Chapter 3

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

3.1 Abstract

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, and As was completely recovered from HFO-doped gels. Arsenic speciation was determined in clear gels through chromatographic separation of the re-equilibrated solution. The relative amount of As(III) and As(V) adsorbed on HFO embedded in gel

was measured using X-ray absorption spectroscopy (XAS) based on calibration standards of known mixtures of HFO doped with As(III) and As(V); spectra were fit with a least-squares linear combination of As(III) and As(V) end-members. 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 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 can also decrease As adsorption by up to 50%, but does not preferentially inhibit As(V) or 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.

3.2 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 (Smedley and Kinniburgh 2002). Sequestration and mobilization of trace elements depends on a complex interaction of mineralogy, sorption, precipitation, porewater composition, organic matter interactions, redox conditions, and microbially-controlled processes. One element of particular concern, because of its toxicity and prevalence, is arsenic (As), which affects drinking water quality around the world (Nordstrom 2002; Smedley and Kinniburgh 2002). 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 (Nickson et al. 2000; Smedley and Kinniburgh 2002). 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 and processing sediment samples can be difficult. The ability to measure porewater composition and specific geochemical processes such as adsorption *in situ* circumvents 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. 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 (Davison et al. 1991; Davison et al. 1994; Krom et al. 1994). 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, also known as peepers, can require several weeks to reach equilibrium, while thin gels (several millimeters thick) equilibrate within

hours. 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 (Davison et al. 1991).

The DET method was extended to trace metals by either using more sensitive detection techniques or incorporating a resin with a large capacity for binding metals as a preconcentration step, known as diffusive gradients in thin films (DGT) (Zhang and Davison 1995; Zhang et al. 1995; Zhang et al. 1998; Kneebone 2000; Docekalova et al. 2002). Porewater concentrations of certain trace metals can be calculated from DGT probes by measuring the flux onto resin embedded in the gel. An alternate approach for measuring concentrations of sulfide in marine sediments was to dope a polymer with lead acetate and measure the amount of insoluble lead sulfide formed in the gel (Reeburgh and Ericson 1982). Modifications of the gel probe design have been made for other applications. The extent of Mn oxide dissolution in sediments was observed by doping agarose gel with amorphous MnO_2 and measuring the extent of clearing after deployment as solid Mn(IV) was reduced to soluble Mn(II) (Edenborn 2002; Edenborn and Brickett 2002). A novel method of hazardous waste treatment was created by embedding uranium-reducing bacteria into a gel probe (Tucker et al. 1998).

In this study, the gel probe was adapted to study As sorption behavior by incorporating with 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 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 Chapter 4).

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. Chapter 3 presents laboratory validation of the clear and HFO-doped gels, establishing a baseline for behavior in simplified chemical systems. Chapter 4 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.

3.3 Materials and Methods

3.3.1 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%). As(V) stock solutions were made from Na_2HAsO_4 (Sigma). As(III) stock

solutions were made from $NaAsO_2$ (Baker), and used before any oxidation could occur (<2 weeks).

3.3.2 HFO synthesis

HFO was prepared by the drop-wise addition of 0.5 M NaOH to 150 mL of 0.05 M $Fe(NO_3)_3$ until the solution stabilized at pH 8 (Schwertmann and Cornell 1991). 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. HFO stock solutions were used within 10 days to minimize changes in crystallinity (Ford et al. 1997; Raven et al. 1998).

3.3.3 Gel Casting

Gel slabs were made by modifying the methods of Tanaka (Tanaka 1981), Davison, et al. (Davison et al. 1994; Krom et al. 1994), and Kneebone et al. (Kneebone 2000; Kneebone et al. 2002). 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. The acrylamide solution was deoxygenated by bubbling with compressed nitrogen or argon for 30-45 minutes. Polymerization was initiated by the simultaneous addition of 150 µL of 1 g/L sodium persulfate (EM Science, Omnipure) and 25 µL of tetramethylethylenediamine (TEMED, Omnipure, EM Science). The solution was mixed and quickly poured into a heated, acid-washed, 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 hours and increased in size by approximately 30% when fully hydrated (Tanaka 1981). The gel was cut into slabs 2 cm × 0.5 cm × 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.

3.3.4 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 hours. At these acid concentrations, the polyacrylamide gel was unaffected, and the HFO dissolved completely out of the gel slabs. Re-equilibrated gel solutions were analyzed for total As (As(III) + As(V)) and phosphorous (P) by inductively coupled plasma mass spectrometry (ICP-MS, HP 4500).

Iron was measured by the phenanthroline colorimetric method with hydroxylamine (Standard Methods 1995). 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:

$$C = \frac{C_{measured}\left(m_{gel}\omega_{gel} + V_{acid}\right)}{m_{gel}\omega_{gel}} \qquad (3.1)$$

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 (Kneebone 2000).

3.3.5 Arsenic 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-11 column) with a 3 mM phosphate mobile phase at 0.9 mL/min flow rate. Arsenic was measured directly by ICP-MS in series with the LC outflow. This method will be referred to as 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 hours to prevent oxidation of As(III).

Arsenic speciation was measured on the HFO gels using X-ray absorption near edge spectroscopy (XANES) by utilizing the K-edges of As(III) (11871 eV) and As(V) (11875 eV). In order 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 varying ratios of adsorbed As(III) and As(V). 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. Each gel slab was equilibrated for 24 hours with 20 mL of an As(III) and As(V) solution adjusted to pH 7 in 25mM 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, and 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 cryostat maintained at 4 K.

Arsenic K-edge 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 absorption was set to 11867 eV, and a sodium arsenate reference (Sigma) was analyzed to verify calibration with maximum As(V) absorption at 11875 eV. Scans were averaged and background subtracted using the SIXPACK software package. Background subtraction was done with a linear fit through the pre-edge region and extrapolation into the EXAFS region. Spectra were normalized using the height of the edge step just above the absorption maximum. Normalized XANES spectra were fit to a binary reference set by linear combination using the program DATFIT with a least-squares linear combination. Fits were calibrated and verified to be linear by fitting end-member and known mixtures of As(III) and As(V) with DATFIT.

3.3.6 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 solution and allowed to equilibrate for 24 hours unless otherwise noted.

3.3.6.1 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 equation (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.

3.3.6.2 Iron loading in HFO-doped 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.

3.3.6.3 MINEQL modeling

The amount of As adsorbed on the HFO embedded into a gel was modeled using the surface complexation model, MINEQL+ (Schecher and McAvoy 1998). The diffuse double layer model was used to account for surface electrostatics. The specific surface area for HFO was assumed to be 600 m^2/g (Dzombak and Morel 1990), and the surface site density for HFO in the gels was determined from the sorption isotherms. Only ferrihydrite was allowed to precipitate in the model. The ionic strength was set to 0.01 M. Intrinsic surface complexation constants from the Dzomback and Morel database were used in the model (Dzombak and Morel 1990). Activity coefficients were calculated using the Davies equation correction for ionic strength.

3.3.6.4 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 phosphate (EM Science). Arsenic and P were analyzed at each time point by ICP-MS.

3.3.6.5 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.

3.3.6.6 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). After equilibration, each gel slab was removed from the solution, re-equilibration 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 equation (1), and subtracted from the total P measurement, the difference being the amount of P adsorbed to the HFO surface.

3.3.6.7 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 #1S102H) and Suwannee River natural organic matter (SR-NOM, IHSS #1N101). The As concentration was held constant at 10 µM and the organic carbon concentration was varied from 0 to 500 ppm.

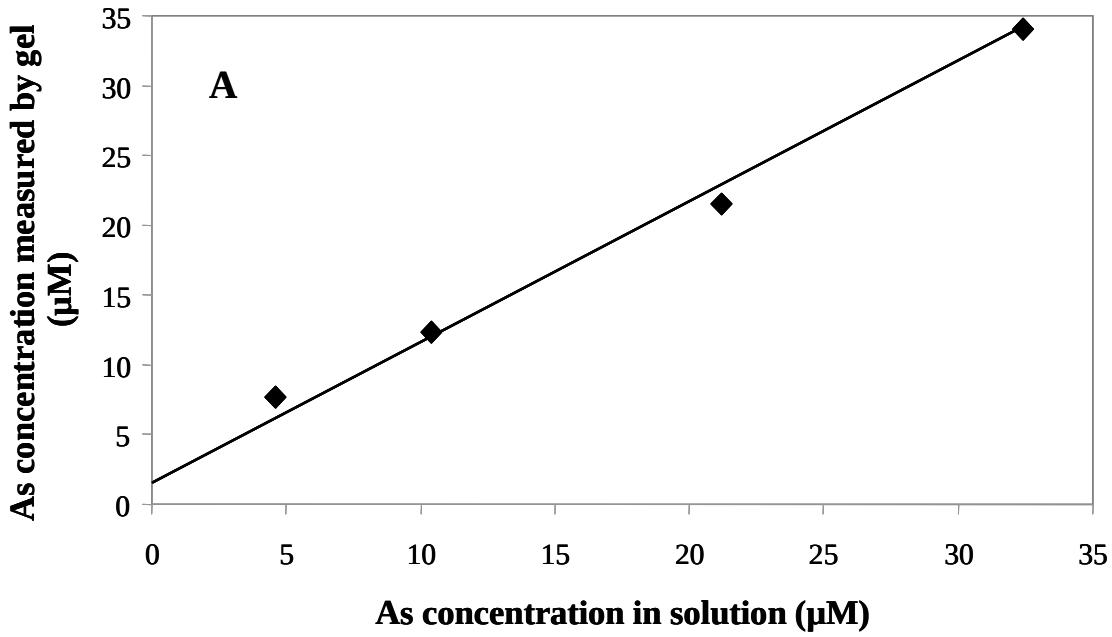
3.4 Results and Discussion

3.4.1 Properties of clear and HFO-doped gels

The polyacrylamide gels are composed of 92% water (ω_{gel} = 0.92) and the mass of each gel (m_{gel}) is equal to 0.286 g. The gel was not affected by nitric acid, even at

concentrations greater than 35%. The XRD of HFO was consistent with an amorphous iron oxyhydroxide, and the solid was readily dissolved in 5% nitric acid.

For both clear and HFO-doped gels, As recovery was >95% (Figure 3.1 A, B). 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% as the amount of Fe per gel slab was varied between 1×10^{-6} to 8×10^{-6} mol Fe/slab (Figure 3.2). All loadings of HFO were sufficient to ensure that the amount of adsorbed As to the HFO in the gel is in excess of the dissolved As in the solution phase in the gel, and that the contribution of dissolved As can be neglected in the HFO-doped gels. 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 (Chapter 4).



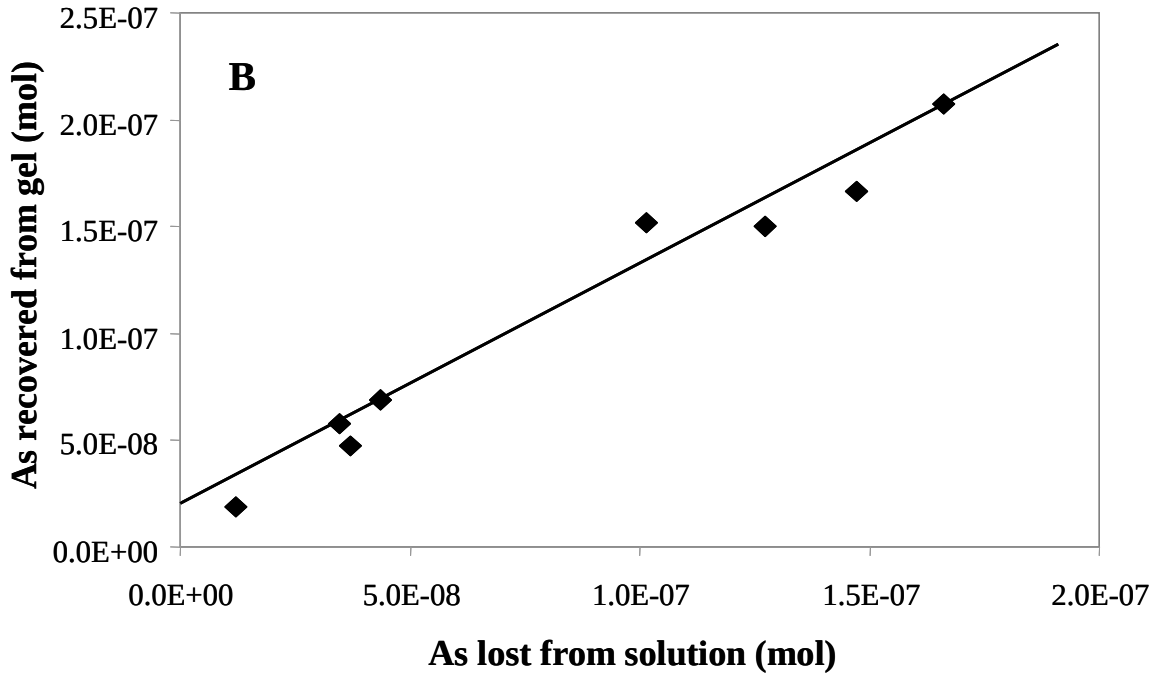


Figure 3.1. Arsenic recovery from clear (A) and HFO-doped gels (B). One gel was equilibrated in a solution of known As concentration. Gels were equilibrated for 24 hours before re-equilibration in acid, and analysis by ICP-MS.

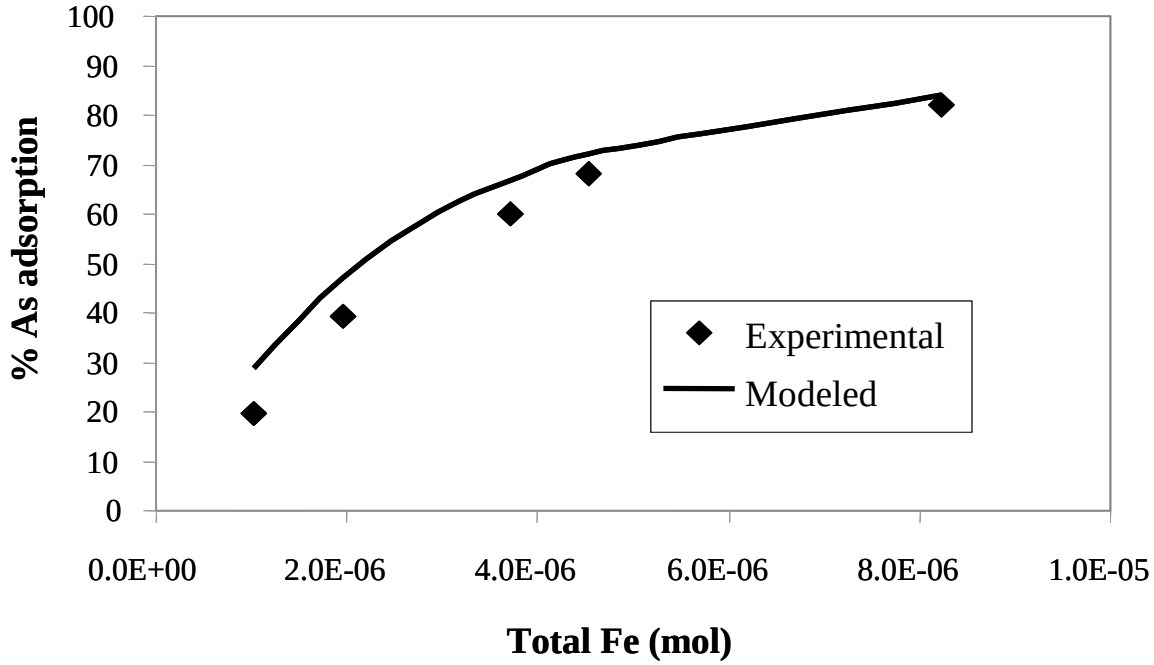


Figure 3.2. Amount of adsorbed As as a function of Fe per gel slab. MINEQL+ was used to simulate As sorption.

3.4.2 Gel equilibrium kinetics

A previous study found that clear gels reached equilibrium within 1-2 hours 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 (Kneebone 2000). This is comparable to other studies for similar types of gels (Davison et al. 1994; Docekalova et al. 2002). Sorption equilibrium with As(III) on an HFO-doped gel was reached in approximately 18 hours. The presence of phosphate did not alter the sorption kinetics, although the maximum amount of As adsorbed decreased by approximately 18% (Figure 3.3). Equilibration in both HFO and clear gels is controlled by diffusion. HFO-doped gels can take up to 10 times longer to equilibrate than clear gels, since the HFO concentrates As in the gel. The kinetics of adsorption onto HFO embedded in gel is consistent with other HFO sorption experiments without gel where equilibration can take up to 24 hours (Pierce and Moore 1982; Fuller et al. 1993).

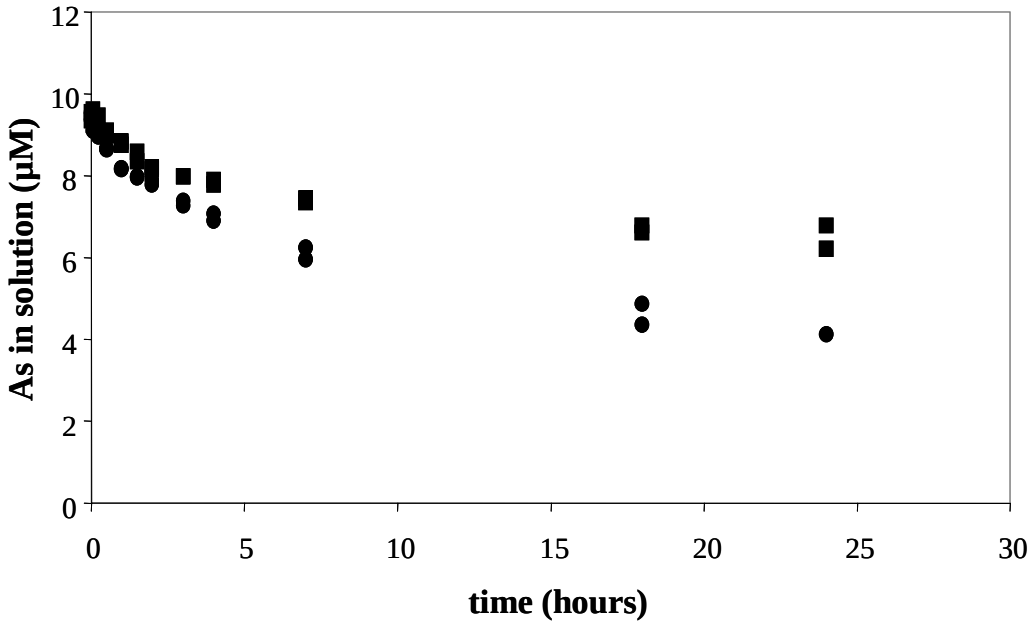


Figure 3.3. Kinetics of As(III) adsorption onto HFO-doped gels equilibrated with 10 µM As(III) in the presence of 50 µM phosphate (●) or the absence of phosphate (■).

3.4.3 XANES Calibration

Calibration standards for XANES were prepared by sorbing only As(III) or As(V) onto HFO-doped gel slabs. The XANES spectra of a set of HFO-doped gel slabs with varying proportions of adsorbed As(III) and As(V) were then collected.

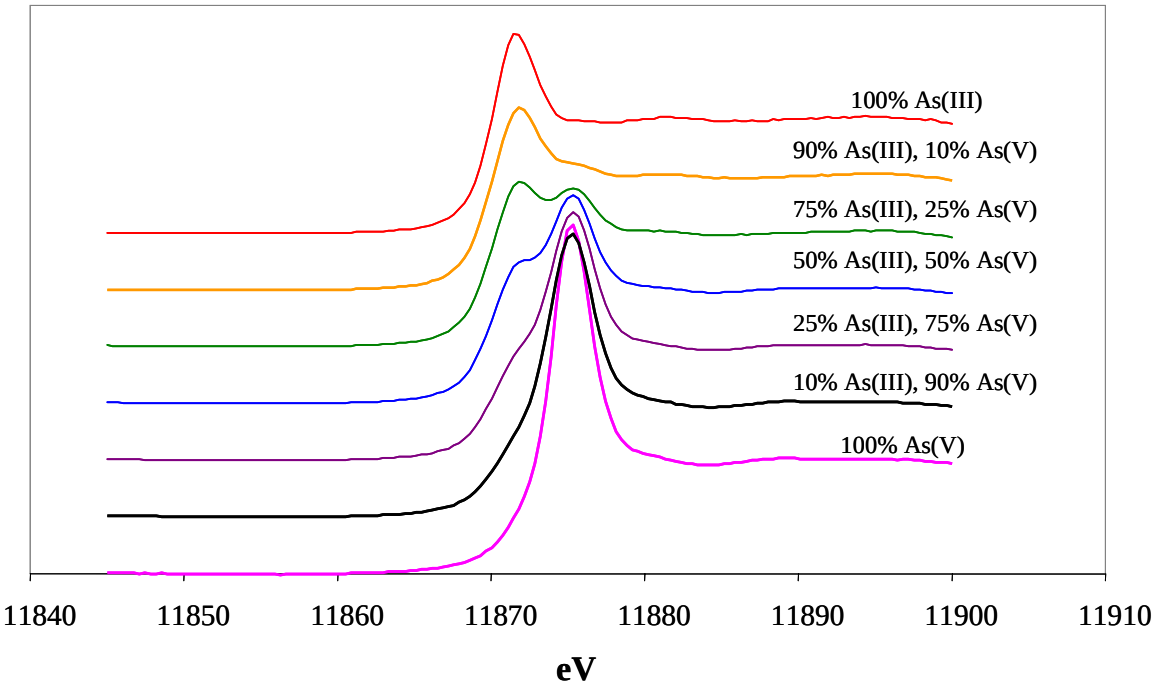


Figure 3.4. XANES calibration of As(III) and As(V) adsorbed on HFO embedded in gel. XANES edges are background normalized.

As seen in Figure 3.4, the As(V) signal is substantially stronger than the As(III) signal. As a result, peak heights are insufficient to quantitatively determine relative fractions of adsorbed As(III) and As(V) from a XANES edge. A least-squares linear combination of As(III) and As(V) end-members was chosen as an alternative. The results obtained for XANES spectra were compared with the value calculated from the residual dissolved concentrations of As(III) and As(V) measured by LC-ICP-MS after equilibration with HFO-doped gels (Table 3.1). For low As(III) fractions (<50%), the fit

has less than 1% error. However, once As(III) and As(V) are in equal abundance, a bias toward overestimating As(V) is observed. This effect is more pronounced at high As(III) fractions, where As(III) is underestimated by >10%. Nevertheless, the XANES calibration is a useful tool for determining the relative fraction of As(III) and As(V) on HFO-doped gels deployed in the field. The difference in signal response for adsorbed As(III) and As(V) may have implications for XANES edges collected on material other than HFO-doped gels, but further research is needed to compare the relative signal when the As is adsorbed on other synthetic and natural minerals.

Table 3.1. Analysis of XANES calibration by principal component analysis compared to measured values.

	LC-ICP-MS		***XANES***	
As(III):As(V)	**% As(III)**	**% As(V)**	**% As(III)**	**% As(V)**
10/90	7.9	92.1	8.0	91.7
25/75	22.4	77.6	21.4	78.5
50/50	47.4	52.6	54.6	45.6
75/25	73.9	26.1	61.2	39.1
90/10	89.5	10.5	76.7	23.5

3.4.4 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 3.5). 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} (Figure 3.6).

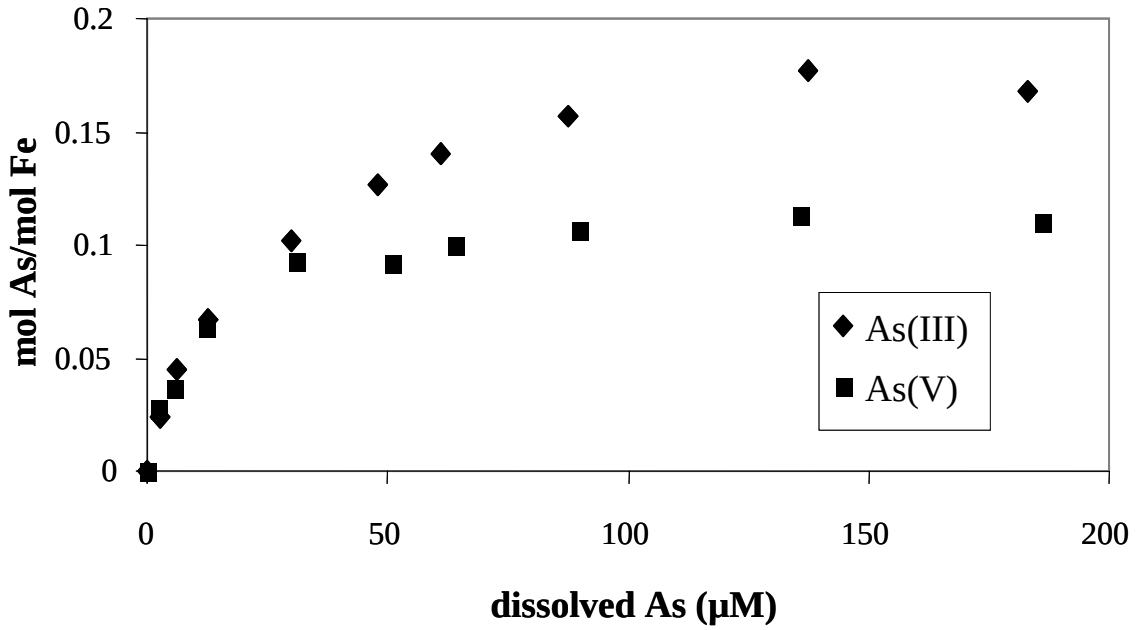


Figure 3.5. Sorption isotherms of As(III) (♦) and As(V) (■) on HFO embedded in polyacrylamide gel. One HFO-doped gel (2×10^{-6} mol Fe/gel) was equilibrated for 24 hours with 20mL of buffered arsenic solution (pH 7.1, I = 0.01 M).

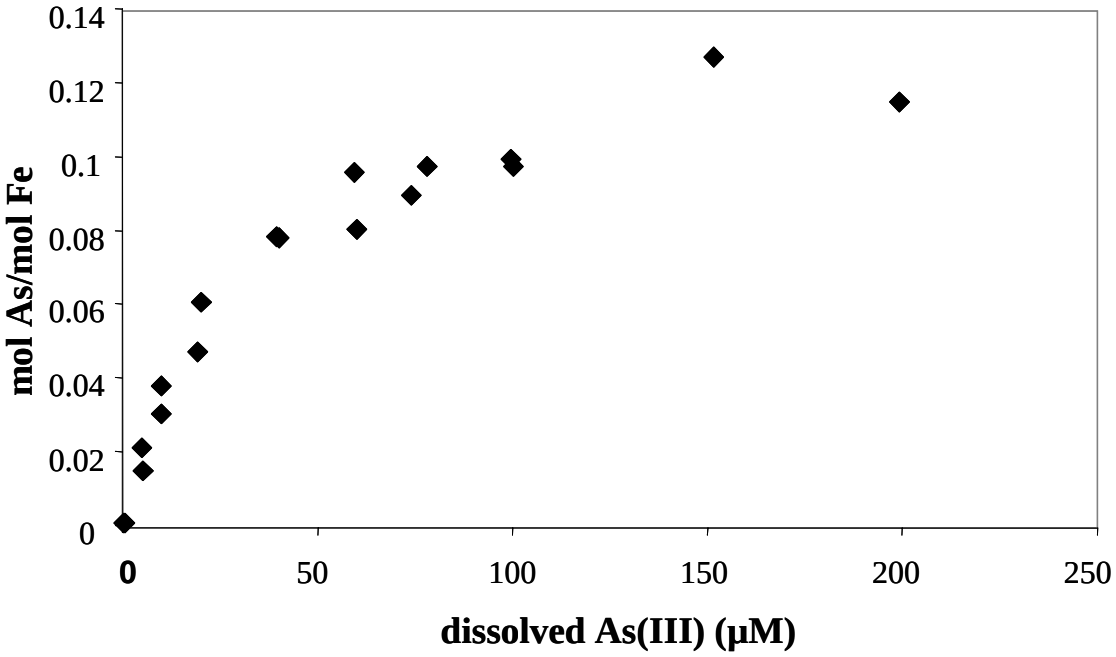


Figure 3.6. Sorption isotherm for As(III), pH 8. One HFO-doped gel (2×10^{-6} mol Fe/gel) was equilibrated for 24 hours with 20mL of buffered arsenic solution (I = 0.01 M).

The maximum sorption capacity of adsorbed As(III) onto HFO embedded in gel is less than most literature values, although the reported site density for As(III) varies considerably, from 0.043 mol As/mol Fe (Pierce and Moore 1980; Pierce and Moore 1982) to 0.31 mol As/mol Fe at pH 8 (Dixit and Hering 2003). Estimated site densities in excess of the theoretical number of surface sites have also been reported, possibly attributable to surface precipitation (Pierce and Moore 1982; Raven et al. 1998). The amount of As(III) adsorbed onto HFO depends strongly on pH (Pierce and Moore 1982; Wilkie and Hering 1996; Raven et al. 1998; Goldberg and Johnston 2001; Dixit and Hering 2003). This effect is observed in the difference in site densities at pH 7.1 and pH 8.

The site density of As(V) on HFO embedded in gel falls within the range of literature values, which vary from 0.02 mol As/mol Fe (Pierce and Moore 1982) to 0.25 mol As/mol Fe at pH 8 (Fuller et al. 1993). Co-precipitated HFO and As(V) can yield higher sorption densities (Fuller et al. 1993; Jia et al. 2006), but is not applicable to the HFO-doped gel probe, since field deployment will necessarily limit the conditions to neutral pH and post-synthesis sorption.

The maximum sorption densities of As(III) and As(V) are slightly less than reported values at comparable pH values possibly because some surface sites may be obstructed by 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 (Dzombak and Morel 1990), and provide a valuable estimate for available surface sites in the gel probe when it is deployed in natural sediments.

3.4.5 Competitive sorption of Phosphate

It is well known that phosphate inhibits the sorption of both As(V) and As(III) on Fe (oxyhydr)oxides (Manning and Goldberg 1996; Jain and Loeppert 2000; Hongshao and Stanforth 2001; Liu et al. 2001; Holm 2002; Violante and Pigna 2002; Dixit and Hering 2003; Antelo et al. 2005). Phosphate inhibits the adsorption of both As(III) and As(V), but has a stronger effect on As(V) (Figure 3.7). 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 (Figure 3.8). In the mixed As(III)/As(V) condition, total As sorption is slightly less than the As(III) only condition.

Previous studies have found that As(V) sorption is suppressed by phosphate to the greatest extent between pH 7 and 10, while As(III) sorption is inhibited the most at low pH (Jain and Loeppert 2000). As(V) and phosphate directly compete for surface sites, especially at neutral and alkaline pH (Manning and Goldberg 1996; Jain and Loeppert 2000). Similar maximum site densities for As(V) and phosphate in this study support this observation.

The order of sorbate addition strongly affects the extent of sorption, especially in the case of phosphate and As, which is indicative of incomplete equilibration. The sorbate added first adsorbs to a greater extent (Hongshao and Stanforth 2001; Liu et al.

2001). In this study, the sorbates (As(III), As(V), and phosphate) were added simultaneously to simulate sorption conditions in a field-deployed gel probe.

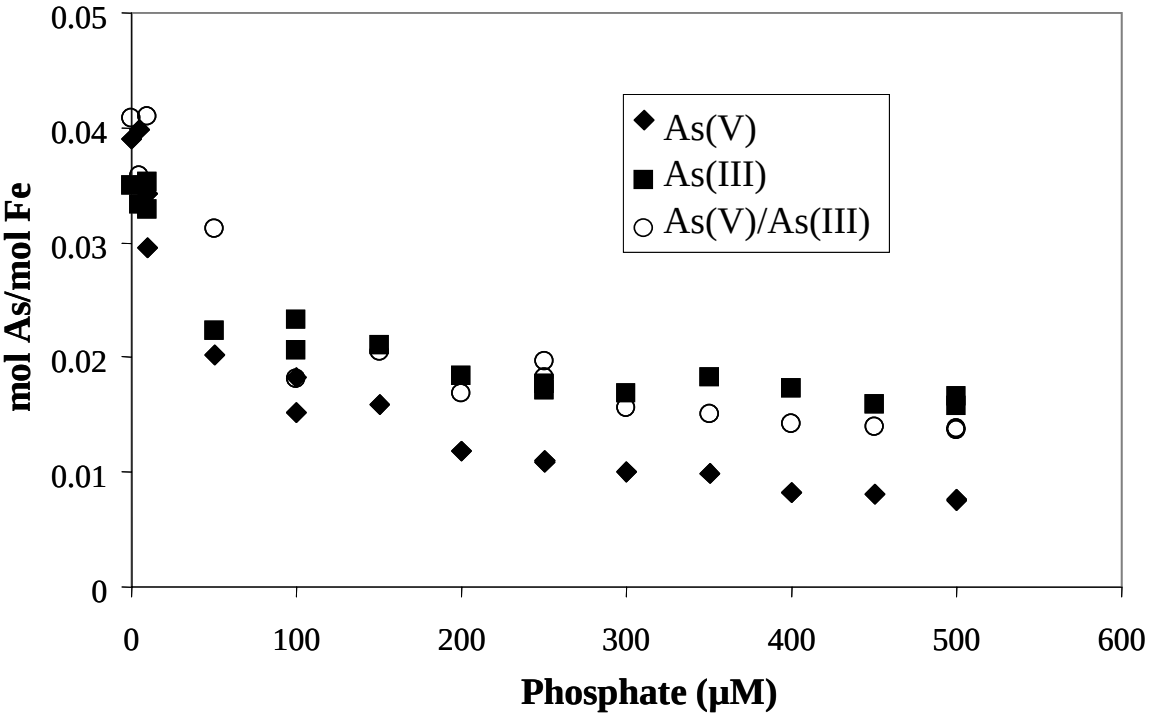


Figure 3.7. The effect of phosphate on adsorption of As(III) and As(V) on HFO-doped gels. One gel slab (2×10^{-6} mol Fe/gel) was added to a 20 mL buffered solution (pH 7.1, I = 0.01 M) of variable phosphate concentration and 10 µM As(III) (■), 10 µM As(V) (♦), or 5 µM As(III) and 5 µM As(V) (○) and equilibrated for 24 hours.

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 As(III) and As(V)), Jain and Loeppert 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% (Jain and Loeppert 2000). Phosphate has a much stronger inhibitory effect under our experimental conditions.

At high 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. Fe(III) minerals exhibit a slight preference for As(V) adsorption over phosphate (Hongshao and Stanforth 2001; Liu et al. 2001; Violante and Pigna 2002). 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 (Violante and Pigna 2002). The presence of adsorbed As(V), even at very high phosphate concentrations, may be due to slight preference for As(V) at equilibrium rather than sorption kinetics, although further investigation is needed to constrain this mechanism.

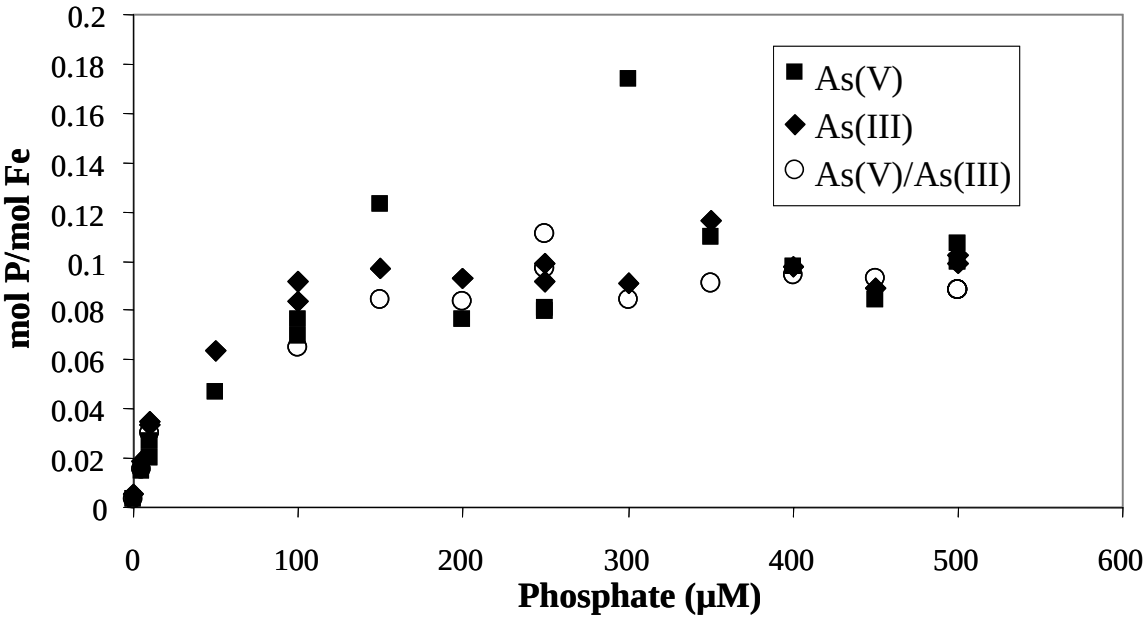


Figure 3.8. Phosphate adsorption onto HFO gels from the same experiment as Figure 3.7.

3.4.6 Competitive Sorption of Organic Matter

Soil HA and SR-NOM also inhibited adsorption of As(V) and As(III) onto HFO embedded in gel (Figure 3.9 A, B). Both types of organic matter had comparable effects and both As(V) and As(III) were similarly affected.

As(V) reduction and As(III) oxidation have both been observed in the presence of organic carbon, but this varies with the carbon source (Redman et al. 2002; Ko et al. 2004). 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 effects were observed for As added nominally as either As(III) or As(V).

The presence of Soil HA and SR-NOM reduced the amount of As adsorbed by ~50% at high organic carbon concentrations. While phosphate had a stronger competitive effect than organic matter, both are effective at inhibiting As sorption onto HFO. The mechanism of As sorption inhibition is not known by organic carbon, but could be due to several processes. Organic carbon can sorb directly to Fe(III) mineral surfaces (Kaiser et al. 1997) and may affect As sorption through steric effects by blocking the oxide surface (Grafe et al. 2002) or electrostatic effects (Xu et al. 1991). Organic matter may also complex As in solution, most likely by inorganic bridging between Fe(III) stabilized in the dissolved phase by NOM (Redman et al. 2002; Ko et al. 2004; Warwick et al. 2005; Ritter et al. 2006). Organic carbon complexation exhibits a slight preference for As(V), but this observation is not consistent across all types of organic matter (Redman et al. 2002). 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.

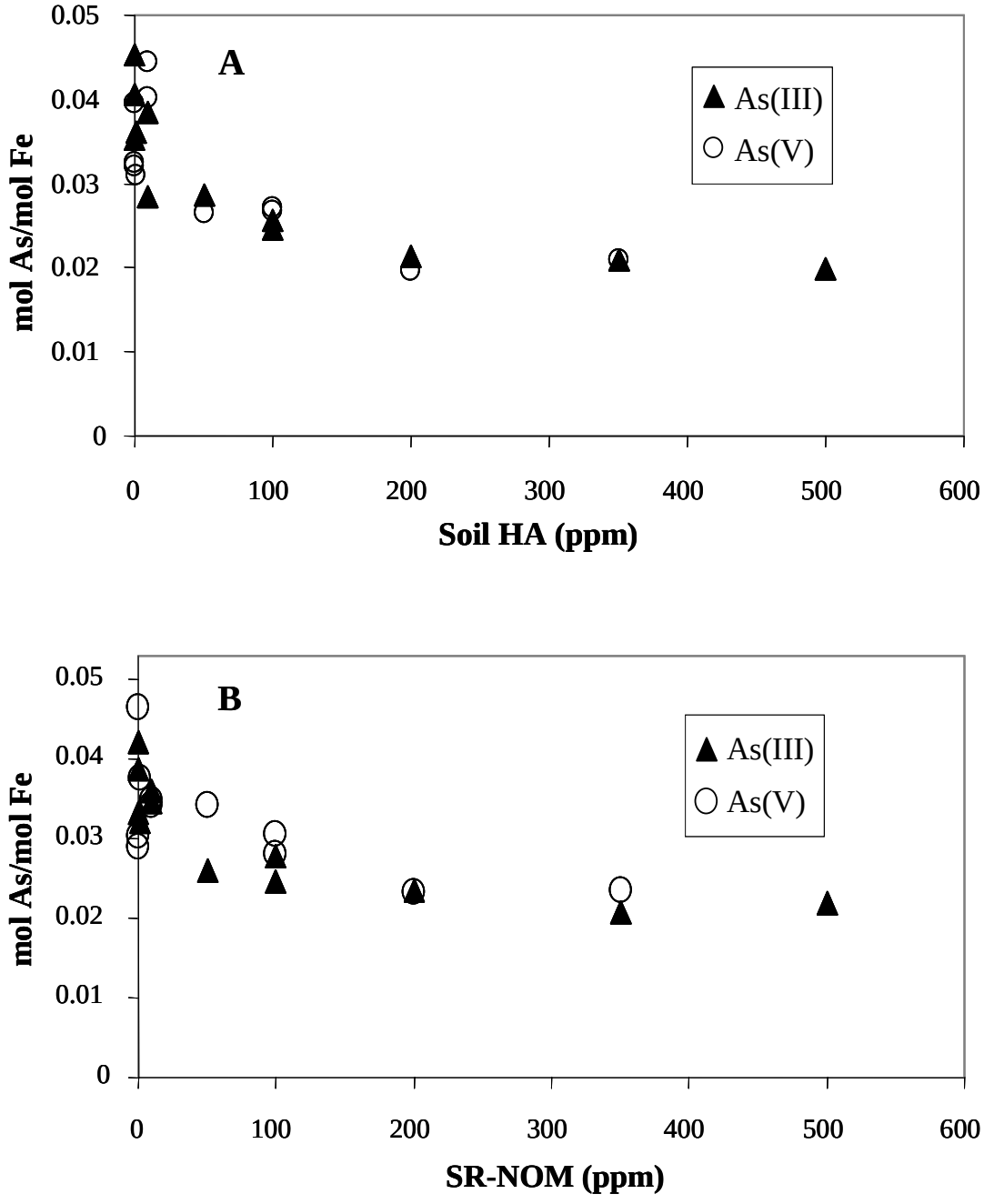


Figure 3.9. The effect of Soil HA (A) and SR-NOM (B) on As adsorption onto HFO-doped gels. One gel slab (2×10^{-6} mol Fe/gel) was added to 20 mL of buffered (pH 7.1, I = 0.01 M) solution with 10 μM arsenic and variable concentrations of organic matter. The gel was equilibrated for 24 hours, and re-equilibrated in acid.

Similar to phosphate, the extent of organic carbon inhibition on As sorption may depend on the order of sorbate addition. This was seen by Grafe and co-workers in an experiment where As adsorption onto goethite was inhibited by the presence of humic acid (HA) and fulvic acid (FA) when organic carbon and As were added simultaneously (Grafe et al. 2001). However, the opposite effect was seen on ferrihydrite-coated sand in column studies, where organic carbon was equilibrated with the solid phase first, followed by As (Grafe et al. 2002). Simultaneous addition of organic carbon and As in these experiments mimics the conditions to which an HFO-doped gel would be exposed in the field.

3.4.7 Application to field measurements

The results presented here establish a baseline of laboratory behavior for clear and HFO-doped gels. The clear gels can accurately measure the amount of As over a range of environmentally relevant concentrations. Arsenic sorption capacities for the HFO-doped gels and As behavior in simple competitive systems are essential in order to identify competitive sorption effects in a sedimentary system. By applying the XANES calibration to HFO-doped gels and LC-ICP-MS for the clear gels, both porewater and sorption speciation 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.

3.4 Acknowledgements

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