# Chapter 4

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

## 4.1 Abstract

Arsenic (As) geochemistry and sorption behavior was measured in Haiwee Reservoir sediments by deploying undoped (clear) polyacrylamide gels and hydrous ferric oxide (HFO)-doped gels in a gel probe equilibrium sampler. The As- and iron (Fe)-rich sediments provide a unique field site to study the effects of sediment diagenesis and porewater chemistry on As partitioning between solid and aqueous phases. Gel probe measurements were accompanied by sediment core analysis. Arsenic was deposited at the sediment surface as As(V) but was reduced to As(III) in the upper layers of the sediment. Reduction of As(V) did not cause mobilization into the porewater, as a negligible about of dissolved As was observed at the sediment-water interface. Dissolved As and Fe concentrations increased at depth in the sediment column driven by the reductive dissolution of amorphous Fe(III) oxyhydroxides. As organic matter was mineralized to dissolved inorganic carbon, sorption onto the HFO-doped gels was most likely inhibited by carbonate. In this region, dissolved As concentrations were at least partially controlled by porewater composition rather than surface site availability. Deeper in the sediment column, the Fe(III) oxyhydroxides partially converted to

carbonate green rust, possibly sequestering dissolved carbonate into the solid phase. Arsenic adsorption onto the HFO-doped gels increased in this region, and the extent of adsorption was most likely controlled by the competitive effects of dissolved phosphate. The persistence of dissolved As in the porewaters may be due to the loss of sorption sites upon conversion to green rust. When sediments were recently exposed to air, the region of sorption inhibition was not observed, suggesting that oxidation affects the extent of reductive dissolution. The HFO-doped gel probe equilibrium sampler is a novel technique for measuring the effects of porewater composition on As mobilization when combined with core analysis.

## 4.2 Introduction

Complex biogeochemistry governs the partitioning of arsenic (As) between solid and aqueous phases in freshwater sedimentary environments. In non-sulfidogenic 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 (Smedley and Kinniburgh 2002). Adsorption is controlled by As redox state, solution chemistry, and sorbent properties, and is sensitive to 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, carbonate, silicate, organic carbon, and other compounds (Jain and Loeppert 2000; Grafe et al. 2001; Holm 2002; Dixit and Hering 2003). Changes in solid-phase properties during early sediment diagenesis can

alter As partitioning. Reductive dissolution and the resulting secondary mineral transformations can promote As mobilization under some conditions and may be important in many types of reducing sediments and aquifers (Aggett and O'Brien 1985; Peterson and Carpenter 1986; Azcue and Nriagu 1994; Nickson et al. 2000; Welch et al. 2000).

The sediment in North Haiwee Reservoir (Olancha, 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/co-precipitation. The As- and Fe-rich floc is removed from the water via sedimentation at Haiwee Reservoir. Some initial sedimentation occurs in the inlet channel to the reservoir (Figure 4.1), which provides a location for the study of effects of early diagenesis on Fe and As distribution. Arsenic is deposited as As(V), but reduction to As(III) occurs in the surficial sediment. The change in oxidation state does not result in release of As to the porewaters (Root et al. 2006). The reduction of As(V) is most likely due to biological metabolism related to respiration (Malasarn et al. 2004; Campbell et al. 2006).

Reductive Fe(III) dissolution drives the mobilization of As in Haiwee sediments and is most likely microbially mediated. Reductive dissolution can proceed through abiotic or biotic pathways, although biological reductive dissolution is thought to be more significant in freshwater sediments (Lovley et al. 1991). Biological Fe(III) oxide

reduction can be catalyzed by a very metabolically-diverse group of organisms present in a wide variety of sediment environments (Lovley et al. 1991; Thamdrup 2000). Less crystalline Fe oxides are more bioavailable due to higher reactive surface areas and, consequently, more readily reduced by bacteria (Jones et al. 2000).

Secondary mineral transformations can be catalyzed by the Fe(II) produced during reductive dissolution (Schwertmann 1991; Zachara et al. 2002; Hansel et al. 2005; Pedersen et al. 2005). A mixed Fe(II)-Fe(III) hydroxide phase, carbonate green rust ($[Fe^{II}_4Fe^{III}_2(OH)_{12}]^{2+}\cdot[CO_3,\ nH_2O]^{2-}$), was found to be a significant mineralogical component below ~15 cm in Haiwee sediments (Root et al. 2006). Green rust is a metastable mineral resulting from bacterial Fe(III) reduction. The presence of adsorbed As, phosphate, and other anions can stabilize green rust in sediment (Bocher et al. 2004; Su and Wilkin 2005). While green rust generally has a high surface area, the effect of conversion from amorphous Fe(III) oxide to green rust on As partitioning is not well understood.

Iron reduction is not complete; Fe(III)-containing solids persist in the sediments, and are efficient sorbents for As. When sorption sites remain available on the solid, As can re-adsorb onto the solid phase even as reductive dissolution progresses (McArthur et al. 2004). 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. 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. We also demonstrate the utility of a Fe(III)-doped gel probe equilibrium sampler (Chapter 3) for investigating *in situ* sorption processes.

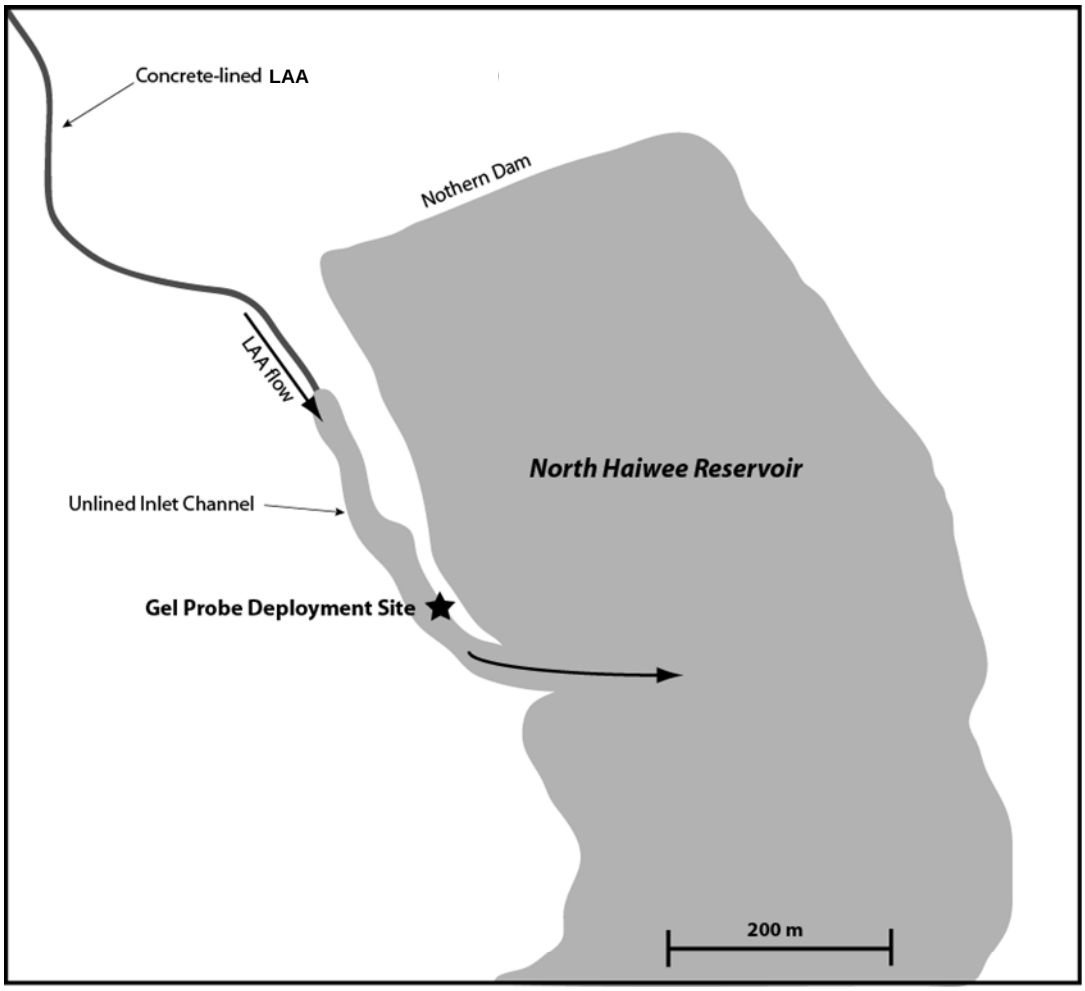



**Figure 4.1**. Map of North Haiwee Reservoir and the Los Angeles Aqueduct (LAA) inlet.

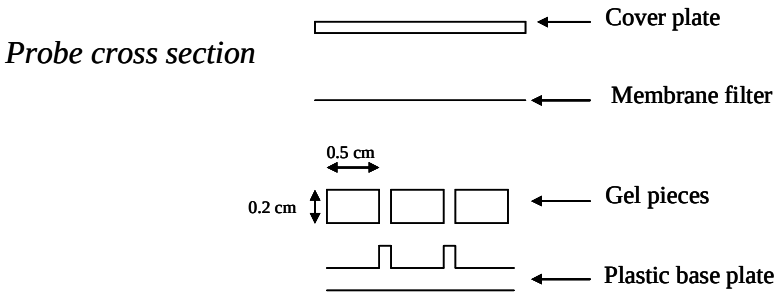
## 4.3 Materials and Methods

### 4.3.1 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%).

### 4.3.2 Clear and HFO-doped gels

Hydrous ferric oxide (HFO) was synthesized as described in Chapter 3. Both clear and HFO-doped gels were used in this study. A detailed description of gel synthesis, casting and cutting methodology is presented in Chapter 3. All gels were cut to the final dimensions of 2 cm × 0.5 cm × 0.2 cm. The iron content of HFO-doped gels was $2 \times 10^{-6}$ mol Fe/gel slab. A complete description of gel re-equilibration and analytics is provided in Chapter 3. Porewater composition (clear gels) was calculated with equation (3.1). Sorption onto HFO-doped gels is normalized to the amount of Fe in each gel slab (mol sorbate/mol Fe).




*Generalized Gel Probe schematic*

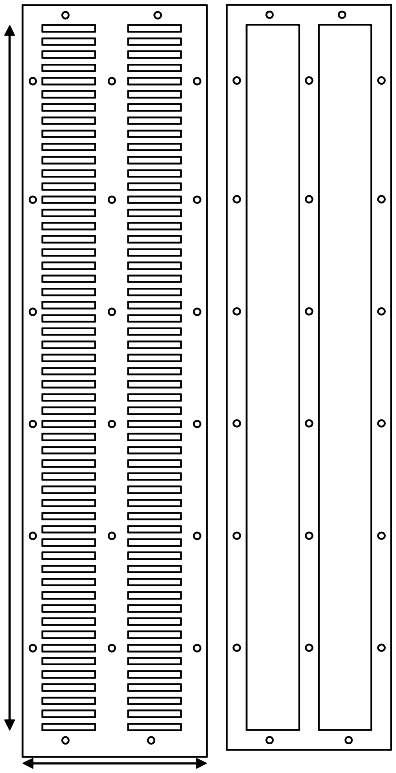


**Figure 4.2A.** Gel probe equilibrium sampler schematic with cross section.

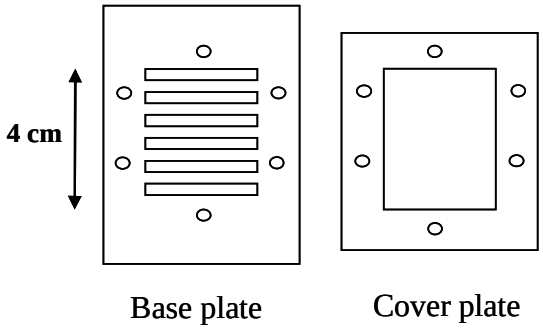



**Figure 4.2B.** "Mini-probe" gel probe equilibrium sampler schematic for sediment microcosms.

### 4.3.3 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 μm 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 $N_2$ 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. A double gel probe schematic is shown in Figure 4.2a.

For sediment laboratory microcosm experiments, 6 "mini-probes" were constructed. The mini-probes had a single column of 6 slots for gel slabs, and were 4 cm long. Preparation was identical to the field probe procedure. A mini-probe schematic is shown in Figure 4.2b.

### 4.3.4 Field Deployment

Gel probes were deployed in Haiwee Reservoir sediments at the location marked in Figure 4.1. The gel probes contained both HFO and clear gels unless otherwise noted, and were deployed in July 2003 (Appendix A), October 2003 (clear gels only), October 2004, August 2005, and May 2006. 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 overlying water was ~0.5 m deep above the probes. The gel probes were deployed in an area of relatively slow flow close to the shore, and were allowed to equilibrate undisturbed for 24 hours before being gently extracted from the sediment. The outside of the probe was quickly washed with water to remove excess sediment. The membrane was then removed, and the gels were immediately extracted and placed in individual 2 mL tubes (Eppendorf). A subset of clear gels was placed in tubes pre-filled with 1.25 mL of 25 mM $H_3PO_4$ for As speciation measurement (August 2005 and May 2006). These gels were allowed to re-equilibrate for 6-12 hours before analysis. A subset of HFO-doped gels were preserved for X-ray absorption spectroscopy (XAS) analysis and immediately frozen on dry ice in the field until placed in a -20°C freezer (August 2005 and May 2006). 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.

### 4.3.5 Gel Probe Analytics

Clear gels were re-equilibrated in 1% $HNO_3$ for inductively-coupled plasma mass spectrometry (ICP-MS) analysis, or 25 mM $H_3PO_4$ for liquid chromatography coupled to ICP-MS (LC-ICP-MS) for As speciation measurements. HFO-doped gels were re-equilibrated in 5% $HNO_3$ for ICP-MS analysis or were frozen for As speciation measurements by X-ray absorption spectroscopy (XAS). Both clear and HFO-doped gels were analyzed for manganese (Mn), As, strontium (Sr), molybdenum (Mo), antimony (Sb), barium (Ba), tungsten (W), phosphorous (P), chromium (Cr), nickel (Ni), copper (Cu), lead (Pb), uranium (U), selenium (Se), and Fe. Fe was measured by the

phenanthroline Fe assay (Standard Methods 1995). Only As, Mn, Fe, and P were measured in July 2003, October 2003, and October 2004.

Arsenic K-edge spectra of HFO-doped gels from the May 2006 deployment were collected at the Stanford Synchrotron Radiation Laboratory (SSRL), Menlo Park, California, on wiggler beamline 11-2 at a beam energy of 80-100 mM, 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. X-ray absorption near edge structure (XANES) edges were collected on HFO-doped gels that were equilibrated below 20 cm in the sediment. 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 extended x-ray absorption fine structure (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 endmember and known mixtures of As(III) and As(V) with DATFIT (see Chapter 3 for HFO-doped gel XANES calibration details).

### 4.3.6 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 6 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 $N_2$ for 24 hours to allow anoxic conditions in the sediment to be established. Even after freezing, anoxia is readily established, presumably due to the ambient bacterial population. Six mini-probes were filled with alternating clear and HFO-doped gels, deoxygenated, and inserted into the sediment, one probe per container. Compressed $N_2$ 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.

### 4.3.7 Gravity Core Processing and Analysis

Several acid-washed core tubes were inserted adjacent to the gel probes at the time of deployment, and were left undisturbed until after the gel probes were removed. Once recovered, they were stored upright on ice for transport and frozen at -20°C upon return to the laboratory. An additional set of cores was taken in May 2006, four weeks prior to the gel probe deployment, and in November 2004. Cores were defrosted under $N_2$ 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 µm, Pallman), and acidified with 1% $HNO_3$ for ICP-MS and colorometric analyses.

Core sections from two August 2005 cores were dried at 60°C in a drying oven. Solid phase organic carbon was analyzed 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).

Cores from November 2004 and August 2005 were analyzed for solid-phase As speciation by XANES at SSRL. In addition, core sections from May 2006 were extracted with 25 mM $H_3PO_4$, syringe-filtered (0.2 µm), and analyzed for As speciation by LC-ICP-MS.

## 4.4 Results

### 4.4.1 Sediment Microcosm

The clear gels in the sediment microcosms stabilized to a constant As concentration of ~10 µM within 10 hours (Figure 4.3a). The HFO-doped gels in the sediment microcosm required about 18 hours to reach equilibrium with the sediment porewaters (Figure 4.3b). Based on laboratory kinetics (Chapter 3), it is reasonable to expect that the HFO-doped gels require longer equilibration times than clear gels. An acceptable deployment time was determined to be 24 hours based on the sediment microcosm results.

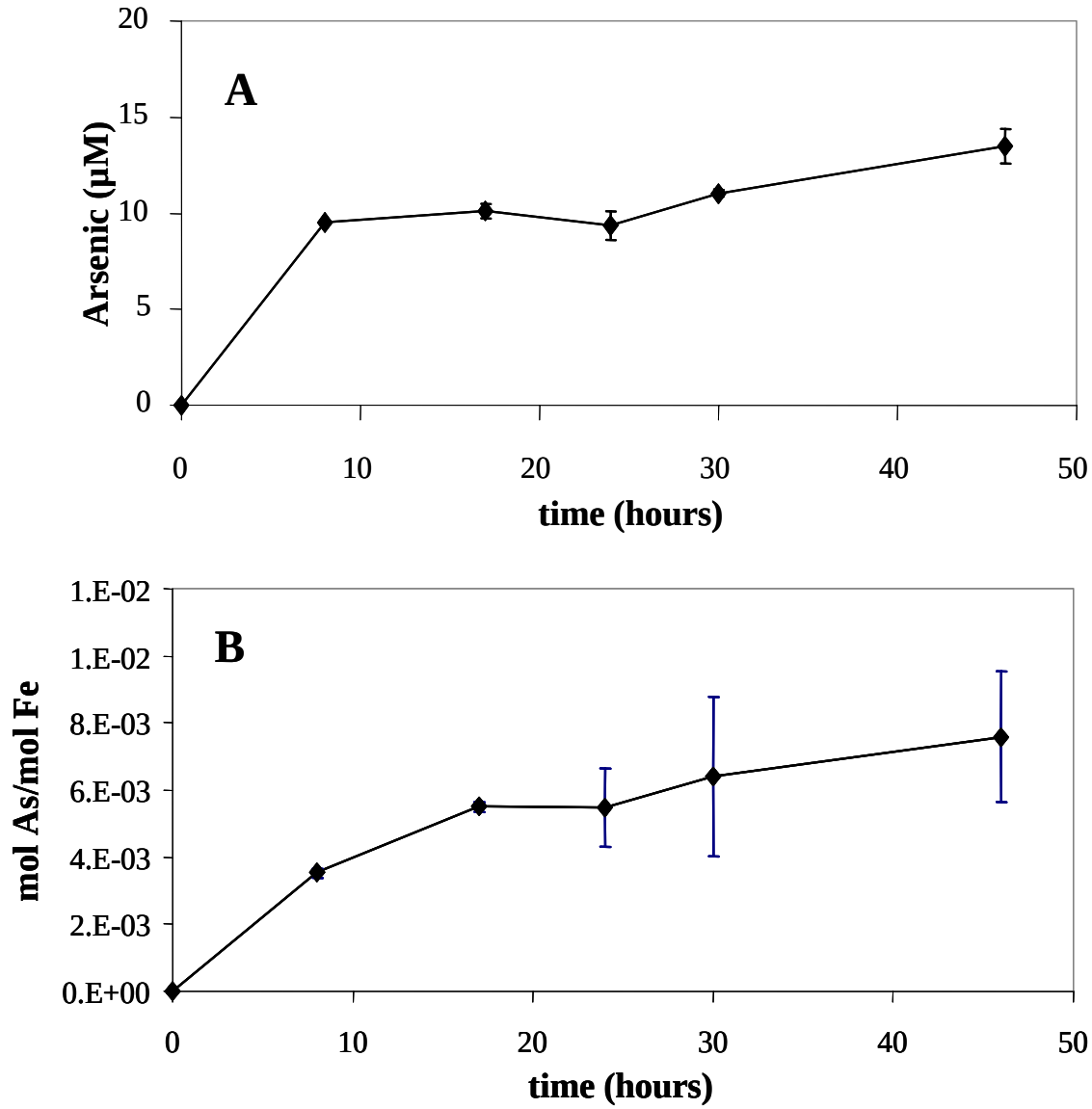



**Figure 4.3.** Arsenic in the porewaters (A) and adsorbed onto HFO-doped gels (B) in mini-probes equilibrated in Haiwee sediment microcosms. One probe was removed at each time point and the gels re-equilibrated in acid.

### 4.4.2 Comparison of clear gel concentrations and core porewater extractions

Porewater As concentrations measured by clear gels in a double gel probe are compared to porewater extractions from a core taken adjacent to the gel probe (~10 cm) in May 2006, in Table 4.1. Since the gel probe has a finer resolution than the core

sections, the gel probe porewater concentrations are reported as an average over the same depth interval as the core sections (n=4). The porewater As concentrations are consistent between the two measurement techniques. Although there is some variability, it is most likely due to natural spatial variability since there is no systematic bias between the two methods. This result also confirms the accuracy of clear gels for porewater measurements when placed in a double probe adjacent to HFO-doped gels.

**Table 4.1.** Comparison of porewater As concentrations from clear gels in a double gel probe and porewater extractions from a gravity core. The core was taken immediately adjacent to the gel probe in May 2006. Porewater was extracted from the core by centrifugation and the clear gels were re-equilibrated in 1% nitric acid. Gel probe values are an average over the same depth interval as the core sections (n=4).

| depth (cm) | core sections (µM) | gel probe (µM) |
|---|---|---|
| 0-3 | 0.38 | 0.43 |
| 3-6 | 0.74 | 1.01 |
| 6-9 | 0.70 | 0.99 |
| 9-12 | 1.73 | 1.36 |

### 4.4.3 Gel Probe Porewater profiles (clear gels)

Porewater concentrations as a function of depth below the sediment-water interface for October 2004 (2 double probes), August 2005, and May 2006, are presented in Figures 4.4-4.7. Porewater profiles from October 2003 are similar to October 2004; data can be found in Appendix D. In all cases, 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 and As for all sample dates, with As and Fe porewater data from October 2004 shown in Figure 4.8 as an example. Dissolved As is also correlated with dissolved P (all sample dates) and W (August 2005 and May 2006) (August 2005 shown in Figure 4.9, as an example). Since measurements were made using ICP-MS, the oxidation states of As, P, and W were not preserved. However, it is likely that P is present as phosphate and W present as tungstate, which are chemically similar to the oxyanions of As. Trace amounts of Cu, Cr, Mo, Sr, and Ba were detected in porewaters, but there was no correlation of these elements to dissolved As or Fe concentrations.

In August 2005, the fractions of dissolved As(III) and As(V) were approximately equal to 20 cm, below which about 60% of the total As was present as As(III) (Figure 4.6A). 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 4.7A).

Dissolved As, Fe, Mn, P and W concentrations varied substantially both temporally and spatially. Maximum As concentrations varied from 5 to 25 µM, and maximum Fe concentrations varied between 200 and 2000 µM. In October 2004, the maximum As concentration in one gel probe was 5 µM while maximum concentration in another gel probe placed within 2 meters was ~25 µM, highlighting the substantial spatial variability at the site.

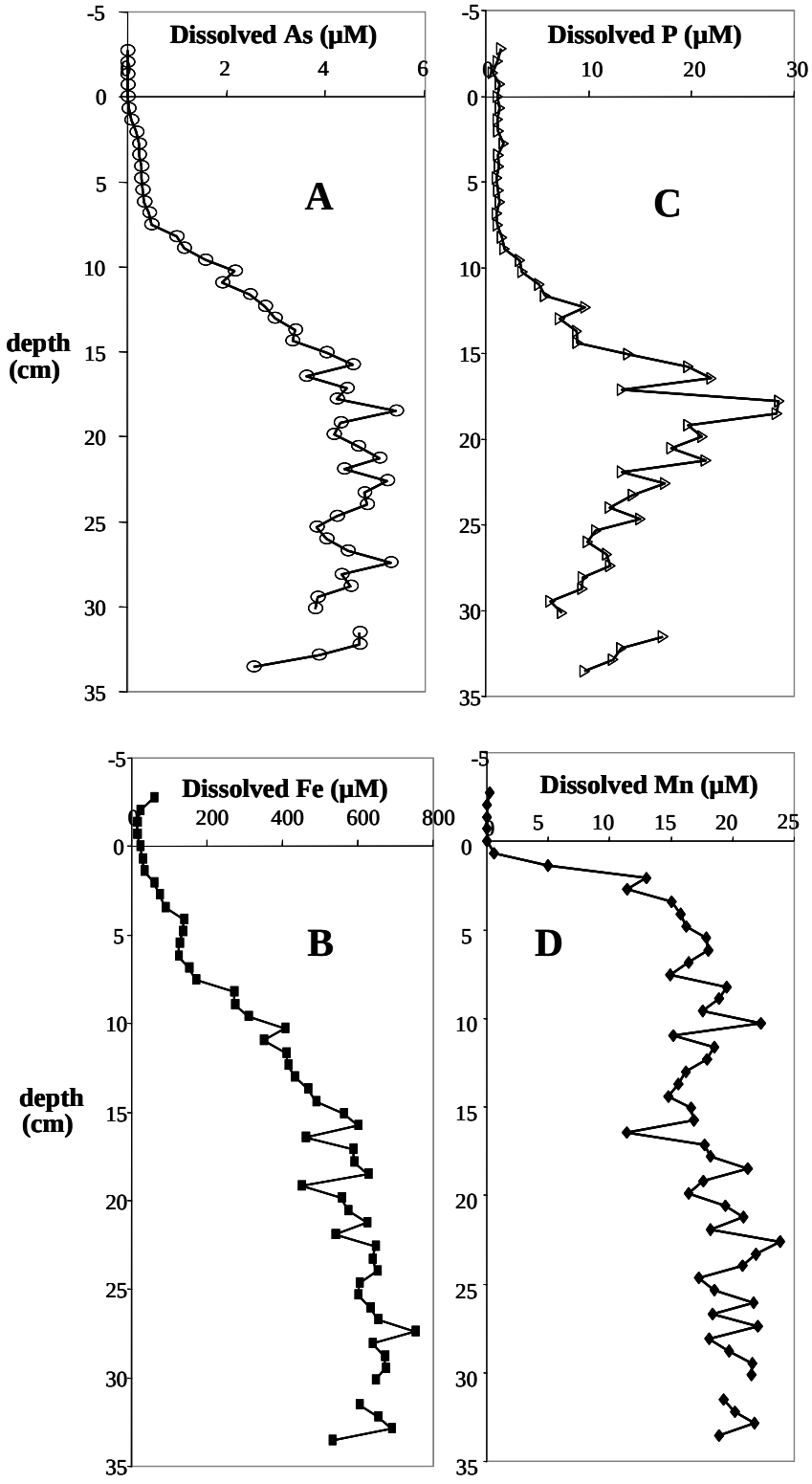



**Figure 4.4.** Porewater concentrations of As (A), Fe (B), P (C), and Mn (D) from double gel probe #1 deployed October 2004. The probe was equilibrated for 24 hours in the sediment. The sediment was soft and had not been recently exposed to the air.

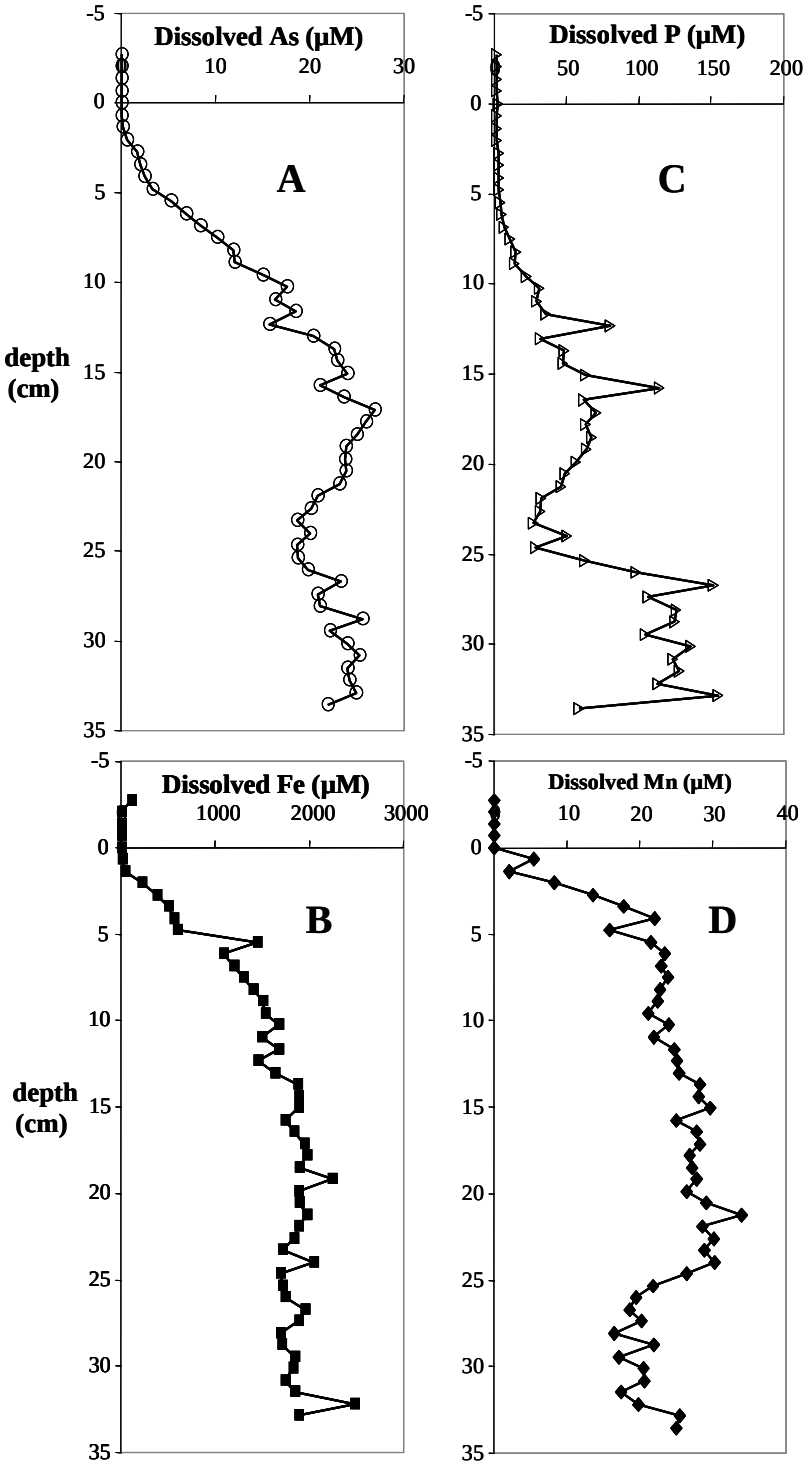



**Figure 4.5.** Porewater concentrations of As (A), Fe (B), P (C), and Mn (D) from double gel probe #2 deployed October 2004. The probe was deployed within 2 m of probe #1, and equilibrated for 24 hours in the sediment. The sediment was soft and had not been recently exposed to the air.

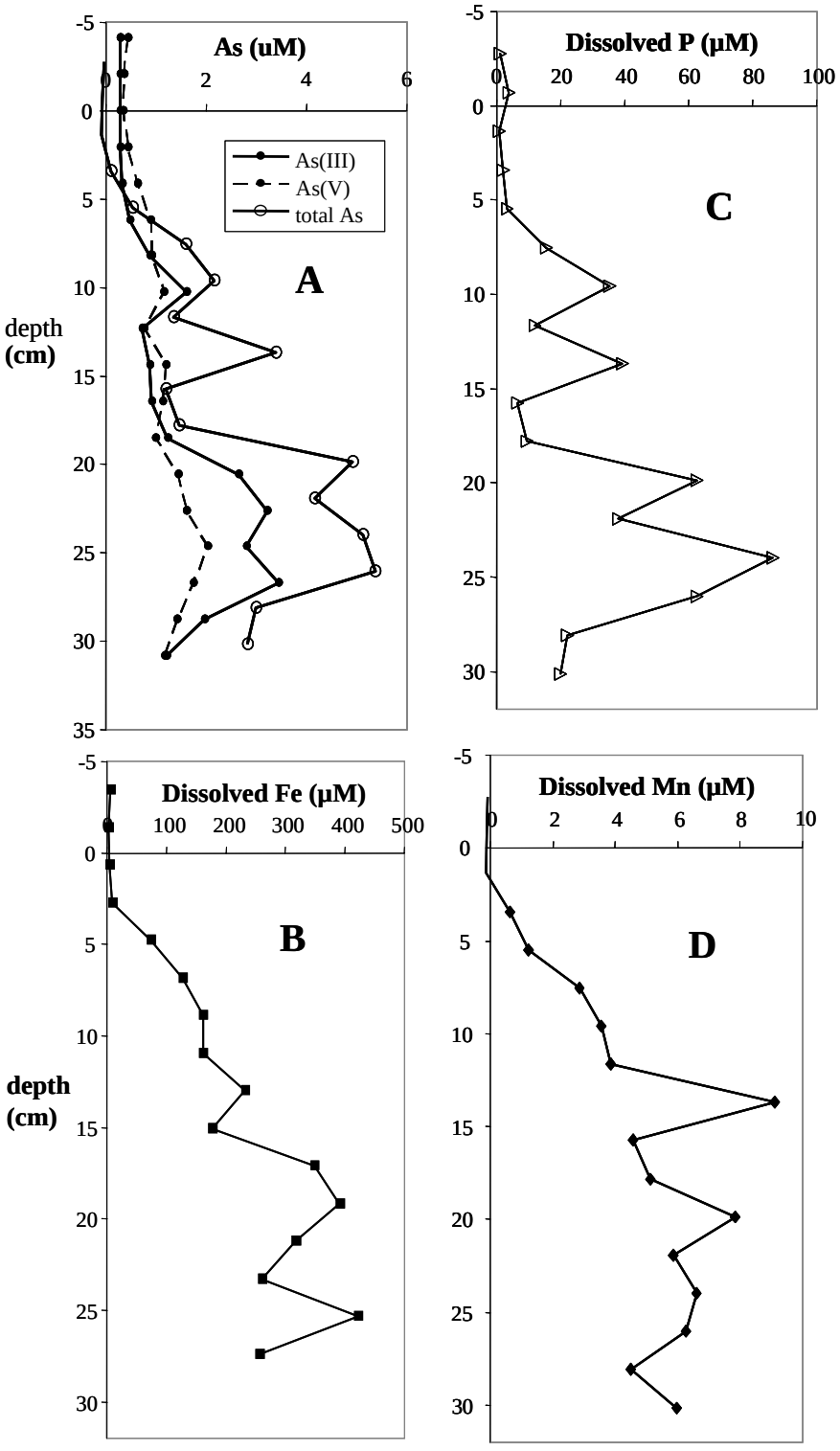



**Figure 4.6.** Porewater concentrations of As (A), Fe (B), P (C), and Mn (D) from a double probe deployed in August 2005. The probe was equilibrated for 24 hours. The sediment was hard and had been recently exposed to air. Arsenic speciation measurements were made by LC-ICP-MS.

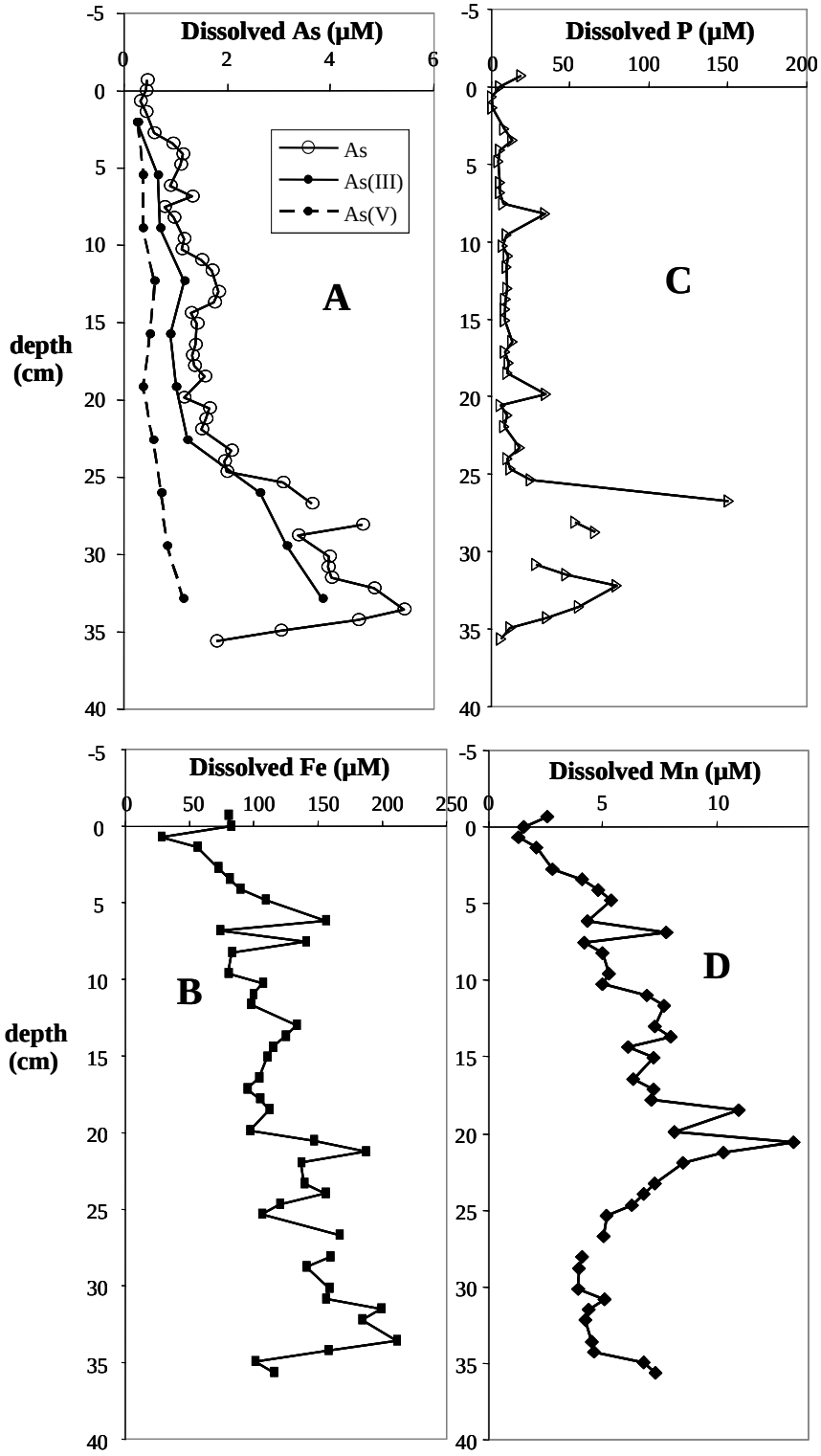



**Figure 4.7.** Porewater concentrations of As (A), Fe (B), P (C), and Mn (D) from a double probe deployed in May 2006. The probe was equilibrated for 24 hours. The sediment was hard and had been recently exposed to air. Arsenic speciation measurements were made by LC-ICP-MS.

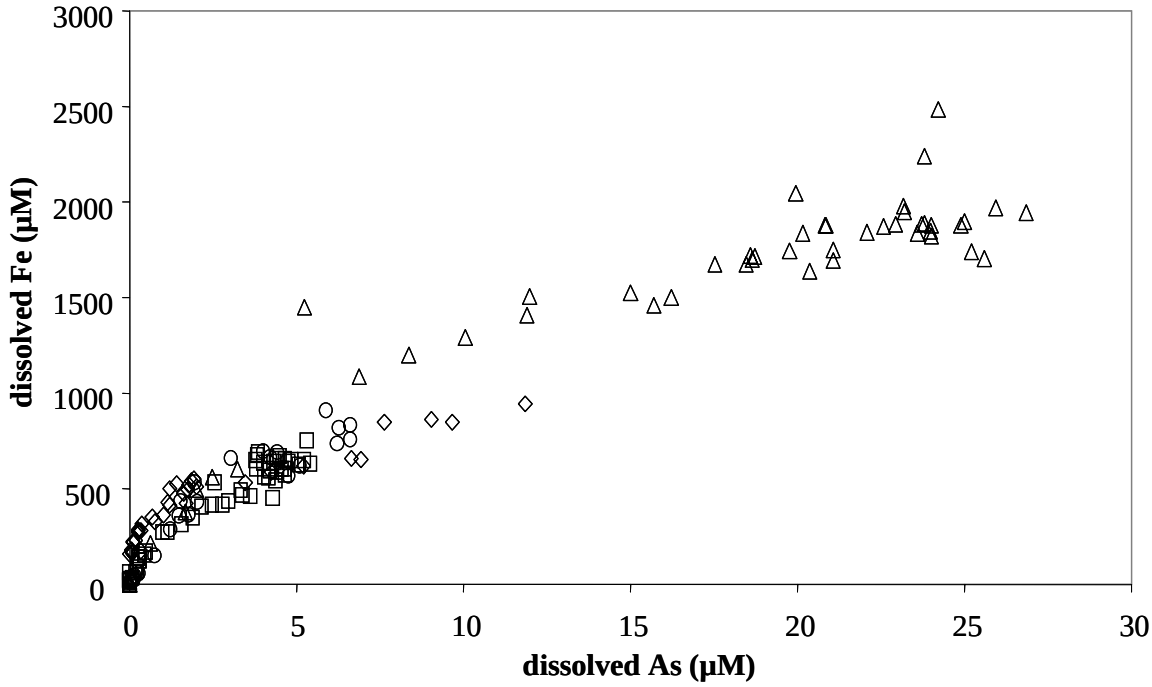



**Figure 4.8.** Correlation between Fe and As in porewaters from October 2004. Squares are data from gel probe #1, triangles are from gel probe #2, diamonds are from gel probe #3, and circles are from gel probe #4 (data are tabulated in Appendix D).

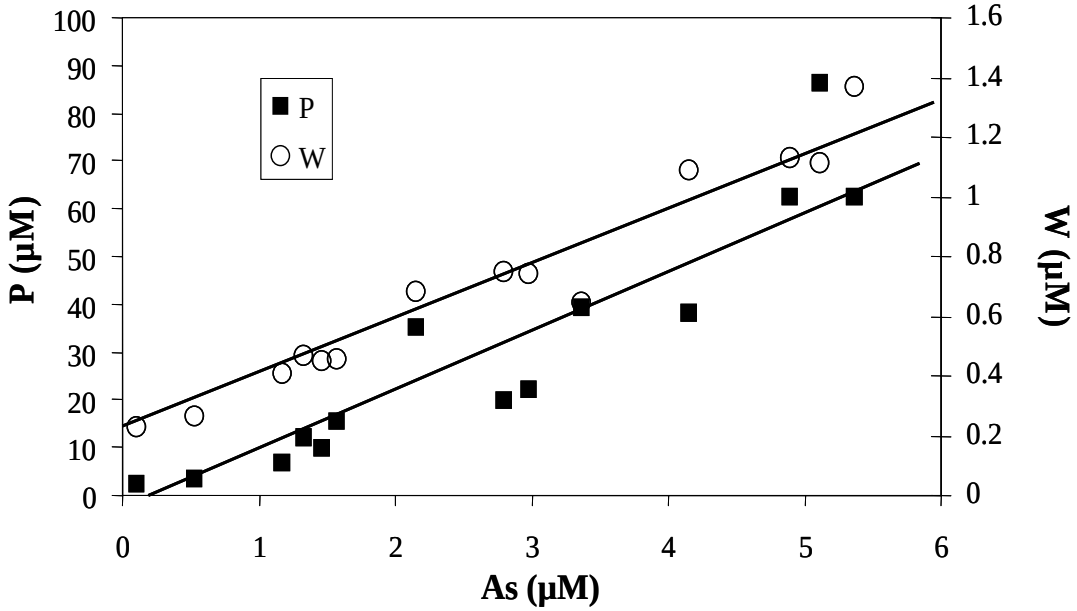



**Figure 4.9.** Correlation between As, P, and W in porewaters from gel probe deployed in August 2005.

### 4.4.4 Gel Probe Sorption profiles (HFO-doped gels)

Arsenic and P adsorption profiles from October 2004 and May 2006 are shown in Figures 4.10-4.12. The amount of As and P adsorbed onto HFO-doped gels in each field deployment is substantially less than the total available surface sites determined from sorption isotherms presented in Chapter 3. At 10 μM dissolved As(III) or As(V), about 0.05 mol As/mol Fe would adsorb if As was the only sorbate present. A maximum of only 0.01 mol As/mol Fe is observed on HFO-doped gels in the field. Similarly, adsorbed phosphate reached values between 0.05 and 0.1 mol P/mol Fe in laboratory studies as dissolved phosphate concentrations were varied between 50 – 150 μM, but a maximum of only 0.03 mol P/mol Fe was observed in the field. Although the maximum amount of As and P adsorbed onto the HFO-doped gels in the field is less than the total site content, the presence of other sorbates such as silicate and organic carbon can decrease the overall adsorption of As and P.

Adsorption of As and P onto HFO-doped gels was correlated with dissolved concentrations for some sampling events (e.g., May 2006), but not for all deployments. In October 2004, dissolved As concentrations increased between 10-20 cm without a corresponding increase in adsorption onto the HFO-doped gels. Most of the As adsorbed onto the HFO-doped gels was As(III) (>90% As(III)) in May 2006 (Table 4.2).

**Table 4.2.** Relative amount of As(V) and As(III) adsorbed onto HFO-doped gels deployed in May 2006. Gels were frozen in the field and analyzed by XANES at SSRL.

| depth (cm) | % As(V) | % As(III) |
|---|---|---|
| 26 | 89 | 11 |
| 29 | 90 | 9 |
| 32.5 | 88 | 10 |

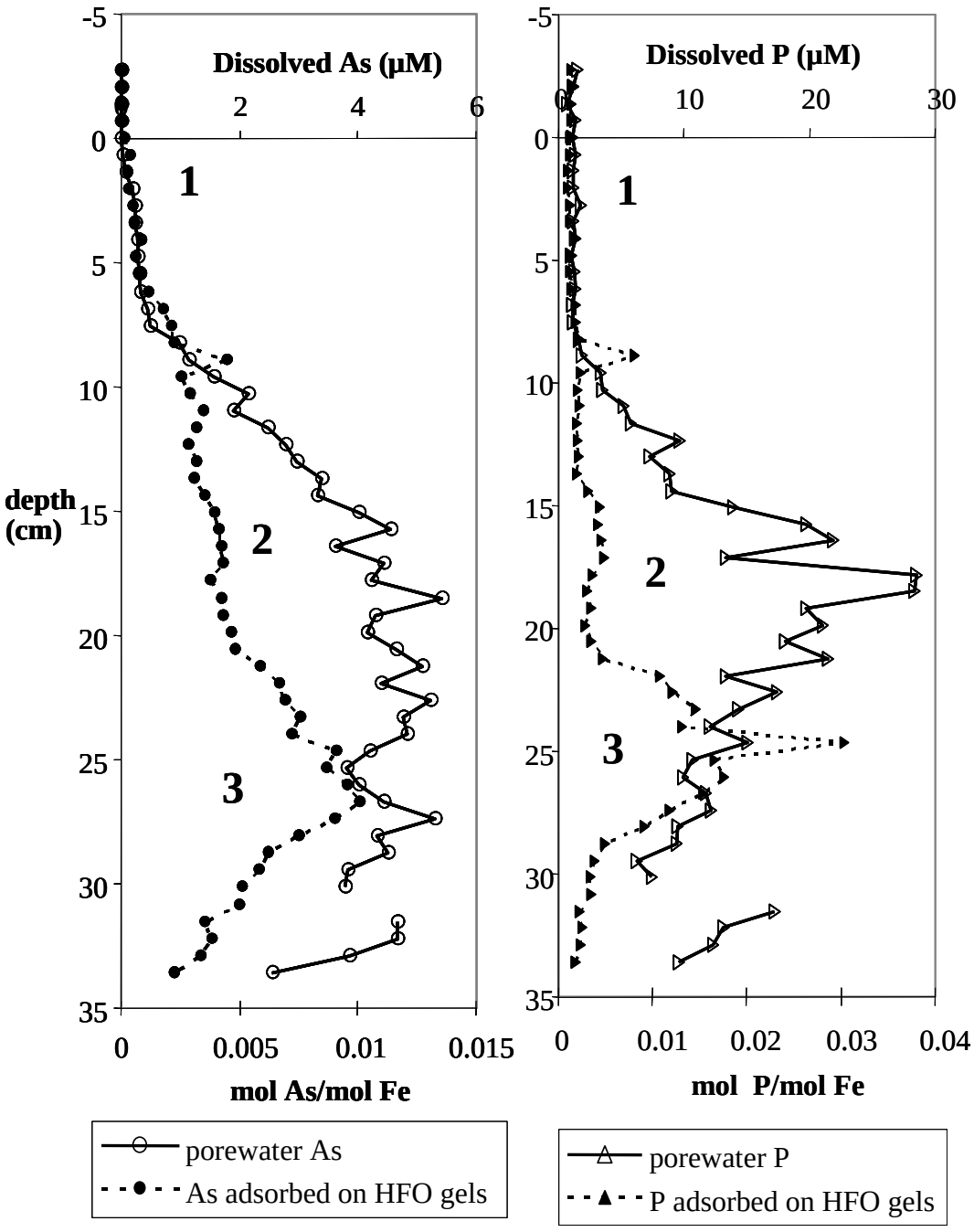



**Figure 4.10.** Porewater and adsorption profiles for As and P from double probe #1 deployed in October 2004. Region 1 denotes the low porewater concentrations of As and P. Region 2 denotes the region of sorption inhibition onto the HFO-doped gels. Region 3 denotes the region where As and P adsorption on HFO-doped gels increase at depth.

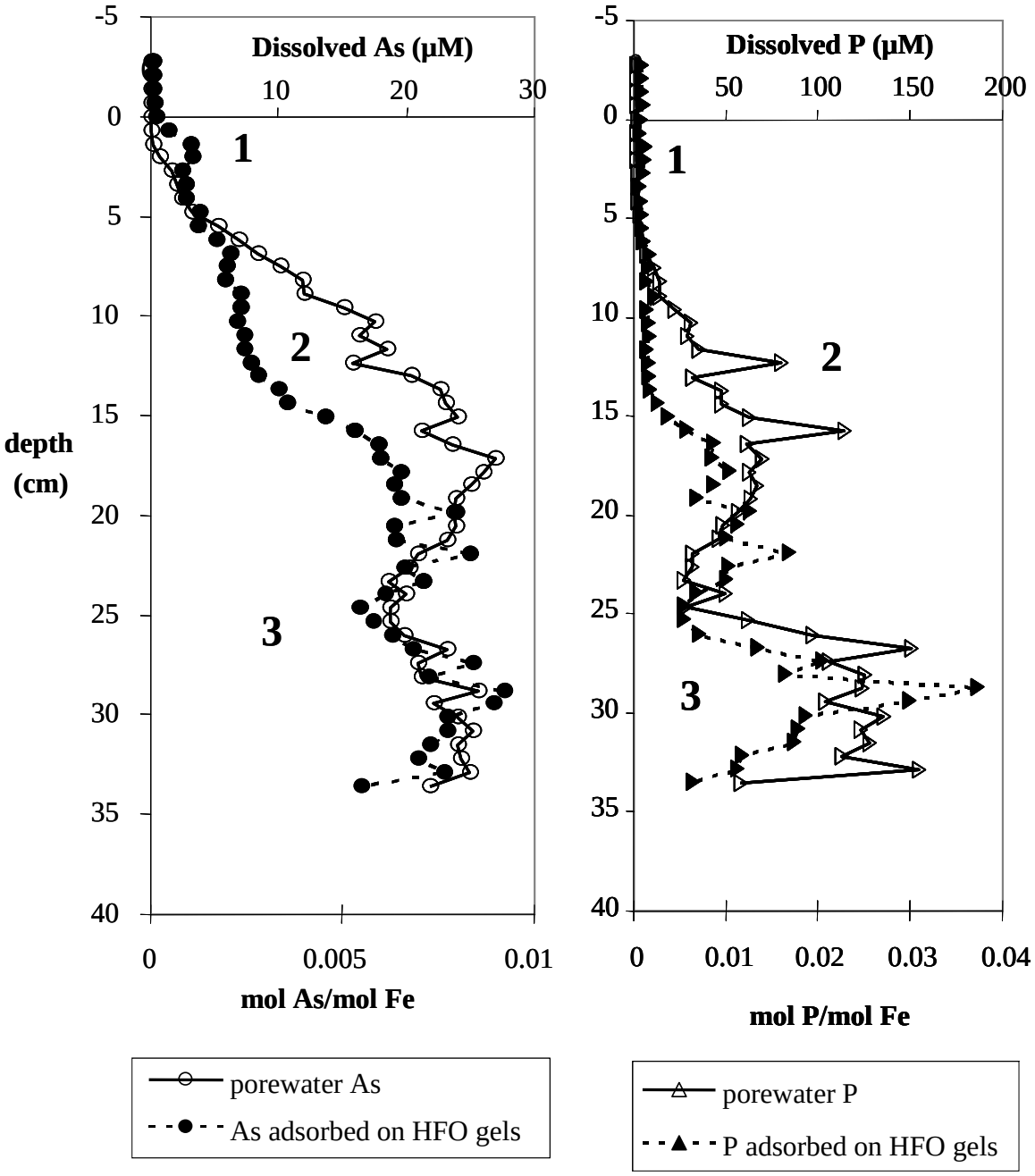



**Figure 4.11.** Porewater and adsorption profiles for As and P from double probe #2 deployed in October 2004. Region 1 denotes the low porewater concentrations of As and P. Region 2 denotes the region of sorption inhibition onto the HFO-doped gels. Region 3 denotes the region where As and P adsorption on HFO-doped gels increase at depth.

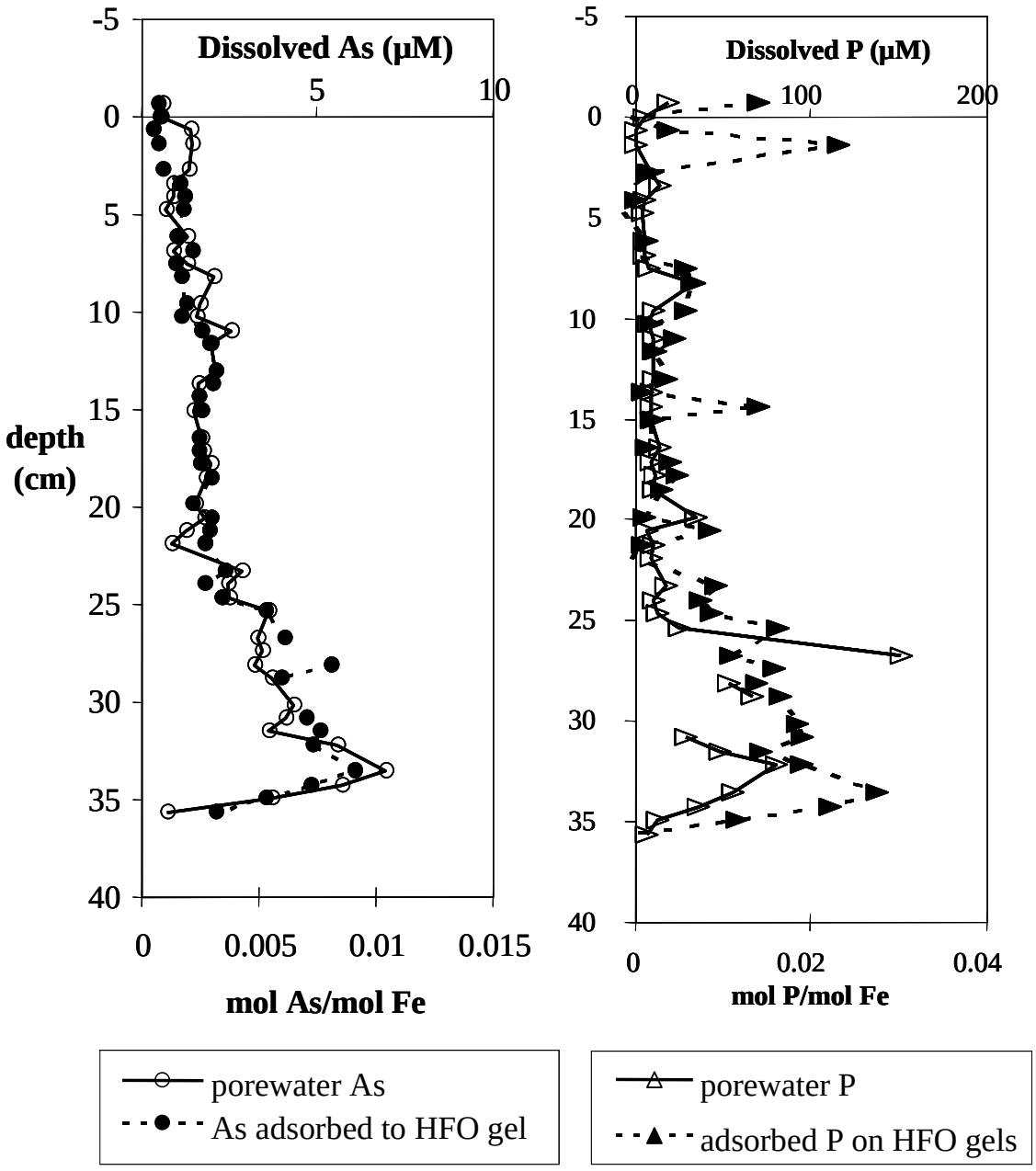



**Figure 4.12.** Porewater and adsorption profiles for As and P from a double probe deployed in May 2006, when the sediment was hard from recent exposure to air.

The ratio of As/P on the HFO gels is greater than the ratio in the porewaters for all sample dates (Figure 4.13, October 2004 as an example). A similar effect was observed in the competitive phosphate laboratory study, where As was adsorbed onto the HFO-doped gels even at high P concentrations (Chapter 3).

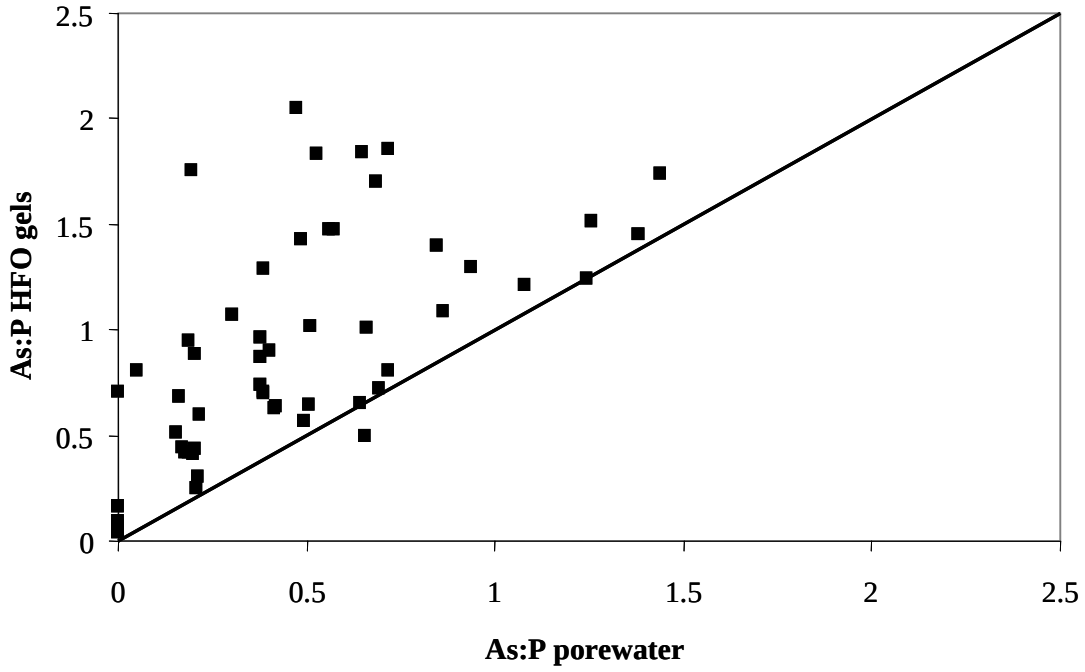



**Figure 4.13.** The As-to-P ratio in the HFO-doped gels versus in the porewater. The data were taken from double probe #2 from October 2004. The line indicates a perfect correlation between the As-to-P ratio in the gels and porewater.

### 4.4.5 Results from Sediment Cores

Bulk sediment elemental composition averaged over the sediment column is summarized in Table 4.3. The total Fe and As content is 7.89% and 210 mg/kg, respectively, consistent with previous sediment extractions (Kneebone 2000). The variation between duplicate cores was small (<0.4% for Fe and <7% for As).

**Table 4.3**. XRF bulk composition of cores from August 2005. Analysis was performed on a composite sample, resulting in an average over the sediment column.

| | % | | % | ppm | | ppm | | ppm |
|---|---|---|---|---|---|---|---|---|
| **SiO2** | 56.5 | **Al** | 5.70 | -- | **Cs** | 27.80 | **Lu** | 0.29 |
| **Al2O3** | 11.3 | **Ba** | -- | 691.00 | **La** | 33.50 | **Mo** | 8.00 |
| **CaO** | 2.515 | **Ca** | 1.64 | -- | **Nd** | 24.55 | **Nb** | 12.50 |
| **MgO** | 2.275 | **Cr** | -- | 160.00 | **Pb** | 23.50 | **Pr** | 6.69 |
| **Na2O** | 2.07 | **Cu** | -- | 57.00 | **Be** | -- | **Sm** | 4.20 |
| **K2O** | 2.47 | **Fe** | 7.89 | -- | **Ni** | 19.00 | **Sn** | 15.50 |
| **Fe2O3** | 12.15 | **K** | 1.93 | -- | **Sc** | 7.50 | **Ta** | 1.10 |
| **MnO** | 0.1 | **Li** | -- | 70.00 | **Ag** | -- | **Tb** | 0.60 |
| **TiO2** | 0.52 | **Mg** | 1.27 | | **Bi** | 0.60 | **Th** | 16.35 |
| **P2O5** | 0.32 | **Mn** | -- | 675.00 | **Cd** | 0.25 | **Tl** | 0.60 |
| **Cr2O3** | 0.03 | **P** | 0.14 | -- | **Co** | 12.00 | **Tm** | 0.30 |
| **LOI** | 8.90 | **Sr** | -- | 206.00 | **Dy** | 3.15 | **U** | 15.80 |
| ***SUM*** | 99.15 | **Ti** | 0.28 | -- | **Er** | 1.90 | **Y** | 18.4 |
| | | **V** | -- | 171.50 | **Eu** | 0.82 | **Yb** | 1.9 |
| | | **Zn** | -- | 96.00 | **Ga** | 15.00 | | |
| | | **Zr** | -- | 132.00 | **Gd** | 4.01 | | |
| | | **As** | -- | 210.00 | **Ge** | 8.00 | | |
| | | **Ce** | -- | 57.50 | **Hf** | 4.50 | | |
| | | **Rb** | -- | 121.00 | **Ho** | 0.65 | | |
| | | **W** | -- | 49.00 | **In** | -- | | |

The As XANES edges of sediment core sections show a distinct transition zone between 8-10 cm in August 2005 where the dominant solid phase As species changed from As(V) to As(III) (Figure 4.14). Phosphoric acid extractions of a sediment core corroborate this result (Appendix E). The As(V) redox transition was deeper in the sediment column than observed in a previous study at Haiwee Reservoir, where the transition occurred in the upper 3 cm of sediment (Kneebone 2000).

Dissolved Fe in the porewater was mainly Fe(II), based on porewater extractions from core sections (Figure 4.15). The difference between total Fe and Fe(II) could be dissolved Fe(III) complexed by organic carbon (Ritter et al. 2006), colloidal Fe(III)

caused by bacterially induced deflocculation (Tadanier et al. 2005), or an analytical artifact due to core processing.

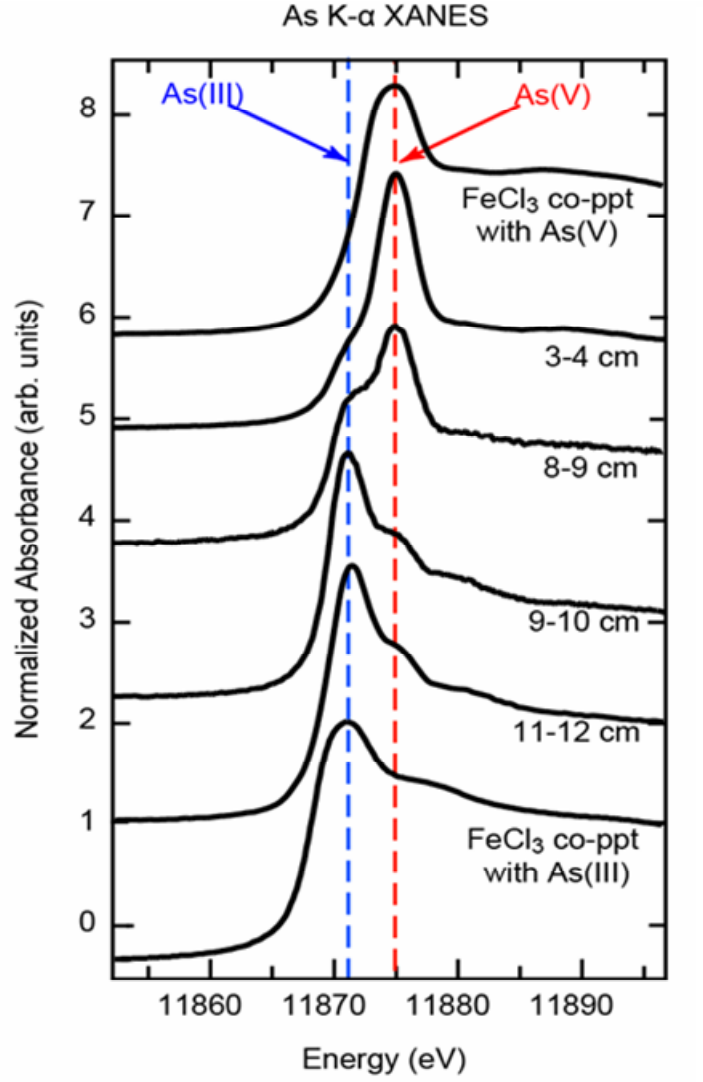



**Figure 4.14.** Arsenic XANES edges from core sections from August 2005. The As(III) and As(V) reference spectra are As co-precipitated with HFO. Figure courtesy of Rob Root, University of California, Merced.

Solid phase organic carbon decreased with depth (Table 4.4), and ranged from 20-34 g C/kg sediment. Between 75 and 90% of the total solid phase carbon was organic carbon.

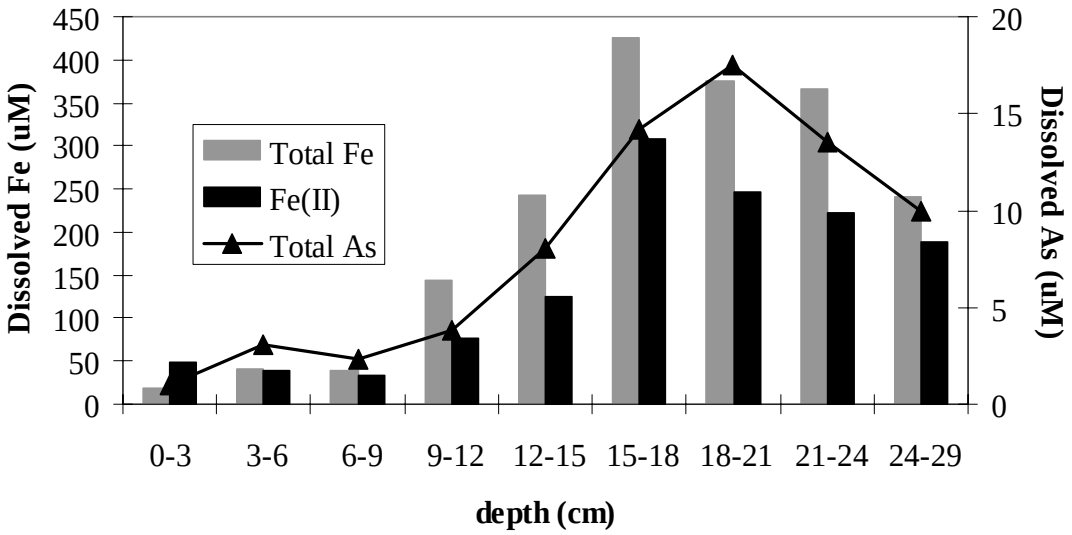



**Figure 4.15.** Iron and As extractions from sediment core from May 2006 prior to gel probe deployment. The sediment was soft, unlike the May 2006 gel probe deployment. Extractions were performed in an anaerobic chamber with 1% HCl.

**Table 4.4**. Solid phase total carbon and organic carbon measurements on dry core sections from duplicated cores sampled in August 2005. The organic carbon fraction was obtained by fumigating a dry sample with HCl before analysis.

| ***Core 1*** | ***Total carbon*** | ***organic carbon*** | |
|---|---|---|---|
| **depth (cm)** | **g C/kg sed** | **g C/kg sed** | **% of total C as organic C** |
| 3-6 | 40.7 | 31.6 | 78 |
| 6-9 | 42.8 | 32.0 | 75 |
| 9-12 | 40.3 | 32.3 | 80 |
| 12-15 | 25.1 | 20.7 | 82 |
| ***Core 2*** | ***Total carbon*** | ***organic carbon*** | |
| **depth (cm)** | **g C/kg sed** | **g C/kg sed** | **% of total C as organic C** |
| 6-9 | 42.8 | 33.9 | 79 |
| 9-12 | 37.9 | 30.8 | 81 |
| 15-18 | 29.8 | 24.3 | 81 |
| 21-29 | 22.8 | 20.3 | 89 |

### 4.4.6 Variability

Based on LAA flow data and ferric chloride dosage records, the rate and amount of Fe and As deposited in the inlet channel is not constant. The water level at the sample deployment location changes as flow varies. In addition, the aqueduct is occasionally drained to a minimal flow for repair. The floc deposited in the inlet channel may periodically be exposed to air and resubmerged as the LAA flow varies. Variation in flow also causes erosion and re-deposition of the sediment.

Because water level and floc deposition are not constant, the profiles taken at this site probably do not represent processes that result from uniform sediment aging. The depositional variability may explain the spatial and temporal variations in porewater concentrations and sorption profiles.

Gel probes deployed August 2005 and May 2006 were deployed in sediment that may have been recently exposed to air prior to sampling either due to a drop in aqueduct flow or substantial increase in base flow. The profiles for August 2005 and May 2006 were different from October 2004 with a peak of dissolved As occurring deeper (~20-25 cm, Figure 4.6-4.7) in the sediment rather than a plateau of dissolved As below ~15 cm (Figure 4.4-4.5). In addition, the solid phase As(V) transition was deeper in the sediment column than previous study results when sediment conditions were more similar to the October 2004 sampling.

## 4.5 Discussion

### 4.5.1 Equilibration of sediments and porewater

The gel probe sampler used in this study assumes that the gels inside the probe are in equilibrium with the surrounding porewater. For this to be true, one of two conditions must exist. The first condition requires that the amount of As exchanged with or concentrated into the gel is negligible compared to the amount of As in the surrounding porewater. If the first condition is not met, then the sediment must be able to resupply the amount of As lost from the porewaters to re-establish equilibrium within 24 hours. If neither of these conditions is met, then the gel probe will measure a diffusive flux (Zhang et al. 1995). The clear gels satisfy the first condition, since the volume of water inside each gel (~250 μL) is small. The HFO-doped gels do not satisfy the first condition, but the sediment is able to resupply the As to the porewaters within 24 hours, thus satisfying the second condition. The sediment microcosm showed an equilibrium state reached by both clear and HFO-doped gels within 24 hours. In addition, the porewater concentrations measured by a double probe with clear and HFO-doped gels were consistent with porewater extracted from a core (Table 4.1), confirming that the sediment was able to resupply As to the porewaters and equilibrate within 24 hours of deployment.

### 4.5.2 Effect of dissolved carbonate and green rust formation 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 (≤80%) of

amorphous carbonate green rust below ~15 cm (Root et al. 2006). The presence of green rust indicates that production of Fe(II) from reductive dissolution of the Fe(III) oxide and other chemical conditions was sufficient to transform the primary mineral phase. Mineralogical transitions in the sediment can be seen visually in a fresh core taken from Haiwee in October 2003 (Figure 4.16A). Cores with similar layers were observed in October 2004. The upper layers are red-orange, consistent with amorphous Fe(III) oxyhydroxide. The middle layers (~5-15 cm) are dark brown, indicative of Fe(II) re-adsorption to the Fe(III) surface. Deeper in the sediment column (~15-20cm) there is a layer of grey sediment, which may correlate to the formation of green rust. In August 2005, the sediment does not transition through a dark brown intermediate but changes directly from red-orange to grey at ~20 cm (Figure 4.16B).

Early sediment diagenesis is characterized by the mineralization of organic carbon coupled to the reduction of $O_2$, nitrate, Mn (III,IV) oxides, and Fe(III) oxides and is usually driven by microbial metabolism (Song and Muller 1999). As organic carbon is oxidized, the dissolved inorganic carbon in the porewaters is expected to increase with depth. 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 confirms that diagenetic processes are occurring in the sediment, and these processes are most likely coupled to organic carbon oxidation.


**Figure 4.16.** Pictures of cores taken from October 2003 (A) and August 2005 (B).

The porewater and sorption profiles for October 2004 can be divided into three regions, as denoted on Figures 4.10-4.11. 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. 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 As and P did not adsorb onto the HFO-doped gels, indicative of As and P sorption inhibition (region 2). Region 3 correlates to the depth where carbonate green rust was measured, as well as where the grey sediment layer was observed.

Inorganic carbon has been shown to inhibit As adsorption to Fe(III) oxides at concentrations of ~4 mM (Radu et al. 2005), which is possible in microbially active sediments. Elevated concentrations of dissolved carbonate from organic carbon mineralization may inhibit the re-adsorption of As and P onto the HFO-doped gels in region 2. Deeper in the sediment column, the formation of carbonate green rust may sequester enough of the dissolved carbonate to allow As and P to adsorb to the HFO-doped gels (region 3).

The sediment in August 2005 and May 2006 may have been exposed to air, and gel probes deployed on these dates exhibited slightly different porewater and sorption profiles than October 2004. In May 2006, there was a strong correlation between dissolved As and P concentrations and adsorption to HFO-doped gels even as As and P concentrations increased sharply between 25-35 cm. It is possible that due to the oxidative changes in the sediment, region 2 was absent because reductive dissolution in the upper layers (0-20 cm) had not progressed to the same extent as in October 2004. This result is corroborated by the visual transition directly from red-orange to grey sediments at ~25 cm in a core from August 2005.

### 4.5.3 Effect of P on As adsorption

The adsorption behavior of As onto the HFO-doped gels in region 3 (20-35 cm) in October 2004 and May 2006 is consistent with the competitive sorption effects of phosphate. An operationally-defined partition coefficient for sorption onto HFO-doped gels was calculated with equation (4.1).

$$K_D^{*} = \frac{\left(mol_{As} / mol_{Fe}\right)_{HFOgel}}{[As_{dissolved}]_{porewater}} \tag{4.1}$$

where the concentration of dissolved total As is expressed in mol/L. Although this is not a true partition coefficient, it is useful for comparing HFO-doped gel data from field deployments and laboratory experiments. $K_D^{*}$ values are valid only when the amount of As adsorbed to the HFO is far from surface site saturation. The plots of $K_D^{*}$ as a function of depth for the field deployments in October 2004 and May 2006 are shown in Figure 4.17 A, B. The $K_D^{*}$ values for Figure 4.11 (October 2004, double probe #2) have not been included because the dissolved As concentrations are >20 μM. Based on sorption isotherms from Chapter 3, when As concentrations are >20 μM, As sorption is close to surface site saturation where $K_D^{*}$ is not valid.

The large $K_D^{*}$ values at shallow depths are due to 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, $K_D^{*}$ as a function of phosphate concentration is plotted in Figure 4.18, using data from the competitive phosphate study presented in Chapter 3. When phosphate concentrations are 150-200 μM in the laboratory study, $K_D^{*}$ values are approximately 1500-2000 for As(V) and 2000-2800 for As(III). 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 region 3 (20-35 cm).

In the competitive phosphate study from Chapter 3, 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), but As(III) comprised >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 (20-35 cm).

### 4.5.4 Conclusions

Reductive Fe(III) dissolution in the sediments at Haiwee Reservoir causes the release of As and P into the porewaters and drives the mineralogical change to green rust deeper in the sediment column. The mineralization of organic carbon may cause increased concentrations of dissolved inorganic carbon, which inhibits As re-adsorption onto the HFO-doped gels. This implies that As accumulation into the porewater may be at least partially controlled by porewater composition rather than available sorption sites on the sediment. Green rust formation may sequester dissolved carbonate, allowing As and P adsorption to the HFO-doped gels. The amount of As adsorbed onto the HFO-doped gels in this region 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 convert to green rust.

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. Combined with core measurements, the complex mechanisms that control As partitioning between the solid and dissolved phases in sediment systems can be observed in the field.

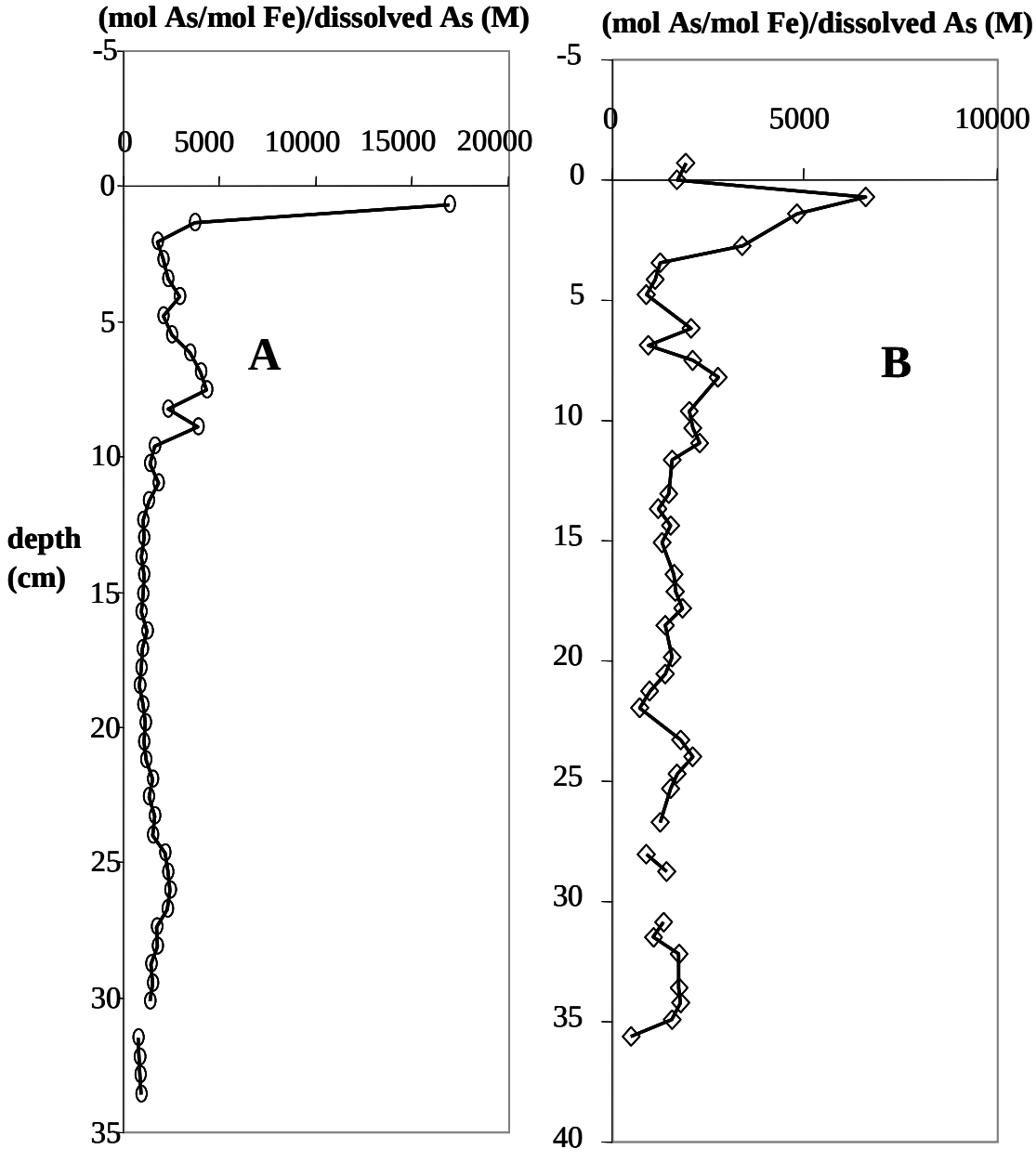



**Figure 4.17.** $K_D^*$ plots for October 2004 double probe #1 (A) and May 2006 (B).

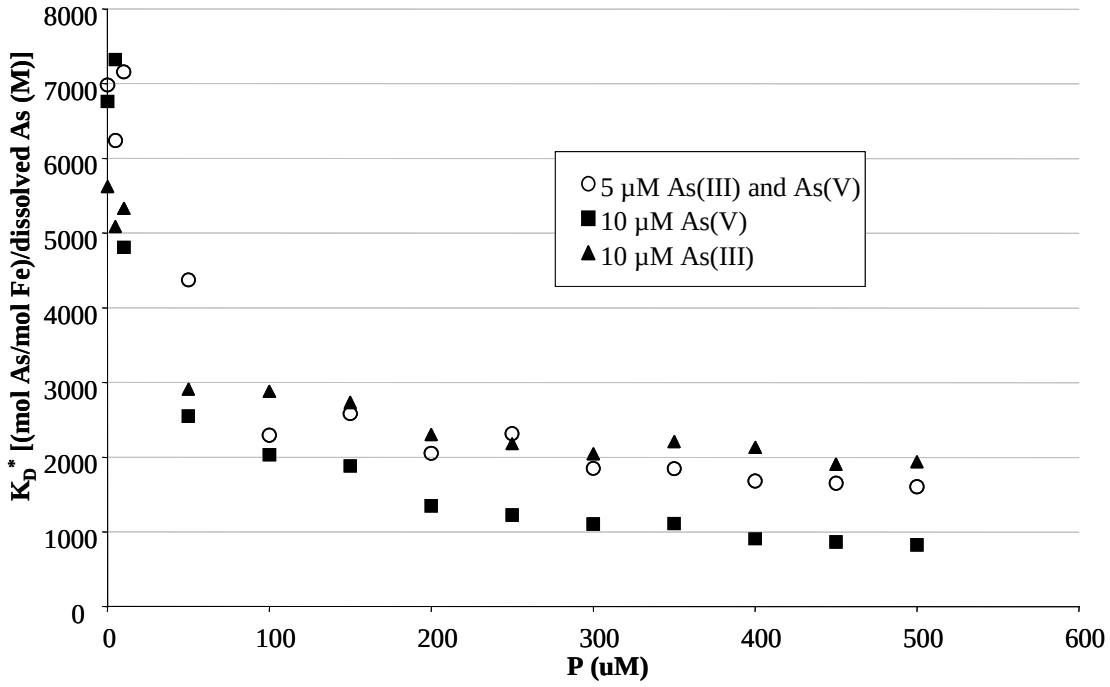



**Figure 4.18.** $K_D^*$ plot for the laboratory study of the competitive effects of phosphate on As adsorption (data presented in Chapter 3). In each case, the total As concentration was 10 µM.

## 4.6 Acknowledgement

This work was done in collaboration with Rob Root and Dr. Peggy O'Day. The As XANES edges on core sections and the quantification of As species on HFO-doped gels were performed by Rob Root. This work was supported by funding from NSF BES-0201888 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.