acid sites as monodentate sites (HA, HB, HC, HD), keeping the total sum at 39.2 mM. The fit gave a concentration profile of [HA]_{tot} = 10.5 mM, [HB]_{tot} = 14.5 mM, [HC]_{tot} = 10.5 mM, and [HD]_{tot} = 3.1 mM with pKₐ = 0.98 (±0.04) and a U
value of 4.7. To visualize how the model fits the data, a Z-curve was calculated and plotted for both the experimental data and the model (Fig. 27). The Z-plot indicates a small systematic deviation above pH 4.5 and the buffer capacity seems to be too low at pH = 4.5-6 and too high at pH = 6.5-7.5 indicating an error in $pK_{a2}$ (3.66) and/or $pK_{a3}$ (5.66). Due to these deviations, a final model was constructed where all $pK_a$ values were co-varied and the concentrations were refined. A fifth $pK_a$ value at 9.52 was also introduced in the model to account for the present phenolic OH-groups at pH around 8 and above (for more in-depth explanation of this, see paper V). By introducing these changes to the model the best fit to the experimental data resulted in the following $pK_a$-values and corresponding total concentrations (mM): (1.09 ±0.05, 10.8); (3.75 ±0.10, 14.7); (5.30 ±0.16, 8.4); (7.22 ±0.16, 5.3) giving a U value of 0.7 (compared to the previous 4.7). The obtained model showed a very good fit to the data (Fig. 27) which was not so surprising considering relatively high number of adjustable parameters (7). The present model shows upon the complexity of the fulvic acid and simpler models (with fewer $pK_a$-values and no site heterogeneity) are in conflict with the present spectroscopic findings.

From these results it can be deduced that the SRFA material contains a relative high amount (ca. 28 %) of strong acidic groups ($pK_a$ 1.09). The results are in good agreement with previous studies showing an upper limit of these acids of 43 % with a $pK_a$ of about 1.67 in SRFA. (Leenheer et al., 1995a; 1995b). The same study suggested that polycarboxylic acids can

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**Figure 27.** Z-plot of the experimental data (circles) and the two different models. Figure modified from paper V.
account for the lower pKₐ and give rise to the high acidity of the SRFA, e.g., tetrahydrofuran tetracarboxylic acid have pKₐ-values of 0.95, 3.40, 5.55, and 6.42, showing clear similarities with the results in the present study. Furthermore, the average pKₐ value of 3.8 determined by Ritchie and Perdue (2003) is in good agreement with our second pKₐ value of 3.66-3.75. The fourth pKₐ value of 7.22 can seem a bit high for a carboxylic acid, but similar values can be found in the literature (e.g., butane-1,2,3,4-tetracarboxylic acid, pKₐ₄ = 7.16; Martell and Smith, 1982) showing that this is a reasonable result. Also, the IR data do not conclusively show that the highest pKₐ-value is originating from a carboxyl group but could be related to other functional groups of SRFA.
“If I have seen further it is by standing on ye shoulders of Giants.”

*Isaac Newton, 1676*
6. Summary

In this thesis the complexation of Al(III) by NOM have been in focus. The characterization of the Al(III)-NOM system indicated the formation organic Al(III) complexes that were stable enough to suppress the hydrolysis and polymerization of Al(III). Moreover, Al(III) forms mononuclear chelate complexes with carboxylic groups in NOM and according to the results in paper I and II, pH and metal concentration do not seem to have a large impact on the formed complex. However, the natural systems are a lot more complex than the reference system studied in paper I and II, so the results from the environmental system in paper II gives valuable information and indicates the presences of both organic Al(III) complexes and precipitated Al(III) phases (Al-hydroxide and/or Al-silicate). Because of the high stability of the Al(III)-NOM complexes, the question was raised if these complexes could be strong enough to induce dissolution of Al(III)-based minerals. Results from the dissolution experiment in paper III indicated a small but significant dissolution of the mineral that was related to the stability of the Al(III)-NOM complexes formed. In the same paper, IR spectroscopy data showed clear indications of inner-sphere Al(III)-NOM species at the gibbsite surface. However, the exact structure of the formed inner-sphere Al(III) complexes could not be determined by the IR measurements leading to paper IV where the ternary Ga(III)-NOM gibbsite system was investigated using EXAFS. This study showed that there is a possibility that Ga(III)-NOM adsorbs inner-spherically to gibbsite by forming ternary surface complexes with a type A configuration meaning that Ga(III)-NOM interacts with the surface through a Ga(III)-gibbsite bond. As a side-track to the studies of the Al(III)-NOM system, a new method to characterize NOM was developed. In paper V ATR-FTIR and MCR-ALS were utilized to get estimations of number of species and pKₐ values of the studied NOM. By using this information a chemical equilibrium model, describing the acid/base properties of the studied material with high accuracy and specificity, was constructed.

Even though a lot of progress have been done on the characterization of the complexes formed between Al(III) and NOM, the presented results raises new and interesting questions that I did not have the time to investigate further within this project. I have tried to summarize the most important aspects of this thesis and a few thoughts about important work for the future in three sections below.
6.1. Implications

6.1.1. The importance of NOM for metal speciation and mineral dissolution

To understand the mobility and bioavailability of metals in environment knowledge about the distribution between solid and dissolved phases in these systems is of great importance. The fact that NOM have proven to have an impact on the solubility of Al(III), indicates a possibility that it also effects the concentrations of potentially toxic soluble Al species. Furthermore, the interactions between NOM and metals will most likely lead to an effect on the geochemistry of other elements, such as phosphorus and arsenic that are known to be strongly adsorbed to e.g., Al(III)-hydroxide surfaces. The high affinity of NOM to mineral surfaces influences the weathering of these minerals (e.g., Furrer and Stumm, 1986; Hering and Stumm, 1991; Ludwig et al., 1996; Oliva et al., 1999) having an impact on the bioavailability of metal ions and also the pH-regulation and nutrient supply in natural systems. Furthermore, the formation of inner-sphere complexes between NOM and mineral surfaces has shown to increase the dissolution of minerals (Furrer and Stumm, 1986; Stumm, 1995) and therefore studies of mineral-NOM systems are of great importance. The results from paper III indicate a significant dissolution of gibbsite in presence of NOM but the cause of the dissolution could not be derived clearly from the obtained results. Furthermore, in paper IV the EXAFS results from the ternary Ga(III)-NOM-gibbsite system could be explained in two ways; either that Ga(III)-NOM type A ternary complexes where Ga(III) acts as a bridge between NOM and the gibbsite surface are formed, or that Ga(III) is present as two separate species; Ga(III)-NOM complexes in solution and a precipitated Ga(OH)₃(s) phase. If ternary metal surface complexes are formed they could influence the way NOM interacts with surfaces and these results are probably also relevant for other trivalent metals like Al(III) and Fe(III). Thus, although there were indications of inner-sphere Al(III)-NOM complexes at the surface of gibbsite, further studies are needed to fully understand how and under what conditions organic matter can promote or inhibit dissolution of minerals.

6.1.2. Using Ga(III) as a probe for other metals

In this thesis Ga(III) have been used to study the complexation between Ga(III) and NOM (paper I). The same study together with the results in paper II, show the similarities between Ga(III)-NOM and Al(III)-NOM complexes. Furthermore, the EXAFS results from the Ga(III)-NOM system are similar to that reported by Karlsson and Persson (2012) for Fe(III) complexed by NOM. This demonstrates that Ga(III) can be utilized as a probe to study other important metals like Fe, Al, and in some cases even Cu,
in environmental system. When studying systems including NOM it is important to not alter the NOM by treating it too harshly. This makes it difficult to clean the material from all the metals bound to it. Thus, due to the very low native concentration of Ga(III) in environmental samples, there is a possibility of using Ga(III) instead of e.g., Al(III) (that generally have a high native concentration) to study low concentration systems. In particular, Ga(III) can be utilized to study Al(III) systems where NOM and/or Al based minerals are present. The combined results presented in this thesis shows that Ga(III) can indeed be used as a probe in order to improve our knowledge about Me(III)-NOM interactions in general as well as Me(III)-NOM interactions with mineral surfaces.

6.1.3. A new method for the characterization of NOM

Developing new and more reliable methods for the characterization of organic matter are of great importance since NOM contributes to the acid/base balance of natural waters and is one of the major factors that determines the fate and behavior of many organic and inorganic compounds in the environment. A deeper understanding of the reactivity of different functional groups in NOM is necessary to accurately model proton and metal binding. The work in paper V demonstrates how information about functional groups and their pKₐ values, obtained from vibrational spectroscopy and multivariate data analysis, can be utilized in the construction of chemical equilibrium models for NOM. This opens up new possibilities to study the acid/base and metal complexing properties of NOM, in which the presence of carboxylic acid groups predominate, and to design equilibrium models more reliable than presented before.

6.2. The bigger picture

At the end of this thesis I would like to dedicate some space to the attempt of putting my research in a bigger perspective. When doing science, it is very easy to lose the reason why the things we do are of importance. Results are usually what we measure our success in, but sometime researchers forget about the real world applications. Without the need and support from society, the obtained results have little meaning. Therefore, in this chapter, I will discuss the importance of my findings using a wider perspective.

Natural organic matter exists almost everywhere in nature and increased knowledge about different chemical properties of organic materials can be of great importance in everyday life. It is hard to evaluate the impact NOM has on different environmental systems, and the gathered research in the field has indicated a diverse spectra of positive and negative effects. As NOM is known to bind metals in the environment, an increase in its mobility will
have an effect on the bioavailability of the metals. It have also been proven, in this thesis and in other articles, that NOM have an impact on the dissolution of different minerals. Furthermore, in the literature there is a number of studies showing the effect of NOM on the weathering of minerals in soils and waters. But what is the environmental impact of these organic matter-metal/mineral interactions? The presence of NOM in Al rich waters has been proven to have a positive effect on the toxicity of Al(III) towards fish. In contrast, the presence of Al(III)-NOM complexes can affect bacteria in a negative way since organic matter is an important source of carbon and with it Al(III) will enter the bacteria putting them to stress. Furthermore, increasing amounts of bioavailable Al(III) has shown to have a negative effect on the growth of plants. Hence, the raised question is not so easy to answer without looking at it from different perspectives. Foremost, there is a great need of more research to get a better understanding of the importance of organic matter for different environmental processes. The results presented in this thesis can give guidance for further studies of the metal-NOM system and I hope my work will guide other researchers towards acquiring an answer to the question “What is the environmental impact of metal-NOM complexation?”
7. Acknowledgements

First of all I would like to acknowledge the different sources of funding that have, in a fundamental way, made this work possible: the department of chemistry and the faculty of science and technology at Umeå University, Carl Trygger Foundation, Kempe Foundation, Max-lab, SSRL, SOLEIL, The Swedish Research Council, Formas (ForWater), Future Forest and SKB. Furthermore, the support from Knut and Alice Wallenberg Foundation, Kempe foundation, and Ångpanneföreningens forskningsstiftelse and Helge Ax:son Johnson are acknowledged for travel grants to conferences and trips to synchrotrons. Hjalmar Laudon and Peder Blomkvist are acknowledged for providing samples from the boreal Krycklan catchment. Ulf Skyllberg is acknowledged for providing us with the soil samples and the Ultra filtrated stream water sample. The staff at beamline I811 at MAX-Lab, beamline 4-1 at SSRL, and beamline LUCIA at SOLEIL are gratefully acknowledged for their help and advice.

My supervisor Torbjörn, thanks for giving me the opportunity to do this PhD. It has been an eventful, and sometimes really stressful, period in my life. I have learned so much from you and thanks for having the patience to deal with my countless mistakes and misunderstandings. Thanks for always being a support during my more stressful periods especially during the last months. Per, my second supervisor, thanks for taking me under your wings and guiding me through the world of IR spectroscopy and contributing with your expertise to my work. I’m truly grateful for the time we have worked together. Lars, we have not worked together so much, but thanks for all the work with the writing of this thesis. As a member of the old inorganic chemistry section you have always seemed interested in my work and supporting me during hard times, thank you for that!

Two of the first persons I met when I started my undergraduate studies 9 years ago at Umeå University were Thomas and Staffan. Thomas, thanks for all the help with the “everyday life” in the corridor. You always have an idea of how to solve practical and theoretical problems, thanks for taking the time to answer my more or less relevant questions. Staffan, you are truly a source of inspiration. As a person with seemingly endless amount of knowledge, experience, and kindness you have made my time at Umeå University a lot more fun and interesting. I also would like to thank you for all the help with paper V, without you the paper would have been impossible to write.

I also would like to take the opportunity to thank Madeleine for always being there when I needed it the most. Thanks for the support and for taking the time to help me with everything from finding books in the library to helping me with thermodynamic calculations. You are amazing! I would also
like to thank Andras for all the help with IR and MCR. You are a great teacher and I have you to thank for understanding MCR and how to apply it to my research. Furthermore, you have been an amazing friend during my time in the corridor. Janice, I don’t know where to start, thank you for everything! You are an incredibly kind and wonderful person as well as a talented researcher. You have helped me with more than you know and I missed you a lot when you moved.

Through the years I have had the opportunity get to know a lot of people. Some are still here but many have come and left during the years. To all of you, without naming anyone, and hence not forgetting anyone, thanks for all the help, all the discussions, all the laughs and all the “fikas”. Without you the time as a PhD would be a lot less satisfying. I would also like to thank all my friends outside of work for being there when I needed to get a different perspective or just have a break from everything. I would also like to thank my family for always supporting my choices in life and for being there in all situations. Finally, Gustav, I love you and without you this would have been impossible!
8. References


Bethke C. M.  **2002.** The Geochemist’s Workbench. University of Illinois, Champaign, IL.


