A Gel Probe Equilibrium Sampler for Measuring Arsenic Porewater Profiles and Sorption Gradients in Sediments: I. Laboratory Development

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A gel probe equilibrium sampler has been developed to study arsenic (As) geochemistry and sorption behavior in sediment porewater. The gels consist of a hydrated polyacrylamide polymer, which has a 92% water content. Two types of gels were used in this study. Undoped (clear) gels were used to measure concentrations of As and other elements in sediment porewater. The polyacrylamide gel was also doped with hydrous ferric oxide (HFO), an amorphous iron (Fe) oxyhydroxide. When deployed in the field, HFO-doped gels introduce a fresh sorbent into the subsurface thus allowing assessment of in situ sorption. In this study, clear and HFO-doped gels were tested under laboratory conditions to constrain the gel behavior prior to field deployment. Both types of gels were allowed to equilibrate with solutions of varying composition and re-equilibrated in acid for analysis. Clear gels accurately measured solution concentrations ($\pm 1\%$), and As was completely recovered from HFO-doped gels ($\pm 4\%$). Arsenic speciation was determined in clear gels through chromatographic separation of the re-equilibrated solution. For comparison to speciation in solution, mixtures of As(III) and As(V) adsorbed on HFO embedded in gel were measured in situ using X-ray absorption spectroscopy (XAS). Sorption densities for As(III) and As(V) on HFO embedded in gel were obtained from sorption isotherms at pH 7.1. When As and phosphate were simultaneously equilibrated (in up to 50-fold excess of As) with HFO-doped gels, phosphate inhibited As sorption by up to 85% and had a stronger inhibitory effect on As(V) than As(III). Natural organic matter (>200 ppm) decreased As adsorption by up to 50%, and had similar effects on As(V) and As(III). The laboratory results provide

a basis for interpreting results obtained by deploying the gel probe in the field and elucidating the mechanisms controlling As partitioning between solid and dissolved phases in the environment.

INTRODUCTION

Trace element concentrations in sediment porewaters are strongly affected by solid−solution interactions, especially associations with iron (Fe), aluminum (Al), and manganese (Mn) oxides (*1*). Sequestration and mobilization of trace elements depend on a complex interaction of mineralogy, sorption, precipitation, porewater composition, and the microbial community through the processes of sorption, precipitation−dissolution, and microbial transformations. One element of particular concern, because of its toxicity and prevalence, is arsenic (As), which affects drinking water quality around the world (*1, 2*). Understanding the range of geochemical conditions that contribute to the presence of As in porewaters may help predict and mitigate As contamination.

Arsenic is often found to be associated with Fe mineral phases through adsorption to mineral surfaces (*1, 3*). When Fe(III) (oxyhydr)oxides are reductively dissolved, As can be released to sediment porewaters. Since reductive dissolution of Fe (oxyhydr)oxides occurs in anoxic environments, collecting, processing and preserving sediment samples without exposing them to air can be difficult. Measurement of porewater composition and specific geochemical processes such as adsorption in situ would circumvent many of these problems.

This study builds upon the concept of an in situ gel probe equilibrium sampler for measuring porewater composition first developed by Davison and co-workers (*4, 5*). In previous studies, probes were constructed based on diffusive equilibration in a thin film (DET) to measure porewater concentrations of elements and compounds such as Fe, Mn, chloride, nitrate, sulfate, and ammonium in sediments where convection is limited (*4–6*). A thin sheet of polyacrylamide or agarose gel was placed into a plastic holder, covered with a permeable membrane, and allowed to equilibrate with sediment porewaters. The water inside the gel equilibrated with porewaters by solute diffusion through the membrane. Upon removal from the sediment, the gel was either chemically fixed or quickly sliced to preserve concentration gradients of target elements.

Gel probes have several advantages over other techniques for measuring porewater composition. Dialysis devices can require several weeks to reach equilibrium, whereas thin gels (several millimeters thick) equilibrate within hours to days. Extracting porewaters from sediment cores requires substantial sample processing and has lower vertical resolution than gel probes, which can measure vertical gradients with several millimeters resolution (*4*).

The DET method was extended to trace metals either by using more sensitive detection techniques, or by incorporating a resin with a large capacity for binding metals as a preconcentration step, known as diffusive gradients in thin films (DGT) (*7–10*). Porewater concentrations of certain trace metals can be calculated from DGT probes by measuring the flux onto resin embedded in the gel.

In this study, the gel probe was adapted to study As sorption behavior by incorporating two types of gels in a single probe device. One type of gel is a clear polyacrylamide gel, similar to the gels used in DET probes. The second type of gel is polyacrylamide doped with hydrous ferric oxide (HFO), an amorphous iron oxyhydroxide. The HFO-doped

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gels were designed to measure the amount of As adsorbed upon equilibration with sediment porewaters. Both types of gels were precut into slabs and seated into slots etched into a plastic ladder-like holder; this constrained gel probe configuration eliminates the necessity of chemical fixing or cutting in the field, but limits resolution based on the separation and width of the gel slabs. The gel probe has two parallel columns of gels, allowing for simultaneous measurement of porewater concentrations (clear gels) and sorption profiles (HFO-doped gels) as a function of depth in sediments (for field results and probe design details, see Part II, ref *11*).

The purpose of this study was to develop and validate a method for measuring As porewater and adsorption profiles using a constrained gel probe equilibrium sampler. This study (Part I) presents laboratory validation of the clear and HFO-doped gels, establishing a baseline for behavior in simplified chemical systems. Part II demonstrates field application in a series of deployments at Haiwee Reservoir (Olancha, CA), a field site with Fe- and As-rich sediments where elevated As concentrations have been observed in sediment porewaters.

EXPERIMENTAL SECTION

Reagents. All chemicals used were reagent grade and used without further purification unless otherwise noted. All water used was 18 MΩ-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 HNO_3 (EM Science, Omnipure, 70%). Arsenic(V) stock solutions were made from Na_2HAsO_4 (Sigma). Arsenic(III) stock solutions were made from $NaAsO_2$ (Baker), and used before any oxidation could occur (<2 weeks).

HFO Synthesis. Hydrous ferric oxide was prepared by the dropwise addition of 0.5 M NaOH to 150 mL of 0.05 M $Fe(NO_3)_3$ until the solution stabilized at pH 8 (*12*). The suspension was equilibrated for 4 h under constant stirring, adjusting any pH drift as necessary with 0.5 M NaOH. The HFO was then washed three times with water. The solid was resuspended in 150 mL water to yield a 4.5 g/L stock solution. The crystallinity of a concentrated hydrated HFO slurry was analyzed by X-ray diffraction (XRD) on a Phillips X'Pert PRO with a Cu Kα X-ray source. Hydrous ferric oxide stock solutions were used within 10 days to minimize changes in crystallinity (*13, 14*).

Gel Casting. Gel slabs were made by modifying the methods of Davison et al. (*5, 6*), and Kneebone et al. (*15, 16*). Gels were made by dissolving 3.75 g acrylamide (C_3H_5NO, Omnipure, EM Science) and 0.075 g N-N′-methylene-bis-acrylamide (($CH_2CHCONH)_2CH_2$, Omnipure, EM Science) in 25 mL water for clear gels or HFO stock diluted with water for HFO-doped gels. In experiments where the amount of HFO in the gels was held constant at 2×10^{-6} mol Fe/gel slab, 7.5 mL of HFO stock was diluted with 12.5 mL water. In experiments with variable amounts of HFO per gel, the amount of HFO stock solution was adjusted accordingly, and water was added to a total volume of 25 mL. No As was present in the gel casting step. The acrylamide solution was deoxygenated by bubbling with compressed nitrogen or argon for 30–45 min. Polymerization was initiated by the simultaneous addition of 150 μL of 1 g/L sodium persulfate (Omnipure, EM Science) and 25 μL of tetramethylethylenediamine (TEMED, Omnipure, EM Science). The solution was mixed and quickly poured into a heated glass Petri dish to increase the polymerization rate. The gel was allowed to completely solidify (∼5 min) before removing the dish from the heat. After the gel cooled to room temperature, it was gently extracted from the Petri dish with a flexible plastic spatula and transferred directly into a container with 1–2 L

of water. The gel was hydrated for ≥12 h and increased in size by approximately 30% when fully hydrated. The gel was cut into slabs $2 \times 0.5 \times 0.2$ cm by aligning the gel over a template and cutting it with a plastic, acid-washed blade. The gel slabs were placed into water and gently shaken to remove any excess reagents or loose HFO. Gel slabs were stored in water for up to one week to prevent dehydration.

Gel Re-equilibration. Once a gel slab was equilibrated with a solution, target analytes were measured by re-equilibrating the gel slab in 1.25 mL of 1% nitric acid (clear gels) or 1.25 mL of 5% nitric acid (HFO gels) for at least 12 h with only occasional mixing. At these acid concentrations, the polyacrylamide gel was unaffected, the HFO dissolved completely out of the gel slabs, and solution equilibrium was reached. Re-equilibrated gel–solutions were analyzed for total As (As(III) + As(V)) and phosphorus (P) by inductively coupled plasma mass spectrometry (ICP-MS, HP 4500, detection limit for As and P = 0.1 μM). Iron was measured by the phenanthroline colorimetric method with hydroxylamine (*17*), with a detection limit of 2 μM. For HFO gels, analyte concentrations were normalized to the measured amount of Fe per gel slab (mol analyte/mol Fe). For the clear gels, the original concentration was calculated from the concentration in the re-equilibrated solution by the equation:

$$C = \frac{C_{measured}(m_{gel}\omega_{gel} + V_{acid})}{m_{gel}\omega_{gel}} \quad (1)$$

where $C_{measured}$ is the concentration in the re-equilibration solution, m_{gel} is the mass of the gel, ω_{gel} is the fraction of the gel mass that is water, and V_{acid} is the volume of acid added for re-equilibration (*15*). The polyacrylamide does not interact with the target analytes, and serves as an inert polymer framework for the porewater and HFO.

Gel Probe Design. Gel probes were designed to hold the gel slabs in slots etched into a plastic holder. Further information on gel probe design can be found in Part II (*11*) and in reference (*18*).

As Speciation. Arsenic speciation was measured in the experiments described below by separating As(III) and As(V) on a liquid chromatography (LC) column (Agilent As speciation column) with a 3 mM phosphate mobile phase (pH 5.99) at 0.9 mL/min flow rate. Arsenic was measured directly by ICP-MS in series with the LC outflow (LC-ICP-MS). For As speciation in the clear gels, the gels were re-equilibrated in 25 mM H_3PO_4 and analyzed within 24 h to prevent oxidation of As(III).

For comparison to LC-ICP-MS speciation measurements, the relative fraction of As(III) and As(V) adsorbed on the HFO gels determined in situ using X-ray absorption near edge spectroscopy (XANES). The energy of maximum absorption of the As K-edge differs slightly for As(III) (11871 eV) versus As(V) (11875 eV). To quantify the relative amount of As(III) and As(V) adsorbed onto the HFO gels, a series of gel slabs was equilibrated with appropriate solutions to obtain a range of adsorbed As(III) and As(V) ratios. Calibration end-members for XANES were prepared by sorbing an equivalent amount of only As(III) or As(V) onto HFO-doped gel slabs. The gel slabs for the XANES calibration contained 3.3 times more Fe than typical HFO gels since 25 mL of HFO stock solution was used without dilution in the gel casting step. The increased Fe and As in the calibration gels improved the XANES signal, but does not affect the resulting application to field gels since this technique measures the relative fraction of As(III) and As(V) adsorbed onto the HFO (i.e., percent of each species) normalized to total absorption. Each gel slab was equilibrated for 24 h with 20 mL of an As(III) and As(V) solution adjusted to pH 7 in 25 mM HEPES buffer (Omnipure, EM Science). The amount of As(III) and As(V) adsorbed onto the gel slab after equilibration was determined by removing the gel slab and measuring the total As concentration (ICP-

MS) and speciation (LC-ICP-MS) in the remaining solution. The gel slabs were immediately frozen upon removal from the solution (≤ 20 °C), and they remained frozen until loaded into an acid-washed Teflon holder and secured with Kapton tape. The mounted gel slabs were then refrozen in liquid nitrogen until loaded into a helium cryostat maintained between 5 and 20 K.

Arsenic K-edge absorption spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) (Menlo Park, CA) on wiggler beamline 11–2 at a beam energy of 80–100 mA, using a 30-element Ge detector and a Si(220) monochromator crystal. Energy was calibrated using an As foil where the energy of first inflection of the main absorption edge was set to 11867 eV. Sodium arsenate reference (Sigma) was used as a secondary reference to verify calibration with maximum As(V) absorption at 11875 eV. Scans were averaged ($n = 4$–7) and background was subtracted using the SIXPACK software package (19). Background subtraction was done with a linear fit through the pre-edge region and extrapolation into the postedge region. Spectra were normalized using the height of the edge step at energies above the absorption maximum. To calibrate the binary mixtures, XANES spectra were fit with end-member As(III) and As(V) constituents by linear least-squares using the DATFIT package in EXAFSPAK (20). The fitting program generates an estimated standard deviation (esd) for each fractional reference spectrum fit to the unknown spectrum. The reported errors are from the component with the greatest esd. The goodness-of-fit is reported as a 99% confidence limit (three times the esd). Although the confidence limit is a measure of the precision of a varied parameter in the fit and not necessarily the accuracy of the fit (20), there are only two possible reference spectra for the calibration samples. Therefore, the reference library is deemed appropriate by design.

Laboratory Experiments. The following experiments were performed in 25 mM HEPES buffer (Omnipure, EM Science) and 5 mM NaNO$_3$ (Fisher). The pH was adjusted with 0.5 M NaOH or 0.2 M HNO$_3$. One gel slab was directly added to 20 mL of well-stirred solution in equilibrium with ambient atmospheric composition and allowed to equilibrate for 24 h unless otherwise noted.

Recovery Experiments. To verify the accuracy of the concentration obtained from re-equilibrated clear gel slabs, a gel slab was added to a buffered solution (pH 8) with As(III) concentrations comparable to field values (0–35 μM As). The original solution concentration was calculated from the re-equilibrated solution using eq 1 and compared to the actual solution concentration. A similar experiment was performed for the HFO-doped gels with an HFO loading of 2×10^{-6} mol Fe/slab. The recovery of As(III) adsorbed onto the HFO-doped gel at pH 8 was determined by comparing the amount of As lost from solution after equilibration with the HFO gel, and the amount of As released from the gel slab after re-equilibration in acid.

Fe Loading in HFO Gels. The optimal amount of Fe loading per gel slab was determined by varying the amount of Fe from 1×10^{-6} to 8×10^{-6} mol Fe/slab. Each gel slab was added to 20 mL of 10 μM As(III) at pH 8 and allowed to equilibrate for 24 h. The amount of As adsorbed onto HFO in the gel was measured by re-equilibration in acid. The amount of Fe in subsequent experiments was 2×10^{-6} mol Fe/slab unless otherwise noted.

Adsorption Time Series. The rate of As adsorption onto HFO gels was measured by adding an HFO-doped gel slab to a 10 μM As(III) solution at pH 8. Aliquots of solution were removed at each time point, acidified in nitric acid, and analyzed for As by ICP-MS. The effect of phosphate on the rate of As adsorption was measured under similar conditions with the addition of 50 μM sodium phosphate (EM Science). Arsenic and P were analyzed at each time point.

Adsorption Isotherms. Arsenic adsorption onto HFO-doped gels as a function of As concentration was measured for As(III) and As(V) at pH 7.1. Arsenic concentrations were varied from 0 to 200 μM. An additional isotherm was done for As(III) at pH 8.

Competitive Effects of Phosphate on As Adsorption. The effects of phosphate on As(III) and As(V) adsorption onto HFO embedded in a gel were investigated by holding the As concentration constant and varying the phosphate concentration between 0 and 500 μM. One HFO-doped gel slab was equilibrated in a buffered solution at pH 7.1 at a given As and P concentration. Ten μM As was added as either all As(III), all As(V), or a 1:1 mixture of As(III) and As(V). The HFO-doped gel was equilibrated with As and P simultaneously. After equilibration, each gel slab was removed from the solution, re-equilibrated in acid, and analyzed for As and P. Phosphate concentrations were sufficiently large to require correction for the dissolved P in the HFO-doped gels. The amount of dissolved P was calculated using eq 1, and subtracted from the total P measurement, the difference being the amount of P adsorbed to the HFO surface.

Competitive Effects of Organic Matter on As Adsorption. The effect of organic matter on As adsorption onto HFO gels was investigated in solutions of As(III) or As(V) at pH 7.1. Two types of natural organic compounds were used: Soil humic acid (Soil HA, IHSS no. 1S102H) and Suwannee River natural organic matter (SR-NOM, IHSS no. 1N101). The As concentration was held constant at 10 μM, and the organic carbon concentration was varied from 0 to 500 ppm. The HFO-doped gel was equilibrated with the As and organic carbon simultaneously.

RESULTS AND DISCUSSION

Properties of Clear and HFO-doped Gels. The polyacrylamide gels are composed of 92% water ($\omega_{gel} = 0.92$) and the mass of each gel (m_{gel}) is equal to 0.29 g $\pm$ 0.02 g ($n = 20$). The gel was not affected by nitric acid, at concentrations <35%. The HFO was amorphous and readily dissolved in 5% nitric acid.

Clear gels accurately measured solution concentrations ($\pm$1%) and As(III) was completely recovered from HFO-doped gels ($\pm$4%) (for data, see Supporting Information Figure S1). The variation in Fe concentration in HFO-doped gel slabs was less than 10%. The amount of As adsorbed was found to vary between 20 and 80% of the total As in solution as the amount of Fe per gel slab was varied between 1×10^{-6} to 8×10^{-6} mol Fe/slab (Supporting Information Figure S2). All loadings of HFO were sufficient to ensure that the amount of As in the re-equilibrated solution can be attributed solely to the As adsorbed onto the HFO, and that the contribution of dissolved As in the solution phase of the gel can be neglected. Since high Fe loadings have a greater probability of perturbing a natural sediment system and may require extended equilibration times, an intermediate Fe loading of 2×10^{-6} mol Fe/slab was used in laboratory experiments and in field deployments (Part II).

Gel Equilibrium Kinetics. A previous study found that clear gels reached equilibrium within 1–2 h when directly in contact with the solution (i.e., not in a probe) but equilibration time increased to 5–7 h when placed in a probe (15). This is comparable to other studies for similar types of gels (5, 10). Sorption equilibrium with As(III) on an HFO-doped gel directly in contact with the solution was reached in approximately 18 h. The presence of phosphate did not alter the sorption kinetics, although the maximum amount of As adsorbed decreased by approximately 18% (Supporting Information Figure S3). HFO-doped gels can take up to 10 times longer to equilibrate than clear gels, since the HFO concentrates As in the gel. Although it was expected that the equilibration of As with HFO embedded in gel would take
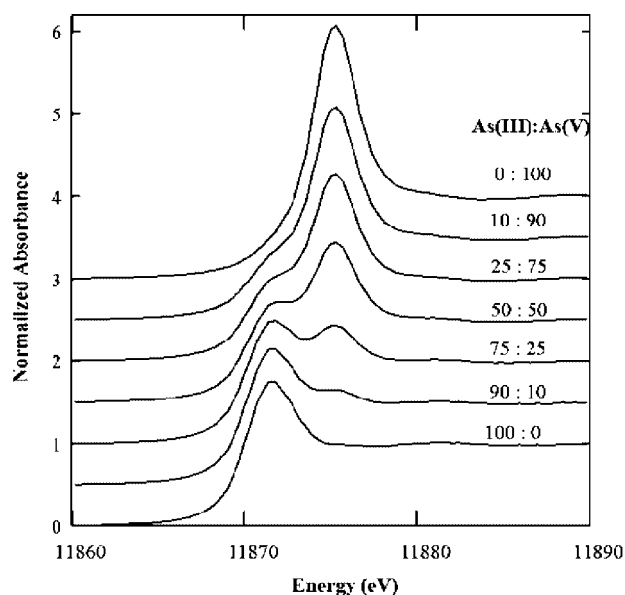
FIGURE 1. XANES spectra of As(III) and As(V) mixtures adsorbed on HFO embedded in gel. Spectra are background-subtracted and normalized to postedge step height.

longer than As adsorption onto HFO alone, equilibration with the HFO-doped gel is reached within 24 h, consistent with kinetics of As adsorption onto HFO alone (*21, 22*). The equilibration kinetics of gels mounted in a gel probe sampler and deployed in sediments is discussed in Part II (*11*).

Comparison of As Speciation Determined by XANES and LC-ICP-MS. The fractional amount of As(III) and As(V) adsorbed on HFO embedded in gel was determined in situ by solid-phase XANES analysis using known mixtures in solution of As(III) and As(V). The results from the XANES analysis of solid samples can be directly compared to the LC-ICP-MS measurement of the solution phase after equilibration, assuming mass balance. The maximum X-ray absorption from As(V) is substantially stronger than absorption from As(III) (Figure 1). Therefore, normalized peak height measurements alone are insufficient to quantify the relative fractions of adsorbed As(III) and As(V) from a XANES edge and may lead to substantial error in estimating relative fractions. The proportions of As(III) and As(V) obtained from linear least-squares XANES fits using As(III) and As(V) end-member spectra were compared with the amounts determined from the residual dissolved concentrations of As(III) and As(V) measured by LC-ICP-MS after equilibration with HFO-doped gels (Table 1). The difference between As(III) and As(V) proportions determined by XANES fits and

solution uptake measurements is minimal (<5%) when the fraction of As(V) is <50%. However, once As(III) and As(V) are in equal abundance, the stronger absorption of As(V) tends to overestimate the As(III) fraction and underestimate the As(V) fraction in the least-squares fit, compared to the As(III)/As(V) ratio measured in the residual solution. This effect is more pronounced at high As(V) fractions, where As(V) is underestimated by 15% compared to the speciation in solution. The XANES and LC-ICP-MS comparison provides a correction factor for determining the relative fraction of As(III) and As(V) on HFO-doped gels deployed in the field.

As(III) and As(V) Isotherms. Adsorption site density for As(III) and As(V) on HFO embedded in gel was calculated based on sorption isotherms (Figure 2). The maximum sorption site capacity for As onto HFO embedded in gel is 0.12 mol_{sites}/mol_{Fe} for As(V) and 0.17 mol_{sites}/mol_{Fe} for As(III) at pH 7.1. At pH 8, the site density of As(III) drops to 0.12 mol_{sites}/mol_{Fe} (Supporting Ingotmation Figure S4).

The maximum sorption densities of As(III) and As(V) are slightly less than values reported in the literature in a similar pH range (*21–25*), possibly because some surface sites may be obstructed by the gel. However, the site densities measured in these experiments are within the range of 0.05–0.18 mol_{sites}/mol_{Fe} reported for arsenic sorption on HFO surface sites (*26*), and provide an estimate for available surface sites in the gel probe when it is deployed in natural sediments.

Competitive sorption of Phosphate. It is well-known that phosphate inhibits the sorption of both As(V) and As(III) on Fe (oxyhydr)oxides (*24, 27–33*), but it has a stronger effect on As(V) (Figure 3). At high phosphate concentrations, only 7% of total As(V) and 16% of total As(III) is adsorbed, compared to 45% adsorbed As(III) and As(V) in the absence of phosphate. The amount of As adsorbed onto the HFO in the absence of phosphate is consistent with the sorption isotherms. The maximum amount of phosphate adsorbed onto the HFO approaches 0.12 mol P/mol Fe, indicating that the maximum sorption density for phosphate is similar to As(V) at pH 7.1 (Supporting Information Figure S5). In mixed As(III)/As(V) solutions, total As sorption is slightly less than with As(III) only.

Previous studies have found that As(V) sorption is suppressed by phosphate to the greatest extent between pH 7 and 10, whereas As(III) sorption is inhibited the most at low pH (*30*). Arsenic(V) and phosphate directly compete for surface sites, especially at neutral and alkaline pH (*29, 30*), which is consistent with the similar maximum site densities observed for As(V) and phosphate in this study.

Competition between As(III) and As(V) for surface sites is minimal under the conditions of our experiments. At pH 7 and comparable concentrations (0.048 mol As/mol Fe for

TABLE 1. Comparison of XANES Spectra of HFO-dDoped Gels Fit with Least-Squares Linear Combinations As(III) and As(V) End-Members and Proportions of As Remaining in Solution, as Measured by LC-ICP-MS[a]

LC-ICP-MS		XANES			goodness of fit	
As(III) %	As(V) %	As(III) %	As(V) %	Total %	Esd	3x esd
0	100	0	100	100	n/a	n/a
7.9	92.1	23.5	76.6	100.1	8.59E-03	2.58E-02
22.4	77.6	39.1	61.1	100.2	7.67E-03	2.30E-02
47.4	52.6	54.6	45.6	100.2	7.36E-03	2.21E-02
73.9	26.1	78.5	21.4	99.9	5.14E-03	1.54E-02
89.5	10.5	91.7	8.0	99.7	4.24E-03	1.27E-02
100	0.0	100	0.0	100	n/a	n/a

[a] The relative amount of As(III) and As(V) measured by the LC-ICP-MS method was calculated by normalizing the ratio of As(III) and As(V) peak heights to the total amount of As measured in the sample by ICP-MS (total As = 60 μM $\pm$ 0.3 μM). The error on the LC-ICP-MS data reported below is 0.1%. The end-members used to fit the XANES spectra (100% As(III) and 100% As(V)) do not have a reported goodness of fit (n/a). The goodness of fit is reported as estimated standard deviation (esd) and the 99% confidence limit (3x esd).
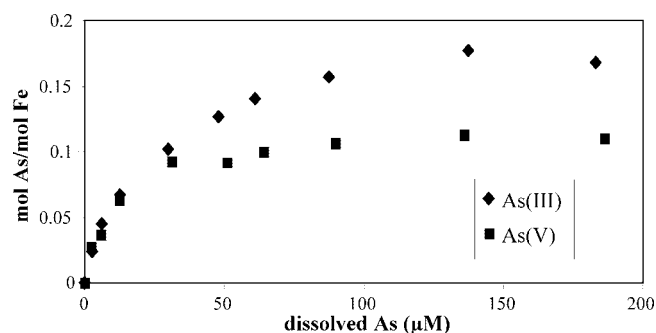
FIGURE 2. Sorption isotherms of As(III) (♦) and As(V) (■) on HFO embedded in polyacrylamide gel. One HFO-doped gel (2×10^{-6} mol Fe/gel) was equilibrated for 24 h with 20 mL of buffered As solution (pH 7.1, $I = 0.01$ M).
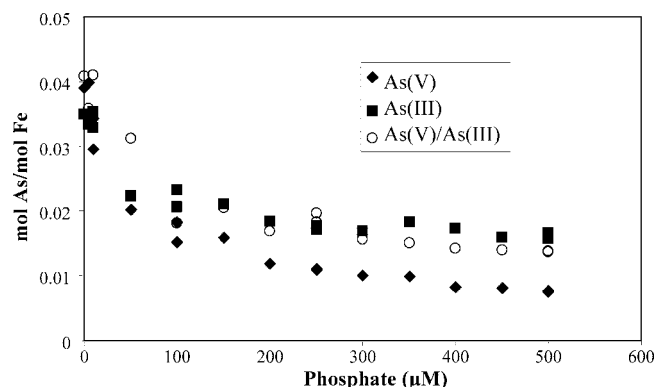

FIGURE 3. The effect of phosphate on adsorption of As(III) and As(V) on HFO-doped gels. One gel slab (2×10^{-6} mol Fe/gel) was added to a 20 mL buffered solution (pH 7.1, $I = 0.01$ M) of variable phosphate concentration and 10 μM As(III) (■), 10 μM As(V) (♦), or 5 μM As(III) and 5 μM As(V) (○) and equilibrated for 24 h.
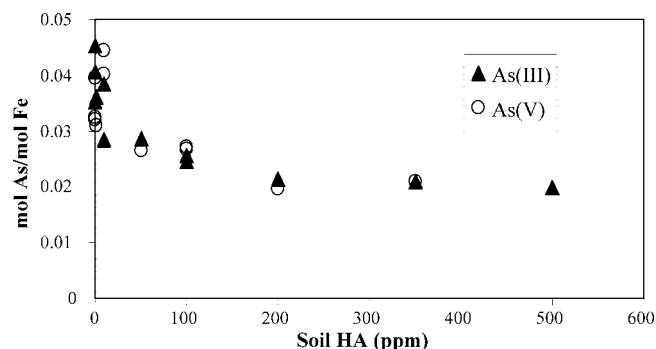

FIGURE 4. The effect of Soil HA on As adsorption onto HFO-doped gels. One gel slab (2×10^{-6} mol Fe/gel) was added to 20 mL of buffered (pH 7.1, $I = 0.01$ M) solution with 10 μM As and variable concentrations of organic matter. The gel was equilibrated for 24 h and re-equilibrated in acid.

As(III) and As(V)), Jain and Loeppert (*30*) observed that As(V) sorption is unaffected by the presence of As(III), and As(III) sorption is inhibited by As(V) by only ~1%. Phosphate has a much stronger inhibitory effect under our experimental conditions.

At high phosphate (P) concentrations (P:As > 10), sorption of As(V) is expected to be minimal if As(V) and phosphate directly compete for the same surface sites. Even though As(V) sorption is suppressed at large P:As ratios, a significant amount of As(V) is still adsorbed. This observation can be explained by relative surface affinity or sorption kinetics. Iron(III) minerals exhibit a slight preference for As(V) adsorption over phosphate (*27, 28, 31*). However, the rate of phosphate sorption is initially faster than that of As(V) although the amount of adsorbed As(V) increases with reaction time until equilibrium is reached (*27*). The presence of adsorbed As(V), even at very high phosphate concentrations, may be due to slight preference for As(V) at equilibrium, although further investigation is needed to constrain this mechanism.

Competitive Sorption of Organic Matter. Soil HA and SR-NOM inhibited adsorption of As(V) and As(III) onto HFO embedded in gel by 50% at high organic carbon concentrations (Figure 4, Supporting Information Figure S6). Both types of organic matter had similar effects and both As(V) and As(III) were equally affected.

Arsenic(V) reduction and As(III) oxidation have both been observed in the presence of organic carbon, but this effect varies with the carbon source (*34, 35*). The oxidation state may also be unaffected by organic matter. Since the nominal As oxidation states were not confirmed after exposure to organic matter in our experiments, possible interconversion of As(III) and As(V) cannot be excluded. However, similar uptake behavior was observed for As added nominally as either As(III) or As(V).

While phosphate had a much stronger competitive effect than organic matter when compared on a molar basis, both were effective at inhibiting As sorption onto HFO at environmentally relevant concentrations for each. The mecha-

nism of As sorption inhibition by organic carbon is not known, but it could be due to several effects. Organic carbon can sorb directly to Fe(III) mineral surfaces (*36*) and may affect As sorption through steric effects by blocking the oxide surface (*37*) or electrostatic effects (*38*). Organic matter may also complex As in solution, most likely by inorganic bridging between Fe(III) stabilized in the dissolved phase by NOM (*34, 35, 39, 40*). Organic carbon exhibits a slight preference for As(V) complexation, but this observation is not consistent across all types of organic matter (*34*). Arsenic interactions with organic carbon are highly dependent on the type of organic matter, and preferential sorption or complexation of As(III) or As(V) is sometimes, but not always, detected. Thus, it is not unreasonable to observe that organic carbon inhibits As(III) and As(V) sorption equally.

Application to Field Measurements. The laboratory results presented here establish a baseline of laboratory behavior for clear and HFO-doped gels. The clear gels can accurately measure the amount of aqueous As over a range of environmentally relevant concentrations. Measurement of As sorption capacities for the HFO-doped gels and As behavior in simple competitive systems enable identification of competitive sorption effects in a sedimentary system. With comparison of XANES spectra for HFO-doped gels and LC-ICP-MS analyses of clear gels, speciation of both porewater and adsorbed As can be measured in field deployments. Porewater chemistry that controls As partitioning in sediments can be elucidated by comparing the sorption data presented here to the results of a field deployment of clear and HFO-doped gels.

Acknowledgments

Supporting Information Available

Plots of As recovery from clear and HFO-doped gels, variation in As sorption as a function of Fe concentration, As adsorption kinetics, As adsorption isotherm at pH 8, amount of P adsorbed in competitive phosphate experiments, adsorption of As in presence of SR-NOM. This material is available free of charge via the Internet at http://pubs.acs.org.

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ES071119B