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ESRF	Experiment title: Binding form of arsenic in arsenic-contaminated peatlands	Experiment No. 01-01-787					
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Report:

Introduction

Field and laboratory reseach on environmental systems has shown that the solid-solution partitioning of arsenic (As) is often controlled by the cycling of Fe. Analyzing the Fe and As speciation in our As-contaminated peatland *Gola di Lago* in canton Ticino (Switzerland), we found that even under anoxic conditions, some As was quantitatively sequestered as As(V) by Fe(III)-(hydr)oxides [1]. In a previous beamtime session at beamline BM01B, we analyzed the influence of citrate, a polyhydroxycarboxylate, on the local coordination of Fe in poorly crystalline Fe(III)-(hydr)oxides [2] and found, in short, that citrate decreased the number of octahedral linkages within the solid [3]. Thus we hypothesized that low molecular weight polyhydroxycarboxalates, omnipresent in peat soil solutions, may impact the surface speciation of As(V) immobilized by poorly crystalline Fe(III)-(hydr)oxides. In the past, three innersphere surface complexes of As(V) have been suggested based on extended X-ray absorption fine structure (EXAFS) spectroscopy: (i) a monodentate surface complex resulting from corner-sharing between AsO₄ tetrahedra and Fe(O,OH)₆ octahedra labeled ¹V, (ii) a bidentate surface complex resulting from corner-sharing with two adjacent edge-sharing Fe(O,OH)₆ octahedron denoted ¹E [4-8]. Here we studied the influence of citrate on the coordination mode of As(V) on 2-line ferrihydrite (Fh) in order to understand the binding of As(V) to poorly crystalline Fe(III)-(hydr)oxides in environments rich in dissolved organic matter.

Methods

We synthesized Fh in the presence of citrate and As(V). In these syntheses we varied the initial citrate concentration and kept the initial molar As/Fe ratio constant at 5 mol% (Table 1). The syntheses were conducted by titrating a 200 mM Fe(NO₃)₃ solution containing 10 mM As(V) and increasing amounts of citrate with 1 M KOH (Titrisol[®]) at a rate of 300 µmol/min up to a final pH of 6.5. Afterwards, the suspensions were centrifuged at 5000 x g for 60 min. The supernatants were decanted and subsequently ultrafiltered through 4-kDa membranes to separate Fh from dissolved Fe species. The centrifugate was shock-frozen in liquid N₂ and freeze-dried. In all three fractions (centrifugate, suspernatant, ultrafiltrate), we measured the total content of Fe and As. Arsenic K-edge X-ray absorption spectra of the samples were measured in both transmission and fluorescence mode at the BM01B beamline. Data reduction and shellfit analysis was performed with the software package IFEFIT [9].

Table 1. Molar ratios and concentrations of Fe(III), citric acid, and As(V) in the initial 50-mL stock solutions used for coprecipitate formation.

Treatment	Millimo	oles in Stock S	Solution	Concentration (mM)			
	Fe(III)	Citric acid	As(V)	Fe(III)	Citric acid	As(V)	
$Fe_{10}As_{0.5}$	10	0	0.5	200	0	10	
$Fe_{10}C_{0.5}As_{0.5}$	10	0.5	0.5	200	10	10	
$Fe_{10}C_{2.5}As_{0.5}$	10	2.5	0.5	200	50	10	
$Fe_{10}C_5As_{0.5}$	10	5	0.5	200	100	10	

Results

Arsenic K-edge EXAFS as well as magnitude and real part of the Fourier transform of the samples analyzed are shown in Fig. 1. EXAFS fit parameters obtained from shell-fits are summarized in Table 2. The white line position at 11,875 eV in the As K-edge XANES spectra of all our samples matched those of the As(V) references (not shown), implying that a net reduction of As(V) during the experiment was negligible. Data in Table 2 reveal that citrate had no effect on the As-O bond distance, which remained constant at a mean value of 1.69 Å, which is in line with previous results [8, 10]. Citrate had also no effect on the As-Fe bond distance in the coprecipitated samples, which stayed constant within error at 3.32 Å. This value is identical to that fitted by Voegelin et al. [10] to As(V)-adsorbed Fh, and is also in agreement with the mean As-Fe distance (fitted with two As-Fe contributions) in Fh coprecipitated with As(V) at pH 4 [8].



Figure 1. Arsenic K-edge EXAFS as well as magnitude and real part of the Fourier transform of the solids and suspensions analyzed. Solid lines are experimental data and open circles represent best model fits. Vertical lines indicate peaks in the Fourier transform magnitude assigned to multiple scattering within the AsO₄ tetrahedron (1) and As-Fe single scattering paths of ²C surface complexes in which As(V) shares two corners with edge-sharing Fe(O,OH)₆ octahedra (2). *R* was not corrected for phase shift.

Coordination numbers of second-shell Fe correspond well to our As(V)-adsorbed Fh reference and suggest that the binding mode of coprecipitated As(V) is not significantly different from adsorbed As(V). All data are in accordance with a bidentate binuclear As(V) surface complex (²C) in which As(V) binds to the corners of two adjacent ege-sharing Fe(O,OH)₆ octahedra. Implementation of a bidentate mononuclear ¹E surface complex in our shell-fit scheme yielded negative coordination numbers for an As-Fe path with a mean half path length of about 2.85 Å, which implies the absence of ¹E complexes in agreement with Waychunas et al. [6]. In addition, coordination numbers of the As-Fe path (Table 2) were significantly greater than those for As(V) on goethite (0.8 - 1.1 ± 0.7; [11]) and do not support the exclusive formation of a monodentate As(V) complex on Fh. It follows that during rapid coprecipitation of As(V) with Fh in the presence or absence of citrate, no energetically less favorable innersphere surface complexes (¹E) are formed, even when the molar concentration of citrate exceeds that of As(V) ten-fold. Our results suggest that under the experimental conditions used in this study (pH 4.3 - 6.6, *I* ~ 0.45 M) low molecular weight polyhydroxycarboxylates do not change the surface speciation of As(V) on poorly crystalline Fe(III)-(hydr)oxides.

Sample	$\Delta E_0 (eV)^a$	Path	CN ^b	$\sigma^2 (\text{\AA}^2)^c$	$\mathbf{R}^{\mathbf{d}}(\mathbf{\mathring{A}})$	R-factor ^e	Red χ^{2f}
As(V) adsorbed	12.8 +/- 1.1	As-O	4.00	0.0023 +/- 0.0003	1.69 +/- 0.00	0.011	32
to ferrihydrite		As-Fe	2.14 +/- 0.65	0.0120	3.30 +/- 0.02		
		MS1-3 ^g					
$Fe_{10}As_{0.5}$	13.5 +/- 1.3	As-O	4.00	0.0023 +/- 0.0003	1.69 +/- 0.01	0.015	65
		As-Fe	2.09 +/- 0.78	0.0120	3.32 +/- 0.03		
		MS1-3 ^g					
$Fe_{10}C_{0.5}As_{0.5}$	13.2 +/- 1.5	As-O	4.00	0.0023 +/- 0.0004	1.69 +/- 0.01	0.019	110
		As-Fe	2.31+/- 0.87	0.0120	3.31 +/- 0.03		
		MS1-3 ^g					
$Fe_{10}C_{2.5}As_{0.5}$	13.4 +/- 1.5	As-O	4.00	0.0023 +/- 0.0004	1.69 +/- 0.01	0.019	96
		As-Fe	2.74 +/- 0.87	0.0120	3.30 +/- 0.02		
		MS1-3 ^g					
Fe ₁₀ C _{2.5} As _{0.5}	12.7 +/- 1.3	As-O	4.00	0.0027 +/- 0.0003	1.69 +/- 0.01	0.015	149
(Suspension)		As-Fe	3.06 +/- 0.76	0.0120	3.32 +/- 0.02		
		MS1-3 ^g					
$Fe_{10}C_5As_{0.5}$	12.5 +/- 1.1	As-O	4.00	0.0022 +/- 0.0004	1.69 +/- 0.01	0.024	162
		As-Fe	2.44 +/- 0.84	0.0120	3.30 +/- 0.03		
		MS1-3 ^g					

Table 2. EXAFS shell-fit parameters determined from the As K-edge EXAFS spectra. The passive amplitude reduction factor, S_0^2 , was set to 1 for all samples. Bold values: parameter fixed in the fit. Errors are given as standard errors.

energy shift parameter

^b CN = coordination number (path degeneracy)

^c Debye-Waller parameter; the value for the As-Fe path was fixed to that of arsenate adsorbed to ferrihydrite [10]

 d R = half path length uncorrected for phase shift. The half path length of the Fe-O path was identical within error for all samples. Hence, its value was fixed to the one determined from a simultaneous fit of all spectra.

^{e, f} R-factor =
$$\frac{\sum_{i} (data_{i} - fit_{i})^{2}}{\sum_{i} data}$$
 and reduced $\chi^{2} = \frac{N_{idp}}{N_{pts}} \sum_{i} \left(\frac{data_{i} - fit_{i}}{\epsilon_{i}}\right)^{2} (N_{idp} - N_{var})^{-1}$. N_{idp} , N_{pts} , and N_{var} are,

respectively, the number of independent points in the model fit, the total number of data points, and the number of variables in the fit. ε_i is the uncertainty of the ith data point [12]. Fit range: 0.9-3.6 Å; $N_{idp} = 15$, $N_{var} = 5$. ^g Multiple scattering paths: MS1 = triangular As-O-O MS path, path degeneracy = 12, $R = 1.8165 \times R_{As-O}$, $\sigma^2 = \sigma^2_{As-O}$; MS2 = collinear As-O-As-O MS path, path degeneracy = 4, $R = 2 \times R_{As-O}$, $\sigma^2 = 4 \times \sigma^2_{As-O}$; MS3 = non-collinear As-O-

As-O MS path, path degeneracy = 12, $R = 2 \times R_{As-O}$, $\sigma^2 = 2 \times \sigma^2_{As-O}$.

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