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

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ABSTRACT

Interactions between metals and natural organic matter (NOM) are of great environmental importance and one of the key factors influencing hydrolysis, solubility, and speciation of the metals. However, studying geochemically relevant metals like Al, Fe, and Cu is sometimes associated with analytical problems; for example Fe and Cu are both redox active. Gallium (Ga) is a non-redox active metal that usually occurs at very low concentrations in environmental samples and therefore a wide concentration range of Me(III)-NOM species can be explored by adding Ga(III) to such samples. This makes Ga(III) a good probe and analogue for other metal ions, in particular Al. In addition, due to the increased usage of Ga in society, a better understanding of how Ga interacts with NOM is of importance but such studies are scarce. In this work, Ga(III) interactions with two different organic materials (Suwannee River natural organic matter and Suwannee River fulvic acid) were studied using infrared (IR) and extended X-ray absorption fine structure (EXAFS) spectroscopy in a large experimental range (101–84,076 $\mu\text{g Ga g}^{-1}$ dry weight; pH 3–8). Our IR spectroscopic results showed that Ga(III) is bonded mainly to carboxylic functional groups and suggested that only a fraction of the total number of carboxylic sites in the samples was actively involved in the bonding. Modeling of the EXAFS data revealed that Ga(III) formed mononuclear chelate complexes with NOM that strongly suppressed the hydrolysis and polymerization of Ga(III). At low Ga(III) concentrations (1675–16,649 $\mu\text{g g}^{-1}$) organic complexes, consisting of 1 to 3 chelate ring structures, were the dominating species in the entire pH range while at higher concentrations (67,673–84,076 $\mu\text{g g}^{-1}$, pH 3.0–7.0) we detected mixtures of mononuclear organic Ga(III) complexes, Ga(III) (hydr)oxide, and free Ga(III) (here defined as the

hydrated Ga(III) ion and its soluble hydrolysis products). Moreover, the EXAFS results showed significantly higher contribution from second-shell C atoms (9–11) for the Ga(III)-organic complexes at the lowest concentration (101–125 $\mu\text{g g}^{-1}$, pH 4.9–5.1), indicating formation of cage-like structures similar to Ga(III)-EDTA. Our combined results showed that Ga(III)-NOM interactions can be of importance for the solubility and speciation of Ga in environmental systems. Furthermore, the similarities between Ga(III) and previous Fe(III) results demonstrates that Ga(III) can be utilized as a probe for Me(III)-NOM interactions over an extended experimental range (e.g., pH and metal concentration) and thereby improve our knowledge about these interactions in general.

1. Introduction

The fate and behavior of many metals in the environment are strongly influenced by interactions with natural organic matter (NOM). These interactions influence hydrolysis, solubility and thus the speciation of the metals (e.g., Elkins and Nelson, 2002; Xu et al., 2010; Karlsson and Persson, 2012), which in turn affects their mobility, bioavailability and potential toxicity. NOM is formed primarily through degradation of organic material from plants and animals in the environment and consists of a mixture of low molecular weight substances and macromolecules produced by hydrolytic and oxidative decomposition of complex organic compounds such as proteins, carbohydrates, lignins, lipids, and fats (e.g., Ogner and Schnitzer, 1971; Rouhi, 2000). It is abundant in most natural systems such as soils and surface waters and contributes greatly to the accessible terrestrial and aquatic carbon in the environment. Generally, NOM has a high capacity to complex metal ions via the coordination to a variety of functional groups (e.g., carboxyls,

phenols, amine, thiols) present in this material (Essington, 2004). Gallium (Ga) is known to form stable complexes with organic functional groups (Clausén et al., 2003; Clausén et al., 2005) and interactions with NOM will probably have a significant influence on the speciation of Ga in environmental systems. Due to the toxicity of Ga (Lin and Hwang, 1998; Yang and Chen, 2003) the increased usage in society, e.g., in the electronic industry (Yu and Liao, 2011) and cancer treatment (Collery et al., 2002), could potentially cause environmental problems and therefore it is important to increase our understanding of how Ga interacts with NOM, but studies of these interactions are scarce.

In order to get detailed molecular-level information about the interactions between metals and organic matter in environmental systems, different spectroscopic techniques can be applied. Synchrotron-based extended X-ray absorption fine structure (EXAFS) spectroscopy and X-ray absorption near edge structure (XANES) spectroscopy as well as infrared (IR) spectroscopy have been shown to provide useful molecular-scale information on metal-NOM interactions (e.g., Elkins and Nelson, 2002; Duckworth et al., 2009; Xu et al., 2010; Karlsson and Persson, 2012). These techniques are complementary and make it possible to probe both the metal (EXAFS/XANES) and the functional groups (IR) involved in the interactions. However, in some cases, the properties of the studied systems limit the applicability of the techniques. For example, the low K-edge energy (1.5596 keV) of aluminum (Al) results in strong background absorption and, as a consequence, only highly concentrated samples can be analyzed. In the case of the redox-active metal iron (Fe), the intense X-ray beam can induce redox transformations during the measurements. Furthermore Al and Fe occur at relatively high concentrations in natural samples making it difficult to determine the coordination of complexes formed at

low concentrations without somehow pre-washing NOM with the risk of further altering the material. In this respect, Ga(III) can be used as a suitable probe and analogue for metal ions with high charge-to-radius ratios. Gallium has a high K-edge energy (10.367 keV) making it readily accessible with EXAFS; it is not redox active and usually occurs at very low concentrations in environmental samples. Furthermore, since the hydrolysis and coordination chemistry of Fe(III), Al(III) and Ga(III) are very similar (Baes and Mesmer, 1976; Bénézech et al., 1997; Clausén et al., 2003; Clausén et al., 2005; Persson and Axe, 2005), studies of Ga(III)-NOM systems may be used to increase our understanding of Fe(III)/Al(III)-NOM interactions. To our knowledge, there are no previous EXAFS or XANES studies on Al(III)- or Ga(III)-NOM interactions but some infrared spectroscopic results from Al(III)-fulvic acid systems have been published (e.g., Patterson et al., 1992; Elkins and Nelson, 2002). In these studies, salicylic- and phthalic-acid-like sites were suggested as likely coordination sites for Al(III). Interactions between Fe(III) and NOM have been studied using both EXAFS and IR spectroscopy and the results showed that the interactions are mainly due to carboxylic functional groups in the pH range 3–7 (Karlsson and Persson, 2010; Sharma et al., 2010; Karlsson and Persson, 2012). However, these studies were performed at rather high metal concentrations ($>90 \mu\text{mol Fe g}^{-1}$ organic matter) and problems with beam-induced reduction during EXAFS measurements were reported at low Fe concentrations (Karlsson and Persson, 2012).

In this work we have used infrared and EXAFS spectroscopy to study Ga(III) interactions with aquatic NOM, from the Suwannee River, at varying metal concentrations and pH values. The main aims were to determine the structure of the Ga(III)-NOM complexes formed, follow the hydrolysis and polymerization of Ga(III) in

this system, and evaluate if Ga(III) can be used as a probe to extend our knowledge about metal-NOM interactions in general. Knowledge about these interactions is needed to better understand the behavior metals in soils and waters.

2. Material and methods

2.1. Samples and sample preparation

Suwannee River Natural Organic Matter (SRN; 1R101N) and Suwannee River Fulvic Acid (SRFA; 1S101F) were purchased from the International Humic Substances Society (IHSS). Selected chemical data for these materials are presented in Table S1, Supplementary data. The Suwannee River is classified as a blackwater river that receives water from the Okefenokee Swamp. The area consists of extensive peat deposits but the majority of the dissolved organic carbon (DOC) in the Suwannee River is believed to come from decomposing vegetation. The DOC content of the river ranges from 25 to 75 mg L⁻¹, which lowers the pH to less than 4.0 (Averett et al., 1994). The SRN material was collected through reverse osmosis (Serkiz and Perdue, 1990), and the isolated freeze-dried organic matter contained hydrophobic and hydrophilic acids and other soluble organic molecules present in the river water, with no fractionation dependent on size or structure of the molecules present. To isolate the SRFA material, the XAD-8 resin adsorption method was used. This method fractionates the DOC into hydrophobic and hydrophilic fractions through preferential adsorption of the hydrophobic fraction on the XAD-8 resin. The hydrophobic fraction is then eluted from the resin by the addition of aqueous NaOH. Small organic acids (MW<200 Da) are eluted in one fraction and what is considered aquatic humus in another fraction, resulting in a size fractionation of the

material. The humic acid is then removed from the aquatic humus fraction by precipitation at low pH. Finally, a desalting step involving cation exchange is used to obtain the fulvic acid. Thus, the freeze-dried fulvic acid used (SRFA) contained only hydrophobic organic acids with molecular weights larger than 200 Da (Thurman and Malcolm, 1981).

2.1.1. Infrared spectroscopy

Samples for infrared analysis were prepared by adding 28 mg of the SRN and 27 mg of the SRFA material (dry weight) into 1.5 mL Eppendorf tubes followed by addition of GaCl_3 (anhydrous beads 99.99%, Sigma-Aldrich) dissolved in Milli-Q water (pH 1.1). The suspensions with Ga and organic matter were allowed to equilibrate for 10 minutes before pH was adjusted to 3.1–7.9 with NaOH (2 M), and the ionic strength to 0.270 M by addition of NaCl (0.6 M). This resulted in Ga(III) concentrations of 23,451–67,673 $\mu\text{g g}^{-1}$ and 84,076 $\mu\text{g g}^{-1}$ for SRN and SRFA, respectively. All concentrations were on a dry mass basis and corresponded to a molar ratio of 0.070–0.202 mol Ga(III) per mol of carboxylic functional groups (R-COOH) for SRN and 0.202 mol Ga(III) per mol R-COOH for SRFA. The total volume of each sample was adjusted to 0.5 mL by addition of Milli-Q water followed by equilibration on a rotating mixer for 24–72 h. The samples were stored in a refrigerator at 8°C until the infrared analysis, and the pH was measured using a pH combination electrode (InLab®Micro, Mettler Toledo) and a pH meter (SevenMulti modular meter system, Mettler Toledo) prior to the infrared analysis. Reference samples were prepared in the same way but without addition of GaCl_3 in the pH range 3.1–8.1 for SRN and 3.0–6.9 for SRFA and with a total volume of 0.3 mL. For

the deuterium samples (IR_SRN_16–21; Table S2, Supplementary data), the SRN material was washed with D₂O (99.5%, purchased from Cambridge Isotope Labs) once and then freeze-dried. The NaCl, as well as the GaCl₃, was dried and dissolved in D₂O before use. NaOD was purchased from Cambridge Isotope Labs (99.5%, 40% in D₂O) and added to the samples to get the desired pD values. pH was measured using a pH combination electrode (as above) and a correction factor of +0.44 was used to calculate pD (Mikkelsen and Nielsen, 1960). Data for the IR SRN samples, for which spectra are shown in 3.1, are presented in Table 1 and data for the remaining IR samples are presented in Table S2, Supplementary data.

Table 1

2.1.2. EXAFS spectroscopy

The EXAFS samples were prepared by adding 18–46 mg of SRN or SRFA, based on dry weight, to 1.5 mL Eppendorf tubes. GaCl₃ dissolved in Milli-Q water (pH 1.1) were added to the samples resulting in Ga(III) concentrations in the range 101–67,673 $\mu\text{g g}^{-1}$ for the SRN samples and 125–84,076 $\mu\text{g g}^{-1}$ for SRFA. All concentrations were on a dry mass basis and correspond to molar ratios of 0.0003 to 0.202 mol Ga(III) per mol R-COOH. The suspensions with Ga and organic matter were equilibrated for 10 minutes and then pH was adjusted to between 3.0 and 6.9 for SRN and to between 2.9 and 7.0 for SRFA by addition of NaOH (2 M). The ionic strength was adjusted to 0.270 M by addition of NaCl (0.6 M) and the total volume to 0.25 or 0.5 mL by addition of Milli-Q water. Subsequently, the samples were equilibrated on a rotating mixer for 24–72 h.

Finally, pH was measured using a pH combination electrode (as above), and the samples were stored for 5–12 days in a refrigerator at 8°C prior to EXAFS analysis. At the beamline, the samples were transferred to a Teflon holder and sealed with Kapton tape (CHR-Furon). Characteristics of the EXAFS samples are presented in Table 2.

Table 2

An aqueous paste of amorphous $\text{Ga}(\text{OH})_{3(s)}$ (Persson et al., 2006) and aqueous solutions of Ga(III)-EDTA $[\text{Ga}(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)^-]$ (Norén and Persson, 2010), Ga(III)-Oxalate $[\text{Ga}(\text{C}_2\text{O}_4)_3^{3-}]$ (Clausén et al., 2003), Ga(III)-Citrate $[\text{Ga}(\text{C}_6\text{H}_5\text{O}_7)_2^{3-}]$ (Clausén et al., 2005) and Ga(III)-Nitrate $[\text{Ga}(\text{NO}_3)_3]$ (Clausén et al., 2002) were selected as EXAFS reference samples for comparison with the Ga(III)-NOM samples.

2.2. Data collection and treatment

2.2.1. Infrared spectroscopy

The infrared spectra were collected using a Bruker Vertex 80v FTIR spectrometer equipped with a RT-DLaTGS (deuterated triglycine sulfate) detector and a single-reflection, 45°, ZnSe ATR crystal (FastIR, Harrick Scientific). Each sample was scanned 512 times in the range 520–7500 cm^{-1} at a resolution of 4 cm^{-1} . The samples were added directly onto the ZnSe crystal and analyzed at room temperature. During data collection the sample compartment was kept under vacuum, but a vacuum-tight lid protected the sample. To extract the spectra of the NOM (SRN and SRFA) samples, the absorption of the empty cell was collected as the background and a spectrum of the ionic medium was

collected in order to remove this contribution from the sample spectra. The resulting spectra show the IR spectral features of the organic matter with and without addition of Ga(III). To isolate the IR spectral characteristics of the Ga(III)-NOM complexes, difference spectra were calculated by subtracting the spectra of protonated and non-protonated NOM from NOM spectra with added Ga(III). The isolation of the non-protonated NOM was done by subtracting a spectra where the NOM was fully protonated (e.g., IR_SRN1; pH 3.1) from a spectra of the fully non-protonated NOM (e.g., IR_SRN6; pH 8.1) focusing on the protonated carboxylic stretching mode at ca. 1700 cm^{-1} . The isolation of the protonated NOM was done in the same way focusing on the symmetric carboxylic stretching mode at ca. 1400 cm^{-1} . The data treatment (as well as controlling the spectrometer) was accomplished by the OPUS software (Bruker).

2.2.2. EXAFS spectroscopy

The Ga K-edge (10.367 keV) EXAFS spectra were collected at the multi-pole wiggler beamline 4-1 at Stanford Synchrotron Radiation Lightsource (SSRL), Stanford University, USA. SSRL was operated at 3.0 GeV ring energy and at currents around 350 mA in top-up mode. The detector system included three consecutive ion chambers that were filled with N₂ to monitor the transmitted beam and an Ar-filled Lytle detector for fluorescence measurements. The beamline was equipped with a Si [2 2 0] double-crystal monochromator, and to eliminate higher order harmonics it was detuned by 30%. The spectra of the SRN and SRFA samples were collected at room temperature in fluorescence mode using the Lytle detector. Samples were positioned at a 45° angle to the beam and, to reduce unwanted fluorescence and scattering contributions to the signal, a

Zn 3- μ x filter and Soller slits were used. The spectra (I_t/I_0 versus energy) were collected in the energy range from 227 eV before the edge to 880 eV after the edge in a step-scan mode. The scan step-sizes were 10 eV before the edge, 0.35 eV over the edge, and 0.05 $\text{\AA}^{-1}$ in the EXAFS region. Internal calibration was performed by simultaneously measuring the spectra of a Ga 3- μ x filter (gallium(III) oxide; K-edge set to 10.3728 keV) in transmission mode throughout the duration of all scans. The spectrum for each sample represents the average of 1–39 scans. Spectra of SRN1-7 and SRFA1-3 and 5 are from one scan only; for the rest of the samples all individual scans were checked for possible beam damage, but no beam-induced changes were detected.

The EXAFS data treatment was performed using SIXPack v1.01 (Webb, 2005). To normalize the data over the edge, a linear pre-edge function and a second-order polynomial post-edge function was subtracted from each averaged spectrum. Above the absorption edge a cubic spline was used to remove the background. The normalized and background subtracted spectra were k^3 -weighted to enhance the higher k -values and Fourier transformed over the k -interval from ca. 3.0 to 10.3–15.0 $\text{\AA}^{-1}$ (depending on data quality), using a Kaiser-Bessel window function. The spectra were quantitatively evaluated in R -space 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). $\text{Ga}(\text{C}_2\text{O}_4)_3^{3-}$ and $\text{GaO}(\text{OH})$ (Clausén et al., 2003; Li et al., 2003) were used as input structures in the FEFF calculations. The EXAFS amplitudes are proportional to the coordination number (CN) and the amplitude reduction factor, S_0^2 , hence reference samples with known structures were used to determine S_0^2 . For all the SRN and SRFA samples the EXAFS spectrum of an acidic $\text{Ga}(\text{NO}_3)_3$ solution, where the

CN for Ga-O in $\text{Ga}(\text{H}_2\text{O})_6^{3+}$ is known to be 6 (Lindqvist-Reis et al., 1998), was used. By fitting this spectrum with a fixed CN of 6.0 in the first coordination shell, a S_0^2 value of 1.21 ± 0.09 was obtained. The threshold energy (ΔE_0) was varied but correlated to be the same for all shells. Whenever possible, the quantitative EXAFS modeling was further constrained by correlating CNs and fixing Debye-Waller factors (σ^2). The scattering paths used to model organic Ga structures were those from a mononuclear $\text{Ga}(\text{C}_2\text{O}_4)_3^{3-}$ complex (Fig. 1), a choice motivated by the IR spectroscopic results (see below) indicating Ga(III) coordination to carboxylate groups of the SRN and SRFA materials. The Debye-Waller factors of the Ga-C, Ga-O-C, and Ga-C-O scattering paths (Fig. 1) were determined via fits of SRN and SRFA spectra (SRN9 and SRFA7; Table 2) that showed no indications of Ga-Ga contributions in higher coordination shells and were prepared at pH 4.9 and 4.7, respectively, where contribution from free Ga(III) (here defined as the hydrated Ga(III) ion and its soluble hydrolysis products) was considered to be small. These Debye-Waller factors were used as fixed parameters during the refinement of the remaining SRN and SRFA samples (Table 3). The Debye-Waller factors of the Ga-Ga scattering paths were obtained by fitting the $\text{Ga}(\text{OH})_{3(s)}$ spectrum with fixed CN:s for the Ga-Ga paths, according to data presented by Pokrovski et al. (2002) for α -GaOOH, and used as fixed parameters for the SRN and SRFA samples. The idea behind these relatively constrained fits was to facilitate the comparison between samples and to reveal trends in the data depending on pH and Ga(III) concentration. As a result of these constraints, the number of free variables in the fitting procedure (4–11) never exceeded the number of independent points (12–20) as calculated by the Nyquist theorem ($N_{\text{ind}} = (2 \times \Delta k \times \Delta R) / \pi$, where Δk is the k -range of the EXAFS spectrum and ΔR is the R-range of the FT

considered) and the degree of freedom was never below 4. Further details of the fitting procedure are found in Table 3.

In addition to the quantitative fitting procedure described above, a qualitative interpretation of the nature of backscattering of atoms in higher coordination shells was carried out using the wavelet transform (WT) method as implemented in the Igor Pro script developed by Funke et al. (2005). The WT results are typically visualized as a contour plots in three dimensions: the wave vector (k), the interatomic distance uncorrected for phase shifts (R), and the WT modulus. The different backscattering atoms appear as ridges with high intensity and since heavy elements show contributions at higher k -values compared to lighter elements the locations of these ridges help to differentiate between light and heavy backscattering atoms. All EXAFS spectra were analyzed using the Morlet-wavelet function and different values of η and σ were used depending on the resolution of the wavelet plot. Since the resolution of the plots critically depends on the selection of these Morlet parameters (Funke et al., 2005), different values were tested in order to optimize the resolution in both k and R space for our samples.

Fig. 1.

3. Results and discussion

3.1. Infrared spectroscopy

IR spectroscopic data collected for both the Ga(III)-SRN and Ga(III)-SRFA systems showed that they behaved in a very similar fashion. Hence, the discussion will be focused on the Ga(III)-SRN results, and the fulvic acid results will primarily be presented as

Supplementary data (Fig. S1). Fig. 2 shows IR spectra of SRN collected in the absence and presence of Ga(III) as a function of pH, and the region displayed is dominated by bands originating from carbohydrates as well as carboxylic functional groups, as discussed in previous works (Persson and Axe, 2005; Karlsson and Persson, 2012). Furthermore, protonation/deprotonation reactions of these carboxylic groups are the primary cause of the pH-dependent IR spectroscopic features of SRN (Karlsson and Persson, 2012). These pH-induced spectroscopic changes were manifested as an increase of the symmetric and asymmetric carboxylate stretching frequencies at ca. 1400 and 1600 cm^{-1} , respectively, with increasing pH whereas the carbonyl and the C-O-H modes of the carboxylic acid decreased concomitantly (Fig. 2). In the presence of Ga(III), two key observations were the loss of carbonyl intensity relative to the asymmetric carboxyl band at low pH as well as a shift of the latter to a higher frequency (Fig. 2). These observations suggested that Ga(III) outcompeted some of the carboxylic protons and thus become coordinated directly to carboxylate groups. We detected no major involvement from other functional groups such as hydroxyls under the current experimental conditions; note that there are 2.5 and 3.9 times more carboxyl groups than phenols in SRN and SRFA, respectively (Table S1, Supplementary data). However, we cannot rule out coordination via other functional groups, especially at lower concentrations, as the detection limits of IR spectroscopy may prevent observation of these interactions.

Fig. 2.

In order to isolate the IR spectral characteristics of the Ga(III)-SRN complexes, difference spectra were calculated by subtracting the spectra of protonated and non-protonated SRN from the spectra of Ga(III)-SRN as explained in the experimental section (Fig. 3). The difference spectra displayed symmetric and asymmetric carboxylate stretching frequencies at 1432 and 1615 cm^{-1} , respectively, and these were substantially different from the two groups of SRN carboxylate frequencies previously identified in the absence of metal ions at 1394 and 1566 cm^{-1} and 1390 and 1590 cm^{-1} (Karlsson and Persson, 2012). The shift of the asymmetric stretching vibration to higher wavenumbers in the presence of Ga(III) was in accordance with previous studies on Ga(III)-carboxylate complexes and indicated inner-sphere coordination between Ga(III) and the carboxylate groups of SRN (Clausén et al., 2003; Clausén et al., 2005). As the strong bending mode of water at ca. 1640 cm^{-1} may cause problems in properly isolating the asymmetric carboxylate stretching band, we also conducted an experiment in D_2O . In this solvent there is no overlap between these bands and the results obtained corroborated the existence of a Ga(III)-carboxylate interaction in SRN characterized by an asymmetric carboxylate stretching vibration around 1610–1620 cm^{-1} (Fig. S2, Supplementary data). Furthermore, the difference spectra showed that the concentration of SRN Ga(III)-carboxylate complexes decreased with increasing pH, and that these changes were concomitant with an increase in the carbohydrate bands (Figs. 2 and 3). These trends were in accordance with previous Fe(III)-SRN results that showed that mononuclear Fe(III)-carboxylate complexes were consumed and converted into ferrihydrite by raising the pH (Karlsson and Persson, 2012). The increase of the carbohydrate bands indicated that such molecules could play a role in the formation and stabilization of the presumably

small ferrihydrite particles. By analogy, the results presented in Figs. 2 and 3 suggest that an increase in pH causes a conversion of mononuclear Ga(III)-SRN complexes into $\text{Ga}(\text{OH})_{3(s)}$, where the latter species is somehow interacting with carbohydrates. Similar observations were made for the Ga(III)-SRFA system (Fig. S1, Supplementary data), although in this case the pH-dependent changes of the carbohydrate bands were not as pronounced.

Fig. 3.

If we assume that the carboxylate peak areas of the difference spectra (Fig. 3) are representative of the amount of Ga(III)-SRN complexes, then these can be used to estimate the fraction of carboxylate groups involved in the interaction with Ga(III) by calculating the ratios between these areas and the total area of the carboxyl bands (Fig. 4). The calculated ratios showed that Ga(III)-SRN complexes were favored at low pH, as already discussed, and at a total Ga(III) to R-COOH molar ratio of 0.202, a maximum of ca. 20% of the carboxylate groups were indeed coordinated to Ga(III) (Fig. 4). Accordingly, the 1:1 ratio between Ga(III) and coordinated carboxylate groups together with previous observations that metal ions coordinate to NOM as chelate structures involving several functional groups (Manceau and Matynia, 2010; Karlsson and Persson, 2012) implies that at the 0.202 Ga(III) to R-COOH molar ratio, a substantial fraction of Ga(III) must not be coordinated to carboxyl groups, as will be discussed in the EXAFS section. Interestingly, the results indicated that fulvic acid has an even smaller fraction of carboxyl groups available for Ga(III) coordination (Fig. 4). This difference could be due

to the methods used to isolate the two materials (Thurman and Malcolm, 1981; Serkiz and Perdue, 1990). In the SRFA material, small organic acids (<200 Da) are removed during isolation while they are included in the SRN material. Thus, the small organic acids present in the SRN material could make more carboxylic sites available for binding.

Fig. 4.

3.2. EXAFS spectroscopy

3.2.1. Wavelet transform analysis

The results from the WT analysis for the SRN and SRFA samples showed similar first-shell contributions with a backscattering maximum around $6 \text{ \AA}^{-1}$, in accordance with the Ga-O scattering of the $\text{Ga}(\text{C}_2\text{O}_4)_3^{3-}$ reference sample (Fig. S3, Supplementary data). The WT results of the higher coordination shells in SRN and SRFA displayed similar features (Fig. 5 and Fig. S4, Supplementary data). At the highest Ga(III) concentration (0.202 mol Ga/mol R-COOH) and pH values of 4.8–7.0, the high-resolution WT showed a distinct feature at ca. $7\text{--}8 \text{ \AA}^{-1}$ and $2.7 \text{ \AA}$ corresponding to the second peak in the Fourier transform (FT) (Fig. 5c and d; Fig. S4h, Supplementary data). This feature was also present in the $\text{Ga}(\text{OH})_{3(s)}$ reference sample (Fig. 5a) and originates from Ga-Ga backscattering. At the same Ga(III) concentration but lower pH values (3.0–4.2), no signals were detected from Ga in the second shell probably due to a substantial amount of free Ga(III) in these samples (Fig. 5b and Fig. S4f, Supplementary data).

At lower concentrations (0.0003–0.04 mol Ga/mol R-COOH), no contribution from Ga was detected in the investigated pH range (2.9–6.9). Instead, these samples displayed

strong FT features at distances of about 2.0–2.5 Å and 3.0–3.8 Å that appeared at lower energies (2–6 Å⁻¹) in the WT plots, which indicated backscattering from lighter atoms (Fig. 5f, g and h and Fig. S4j, l and n, Supplementary data). These features were in fair agreement with those of single and multiple backscattering from C/O in the second and third coordination shells of Ga(C₂O₄)₃³⁻, Ga(C₆H₅O₇)₂³⁻, and Ga(C₁₀H₁₂N₂O₈)⁻ (Fig. 5e and Fig. S4c and d, Supplementary data), suggesting that mononuclear organic Ga(III) complexes were the predominating species in the SRN and SRFA samples under these conditions. These observations divided the samples into two main categories depending on Ga(III) concentration and pH, one with only light atoms in higher coordination shells and the other with a mixture of light and Ga(III) atoms.

Fig. 5.

3.2.2. Quantitative EXAFS analysis

The quantitative EXAFS fits showed that Ga(III) in both the SRN and SRFA systems was coordinated to O/N atoms at a first-shell distance of about 1.96 Å. This was in agreement with 6-coordinated complexes, presumably in an approximate octahedral configuration (Lindqvist-Reis et al., 1998; Table 3 and Table S4, Supplementary data). In the samples with the highest Ga(III) concentrations (0.202 mol Ga/mol R-COOH), a slight decrease in the distance of the Ga-O scattering path with increasing pH was observed, from 1.96 Å at pH 3.0–3.1 to 1.93–1.94 Å at pH 6.8–7.0 (Table 3, SRN1–5 and SRFA1–3). This could indicate a partial shift from a 6-coordinated structure to a 4-coordinated Ga(OH)₄⁻ structure, which is supported by the distribution diagram (Fig. 6). However, the XANES

spectra show similar edge positions in the whole pH range for these samples indicating that 6-coordination dominates (Figs. S5 and S6, Supplementary data).

Table 3

In accordance with the WT results, the samples with a Ga(III) to R-COOH ratio of 0.04 and below (21.5–0.27 mM Ga, pH 2.9–6.9; Table 2) were successfully modeled using 2nd and 3rd shell scattering paths from organic structures only (Table 3 and Figs. 1 and 7 and Fig. S7, Supplementary data). This should be compared to the distribution diagrams of Ga(III), which are dominated by amorphous $\text{Ga}(\text{OH})_{3(s)}$ from pH 3–3.5 to about 6–8.5, depending on total Ga(III) concentration (Fig. 6). Thus, the addition of organic matter suppresses the hydrolysis and polymerization of Ga(III) and this effect has been demonstrated for other metals ions, e.g., Fe(III) (Mikutta, 2011; Karlsson and Persson, 2012). Very recently the high stability of metal-NOM complexes has also been revealed by Fe isotope studies of organic-rich waters (Ilina et al., 2013). The obtained Ga-C, Ga-O-C, and Ga-C-O distances were in fair accordance with distances in $\text{Ga}(\text{C}_2\text{O}_4)_3^{3-}$ (Table 3 and Table S4, Supplementary data), indicating a chelate structure as described by Clausén et al. (2003, 2005) for oxalate, malonate, and citrate. Recent studies have shown that Fe and Cu 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). The observed ability of NOM to suppress the hydrolysis and polymerization of Ga(III) is also in accordance with formation of chelate ring structures. A comparison between stability constants ($\log K_1$; $[\text{ML}]/[\text{M}][\text{L}]$) for

Ga(III) complexes with O- and N-functional groups typical of natural organic matter, e.g., carboxylic acids (oxalic 7.06 (I=1.0 M; Perrin, 1979) and salicylic 14.5 (I=0.1 M; Martell and Smith, 1982)), phenols (catechol 18.9 (I=0.1 M; Perrin, 1979), and amines (glycine 9.33 (I=0.1 M; Perrin, 1979)), shows that Ga(III) also has a high affinity for catechol-like sites. Furthermore, the affinity for artificial chelating agents like EDTA is even higher than for catechol ($\log K_1$ 21.0 (I=0.1 M); Martell and Smith, 1982). Thus, especially at the lower concentrations involvement from other functional groups than carboxyls is a possibility and cannot be ruled out, but this cannot be ascertained by our spectroscopic data. Phosphoryl groups could theoretically also be of importance as shown for other metals (e.g., Cd; Boyanov et al., 2003). However, the phosphorus content in SRN and SRFA is too low for these groups to have any influence on the average coordination of Ga at the studied concentrations (Table S1, Supplementary data). The obtained Ga-C, Ga-O-C, and Ga-C-O distances in our samples could be averages of several distances originating from different functional groups, but it should be noted that the concentration of carboxylic groups in SRN and SRFA are substantially higher than the concentrations of these other groups (Table S1, Supplementary data).

Fig. 6.

Fig. 7.

At a molar ratio of 0.04 mol Ga/mol R-COOH, a decrease in the CN for C is observed for both SRN and SRFA with decreasing pH (Table 3, SRN6–8 and SRFA4–6).

This indicated a contribution from free Ga(III) in the samples with the lowest pH (pH 2.9–3.3) and that a greater proportion of the Ga(III) is bonded to NOM at higher pH. Although the CN for Ga-C at pH 5.0 to 6.9 is between 3.0 and 3.8, Ga(III) is most probably completely complexed by NOM since these samples are supersaturated with respect to precipitation of $\text{Ga}(\text{OH})_{3(s)}$ (Fig. 6). At lower molar ratio (0.005 mol Ga/mol R-COOH) and a pH around 5, the CN of the Ga-C scattering path is around 6–7 (Table 3), in accordance with $\text{Ga}(\text{C}_2\text{O}_4)_3^{3-}$, which has a structure with three 5-membered chelate rings (Fig. 1 and Table S4, Supplementary data). A visual comparison between the spectra in Fig. 7 (spectra **c** and **e**) also indicated a change towards a structure similar to $\text{Ga}(\text{C}_2\text{O}_4)_3^{3-}$ with decreasing molar ratio.

The lowest Ga(III) concentrations (0.0003–0.0012 mol Ga/mol R-COOH; pH 4.9–5.2) showed the most pronounced second and third coordination shell contributions and also a more distinct split at the top of the second oscillation in k -space (Fig. 5h; Fig. 7 spectra **f** and **g** and Fig. S4n, w, and x and Fig. S7 spectra **e** and **f**, Supplementary data). This was accompanied by an increase in the CN for the Ga-C scattering path from around 6–7 (at 0.005 mol Ga/mol R-COOH) to 7.2–10.9 and indicated that we have a different dominant complex in these samples or mixtures of complexes instead of the supposed domination of oxalate-like Ga(III) carboxylic complexes (Table 3, SRN9–11 and SRFA7–9). High CNs for second-shell C atoms 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). In EDTA and NOTA, Ga(III) is complexed by five and six 5-membered chelate rings, respectively, and surrounded by 10 to 12 C atoms (Wadas et al., 2010). For EDTA, which is the most commonly used chelating agent,

concentrations have been reported for natural waters ($0.52\text{--}1120\ \mu\text{g L}^{-1}$; Oviedo and Rodriguez, 2003) that potentially could complex all Ga(III) in the SRN and SRFA samples with the lowest concentrations ($1.7\text{--}7.2\ \mu\text{mol g}^{-1}$). Another possibility is that ligands capable of forming cage-like structures, as in Ga(III)-EDTA/NOTA, exist within the NOM material and we cannot discern whether the ligands forming these complexes with Ga(III) are of anthropogenic or natural origin.

It should be noted that the decrease in CN for Ga-C with increasing Ga(III) to R-COOH molar ratios, at pH around 5 (Table 3), could theoretically be a dilution effect. If there is an increase of free Ga(III) ions with increasing molar ratios (increase in total Ga(III) concentration), the CN of Ga-C would decrease even though the coordination of the organic Ga(III) complexes remain the same. However, the distribution diagrams show (Fig. 6) that all samples would be supersaturated with respect to formation of $\text{Ga}(\text{OH})_{3(s)}$ if they had been prepared in the absence of NOM. This suggest an actual change in coordination of the organic Ga(III) complexes and a probable explanation is that the ligands/functional groups involved in the complexation at the lowest Ga(III) to R-COOH ratios become saturated at increased Ga(III) concentration. Another interesting thing to note is that, at a molar ratio of $0.012\text{--}0.04$ (Me/R-COOH), the structures of the organic Ga(III) complexes formed are similar to structures obtained for Fe(III) and Cu(II) in association with SRN (Karlsson et al., 2006; Karlsson and Persson, 2012). This indicates that the structures obtained for the Ga(III)-SRN complexes at lower molar ratios ($0.0003\text{--}0.005$), having 6–11 C atoms in the second shell, also could exist for Fe and Cu. However, studies of Fe at these low concentrations are lacking, and would be difficult to

conduct for reasons discussed above. This clearly demonstrates the benefit of using Ga(III) as a probe for other metals.

For the samples with highest Ga(III) concentrations (0.202 mol Ga/mol R-COOH) and pH values of 4.8–7.0, features characteristic of both C/O/N and Ga backscattering appeared in the EXAFS spectra (Fig. 5c and d and Fig. 8; Fig. S4h, q and r and, Fig. S8, Supplementary data). Contributions from organic complexes were weaker than at lower Ga(III) concentrations, which are reflected by lower CN for the Ga-C scattering path (1.1–2.2) and that fewer scattering paths from the organic structures could be fitted to these spectra (Table 3). This is in line with the IR results indicating that only ca. 10–20% of the carboxylic sites are available for metal complexation (Fig. 4). Thus, at the highest concentration of Ga(III), the number of available sites (the same as the amount of added Ga(III)) are too few to form chelate complexes with all the added Ga(III) and the observed CN for Ga-C can be explained by a mixture of Ga(III)-NOM complexes and Ga(OH)_{3(s)} and probably some free Ga(III) at pH 4.8. The determined distances for Ga-C and Ga-C-O at pH 4.2–7.0 are in fair agreement with the Ga(C₂O₄)₃³⁻ reference (Table 3 and Table S4, Supplementary data). The contribution from Ga backscattering in the samples with highest Ga(III) concentrations (0.202 mol Ga/mol R-COOH) and pH values of 4.8–7.0 were fitted with two Ga-Ga scattering paths and the determined distances are in fair agreement with the amorphous Ga(OH)_{3(s)} reference (Table 3) and with data reported by Pokrovski et al. (2002) for α-GaOOH (Table S4, Supplementary data). Addition of a third Ga-Ga scattering path, as in Ga(OH)_{3(s)} and α-GaOOH, did not significantly improve the fit and an explanation for this could be the complexity of these samples with different Ga species possibly causing interferences

between scattering paths at similar distances. For all these samples except one (SRN3 at pH 4.8) a significant improvement was obtained by including the two Ga-Ga scattering paths in the fit (see Supplementary data, Table S3). For the samples at pH 6.2–7.0, the CNs for Ga-Ga show approximately the same relationship between the short and the long scattering paths (Table 3) indicating a similar structure of the $\text{Ga}(\text{OH})_{3(s)}$ phase. However, at pH 4.8 there is lower relative contribution from the short Ga path suggesting a difference in the structure and/or the particle size (Table 3, SRN3 and SRFA2). At pH 3.0–3.1 (0.202 mol Ga/mol R-COOH), the contributions from higher coordination shells were weak and these spectra were similar to the spectrum for $\text{Ga}(\text{NO}_3)_{3(aq)}$, i.e., free Ga(III) (Fig. 8f and g and Fig. S8d, Supplementary data). However, since the wavelet plots (Fig. 5b and Fig. S4p, Supplementary data) and the IR results indicated occurrence of organic Ga(III) complexes, an attempt was made to fit Ga-C and Ga-C-O in the second and third shells to these spectra (SRN1 and SRFA1). However, the contribution from these paths were statistically insignificant and resulted in unreasonable fit parameters; therefore only Ga-O in the first shell was used in the fit to these samples giving a distance of 1.96 Å (Table 3).

Fig. 8.

4. Conclusions and implications for other metals

The results discussed herein demonstrate similarities between the Ga(III)-NOM system investigated and other metals complexed by NOM, e.g., Fe(III) (Karlsson and Persson, 2012). As for Fe(III), we detected two predominant Ga(III) species: mononuclear Ga(III)-

NOM complexes and a $\text{Ga}(\text{OH})_{3(s)}$ phase and a complete domination of organically complexed Ga(III) at molar ratios of 0.04 Ga/R-COOH ($16,649 \mu\text{g Ga g}^{-1}$) and below. In addition, our combined EXAFS and IR results showed that NOM interacts with Ga(III) primarily through carboxylic groups, in a large concentration range, forming mononuclear chelate structures stable enough to suppress the hydrolysis and polymerization of the metal. This highlights the importance of these interactions for the solubility and speciation of Ga and other hydrolyzing metals (e.g., Fe, Al). Knowledge about the distribution between solid and dissolved phases is necessary for understanding the mobility and bioavailability of metals in environmental systems. We detected no significant differences between the two organic materials regarding the structure of the Ga(III)-NOM complexes, but the IR results indicated that the NOM material (SRN) had more active carboxylic sites for metal binding than the fulvic acid (SRFA), ca. 20% for SRN compared to ca. 10% for SRFA. This shows that the size and molecular structure of the organic material is probably very important for the complexation of metals. At the lowest concentration of Ga(III) ($101\text{--}125 \mu\text{g g}^{-1}$; $0.0003 \text{ mol Ga(III)/mol R-COOH}$), substantially lower than what has been analyzed for Fe(III)-NOM systems, the EXAFS results revealed a change in coordination of the Ga(III)-NOM complexes with significantly higher contribution from second-shell C atoms (9–11). This could indicate formation of cage-like structures as in Ga(III)-EDTA, but in order to describe these complexes in more detail additional studies at these low concentrations are needed. The spectroscopic results presented herein for Ga(III)-NOM interactions can be used to better understand the behavior of Ga in soils and surface waters via improvements of thermodynamic speciation models. Furthermore, the similar coordination chemistries of

Ga(III) and other metals in NOM, and the fact that Ga can be utilized to extend the experimental range and avoid analytical problems, clearly demonstrates that Ga(III) indeed can be used as a probe in order to improve our knowledge about Me(III)-NOM interactions in general. In particular, due to the difficulties of analyzing Al using synchrotron-based techniques and similar chemical behavior of Al(III) and Ga(III), using Ga(III) as a probe could be very useful in order to determine the coordination chemistry of Al(III) in environmental systems.

Acknowledgements

Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource, a Directorate of SLAC National Accelerator Laboratory and an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Stanford University. The SSRL Structural Molecular Biology Program is supported by the DOE Office of Biological and Environmental Research, and by the National Institutes of Health, National Institute of General Medical Sciences (including P41GM103393). The contents of this publication are solely the responsibility of the authors and do not necessarily represent the official views of NIGMS, NCRR, or NIH. Matthew Latimer and the rest of the staff at beamline 4-1 are gratefully acknowledged for their help and advice. We also thank Anneli Sundman from the Department of Chemistry, Umeå University, for help with the EXAFS data collection. The infrared spectroscopy measurements were conducted at the Vibrational Spectroscopy Platform at Umeå University. We also thank three anonymous reviewers and the associate editor, Gleb Pokrovski, for constructive

suggestions which substantially improved this manuscript. The Knut and Alice Wallenberg foundation is acknowledged for financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at

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Figure captions

Fig. 1. A mononuclear $\text{Ga}(\text{C}_2\text{O}_4)_3^{3-}$ complex with three five-membered chelate rings and indicated interatomic distances from Clausén et al. (2003). The single scattering paths (Ga-O and Ga-C) used to model the organic structures in the Ga(III)-NOM samples are indicated with dashed lines and the multiple scattering paths (Ga-O-C and Ga-C-O) with dotted lines.

Fig. 2. Infrared spectra illustrating the differences between the Ga(III)-SRN system and the reference SRN system in the pH range 3–8 (the two groups of spectra are offset vertically for clarity). Spectra of the Ga(III)-SRN samples, IR_SRN7–12, (top) and spectra of the reference samples, IR_SRN1–6, (bottom) at pH 7.9 (top)/8.1 (bottom) (orange lines), 6.7/6.7 (black), 5.8/5.9 (purple), 4.7/5.1 (green), 3.8/4.1 (red), and 3.2/3.1 (blue). The arrows shows if the absorbance of the IR peaks increase ($\uparrow$) or decrease ($\downarrow$) when pH increases. The two vertical lines indicate the start- (left line) and end-position (right line) of the asymmetric carboxylate peak in the reference SRN system when going from low to high pH.

Fig. 3. Difference spectra showing the contribution from the Ga(III)-SRN complex in the carboxylate region, isolated by subtracting the spectra of protonated and non-protonated SRN from the spectra of Ga(III)-SRN at pH 3.2 (IR_SRN7), pH 3.8 (IR_SRN8), pH 4.7 (IR_SRN9), pH 5.8 (IR_SRN10), pH 6.7 (IR_SRN11), and pH 7.9 (IR_SRN12) (the spectra are offset for clarity). Vertical dashed lines mark the symmetric and asymmetric carboxylate stretching frequencies at 1432 and 1615 cm^{-1} , respectively.

Fig. 4. Fraction of coordinated carboxyl groups in SRN and SRFA as a function of pH and at different Ga(III):R-COOH ratios: 0.202 (IR_SRN7-12, IR_SRN22-26, and IR_SRFA1-3) and 0.17–0.07 (IR_SRN13-15). Data for the IR_SRN22-26, IR_SRN13-15, and IR_SRFA1-3 samples are found in Table S2 (Supplementary data).

Fig. 5. High resolution WT modulus displaying the second and third coordination shells (MORLET parameters, $\eta = 10$, $\sigma = 1$) of a) Ga(OH)_{3(s)}, b) SRN1 (pH 3.0; Ga:R-COOH ratio 0.202), c) SRN3 (pH 4.8; Ga:R-COOH ratio 0.202), d) SRN5 (pH 6.8; Ga:R-COOH ratio 0.202), e) Ga(C₂O₄)₃³⁻, f) SRN7 (pH 5.2; Ga:R-COOH ratio 0.04), g) SRN9 (pH 4.9; Ga:R-COOH ratio 0.005), and h) SRN11 (pH 5.1; Ga:R-COOH ratio 0.0003), 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 (not corrected for phase shift). The white/brown areas indicate strong contribution from back-scattering atoms whereas the blue/green areas indicate no or weak contribution.

Fig. 6. Distribution of Ga(III) species as a function of pH at **A**) [Ga(III)]_{tot} = 44.8 mM, and **B**) [Ga(III)]_{tot} = 0.27 mM. Calculations were performed with stability constants from Clausén et al. (2002), Bénézech et al. (1997), and Baes and Mesmer (1976). The solid phase considered is amorphous Ga(OH)_{3(s)}.

Fig. 7. k^3 -weighted EXAFS spectra (solid line) with fit results (dotted line) **A**) and the corresponding Fourier Transforms (solid line), not corrected for phase shift, together with fit results (dotted line) **B**) of the Suwannee river NOM and fulvic acid at pH and Ga(III) to R-COOH ratio of a) 5 and 0.005 (SRFA7), b) 3 and 0.04 (SRN6), c) 5 and 0.04 (SRN7), d) 7 and 0.04 (SRN8), e) 5 and 0.005 (SRN9), f) 5 and 0.0012 (SRN10), g) 5 and 0.0003 (SRN11), and h) $\text{Ga}(\text{C}_2\text{O}_4)_3^{3-}$ (Clausén et al., 2003). The vertical dashed lines indicate approximate positions for the main atomic neighbors and multiple scattering (MS) contributions in $\text{Ga}(\text{C}_2\text{O}_4)_3^{3-}$.

Fig. 8. k^3 -weighted EXAFS spectra (solid line) with fit results (dotted line) **A**) and the corresponding Fourier Transforms (solid line), not corrected for phase shift, together with fit results (dotted line) **B**) of the Suwannee river NOM samples at a Ga(III) to R-COOH ratio of 0.202 and a pH of a) $\text{Ga}(\text{OH})_{3(s)}$, b) 7 (SRN5), c) 6 (SRN4), d) 5 (SRN3), e) 4 (SRN2), f) 3 (SRN1), and g) $\text{Ga}(\text{NO}_3)_{3(aq)}$. The vertical dashed lines indicate approximate positions for the main atomic neighbors in $\text{Ga}(\text{OH})_{3(s)}$.

Table 1

Data for the Suwannee River NOM (SRN) samples prepared for infrared analysis.

Sample	NOM (mg) ^a	Volume (mL) ^b	pH	[Ga(III)] ($\mu\text{g g}^{-1}$) ^c	Ga(III) (μmol) ^d	[Ga(III)] (mM) ^e	Ga(III) /R-COOH ^f
IR_SRN1	28	0.30	3.1	0	0	0	0
IR_SRN2	28	0.30	4.1	0	0	0	0
IR_SRN3	28	0.30	5.1	0	0	0	0
IR_SRN4	28	0.30	5.9	0	0	0	0
IR_SRN5	28	0.30	6.7	0	0	0	0
IR_SRN6	28	0.30	8.1	0	0	0	0
IR_SRN7	28	0.50	3.2	67,673	26.8	53.6	0.202
IR_SRN8	28	0.50	3.8	67,673	26.8	53.6	0.202
IR_SRN9	28	0.50	4.7	67,673	26.8	53.6	0.202
IR_SRN10	28	0.50	5.8	67,673	26.8	53.6	0.202
IR_SRN11	28	0.50	6.7	67,673	26.8	53.6	0.202
IR_SRN12	28	0.50	7.9	67,673	26.8	53.6	0.202

^a The amount of natural organic matter (NOM) in dry weight.^b The total solution volume.^c The weight of Ga per gram of NOM.^d The amount of Ga in micromoles.^e The concentration of Ga in millimolar.^f Mol Ga per mol of carboxylic acid.

Table 2

Composition of the Suwannee River NOM (SRN) and fulvic acid (SRFA) samples prepared for EXAFS analysis.

Sample	NOM (mg) ^a	Volume (mL) ^b	pH	[Ga(III)] ($\mu\text{g g}^{-1}$) ^c	Ga(III) (μmol) ^d	[Ga(III)] (mM) ^e	Ga(III) /R-COOH ^f
SRN1	18	0.50	3.0	67,673	17.9	35.8	0.202
SRN2	18	0.50	4.2	67,673	17.9	35.8	0.202
SRN3	18	0.50	4.8	67,673	17.9	35.8	0.202
SRN4	18	0.50	6.2	67,673	17.9	35.8	0.202
SRN5	18	0.50	6.8	67,673	17.9	35.8	0.202
SRN6	23	0.25	3.3	13,401	4.48	17.9	0.04
SRN7	23	0.25	5.2	13,401	4.48	17.9	0.04
SRN8	23	0.25	6.9	13,401	4.48	17.9	0.04
SRN9	37	0.25	4.9	1675	0.90	3.58	0.005
SRN10	37	0.25	5.0	402	0.21	0.85	0.0012
SRN11	46	0.25	5.1	101	0.07	0.27	0.0003
SRFA1	18	0.50	3.1	84,076	22.4	44.8	0.202
SRFA2	18	0.50	4.8	84,076	22.4	44.8	0.202
SRFA3	18	0.50	7.0	84,076	22.4	44.8	0.202
SRFA4	23	0.25	2.9	16,649	5.37	21.5	0.04
SRFA5	23	0.25	5.0	16,649	5.37	21.5	0.04
SRFA6	23	0.25	6.5	16,649	5.37	21.5	0.04
SRFA7	27	0.25	4.7	2081	0.81	3.26	0.005
SRFA8	32	0.25	5.2	499	0.23	0.93	0.0012
SRFA9	46	0.25	4.9	125	0.08	0.32	0.0003

^a The amount of natural organic matter (NOM) in dry weight.

^b The total solution volume.

^c The weight of Ga per gram of NOM.

^d The amount of Ga in micromoles.

^e The concentration of Ga in millimolar.

^f Mol Ga per mol of carboxylic acid.

Table 3

Fits to Fourier-transformed EXAFS data for Ga(OH)_{3(s)} and the Suwannee River NOM (SRN) and fulvic acid (SRFA) samples.

Sample	pH	Molar ratio	Ga-O/N (SS)			Ga-C (SS) ^{c,f}		Ga-O-C (MS) ^{d,f}		Ga-C-O (MS) ^{e,f}		Ga-Ga (SS) ^g		Ga-Ga (SS) ^g		ΔE_0 (eV)	R-factor
			CN	R (Å) ^b	σ^2 (Å ²)	CN ^f	R (Å)	CN ^f	R (Å)	CN ^f	R (Å)	CN	R (Å)	CN	R (Å)		
Ga(OH) ₃ ^a			6.0±0.8	1.96	0.0111±0.002							2	2.99±0.03	4	3.52±0.04	3.4±1.5	0.0093
												2	3.10±0.03				
SRN1	3.0	0.202	5.6±0.5	1.96	0.0071±0.001											6.8±1.1	0.0238
SRN2	4.2	0.202	5.6±0.4	1.96	0.0072±0.001	1.7±0.6	2.70±0.03			3.4	4.16±0.06					6.2±0.8	0.0117
SRN3*	4.8	0.202	5.3±0.7	1.95	0.0073±0.001	2.2±1.1	2.70±0.05			4.4	4.08±0.11	0.4±0.3	3.06±0.06	3.2±2.3	3.56±0.05	6.5±1.5	0.0140
SRN4	6.2	0.202	5.3±0.6	1.95	0.0089±0.001	1.7±0.8	2.72±0.05			3.4	4.06±0.10	1.1±0.3	3.06±0.01	3.4±1.6	3.55±0.03	7.0±1.2	0.0082
SRN5	6.8	0.202	5.3±0.7	1.94	0.0112±0.001	1.6±0.8	2.76±0.05			3.2	4.06±0.10	1.0±0.3	3.06±0.02	3.1±1.5	3.56±0.04	7.4±1.3	0.0091
SRN6	3.3	0.04	5.5±0.3	1.97	0.0068±0.001	3.0±0.6	2.78±0.02	6.0	3.05±0.08	6.0	4.12±0.03					7.6±0.7	0.0083
SRN7	5.2	0.04	5.5±0.3	1.96	0.0076±0.001	3.8±0.5	2.76±0.01	7.6	3.02±0.05	7.6	4.09±0.02					7.3±0.6	0.0059
SRN8	6.9	0.04	5.5±0.3	1.95	0.0100±0.001	3.8±0.3	2.77±0.01	7.6	3.02±0.04	7.6	4.09±0.02					7.7±0.5	0.0046
SRN9	4.9	0.005	5.3±0.4	1.97	0.0060±0.001	6.9±1.1	2.76±0.01	13.8	3.06±0.06	13.8	4.09±0.02					7.6±0.9	0.0153
SRN10	5.0	0.0012	5.0±0.6	1.97	0.0061±0.001	7.2±1.1	2.74±0.02	14.4	3.04±0.07	14.4	4.08±0.03					6.5±1.2	0.0141
SRN11	5.1	0.0003	5.6±1.1	1.97	0.0046±0.002	10.9±2.1	2.76±0.02	21.8	3.07±0.09	21.8	4.11±0.04					6.2±1.7	0.0231
SRFA1	3.1	0.202	5.4±0.5	1.96	0.0062±0.001											6.3±1.3	0.0234
SRFA2	4.8	0.202	5.6±0.5	1.95	0.0079±0.001	1.4±0.6	2.68±0.04			2.8	4.06±0.09	0.6±0.2	3.06±0.02	3.3±1.5	3.55±0.03	5.9±1.0	0.0074
SRFA3	7.0	0.202	5.1±0.5	1.93	0.0094±0.001	1.1±0.6	2.66±0.05			2.2	3.98±0.11	1.4±0.2	3.04±0.01	3.1±1.3	3.50±0.04	6.3±1.2	0.0098
SRFA4	2.9	0.04	5.8±0.3	1.96	0.0065±0.001	2.4±0.6	2.77±0.02	4.8	3.05±0.09	4.8	4.10±0.04					6.0±0.7	0.0090
SRFA5	5.0	0.04	5.7±0.3	1.96	0.0071±0.001	3.0±0.4	2.76±0.01	6.0	3.04±0.06	6.0	4.08±0.02					6.1±0.6	0.0059
SRFA6	6.5	0.04	6.1±0.4	1.95	0.0098±0.001	3.5±0.5	2.76±0.01	7.0	3.07±0.06	7.0	4.09±0.02					6.5±0.7	0.0088
SRFA7	4.7	0.005	5.4±0.6	1.97	0.0058±0.001	6.4±1.2	2.76±0.01	12.8	3.06±0.06	12.8	4.08±0.03					7.6±1.1	0.0216
SRFA8	5.2	0.0012	5.5±0.4	1.98	0.0056±0.001	7.6±0.7	2.76±0.01	15.2	3.06±0.04	15.2	4.10±0.02					8.2±0.8	0.0097
SRFA9	4.9	0.0003	5.7±1.2	1.98	0.0050±0.002	9.4±1.9	2.76±0.02	18.8	3.11±0.09	18.8	4.12±0.04					5.7±1.6	0.0265

The following abbreviations are used: single scattering (SS), multiple scattering (MS), coordination number (CN), bond distance (R), Debye–Waller factor (σ^2) and edge energy (ΔE_0). S_0^2 was set to 1.21 for the SRN and SRFA samples (see text) and determined to 0.98 for Ga(OH)₃ by fitting the first coordination shell with a fixed CN of 6.0.

^a CNs for the three Ga-Ga scattering paths were fixed according to data reported by Pokrovski et al. (2002) for α -GaOOH and the σ^2 :s were determined to be 0.0078 ± 0.006 (at 2.99 Å), 0.0057 ± 0.004 (at 3.10 Å) and 0.0185 ± 0.005 (at 3.52 Å).

^b The uncertainty for the determined Ga-O distances is ± 0.01.

^c For SRN9 σ^2 was determined to be 0.0092 ± 0.005 and this value was used for the samples SRN2–11. Similarly, σ^2 was determined to be 0.0071 ± 0.005 for SRFA7 and this value was used for the samples SRFA2–9.

^d For SRN9 σ^2 was determined to be 0.0099 ± 0.008 and this value was used for the samples SRN6–11. Similarly, σ^2 was determined to be 0.0076 ± 0.007 for SRFA7 and this value was used for the samples SRFA4–9.

^e For SRN9 σ^2 was determined to be 0.0145 ± 0.003 and this value was used for the samples SRN2–11. Similarly, σ^2 was determined to be 0.0128 ± 0.004 for SRFA7 and this value was used for the samples SRFA2–9.

^f CNs of these scattering paths were correlated as follows: 2×CN (Ga-C (SS)) = CN (Ga-O-C (MS)) = CN (Ga-C-O (MS)), in accordance with the Ga(C₂O₄)₃³⁻ structure.

^g For the samples SRN3-5 and SRFA2-3 the σ^2 :s for the short and the long Ga-Ga scattering paths were fixed at 0.0078 and 0.0185, respectively, which are the values determined for Ga(OH)₃.

*Inclusion of the two Ga-Ga scattering paths in the fit did not result in a significant improvement (see Table S3, Supplementary data). However, since the WT analysis showed a clear contribution from Ga-Ga backscattering in this sample we decided to keep these paths in the reported fit.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8