



	Experiment title: Mechanism of arsenite binding to natural organic matter: Effect of pH and organic sulfur content	Experiment number: EC-1005
Beamline: BM26A	Date of experiment: From 20.06. to 24.06.2012	Date of report: 2 September 2012
Shifts: 12	Local contact(s): Sergey Nikitenko, Dipanjan Banerjee	<i>Received at ESRF:</i>
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1. Introduction

The fate of the toxic trace element arsenic (As) in aquatic and terrestrial ecosystems is strongly controlled by its interaction with solid phases.¹ While interactions of both arsenite (As(III)) and arsenate (As(V)) with mineral matter, notably Fe(III)-oxyhydroxides, were extensively studied in the past,² the role natural organic matter (NOM) plays in As sequestration is still poorly understood. Several binding mechanisms have been proposed for As-NOM interactions, which include (i) the formation of covalent bonds between phenolic/carboxylic groups of NOM and As(III) or As(V),³ (ii) the formation of outersphere complexes with protonated amino groups of NOM,⁴ (iii) the formation of covalent bonds between As(III) and organic sulfur groups of NOM,⁵ and (iv) the formation of ternary complexes in which a polyvalent metal cation forms a bridge between a negatively charged As oxyanion and an organic ligand.⁶ Based on As and Fe K-edge X-ray absorption spectroscopy (XAS) measurements conducted at ESRF (Exp. No. EC-818), we recently succeeded in providing the first spectroscopic evidence for ternary complex formation between arsenate, As(V), and Fe(III) complexes of humic substances.⁷ Yet, there is no spectroscopic evidence for ternary complex formation between arsenite, As(III), and Fe(III)-NOM complexes. For this reason we performed As K-edge XAS measurements at beamline BM26A (Exp. No. EC-1005) in order to explore the local coordination environment of As in As(III)- and Fe(III)-enriched particulate NOM. These measurements were complemented by Fe K-edge XAS measurements at beamline BM23 (Exp. No. EC-999). The results of both XAS experiments will increase our understanding of As cycling in sub- and anoxic NOM-rich environmental systems such as floodplains, peatlands, or rice paddies.

2. Materials and Methods

Peat was collected from a natural ombrotrophic peatland near Bad Buchau, Germany. For our sorption experiments, we used its 40-250- μm size fraction as a proxy for particulate NOM. The peat was spiked with varying amounts of Fe(III) as FeCl_3 at pH <2. After filtration and washing of the Fe(III)-

loaded peat with doubly deionized (DDI) water, As(III) (0.3 mmol/mol C) was added under anoxic conditions ($pO_2 < 10$ ppm). After equilibration of the peat with As(III) for 72 hours in 0.1 M NaCl solution at pH 7.0, 8.4 and 8.8, respectively, the peat was filtered, rinsed with DDI water, freeze-dried, and homogenized in an anoxic glove box. For XAS analysis the samples were filled into Al sample holders and sealed with Kapton® tape. Arsenic K-edge (11,867 eV) X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were recorded in fluorescent-yield mode at ~ 12 K using a 9-element Ge detector and a He cryostat. The monochromator was calibrated to the first maximum in the first derivative of the L3-edge absorption spectrum of a metallic Au foil (11,919 eV), which was continuously monitored to account for slight energy shifts during the sample measurements. For each sample 9-15 scans were averaged. Spectral processing was done according to standard procedures using the IFEFIT program suite.⁸ Fourier transforms of the $\chi(k)$ data were calculated over a k -range of 2.0-12.0 \AA^{-1} using a Kaiser-Bessel apodization window with a sill width of 3 \AA^{-1} .

3. Results and Discussion

First derivatives of the As K-edge XANES spectra of Fe(III)-peat complexes reacted with As(III) are shown in **Figure 1**. They exhibit maxima at $\sim 11,869$ eV, which are comparable to those of As(III) reference compounds. Hence, the oxidation of As(III) to As(V) was negligible in our experiments.

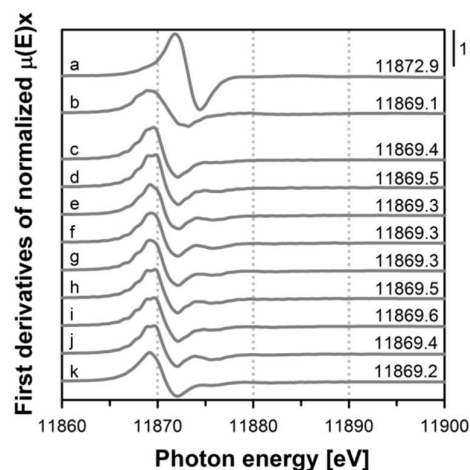


Figure 1. First derivatives of normalized As K-edge XANES spectra of (a) As(V) adsorbed to ferrihydrite, (b) As(III) adsorbed to ferrihydrite, and peat samples with increasing Fe(III) loadings, which were reacted with As(III) at pH 7.0 (c-g), pH 8.4 (h, i), and pH 8.8 (j, k). Energy values indicate the maximum of the first derivatives.

The k^3 -weighted As K-edge EXAFS spectra of Fe(III)-peat complexes reacted with As(III) (**Figure 2A**) had a fair signal-to-noise ratio up to $k \sim 12 \text{ \AA}^{-1}$. The corresponding Fourier transforms are illustrated in **Figure 2B**. The location of first Fourier-transform peak at $R + \Delta R \sim 1.4 \text{ \AA}$ (**Figure 2B**) accords with the interatomic As-O distance commonly observed for the pyramidal As(III) molecule.² The Fourier transforms also showed backscattering signals at $R + \Delta R \sim 2.2$ and $\sim 2.7 \text{ \AA}$ (**Figure 2B**). While the first peak may arise from C backscatterers located in higher coordination shells of As,^{9,10} the second Fourier-transform peak at $\sim 2.7 \text{ \AA}$ is clearly indicative of Fe neighbors in the second coordination shell of As (ref. 2, see spectrum for As(III) adsorbed to ferrihydrite in **Figure 2**). Our result thus implies the formation of inner-sphere complexes of As(III) with Fe(III) species of the peat. A qualitative spectra comparison also showed that the 2.7- \AA peak becomes more pronounced (i) with increasing Fe(III) loading of the peat (samples b-f) and (ii) with increasing pH during As(III) sorption to peat with an identical Fe(III) loading (samples d, g). At present, we are investigating the local As coordination in our samples by means of shell fitting. These results will complement our Fe speciation analysis (see report for experiment EC-999). Reconciling shell-fit results obtained from both As and Fe K-edge

EXAFS spectroscopy will allow us to either dismiss or prove the existence of ternary As(III) complexes in particulate NOM.

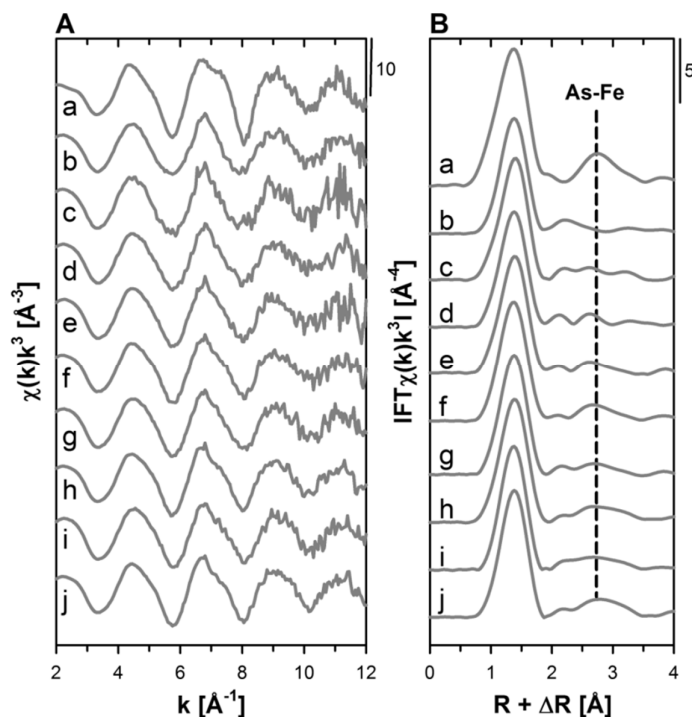


Figure 2. (A) k^3 -weighted As K-edge EXAFS spectra, and (B) Fourier-transform magnitudes of (a) As(III) adsorbed to ferrihydrite, and peat samples with increasing Fe(III) loadings, which were reacted with As(III) at pH 7.0 (c-g), pH 8.4 (h, i), and pH 8.8 (j, k). The dashed vertical line marks the position of Fe in the second coordination shell of As at $R + \Delta R \sim 2.7 \text{ \AA}$.

4. References

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