

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

Kate M. Campbell^{1,4,*}, Robert Root², Peggy A. O’Day², Janet G. Hering^{1,3}

¹Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA 90025, ² School of Natural Sciences, University of California, Merced, CA, 95344, ³(current address) Swiss Federal Institute of Aquatic Science & Technology (EAWAG), Dübendorf, Switzerland, ⁴(current address) U.S. Geological Survey, Menlo Park, CA 94025

Corresponding author: USGS, 345 Middlefield Rd, MS 465, Menlo Park, CA 93025, phone (650) 329-4604, e-mail: kcampbell@usgs.gov

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11 pages including 6 figures and 4 tables

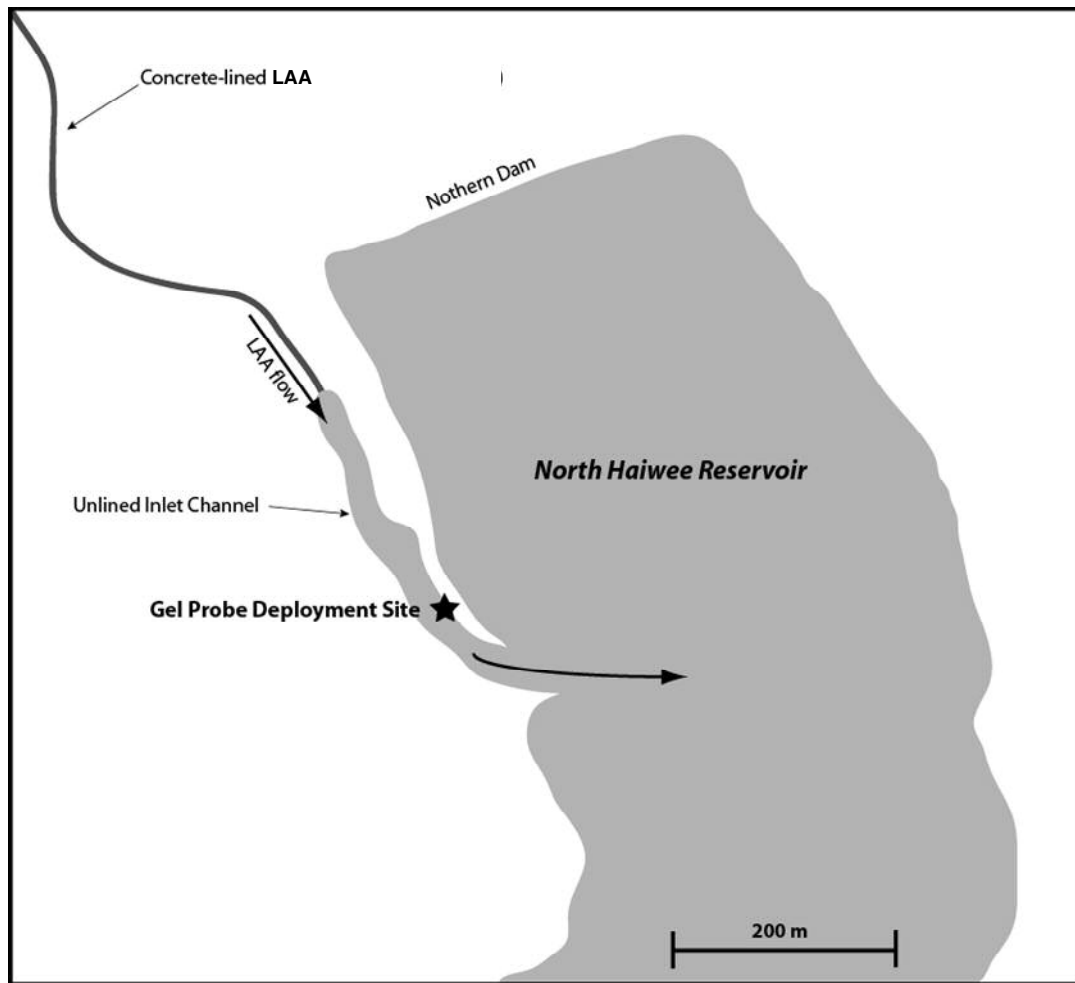


Figure S1. Map of North Haiwee Reservoir and the Los Angeles Aqueduct (LAA) inlet.

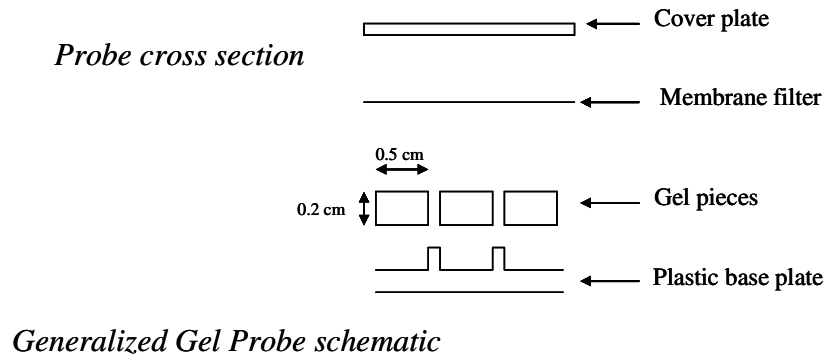


Figure S2-A. Double gel probe equilibrium sampler schematic with cross section.

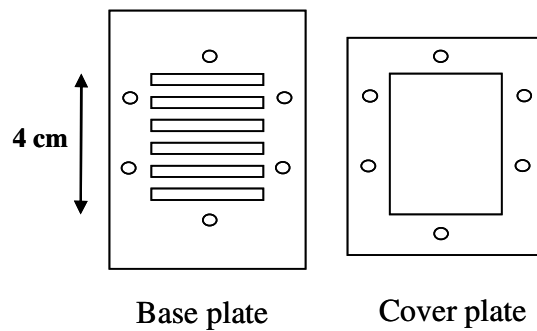


Figure S2-B. Mini-probe equilibrium sampler schematic for sediment microcosms.

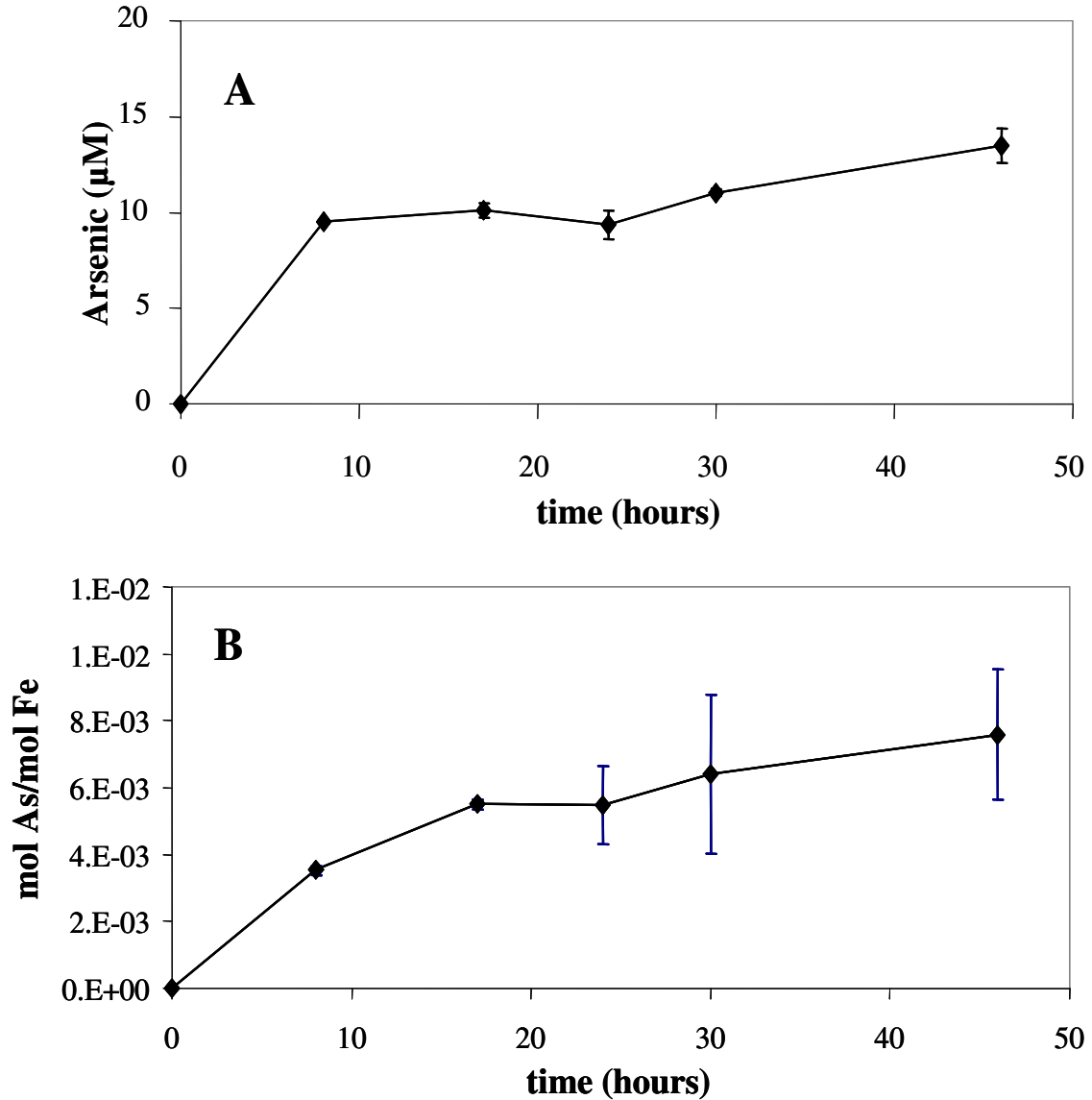


Figure S3. Arsenic in the porewaters (A) and adsorbed onto HFO-doped gels (B) in mini-probes equilibrated in Haiwee sediment microcosms. One probe was removed at each time point and the gels were immediately extracted from the probe and re-equilibrated in acid. The increase in As in the clear and HFO-doped gels at 48 h of equilibration was most likely due to slightly changing conditions in the sediment containers at longer times. The sediment collected for this experiment was a mixture of surficial and deeper sediment (<0.5 m), with potential for further Fe reduction and release of As from the sediment. The plateau of As in the clear gels at 8-24 h and HFO-doped gels at 18-24 h strongly supports the equilibration of gel probes with sediment porewaters, despite the ongoing reductive dissolution in the sediment.

Table S1. 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	0.4 \pm 0.1	0.4 \pm 0.1
3-6	0.7 \pm 0.1	1.0 \pm 0.1
6-9	0.7 \pm 0.1	1.0 \pm 0.2
9-12	1.7 \pm 0.1	1.4 \pm 0.3

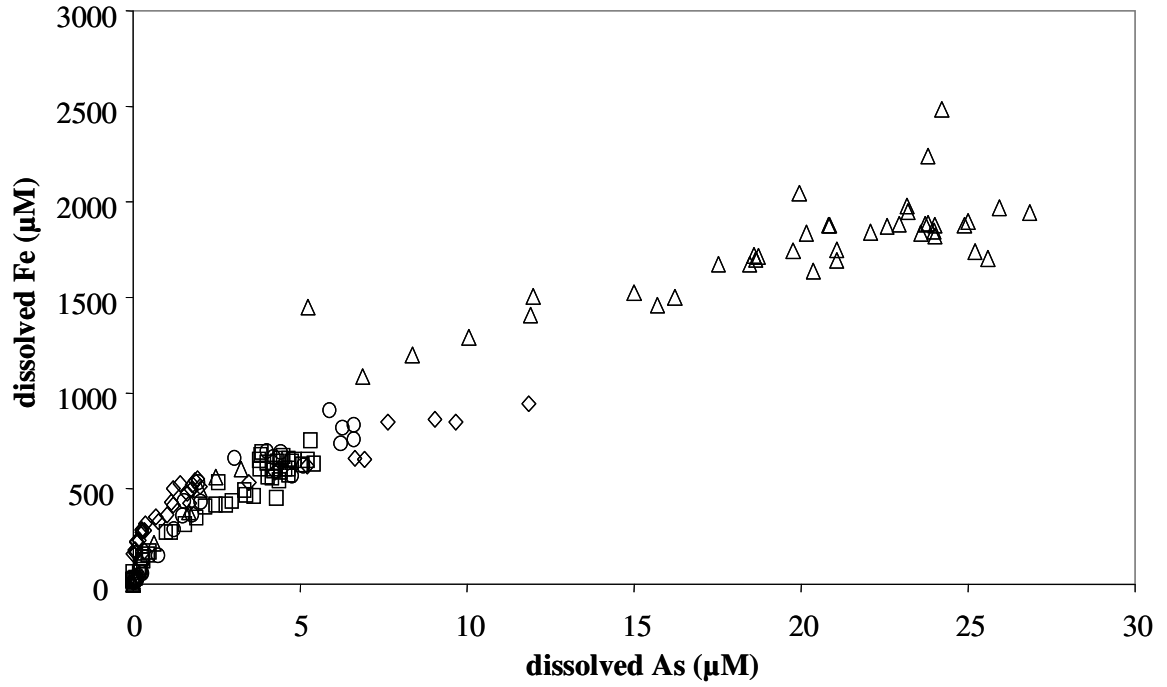


Figure S4. Correlation between Fe and As in porewaters from October 2004. Squares, triangles, diamonds, and circles represent data from different gel probes deployed at the same site.

Table S2. The relative amount of As(III) and As(V) adsorbed onto HFO-doped gels deployed in May 2006. Gels were frozen in the field and analyzed by XANES at SSRL. Reported are the XANES linear combination fits of the field samples to As(III) and As(V) spectra shown in Figure S5 and the corrected (As III:V) distribution. The corrected fit is based on the calibration of HFO-doped gel probes from Campbell et al. 2007 (1). The goodness of fit is reported as the estimated standard deviation (esd) and the 99% confidence limit (3x esd). Methods are described in Campbell et al. 2007 (1).

depth (cm)	XANES		Corrected		goodness of fit	
	As(III) %	As(V) %	As(III) %	As(V) %	esd %	3x esd %
26	89	11	91	9	0.6	1.8
29	90	9	92	8	0.5	1.5
32.5	88	10	90	10	0.6	1.8

Figure S5. XANES spectra and corrected fit proportions of arsenic species in field deployed HFO-gel probes and the spectra of the As(III) and As(V) on gel probes used in the fits in Table S2. XANES are background-subtracted and normalized to post-edge step height. The corrected fit distributions between As(III) and As(V) are based on the calibration from Campbell et al, 2007 (1).

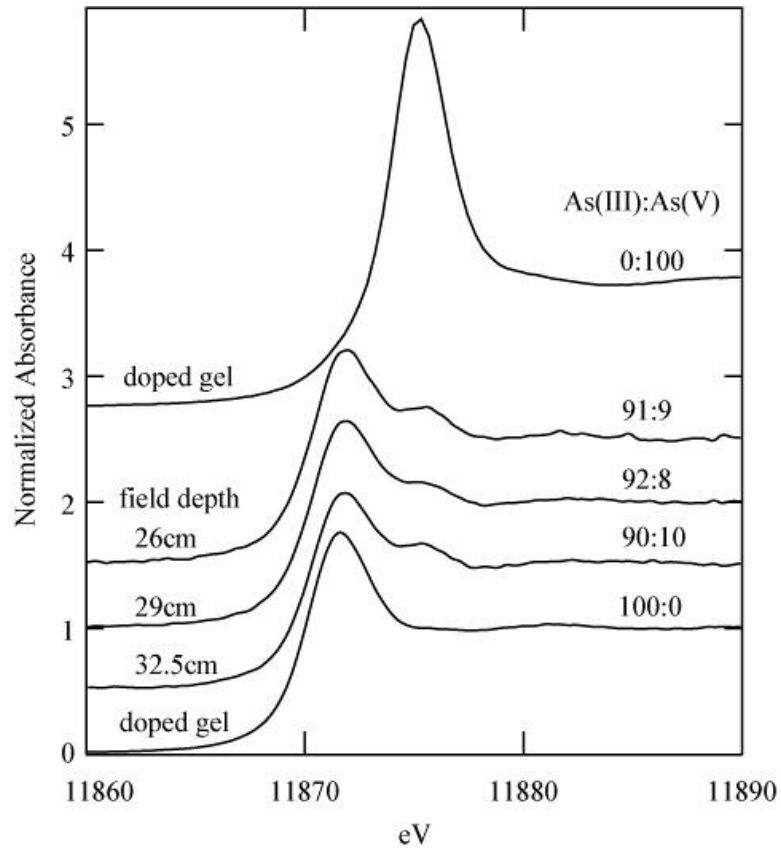


Table S3. XRF bulk composition of cores from August 2005. Analysis was performed on a composite sample, resulting in an average over the sediment column. The variation between duplicate cores was small (<0.4% for Fe and <7% for As).

	%		%	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	--		

Table S4. 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.

<i>Core 1</i>	<i>Total carbon</i>	<i>organic carbon</i>	
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
<i>Core 2</i>	<i>Total carbon</i>	<i>organic carbon</i>	
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

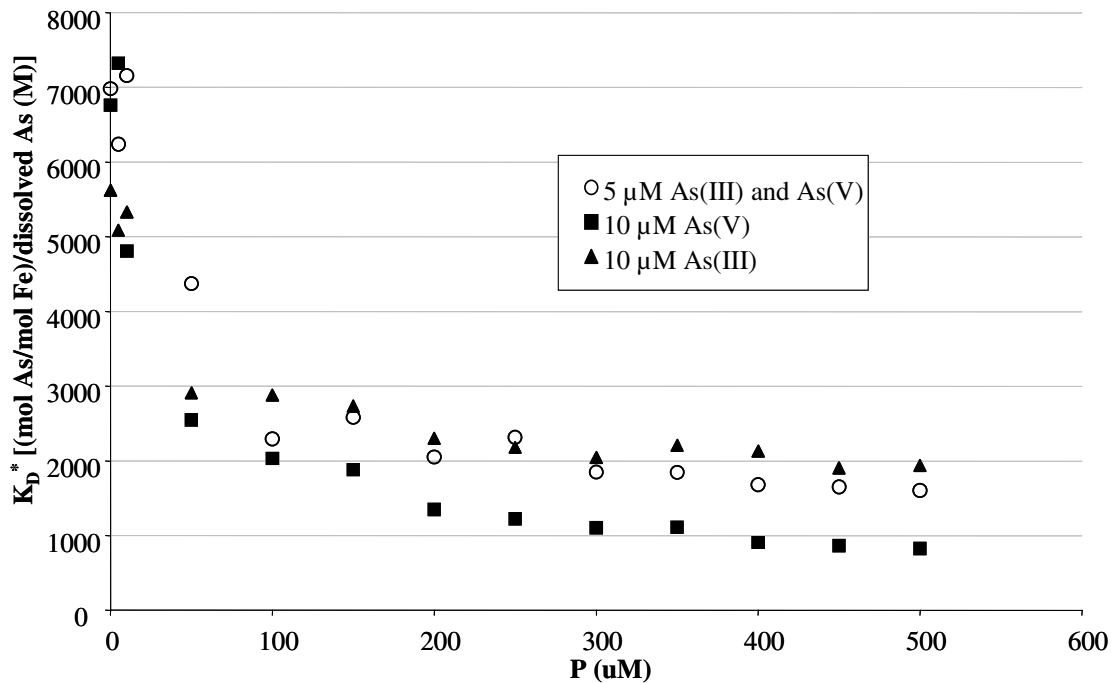


Figure S6. K_D^* plot for the laboratory study of the competitive effects of phosphate on As adsorption (data and experimental details presented in Part I (ref. (1))). In each case, the total As concentration was 10 μM .

REFERENCES

- (1) Campbell, K. M.; Root, R.; O'Day, P. A.; Hering, J. G. A Gel Probe Equilibrium Sampler for Measuring Arsenic Porewater Profiles and Sorption Gradients in Sediments: I. Laboratory Development. *Submitted to Environ. Sci. Technol.* **2007**.