Reactivity of Fe from a natural stream water towards As(V)

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ABSTRACT

Interactions between iron (Fe) and arsenic (As) play a vital role in aquatic and terrestrial ecosystems influencing the reactivity and transport of arsenic. A key aspect is the effect of natural organic matter (NOM) on these interactions, and previous investigations have reported the existence of ternary As-Fe-NOM species. In this study, the reactivity of Fe, from a boreal stream water, towards As(V) was investigated using Fe and As K-edge X-ray absorption spectroscopy (XAS). The native stream water was shown to contain mononuclear Fe-NOM complexes together with Fe(III) (hydr)oxides associated with the NOM. Addition of As(V) to this water at Fe to As ratios of 2.0-15.6 resulted in substantial changes in the Fe speciation; the Fe(III) (hydr)oxides were partly converted into $\text{FeAsO}_4(\text{s})$ or a solid solution where As(V) was incorporated into Fe(III) (hydr)oxide structures. Under the same conditions no or only small effects of As(V) on the Fe-NOM complexes initially present were observed, and the concurrent existence of these complexes and free As(V) showed that a large fraction of the Fe-NOM complexes were non-reactive towards As(V). This study suggests that complexation of Fe by NOM in organic rich environments may lead to elevated free, aqueous arsenic levels as these complexes do not interact with As(V). Moreover, the formation of Fe-NOM complexes also reduce the tendency of Fe to form reactive Fe(III) (hydr)oxides particles and Fe(III)-arsenate precipitates.

KEYWORDS: XAS, iron, arsenic, natural organic matter, stream water, Krycklan catchment

1. Introduction

Iron (Fe) plays a vital role in the environment by taking part in a variety of different processes such as redox and precipitation/dissolution reactions, as well as adsorption/desorption of nutrients and contaminants at Fe-bearing mineral surfaces (Borch et al., 2010). An important factor in these processes is the chemical form of Fe (i.e. the chemical speciation), and the Fe speciation is strongly influenced by interactions with microorganisms and natural organic matter (NOM) (Borch et al., 2010). As a result, Fe speciation in natural waters has received increased attention over the last years, e.g. Ingri et al. (2006), Kleja et al. (2012), Ilina et al. (2013), Neubauer et al. (2013), Sjöstedt et al. (2013) and Sundman et al. (2013, 2014a). A growing pool of evidence suggests that Fe speciation in oxygenated, aquatic systems can be divided into two main categories; organically complexed Fe(III)/Fe(II) and Fe(III) (hydr)oxides (Karlsson and Persson, 2012; Neubauer et al., 2013; Sjöstedt et al., 2013; Sundman et al., 2013, 2014a). The limited solubility of Fe(III) (hydr)oxides indicates that they should be the predominant form of Fe at environmentally relevant conditions, but these solid phases can be dissolved via complexation by NOM, and both Fe(III) and Fe(II) may be stabilized as organic complexes (Karlsson and Persson, 2010, 2012; Neubauer et al., 2013; Sundman et al., 2014a). Thus, NOM, together with pH, total Fe concentration and redox potential are among the most important factors controlling the speciation of Fe (Karlsson et al., 2008; Neubauer et al., 2013; Sundman et al., 2014a), and NOM also affects the structure of the Fe minerals formed (Mikutta, 2011). Furthermore, NOM is assumed to play an important role in the three component system As(III/V)-Fe(III)-NOM, where Fe often is assumed to act as a bridge between As and NOM (Hoffmann et al., 2013; Mikutta et al., 2010; Mikutta and Kretzschmar, 2011; Neubauer et al., 2013). These ternary phases are believed to contribute to the As-mobility in the environment (Mikutta et al., 2010; Sharma et

al., 2010; Mikutta and Kretzschmar, 2011). Most previous studies of ternary As(V)-Fe(III)-NOM systems have investigated Fe(III):As(V) molar ratios in the range from 10-30 (Sharma et al., 2010; Mikutta and Kretzschmar, 2011) to several hundred (Neubauer et al., 2013). Recently, we have shown that speciation in these ternary systems are very sensitive to the experimental conditions, and that high concentrations and Fe(III):As(V) ratios generally favor precipitation of $\text{FeAsO}_4(\text{s})$ or As(V)-containing Fe(III) (hydr)oxide (Sundman et al., 2014b). In order to better understand these systems it is thus important to probe a range of experimental conditions. In the present study, we have investigated the reactivity of aquatic Fe species towards As(V) in a natural stream water from the well-studied Krycklan Catchment (Laudon et al., 2011, 2013). This has been accomplished by adding increasing amounts of As(V) to the stream water while following the Fe and As speciation by means of As and Fe K-edge X-ray absorption spectroscopy (XAS). Two main questions were addressed: do the different Fe pools typically present in natural samples react differently towards elevated As concentrations, and are the Fe-NOM complexes sufficiently stable to prevent reaction with As(V)? The results from this study will also serve as an important link between the previously studied model systems and naturally occurring Fe-NOM species.

2. Experimental section

2.1 Chemicals and sample preparation

A 20 mM stock solution of As(V) was prepared by dissolving $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ($\geq 98\%$ Sigma) in Milli-Q water. The stock solution was adjusted to pH 5.7 by adding HCl yielding a final As(V) concentration of 18.82 mM. The stream water was collected from the C2 site, in December 2010, at the boreal Krycklan catchment, in northern Sweden (64° , $16'\text{N}$, 19° , $46'\text{E}$). C2 is a small stream surrounded by a forested landscape; for more information about the sampling site, see Buffam et al. (2007) and Laudon et al. (2011, 2013). The stream water

was collected in a thoroughly acid-washed polyethylene bottle, rinsed three times in the sampled stream, and filled under water to avoid air bubbles. Before sample preparation the pH of the natural stream water was measured, using a calibrated Mettler Toledo DGI 112-Pro combination electrode. 800 mL aliquots of the C2 stream water sample were transferred to four new acid-washed polyethylene bottles while maintaining an atmosphere of N₂ in the bottles. Three of these were spiked with As(V) to final Fe/As molar ratios of 15.6, 4.0 and 2.0, respectively. The As(V)-spiked samples were equilibrated, at room temperature, for 24 h prior to pre-concentration via addition of ion exchange resins (Dowex 1x8, chloride form, Sigma Aldrich), according to the experimental protocol described in Sundman et al. (2013). All samples were covered with aluminum foil and manually rotated on a regular basis for 5 days. The resins were separated from the stream water through centrifugation at 5000 rpm for 5 minutes and then transferred to 1.5 mL test tubes that were filled with N₂ (g). Finally, the resin samples were sealed with plastic film, covered with aluminum foil and refrigerated until XAS analysis. Aliquots for total organic carbon (TOC), Fe and As analyses were sampled before and after the adsorption onto the resins. TOC was measured on a Shimadzu TOC-5000 and total concentrations of As and Fe were determined by a Perkin Elmer SCIEX ELAN DRC-e ICP-MS. The wet resin paste samples were mounted into Teflon sample holders and sealed with Kapton tape (CHR-Furon) at the XAS beamline. In addition to these samples, a 150 mM H₂AsO₄⁻ solution (Loring et al., 2009), 6489 ppm Fe complexed by Suwannee river NOM (SRN) at pH 5 with C/Fe molar ratio $\approx$ 85 (Karlsson and Persson, 2012), 6-line ferrihydrite (Karlsson and Persson, 2012), amorphous FeAsO₄(s) (Sundman et al., 2014b) and 1.8 μ mol/m² arsenate adsorbed on goethite at pH 5.3 (Loring et al., 2009) were used as XAS references for comparison with the stream water samples.

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2 **2.2 XAS data collection and analysis**

3 Fe and As K-edge spectra were collected at beamline 4-1 at the Stanford Synchrotron
4 Radiation Lightsource (SSRL), California, USA. SSRL was operated in top-up mode at 3.0
5 GeV beam energy and 300–350 mA ring current. The beamline was equipped with three
6 consecutive ion chambers to monitor the transmitted beam and one Lytle detector for
7 fluorescence measurements. The ion chambers were filled with N₂ (g) while the Lytle
8 detector contained Ar (g). A pair of silicon crystals ([2 2 0], $\Phi=90^\circ$) was used to
9 monochromatize the beam. XAS spectra were collected at room temperature in fluorescence
10 mode using the Lytle detector, and a 3 x Mn filter at the Fe-K edge and a 6 μ x Ge filter at the
11 As-K-edge were used to reduce unwanted elastic and inelastic scattering contributions. The
12 samples were aligned at 45° with respect to the incident beam and the hutch slit was set to 2 ×
13 12 mm. The spectrum of an Fe(0) or As(III) foil was recorded simultaneously during all
14 scans to allow for internal energy calibration. 12-29 spectra were recorded at the Fe K-edge
15 and 3-9 spectra at the As K-edge. The first-derivative XANES spectra of each individual scan
16 were carefully compared and indicated no beam-induced changes in any of the spectra. Each
17 spectra was energy calibrated and averaged using SixPack (Webb, 2005). X-ray absorption
18 near-edge structure (XANES) analysis was also performed in SixPack. To qualitatively
19 differentiate between different backscatters, wavelet transform (WT) analysis was performed
20 using an Igor Pro script (Funke et al., 2005); k -ranges between 3.0 to 12.0 Å⁻¹ and 3.0 to 13.4
21 Å⁻¹ were used for Fe-WT and As-WT analysis, respectively. Self-absorption was investigated
22 using Viper (Klementiev, 2001) by comparing the transmission and fluorescence spectra of
23 the same sample.

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Subsequent data processing followed the standard procedures in Viper (Klementiev, 2001). Pre- and post-edge functions were subtracted from the spectra, and the subtracted spectra were normalized. A spline function was used to subtract a background beyond the absorption edge. The obtained EXAFS spectra were analyzed over the same k -ranges as used in the Fe- and As-WT analyses, and the spectra were k^3 -weighted in order to enhance oscillations at higher k -values. Goethite (Szytula et al., 1968), scorodite (Kitahama et al., 1975) and trisoxalatoiron(III) (Persson and Axe, 2005) were used as input structures for the ab initio FEFF calculations (Zabinsky et al., 1995). The amplitude reduction factor (S_0^2) was set to 0.85 and 1.0 for the Fe and As K-edge spectra, respectively. These S_0^2 values were obtained from fitting spectra of reference compounds (aqueous trisoxalatoiron(III) and $\text{FeAsO}_4(\text{s})$) and fixing the coordination numbers to known values. The number of free variables was restricted by correlating the threshold energy (E_0) to be identical for all shells, by correlating coordination numbers and when available fixing the Debye-Waller factors (σ^2) to literature values. The limit for free variables, given by the Nyquist theorem ($N_{\text{max}} = 2 \times \Delta k \times \Delta R / \pi$, where Δk is the k -range of the extended X-ray absorption fine structure (EXAFS) spectrum and ΔR is the R -range of the Fourier transformed range), was never exceeded.

2.3 Thermodynamic equilibrium calculations

A distribution diagram describing the speciation in the ternary As(V)-Fe(III)-NOM system was obtained via modelling in WinSGW (Karlsson and Lindgren, 2006). The model was based on stability constants from our previous work (Sundman et al., 2014b). The input data consisted of the pH, Fe and active dicarboxylic acid concentrations analyzed in this work (pH and Fe concentration) or extrapolated from related data presented in Neubauer et al. (2013) (carboxylic acid concentration). The concentration of all soluble and solid species described

by the model were calculated under conditions where the As(V) concentration was increased from 0 μM to 15 μM while all other parameters were constant.

3. Results and discussion

Treatment of pure and As-spiked and equilibrated pH 5.5 C2 water, containing 29.7 μM Fe and 13.9 mg L^{-1} TOC, with anion-exchange resins resulted in ca. 65% of Fe and between 35-40% of TOC adsorption onto the resin particles irrespective of total As concentrations (Table 1). This showed that a large fraction of Fe was associated with negatively charged NOM. The extent of Fe adsorption was in line with previous studies (Sundman et al., 2013, 2014a), which also have shown that adsorption of Fe-NOM species onto the resins was partly selective favoring for example Fe(III)-NOM over Fe(II)-NOM. Concomitantly, the percentage of As adsorption remained constant at 85% in the As-spiked samples (Table 1) implying that the Fe to As molar ratio on the resins decreased with increasing As concentrations. This decrease in Fe to As molar ratio on the resins could be the result of changes in the stoichiometry of the adsorbed Fe-As-NOM species. Another likely explanation is that increasing total As concentrations leads to higher levels of free As(V) in solution and these negatively charged anions may therefore adsorb to the positively charged resins without being associated with NOM; this will be further discussed below. It follows that the non-adsorbed As fraction will either exist as free As(V) anions or associated with the non-adsorbed fraction of Fe-NOM, or other metal ions present in NOM.

Table 1. Adsorption of Fe, As and TOC from the stream water onto the ion-exchange resins.

Sample	Fe _{start} (μM) ¹	Fe _{adsorbed} (%)	As _{start} (μM)	As _{adsorbed} (%)	TOC _{start} (mg L^{-1})	TOC _{adsorbed} (%)
C2, native	29.7	62.0	0.02 ²	-	13.9	42.9
C2, Fe/As=15.6	29.7	64.5	1.9 ³	85.5	13.9	34.9
C2, Fe/As=4.0	29.7	61.3	7.5 ³	84.7	13.9	33.8

C2, Fe/As=2.0	29.7	66.8	15.0 ³	84.0	13.9	37.4
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The detection limits of Fe and As measurements were 0.04 and 0.004 M, respectively. The TOC detection limit was 1.0 mg L⁻¹.

¹Dilution caused by adding As(V)-stock solution was insignificant.

²Native arsenic concentration.

³Calculated arsenic concentration after spiking with As, but prior to adsorption to the resins.

Analysis of the first derivative As XANES spectra confirmed the conservation of the As(V) oxidation state in all resin samples, as shown by the maximum absorption at 11873.5-11874 eV (Mikutta and Kretzschmar, 2011) (Figure 1 I). Furthermore, the overall shape of these first derivative spectra were similar to that of aqueous H₂AsO₄⁻ suggesting that a fraction of the As(V) in the samples did not interact with the Fe-NOM species (Figure 1 I a-d). The first derivative Fe XANES spectra displayed a main edge between 7123.3-7123.9 eV indicating that Fe(III) was the predominating oxidation state (O'Day et al., 2004), and the ferrihydrite-like shapes suggested a substantial contribution from Fe(III) (hydr)oxides (Figure 1 IIj). Note however, that the shape of these first derivative spectra seemed to vary slightly with As(V) addition suggesting changes in Fe speciation. The Fe redox chemistry was analyzed in more detail via the weak pre-edge feature around 7112-7113 eV following the procedure of Wilke et al. (2001). The pre-edge centroids were in the range 7113.24-7113.44 eV and the integrated pre-edge intensities were 1.39-1.64. This, according to Wilke et al. (2001), indicated a predominance of 6-coordinated Fe(III), which was in agreement with the suggested contribution from a ferrihydrite-like material but was also consistent with Fe(III)-NOM complexes.

Figure 1. First derivative absorbance XANES spectra of **I**) As-edge data according to a) 150 mM H_2AsO_4^- solution (Loring et al., 2009), b) C2 stream water spiked to Fe/As=15.6, c) C2 stream water spiked to Fe/As=4.0, d) C2 stream water spiked to Fe/As=2.0, e) amorphous $\text{FeAsO}_4(\text{s})$ (Sundman et al., 2014b), and **II**) Fe-edge data according to f) 6489 ppm Fe SRN sample at pH 5 with C/Fe molar ratio ≈ 85 (Karlsson and Persson, 2012), g) native C2 stream water, h) C2 stream water spiked to Fe/As=15.6, i) C2 stream water spiked to Fe/As=2.0, j) 6L-ferrihydrite (Karlsson and Persson, 2012) and k) amorphous $\text{FeAsO}_4(\text{s})$. The vertical dashed lines are for visual guidance.

The As WT of the three As-spiked samples were similar (Fig. 2c-e) and displayed a maximum at ca. ($6 \text{ \AA}^{-1}$, $2.5 \text{ \AA}$). This has previously been shown to be characteristic of Fe backscatters (Sundman et al., 2014b), and the elongated shape resembles that of $\text{FeAsO}_4(\text{s})$ (Fig. 2b). These features were also in agreement with those of Fe(III)-As(V) solids formed in

synthetic As(V)-Fe(III)-NOM systems previously studied (Sundman et al., 2014b). In addition to signatures of As-Fe back-scattering, the As WTs of the C2 samples displayed high intensity regions at ca. ($3 \text{ \AA}^{-1}$, $2.5 \text{ \AA}$) and ($3 \text{ \AA}^{-1}$, $3.8 \text{ \AA}$) which were attributed to multiple scattering within the symmetric arsenate tetrahedron (Loring et al., 2009); these features were strong in the WT of the arsenate solution (Fig. 2f) while they were very weak or not detectable in WTs of surface complexes/solids in presence of strong Fe back-scattering (Fig. 2a and b). Noteworthy was the gradual increase of these arsenate multiple scattering features with increasing As(V) concentrations best seen at ($3 \text{ \AA}^{-1}$, $3.8 \text{ \AA}$) (Fig. 2c-e). This pointed to the presence of free As(V) on the resins at all conditions and that this fraction increased with increasing total As. Thus, free arsenate seemed to be present even at the highest Fe to As ratio employed in this study which suggests only a moderate reactivity of the Fe-NOM species towards As(V).

The Fe WTs of the C2 samples displayed strong features at ($2\text{-}4 \text{ \AA}^{-1}$, $2\text{-}2.5 \text{ \AA}$) which were characteristic of a single scattering Fe-C path, indicating Fe complexed to organic matter (Fig. 2i-l) (Karlsson et al., 2008; Karlsson and Persson, 2010, 2012). This Fe-C path was accompanied by Fe-C-O multiple scattering expressed as weaker features at ($2\text{-}4 \text{ \AA}^{-1}$, $3.2\text{-}4 \text{ \AA}$). In addition, the Fe WT of the native C2 sample also displayed signatures of Fe-Fe back scattering at ca. ($8 \text{ \AA}^{-1}$, $2.8 \text{ \AA}$) (Fig. 2k) (Karlsson and Persson, 2010, 2012). Hence, this sample contained the two pools of Fe identified by Karlsson and Persson (2012) and also previously detected in stream water samples from the field site studied in the present work (Neubauer et al., 2013; Sundman et al., 2013, 2014a). Addition of As(V) to the C2 sample had a substantial effect on the Fe WT, in particular the Fe-Fe feature was diminished (Fig. 2i-k). No clear signal from Fe-As back scattering was detected despite the As WT results that showed the existence of this path. These observations can be explained by destructive

1 interference between Fe-As and Fe-Fe paths in systems containing $\text{FeAsO}_4(\text{s})$ or solid
2 solutions of ferrihydrite and arsenate in combination with structural modification of the
3 Fe(III) (hydr)oxide caused by incorporating arsenate as shown in previous studies of
4 synthetic ternary As(V) - Fe(III) -NOM systems (Sundman et al., 2014b). The WT results thus
5 indicated that addition of As(V) induced phase transformation of the Fe(III) (hydr)oxides
6 associated with the NOM. In contrast, no or only very small effects on the scattering from the
7 organic structure were observed at elevated As concentration, suggesting that most of the
8 mononuclear Fe-NOM species were unaffected by addition of As(V) .

Arsenic

Iron

1

2 **Figure 2.** High resolution As-WT modulus of second and third coordination shells ($\eta=4$,
3 $\sigma=2$) for k^3 -weighted EXAFS spectra of a) $1.8\mu\text{mol}/\text{m}^2$ arsenate adsorbed on goethite at pH
4 5.3 (Loring et al., 2009), b) amorphous $\text{FeAsO}_4(\text{s})$ (Sundman et al., 2014b), c) C2, with
5 $\text{Fe}/\text{As}=2.0$, d) C2, with $\text{Fe}/\text{As}=4.0$, e) C2, with $\text{Fe}/\text{As}=15.6$, f) 150mM H_2AsO_4^- solution
6 (Loring et al., 2009) and Fe-WT modulus of second and third coordination shells ($\eta=4$, $\sigma=2$)
7 for g) 6L-ferrihydrite (Karlsson and Persson, 2012), h) amorphous $\text{FeAsO}_4(\text{s})$, i) C2, with

1 Fe/As=2.0 , j) C2, with Fe/As=15.6, k) native C2 , and l) 6489 ppm Fe SRN sample at pH 5
2 with C/Fe molar ratio ≈ 85 (Karlsson and Persson, 2012) plotted as a function of k ($\text{\AA}^{-1}$) on
3 the x-axis and R ($\text{\AA}$) on the y-axis.

4
5 The findings from the XANES and WT analyses were corroborated by the quantitative fits of
6 the EXAFS spectra. These fits included paths that contributed at the confidence limits 0.6-
7 0.95, and were motivated by the identification of second shell neighbors in the WT plots as
8 well as by the visually poor fits when including only paths significant at the 0.95 confidence
9 limit (Table A1 and Fig. A1 and A2, Supplementary data). The As spectra were adequately
10 fit with a simple model consisting of As-O and As-Fe single scattering paths together with a
11 first-shell As-O-O multiple scattering path (Table 2 and Fig. 3). The As-Fe distance around
12 $3.23 \text{ \AA}$ was consistent with values of amorphous $\text{FeAsO}_4(\text{s})$, arsenate surface complexes on
13 Fe(III) (hydr)oxides (Fendorf et al., 1997; Loring et al., 2009) as well as distances obtained in
14 ternary As(V)-Fe(III)-NOM systems (Mikutta and Kretzschmar, 2011; Sundman et al.,
15 2014b). The coordination numbers ($\text{CN}_{\text{As-Fe}}$) varied between 0.7-1.0 with lower $\text{CN}_{\text{As-Fe}}$ for
16 the sample with the highest total As concentration (Table 2). This decrease, also indicated by
17 the amplitude of the 2nd peak of the Fourier transforms (Fig. 3), was consistent with the As
18 WT results showing increase of free arsenate ions associated with the resins that should lower
19 the average $\text{CN}_{\text{As-Fe}}$. Note that the decrease in $\text{CN}_{\text{As-Fe}}$ was not caused by self-absorption as
20 shown by comparing the EXAFS fluorescence and transmission spectra (Fig. A3 and A4,
21 Supplementary data).

Figure 3. I) k^3 -weighted and II) the corresponding Fourier transforms of As K-edge EXAFS of a) 150mM H_2AsO_4^- solution (Loring et al., 2009), b) C2, with Fe/As=15.6, c) C2, with Fe/As=4.0, d) C2, with Fe/As=2.0, e) $1.8\mu\text{mol/m}^2$ arsenate adsorbed on goethite at pH 5.3 (Loring et al., 2009) and f) amorphous $\text{FeAsO}_4(\text{s})$ (Sundman et al., 2014b). Black lines represent experimental data and red lines models. The dashed vertical line is for visual guidance.

The Fourier transforms of the Fe K-edge EXAFS spectra indicated a gradual decrease of the 2nd shell amplitude as a function of increasing As(V) concentrations (Fig. 4). Although it is difficult to detect in Fig. 4, close comparison indicated that an addition of As(V) to yield Fe/As=15.6 affected this 2nd shell peak, thus corroborating the WT trend of the Fe-Fe interaction (Fig. 2). In agreement with the WT results the Fe EXAFS spectra were successfully modeled with an organic Fe-NOM component together with an Fe(III) (hydr)oxide and at the highest As(V) concentration, a Fe-As path was also statistically significant (Table 2). The fitting strategy for these samples were based on the same assumptions as in Sundman et al. (2014b), i.e. a shell-by-shell fit strategy that included sets of scattering paths corresponding to $\text{FeAsO}_4(\text{s})$, Fe(III)-NOM complexes and Fe(III)

(hydr)oxides. The Fe-Fe fitting parameters showed two trends: (1) the edge-sharing CN_{Fe-Fe} decreased slightly; (2) the corner-sharing CN_{Fe-Fe} became undetectable at high As(V) concentration. These trends indicated that a substantial fraction of the Fe(III) (hydr)oxides was converted upon As(V) addition. A slight decrease of the CN_{Fe-C} was also observed and this was consistent with the small effects on the carbon scattering features in the WT plots (Fig. 2).

These collective XANES and EXAFS results provided information on the mechanism behind the interaction between added As(V) and Fe initially present in the C2 stream water. Possible and previously proposed mechanisms are adsorption of arsenate on Fe(III) (hydr)oxides and the formation of ternary As(V)-Fe(III)-NOM complexes (Ghosh and Yuan, 1987; Mikutta and Kretzschmar, 2011; Pierce and Moore, 1982; Raven et al., 1998; Sharma et al., 2010; Wilkie et al., 1996). However, neither of these was likely to be predominant under the conditions investigated herein. Although both were consistent with the As-Fe distance and coordination numbers determined from As-EXAFS, they were contradicted by the Fe-EXAFS results. The adsorption mechanism should have left the Fe-EXAFS of the Fe-NOM and the Fe(III) (hydr)oxides fractions practically unchanged as the former should not be involved in this reaction and the latter should merely provide adsorption sites without any major structural change. As for ternary As(V)-Fe(III)-NOM species they would also leave the Fe(III) (hydr)oxide fraction unchanged. Instead, we propose that the predominant reactions involved transformation of the Fe(III) (hydr)oxides, and perhaps to a small extent also the Fe-NOM complexes, into $FeAsO_4(s)$ and/or an arsenate-ferrihydrite solid solution, in accordance with recent findings in synthetic ternary As(V)-Fe(III)-NOM systems (Sundman et al., 2014b). Thus, capture of As(V) by Fe in the C2 stream water at these elevated As concentrations should be controlled by the thermodynamic stability of the Fe-NOM

complexes and the solubilities of the Fe(III) (hydr)oxides and the Fe-arsenate phases. It follows that a high stability constant of the Fe-NOM complexes in C2 stream water explains why we find free arsenate despite the excess of Fe.

Finally we compared our XAS spectroscopic results to chemical equilibrium predictions using the thermodynamic model presented by Sundman et al. (2014b), and these predictions were generally in good agreement with the spectroscopic results (Fig. 5 and Table 2). The model corroborated the trend of Fe mineral transformation into the As-bearing solid solution at increasing As concentrations. Moreover, it showed that Fe-NOM complexes were stable over the complete range of As concentrations indicating only a slight decrease of Fe-NOM concentration consistent with the WT (Figure 2 i-k) and EXAFS fit results (Table 2). At higher Fe/As ratios and lower total As concentrations prevalent in natural waters extrapolation of our spectroscopic results and the equilibrium models suggest that As(V) is not sequestered by interactions with the Fe-NOM complexes or by precipitation mechanisms. Thus, under these conditions the only likely sequestering process involving Fe is surface complexation to Fe (hydr)oxides.

Figure 4. I) k^3 -weighted and II) the corresponding Fourier transforms of Fe K-edge EXAFS spectra of a) 6489 ppm Fe SRN sample at pH 5 with C/Fe molar ratio ≈ 85 (Karlsson and Persson, 2012), b) native C2 stream water, c) C2, with Fe/As=15.6, d) C2, with Fe/As=2.0, e) 6L-ferrihydrite (Karlsson and Persson, 2012) and f) amorphous $\text{FeAsO}_4(\text{s})$ (Sundman et al., 2014b). Black lines represent experimental data and red lines model data. The dashed vertical line is for visual guidance.

1 **Table 2.** As and Fe K-edge EXAFS fit results of k^3 -weighted spectra

Sample	Path	CN	R(Å)	σ^2 (Å ²)	ΔE_0^a
			Arsenic		
C2	As-O	4.2	1.69	0.0046	4.9
Fe/As=15.6	As-O-O#	12.7 ^b	3.15	0.0092 ^c	4.9
	As-Fe	1.0	3.24	0.0080 ^d	4.9
C2	As-O	4.0	1.69	0.0034	5.1
Fe/As=4.0	As-O-O#	12.0 ^b	3.14	0.0067 ^c	5.1
	As-Fe	1.0	3.22	0.0080 ^d	5.1
C2	As-O	4.1	1.69	0.0038	5.0
Fe/As=2.0	As-O-O#	12.4 ^b	3.16	0.0076 ^c	5.0
	As-Fe	0.7	3.23	0.0080 ^d	5.0
			Iron		
C2 (native)	Fe-O	5.7	2.00	0.0110	3.5
	Fe-C ^e	1.5	2.85	0.0075 ^f	3.5
	Fe-C-O# ^e	3.0	4.10	0.0150 ^h	3.5
	Fe-Fe	1.7	3.09	0.0100 ^g	3.5
	Fe-Fe	0.4	3.40	0.0100 ^g	3.5
C2	Fe-O	5.8	2.00	0.0117	3.3
Fe/As=15.6	Fe-C ^e	1.2	2.85	0.0075 ^f	3.3
	Fe-C-O# ^e	2.4	4.12	0.0150 ^h	3.3
	Fe-Fe	1.5	3.09	0.0100 ^g	3.3
	Fe-Fe	0.3	3.38	0.0100 ^g	3.3
C2	Fe-O	5.7	2.00	0.0118	2.7
Fe/As=2.0	Fe-C ^e	1.1	2.84	0.0075 ^f	2.7
	Fe-C-O# ^e	2.3	4.12	0.0150 ^h	2.7
	Fe-Fe	1.3	3.09	0.0100 ^g	2.7
	Fe-Fe ⁱ	n.d.	n.d.	n.d.	n.d.
	Fe-As	0.5	3.23	0.0080 ^d	2.7

2 The amplitude reduction factor (S_0^2) was set to 1.0 for arsenic and 0.85 for iron. # MS paths.
3 The following abbreviations are used: coordination number (CN), bond distance (R), and
4 Debye-Waller factor (σ^2). Conservative confidence limits on obtained distances and
5 coordination numbers were estimated by varying each parameter in a step-wise fashion away
6 from its optimal value, while varying all other parameters until $\Delta\chi^2$ increased 1.0 above its
7 minimum value. This resulted in the following confidence limits: CN_{As-O}: ± 0.3 ; CN_{As-Fe}:
8 ± 0.4 ; R_{As-O}: ± 0.01 ; R_{As-Fe}: ± 0.05 ; CN_{Fe-O}: ± 0.5 ; CN_{Fe-C}: ± 0.6 ; CN_{Fe-As}: ± 0.4 ; CN_{Fe-Fe(short)}:
9 ± 0.6 ; CN_{Fe-Fe(long)}: ± 0.2 ; R_{Fe-O}: ± 0.01 ; R_{Fe-C}: ± 0.05 ; R_{Fe-Fe}: ± 0.05 . The contributions from the
10 As-Fe, Fe-C, Fe-Fe and Fe-As paths were evaluated by means of the F-test, and when
11 included in the fits it contributed at a confidence level between 60%-95%.

12 ^a E_0 was assumed to be identical for all coordination shells.

13 ^bCN correlated to 3 times CN_{As-O} according to the triple degeneracy of the multiple scattering
14 path.

15 ^cCorrelated to two times σ^2 of As-O.

^d σ^2 fixed at 0.0080 obtained from Sundman et al. (2014b).

^e The coordination number of the Fe-C-O[#] path was correlated to be $2 \times \text{CN}$ of Fe-C according to carboxylic like structures.

^f Fixed value from Sundman et al. (2014b).

^g Fixed value from Maillot et al. (2011).

^h Fixed according to $2 \times \sigma^2$ for Fe-C.

ⁱ Path not detected (n.d.) in the fit.

Figure 5. Distribution diagram showing the speciation in a system containing As(V), Fe(III) and NOM, and calculated from stability constants and solubility products presented in Sundman et al. (2014b). The calculations were performed at 4 total As-concentration, from 0 μM to 15.0 μM, corresponding to the experimental conditions in this study. The other conditions pH, Fe and active dicarboxylic acid groups were constant at 5.5, 29.7 μM (this study) and 17.5 μequivalents L⁻¹ (adapted from earlier measurements in the Krycklan catchment by Neubauer et al., 2013), respectively. Fe(OH)₃ corresponds to ferrihydrite, Fe(OH)_{1.5}(AsO₄)_{0.5} to the solid solution, Fe-NOM to mononuclear organic complexes, and FeAsO₄(aq) and H₂AsO₄⁻ to soluble As species.

4. Conclusions

Although the present investigation was limited by the fact that only ca. two-thirds of the total Fe concentration was structurally characterized it showed that addition of As(V) to a natural stream water from a boreal catchment had a profound effect on the Fe speciation initially present. At increasing concentrations of As(V) the collective spectroscopic results indicated a transformation of Fe species from Fe(III) (hydr)oxides to $\text{FeAsO}_4(\text{s})$ or a solid solution where As(V) was incorporated into a Fe(III) (hydr)oxide structure. Even though there were weak indications that some of the Fe-NOM complexes initially present also were transformed, the concurrent existence of Fe-NOM complexes and aqueous As(V) showed that a large fraction of stable Fe-NOM complexes were non-reactive towards As(V). These results were in general agreement with previous studies on As-Fe-NOM model systems, and highlight the importance of the thermodynamic stability of the Fe-NOM complexes. The high Fe concentration in combination with the low Fe/As ratios employed in this study correspond to As-contaminated environments but the findings also have implications for other conditions. These suggest that, irrespective of the total As concentration, complexation of Fe by NOM in organic rich environments may lead to elevated free, aqueous As levels as these complexes reduce the propensity to form reactive Fe(III) (hydr)oxides particles and Fe(III)-arsenate precipitates. Another general implication is that whether or not Fe will act as a vector for anions such as As(V) or P(V) depends on the Fe speciation induced by the geochemical conditions.

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Appendix A. Supplementary material

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

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