Complexation and precipitation reactions in the ternary As(V)-Fe(III)-OM (organic matter) system

Anneli Sundman^{a†}, Torbjörn Karlsson^a, Staffan Sjöberg^a and Per Persson^{b*}

^aDepartment of Chemistry, Umeå University, SE-901 87 Umeå, Sweden.

torbjorn.karlsson@chem.umu.se, staffan.sjoberg@chem.umu.se

^bCentre for Environmental and Climate Research & Department of Biology, Lund University, SE-223 62 Lund, Sweden. per.persson@biol.lu.se

Abstract

The predominant forms of arsenic (As) in anoxic and oxic environments are As(III) and As(V), respectively, and the fate of these forms is influenced by interactions with mineral surfaces and organic matter (OM). Interactions between As(V) and OM are believed to occur mainly via iron(Fe)-bridges in ternary Fe-arsenate complexes, but direct evidence for these interactions are scarce. Furthermore, since the speciation of Fe in the presence of organic matter varies as a function of pH and Fe concentration, a central question is how different chemical conditions will affect the As-Fe-OM interactions. In order to answer this, the As(V)-Fe(III)-OM system have been studied under a large range of experimental conditions (6485-67 243 ppm Fe(III) and Fe(III):As(V) ratios of 0.5-20 at pH 3–7), with Suwannee River Natural organic matter and Suwannee River Fulvic acids as sources of OM, using Fe and As K-edge X-ray absorption spectroscopy (XAS), infrared (IR) spectroscopy and chemical equilibrium modeling. Our collective results showed that interactions in the ternary As(V)-Fe(III)-OM system were strongly influenced by pH, total concentrations and ratios among the reactive species. In particular, the high stability of the Fe(III)-OM complexes exerted a strong control on the speciation. The predominant species identified were mononuclear Fe(III)-OM complexes, Fe(III) (hydr)oxides and FeAsO₄ solids. The experimental results also showed that at low concentrations the Fe(III)-SRFA/SRN complexes were sufficiently stable to prevent reaction with arsenate. The chemical equilibrium models developed corroborated the spectroscopic results and indicated that As(V) was distributed over two solid phases, namely FeAsO₄(s) and Fe(OH)_{1.5}(AsO₄)_{0.5}(s). Thus, neither ternary As(V)-Fe(III)-OM complexes nor As(V) surface complexes on Fe(III) (hydr)oxides were necessary to explain the collective results presented in this study.

1. Introduction

Arsenic (As) is a toxic and carcinogenic element found in contaminated ground, surface, and drinking waters as a result of human activities and/or natural processes. It poses a threat to the health of millions of people in countries such as Chile, West Bengal and Argentina (Smedley and Kinniburgh, 2002). The predominant forms of As in anoxic and oxic environments are As(III) and As(V), respectively, and the fate of these forms is influenced by interactions with environmental components such as mineral surfaces and organic matter (OM). Both As(III) and As(V) have been shown to bind to mineral surfaces e.g. gibbsite (Ladeira et al., 2001), ferrihydrite, goethite, hematite and lepidocrocite (Bowell, 1994; Catalano et al., 2008; Fendorf et al., 1997; Loring et al., 2009; Pierce and Moore, 1982; Raven et al., 1998; Xu et al., 1991). At Fe(III)-containing mineral surfaces, arsenic can be affected by microbial Fe(III) reduction which also induces As(V) to As(III) reduction (Tufano et al., 2008; Weber et al., 2010), potentially leading to a rise in solution concentrations of As since As(III) often displays lower affinity for mineral surfaces (Dixit and Hering, 2003).

Organic matter affects As via a range of different mechanisms (Lagner et al., 2012; Redman et al., 2002; Sharma et al., 2011; Thanabalasingam and Pickering, 1986; Wang and Mulligan, 2006; Xu et al., 1991); e.g. via reductive dissolution of iron minerals that may cause desorption of As(III/V) (McArthur et al., 2004) or via direct oxidation/reduction of As(III) or As(V), respectively (Bauer and Blodau, 2006; Buschmann et al., 2005; Redman et al., 2002). Organic matter also competes with As(III/V) for binding sites at mineral surfaces (Bauer and Blodau, 2006; Grafe et al., 2001, Grafe et al., 2002; Redman et al., 2002; Simeoni et al., 2003; Xu et al., 1991) and there are studies suggesting formation of As-OM complexes (Buschmann et al., 2006; Redman et al., 2002). These interactions between As and OM are believed to occur mainly via Fe-bridges in ternary iron-arsenate complexes (Hoffmann et al., 2013; Lin et

al., 2004; Redman et al., 2002; Sharma et al., 2010; Sharma et al., 2011). In most cases this interpretation is based on indirect evidence such as correlations between concentrations of As, Fe and/or OM (Dobran and Zagury, 2006; Ritter et al., 2006; Rothwell et al., 2009) or on results from sequential extraction procedures (González et al., 2006). The lack of direct spectroscopic evidence capturing these complexes was discussed by Mikutta and Kretzschmar (2011) and they also presented spectroscopic support for ternary As(V)-Fe(III)-OM complexes. It was concluded that a majority of the As(V) associated with Fe(III) forms inner-sphere Fe(III)-OM complexes and in these complexes Fe(III) exists as oligomeric clusters (Mikutta and Kretzschmar, 2011). Previous studies have shown that Fe speciation in the presence of organic matter, but in the absence of As, varies as a function of pH and Fe concentration (Bauer and Blodau, 2009; Karlsson and Persson, 2010 and 2012). At low Fe concentrations and low pH, mononuclear Fe(III)-OM complexes predominate, whereas at high Fe concentrations and high pH, Fe(III) is hydrolyzed and precipitated as Fe(III) (hydr)oxides. Considering the close linkage between Fe(III) and As(V) it is likely that changes in Fe speciation will also be reflected in the As speciation. Hence, a central question is how chemical conditions affect As-Fe-OM interactions. In order to answer this, we have studied a wide range of experimental conditions covering a variation in Fe(III) concentrations, Fe(III) to As(V) ratios, and pH, and we have also investigated two different organic materials. The local structures of the ternary As(V)-Fe(III)-OM systems have been probed by Fe and As K-edge X-ray absorption spectroscopy (XAS). These measurements have been complemented by infrared (IR) spectroscopy that provided information on the As-O vibrations and the possibility to quantify the ratio between free and coordinated As(V). In addition, based on the XAS and IR results, a chemical equilibrium model was developed that describe the studied systems within a thermodynamic framework.

2. Material and Methods

2.1 Chemicals and sample preparation

Suwannee River fulvic acid (SRFA; 1S101F) and Suwannee River organic matter (SRN; 1R101N) were purchased from the International Humic Substances Society. The elemental composition of these samples is reported in Table A1, Supplementary data. The freeze-dried SRN and SRFA originate from a blackwater river, with 25-75 mgL⁻¹ DOC and low pH. The SRN material was isolated by filtration, followed by reverse osmosis (Serkiz and Perdue, 1990; Sun et al., 1995). It contains hydrophobic and hydrophilic acids and other soluble organic solutes. The SRFA material was obtained via a multistep isolation procedure (Aiken, 1985). Briefly, the river water was acidified, repeatedly passed over an XAD-8 resin, eluted with NaOH and re-acidified with HCl. The fulvic acids were separated from the humic acids by addition of HCl to pH 1 where the humic acids precipitate. In the final step before freeze-drying, the fulvic acid eluate was passed over a hydrogen-saturated cation-exchange resin to remove Na⁺. As a result of this isolation procedure, the SRFA material only contains hydrophobic organic acids with molecular weights above 200 Da (Thurman and Malcolm, 1981). A stock solution of arsenate was prepared by dissolving Na₂HAsO₄×7H₂O (≥98% Sigma) in Milli-Q water. Stock solutions of Fe(III) (0.09-1.0 M) were prepared by dissolving either FeCl₃×6H₂O (p.a. Sigma-Aldrich) or Fe(NO₃)₃×9H₂O (p.a. MERCK) in Milli-Q water. The nitrate salt was used for the Fe(III)-SRN reference samples (Karlsson and Persson, 2012) and for the majority of the SRN XAS samples (Table 1, Table A2, Supplementary data). Due to possible nitrate interference in the IR spectra, the chloride salt was chosen for the IR samples, as well as for the SRFA XAS samples. The samples were prepared similar to the procedure used by Karlsson and Persson (2010). 25.0-60.0 mg of the aquatic organic material was weighted into 1.5 mL Eppendorf test tubes; subsequently an Fe(III) stock solution (concentration range 0.1-1.0 M depending on the target Fe concentrations) and water were

added to reach the desired total Fe concentration. After 20 minutes pH was adjusted to reach the predetermined value using a 2-4 M NaOH stock solution. The samples were covered with aluminum foil and equilibrated for 2 h on an end-over-end rotator. The samples were further equilibrated for 22 h in an upright position prior to addition of the arsenate stock solution. The equilibration procedure was repeated, i.e. 2 h on an end-over-end rotator and 22 h in an upright position. pH was measured and adjusted when needed, before final dilution with Milli-Q water. After the final dilution the samples were further equilibrated for 3 days and pH was measured again. For selected samples, pH was re-measured 3 weeks after preparation to ensure the pH did not drift and the value was identical with that obtained 3 days after pH adjustment. A set of Fe reference samples was also prepared in absence of arsenate. pH was measured using a 2-point calibrated InLab®Micro (Mettler Toledo) pH combination electrode. The samples were stored in a refrigerator for 5-10 days prior to XAS measurements and 1-3 days prior to IR measurements. The SRN sample characteristics are summarized in Table 1 and Table A2, and the SRFA characteristics in Table 2 and Table A3. In addition to these series a set of aqueous H_2AsO_4^- samples, at pH 4.5, at concentrations from 1 to 250 mM was prepared by diluting the arsenate stock solution with Milli-Q water. The amorphous $\text{FeAsO}_4(\text{s})$ reference compound was prepared by mixing Na_2HAsO_4 and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solutions and then dialyzing the resulting suspension, for more information and identification see Supplementary data and Fig. A1.

Table 1

The characteristics of Suwannee River organic matter (SRN) samples prepared for XAS (SRN ref1-6; SRN1-7) and IR (SRN IR1-10) measurements.

Sample ^a	[Fe] (ppm) ^b	[Fe(III)]/[As(V)] ^c	pH
SRN ref1	6504 ^d	-	3.0
SRN ref2	6489 ^d	-	5.0
SRN ref3	11 953 ^e	-	5.0
SRN ref4	22 818 ^f	-	4.2
SRN ref5	22 879 ^f	-	5.0
SRN ref6	22 818 ^f	-	6.2
SRN1	6485 ^d	1.2	5.0
SRN2	11 971 ^e	1.0	5.2
SRN3	22 916 ^f	1.0	3.2
SRN4	22 916 ^f	1.0	5.3
SRN5	22 916 ^f	0.5	5.0
SRN6	22 916 ^f	4.0	5.3
SRN7	22 916 ^f	1.0	7.0
SRN IR1	22 916 ^f	1.05	2.9
SRN IR2	22 916 ^f	1.0	3.6
SRN IR3	22 916 ^f	1.0	4.0
SRN IR4	22 916 ^f	1.0	4.6
SRN IR5	22 916 ^f	1.05	5.1
SRN IR6	22 916 ^f	1.0	5.6
SRN IR7	22 916 ^f	1.0	6.0
SRN IR8	22 916 ^f	0.5	5.1
SRN IR9	22 916 ^f	2.0	5.1
SRN IR10	11 971 ^e	1.0	5.0

Abbreviations: X-ray absorption spectroscopy (XAS) and infrared (IR).

^a The concentration of carboxylic functional groups is 4807 $\mu\text{mol g}^{-1}$ on a dry mass basis.

^b $\mu\text{g Fe g}^{-1}$ dry SRN, including both added Fe and Fe present in the pristine OM. The latter fraction constitutes a maximum of ca. 15% of the total [Fe].

^c Expressed as a molar ratio.

^d Corresponds to 14.3-17.2 mM Fe.

^e Corresponds to 26.2-31.5 mM Fe.

^f Corresponds to 50.2-58.8 mM Fe. For more information see Table A2, Supplementary data.

Table 2

The characteristics of Suwannee River Fulvic Acid (SRFA) samples prepared for XAS (SRFA ref1-6; SRFA1-10) and IR (SRFA IR1-5) measurements.

Sample ^a	[Fe] (ppm) ^b	[Fe(III)]/[As(V)] ^c	pH
SRFA ref1	13 473 ^d	-	2.9
SRFA ref2	13 473 ^d	-	5.2
SRFA ref3	26 945 ^e	-	2.8
SRFA ref4	26 945 ^e	-	4.9
SRFA ref5	26 94 ^e	-	6.5
SRFA ref6	67 363 ^f	-	5.1
SRFA1	6736 ^g	1.0	5.0
SRFA2	13 473 ^d	1.0	3.1
SRFA3	13 473 ^d	1.0	5.1
SRFA4	26 945 ^e	1.0	3.0
SRFA5	26 945 ^e	1.0	5.1
SRFA6	26 945 ^e	1.0	6.5
SRFA7	26 945 ^e	4.0	5.1
SRFA8	26 945 ^e	20.0	5.0
SRFA9	67 243 ^f	1.0	3.5
SRFA10	67 243 ^f	1.0	5.3
SRFA IR1	33 917 ^h	1.0	3.6
SRFA IR2	33 917 ^h	1.0	4.1
SRFA IR3	33 917 ^h	1.0	4.5
SRFA IR4	33 917 ^h	1.0	5.6
SRFA IR5	33 917 ^h	1.0	5.8

Abbreviations: X-ray absorption spectroscopy (XAS) and infrared (IR).

^a On a dry mass basis, the concentration of carboxylic functional groups is 5972 $\mu\text{mol g}^{-1}$.

^b $\mu\text{g Fe g}^{-1}$ dry SRFA. This value only includes added Fe, as the Fe content of the pristine SRFA material is ca. 1%, or less, of the total [Fe] (Table A1, Supplementary data).

^c Expressed as a molar ratio.

^d Corresponds to 22.0 mM Fe.

^e Corresponds to 44.0-44.7 mM Fe.

^f Corresponds to 66.7 mM Fe.

^g Corresponds to 11.0 mM Fe.

^h Corresponds to 55.4 mM Fe. For more information see Table A3, Supplementary data.

2.2 XAS measurement and data analysis

The Fe K-edge and As K-edge spectra were collected at beamlines 4-1 and 4-3 at Stanford Synchrotron Radiation Lightsource, California. The ring current was 300-350 mA and the energy was 3 GeV. The spectra were collected at room temperature in fluorescence mode using a Lytle detector filled with Ar gas. Both beamlines were equipped with double crystal monochromators; Si ([220], $\Phi=90$) at 4-1 and Si ([111], $\Phi=90$ or $\Phi=0$) at 4-3. To reduce unwanted elastically and inelastically scattered radiation Mn 3 μx (at the Fe K-edge) or Ge 6 μx (at the As K-edge) filters were used. To reduce higher order harmonics, the monochromator was detuned 30-50 % at 4-1 and at 4-3 a nickel coated harmonic rejection mirror was used. The samples were mounted in Teflon sample holders, sealed with Kapton Tape (CHR Furon), and the hutch slit was set to 2×10 mm. Spectra were simultaneously recorded for Fe or As foils to allow for internal calibration. 1-18 spectra per sample were recorded at the Fe-edge and 1-14 spectra at the As-edge, depending on sample concentration. The spectra were energy calibrated and averaged using SixPack (Webb, 2005). Prior to averaging, each individual spectrum was carefully inspected for self-absorption and beam damage. Self-absorption was evaluated by comparing fluorescence and transmission spectra. No self-absorption was observed for any of the samples analyzed in this study (representative spectra in Fig. A2, Supplementary data). To evaluate possible beam damage, the pre-edge and main edge were inspected and compared between the scans. Beam damage was observed in several Fe spectra, and those were not included in the final average spectrum. Beam damage was manifested as changes in the shape and position of the main edge. The majority of the Fe-XAS spectra consist of an average of 2-7 scans. The As-XAS spectra did not display any beam damage, and the position of the edge was consistent with As(V).

Shell-by-shell extended X-ray absorption fine structure (EXAFS) fits as well as investigations of self-absorption effects were accomplished by means of the computer code Viper (Klementiev, 2001). Pre- and post-edge functions were subtracted from the spectra, which were subsequently normalized. A spline function was used to subtract background beyond the absorption edge. Furthermore, spectra were k^3 -weighted in order to enhance oscillations at high k -values. The samples were fitted in k -space, (3.40-13.60 $\text{\AA}^{-1}$ for As and 2.80-11.475 $\text{\AA}^{-1}$ for Fe) using theoretical phase and amplitude functions from FEFF calculations (Zabinsky et al., 1995). Trisoxolatoiron (Persson and Axe, 2005), scorodite (Kitahama et al., 1975) and goethite (Szytula et al., 1968) were used as input structures for the FEFF calculations (Zabinsky et al., 1995). The amplitude reduction factor (S_0^2) was set to 1.0 for the As-edge. This was obtained by fitting the first coordination shell in the amorphous $\text{FeAsO}_4(\text{s})$ sample, assuming a coordination number (CN) of 4 for the As-O path. For the Fe-edge a S_0^2 value of 0.85 was obtained by fitting the first coordination shell in the SRFA ref 1 sample (13 000 ppm Fe, pH 2.9; Table 2) assuming a CN of 6 for the Fe-O path. The numbers of free variables were restricted by correlating coordination numbers and when available, fixing the Debye-Waller factors (σ^2) to values found in literature or determined from fitting spectra of reference compounds. Furthermore, the E_0 -shift was assumed to be identical for all shells. Consequently, the number of free variables never exceeded the limit given by the Nyquist theorem ($N_{\text{max}} = 2 \times \Delta k \times \Delta R / \pi$, where Δk is the k -range of the EXAFS spectrum and ΔR is the R -range of the Fourier transformed range). Wavelet transform (WT) analysis of the EXAFS spectra were accomplished by means of the Igor Pro script developed by Funke et al. (2005).

2.3 IR measurements

The IR measurements were conducted with a Bruker Vertex 80 vacuum FTIR spectrometer equipped with a DTGS detector in a laboratory thermostated at $25.0 \pm 0.15^\circ\text{C}$. The spectra

were collected using an attenuated total reflectance (ATR) accessory equipped with a ZnSe crystal as the internal reflection element. The samples were transferred to the crystal surface using a pipette and were then further sealed from the atmosphere using a stainless steel lid that was not in contact with the sample. 1000 scans, ranging 400-5000 cm^{-1} at a resolution of 4 cm^{-1} , were recorded for each sample. The spectra for a pH-adjusted 0.27 M NaCl solution, SRN dissolved in water adjusted to pH 3 and 6, SRFA dissolved in water adjusted to pH 3 and 6, were also recorded and later used for subtraction of the water and organic material contributions in the spectra. The concentration of free arsenate in solution was evaluated by calculating the ratio between the area of the arsenate bands integrated over 930-860 cm^{-1} and the area of the water bend vibration around 1600 cm^{-1} in a pH region 3-6 where H_2AsO_4^- predominates. This ratio accounts for differences in arsenate peak intensities caused by different water content in the samples and thus isolates true concentration effects. A calibration curve was obtained by plotting this ratio for H_2AsO_4^- standard solutions against arsenate concentration, c.f. Fig. A3. The concentration of free H_2AsO_4^- in the As(V)-Fe(III)-SRFA/SRN samples were evaluated from this calibration-curve.

2.4 Chemical equilibrium modeling

Previous IR studies of the SRN/SRFA systems have shown that only a fraction of the carboxyl groups are reactive towards trivalent metal ions (Hagvall et al., 2014). Herein this fraction was assumed to be 15 % for SRFA and 20 % for SRN (remaining carboxyls are assumed to show a negligible reactivity towards Fe(III)). Furthermore, these carboxylic sites were characterized by the pKa values 2.9 and 5.7 ($I=0.27$ M) (Karlsson and Persson, 2012), values typical for dicarboxylic acids (H_2L) (e.g. malonic acid), with chelating properties. 1:1 Fe(III) - H_2SRFA and Fe(III) - H_2SRN complexes were introduced to describe the complexing

properties of the OM. A compilation of speciation and equilibria in the two H₂OM systems is presented in Table A4, Supplementary data.

The Davies equation (1) (Davies, 1962) was used to account for changes of the activity coefficients as a function of ionic strength (I) in the SRFA and SRN systems.

$$\text{Log } \gamma_i = -0.509 z_i^2 \cdot \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \quad (1)$$

γ_i is the activity coefficient for the i^{th} species, z_i is the charge of the species and I is the ionic strength in molar. The calculation of I considered contributions from high and low reactivity sites and I was found to vary between 0.2-1 M.

The computer code WinSGW, (Karlsson and Lindgren, 2006) which is based on the SOLGASWATER algorithm (Eriksson, 1979) was used to fit the equilibrium model to the experimental data. WinSGW minimizes the total residual sum of squares (U (2)), calculated from experimental input data:

$$U_{\text{tot}} = \sum ([\text{Fe}^{3+}]_{\text{tot sln calc}} - [\text{Fe}^{3+}]_{\text{tot sln exp}})^2 + \sum ([\text{As(V)}]_{\text{tot sln calc}} - [\text{As(V)}]_{\text{tot sln exp}})^2 + \sum (\sum (n_i(s_j)_{\text{calc}} - n_i(s_j)_{\text{exp}}))^2 \quad (2)$$

where $[\text{Fe}^{3+}]_{\text{tot sln exp}} = [\text{Fe}^{3+}]_{\text{tot exp}}$ and $n_i(s_j)_{\text{exp}} = 0$ moles/dm⁻³ in the absence of a solid phase (s_j) and s_j are the j different solid phases.

In addition to the measured pH-values of the solutions/suspensions, the total concentrations, $[\text{Fe(III)}]_{\text{tot}}$, $[\text{As(V)}]_{\text{tot}}$, $[\text{H}_2\text{SRFA}]_{\text{tot}}$, or $[\text{H}_2\text{SRN}]_{\text{tot}}$, were known for each experimental point. Furthermore, the EXAFS provided information on the Fe(III) - OM speciation as well as Fe-Fe and Fe-As interactions indicating presence of precipitated Fe(III) (e.g. ferrihydrite) and/ or

FeAsO₄(s), respectively. In some of the samples (c.f. Table A5, Supplementary data) no solid phases were observed and here the total concentration of Fe(III) in solution, [Fe(III)]_{tot. sln.}, was equal to [Fe(III)]_{tot.}. This observation made it possible to determine stability constants for the Fe(III)-SRFA/SRN complexes greater or equal to a given value. This value was then refined in a final calculation using additional experimental points with precipitated phases.

The quantification of total soluble arsenate concentrations obtained by the IR spectroscopy measurements provided an important piece of information (Table A6, Supplementary data). This concentration reflects the interplay between formed Fe(III)-OM complexes and As(V)-containing solids.

3. Results and Discussion

3.1 Infrared spectroscopy

The main objective of the IR experiments was to monitor the molecular vibrations of arsenate in the ternary As(V)-Fe(III)-SRFA/SRN samples, and specifically the pronounced As-O modes in the wavenumber region 950-700 cm⁻¹ (Loring et al., 2009). The As(V)-Fe(III)-SRN samples displayed four main bands in this region at 980, 910, 877 and 810 cm⁻¹ and comparisons with spectra of model compounds indicated the presence of free, aqueous arsenate as well as an iron arsenate phase (Fig. 1). Similar bands were found in the As(V)-Fe(III)-SRFA system (Fig. 1g, only one SRFA spectrum shown) but in this case the 980 cm⁻¹ band was missing, which is unique to protonated SRN (see Fig. 1h and 1i). The aqueous H₂AsO₄⁻ bands (Fig. 1a) showed a perfect match with the As(V)-Fe(III)-SRFA/SRN bands at 910 and 877 cm⁻¹, which implied that IR spectroscopy was able to detect the fraction of free arsenate, allowing determination of the arsenate associated with the As(V)-Fe(III)-SRFA/SRN species (as described in 2.3 and Supplementary data). The quantitative analysis

was limited to the pH range 3-6 where H_2AsO_4^- predominates; at high pH values HAsO_4^{2-} becomes important which alters the IR spectra and complicates the analysis. Under conditions favoring mononuclear Fe(III)-SRFA/SRN complexes (i.e. 1:1 Fe-to-As ratio and at total Fe concentrations of 22 916 and 33 917 ppm, see Karlsson and Persson, 2012 and section 3.3 below), ca. 65-80% of the arsenate was associated with Fe(III)-SRFA/SRN while the rest remained as aqueous H_2AsO_4^- (Fig. 2). The fraction of this bound arsenate was relatively constant over the investigated pH interval although a weak minimum around pH 5 was observed followed by what seemed to be a sharper increase at higher pH. The reason for this behavior is not clear but will be discussed below in 3.4. At higher Fe(III) to As(V) ratios, the fraction of free As(V) was lowered (Fig. 2), whereas at 1:1 Fe to As ratios but lower total concentrations higher fractions of free arsenate were observed (Table A6, Supplementary data). Accordingly, arsenate interactions with Fe(III)-SRFA/SRN are generally favored by high iron concentrations.

The IR spectra, in particular the band at 810 cm^{-1} , also provided insight into the nature of the Fe(III)-As(V) phases formed. According to the analysis above, the pronounced H_2AsO_4^- bands represented only ca. 20-35 % of the total arsenate concentration in the As(V)-Fe(III)-SRFA/SRN samples, whereas the spectral features of the remaining 65-80 % were less clear (Fig. 1). The weak spectral signature of the fraction of bound arsenate suggested minor or no contribution from arsenate surface complexes on iron oxides and arsenate bonded in mononuclear trivalent metal complexes as these have been shown to display strong and distinct bands (Loring et al., 2009) (examples are provided in Fig. 1k and l). Instead, the intensity increase and the increasing width of the 810 cm^{-1} band as compared to pure SRN (Fig. 1) were consistent with the weak but very broad band centered around 810 cm^{-1} of $\text{FeAsO}_4(\text{s})$ (Fig. 1j). Thus, although a large fraction of arsenate is present as $\text{FeAsO}_4(\text{s})$, the IR

characteristic of this compound explains the comparatively weak spectral effects in our samples.

Figure 1. IR spectra of a) aqueous H_2AsO_4^- , b) SRN IR2, c) SRN IR3, d) SRN IR4, e) SRN IR5, f) SRN IR6, g) SRFA IR2, h) SRN containing protonated carboxyls, i) SRN containing de-protonated carboxyls, j) amorphous $\text{FeAsO}_4(\text{s})$, k) arsenate adsorbed on goethite in D_2O suspension at pD 3.65, and l) arsenate adsorbed on goethite in D_2O suspension at pD 5.79. Spectra h) and i) were obtained by subtracting a high pH SRN spectrum from a low pH, or vice versa, to isolate either protonated or deprotonated carboxyls only.

Figure 2. Estimated bound concentrations (in %) of As(V) in **A**) As(V)-Fe(III)-SRN samples at pH 2.9-6.0 (SRN IR1-7) represented by blue squares, and As(V)-Fe(III)-SRFA samples at pH 3.6-5.8 (SRFA IR1-5) represented by red triangles, and **B**) As(V)-Fe(III)-SRN samples at pH 5.1 and different Fe(III) to As(V) ratios (SRN IR5, 8 and 9).

3.2 X-ray absorption spectroscopy: The As K-edge

3.2.1 Qualitative XANES, EXAFS and WT analysis

For redox sensitive elements such as arsenic there is always a risk of beam-induced redox reactions, but the main absorption edge at 11 873 eV in all XAS spectra (Fig. A4 and A5, Supplementary data) indicated only the presence of As(V) in our samples (Mikutta and Kretzschmar, 2011). Besides information on the arsenic redox state, the featureless As K-edge X-ray absorption near edge structure (XANES) spectra did not provide additional clues about the As speciation, In contrast, the k^3 -weighted EXAFS spectra, and in particular the 2nd shell peak at ca. 2.5 Å of the corresponding Fourier transforms, revealed important trends in the extent of As-Fe interactions (Fig. 3-5). This 2nd shell peak coincided with a similar feature in the Fourier transform of amorphous FeAsO₄(s) (Fig. A2a, Supplementary data), and as shown previously it originates primarily from As-Fe back-scattering, (Loring et al., 2009). The amplitude variations of the As-Fe peak showed that As-Fe interaction was favored at high

total Fe concentrations and Fe(III)/As(V) ratios (Fig. 4 and 5), whereas pH had only very minor effects on the As speciation (Fig. 3).

These variations in As speciation as a function of experimental conditions were also reflected in the high-resolution WT contour plots of the As(V)-Fe(III)-SRFA/SRN samples (Fig. 6 and Fig. A6, Supplementary data), and in agreement with the IR results the WT plots can be explained by contributions from aqueous H_2AsO_4^- (Fig. 6a) and amorphous $\text{FeAsO}_4(\text{s})$ (Fig. 6c). The arsenate solution showed high intensity regions at ca. $(3.5 \text{ \AA}^{-1}, 2.5 \text{ \AA})$ and $(3.5 \text{ \AA}^{-1}, 3.8 \text{ \AA})$ caused by multiple scattering within the arsenate tetrahedron (Loring et al., 2009). The former also contributed to the WT feature of amorphous $\text{FeAsO}_4(\text{s})$ but here the most important contribution was scattering from second nearest Fe neighbors (Mikutta and Kretzschmar, 2011), presumably at a range of different As-Fe distances given the amorphous nature of $\text{FeAsO}_4(\text{s})$, which resulted in a strong feature at higher k -values, ca. $(8 \text{ \AA}^{-1}, 3 \text{ \AA})$. At smaller spread in As-Fe distances, the center of gravity of the As-Fe WT feature has been shown to appear at higher k -values $(9 \text{ \AA}^{-1}, 3 \text{ \AA})$ (Loring et al., 2009). This may be used to distinguish between amorphous $\text{FeAsO}_4(\text{s})$ and arsenate surface complexes (c.f. Fig. 6b and 6c) as well as aqueous mononuclear Me(III)-arsenate coordination complexes (Loring et al., 2009). The largest variation in the contour plots was detected when the total concentrations were varied at constant pH and Fe:As ratio (Fig. 6g-i). At low concentration (6736 ppm) the WT closely resembled that of aqueous arsenate suggesting a predominance of free arsenate. This was also observed in a sample where 4350 ppm As was added to native SRN, indicating that Fe, or other metal ions, associated with the SRN material do not cause detectable interactions with the As(V) under these conditions (Fig. A6i). Increasing total concentrations resulted in increasing As-Fe interactions evidenced by WT features at higher k -values, and at the highest concentration (26 945 ppm) they were in reasonable agreement with $\text{FeAsO}_4(\text{s})$.

Under these chemical conditions the IR results indicated that ca. 6500 ppm did not interact with As(V) (Fig. 2A), thus in quantitative agreement with the fact that the WT of SRFA1 displayed features of aqueous arsenate only (Fig. 6g). Finally, the appearance of the WT contour plots as a function of Fe:As ratios showed a weak trend towards an $\text{FeAsO}_4(\text{s})$ -like feature, with a stronger As-Fe amplitude, at higher ratios (Fig. 6j-l).

Figure 3. A) k^3 -weighted As-EXAFS spectra and B) the corresponding Fourier transforms of representative samples displaying the effect of pH for As(V)-Fe(III)-SRN samples with $[\text{Fe}] = 22\,916$ ppm Fe and $\text{Fe:As} = 1$ at a) pH 3.2 (SRN3), b) pH 5.3 (SRN4), c) pH 7.0 (SRN5), and As(V)-Fe(III)-SRFA samples with $[\text{Fe}] = 26\,945$ ppm Fe and $\text{Fe:As} = 1$ at d) pH 3.0 (SRFA4), e) pH 5.1 (SRFA5), and f) pH 6.5 (SRFA6). Black lines represent experimental data and red lines fit results.

Figure 4. A) k^3 -weighted As-EXAFS spectra and B) the corresponding Fourier transforms of representative samples displaying the effect of concentration for As under Fe:As=1 conditions in As(V)-Fe(III)-SRN samples at pH 5 at a) 11 971 ppm Fe (SRN2), b) 22 916 ppm Fe (SRN4), and for As(V)-Fe(III)-SRFA samples at pH 3 at c) 13 473 ppm Fe (SRFA2), d) 26 945ppm Fe (SRFA4), e) 67 243 ppm Fe (SRFA9), and at pH 5 at f) 6736 ppm Fe (SRFA1), g) 13 473 ppm Fe (SRFA3), h) 26 945ppm Fe (SRFA5), and i) 67 243 ppm Fe (SRFA10). Black lines represent experimental data and red lines fit results.

Figure 5. A) k^3 -weighted As-EXAFS spectra and B) the corresponding Fourier transforms of representative samples displaying the effect of the Fe:As ratio for As(V)-Fe(III)-SRN samples at 22 916 ppm Fe and pH 5.0-5.3 at a) Fe(III):As(V)=0.5 (SRN5), b) Fe(III):As(V)=1.0 (SRN4), c) Fe(III):As(V)=4.0 (SRN6), and for As(V)-Fe(III)-SRFA samples at 26 945 ppm Fe and pH 5.1 at d) Fe(III):As(V)=1.0 (SRFA5), e) Fe(III):As(V)=4.0 (SRFA7), and f) Fe(III):As(V)=20.0 (SRFA8). Black lines represent experimental data and red lines fit results.

395 **Figure 6.** High resolution As-WT modulus ($\eta=4$, $\sigma=2$) between $k=2-14 \text{ \AA}^{-1}$ (x-axis) and $R=2-$
 396 $4 \text{ \AA}$ (y-axis) of k^3 -weighted EXAFS spectra of reference compounds according to a) 150 mM
 397 HAsO_4^{2-} solution, b) $1.8 \mu\text{mol/m}^2$ arsenate adsorbed on goethite at pH 5.3, c) $\text{FeAsO}_4(\text{s})$, and
 398 of As(V)-Fe(III)-SRFA samples displaying the effect of pH at 26 945 ppm Fe and Fe:As=1:
 399 d) pH 3.0 (SRFA4), e) pH 5.1 (SRFA5), f) pH 6.5 (SRFA6); displaying the effect of
 400 concentration at pH 5 and Fe:As=1: g) 6736 ppm Fe (SRFA1), h) 13 473 ppm Fe (SRFA3), i)
 401 26 945ppm Fe (SRFA5); and displaying the effect of Fe(III) to As(V) ratio at pH 5.1 and

26 945 ppm Fe: j) Fe(III):As(V)=1.0 (SRFA5), k) Fe(III):As(V)=4.0 (SRFA7), and l) Fe(III):As(V)=20.0 (SRFA 8).

3.2.2 Quantitative shell-by-shell As EXAFS fits

The qualitative trends discussed above were transferred into quantitative numbers via shell-by-shell fits of the k^3 -weighted EXAFS spectra (Table 3). All spectra were adequately fit with a relatively simple model including first-shell As-O single scattering and As-O-O multiple scattering together with a second-shell As-Fe single-scattering path (Table 3 and Fig. 3-5). This simple model did not include all paths in short-ranged ordered FeAsO₄(s) detected by Mikutta et al. (2013), but our spectral quality did not motivate additional paths as indicated by F-tests. The two first-shell paths showed no variation with the composition of the As(V)-Fe(III)-SRFA/SRN samples whereas the As-Fe coordination number (CN_{As-Fe}) varied in accordance with the As speciation trends already identified. Thus, the largest effect on CN_{As-Fe} was detected when the total concentrations of Fe and As were varied keeping pH and the Fe:As ratio fixed; for the SRFA samples the CN_{As-Fe} increased from non-detectable at 6736 ppm Fe (SRFA1) to 1.3 (SRFA9, pH 3) and 0.9 (SRFA10, pH 5) at 67 243 ppm. The difference in the CN_{As-Fe} for the SRN samples at 11 971 ppm (SRN 2) and 22 916 ppm (SRN 4) was in accordance with the SRFA trend (Table 3), but the effect was smaller due to smaller variation in total concentrations. The fact that no As-Fe interactions were detected at a 1:1 Fe to As ratio at comparatively low total concentrations, which should be optimal for mononuclear ternary As(V)-Fe(III)-OM complexes, indicated that these complexes were not significant. The WT:s and FT:s indicated a slight increase in As-Fe interactions at increasing Fe:As ratios, and these observations were reinforced by the quantitative EXAFS fits (Table 3). The CN_{As-Fe} was roughly doubled when the Fe:As ratio was increased by a factor of 20 and 8 for the SRFA and SRN samples, respectively (Table 3). Also the effect of pH on CN_{As-Fe} was in agreement with previous results; i.e. it remained almost constant over the

investigated pH range (Table 3). Interestingly however, both the SRFA and the SRN samples displayed a weak minimum in CN_{As-Fe} around pH 5, which coincided with minima of the bonded fraction of As estimated from the independent IR data (Fig. 2), again showing the good agreement between the two techniques.

Table. 3

k^3 -weighted As K-edge EXAFS fit results of ternary As(V)-Fe(III)-SRFA/SRN samples and amorphous $FeAsO_4(s)$.

Sample ^a	As-O			As-O-O ^b		As-Fe ^d		ΔE_0	F_i^f
	CN	R (Å)	σ^2 (Å ²)	CN ^c	R (Å)	CN	R (Å)		
SRFA1	4.0	1.69	0.0053	12.0	3.17			4.12	12.04
SRFA2	4.2	1.69	0.0047	12.5	3.15	0.4	3.22	3.64	11.31
SRFA3	4.0	1.69	0.0044	12.1	3.16	0.5	3.27	4.69	11.59
SRFA4	4.0	1.69	0.0038	12.0	3.14	0.9	3.31	4.01	11.65
SRFA5	4.0	1.69	0.0038	11.9	3.15	0.7	3.29	4.63	11.63
SRFA6	3.9	1.69	0.0038	11.8	3.15	0.8	3.24	4.77	12.43
SRFA7	4.1	1.69	0.0037	12.3	3.14	1.2	3.29	4.13	12.64
SRFA8	4.1	1.69	0.0050	12.3	3.14	1.3	3.29	4.07	17.78
SRFA9	4.0	1.69	0.0033	11.9	3.15	1.3	3.32	4.27	12.11
SRFA10	4.0	1.69	0.0036	11.9	3.14	0.9	3.30	4.44	11.72
SRN2	4.0	1.69	0.0037	12.1	3.14	0.8	3.27	4.01	14.26
SRN3	4.0	1.69	0.0037	12.0	3.14	1.1	3.31	3.81	12.61
SRN4	4.0	1.69	0.0036	12.1	3.14	0.9	3.30	4.83	12.23
SRN5	3.8	1.69	0.0037	11.5	3.15	0.7	3.30	4.98	11.34
SRN6	4.1	1.69	0.0033	12.2	3.13	1.5	3.28	4.19	13.39
SRN7	4.0	1.69	0.0033	12.0	3.14	1.2	3.26	4.54	11.88
$FeAsO_4(s)^e$	4.0	1.69	0.0029	12.0	3.14	1.7	3.32	4.21	12.01

Abbreviations: Suwannee River OM (SRN), Suwannee River Fulvic Acid (SRFA), coordination number (CN), bond distance (R), Debye-Waller factor (σ^2), edge energy (ΔE_0) and goodness of fit (F_i).

Conservative confidence limits on obtained distances and coordination numbers were estimated by varying each parameter in a step-wise fashion away from its optimal value, while varying all other parameters until $\Delta\chi^2$ increased 1.0 above its minimum value. This resulted in the following confidence limits: CN_{As-O} : ± 0.3 ; CN_{As-Fe} : ± 0.5 ; R_{As-O} : ± 0.01 ; R_{As-Fe} : ± 0.06 . The contribution from the As-Fe path was evaluated by means of the F-test, and when included in the fits it contributed at a confidence level between 50%-95%.

^a The amplitude reduction factor (S_0^2) was fixed at 1.0 in all fits.

^b σ^2 (Å²) was correlated to $2 \times \sigma^2$ of the As-O path.

^c CN was correlated to 3×CN of the As-O path according to the triple degeneracy of the As-O-O multiple scattering path.

^d σ^2 ($\text{\AA}^2$) fixed at 0.0080 based on the average obtained by fitting SRFA7, 8 and SRN 6 (i.e. samples with strong a As-Fe contribution) treating σ^2 as a variable.

^e In this fit σ^2 was treated as a variable resulting in $\sigma^2=0.0075$ i.e. very close to 0.0080 used to fit the remaining spectra.

^f F_i is defined as $((\sum(k^3\chi_{\text{exp}} - k^3\chi_{\text{fit}})^2)/(\sum(k^3\chi_{\text{exp}})^2)) \times 100$, $k^3\chi_{\text{exp}}$ and $k^3\chi_{\text{fit}}$ represents experimental and fitted data points, respectively.

3.3 X-ray absorption spectroscopy: The Fe K-edge

3.3.1 Qualitative XANES, EXAFS and wavelet transform analysis

As compared to the As K-edge EXAFS spectra of the As(V)-Fe(III)-SRFA/SRN samples, which were composed of free arsenate and arsenate associated with Fe(III), the corresponding Fe K-edge data were more complicated due to the presence of additional binary mononuclear Fe(III)-SRFA/SRN complexes as well as precipitated Fe(III) (hydr)oxides. These two species have previously been identified in the binary Fe(III)-SRN system where the mononuclear Fe(III)-SRN complexes were shown to be favored at low pH and low total Fe concentration whereas Fe(III) (hydr)oxides formed at high pH and high total Fe (Karlsson and Persson, 2012). This is in agreement with the binary Fe(III)-SRFA samples studied herein as will be further discussed in this section and 3.3.2. Thus, the compositional differences between SRN and SRFA seem to have minor effects on the interactions with Fe(III). These Fe(III)-OM interactions are also similar to those previously investigated in Pahokee Peat Humic Acid (PPHA) (Mikutta and Kretschmar, 2011, Sharma et al., 2010 and Sharma et al., 2011); a comparison between the SRN and PPHA materials is provided in Karlsson and Persson (2012).

The complexity of the Fe speciation was expressed as substantial variation in the Fe-XANES spectra of the As(V)-Fe(III)-SRFA/SRN samples (Fig. 7). At low total Fe concentrations and/or high Fe:As ratios the 1st derivative spectra were similar to that of the Fe(III)-OM reference displaying one rather broad and featureless peak (e.g. Fig. 7d, i, p and u). Increasing the total concentrations at 1:1 Fe:As ratios resulted in development of peaks at 7124 and 7136 eV (e.g. Fig. 7f, q, and s). The former was present in both FeAsO₄(s) and ferrihydrite whereas the latter was more pronounced in FeAsO₄(s), thus, when both peaks grew in concomitantly they indicated formation of FeAsO₄(s). These results were consistent with the observations made from the IR and As-EXAFS data indicating the formation of FeAsO₄(s) at high total concentrations. A variation in pH from low to high seemed to induce transformation from predominantly FeAsO₄(s) to increasingly more Fe(III) (hydr)oxide (Fig. 7a-c and m-o).

Figure 7. First derivative Fe K-edge XANES spectra of A) As(V)-Fe(III)-SRN, and B) As(V)-Fe(III)-SRFA samples together with spectra of reference compounds: a) SRN3, b) SRN 4, c) SRN7, d) SRN1, e) SRN2, f) SRN4, g) SRN5, h) SRN4, i) SRN6, j) SRN ref3, k) ferrihydrite, l) FeAsO₄(s), m) SRFA4, n) SRFA5, o) SRFA6, p) SRFA2, q) SRFA9, r) SRFA3, s) SRFA10, t) SRFA5, u) SRFA7, and v) SRFA ref2. For detailed sample characteristics see Table 1 and 2. Spectra a-c and m-o display the effect of pH at 1:1 Fe:As ratio and 22 916 (SRN) or 26 945 ppm Fe (SRFA), respectively, spectra d-f and r-s display the effect of concentration at pH 5, spectra p-q display effect of concentration at pH 3, and spectra g-i and t-u display the effect of Fe:As ratio at constant Fe concentration at pH 5. Spectra of reference compounds are displayed in j-l and v. The vertical dashed lines are for visual guidance.

The complexity of the Fe K-edge EXAFS data of the As(V)-Fe(III)-SRFA/SRN samples was further expressed in the Fourier transforms of the k^3 -weighted EXAFS spectra (Fig. 8-10) as well as the WT contour plots (Fig. 11 and Fig. A7, Supplementary data). Beyond the invariant first shell peak the Fourier transforms displayed large variations in the set of low amplitude peaks between 2-4 Å as a function of experimental conditions. These higher shell features were resolved in the WT:s and compared to the binary Fe(III)-SRFA/SRN systems in Fig. 11. The binary Fe(III)-SRFA system has not previously been studied, but the WT results indicated that it followed the same general pattern as identified for Fe(III)-SRN (Karlsson and Persson, 2012). At low pH and/or low Fe concentration the dominant WT features were contributions from C/O single scattering at ca. (3 Å⁻¹, 2.3 Å) and multiple scattering from C/O at ca. (3 Å⁻¹, 3.5 Å) (Fig. 11d, e, j and k), which indicated the presence of mononuclear Fe(III)-SRFA complexes formed via coordination to carboxyl groups (Karlsson and Persson, 2012). Increased pH and/or total Fe concentration resulted in additional WT features at ca. (7 Å⁻¹, 3 Å) indicative of Fe-Fe scattering and thus formation of Fe(III) (hydr)oxides (Fig. 11f and l) (Karlsson et al., 2008; Karlsson and Persson, 2010 and 2012). The addition of arsenate had a large impact on the Fe-WT contour plots. At a 1:1 Fe to As ratio and a Fe concentration

of 26 945 ppm a new WT feature appeared at 6-10 Å⁻¹ indicative of a heavy backscattering atom (c.f. Fig. 11g). According to the As-EXAFS results (Fig. 3 and 4, and Table 3) this sample (SRFA4) contained substantial amounts of FeAsO₄(s), thus the feature in Fig. 11g was assigned to Fe-As scattering; this is also in agreement with the Fe-XANES results (Fig. 7m). Note that Fe-Fe and Fe-As scattering resulted in quite similar WT features and can be difficult to separate, although the latter was shifted to slightly greater *k*-values (c.f. ferrihydrite Fig. 11a and FeAsO₄(s) Fig. 11b). When pH was increased at a fixed 1:1 Fe to As ratio the Fe-As signal decreased and at pH 6.5 it was not detectable (Fig. 11g-i). This contrasted the As-EXAFS results that indicated an almost constant contribution from FeAsO₄(s) (Fig. 3 and 4, and Table 3). We explain these seemingly conflicting results with destructive interference between Fe-As and Fe-Fe paths, which should be more prevalent at higher pH values favoring the conversion of mononuclear Fe(III)-SRFA/SRN complexes into Fe(III) (hydr)oxides, which was also indicated in the Fe-XANES spectra (Fig. 7m-o). Indeed, theoretically generated Fe-As and Fe-Fe paths at distances in the range of values obtained from the shell-by-shell fitting (see below) showed substantial destructive interference in the *k*-range of the experimental data (*k* = 2.8-12.5 Å⁻¹) (Fig. A8, Supplementary data). A final remark concerning the Fe-WT results was that also in this data set we observed an increased Fe-As interaction at increasing concentrations and fixed ratio and pH (Fig. 11m-o). In particular, the comparison between samples SRFA ref4 and SRFA5 prepared in absence and presence of arsenate, respectively, but otherwise under the same conditions, showed that back-scattering from heavy atoms increased in presence of arsenate (Fig. 11k and n). Since this difference most likely was due to Fe-As interactions it corroborated the trend towards increased contribution from the Fe-As interaction with increasing total Fe(III) and arsenate concentrations.

Figure 8. A) k^3 -weighted Fe-EXAFS spectra and B) the corresponding Fourier transforms of representative samples displaying the effect of pH for As(V)-Fe(III)-SRN samples with Fe:As=1 and [Fe]=22 916 ppm at a) pH 3.2 (SRN3), b) pH 5.3 (SRN4), c) pH 7.0 (SRN7), and As(V)-Fe(III)-SRFA samples with Fe:As=1 and [Fe]=26 945 ppm at d) pH 3.0 (SRFA4), e) pH 5.1 (SRFA5), and f) pH 6.5 (SRFA6). Black lines represent experimental data and red lines fit results. The vertical dashed line is for visual guidance.

Figure 9. A) k^3 -weighted Fe-EXAFS spectra and B) the corresponding Fourier transforms of representative samples displaying the effect of concentration for As(V)-Fe(III)-SRN samples with Fe:As=1 at pH 5 according to a) 6485 ppm Fe (SRN1), b) 11 971 ppm Fe (SRN2), c) 22 916 ppm Fe (SRN4), and for As(V)-Fe(III)-SRFA samples with Fe:As=1 at pH 3 at d) 13 473 ppm Fe (SRFA2), e) 26 945ppm Fe (SRFA4), f) 67 243 ppm Fe (SRFA9), and at pH 5 at g) 13 473 ppm Fe (SRFA3), h) 26 945ppm Fe (SRFA5), and i) 67 243 ppm Fe (SRFA10). Black lines represent experimental data and red lines fit results. The vertical dashed lines are for visual guidance.

Figure 10. A) k^3 -weighted Fe-EXAFS spectra and B) the corresponding Fourier transforms of representative samples displaying the effect of the Fe(III) to As(V) ratio for As(V)-Fe(III)-SRN samples at 22 916 ppm Fe and pH 5.0-5.3 at a) Fe(III):As(V)=0.5 (SRN5), b) Fe(III):As(V)=1.0 (SRN4), c) Fe(III):As(V)=4.0 (SRN6), and for As(V)-Fe(III)-SRFA samples at 26 945 ppm Fe and pH 5.1 at d) Fe(III):As(V)=1.0 (SRFA5), and e) Fe(III):As(V)=4.0 (SRFA7). Black lines represent experimental data and red lines fit results. The vertical dashed line is for visual guidance.

586 **Figure 11.** High resolution Fe-WT modulus ($\eta=4$, $\sigma=2$) between $k=2-12\text{ \AA}^{-1}$ (x-axis) and
587 $R=2-4\text{ \AA}$ (y-axis) of k^3 -weighted EXAFS spectra of reference compounds a) 6L-ferrihydrite
588 (Karlsson and Persson, 2012), b) $\text{FeAsO}_4(\text{s})$, c) , and of
589 Fe(III)-SRFA samples displaying the effect of pH at 26 945 ppm Fe in SRFA in absence of

As(V) at: d) pH 2.8, e) pH 4.9, f) pH 6.5; in presence of As(V) at 1:1 Fe(III):As(V) ratio at: g) pH 3.0 (SRFA4), h) pH 5.1 (SRFA5), i) pH 6.5 (SRFA6); displaying the effect of concentration at pH 5 in SRFA in absence of As(V) at: j) 13 473 ppm Fe, k) 26 945 ppm Fe, l) 67 243 ppm Fe; in presence of As(V) at 1:1 Fe(III):As(V) ratio and pH 5 at: m) 13 473 ppm Fe (SRFA3), n) 26 945 ppm Fe (SRFA5), and o) 67 243 ppm Fe (SRFA10).

3.3.2 Quantitative shell-by-shell Fe EXAFS fits

The binary Fe(III)-SRFA/SRN samples were composed of either mononuclear Fe(III)-SRFA/SRN complexes only or a mixture between these complexes and Fe(III) (hydr)oxides (Table 4), whereas EXAFS spectra of the ternary samples should contain additional effects from Fe-As interactions. We can thus assume that observed variations in the Fe EXAFS spectra were caused by differences in the relative proportions of $\text{FeAsO}_4(\text{s})$, Fe(III)-SRFA/SRN complexes and Fe(III) (hydr)oxides. Based on this basic assumption we have used a shell-by-shell fit strategy including sets of scattering paths characteristic of each of these three components (see Table 4 and Table A7, Supplementary data). A general observation from the obtained fit results was that under all conditions probed we observed Fe(III)-SRFA/SRN complexes while the contributions from $\text{FeAsO}_4(\text{s})$ and Fe(III) (hydr)oxides varied substantially. This high stability of the Fe(III)-SRFA/SRN complexes was in line with recent findings on Fe-OM interactions (Ilina et al., 2013; Neubauer et al., 2013; Sundman et al., 2014). At sufficiently low pH and/or total Fe concentrations no Fe(III) (hydr)oxides were observed, and the $\text{CN}_{\text{Fe-As}}$ and $\text{CN}_{\text{Fe-C}}$ displayed the trends expected from the As EXAFS results. At 1:1 Fe to As ratio and low total concentrations we obtained low coordination numbers of the Fe-As path; $\text{CN}_{\text{Fe-As}}=0.5$ (SRFA2) and $\text{CN}_{\text{Fe-As}}=0.2$ (SRN1). At higher total concentrations and low pH, but still 1:1 ratio, this coordination number increased to 1.3 (SRFA4) and 1.2 (SRN3), and concomitantly $\text{CN}_{\text{Fe-C}}$ decreased by roughly 15-20 % as compared to the reference samples (SRFA ref3 and SRN ref4). Hence, at higher

616 concentrations more Fe(III) was reactive towards arsenate and converted from Fe(III)-
 617 SRFA/SRN complexes to As-containing phases.
 618
 619 The appearance of Fe(III) (hydr)oxides in the spectra of the As(V)-Fe(III)-SRFA/SRN
 620 samples coincided approximately with their formation in the binary systems (Table 4).
 621 However, from the current data it was not possible to exactly pin-point the formation of the
 622 (hydr)oxides, and there were indications of Fe-Fe interactions also at 22 916-26 970 ppm Fe
 623 and pH 3.0-3.2 (SRN3 and SRFA4) although too weak to model as indicated by F-tests. In
 624 samples where Fe-Fe paths were detected it was difficult to distinguish any definitive trends
 625 partly because the strong correlations between CN and R of the Fe-Fe paths as well as of
 626 parameters of Fe-O, Fe-C and Fe-As (correlation factors in the range of |0.5-0.8|). Thus, in
 627 the presence of Fe(III) (hydr)oxide the fit values should be interpreted with caution and
 628 mainly be used as indicators for the presence of the respective species. The strong correlations
 629 between the Fe-Fe and Fe-As paths explained the decreased FT and WT amplitudes when pH
 630 was increased in 1:1 ratio samples (Fig. 8 and 11). These decreased amplitudes were
 631 accompanied with decreasing Fe-As and increasing corner-sharing Fe-Fe distances (SRFA6
 632 and SRN7, Table 4). Whether this was a real structural effect or caused by the strong
 633 interference between the paths could not be ascertained but it is in agreement with a change of
 634 the Fe speciation predicted by the chemical equilibrium models presented below (section 3.4).
 635 One obvious trend, though, was the effect of increasing Fe:As ratio on the relative
 636 contribution from FeAsO₄(s) and Fe(III) (hydr)oxide to the EXAFS spectra. At a 1:2 ratio
 637 (SRN5) the (hydr)oxide was suppressed and the fit yielded a high CN_{Fe-As}, but at 4:1 ratios
 638 (SRFA7 and SRN6) the contribution from FeAsO₄(s) was negligible and the spectra were
 639 dominated by Fe(III)-SRFA/SRN and Fe(III) (hydr)oxide. Note that the opposite trend was
 640 observed for the As-EXAFS spectra. Here the contribution from FeAsO₄(s) increased at

higher ratios because the fraction of this As species increased with respect to the total As concentration in the sample (Fig. 5 and Table 3).

Table 4

k^3 -weighted Fe K-edge EXAFS fit results of binary Fe(III)-SRFA/SRN (ref1-6) and ternary As(V)-Fe(III)-SRFA/SRN (SRFA2-10; SRN1-7) samples. The table only includes single-scattering higher shell paths; for complete models see Table A7, Supplementary data.

Sample	Fe-C		Fe-As		Fe-Fe			
	CN	R (Å)	CN	R (Å)	CN	R(Å)	CN	R (Å)
SRFA ref1	2.3	2.87						
SRFA ref2	2.8	2.86						
SRFA ref3	2.3	2.90						
SRFA ref4	2.4	2.87			0.6	3.05	0.4	3.51
SRFA ref5	2.1	2.87			1.1	3.06	0.7	3.49
SRFA ref6	1.8	2.89			1.3	3.06	0.7	3.49
SRFA2	2.2	2.89	0.50	3.30				
SRFA3	2.4	2.88	0.74	3.33				
SRFA4	1.9	2.92	1.30	3.32				
SRFA5	2.3	2.87	0.80	3.26	1.0	3.07	0.2	3.42
SRFA6	1.9	2.90	0.45	3.19	0.4	3.05	0.7	3.58
SRFA7	2.8	2.86			0.4	3.06	0.9	3.51
SRFA9	1.8	2.84	1.17	3.31	0.9	3.04	0.3	3.40
SRFA10	1.9	2.88	0.93	3.31	1.0	3.06	0.4	3.53
SRN ref1	2.5	2.90						
SRN ref2	3.0	2.90						
SRN ref3	2.9	2.88						
SRN ref4	2.7	2.93						
SRN ref5	2.9	2.92			0.4	3.11	0.6	3.46
SRN ref6	2.4	2.89			0.8	3.07	0.6	3.47

SRN1	2.6	2.87	0.24	3.26				
SRN2	2.5	2.87	0.60	3.30				
SRN3	2.3	2.95	1.16	3.33				
SRN4	2.4	2.87	0.55	3.26	1.1	3.06	0.5	3.35
SRN5	2.0	2.92	1.32	3.34				
SRN6	2.5	2.83			0.7	3.01	0.1	3.52
SRN7	2.2	2.88	0.61	3.22	0.2	3.07	0.6	3.63

Abbreviations: Suwannee River NOM (SRN), Suwannee River Fulvic Acid (SRFA), coordination number (CN) and bond distance (R).

3.4 Chemical equilibrium modeling

The chemical equilibrium models developed were based on the collective experimental results of this study together with literature data. The formation constant of poorly crystalline $\text{Fe}(\text{OH})_3(\text{s})$ (ferrihydrite) was according to Liu and Millero (1999), and no attempt was made to adjust this constant. In contrast, the formation constant of amorphous $\text{FeAsO}_4(\text{s})$ was regarded as an adjustable parameter due to the absence of reliable solubility measurements under similar experimental conditions (i.e. high concentrations of $\text{Fe}(\text{III})$ and $\text{As}(\text{V})$, high ionic strength and presence of OM which may affect particle size (Mikutta et al., 2008) and solubility (Karlsson and Persson, 2010)). Previous studies have reported $\log K_{\text{sp}}$ for amorphous $\text{FeAsO}_4(\text{s})$ in the range -23.0 to -23.3 (Langmuir et al., 2006, Nordstrom and Archer, 2003) and these were in good agreement with our optimized value; note that the apparent big difference in the numerical values of the stability constants is caused by the use of different starting points (AsO_4^{3-} vs H_3AsO_4). The absence of spectroscopic evidence for Fe-Fe interactions in the $\text{Fe}(\text{III})$ -SRFA/SRN species implied mononuclear Fe complexes, and the initial assumption was the formation of $\text{Fe}(\text{III})$ -SRFA/SRN complexes with a 1:1 composition. The proton stoichiometry of the $\text{FeH}_x\text{SRFA}^{3-x}$ and $\text{FeH}_x\text{SRN}^{3-x}$ complexes was determined by testing different values for x. Attempts to add species with a 1:2 stoichiometry did not improve the fit to the experimental data. In total 83 points of spectroscopic

information were used in the evaluation of the equilibrium models (Table A5, Supplementary data), and the agreement with respect to the existence of particular complexes/phases between this information and the final models was better than 91% (Table A5, Supplementary data). We find this satisfactory considering the complexity of the two systems and the simplicity of the models.

3.4.1 The binary Fe(III)-SRFA and ternary As(V)-Fe(III)-SRFA systems

Among the Fe(III)-SRFA stoichiometries tested, the following reaction gave a good fit to the experimental data in the low pH range:

However, the concentration of this species in high-pH samples was predicted to be very low and in disagreement with the EXAFS results. Therefore, an additional species was added with the composition FeSRFAH_{-2}^- :

These two reactions with the corresponding equilibrium constants ($\log\beta_{-3,1,0,1} = -0.33$; $\log\beta_{-4,1,0,1} = -6.42$;) were in good agreement with the EXAFS results, i.e. $[\text{FeSRFAH}_{-1}] + [\text{FeSRFAH}_{-2}^-]$ was formed to 100% of $[\text{Fe(III)}]_{\text{tot}}$ in SRFA ref1-3 while in samples SRFA ref 5-8 parts of the Fe was precipitated as ferrihydrite (Table A5, Supplementary data). The collective EXAFS results indicated that addition of arsenate (samples SRFA1 –SRFA10) generated Fe-As interactions in all samples except SRFA1 (Tables 4 and 5). According to our model, under the present experimental conditions and with a Fe to As ratio of 1:1, $\text{FeAsO}_4(\text{s})$

695 was the only solid phase present with $\text{pH} \leq 5.2$ and $[\text{Fe(III)}]_{\text{tot}} = 22 \text{ mM}$ (SRFA2 and 3).
 696 Thus, the Fe-As interactions from the spectroscopic measurements were explained by the
 697 formation of a thermodynamically favored $\text{FeAsO}_4(\text{s})$ phase. At higher $[\text{Fe(III)}]_{\text{tot}}$ the EXAFS
 698 spectra indicated the presence of Fe(III) (hydr)oxides (SRFA5 – 10). However, the
 699 equilibrium calculations suggested that this compound was substantially more insoluble than
 700 ferrihydrite. The stabilization of Fe(III) (hydr)oxides in systems with arsenate or phosphate
 701 has been reported earlier. Majzlan (2011) assumed that the adsorption of arsenate onto
 702 ferrihydrite occurs at the bulk of the nanoparticles, similar to a solid solution. Thibault et al.
 703 (2009) concluded from X-ray and Mössbauer spectroscopy of analogous Fe(III)-phosphate
 704 samples that P was specifically incorporated within the nanoparticle structure rather than
 705 complexing to the nanoparticle surface. They proposed a solid solution between ferrihydrite
 706 and an end-member of phosphate-rich ferrihydrite with a limiting P:Fe ratio of 1:2.
 707 Including the end-member $\text{Fe(OH)}_{1.5}(\text{AsO}_4)_{0.5}(\text{s})$, and $\log \beta_{-3,1,0.5,0}(\text{Fe}^{3+} + \text{H}_3\text{AsO}_4 \rightleftharpoons$
 708 $\text{Fe(OH)}_{1.5}(\text{AsO}_4)_{0.5}(\text{s}) + 3\text{H}^+ = 0.2)$ and $\log \beta_{-3,1,1} = 3.0$ for $\text{FeAsO}_4(\text{s})$ resulted in
 709 precipitation of $\text{FeAsO}_4(\text{s})$ and/or $\text{Fe(OH)}_{1.5}(\text{AsO}_4)_{0.5}(\text{s})$ in agreement with the Fe-As
 710 interactions detected by EXAFS in the SRFA samples. The solid solution phase
 711 $\text{Fe(OH)}_{1.5}(\text{AsO}_4)_{0.5}(\text{s})$ was predicted in samples SRFA 6 and 7. Furthermore, the total arsenate
 712 concentrations in solution determined from IR spectroscopy in samples SRFA IR6-8 were
 713 12.2, 9.4 and 12.3 mM, which agree reasonably well with the calculated values 9.1, 8.6 and
 714 15.4 mM, respectively. Fig. 12 shows a distribution diagram calculated from the presented
 715 model illustrating chemical speciation at a 4:1 Fe(III) to As(V) ratio.

Figure 12. Distribution diagram for 36.7 mM Fe(III), 9.0 mM As(V) and 38 mM dicarboxylic acid groups from the active fraction of carboxylic acid groups in SRFA. These conditions correspond to the SRFA7 sample (pH=5.1).

The model predicts precipitation/dissolution reactions following the sequence

$\text{FeAsO}_4(\text{s})$: $\text{Fe}(\text{OH})_{1.5}(\text{AsO}_4)_{0.5}(\text{s})$: $\text{Fe}(\text{OH})_3(\text{s})$ as a function of increasing pH. In accordance with As-EXAFS fit results (Table 3) that showed increased As-Fe interactions at increasing Fe(III):As(V) ratio, the thermodynamic model predicted that As speciation under these conditions was dominated by $\text{FeAsO}_4(\text{s})$ and $\text{Fe}(\text{OH})_{1.5}(\text{AsO}_4)_{0.5}(\text{s})$ with low $[\text{As}(\text{V})]_{\text{tot sln.}}$.

According to the model, the As-Fe detected in sample SRFA 7 (Table 3) should originate from the latter solid phase. Interestingly, the model predicted a slight increase in $[\text{As}(\text{V})]_{\text{tot sln.}}$ at the transition between $\text{FeAsO}_4(\text{s})$ and $\text{Fe}(\text{OH})_{1.5}(\text{AsO}_4)_{0.5}(\text{s})$. Thus, the IR spectroscopic

results suggesting a weak minimum of the bound As(V) fraction around pH 5 (Fig. 2) might indicate this transition.

3.4.2 The binary Fe(III)-SRN and ternary As(V)-Fe(III)-SRN systems

The initial model assumptions regarding the formation constants of $\text{Fe}(\text{OH})_3(\text{s})$, $\text{FeAsO}_4(\text{s})$ and $\text{Fe}(\text{OH})_{1.5}(\text{AsO}_4)_{0.5}(\text{s})$ were the same as in the corresponding SRFA system. Furthermore, identical stoichiometries of the 1:1 Fe(III)-SRN species were assumed; i.e. FeSRNH_{-1} and FeSRNH_{-2} . With ($\log\beta_{-3,1,0,1} = -0.39$; $\log\beta_{-4,1,0,1} = -6.65$) a good agreement between the equilibrium model and the Fe(III)-SRN EXAFS results was obtained (Table A5, Supplementary data). The stability constants of the Fe(III)-SRN were also in agreement with those of Fe(III)-SRFA.

In the presence of arsenate, the model predictions were in agreement with the EXAFS data except for SRN4 and SRN9 (Table A5). Under the conditions in sample SRN4 the model predicted no $\text{Fe}(\text{OH})_{1.5}(\text{AsO}_4)_{0.5}(\text{s})$; i.e. no Fe-Fe interactions in contrast to the EXAFS results (Table 4). However, as can be seen in the distribution diagram (Fig. 13) these experimental conditions were close to the onset of precipitation of $\text{Fe}(\text{OH})_{1.5}(\text{AsO}_4)_{0.5}(\text{s})$. Thus, a very small increase in pH or a decrease in the solubility of this phase would increase the amount of the mixed phase. For SRN9, the model predicted $\text{Fe}(\text{OH})_{1.5}(\text{AsO}_4)_{0.5}(\text{s})$, which is in contrast to the EXAFS results that suggested the formation of $\text{FeAsO}_4(\text{s})$. As previously discussed, the strong correlations between the EXAFS fit parameters make it difficult to exactly pin-point where a certain phase starts to form, furthermore, small changes in pH influence the solubility of the two As(V) containing phases. The performance of the equilibrium model was also checked against the quantitative IR results and the experimental concentrations of total

arsenate in solution 9.0, 10.7 and 13.8 mM in samples SRN IR10, 1 and 5, respectively, were reasonably matched by the model predictions of 13.0, 11.0 and 13.2 mM, respectively.

The distribution diagram calculated at high total concentrations and 1:1:1.3 ratio of Fe(III):As(V):SRN illustrated that the free arsenate in solution was regulated by the formation of $\text{FeAsO}_4(\text{s})$ and $\text{Fe}(\text{OH})_{1.5}(\text{AsO}_4)_{0.5}(\text{s})$. Approximately 10 mM Fe(III)-SRN complexes existed within the studied pH range which also affected As(V) concentration in solution. The existence of these complexes over a broad pH interval was in general agreement with the large stability of these complexes as shown by the Fe-EXAFS results presented herein and in a previous study (Karlsson and Persson, 2012). However, from the $\text{CN}_{\text{Fe-C}}$ of samples prepared in absence and presence of As(V) (Table 4) we would expect a larger contribution from Fe(III)-SRN in presence of As(V). This discrepancy between the model and the EXAFS results could be caused by several factors. Generally, EXAFS CNs are associated with large errors and in the present system the CN and distances of various paths were also strongly correlated which added further uncertainties to these numbers. Furthermore, in the EXAFS model Fe-C was treated as one coordination shell, however, it is likely that this consists of several sub-species with different Fe-C coordination numbers, which would make the interpretation of an average Fe-C coordination number difficult. It is also likely that the equilibrium model assumption involving only one 1:1 Fe(III)-SRN complex is too simplistic and fails to capture the actual distribution between Fe(III)-SRN and $\text{FeAsO}_4(\text{s})$. Interestingly, the EXAFS results indicated a decrease in $\text{CN}_{\text{Fe-As}}$ with increasing pH (Tables 4 and 5, SRN3 and 4). This followed the equilibrium model predictions and also indicated that the SRN4 sample was prepared in the vicinity of $\text{Fe}(\text{OH})_{1.5}(\text{AsO}_4)_{0.5}(\text{s})$ precipitation, c.f. Fig. 13.

Figure 13. Distribution diagram for 58 mM Fe(III), 58 mM As(V) and 76 mM dicarboxylic acid groups from the active fraction of carboxylic acid groups in SRN. These conditions correspond to the SRN3 and SRN4 samples (pH=3.2 and pH=5.3, respectively).

The spectroscopic samples as well as the equilibrium models were evaluated at total concentrations substantially higher than those typically found in natural environments. Still, the presented results have implications also for these environments, as the models can be used to make predictions about the speciation at lower total concentrations. Calculations based on input concentrations from 14 boreal streams (Neubauer et al., 2013) indicated predominance of Fe(III)-OM complexes at the lowest pH-values, whereas ferrihydrite precipitated at higher pH values (Fig. 14). These general trends were in agreement with the experimental results presented by Neubauer et al. (2013). Furthermore, under these low As-conditions (8.5 nM), all As was predicted to be soluble. Thus, if Fe-As interactions occur these are likely to be

between arsenate and ferrihydrite surfaces as surface complexes were not included in the model. The formation of mononuclear ternary As(V)-Fe(III)-OM complexes is unlikely as these were shown not to exist at the optimized, high concentration conditions investigated in this study. In absence of surface complexes, our models predict that it is not until the As-concentrations approaches the μM range that precipitation of a solid $\text{Fe}(\text{OH})_{1.5}(\text{AsO}_4)_{0.5}(\text{s})$ occurs and thus As(V) is sequestered.

Figure 14. Distribution diagram calculated for $22 \mu\text{M}$ Fe, 8.5 nM As and $175.2 \mu\text{equiv}$ $\text{RCOO}^- \text{ L}^{-1}$.

4. Summary and conclusions

The collective results from this study have shown that interactions in the ternary As(V)-Fe(III)-SRFA/SRN systems were strongly influenced by pH, total concentrations and the ratios among the reactive species. In particular, the high stability of the Fe(III)-SRFA/SRN

complexes exerted a strong control on the speciation in these systems. The predominant species identified by means of infrared and EXAFS spectroscopy were mononuclear Fe(III)-SRFA/SRN complexes, Fe(III) (hydr)oxides and As-containing solids. The latter were favored by high total concentrations, and large Fe:As ratios, whereas pH only had a minor influence on the amount of As contained in solids within the studied range, pH 3.0-7.0. The experimental results also showed that at low concentrations the Fe(III)-SRFA/SRN complexes were sufficiently stable to prevent reaction with arsenate. The chemical equilibrium models developed corroborated the spectroscopic results and showed that the general spectroscopic trends were reproduced by invoking formation constants of the Fe(III)-SRFA/SRN complexes and solubility products of the solid phases. These models also indicated that arsenate was distributed over two solid phases, namely $\text{FeAsO}_4(\text{s})$ and $\text{Fe}(\text{OH})_{1.5}(\text{AsO}_4)_{0.5}(\text{s})$. Thus, neither ternary As(V)-Fe(III)-SRFA/SRN complexes nor As(V) surface complexes on Fe(III) (hydr)oxides were necessary to explain the spectroscopic results or as components in the equilibrium models under the experimental conditions studied herein. Our results imply that at lower concentrations prevalent in natural environments the Fe(III)-OM species are either unreactive towards arsenate or, in presence Fe(III) (hydr)oxides associated with the OM, aqueous arsenate may be captured as surface complexes. Furthermore, in OM-rich environments and at typical Fe and As concentrations the formation of mononuclear ternary As(V)-Fe(III)-OM species is unlikely due to the high stability of the Fe(III)-OM complexes.

5. Acknowledgement

This manuscript was substantially improved by the comments and suggestions provided by the associate editor and two anonymous reviewers. Portions of the 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.

830 Department of Energy Office of Science by Stanford University. The SSRL Structural
831 Molecular Biology Program is supported by the DOE Office of Biological and Environmental
832 Research, and by the National Institutes of Health, National Institute of General Medical
833 Sciences (including P41GM103393) and the National Center for Research Resources
834 (P41RR001209). The contents of this publication are solely the responsibility of the authors
835 and do not necessarily represent the official views of NIGMS, NCRR or NIH. The vibrational
836 spectroscopy platform at the Chemical Biological Center at Umeå University is
837 acknowledged for use of the Bruker Vertex 80 instrument for IR measurements. Dan Boström
838 is acknowledged for X-ray diffraction analysis of the amorphous ferric arsenate, and
839 Kristoffer Hagvall for help with the XAS data collection. This project was supported by the
840 Swedish Research council.

6. References

- Aiken G. R. (1985) Isolation and concentration techniques for aquatic humic substances. In Aiken G.R., McKnight D.M., Wershaw R.L., MacCarthy P. (Eds). Humic substances in soil, sediment and water: geochemistry and isolation. *Wiley-Interscience*, New York.
- Bauer M. and Blodau C. (2006) Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. *Sci. Total Environ.* **354**, 179-190.
- Bauer M. and Blodau C. (2009) Arsenic distribution in the dissolved, colloidal and particulate size fraction of experimental solutions rich in dissolved organic matter and ferric iron. *Geochim. Cosmochim. Acta* **73**, 529-542.
- Bowell R. J. (1994) Sorption of arsenic by iron oxides and oxyhydroxides in soils. *Appl. Geochem.* **9**, 279-286.
- Buschmann J., Canonica S., Lindauer U., Hug S. J. and Sigg L. (2005) Photoirradiation of dissolved humic acid induces arsenic(III) oxidation. *Environ. Sci. Technol.* **39**, 9541-9546.
- Buschmann J., Kappeler A., Lindauer U., Kistler D., Berg M. and Sigg L. (2006) Arsenite and arsenate binding to dissolved humic acids: Influence of pH, type of humic acid, and aluminum. *Environ. Sci. Technol.* **40**, 6015-6020.
- Catalano J. G., Park C., Fenter P. and Zhang Z. (2008) Simultaneous inner- and outer-sphere arsenate adsorption on corundum and hematite. *Geochim. Cosmochim. Acta* **72**, 1986-2004.
- Davies C. W. (1962) *Ion Association*. Butterworth, London.
- Dixit S. and Hering J. G. (2003) Comparison of arsenic (V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. *Environ. Sci. Technol.* **37**, 4182-4189.

- Dobran S. and Zagury G. J. (2006) Arsenic speciation and mobilization in CCA-contaminated soils: Influence of organic matter content. *Sci. Total. Environ.* **364**, 239-250.
- Eriksson G. (1979) An Algorithm for the computation of aqueous multicomponent, multiphase equilibria. *Anal. Chim. Acta* **112**, 375-383.
- Fendorf S., Eick M. J., Grossl P. and Sparks D. L. (1997) Arsenate and chromate retention mechanisms on goethite. 1. Surface structure. *Environ. Sci. Technol.* **31**, 315-320.
- Funke H., Scheinost A. C. and Chukalina M. (2005) Wavelet analysis of extended x-ray absorption fine structure data. *Phys. Rev. B* **71**, 1-7.
- González A. Z. I., Krachler M., Cheburkin A. K. and Shotyk W. (2006) Spatial distribution of natural enrichments of arsenic, selenium, and uranium in a minerotrophic peatland, Gola di Lago, Canton Ticino, Switzerland. *Environ. Sci. Technol.* **40**, 6568-6574.
- Grafe M., Eick M. J. and Grossl P. R. (2001) Adsorption of arsenate (V) and arsenite (III) on goethite in the presence and absence of dissolved organic carbon. *Soil Sci. Soc. Am. J.* **65**, 1680-1687.
- Grafe M., Eick M. J., Grossl P. R. and Saunders A. M. (2002) Adsorption of arsenate and arsenite on ferrihydrite in the presence and absence of dissolved organic carbon. *J. Environ. Qual.* **31**, 1115-1123.
- Hagvall K., Persson P. and Karlsson T. (2014) Spectroscopic characterization of the coordination chemistry and hydrolysis of gallium(III) in the presence of aquatic organic matter. *Manuscript submitted to Geochim. Cosmochim. Acta.*
- Hoffmann M., Mikutta C. and Kretzschmar R. (2013) Arsenite binding to natural organic matter: spectroscopic evidence for ligand exchange and ternary complex formation. *Environ. Sci. Technol.* **47**, 12165-12173.

- Ilna S. M., Poitrasson F., Lapitskiy S. A., Alekhin Y. V., Viers J. and Pokrovsky O. S. (2013) Extreme iron isotope fractionation between colloids and particles of boreal and temperate organic-rich waters. *Geochim. Cosmochim. Acta* **101**, 96-111.
- Karlsson M. and Lindgren J. (2006) *WinSGW, a user interface for SolGasWater*, www.winsgw.se.
- Karlsson T., Persson P., Skyllberg U., Mörtz C.-M. and Giesler R. (2008) Characterization of iron(III) in organic soils using extended X-ray absorption fine structure spectroscopy. *Environ. Sci. Technol.* **42**, 5449-5454.
- Karlsson T. and Persson P. (2010) Coordination chemistry and hydrolysis of Fe(III) in a peat humic acid studied by X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta* **74**, 30-40.
- Karlsson T. and Persson P. (2012) Complexes with aquatic organic matter suppress hydrolysis and precipitation of Fe(III). *Chem. Geol.* **322-323**, 19-27.
- Kitahama K., Kiriya R. and Baba Y. (1975) Refinement of the crystal structure of scorodite. *Acta Cryst.* **B31**, 322-324.
- Klementiev K. V. (2001) VIPER for Windows, freeware; K.V.Klementev. *J. Phys. D: Appl. Phys.* **34**, 209-17.
- Ladeira A. C. Q., Ciminelli V. S. T., Duarte H. A., Alves M. C. M. and Ramos A. Y. (2001) Mechanism of anion retention from EXAFS and density functional calculations: arsenic(V) adsorbed on gibbsite. *Geochim. Cosmochim. Acta* **65**, 1211-1217.
- Lagner P., Mikutta C. and Kretzschmar R. (2012) Arsenic sequestration by organic sulphur in peat. *Nat. Geosci.* **5**, 66-73.
- Langmuir, D., Mahoney, J. and Rowson J. (2006) Solubility products of amorphous ferric arsenate and crystalline scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) and their application to arsenic behavior in buried mine tailings. *Geochim. Cosmochim. Acta* **70**, 2942-2956.

- Lin H. T., Wang M. C. and Li G. C. (2004) Complexation of arsenate with humic substance in water extract of compost. *Chemosphere* **56**, 1105-1112.
- Liu X. and Millero F. J. (1999) The solubility of iron hydroxide in sodium chloride solutions. *Geochim. Cosmochim. Acta* **63**, 3487-3497.
- Loring J. S., Sandström M. H., Norén K. and Persson P. (2009) Rethinking arsenate coordination at the surface of goethite. *Chem. Eur. J.* **15**, 5063-5072.
- Majzlan J. (2011) Thermodynamic stabilization of hydrous ferric oxide by adsorption of phosphate and arsenate. *Environ. Sci. Technol.* **45**, 4726-4732.
- McArthur J. M., Banerjee D. M., Hudson-Edwards K. A., Mishra R., Purohit R., Ravenscroft P., Cronin A., Howarth R. J., Chatterjee A., Talukder T., Lowry D., Houghton S. and Chadha D. K. (2004) Natural organic matter in sedimentary basins and its relation to arsenic in anoxic groundwater: the example of West Bengal and its worldwide implications. *Appl. Geochem.* **19**, 1255-1293.
- Mikutta C., Frommer J., Voegelin A., Kaegi R. and Kretzschmar R. (2008) Effect of citrate on the local Fe coordination in ferrihydrite, arsenate binding, and ternary arsenate complex formation. *Geochim. Cosmochim. Acta.* **74**, 5574-5592.
- Mikutta C. and Kretzschmar R. (2011) Spectroscopic evidence for ternary complex formation between arsenate and ferric iron complexes of humic substances. *Environ. Sci. Technol.* **45**, 9550-9557.
- Mikutta C., Mandaliev P. N. and Kretzschmar R. (2013) New clues to the local atomic structure of the short-range ordered ferric arsenate from extended X-ray absorption fine structure spectroscopy. *Environ. Sci. Technol.* **47**, 3122-3131.
- Neubauer E., Köhler S. J., von der Kammer F., Laudon H. and Hofmann, T. (2013) Effect of pH and stream order on iron and arsenic speciation in boreal catchments. *Environ. Sci. Technol.* **47**, 7120-7128.

- Nordstrom D. K. and Archer D. G. (2003) Arsenic thermodynamic data and environmental geochemistry. In: Welch, A.H., Stollenwer, K. G., (Eds) *Arsenic in Ground Water*. Kluwer Academic Publishers, Boston, MA pp.1-25.
- Persson P. and Axe K. (2005) Adsorption of oxalate and malonate at the water-goethite interface: molecular surface speciation from IR spectroscopy. *Geochim. Cosmochim. Acta* **69**, 541-552.
- Pierce M. L. and Moore C. B. (1982) Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Water Res.* **16**, 1247-1253.
- Raven K. P., Jain A. and Loeppert R. H. (1998) Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes. *Environ. Sci. Technol.* **32**, 344-349.
- Redman A. D., Macalady D. L. and Ahmann D. (2002) Natural organic matter affects arsenic speciation and sorption onto hematite. *Environ. Sci. Technol.* **36**, 2889-2896.
- Ritter K., Aiken G. R., Ranville J. F., Bauer M. and Macalady D. L. (2006) Evidence for the aquatic binding of arsenate by natural organic matter (NOM)-suspended Fe(III). *Environ. Sci. Technol.* **40**, 5380-5387.
- Rothwell J. J., Taylor K. G., Ander E. L., Evans M. G., Daniels S. M. and Allott T. E. H. (2009) Arsenic retention and release in ombrotrophic peatlands. *Sci. Total Environ.* **407**, 1405-1417.
- Serkiz S. M. and Perdue E. M. (1990) Isolation of dissolved organic matter from the Suwannee River using reverse osmosis. *Water Res.* **24**, 911-916.
- Sharma P., Ofner J. and Kappler A. (2010) Formation of binary and ternary colloids and dissolved complexes of organic matter, Fe and As. *Environ. Sci. Technol.* **44**, 4479-4485.

- Sharma P., Rolle M., Kocar B., Fendorf S. and Kappler A. (2011) Influence of natural organic matter on As transport and retention. *Environ. Sci. Technol.* **45**, 546-553.
- Simeoni M. A., Batts B. D. and McRae C. (2003) Effect of groundwater fulvic acid on the adsorption of arsenate by ferrihydrite and gibbsite. *Appl. Geochem.* **18**, 1507-1515.
- Smedley P. L. and Kinniburgh D. G. (2002) A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **17**, 517-568.
- Sun L., Perdue E. M. and McCarthy J. F. (1995) Using reverse osmosis to obtain organic matter from surface and ground water. *Water Res.* **29**, 1471-1477.
- Sundman A., Karlsson T., Laudon H. and Persson P. (2014) XAS study of iron speciation in soils and waters from a boreal catchment. *Chem. Geol.* **364**, 93-102.
- Szytula A., Burewicz A., Dimitrijević Ž., Kraśnicki S., Rżany H., Todorović J., Wanic A. and Wolski W. (1968) Neutron diffraction studies of α -FeOOH. *Phys. Status solidi (b)* **26**, 429-434.
- Thanabalasingam P. and Pickering W. F. (1986) Arsenic sorption by humic acids. *Environ. Pollut.* **12**, 233-246.
- Thibault P.-J., Rancourt D. G., Evans R. J. and Dutrizac J. E. (2009). Mineralogical confirmation of a near-P:Fe = 1:2 limiting stoichiometric ratio in colloidal P-bearing ferrihydrite-like hydrous ferric oxide. *Geochim. Cosmochim. Acta* **73**, 364-376.
- Thurman E. M. and Malcolm R. L. (1981) Preparative isolation of aquatic humic substances. *Environ. Sci. Technol.* **15**, 463-466.
- Tufano K. J., Reyes C., Saltikov C. W. and Fendorf S. (2008) Reductive processes controlling arsenic retention: Revealing the relative importance of iron and arsenic reduction. *Environ. Sci. Technol.* **42**, 8283-8289.

- Wang S. and Mulligan C. N. (2006) Effect of natural organic matter on arsenic release from soils and sediments into groundwater. *Environ. Geochem. Health*. **28**, 197-214.
- Webb S. M. (2005) SixPack: a graphical user interface for XAS analysis using IFEFFIT. *Phys. Scr.* **T115**, 1011-1014.
- Weber F.-A., Hofacker A. F., Voegelin A. and Kretzschmar R. (2010) Temperature dependence and coupling of iron and arsenic reduction and release during flooding of a contaminated soil. *Environ. Sci. Technol.* **44**, 116-122.
- Xu H., Allard B. and Grimvall A. (1991) Effects of acidification and natural organic materials on the mobility of arsenic in the environment. *Water, Air, Soil, Pollut.* **57-58**, 269-278.
- Zabinsky S. I., Rehr J. J., Ankudinov A., Albers R. C. and Eller M. J. (1995) Multiple scattering calculations of X-ray absorption spectra. *Phys. Rev. B*, **52**, 2995-30.