Introduction

The chemical speciation of arsenic in sediments and porewaters of aquifers is the critical factor that determines whether dissolved arsenic accumulates to potentially toxic levels. Elevated arsenic concentrations in groundwater impact the drinking water of millions of people worldwide (see, e.g., recent reviews in [1-3]). A key question in predicting the concentrations of arsenic in groundwater is that of the timescales for release of arsenic from aquifer sediments to porewaters. Although the general redox conditions that allow such release are known, the timescales for release and factors controlling those timescales are not well understood. In this project, we are studying a field site, North Haiwee Reservoir near Olancha, CA, where the deposition of arsenic in association with iron oxyhydroxides is controlled by additions of ferric chloride to the Los Angeles Aqueduct. Since the timing and extent of arsenic deposition is relatively well defined, the site provides a unique natural laboratory in which to examine the mechanisms and rates of arsenic release to porewaters. A prior study by our research groups has demonstrated that arsenic is remobilized from the deposited floc into the sediment porewaters over a depth of 0-5 cm [4]. We are using a combination of characterization approaches, including bulk analysis, sequential extractions, XRD, and synchrotron XAS, to determine changes in arsenic oxidation state with burial and to address whether changes in the structure and crystallinity of the iron oxyhydroxide floc, and therefore its ability to sequester arsenic, occur with deeper burial (to ~1 m).

Methods and Materials

Sample cores were collected at four locations in the Haiwee Reservoir, CA on July 7, 2003. Three cores were collected along the reservoir inlet and a fourth control core was taken north of the inlet, where no iron floc deposition occurs. Duplicate cores were taken at each sample site. Sample collection was done with 30-cm long poly-butylene tubes with an internal diameter of 2.5 cm. The tubes were hand driven into the soft sediment and were removed using a rubber stopper for suction. After removal cores were kept upright to minimize disruption of the sediment and to keep stratigraphy intact. Cores were immediately sealed with end caps and electrical tape in the field. During transit to the laboratory cores were kept upright on ice and on return, were immediately placed in a –80°C freezer to avoid post-collection oxidation. Cores were sectioned 2-4 days after collection at the reservoir inlet and a fourth control core was taken north of the inlet, where no iron floc deposition occurs. Duplicate cores were taken from least-squares fits indicate As(III)-O distances (1.76-1.78 Å) consistent with previous model studies of arsenite sorption on oxide minerals [10,11]. In EXAFS fits to Core #2, two different oxygen shells were assumed in the fit model to account for the mixture of As(III) and As(V) in the arsenate tetrahedron -0.5 Å shorter than As(III)-O distances [11]. For both cores, second-neighbor atoms were assumed to be Fe based on the known association of arsenic with iron floc as the source of arsenic to the sediments. Second-neighbor backscattering was fit with two shells of iron atoms for most samples, with a closer shell at 2.92-3.01 Å and a longer shell at 3.40-3.48 Å, regardless of whether the absorber was As(III) or a mixture of As(III) and As(V).

Results

XANES data for Core #1 showed that samples A (0.5 cm) and C (6 cm) were composed of entirely As(III) (Fig. 1). Sample 1-B (3.25 cm) indicated mostly As(III) and a small fraction of As(V), which is attributed to oxidation during data collection because the size of the As(V) peak grew slightly with successive scans. Core #2 showed a mixture of both As(III) and As(V) for samples 2-A (1 cm), 2-B (2 cm) and 2-C (4 cm) (Fig. 1). This core showed the greatest amount of As(V) at the top of the core near the sediment/water interface and decreasing As(V) with depth. EXAFS and Fourier Transforms for Core #1 were very similar among the three different samples (Fig. 1). Interatomic distances derived from least-squares fits indicate As(III)-O distances (1.76-1.78 Å) consistent with previous model studies of arsenite sorption on oxide minerals [10,11]. In EXAFS fits to Core #2, two different oxygen shells were assumed in the fit model to account for the mixture of As(III) and As(V), with interatomic As(V)-O distances in the arsenate tetrahedron -0.5 Å shorter than As(III)-O distances [11]. For both cores, second-neighbor backscattering was fit with two shells of iron atoms for most samples, with a closer shell at 2.92-3.01 Å and a longer shell at 3.40-3.48 Å, regardless of whether the absorber was As(III) or a mixture of As(III) and As(V).

Discussion

Ferric chloride and polymer are added to the aqueduct at the Cottonwood Treatment Plant, about 15 km upstream of North...
Haiwee Reservoir. Ferric chloride addition results in the formation of an Fe(III) oxyhydroxide floc that is transported as suspended load in the aqueduct and deposited in Haiwee Reservoir as the flow velocity decreases. Characterization of the iron floc in the aqueduct by EXAFS (unpublished data) indicates that arsenic enters the reservoir as As(V) associated with an amorphous iron (hydr)oxide similar in local structure to ferrihydrite or goethite. The XAS results shown here are in agreement with our previous work [4] that showed the presence of As(III) at or near the sediment-water interface. These data indicate a rapid reduction of arsenic from As(V) to As(III) after deposition in the reservoir, either at the sediment-water interface or a few centimeters below the interface.

![Graphs of XANES and EXAFS spectra](image)

Fig. 1. XANES and EXAFS spectra of sediment samples from Cores #1 (top) and #2 (bottom). XANES spectra are compared to laboratory samples of arsenic sorbed to goethite and green rust. For EXAFS spectra, solid line is the experimental data and dashed line is the non-linear least-squares best fit.

The results of the EXAFS fits indicate the presence of second-neighbor iron atoms at As-Fe interatomic distances that are within the range of those found in previous studies of model systems of As(III) and As(V) sorption to ferric oxides, although there is considerable variability reported in interatomic distances among different studies [11]. Simple geometric comparisons dictate that the sorbed arsenic species must be associated with ferric iron octahedra in at least two distinct inner-sphere bonding modes. A near-neighbor As-Fe distance of ~ 3 Å or less constrains the local atomic geometry to one bonding mode of edge-sharing between an iron octahedra and an arsenic polyhedron (either the As(V) tetrahedron or As(III) pyramid). The longer near-neighbor As-Fe distance of 3.40-3.48 Å indicates a second mode of a corner-shared geometry of arsenic and iron polyhedra, probably bidentate attachment [12]. The variability among spectra suggests mixtures of these modes in different proportions. Furthermore, the low amplitude of backscattering from second-neighbor atoms is consistent with either the presence of a fraction of outer-sphere complexes (for which first-neighbor As-O geometry would be similar to that of corresponding inner-sphere complexes but second-neighbor Fe backscattering would be absent), and/or a high degree of overall static disorder contributing to cancellation of backscattering amplitudes. These observations are supported by analysis of the iron EXAFS spectra from sediment core collected previously that showed the non-detrital iron fraction had a local structure similar to that of ferrihydrite or goethite, and showed no evidence for iron reduction in solid phases [13]. Collectively, field, chemical, and spectroscopic evidence point to reduction of sorbed arsenic from As(V) to As(III) at or near the sediment-water interface, but no corresponding release of excess arsenic to solution. Reduced As(III) remains bound to a ferric iron phase by both inner- and outer-sphere complexation. Increases in porewater concentrations of arsenic and iron at greater burial depths is attributed to reductive dissolution of the host iron phase, and by possible competitive desorption by dissolved phosphate [13].

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**References**


