



	<b>Experiment title:</b> Role of sulfur in the mechanism of arsenite binding to natural organic matter <sup>1</sup>	<b>Experiment number:</b> 01-01/829
<b>Beamline:</b> BM 26	<b>Date of experiment:</b> From 15.04. to 21.04.2011	<b>Date of report:</b> 3 September 2011
<b>Shifts: 15</b>	<b>Local contact(s):</b> Sergey Nikitenko, Miguel Silveira	<i>Received at ESRF:</i>
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<sup>1</sup> The relocation of our intended SNBL beamtime to BM26 caused a postponement of our XAS study on ternary As(V) complexes (01-01/829; "Structure of ferric citrate complexes and their role in arsenate binding"). For this reason we had to use BM26 beamtime for another project on As-NOM interactions.

## 1. Introduction

Arsenic (As) is a ubiquitous, toxic contaminant threatening water resources worldwide. In the past decade, many laboratory studies have demonstrated that natural organic matter (NOM) acts as a sorbent for the metalloid [1-4]. Several binding mechanisms have been proposed to explain the sorptive interaction between As and NOM. These mechanisms include (i) the formation of covalent bonds between phenolic/carboxylic groups of NOM and arsenite, As(III), or arsenate, As(V) [2], (ii) the formation of ternary complexes with a polyvalent cation forming a bridge between As oxyanions and organic ligands [3], and (iii) the formation of covalent bonds between As(III) and sulfhydryl groups of NOM [5]. Based on earlier work on the speciation of As in wetlands, which was conducted at ESRF (EC-489, "Binding form of arsenic in arsenic-contaminated peatlands"), we proposed that process (iii) is the major interaction mechanism for As(III) in NOM-rich soils and sediments subject to sulfate-reducing conditions [5]. In order to verify our field results, we tested the effect of freshly formed sulfhydryl groups in NOM produced by reaction with bisulfide (HS<sup>-</sup>) on the binding of As(III). To this end, we addressed the local coordination environment of As in sulphur (S)-enriched NOM by means of X-ray absorption spectroscopy. Additionally, we investigated the partitioning of As(III) in mixtures of a sulfhydryl-group containing resin and the Fe(III)-oxyhydroxide ferrihydrite. This experiment was used to infer the relative sorption strength of sulfhydryl groups for As(III) in soil and sediment environments.

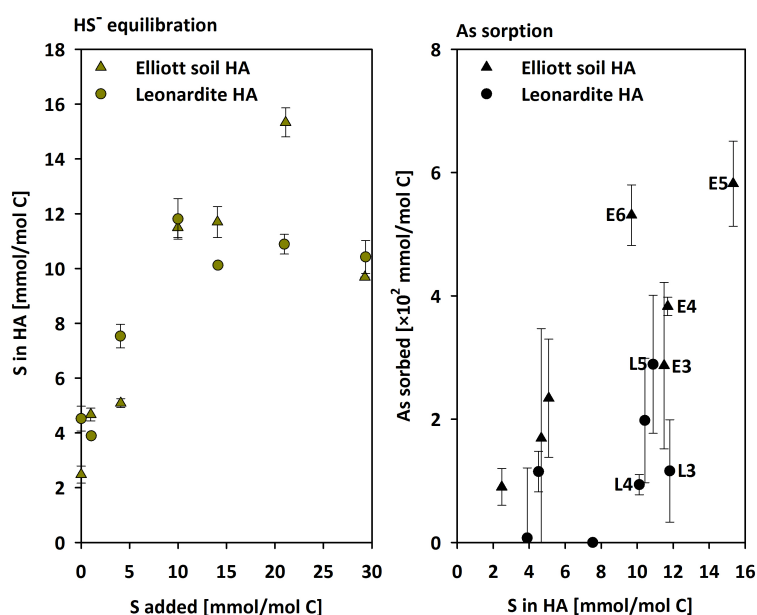
## 2. Materials and Methods

In the first experiment we employed Elliott soil humic acid (HA) and Leonardite humic acid, which were purchased from the International Humic Substances Society. In order to test the effect of increasing S content of HA on the sorption of As, we pre-equilibrated HAs with variable concentrations of HS<sup>-</sup> at pH 5 under anoxic conditions (pO<sub>2</sub> < 1 ppm). After reaction, HA samples were dialyzed (cutoff: 100-500 Da) against ultrapure water, freeze-dried, and analyzed for their S content using X-ray fluorescence spectrometry. The speciation of S both before and after equilibration with HS<sup>-</sup> was investigated by means of S K-edge XANES spectroscopy. Subsequently, S-doped HA samples were equilibrated with As(III) at pH 5. After equilibration, the amount of dissolved As(III) was measured by HPLC ICP-MS to calculate the amount of As(III) sorbed. The HA samples were then again freeze-dried and homogenized in an anoxic glove-box. Based on mass-balance calculations, we selected samples with the highest As concentrations for As K-edge XAS analysis.

In the second experiment we focused on the competitive sorption of As(III) in mixtures of both organic and inorganic sorbents. We used Ambersep GT-74<sup>®</sup> resin as a proxy for sulfhydryl-bearing NOM and utilized ferrihydrite as competitive sorbent. The ratio of sorption sites of the resin and ferrihydrite ('-SH'/'-OH') was systematically varied. In two test series each sorbent was pre-equilibrated with As(III) at pH 7 under anoxic conditions (pO<sub>2</sub> < 1 ppm). After pre-equilibration for 2 days, the second sorbent was added and the mixture was equilibrated for additional two weeks. Afterwards, the amount of dissolved As(III) was determined in solution using HPLC-ICP-MS in order to calculate the total amount of As(III) sorbed. The solids were filtered, washed with ultrapure water, freeze-dried, and homogenized under anoxic conditions. For As K-edge XAS analysis all samples were filled into aluminum sample holders and sealed with Kapton<sup>®</sup> tape. The samples were stored and transported under anoxic conditions until final analysis at beamline BM26 of the European Synchrotron Radiation Facility (ESRF). 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 fluorescence mode at ~12 K using a 9-element Ge detector and a He cryostat. The speciation of As was investigated by means of linear combination fit (LCF) analysis.

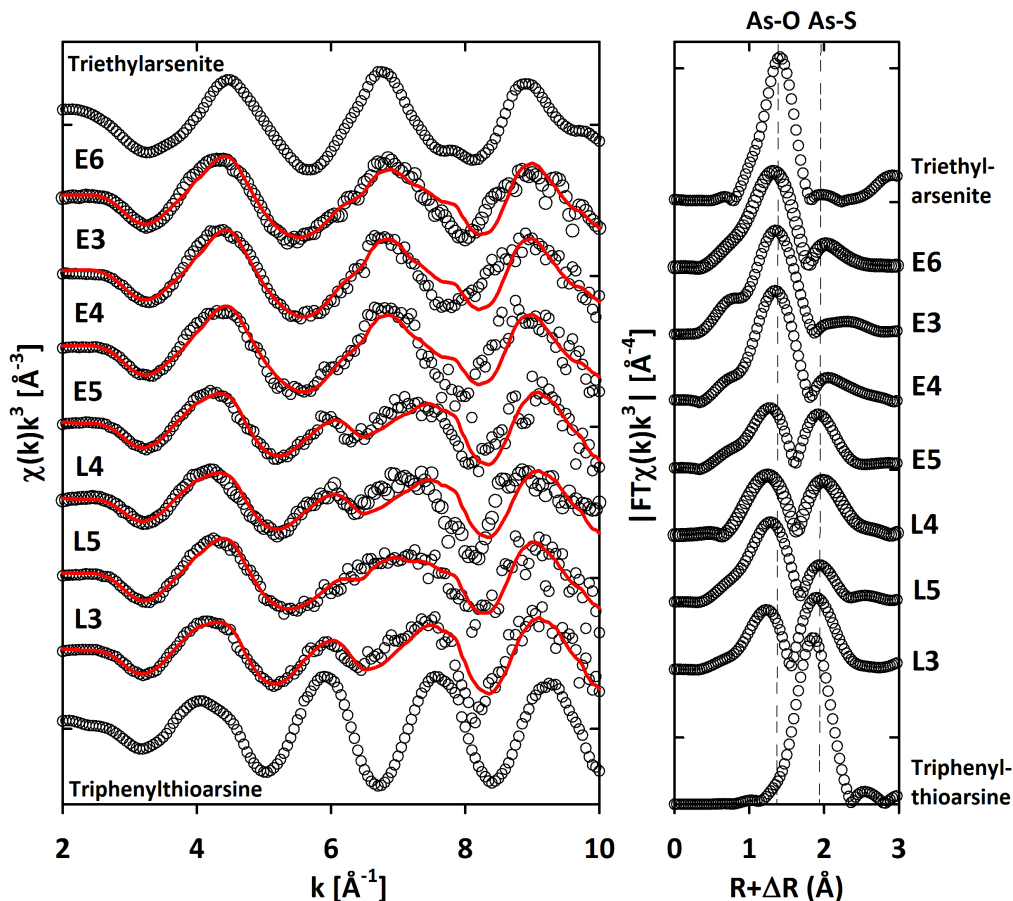
## 3. Results and Discussion

The HS<sup>-</sup> equilibration experiments documented that HAs rapidly incorporated inorganic S into their structure. For both HAs the amount of incorporated S increased with increasing HS<sup>-</sup> concentration (Fig. 1).



**Figure 1.** Results of S incorporation (left) and subsequent As(III) sorption to pure and HS<sup>-</sup>-reacted HAs (right). Labels mark samples chosen for XAS analysis.

Sulfur K-edge XANES of pure and S-doped HAs revealed that reduced S (-II to +I) was formed preferentially. While sorption of As(III) to pure HAs was negligible, it increased with increasing S content of the HAs (Fig. 1). In this respect Elliott soil HA showed a slightly higher reactivity than Leonardite HA. Arsenic K-edge XANES analysis confirmed that sorbed As was only present in its trivalent oxidation state. The Fourier transforms of As K-edge EXAFS spectra depicted in Fig. 2 clearly show that in all samples trivalent As was coordinated to O and S atoms in varying proportions. Preliminary LCF results suggest that As in Leonardite HA was to a greater extent coordinated to organic S atoms than in Elliott soil HA (Table 1).



**Figure 2.** Arsenic K-edge EXAFS spectra (left) and their Fourier transforms (right) of S-doped HAs equilibrated with As(III). Samples of each HA series are ordered by their S content. Linear combination fits are shown as red lines.

**Table 1.** Preliminary linear combination fit results for S-doped HAs equilibrated with As(III). Triethylarsenite and triphenylthioarsenite were used as model compounds for O- and S-coordinated trivalent As, respectively.

Sample ID	Sulfur content [g/kg]	Triethylarsenite [%]	Triphenylthioarsenite [%]	R-factor [-]
Elliott soil 3 (E3)	17.8	88	21	0.048
Elliott soil 4 (E4)	18.2	87	20	0.071
Elliott soil 5 (E5)	23.8	51	51	0.065
Elliott soil 6 (E6)	15.0	82	27	0.056
Leonardite 3 (L3)	20.1	43	60	0.068
Leonardite 4 (L4)	17.2	43	49	0.142
Leonardite 5 (L5)	18.5	69	38	0.049

In the mixed sorbent experiments, about 100% of total As(III) added was immobilized by the sorbents (sulfhydryl resin and ferrihydrite). LCF results (Table 2) show that both sorbents induced the desorption of As(III) from its competitor. At a molar SH/OH ratio of unity and below, ferrihydrite was much more effective in binding As(III) than the sulfhydryl resin. However, when resin functional groups were present in excess, ferrihydrite lost its relative efficiency to sequester As(III); particularly when As(III) was pre-equilibrated with the sulfhydryl resin (Table 2).

**Table 2.** Linear combination fit results for the competitive sorption experiment.

SH/OH ratio <sup>a</sup> [mol/mol]	As(III)-Fh <sup>b</sup> [%]	As(III)-Resin <sup>c</sup> [%]	R-factor [-]	SH/OH ratio [mol/mol]	As(III)-Fh [%]	As(III)-Resin [%]	R-factor [-]
<i>Pre-equilibration of As(III) on ferrihydrite</i>				<i>Pre-equilibration of As(III) on resin</i>			
0.3	98	5	0.013	0.3	85	7	0.004
0.6	76	17	0.055	0.6	70	23	0.062
1	71	18	0.056	1	71	24	0.043
3	54	36	0.068	3	30	52	0.077
6	47	50	0.009	6	12	82	0.023

<sup>a</sup>ratio of sorption sites in sorbent mixtures: SH = sulfhydryl group of resin, OH = surface hydroxyl group of ferrihydrite; <sup>b</sup>As(III) sorbed to synthetic ferrihydrite; <sup>c</sup>As(III) sorbed to resin

#### 4. Conclusions and outlook

Pure HAs did hardly interact with As(III). In contrast, S incorporation into HAs by pre-equilibration with HS<sup>-</sup> resulted in a significantly increased As(III) sorption. LCF results confirmed that the enhanced sorption of As(III) was due to the presence of reactive organic S species. In a next step, we will model our As K-edge EXAFS data by shell-fitting. The mixed sorbent experiments showed that the sorptive power of sulfhydryl groups is slightly lower than that of surface hydroxyls of ferrihydrite. Nonetheless, the sulfhydryl group-bearing resin was capable of causing significant desorption from ferrihydrite. Our laboratory results therefore suggest that at neutral pH sulfhydryl groups of NOM can serve as a geochemical trap for As(III) even in the presence of Fe(III) oxyhydroxides. This finding has important implications for the cycling of As in sub-/anoxic NOM-rich soil and sediment environments.

#### 5. References

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