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Deposition and Fate of Arsenic in Iron- and Arsenic-Enriched Reservoir Sediments

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Deposition of arsenic to the sediments of Haiwee Reservoir (Olancha, CA) has dramatically increased since March 1996 as a result of an interim strategy for arsenic management in the Los Angeles Aqueduct (LAA) water supply. Ferric chloride and cationic polymer are introduced into the Aqueduct at the Cottonwood treatment plant, 27 km north of the Haiwee Reservoir. This treatment decreases the average arsenic concentration from 25 μg/L above Cottonwood to 8.3 μg/L below Haiwee. Iron- and arsenic-rich flocculated solids are removed by deposition to the reservoir sediments. Analysis of sediments shows a pronounced signature of this deposition with elevated sediment concentrations of iron, arsenic, and manganese relative to a control site. Sediment concentrations of these elements remain elevated throughout the core length sampled (ca. 4% iron and 600 and 200 μg/g of manganese and arsenic, respectively, on a dry weight basis). A pore water profile revealed a strong redox gradient in the sediment. Manganese in the pore waters increased below 5 cm; iron and arsenic increased below 10 cm and were strongly correlated, consistent with reductive dissolution of iron oxyhydroxides and concurrent release of associated arsenic to solution. X-ray absorption near-edge spectroscopy revealed inorganic As(V) present only in the uppermost sediment (0−2.5 cm) in addition to inorganic As(III). In the deeper sediments (to 44 cm), only oxygen-coordinated As(III) was detected. Analysis of the extended X-ray absorption fine structure spectrum indicates that the As(III) at depth remains associated with iron oxyhydroxide. We hypothesize that this phase persists in the recently deposited sediment despite reducing conditions due to slow dissolution kinetics.

Introduction

Arsenic concentrations in the Los Angeles Aqueduct (LAA) are elevated due to geothermal inputs to tributary streams. Although geothermal fluxes are relatively constant (*1*), seasonal cycles of snowmelt and storage in the Eastern Sierra Nevada result in significant variations in arsenic concentration in the LAA. The historical annual average arsenic concentration in the LAA water supply is 20 μg/L (0.3 μM) (*2*), which is well below the currently enforceable U.S. drinking water standard of 50 μg/L (0.7 μM). A standard of 10 μg/L (0.07 μM) was promulgated by the U.S. Environmental Protection Agency in January 2001, but the effective date of this rule was delayed until February 2002 pending reevaluation of the standard (*3*). In anticipation of the new drinking water standard and to accommodate the ocean discharge standard for arsenic in wastewater effluent, the Los Angeles Department of Water and Power (LADWP) implemented an interim arsenic management plan in 1996 to decrease arsenic concentrations in the LAA.

The Cottonwood Treatment Plant, located 27 km north of Haiwee Reservoir, has been intermittently operated to control turbidity in the LAA, using an average dose of 1.7 g/m^3 cationic polymer. Since 1996, ferric chloride has also been added, at an average dose of 5.7 g/m^3. The coagulant dose is regulated so that approximately 67% of the dissolved arsenic in the influent to the Cottonwood Treatment Plant is removed by sedimentation of arsenic- and iron-rich floc in North Haiwee Reservoir. Since 1996, average arsenic concentrations have been 25 μg/L above Cottonwood and 8.3 μg/L below Haiwee (*2*). On the basis of average removal and flow (17 m^3/s) rates, some 40 t of arsenic has been deposited in Haiwee sediments since March 1996.

The biogeochemical cycling of arsenic and iron are closely coupled in natural systems. Iron oxyhydroxides provide a carrier phase for the deposition of arsenic in sediments and their reductive dissolution releases arsenic to interstitial waters (*4*−*7*). In strongly reducing sediments, arsenic may be sequestered in authigenic sulfide or iron sulfide solids (*8*). North Haiwee Reservoir provides an opportunity to study arsenic geochemistry in a system where the natural deposition of arsenic and iron have been subject to substantial perturbation and the recent inputs are relatively well-defined. The diagenesis of arsenic deposited with the iron hydroxide floc on the time scale of a few years can thus be examined in these sediments.

Experimental Methods

Site Description. Storage in the North Haiwee Reservoir varies with aqueduct operation. For a storage of 12.4 × 10^6 m^3, the surface area of the reservoir is 2.36 × 10^6 m^2, the average depth is 5.3 m, and the maximum depth is 6.8 m (*9*). The aqueduct flow enters the reservoir in a narrow inlet channel (Figure 1), which is the site of initial sediment deposition. A sediment plume runs east to west across the reservoir below the inlet, forming a berm, which can isolate a small portion of the northern end of the reservoir at low reservoir elevations (*10*). The berm was submerged at the time that samples were collected.

Sample Collection and Processing. Samples were collected on December 22, 1999, at four sites in North Haiwee Reservoir (Figure 1). Water and sediment samples were collected at the NW and SW sites 0.8 m from the water's edge where the water depth was 0.2 m and, at the NE site, 8 m from the bank, in water 0.8 m deep. Pore water samples were collected at the NW site using a gel probe sampler prior to collection of the sediment core, which was taken at a distance of 0.5 m from the location of insertion of the gel probe sampler. Only water samples were collected at the bridge site.

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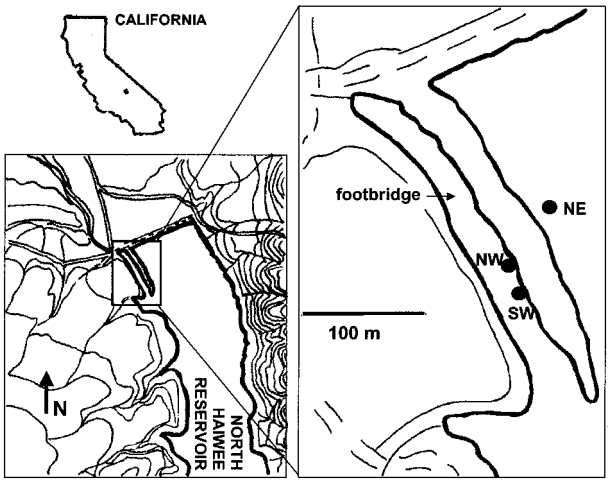

FIGURE 1. Sample collection sites in North Haiwee Reservoir, Olancha, CA, December 22, 1999. Isoclines in lower left panel at 6 m, with spillway at north end at 1128 m (adapted from ref *34*).

Surface water samples were collected in 1-L, acid-washed, HDPE jars by immersion or, for the bridge sample, through Tygon tubing using a hand vacuum pump. Immediately following collection, an aliquot of the bulk sample was filtered through a 0.45-μm, cellulose nitrate syringe filter (Nucleopore). A second aliquot was processed for inorganic arsenic speciation using the anion-exchange technique as previously described and validated (*11, 12*). The anion-exchange column influent was subsampled for total metals analyses, and the effluent was collected for arsenite determination. All samples were stored on ice. The samples for metals analysis were acidified to 1% HNO_3 upon return to the laboratory (within 9 h of collection).

Pore waters were sampled using a gel probe sampler modified from Krom et al. (*13*) in which slabs of precast (0.5 × 2.5 × 0.2 cm) polyacrylamide gel were supported in a plexiglass ladder and protected by a 0.45-μm cellulose nitrate membrane filter and a plexiglass face plate. Design and performance of the modified sampler have been described by Kneebone (*14*); in laboratory tests using streamwater spiked with As(V), recoveries were >95%. In the modified sampler, vertical resolution is defined by the 0.5 cm length of the gel slabs. Although this sacrifices some of the vertical resolution (ca. 1 mm) that can be obtained with a single continuous gel (*15*), substantial ease of handling in the field is gained with this design. The sampler was stored in deoxygenated, 18.2 MΩ·cm water (Millipore) before being inserted in the sediment for 6.5 h. Upon retrieval of the sampler, the gel slabs were placed into preweighed test tubes containing 1.5 mL of 1% (v/v) nitric acid for back equilibration. Solutions were subsequently analyzed for total arsenic, iron, and manganese and the concentrations in the pore waters were calculated based on the mass and water content of the gel slabs.

Sediment cores were collected using 44-cm polycarbonate tubes with an internal diameter of 7.5 cm. The core tubes were not long enough to collect the deepest sediment at the NW site. Cores were transported on ice to the laboratory where they were frozen until use. In the laboratory, sediment cores were sectioned in a nitrogen-filled glovebag. Sections were double-bagged, homogenized, and subsectioned (for digestion and XAS analysis) under a nitrogen atmosphere.

Solid-phase concentrations of iron, manganese, and arsenic were determined using EPA Method 3050b, modified by excluding the final addition of hydrochloric acid and using ICPMS for analysis. This method achieves partial digestion; the sample is heated with nitric acid, and hydrogen peroxide is added. The digestate was diluted appropriately for ICPMS analysis. A blank and a standard reference soil, SRM 4711 (NIST), were analyzed with each set of digestions. Recoveries from the standard soil were approximately 80% of the (certified) X-ray fluorescence values for iron and manganese and greater than 90% for arsenic.

Bulk sediment (upper 20 cm) and water samples were collected near the SW site for use in microcosms. The water was filtered in the field (0.2 μm, cellulose acetate), and samples were transported to the laboratory on ice.

Incubation of North Haiwee Reservoir Sediments. Bulk wet sediment was homogenized and deaerated under argon, and 250 mL (i.e., 60 g dry sediment) was transferred to each of 6 jars. One jar (no. 5) was amended with 20 mL of Provosoli's concentrated antibiotic solution (Sigma). The jars were capped under argon and transferred to a freezer for 30 min, until a thin layer of ice formed on the surface, to minimize subsequent disturbance of the surface sediment. Filtered surface water (0.6 L) was carefully added to each of the jars; the water was dearated with argon before addition to jars 3−5. Jars were bubbled continuously with air (nos. 1 and 2) or argon (nos. 3−5) throughout the experiment at flow rates that kept solutions well mixed without disturbing the sediment. Periodically over 48 h, 10-mL samples were removed via Teflon tubing. The initial pH of the filtered surface water (determined with a pH electrode) was between 8.6 and 8.7; the pH of samples was checked using indicator paper during the experiment and remained between 7 and 8. Samples were collected for analysis of arsenic, manganese, and iron and further processed to determine arsenic speciation (see above).

Analysis. Arsenic, iron, and manganese were quantified by ICPMS (Perkin-Elmer/Sciex Elan 5000A). An arsenic stock solution (1.0 g/L) was prepared from sodium arsenate. Iron and manganese stocks (1.0 g/L) were obtained commercially (VWR Scientific). Calibration standards were prepared immediately prior to each analysis by dilution of the stocks. All chemicals were reagent grade or better and used without further purification.

Arsenic K-edge X-ray absorption spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) on wiggler beamline 4-3 under dedicated conditions (3 GeV, 70−90 mA) using an unfocused beam. Sediment samples were loaded into 2-mm-thick Teflon sample holders and sealed with Kapton tape. Arsenic K-edge and EXAFS (to k = 12 Å^{-1}) fluorescence spectra were collected using Si(220) monochromator crystals (vertical beam size = 1 mm) with a 13-element solid-state germanium-array fluorescence detector at cryogenic temperature (~20 K). Beam energy was calibrated on arsenic foil at 11 867 eV, and 5−8 scans were collected and averaged for edge spectra; 20 scans were averaged for the EXAFS spectrum of one sample. Solid reference compounds were diluted with inert $B(OH)_3$ and collected at 20 K in transmission mode using gas-filled ion chambers. Aqueous reference compounds were quenched in liquid N_2 and run at 20 K in fluorescence.

XANES spectra were analyzed user the computer package WinXAS (*16*); the EXAFS spectrum was analyzed with the package EXAFSPAK (*17*). EXAFS was extracted from background-subtracted spectra using a Victoreen polynomial and tabulated McMaster coefficients (*18*) and was weighted by k^3 (where k is the photoelectron wave vector). The spectrum was fit with theoretical functions calculated by the ab initio computer code FEFF6 (*19, 20*) using atomic clusters generated from the crystal structures of the reference compounds. Interatomic distance (R), backscatterer number (N), and Debye−Waller factor (σ^2) were varied in nonlinear least-squares fits to the normalized experimental spectrum. Trial-and-error fits indicated that backscattering beyond the first coordination shell could not be uniquely fit with more than one iron shell because of overlapping shells at similar

TABLE 1. Composition of Surface Water Samples, North Haiwee Reservoir, December 1999

site	temp (°C)	pH	unfiltered concn (μg/L) As_T	As(III)	Mn	Fe	filtered concn (μg/L) As	Mn	Fe
bridge			17	1.8	27	1900	3.3	5.7	130
NW	6.1	7.8	5.7	1.3	9.9	480	2.5	6.0	80
NE	5.8	8.2	5.7	1.5	11	250	4.6	5.5	78

distances and poor signal-to-noise at high k. To reduce the number of adjustable parameters, second-neighbor backscattering was fit assuming a single shell of iron atoms. Estimated errors based on empirical fits to reference compounds are as follows: first shell: $R \pm 0.01$ Å; $N \pm 10\%$; >first shell: $R \pm 0.02$ Å; $N \pm 30\%$ (*21*, *22*).

Results and Discussion

Removal of Arsenic from Water Column with Deposition of Suspended Sediment. In December 1999, an orange-brown floc was observed in suspension in the water column at the bridge site and was visible settling near the banks of the channel where flow velocity was reduced. Consistent with these observations, the concentrations of arsenic, iron, and manganese were highest in unfiltered samples collected at the bridge site (Table 1). Ninety percent of the iron and 80% of the manganese and arsenic in this sample were retained on a 0.45-μm filter. The material removed by filtration also appears to settle rapidly in the channel since filtered arsenic concentrations were comparable at all sites. The molar ratio of iron to arsenic in the particulate material from the bridge site is 160. The same value is calculated based on the 4-yr average values of the arsenic concentrations above the Cottonwood Treatment Plant and below Haiwee Reservoir and the ferric chloride dose. This correspondence demonstrates that the in situ treatment governs the transport of particulate iron and arsenic to Haiwee Reservoir and their deposition in the sediments. These observations confirm the effectiveness of the interim arsenic management plan in controlling the concentration of arsenic in the LAA water supply below Haiwee Reservoir.

Sediment Concentrations. Settling of the orange-brown floc was observed at the NW and SW sites but not at the protected NE site. The appearance of the sediment cores was also different at these sites. At the NW and SW sites, the surface sediment was a fine, orange-brown material that was easily resuspended, while the deep sediment was fine, black, and gelatinous. At the NE site, the sediment was sandy with brown and black striations throughout. Sediment concentrations of iron, arsenic, and manganese at the NW site are significantly greater than those at the NE site (Figure 2), confirming that the NE site provides a control site that is not subject to deposition of solids generated by the in situ treatment. Note that sediment data are not presented here for the SW site but that sediment concentrations at the NW and SW sites were comparable (*14*).

Iron, arsenic, and manganese concentrations were relatively constant below a depth of 10 cm in the sediment column sampled at the NW site (Figure 2A), averaging 4.4% iron and 240 μg/g arsenic (dry weight). Some decrease in iron, arsenic, and manganese concentrations with depth was observed in the surficial sediment; this effect was most pronounced for manganese. The average molar ratio of iron to arsenic in the sediment is 180, which is consistent with both the composition of the particulate material collected at the bridge site and the average (calculated) composition of the original floc. This again suggests that the deposition of the iron oxyhydroxide floc generated by the in situ treatment is the predominant source of both iron and arsenic in the sediments. The molar ratio in the sediment, however, varies fairly widely (from 92 to 410).

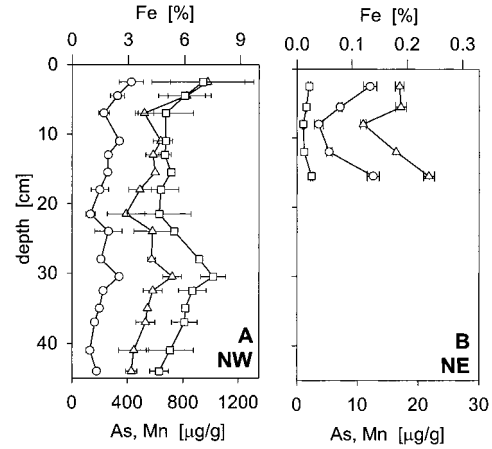

FIGURE 2. Iron (△), manganese (□), and arsenic (○) concentrations measured in sediments collected from NW (A) and NE (B) sites. Note the scale change between A and B. Concentrations, determined by partial digestion, are reported on a dry weight basis. The bars correspond to the concentrations determined in duplicate digestions, and the symbols correspond to the average of the two values. Symbols are positioned at the depth of the bottom of each core section.

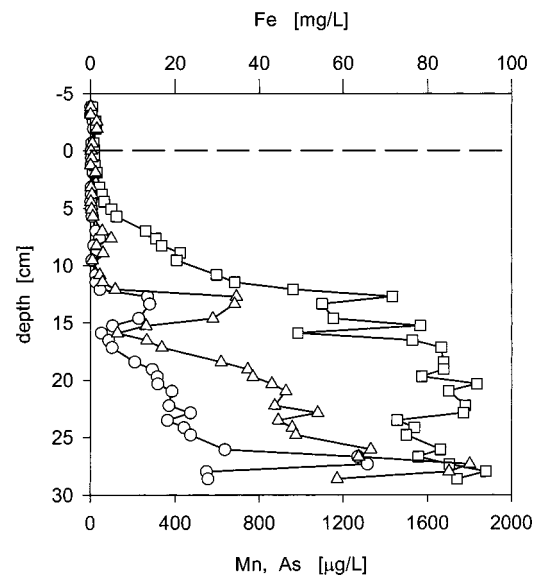

FIGURE 3. Pore water concentrations of manganese (□), iron (△), and arsenic (○) at the NW site, determined using a polyacrylamide gel probe sampler. Error associated with instrumental measurement is smaller than the size of the symbols. The dashed line indicates the position of the sediment−water interface.

Redox Status of the Sediment. Profiles of iron, arsenic, and manganese in the pore water at the NW site obtained with the gel probe sampler (Figure 3) indicate a distinct redox gradient below the sediment−water interface. In the surface sediment, pore water concentrations of iron, manganese, and arsenic are low and comparable to those in the overlying water. Manganese concentrations increase below 5 cm. Arsenic and iron concentrations increase below 10 cm and are strongly correlated (with an r^2 of 0.93). These pore water profiles are consistent with reductive dissolution of manganese and iron oxyhydroxides. The mobilization of iron requires more strongly reducing conditions than does manganese and consequently occurs lower in the sediment profile. The arsenic associated with the iron oxyhydroxide is

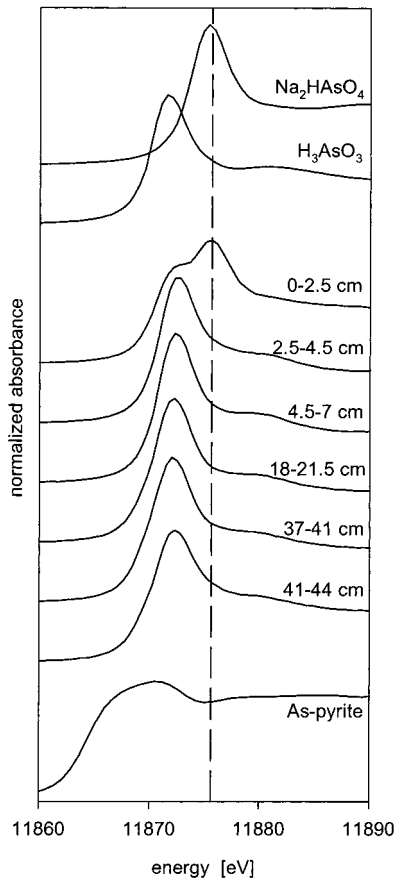

FIGURE 4. Normalized X-ray absorption spectra for model compounds Na_2HAsO_4 and H_3AsO_3 (top) and As-pyrite (bottom) together with sediment samples collected at the NW site.

congruently released upon the reductive dissolution of the carrier phase.

Although the concentration of arsenic in the pore water reaches values as high as 1.3 mg/L, arsenic in the pore water constitutes less than 0.4% of the total arsenic in a given volume of wet sediment (based on the average sediment concentration). Thus, it is not surprising that the sediment concentrations profiles remain constant with depth (Figure 2) despite the increase in the pore water profiles.

Sulfate concentrations are approximately 15 mg/L in Haiwee Reservoir (*10*), and the odor of sulfide was detectable in the deeper NW site sediments. However, the pore water arsenic profiles do not show the decreased concentrations at depth that would be indicative of the sequestration of arsenic in sulfide solids. XAS spectra are also consistent with the absence of sulfide phases (see below).

XAS Characterization of Sediment-Bound Arsenic. XANES spectra obtained for samples taken from several depths in the core from the NW site are shown in Figure 4. The two upper reference spectra, for the salt Na_2HAsO_4 and for a 10 mM solution of $NaAsO_2$, illustrate the separation between the position of the absorption edge maxima at 11876 eV for As(V) as arsenate and at 11871 eV for As(III) as H_3AsO_3(aq). [Note that the $HAsO_2$ species does not occur in aqueous solution (*23*).] Signals for both As(V) and As(III) species are observed in the XANES spectra of the surficial sediment, but only the As(III) species is present in the deeper sediment. The XAS signal can be attributed to arsenic in the solid phase rather than to H_3AsO_3(aq) that may be present in the pore water because of the minor contribution of the pore water to the total arsenic in the sediment sample (see above). The position of the absorption edge maximum in the lower reference spectrum, for arsenic substituted for sulfur in pyrite, is shifted to a distinctly lower value than that observed for the As(III) species in the deeper sediment. Evidence for arsenic in oxidation states lower than +III is not found in the sediment spectra.

The EXAFS spectrum for arsenic in the 41−44-cm sediment sample indicates trigonal coordination of As(III) by oxygen and the presence of second-neighbor iron atoms at longer interatomic distances (Figure 5). The first-neighbor interatomic distance derived from least-squares fitting (As−O = 1.78 Å) indicates As(III) coordinated by three oxygen atoms, similar to As(III)−O distances in reference compounds (*24*, *25*). Arsenic−oxygen distances characteristic of tetrahedral oxygen coordination of As(V) are shorter (As−O = 1.68−1.70 Å) (*26*, *27*) than As(III)−O distances and cannot be fit to the EXAFS spectrum of the sediment. The second-neighbor As−Fe distance derived from fitting (As−Fe = 3.42 Å) assuming a single shell of iron atoms is similar to the range (As−Fe = 3.36−3.40 Å) observed for As(III) sorbed to goethite (*28*). Although a single iron shell was assumed, the best fit does not exactly match the sediment experimental spectrum because there is not a single well-defined set of iron backscatterers (Figure 5). This implies disorder in the position of backscattering iron atoms (i.e., a range of narrowly separated As−Fe interatomic distances) and is consistent with arsenic associated with a disordered or noncrystalline iron phase in which iron backscattering atoms are present over a range of distances. The sorption studies of Manning et al. (*28*) suggested bidentate bonding of As(III) to iron octahedra in goethite ($N_{As-Fe} = 2$). The number of iron backscatterers ($N = 1.6$) derived from the EXAFS fit for the sediment spectrum is probably not diagnostic of the true average because of amplitude cancellation when backscatterer wave functions are slightly out of phase in disordered systems. The observed amplitude is consistent with a mixture of mono- and multi-dentate bonding sites.

Thus, both XANES and EXAFS spectra indicate that As(III) remains associated with iron oxyhydroxides at depth in the sediment column. The presence of As(V) in the surface sediment is consistent with the redox speciation of arsenic in the overlying water (Table 1) and in oxygenated surface waters of the LAA upstream of Haiwee (*11*, *29*). It is likely that arsenic is deposited to the sediments in the +V oxidation state in association with the iron oxyhydroxide floc and that sorbed As(V) is reduced to As(III) at the oxyhydroxide surface (i.e., without release of As(III) to the pore water). Bacterial reduction of As(V) sorbed onto ferrihydrite has been observed in laboratory cultures; the product As(III) remained sorbed to the solid (*30*). It is notable that the signal for As(III) appears in the XANES spectra of the shallowest sediment sample (0−2.5 cm), well above the depth (ca. 10 cm) at which elevated arsenic and iron concentrations (attributable to the reductive dissolution of a small fraction of the iron oxyhydroxides and congruent release of associated arsenic) are observed in the pore water. The occurrence of As(III) in the solid phase in the surficial sediment may also reflect upward mixing of deeper sediment by bioturbation or particle diffusion (*31*).

Release of Arsenic from Microcosm Sediments. The release of iron and arsenic from sediments was followed over 48 h in a microcosm study. Despite attempts to minimize disturbance of the sediments upon addition of filtered surface water, an immediate increase in the iron concentration of the overlying water was observed from 120 μg/L (before addition to the microcosm) to between 240 and 330 μg/L at the first time point (0.5 h). Subsequently, iron concentrations remained constant for about 20 h and then, after 20 h, increased slightly in the jars bubbled with argon and decreased slightly in jars bubbled with air (Figure 6A).

In contrast, arsenic concentrations in the overlying water increased over the course of the experiment in both the aerated and deaerated systems (Figure 6B,C). Release from

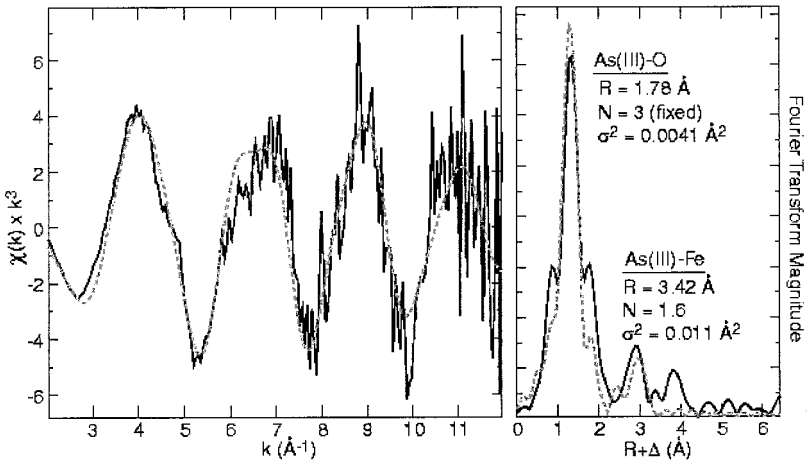

FIGURE 5. Normalized arsenic EXAFS spectrum (left) and the corresponding Fourier transform (right; *x*-axis not corrected for phase shifts) for the 41−44-cm section of the NW core. Solid line is the experimental data; dashed line is the nonlinear least-squares fit assuming one oxygen first shell and one iron second shell. Numerical fit results (inset) are true distances (*R*) corrected for backscatterer phase shifts; *N* is average number of backscatterers, and σ^2 is the Debye−Waller disorder parameter.

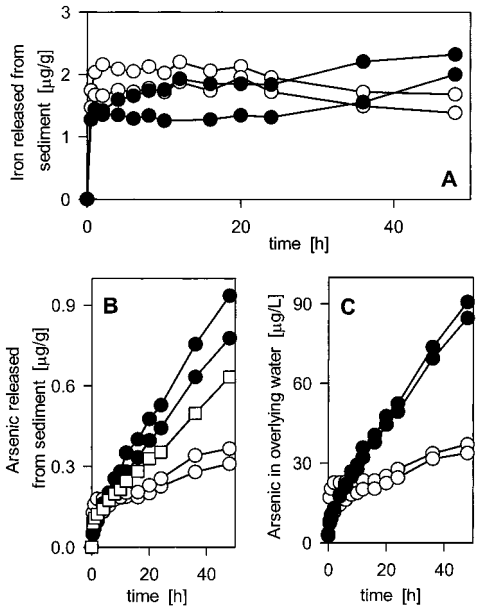

FIGURE 6. Iron (A) and arsenic (B and C) released from sediments in incubations of Haiwee Reservoir sediments under aerated (○) and deaerated (●) conditions. A deaerated, antibiotic-treated control (□) was also monitored for arsenic release. In panels A and B, concentrations measured in solution were corrected for initial solution concentration, then normalized to initial sediment mass and solution volume in each jar, and reported as the mass released from the sediment per mass of dry sediment. Panel C shows the actual arsenic concentration measured in the overlying water. The initial sediment concentrations were 5.9% iron and 225 μg/g arsenic (dry weight basis).

the sediments was fairly comparable in both systems for the first 10 h but then slowed substantially under air while continuing at a steady rate under argon, reaching a final arsenic concentration approximately twice that in the aerated system (Figure 6B). Between 60 and 80% of the arsenic in the overlying water was present as As(III); the redox speciation of arsenic showed neither any consistent trend over time nor any consistent difference between aerated and deaerated systems.

Release of arsenic from the (deaerated) microcosm treated with antibiotics was intermediate between that in the microcosms bubbled with argon and air (Figure 6C). Although the antibiotic treatment did not dramatically decrease arsenic release, the extent to which microbial activity was actually inhibited by this treatment is not known. In a previous microcosm study with arsenic-contaminated sediments, reduction of As(V) to As(III) was observed to be stimulated by addition of organic acids and inhibited by formaldehyde, consistent with the enumeration of cultivable arsenate-reducing bacteria in these sediments (*32*).

Some differences were observed in the behavior of iron and arsenic in the field and microcosm study. Although both iron and arsenic were released into the overlying water in the microcosms, their behavior was not nearly as closely coupled as observed in the pore water. In the microcosms, arsenic was released from the sediments even when the overlying water was aerated. In the field, however, diffusion of arsenic from the sediments into the overlying water was not observed. This difference might be due to the homogenization of deep and surface sediment in the microcosm study but could also imply that the continued deposition of iron oxyhydroxide floc is partly responsible for maintaining a zone of oxidized sediment that prevents diffusion of arsenic into the overlying water in the field.

Implications for Arsenic Geochemistry in Haiwee Reservoir. Ferric chloride additions at Cottonwood Treatment Plant effectively decrease the concentration of arsenic in the water supplied to the City of Los Angeles. However, elevated concentrations of arsenic are present throughout the sediment column in North Haiwee Reservoir as well as in the pore waters at depth in the sediments as a result of the deposition of iron- and arsenic-bearing floc. Because Haiwee Reservoir is a protected water body, our sampling was conducted only in the inlet channel where initial sediment deposition occurs. Sediment transport from this region is restricted by a berm that runs across the reservoir below the inlet (*10*). The composition of the sediment at the protected NE site clearly demonstrates that not all of the reservoir is subject to the effects of deposition of the arsenic- and iron-rich floc.

Although removal of the deposited solids from Haiwee Reservoir is a component of the LADWP's interim arsenic management plan (*2*), this has not (as of September 2001) been attempted. Considerations in sediment removal include the generation of turbidity and transport of arsenic from the reservoir. Options for removing the sediments are currently being assessed by the LADWP (*33*).

Diffusive fluxes of arsenic from pore waters enriched in arsenic to the overlying water are prevented by an oxic zone in the surficial sediments. Iron, arsenic, and manganese

diffusing up through the sediments in response to the observed concentration gradient are trapped in the surficial sediment through a combination of sorption and oxidative precipitation processes. If these oxic conditions are maintained by contact between the surficial sediments and the overlying water, diffusion rates and the adsorptive capacity of the surface sediment will determine whether arsenic will be released from the sediment. If rapid deposition of particles helps to keep the surface sediment oxic, slowing sedimentation by halting the in situ treatment may cause migration of the redox boundary to the sediment−water interface, allowing release of arsenic to the overlying water. Extensive remineralization of organic carbon could also promote such a migration of the redox boundary. To predict the long-term fate of arsenic in the reservoir as a whole, however, the patterns of water circulation and stratification would need to be evaluated and the locations of major sediment accumulation identified and sampled.

Acknowledgments

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Literature Cited

(1) Farrar, C. D.; Sorey, M. L.; Rojstaczer, S. A.; Janik, C. J.; Winnett, T. L.; Clark, M. D. *Water-Resour. Invest.* (*U.S. Geol. Surv.*) **1987**, *No. 87-4090*.
(2) Stolarik, G. F.; Christie, J. D. Interim Arsenic Management Plan for Los Angeles. In *Proceedings of the 1999 American Water Works Association Annual Conference*, Chicago, IL; 1999.
(3) *Fed. Regist.* **2001**, *66* (139), 37617−37631; http://www.epa.gov/safewater/ars/ars_july01proposal.html.
(4) Aggett, J. A.; O'Brien, G. *Environ. Sci. Technol.* **1985**, *19* (3), 231−238.
(5) Edenborn, H. M.; Belzile, N.; Mucci, A.; Lebel, J.; Silverberg, N. *Biogeochemistry* **1986**, *2*, 359−376.
(6) Kuhn, A.; Sigg, L. *Limnol. Oceanogr.* **1993**, *38*, 1052−1059.
(7) Spliethoff, H. M.; Mason, R. P.; Hemond, H. F. *Environ. Sci. Technol.* **1995**, *29*, 2157−2161.
(8) Moore, J. N.; Ficklin, W. H.; Johns, C. *Environ. Sci. Technol.* **1988**, *22* (4), 432−437.
(9) Hopper, W. Los Angeles Department of Water and Power, personal communication, 2000.
(10) Ball, D. LADWP, personal communication, 2000.
(11) Wilkie, J. A.; Hering, J. G. *Environ. Sci. Technol.* **1998**, *32*, 657−662.
(12) Wilkie, J. A. Ph.D. Thesis, University of California, Los Angeles. 1997.
(13) Krom, M. D.; Davison, P.; Zhang, H.; Davison, W. *Limnol. Oceanogr.* **1994**, *39* (8), 1967−1972.
(14) Kneebone, P. E. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 2000.
(15) Shuttleworth, S. M.; Davison, W.; Hamilton-Taylor, J. *Environ. Sci. Technol.* **1999**, *33*, 4169−4175.
(16) Ressler, T. *J. Synchrotron Radiat.* **1998**, *5*, 118−122.
(17) George, G. N.; Pickering, I. J. *EXAFSPAK: A suite of computer programs for analysis of X-ray absorption spectra*; Stanford Synchrotron Radiation Laboratory: 1993.
(18) McMaster, W. H.; Kerr Del Grande, N.; Mallett, J. H.; Hubbell, J. H. *Compilation of X-ray cross sections*; National Bureau of Standards: Gaithersburg, MD, 1969; UCRL-50174.
(19) Rehr, J. J. *Jpn. J. Appl. Phys.* **1993**, *32-2*, 8−12.
(20) Rehr, J. J.; Albers, R. C.; Zabinsky, S. I. *Phys. Rev. Lett.* **1992**, *69*, 3397−3400.
(21) O'Day, P. A.; Carroll, S. A.; Waychunas, G. A. *Environ. Sci. Technol.* **1998**, *32*, 943−955.
(22) O'Day, P. A.; Newville, M.; Neuhoff, P. S.; Sahai, N.; Carroll, S. A. *J. Colloid Interface Sci.* **2000**, *222*, 184−197.
(23) Loehr, T. M.; Plane, R. A. *Inorg. Chem.* **1968**, *7* (9), 1708−1714.
(24) Pertlik, F. *Monatsh. Chem.* **1978**, *109*, 277−282.
(25) Pertlik, F. *Czech. J. Phys.* **1978**, *28*, 170−176.
(26) Foster, A. L.; Brown, G. E., Jr.; Tingle, T. N.; Parks, G. A. *Am. Mineral.* **1998**, *83*, 553−568.
(27) Savage, K. E.; Tingle, T. N.; O'Day, P. A.; Waychunas, G. A.; Bird, D. K. *Appl. Geochem.* **2000**, *15*, 1219−1244.
(28) Manning, B. A.; Fendorf, S. E.; Goldberg, S. *Environ. Sci. Technol.* **1998**, *32*, 2383−2388.
(29) Kneebone, P. E.; Hering, J. G. *Environ. Sci. Technol.* **2000**, *34* (20), 4307−4312.
(30) Zobrist, J.; Dowdle, P. R.; Davis, J. A.; Oremland, R. S. *Environ. Sci. Technol.* **2000**, *34*, 4747−4753.
(31) Meile, C.; Koretsky, C. M.; Van Cappellen, P. *Limnol. Oceanogr.* **2001**, *46*, 164−177.
(32) Harrington, J. M.; Fendorf, S. E.; Rosenweig, R. F. *Environ. Sci. Technol.* **1998**, *32*, 2425−2430.
(33) Christie, D. LADWP, personal communication, 2000.
(34) USGS. Haiwee Reservoirs, CA, 36117-B8-TF-024, 7.5′ Map Series. U.S. Geological Survey: Denver, 1994,

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