

A Gel Probe Equilibrium Sampler for Measuring Arsenic Porewater Profiles and Sorption Gradients in Sediments: II. Field Application to Haiwee Reservoir Sediment

KATE M. CAMPBELL,^{*,†,‡,||} ROBERT ROOT,[‡] PEGGY A. O'DAY,[‡] AND JANET G. HERING^{†,§}

Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA 91125, and School of Natural Sciences, University of California, Merced, CA, 95344

Received May 13, 2007. Revised manuscript received October 02, 2007. Accepted October 05, 2007.

Arsenic (As) geochemistry and sorption behavior were measured in As- and iron (Fe)-rich sediments of Haiwee Reservoir by deploying undoped (clear) polyacrylamide gels and hydrous ferric oxide (HFO)-doped gels in a gel probe equilibrium sampler, which is a novel technique for directly measuring the effects of porewater composition on As adsorption to Fe oxides phases in situ. Arsenic is deposited at the sediment surface as As(V) and is reduced to As(III) in the upper layers of the sediment (0–8 cm), but the reduction of As(V) does not cause mobilization into the porewater. Dissolved As and Fe concentrations increased at depth in the sediment column driven by the reductive dissolution of amorphous Fe(III) oxyhydroxides and conversion to a mixed Fe(II, III) green rust-type phase. Adsorption of As and phosphorous (P) onto HFO-doped gels was inhibited at intermediate depths (10–20 cm), possibly due to dissolved organic or inorganic carbon, indicating that dissolved As concentrations were at least partially controlled by porewater composition rather than surface site availability. In sediments that had been recently exposed to air, the region of sorption inhibition was not observed, suggesting that prior exposure to air affected the extent of reductive dissolution, porewater chemistry, and As adsorption behavior. Arsenic adsorption onto the HFO-doped gels increased at depths > 20 cm, and the extent of adsorption was most likely controlled by the competitive effects of dissolved phosphate. Sediment As adsorption capacity appeared to be controlled by changes in porewater composition and competitive effects at shallower depths, and by reductive dissolution and availability of sorption sites at greater burial depths.

Introduction

Complex biogeochemistry governs the partitioning of arsenic (As) between solid and aqueous phases in freshwater

sedimentary environments. In nonsulfidogenic environments where dissolved As concentrations are not controlled by As-sulfide mineral precipitation, adsorption onto iron (Fe)-(oxyhydr)oxides can be an important sequestration mechanism (1). Adsorption is controlled by As redox state, solution chemistry, sorbent properties, and pH. The availability of sorption sites and surface affinity will determine the extent of adsorption onto a mineral substrate.

Adsorption of As can be suppressed in the presence of competitively sorbing ions such as phosphate, inorganic carbon, organic carbon, and other compounds through electrostatic, steric, or competitive effects (2–5). Phosphate competes directly with both As(III) and As(V) for surface sites on Fe oxides (2, 3, 5–10), but has a stronger inhibitory effect on As(V) (see Part I, 11). Inorganic carbon may also suppress As adsorption when concentrations are elevated in groundwater because of microbial respiration of organic carbon and/or carbonate mineral dissolution (12–15). Interactions of organic carbon with As are highly dependent on the type of organic matter, although it is possible for organic carbon to inhibit As adsorption onto Fe oxides (11, 16–18).

Changes in solid-phase properties during early sediment diagenesis can also alter As partitioning. Reductive dissolution of Fe(III) oxides and the resulting secondary mineral transformations can promote As mobilization under certain conditions and may be important in many types of reducing sediments and aquifers (19–23). When sorption sites remain available on the solid, As can re-adsorb onto the solid phase even as reductive dissolution progresses (24). Re-adsorption is affected strongly by the porewater composition, and the presence of competitively adsorbing ions can increase the amount of As in the porewater. Once the surface sites are saturated, As mobilization into the porewaters is directly related to the amount of solid reductively dissolved.

The sediment in North Haiwee Reservoir (Olancho, CA) is a unique field site for the study of various mechanisms controlling As partitioning in the subsurface environment. A natural geothermal input of As results in elevated As concentrations in the Los Angeles Aqueduct (LAA), a source of drinking water for the city of Los Angeles. Currently, the water is being treated by injecting ferric chloride into the LAA, producing an amorphous Fe oxyhydroxide floc that removes As from the dissolved phase by sorption/coprecipitation. The As- and Fe-rich floc is removed from the water via sedimentation at Haiwee Reservoir (for map, see Supporting Information, Figure S1). Arsenic is deposited as As(V), but reduction to As(III) occurs at or just below the sediment–water interface (25, 26). The change in oxidation state does not result in release of As to the porewaters (26). Below ~10 cm depth, sediment X-ray spectroscopic data suggests reductive dissolution of the Fe(III) oxyhydroxide floc and formation of an amorphous mixed Fe(II, III) phase with local structure similar to that of carbonate green rust ($[\text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}]^{2+} \cdot [\text{CO}_3, n\text{H}_2\text{O}]^{2-}$) (26). Reductive Fe(III) dissolution in Haiwee sediments is also likely to be microbially mediated. The presence of adsorbed As, phosphate, and other anions can stabilize green rust phases in sediment (27, 28). However, the As sorption properties of green rust-type solids compared to Fe(III) oxide phases are not well known.

Reductive dissolution in Haiwee Reservoir sediments drives the mobilization of As, but the role of porewater chemistry in controlling As partitioning is unclear. The purpose of this study is to identify the geochemical controls on As mobilization in Haiwee Reservoir sediment using evidence from a novel Fe(III)-doped gel probe equilibrium sampler.

* Corresponding author phone (650) 329-4604; e-mail kcampbell@usgs.gov.

† California Institute of Technology.

‡ University of California.

§ Current address. Swiss Federal Institute of Aquatic Science & Technology (EAWAG), Dübendorf, Switzerland.

|| Current address. U.S. Geological Survey, Menlo Park, CA 94025.

Experimental Section

Reagents. All chemicals used were reagent grade and used without further purification unless otherwise noted. All water used was 18 M Ω -cm deionized water (Elix/Milli-Q, Millipore). Solutions were stored in plastic containers that had been acid-washed in 2–5% hydrochloric acid. Experiments were performed in trace metal-free plastic tubes. All nitric acid solutions were made with trace metal grade HNO₃ (EM Science, Omnipure, 70%).

Clear and HFO-Doped Gels. Hydrous ferric oxide (HFO) was synthesized as described previously (11, 29, 30). Both clear and HFO-doped gels were used in this study. All gels were cut to the final dimensions of 2 × 0.5 × 0.2 cm. The iron content of HFO-doped gels was 2 × 10⁻⁶ mol Fe/gel slab. A complete description of gel synthesis, re-equilibration and analytical methods is provided in Part I (11). Sorption onto HFO-doped gels is normalized to the amount of Fe in each gel slab (mol sorbate/mol Fe).

Gel Probe Design. Gel probes were designed to hold the gel slabs in individual slots etched into a plastic holder. The slots were arranged vertically in either one or two columns, holding between 54 and 80 slabs per column. The probes were between 35 and 55 cm long, measured from the top gel to the bottom gel. The probes with two parallel columns ("double probes") were designed to hold clear and HFO-doped gels at the same depth for simultaneous porewater and adsorption measurements. The gel slabs were secured with a 0.45 μ m nitrocellulose membrane filter (Schleicher and Schuell) and held in place with a plastic face plate. The probes were placed in deoxygenated water and bubbled with compressed N₂ gas for at least 12 hours prior to deployment to deoxygenate the water inside the gels. The probes were transported to the field site in deoxygenated water.

For sediment laboratory microcosm experiments, six "mini-probes" were constructed. The mini-probes had a single column of six slots for gel slabs, and were 4 cm long. Preparation was identical to the field probe procedure. Double and mini gel probe schematics are given in Supporting Information Figure S2.

Sediment Microcosms. Laboratory sediment microcosms were designed to determine the amount of time required for clear and HFO-doped gels in a gel probe sampler to equilibrate with sediment porewater. Surficial sediment was collected in the field, kept on ice during transport, and homogenized in a large container prior to being frozen at -20°C. After being defrosted, the sediment was again homogenized and distributed into six acid-washed plastic containers in 600 mL aliquots. As the sediment settled, the overlying water at the surface of the sediment was continuously bubbled with compressed N₂ for 24 hours to allow anoxic conditions in the sediment to be established. Six mini-probes were filled with alternating clear and HFO-doped gels, deoxygenated, and inserted into the containers filled with sediment, one probe per container. Compressed N₂ continued to bubble in the overlying water for the entire course of the experiment. One probe was removed at each time point. The gels were immediately recovered from the mini-probes and re-equilibrated in acid for analysis.

Field Deployment. Gel probes were deployed in Haiwee Reservoir sediments in the shallow waters of the inlet channel. The gel probes contained both HFO and clear gels, and were deployed in October 2004 and May 2006. The sediments in October 2004 were soft and porous, whereas the sediments in May 2006 were hard and were recently exposed to air. The probes were inserted vertically into the sediments parallel to the direction of overlying water flow, with several gels above the sediment–water interface. The gel probes were allowed to equilibrate undisturbed for 24 hours before being extracted from the sediment. The gels were immediately removed from the probe and placed in individual 2 mL tubes (Eppendorf).

A subset of clear gels (collected in May 2006) was placed in individual tubes pre-filled with 1.25 mL of 25 mM H₃PO₄ for determination of As speciation. These gels were allowed to re-equilibrate for 6–12 hours before analysis. A subset of HFO-doped gels (collected in May 2006) were preserved for X-ray absorption spectroscopy (XAS) analysis by immediately freezing the tubes on dry ice in the field until placement in a -20°C freezer. The rest of the clear and HFO-doped gels were placed on ice until they were acidified in the laboratory and allowed to re-equilibrate for at least 24 hours before analysis.

Gel Probe Analyses. Clear gels were re-equilibrated in 1% HNO₃ for inductively-coupled plasma mass spectrometry (ICP-MS) analysis (detection limit = 0.1 μ M), or 25 mM H₃PO₄ for liquid chromatography coupled to ICP-MS (LC-ICP-MS, detection limit = 0.2 μ M) for As speciation measurements. HFO-doped gels were re-equilibrated in 5% HNO₃ for ICP-MS analysis (detection limit = 0.001 mol As/mol Fe) or were frozen without further treatment for As speciation measurements by X-ray absorption spectroscopy (XAS). Iron was measured by the phenanthroline Fe assay (31).

Arsenic K-edge X-ray absorption spectra of select HFO-doped gels from the May 2006 deployment were collected at the Stanford Synchrotron Radiation Laboratory (SSRL), Menlo Park, California. Analytical methods are described in detail in Part I (11). The same fitting protocol was employed for gel samples deployed in Haiwee sediments as for the known mixtures analyzed in Part I.

Gravity Core Processing and Analysis. Several acid-washed core tubes were inserted in sediments adjacent to the gel probes at the time of deployment, and were left undisturbed until after the gel probes were removed. Once recovered, sediment cores were stored upright on ice for transport and frozen at -20°C upon return to the laboratory. Cores were defrosted under N₂ in a glove box and cut into 2–4 cm sections. These sections were centrifuged to separate the bulk solid from the porewater. The porewater from each section was syringe-filtered (0.2 μ m, Pallman), and acidified with 1% HNO₃ for ICP-MS and colorimetric analyses.

Core sections from two cores were dried at 60°C in a drying oven for solid phase organic carbon measurement by CHN analysis (Europa Hydra 20/20 IRMS, University of California, Davis). Two samples from each section were analyzed: one sample was fumigated with HCl to remove the inorganic carbon and the other was directly analyzed for total carbon (organic and inorganic). X-ray fluorescence (XRF) on composite samples was performed to measure bulk elemental composition (SGS Minerals, Toronto).

Results

Sediment Microcosm. The clear gels in the sediment microcosms stabilized to a constant As concentration of ~10 μ M within 10 hours. The HFO-doped gels in the sediment microcosm required about 18 hours to reach equilibrium with the sediment porewaters. An acceptable deployment time was determined to be 24 hours based on the sediment microcosm results (Supporting Information Figure S3). Haiwee Reservoir sediments are relatively porous and exhibit fast resupply behavior to the porewater compared to other lacustrine sediments. Equilibration times in other natural systems may vary with sediment porosity and solute transport characteristics.

Comparison of Clear Gel Concentrations and Core Porewater Extractions. Porewater As concentrations measured by clear gels in a double gel probe are comparable to those in porewaters extracted from a core taken immediately adjacent (<10 cm) to the gel probe (Supporting Information Table S1). The porewater As concentrations determined by both methods range from 0.4 to 1.7 μ M and show the same

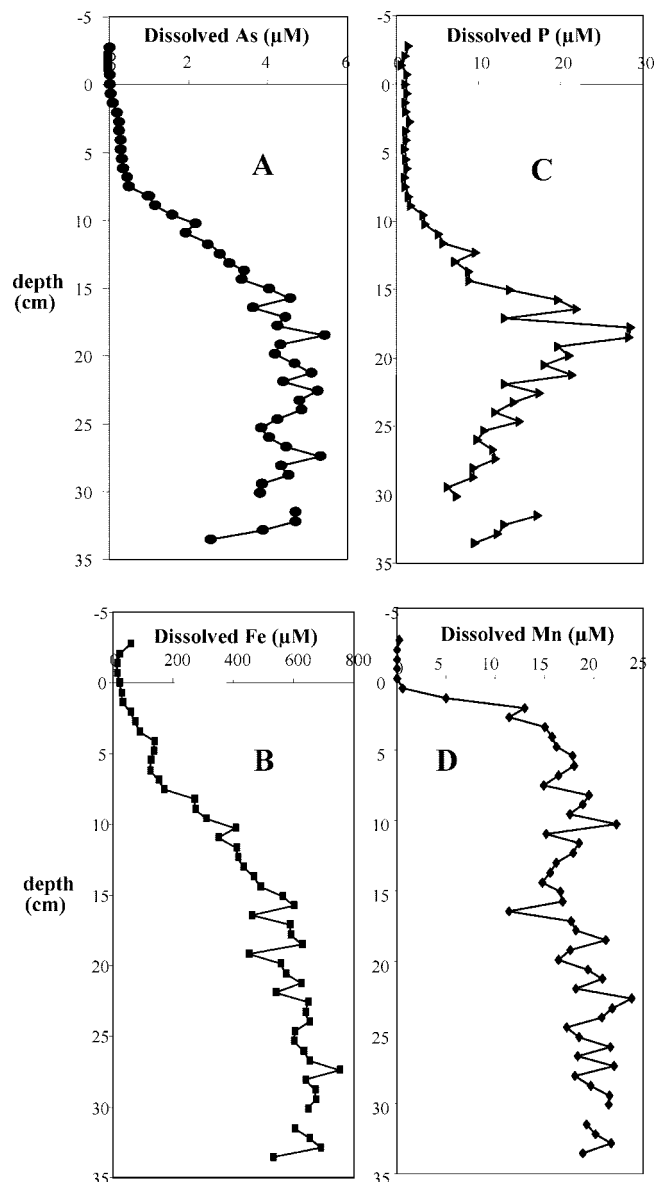


FIGURE 1. Porewater concentrations of As (A), Fe (B), P (C), and Mn (D) from a double gel probe deployed October 2004. The probe was equilibrated for 24 hours in the sediment. The sediment was soft and had not been recently exposed to the air.

trends with depth from 0 to 12 cm. The lack of any systematic bias between the values obtained by the two methods suggest that the observed variability reflects natural spatial variations. The consistency between clear gel and core porewater concentrations also verifies the sufficiency of 24 hour deployment time to reach equilibrium between the sediment, porewater, and gel probe sampler.

Gel Probe Porewater Profiles (Clear Gels). Porewater concentrations as a function of depth below the sediment–water interface for October 2004 and May 2006 are presented in Figures 1 and 2, respectively. Dissolved As concentrations began to increase between 2 and 5 cm depth, with very little dissolved As observed at the sediment–water interface. Arsenic concentrations peaked between 15 and 35 cm below the sediment–water interface. There is a strong correlation between dissolved Fe, As and P (Supporting Information Figure S4 and ref (30)). In May 2006, about 60% of the total dissolved As was present as As(III) between 5 and 25 cm depth. Below 25 cm, As(III) constituted ~80% of the total dissolved As (Figure 2).

Gel Probe Sorption Profiles (HFO-Doped Gels). Arsenic and P adsorption profiles from October 2004 and May 2006 are shown in Figures 3 and 4, respectively. In both deploy-

ments, sorption is low near the sediment–water interface where dissolved As concentrations are low, and increases at depth. Approximately 90% of the As adsorbed onto the HFO-doped gels was As(III) in May 2006, as determined by in situ XANES analysis of the gels (Supporting Information Table S2 and Figure S5). Adsorption of As and P onto HFO-doped gels was correlated with dissolved concentrations for the May 2006 deployment, but not for the October 2004 deployment. In October 2004, dissolved As concentrations increased between 10–20 cm without a corresponding increase in adsorption onto the HFO-doped gels (Figure 3).

Results from Sediment Cores. The total solid-phase Fe and As content is 7.89% and 210 mg/kg, respectively (Supporting Information Table S3), consistent with previous sediment extractions (32). Solid phase organic carbon ranged from 20–34 g C/kg sediment, decreasing with depth by 35–40% (Supporting Information Table S4). Between 75 and 90% of the total solid phase carbon was organic carbon.

Discussion

Variability. Water level and floc deposition in the LAA are not constant, and the profiles taken at this site probably do not represent processes that result from uniform sediment

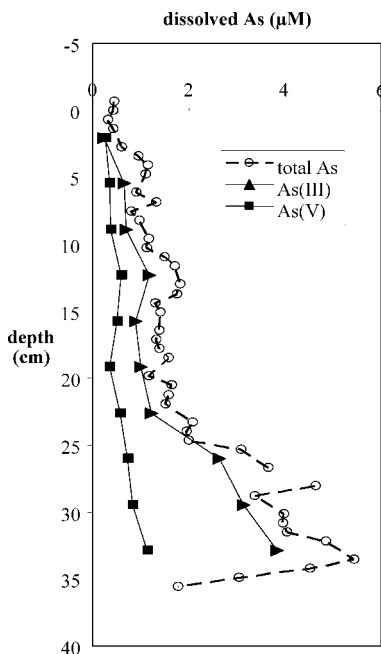


FIGURE 2. Porewater concentration and speciation of As from a double probe deployed in May 2006. The probe was equilibrated for 24 hours. The sediment was hard and had been recently exposed to air. Arsenic speciation measurements were made by LC-ICP-MS.

aging. The floc deposited in the inlet channel may periodically be exposed to air and resubmerged. Variation in flow also causes erosion and re-deposition of the sediment. The depositional variability may explain the spatial and temporal variations in porewater concentrations and sorption profiles.

Gel probes deployed May 2006 were deployed in sediment that may have been recently exposed to air prior to sampling. The profiles in May 2006 were different from October 2004, with a peak of dissolved As occurring deeper (~25–35 cm, Figure 4) in the sediment rather than a plateau of dissolved As below ~15 cm (Figure 3). It is possible that due to the oxidative changes in the sediment, the region of sorption inhibition (10–20 cm) was absent in May 2006 because reductive dissolution in the upper layers (0–20 cm) had not progressed to the same extent as in October 2004. In addition, the solid phase As(V) transition was deeper in the sediment column (~8 cm) after recent exposure to air than when sediment conditions were more similar to the October 2004 sampling (<2 cm) (unpublished data and ref. 30).

Effect of Sediment Diagenesis on As Partitioning. Sediment diagenesis has significant implications for As mobilization in Haiwee sediments, since reductive dissolution not only drives As mobilization, but also mineralogical changes in the sediment. In November 2004, core sections analyzed by X-ray absorption spectroscopy (XAS) were found to have significant fractions of an amorphous carbonate green rust-type phase below ~10 cm (26). The presence of green rust indicates that production of Fe(II) from reductive dissolution of the Fe(III) oxide and other chemical conditions were sufficient to transform the deposited As-bearing amorphous iron phase.

Early sediment diagenesis is characterized by the mineralization of organic carbon coupled to the reduction of O₂, nitrate, Mn (III, IV) oxides, and Fe(III) oxides and is usually driven by microbial metabolism (33). Solid-phase organic carbon in Haiwee cores decreased with depth, suggesting that organic carbon was being metabolized, possibly to dissolved inorganic carbon. The presence of dissolved Mn and Fe in the porewaters (Figure 1) confirms that diagenetic processes were occurring in the sediment.

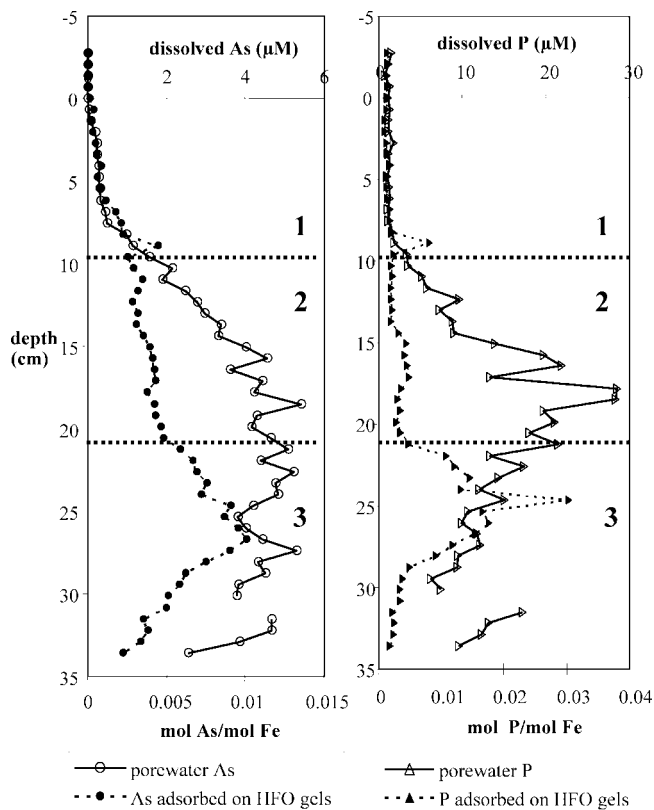


FIGURE 3. Porewater and adsorption profiles for As and P from a double probe deployed in October 2004. Region 1 denotes the low porewater concentrations of As and P. Region 2 denotes the region of sorption inhibition onto the HFO-doped gels. Region 3 denotes the region where As and P adsorption on HFO-doped gels increase at depth.

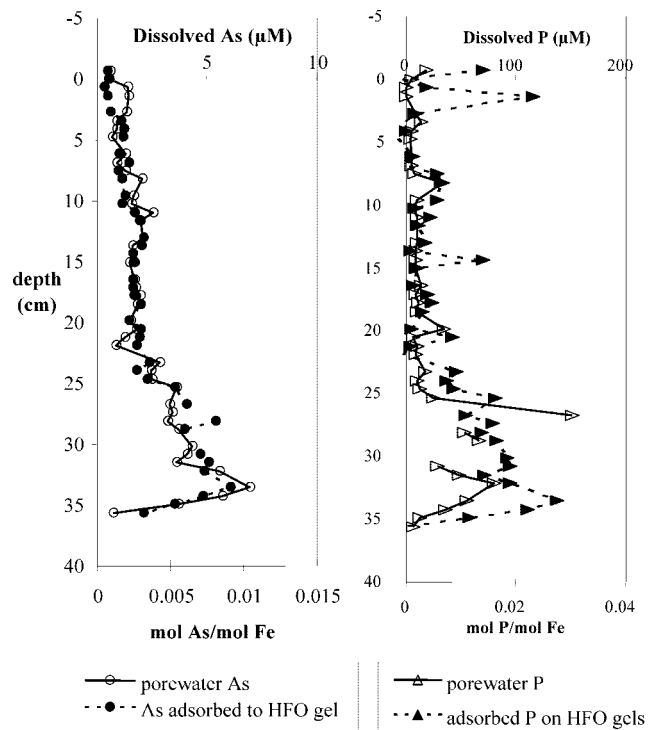


FIGURE 4. Porewater and adsorption profiles for As and P from a double probe deployed in May 2006, when the sediment was hard from recent exposure to air.

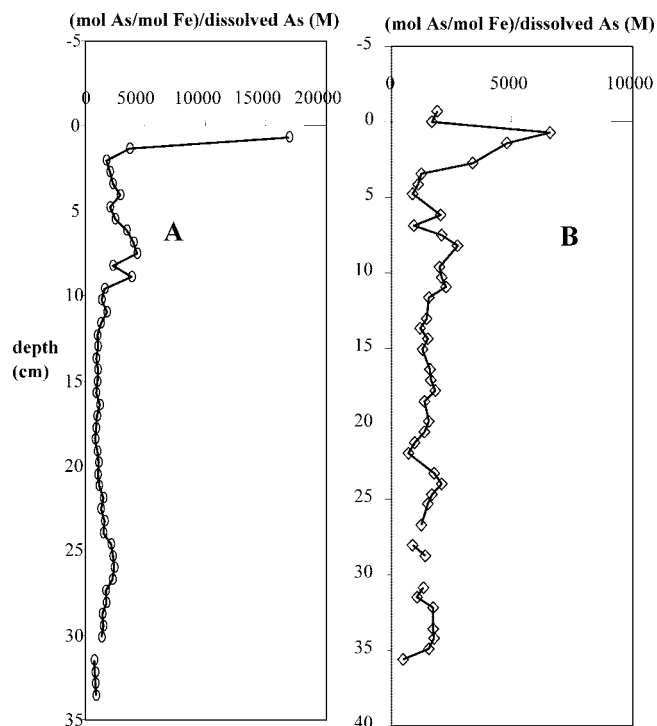


FIGURE 5. K_0^* plots for October 2004 double probe (A) and May 2006 (B).

The porewater and sorption profiles for October 2004 can be divided into three regions, as denoted in Figure 3. The surficial sediment (region 1) had negligible dissolved As, P, and Fe concentrations and minimal sorption onto the HFO-doped gels. In this region, fresh floc was being deposited, and O_2 diffusing from the overlying water was consumed in the sediment (unpublished data). Between 10–20 cm, the correlation between dissolved As, P, and Fe indicates that reductive dissolution released As and P to the porewaters (region 2). Although the dissolved Fe and As concentrations

were constant below ~15 cm, As and P adsorption onto the HFO-doped gels did not peak until 20–30 cm (region 3). The result is a region between 10–20 cm where dissolved As and P increased in the porewaters but minimal adsorption of As and P onto the HFO-doped gels was observed, indicative of sorption inhibition of both As and P (region 2). Sorption inhibition may be caused by dissolved organic or inorganic carbon, both of which are expected to be present as sediment diagenesis occurs. The change in sorption behavior in region 3 suggests a transition in porewater chemistry that greatly

affects As partitioning; this effect would not have been observed by clear gels or core analysis alone.

Effect of P on As Adsorption. The adsorption behavior of As onto the HFO-doped gels in May 2006 and in region 3 (20–35 cm) of October 2004 is consistent with the competitive sorption effects of phosphate. An operationally-defined partition coefficient for sorption onto HFO-doped gels, K_D^* , can be expressed as shown in eq 1,

$$K_D^* = \frac{(\text{mol}_{\text{As}}/\text{mol}_{\text{Fe}})_{\text{HFOgel}}}{[\text{As}_{\text{dissolved}}]_{\text{porewater}}} \quad (1)$$

where the concentration of dissolved total As is expressed in mol/L. This value is useful for comparing HFO-doped gel data from field deployments and laboratory experiments. The plots of K_D^* as a function of depth for the October 2004 and May 2006 field deployments are shown in Figure 5.

The large K_D^* values at shallow depths are due to very low dissolved As concentrations. The K_D^* values deeper in the sediment column range from 1500–2500 when the maximum dissolved P concentrations are 150–200 μM . For comparison, a competitive phosphate study was conducted, where the amount of As adsorbed onto an HFO-doped gel was measured in the presence of 10 μM As and variable (0–500 μM) concentrations of P (data presented in Part I (ref (11))). When phosphate concentrations were 150–200 μM in the laboratory study, the calculated K_D^* values were approximately 1500–2000 for As(V) and 2000–2800 for As(III) (Supporting Information Figure S6). The agreement between the laboratory and field values for K_D^* suggest that phosphate controls the amount of As adsorbed onto the surface of HFO-doped gels in the field in May 2006 and in region 3 (20–35 cm) for October 2004.

In the competitive phosphate study from Part I (11), phosphate inhibited As(V) sorption onto HFO-doped gels to a greater extent than As(III). In May 2006, 80% of the dissolved As in the porewater was present as As(III) (as determined by LC-ICP-MS), and As(III) comprised $\geq 90\%$ of the As adsorbed onto the HFO-doped gels. The enrichment of adsorbed As(III) on the HFO surface supports the hypothesis that phosphate controls As re-adsorption at depth (> 20 cm).

This study illustrates a novel way to measure the effect of porewater composition on As re-adsorption upon reductive dissolution using an HFO-doped gel probe equilibrium sampler. Arsenic accumulation into the porewater at intermediate depths (10–15 cm) may be at least partially controlled by porewater composition rather than available sorption sites on the sediment, whereas the amount of As adsorbed onto the HFO-doped gels at depths greater than 20 cm is controlled by the competitive effects of P. This suggests that the elevated dissolved As concentrations at depth may be due to the lack of available surface sites as the amorphous Fe(III) oxides undergo sediment diagenesis.

Acknowledgments

This work was supported by funding from NSF BES-0201888, BES-0201943, and EAR-0525387. We thank the Los Angeles Department of Water and Power (LADWP), particularly Gary Stolarik, Stanley Richardson, and Fred Richardson, for access to Haiwee Reservoir. We also thank Nathan Dalleska for analytical support and Mike Vondrus for gel probe construction. Portions of this research were carried out at the Stanford Synchrotron Radiation Laboratory, a national users facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences.

Supporting Information Available

Map of Haiwee reservoir, gel probe schematics, microcosm results, comparison of porewater measurement techniques, correlation between As and Fe (October 2004), amount of

As(III) and As(V) in HFO-doped gels, XANES spectra for field gels, XRF bulk sediment composition and solid phase organic carbon data, K_D^* for competitive phosphate laboratory study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Smedley, P. L.; Kinniburgh, D. G. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **2002**, *17*, 517–568.
- (2) Holm, T. R. Effects of CO_3^{2-} /bicarbonate, Si, and PO_4^{3-} on arsenic sorption to HFO. *J. Am. Water Works Assoc.* **2002**, *94*, 174–181.
- (3) Jain, A.; Loeppert, R. H. Effect of Competing anions on the adsorption of arsenate and arsenite by ferrihydrite. *J. Environ. Qual.* **2000**, *29*, 1422–1430.
- (4) Grafe, M.; Eick, M. J.; Grossl, P. R. Adsorption of arsenate (V) and arsenite (III) on goetite in the presence and absence of dissolved organic carbon. *Soil Sci. Soc. Am. J.* **2001**, *65*, 1680–1687.
- (5) Dixit, S.; Hering, J. G. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility. *Environ. Sci. Technol.* **2003**, *37*, 4182–4189.
- (6) Manning, B. A.; Goldberg, S. Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. *Soil Sci. Soc. Am. J.* **1996**, *60*, 121–131.
- (7) Hongshao, Z.; Stanforth, R. Competitive adsorption of phosphate and arsenate on goethite. *Environ. Sci. Technol.* **2001**, *35*, 4753–4757.
- (8) Liu, F.; Cristofaro, A. D.; Violante, A. Effect of pH, phosphate and oxalate on the adsorption/desorption of arsenate on/from goethite. *Soil Sci.* **2001**, *166*, 197–208.
- (9) Violante, A.; Pigna, M. Competitive sorption of arsenate and phosphate on different clay minerals and soils. *Soil Sci. Soc. Am. J.* **2002**, *66*, 1788–1796.
- (10) Antelo, J.; Avena, M.; Fiol, S.; Lopez, R.; Arce, F. Effects of pH and ionic strength on the adsorption of phosphate and arsenate at the goethite-water interface. *J. Colloid Interface Sci.* **2005**, *285*, 476–486.
- (11) Campbell, K. M.; Root, R.; O'Day, P. A.; Hering, J. G. A gel probe equilibrium sampler for measuring arsenic porewater profiles and sorption gradients in sediments: I. Laboratory development. *Environ. Sci. Technol.* **2008**, *42*, 497–503.
- (12) Radu, T.; Subacz, J. L.; Phillippi, J. M.; Barnett, M. O. Effects of dissolved carbonate on arsenic adsorption and mobility. *Environ. Sci. Technol.* **2005**, *39*, 7875–7882.
- (13) Fuller, C. C.; Davis, J. A.; Waychunas, G. A. Surface chemistry of ferrihydrite: Part 2. Kinetics of arsenate adsorption and coprecipitation. *Geochim. Cosmochim. Acta* **1993**, *57*, 2271–2282.
- (14) Arai, Y.; Sparks, D. L.; Davis, J. A. Effects of dissolved carbonate on arsenate adsorption and surface speciation at the hematite-water interface. *Environ. Sci. Technol.* **2004**, *38*, 817–824.
- (15) Appelo, C. A. J.; Van der Weiden, M. J. J.; Tournassat, C.; Charlet, L. Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environ. Sci. Technol.* **2002**, *36*, 3096–3103.
- (16) Grafe, M.; Eick, M. J.; Grossl, P. R.; Saunders, A. M. Adsorption of arsenate and arsenite of ferrihydrite in the presence and absence of dissolved organic carbon. *J. Environ. Qual.* **2002**, *31*, 1115–1123.
- (17) Redman, A. D.; Macalady, D. L.; Ahmann, D. Natural organic matter affects arsenic speciation and sorption onto hematite. *Environ. Sci. Technol.* **2002**, *36*, 2889–2896.
- (18) Xu, H.; Allard, B.; Grimvall, A. Effects of acidification and natural organic materials on the mobility of arsenic in the environment. *Water, Air, Soil Pollut.* **1991**, *57–58*, 269–278.
- (19) Aggett, J.; O'Brien, G. A. Detailed model for the mobility of arsenic in the lacustrine sediments based on measurements in Lake Ohakuri. *Environ. Sci. Technol.* **1985**, *19*, 231–238.
- (20) Peterson, M. L.; Carpenter, R. Arsenic distributions in porewaters and sediments of Puget Sound, Lake Washington, the Washington coast and Saanich Inlet, B.C. *Geochim. Cosmochim. Acta* **1986**, *50*, 353–369.
- (21) Azcue, J. M.; Nriagu, J. O. Role of sediment porewater in the cycling of arsenic in a mine-polluted lake. *Environ. Int.* **1994**, *20*, 517–527.
- (22) Nickson, R. T.; McArthur, J. M.; Ravencroft, P.; Burgess, W. G.; Ahmed, K. M. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. *Appl. Geochem.* **2000**, *15*, 403–413.

- (23) Welch, A. H.; Lico, M. S. Factors controlling As and U in shallow groundwater, southern Carson Desert, Nevada. *Appl. Geochem.* **1998**, *13*, 521–539.
- (24) McArthur, J. M.; Banerjee, D. M.; Hudson-Edwards, K. A.; Mishra, R.; Purohit, R.; Ravenscroft, P.; Cronin, A.; Howarth, R. J.; Chatterjee, A.; Talukder, T.; Lowry, D.; Houghton, S.; Chadha, D. K. Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications. *Appl. Geochem.* **2004**, *19*, 1255–1293.
- (25) Kneebone, P. E.; O'Day, P. A.; Jones, N.; Hering, J. G. Deposition and fate of arsenic in iron- and arsenic-enriched reservoir sediments. *Environ. Sci. Technol.* **2002**, *36*, 381–386.
- (26) Root, R.; Dixit, S.; Campbell, K. M.; Jew, A.; Hering, J. G.; O'Day, P. A. Arsenic sequestration by sorption processes in high-iron sediments. *Geochim. Cosmochim. Acta* **2007**, in press.
- (27) Bocher, F.; Gehin, A.; Ruby, C.; Ghanbaja, J.; Abdelmoula, M.; Genin, J.-M. R. Coprecipitation of Fe(II-III) hydroxycarbonate green rust stabilised by phosphate adsorption. *Solid State Sci.* **2004**, *6*, 117–124.
- (28) Su, C.; Wilkin, R. T. Arsenate and Arsenite Sorption on and Arsenite Oxidation by Iron(II,III) Hydroxycarbonate Green Rust. In *Advances in Arsenic Research: Integration of Experimental and Observational Studies and Implications for Mitigation*; O'Day, P. A., Vlassopoulos, D., Meng, X., Benning, L. G., Eds.; American Chemical Society: Washington, DC, 2005; Vol. 915, pp 25–40.
- (29) Schwertmann, U.; Cornell, R. M. *Iron Oxides in the Laboratory*; Wiley-VCH: Weinheim, 1991.
- (30) Campbell, K. M. Ph.D. Thesis, California Institute of Technology, 2006.
- (31) *Standard Methods for the Examination of Water and Wastewater*; 20 ed.; American Public Health Association: Washington, DD, 1998.
- (32) Kneebone, P. Ph.D. Thesis, California Institute of Technology, 2000.
- (33) Song, Y.; Muller, G. *Sediment-Water Interactions in Anoxic Freshwater Sediments: Mobility of Heavy Metals and Nutrients*; Springer-Verlag: Berlin, 1999; Vol. 81.

ES071120A