Supporting Information

MANUSCRIPT TITLE: Field, Experimental, and Modeling Study of Arsenic Partitioning across a Redox Transition in a Bangladesh Aquifer

AUTHOR NAMES: Hun Bok Jung[1,#], Benjamin C. Bostick[2], and Yan Zheng[1,2]∗

AUTHOR ADDRESSES:

[1]School of Earth and Environmental Sciences, Queens College, and Graduate School and University Center of the City University of New York, Flushing, NY 11367 United States

[2]Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964 United States

#Present address for Hun Bok Jung: Pacific Northwest National Laboratory, Richland WA 99354, USA

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Sampling method for sediment core, porewater, groundwater and river water

Riverbank sediment and porewater samples for sorption and desorption experiments were collected in Jan. 2006 and Nov. 2007 at sandy beaches within ~30 m from the shore of the Meghna River in Gazaria, Bangladesh. Sediment core samples were obtained by a soil probe (AMS Inc., USA), consisting of a probe (1.9 cm diameter and 30.5 cm length), extension rods (60 cm each section), and a slide hammer. Before collecting a sediment core sample at any depth, a drill hole was deepened with a 5 cm diameter PVC pipe by the so-called "hand-flapper" method used by local driller (Horneman et al, 2004). Then the soil probe with liner connected to the extension rods was inserted in the PVC pipe and hammered into the sediment. After the probe was raised, the plastic liner was capped, and immediately placed into an N_2 flushed anaerobic glove box on site for sorption experiment. Other sediment samples were stored in a Mylar bag with oxygen absorbers (SorbentSystems) flushed with nitrogen and kept on ice. Sediment samples from RS19-4 were stored at 4 ^{o}C in double sealed Mylar bag flushed with N_2 until the desorption experiment 11 months later.

Three riverbank porewater samples from 1.5, 3.6 and 5.4 m depth at PZ10, corresponding to the same depth as the sediment core samples from RS39, were used in batch sorption experiment. The porewater samples were obtained using a stainless steel drive point piezometer system ("Retract-A-Tip", AMS Inc) (Charette and Allen 2005). Porewater samples were drawn to the surface through acid-cleansed nylon tubing using a peristaltic pump at a flow rate of 500 ml min^{-1}. After stabilization of the reading of the oxidation reduction potential (ORP), pH, dissolved oxygen, and temperature that were measured using a YSI 600XLM in a flow through cell (YSI Inc), samples filtered through

an inline 0.45 μm Pall AquaPrep 600 filter were collected into 250 mL serum bottles (Wheaton Science) and crimp sealed. Other aliquots of porewater samples were collected in acid-cleaned high-density polyethylene (HDPE) liquid scintillation vials (Wheaton Science) for chemical analysis. Arsenic speciation cartridge packed with 2.5 g of aluminosilicate adsorbent (Meng et al., 2001) was used to separate As(III) from As(V) in the field. Groundwater samples were collected from shallow tube wells in villages nearby the riverbank sampling sites after pumping continuously for 15-30 min until the temperature, conductivity, pH and ORP reading monitored by a HORIBA multiprobe (U22XD) had stabilized. Samples were not filtered but acidified to 1% HCl (Fisher Optima) for cation analysis, while not acidified for anion analysis. River water samples were collected in 20 mL scintillation vials on boat after filtration through a 0.45 μm membrane filter, and acidified to 1% HCl (Fisher Optima). Temperature, pH, conductivity, and ORP were measured using a HORIBA or YSI multiprobe.

Water Analysis

Concentrations of dissolved Fe, Mn, S, P, and As in filtered and acidified porewater and supernatant samples after sorption and desorption experiments were analyzed by high resolution inductively coupled plasma mass spectrometry (HR ICP-MS) on an Axiom (Thermo Elemental, Germany) (Cheng et al., 2004). For quality assurance, one or more laboratory control samples (LDEO) or NIST 1643E were included with each run, resulting in error within 5 to 10%. Anions (F, Cl, NO_3, PO_4, SO_4) in filtered but not acidified samples of supernatant of sediment slurry and porewater were measured by Ion Chromatography (Dionex DX500), following a standard EPA protocol. Immediately after

sampling, the concentrations of As(III) and Fe(II) in the supernatant were determined by differential pulse cathodic stripping voltammetry (DPCSV) on an Eco-Chemie μautolab with a Metrohm 663A stand, by Brinkmann Instrument (He et al., 2004) and ferrozine colorimetric method (Stookey, 1970) on a HACH DR2010 photospectrometer, respectively.

In desorption experiment (Table S7), dissolved Fe(II) concentration determined by ferrozine colorimetric method was higher than dissolved total Fe concentration determined by ICP-MS usually for samples with total Fe concentration between 0.1 to 0.2 mg/L. Although the colorimetric method used to determine Fe(II) can be as sensitive as 0.02 mg/L (Viollier et al., 2000), we could only quantify it at 0.1 mg/L or above due to sometimes high blank corrections. Hence for these samples with Fe(II) concentration at close to quantification limit, results are not very accurate. In both adsorption (Table S4) and desorption (Table S7) experiments, As(III) concentration was significantly higher than total As (> 10%) when As concentration is higher than ~3000 μg/L (2 of 22 samples in adsorption experiment and 3 of 20 samples in desorption experiment) because such high As concentration required dilution by a factor of more than 100 to lower the As concentration to below 50 μg/L, which is the optimum range of As concentration for DPCSV analysis, and consequently analytical errors appeared to take place during the dilution process. Additionally, high concentration of dissolved substances such as Fe and Mn or organic matter in supernatant could have affected the analytical accuracy of DPCSV measurement due to interference with As (III) (Gibbon-Walsh et al., 2011), affecting the calibration curve by standard addition.

Sediment Analysis

Sediment HCl-leachable Fe(II) and total Fe were analyzed in the field, and the concentrations of Fe, Mn, S, P, and As in the HCl leachate were also quantified. Within hours of sample collection, samples were leached with 10 mL of 1.2N HCl in 15 mL centrifuge tube (BD Falcon) at 80 ℃ for 1hr to liberate elements associated with amorphous and labile crystalline Fe oxyhydroxides phases (Horneman et al, 2004). Total Fe and Fe(II) in the leachates were determined by a colorimetric technique using ferrozine solution in the field (Stookey, 1970; Horneman et al., 2004). The sediment HCl leachates were also analyzed by HR ICP-MS for Fe, Mn, S, P, and As. To evaluate sorbed sediment As, 1M sodium phosphate (NaH_2PO_4) solution with 0.1M L-ascorbic acid was adjusted to pH 5 using NaOH pellets and purged with nitrogen. The solution was then added to serum bottles containing sediment, again crimp sealed with rubber stopper and aluminum cap under pure N_2 condition. Samples were shaken for 36 hours and then filtered through a 0.2 μm membrane syringe filter (Jung and Zheng, 2006). Concentrations of As(III) in the phosphate extract were determined by DPCSV in the field. Total As concentrations in phosphate extracts were determined by HR ICP-MS in the laboratory. All solid phase concentrations were reported on dry weight basis after the correction of average moisture content of about 10% measured on these samples.

X-ray Absorption Spectroscopy

Samples were prepared by mounting a small quantity of the solids on Whatman filter paper, saturating the paste with a small quantity of glycerol to prevent oxidation prior to and during measurement, and then sealing the filtrate in Teflon sample holders with

Kapton® film. All samples were prepared in the glove box then transferred in anaerobic containers with gasket seals to a lab freezer until analysis.

At the Stanford Synchrotron Radiation Laboratory, samples were analyzed on either beamline 10-2 or 11-2 using an unfocused beam and a Si(200) crystal monochromator. Data were collected in fluorescence mode using either a 13-element (beamline 2-3) or 30 element (beamline 11-2) Ge detector. EXAFS spectra were collected from -235 to 875 eV about the Fe K edge (defined as 7112.0 eV for the maximum in the first derivative spectrum of an iron metal foil). XANES spectra were collected from -235 to 425 eV about the As K edge (defined as 11874.0 eV for a calcium arsenate standard).

Linear combination fitting were done with SIXPack software (Webb, 2005). Final fitting of As spectra used three spectra: arsenate and arsenite adsorbed on ferrihydrite as As(V) and As(III) standards (50 mg kg^{-1} total As), and orpiment (As$_2$S$_3$) as a model arsenic(III) sulfide. Linear combination fitting of Fe K-edge EXAFS spectra used k^3-weighted chi functions. For Fe EXAFS analysis, k^3-weighted EXAFS spectra of sediments were compared to a spectral library of commonly encountered reference compounds to identify the major iron minerals present in the sample suite. The fraction concentration of each Fe phase was then determined by linear combination fitting of Fe spectra with the spectra of their mineral components. Final fits included hematite (Fe$_2$O$_3$), ferrihydrite (Fe(OH)$_3$), crystalline goethite (α-FeOOH), siderite (FeCO$_3$), mackinawite (nominally FeS), and biotite (KFe$_3$(Si$_3$Al)O$_{10}$(OH)$_2$, representative of Fe(II) silicates) as spectral components. Because of similar XANES and EXAFS spectra, siderite standard represents a variety of Fe(II) phases such as Fe(II) phosphate, sulfate, carbonate, and

some oxides that include a wide variety of oxygen-bound Fe(II) that is in tetrahedral coordination.

The goethite chosen as a reference spectrum is crystalline and has XAS spectra easily distinguished from ferrihydrite. Other reference spectra were also considered (including magnetite (Fe_3O_4), pyrite (FeS_2), lepidocrosite (γ-FeOOH), green rust, and hornblende), and chlorite (representative of model Fe(III) silicates) but were not included because they were consistently negligible in fits or were not easily differentiated from other model phases. Errors calculated using SixPack include error from fitting, from reference spectrum quality and orthogonality (how unique they are from each other). In each case, calculated errors were <7% for all minerals except ferrihydrite, in part because of the spectral similarity between goethite and ferrihydrite. These errors are in line with those typical of linear combination fitting in other studies (~7%) based on fitting statistics and fits of known mixtures of As and Fe minerals (O'Day et al., 2004).

Fe EXAFS vs. Chemical Extraction

The sum of Fe(III) oxyhydroxides (e.g. ferrihydrite, goethite, and hematite) percentage determined by XAS, excluding a sample with HCl leachable Fe(III)/Fe of 0.74 and Fe(III) concentration of 7715 mg kg^{-1} shows a good correlation with HCl leachable Fe(III) concentration (R2=0.63; n=8) or Fe(III)/Fe ratio (R2=0.78; n=8) (Fig. S3), suggesting that HCl leachable Fe(III) concentration or Fe(III)/Fe ratio reflects the relative abundance of Fe(III) oxyhydroxides, and that the fraction of oxides determined by XAS is a reasonable representation of what is found in the sediments.

Sediment Arsenic Speciation

Anaerobic P-extraction of As enriched sediment (>~50 mg kg-1; n=3) found that As(III) is dominant in RS19 (7 m from shore) with 71% and 90% As(III), but As(V) is dominant in RS21 (14 m from shore) with 89% As(V) (Fig. 1). XANES spectra also reveal that both arsenite and arsenate are present in variable proportions (43±20% As(III) and 56±20% As(V); n=9) usually with higher proportion as As(III) when the samples are collected from deeper depths (Fig. S2, Table S6). Sulfide phases are insignificant in all samples (1±2%, n=9) (Table S6). Solid phase speciation indicates that there is higher proportion of As(V), either in total or extracted fractions, in sediments than in porewaters. This may reflect the preferential adsorption of As(V) from solution or preferential reduction to mobilize sorbed As(V) (essentially a difference in the effective K_d), or the oxidation and retention of adsorbed As(III).

In sorption experiment, the higher P-extractable As(III) than P-extractable total As (Table S2) is most likely attributed to change of As concentration during sample storage. P-extractable As(III) was determined by DPCSV in the field immediately after extraction, while P-extractable total As was analyzed by ICP-MS a few weeks later. Higher As(III) than total As in P-extraction may be attributed to precipitation of Fe-As-Phosphate in P-extraction samples that are not-acidified during sample storage.

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Table S1. Summary of the average chemical composition of groundwater, riverbank porewater, and river water collected during Jan. 2006 and Nov. 2007.

Sample type	Sampling Date	Number of sample	Depth m	EC mS/cm	DO mg/L	pH	Na	K	Ca	Mg	Si	HCO$_3$	SO$_4$ (mg/L)	Cl	NO$_3$	NO$_2$	Fe	Mn	S	As	P (µg/L)
Well grondwater	Jan 2006	11	14~21				8.4	3.4	71.2	10.5	20.3						8.75	1.53	0.61	238	1875
	Nov 2007	11	15~23	0.569	0.05	6.87	14.2	3.1	98.2	20.2	18.6	269.2	0.9	58.4	0.00	0.13	9.77	1.79	1.67	385	1258
Riverbank porewater	Jan 2006	1	0~2				3.9	1.4	15.8	4.7	10.2						1.02	0.34	4.93	1	15
		5	2~5				3.9	2.1	107.1	16.3	24.4						5.46	3.54	0.89	99	420
		5	5~7				4.4	1.9	80.1	12.5	23.8						1.72	2.84	0.29	90	436
		8	0~2	0.228	0.29	6.19	4.4	1.5	17.2	6.8	8.9	49.0	12.4	8.9	0.00	0.28	0.13	0.58	5.89	1	25
	Nov 2007	18	2~5	0.482	0.12	6.55	4.1	1.9	60.0	15.3	22.7	194.6	2.6	4.5	0.00	0.09	11.57	3.84	1.26	118	760
		6	5~6	0.401	0.19	6.56	3.6	1.2	39.3	11.7	21.2	129.7	1.9	3.3	0.00	0.28	1.14	1.52	0.90	28	211
River water	Jan 2006	3		0.011	8.74	6.28	3.2	0.8	11.1	2.3	5.4						0.04	0.07	1.48	2	9
	Nov 2007	6		0.062	5.51	6.96	1.9	0.5	3.5	0.9	3.9	8.8	2.3	1.2	1.08	0.07	0.18	0.01	0.93	2	6

Table S2. Characteristics of sediment and Langmuir isotherms from sorption experiment spiked with As(III) and As(V); Sand fraction is on average 94% for RS39; Porewater samples from PZ10 (23° 35.0' N, 90° 35.2' E) were used for the batch sorption experiment with sediment samples from RS39; PZ10 was collected simultaneously at the same depth as RS39 sediment core, both of which are in 1 m distance from each other along the shore.

Sample	Depth		Characteristics of sediment					Langmuir sorption model							
								As(III) spiking experiment				As(V) spiking experiment			
ID	m	Color	1.2N HCl leach FeIII/Fe	1.2N HCl leach Fe	1.2N HCl leach As	1M P-ext As	1M P-ext As(III)	K_{La}	Kd	Sorption capacity	R^2	K_{La}	Kd	Sorption capacity	R^2
				mg/kg	mg/kg	mg/kg	mg/kg	L/kg	L/kg	mg/kg		L/kg	L/kg	mg/kg	
RS39-1	1.5	Brown	0.58	4585	0.55	-	-	670900	7.9	12.5	0.99	311111	6.9	22.9	1.00
RS39-4	3.6	Grey	0.38	3093	0.45	0.92	1.10	322738	1.2	3.8	0.98	189250	1.7	9.4	0.96
RS39-6	5.4	Grey	0.37	3305	0.71	1.05	1.51	377070	1.2	3.4	0.98	201205	1.3	6.8	1.00

Table S3. The chemical composition of porewater samples from PZ10 (23° 35.0' N, 90° 35.2' E), located 1 m away from sediment core RS39. Porewater from PZ10 and sediment core RS39 collected simultaneously at the same depth were used for As(III) and As(V) batch sorption experiment.

Piezometer	Sample ID	Depth	Temp	EC	DO	pH	Na	K	Ca	Mg	Si	HCO_3	SO_4	Cl	Br	F	Sr	NO_3	NO_2	Fe	Mn	S	As	P
		m	°C	mS/cm	mg/L										mg/L									µg/L
PZ10	GBPW-44	1.5	29.3	0.220	0.30	5.97	4.3	1.3	11.5	3.7	9.4	-	20.99	11.24	0.00	0.14	0.08	< 0.1	0.44	0.55	0.41	6.61	1	28
	GBPW-45	3.6	29.0	0.872	0.20	6.15	3.4	2.1	64.0	18.8	24.3	-	2.10	3.86	0.15	0.19	0.42	< 0.1	0.45	2.52	3.02	0.88	28	292
	GBPW-46	5.4	28.1	0.524	0.20	6.52	2.4	1.2	38.8	11.9	24.7	-	3.77	5.66	0.00	0.15	0.22	< 0.1	0.45	1.16	1.37	1.35	58	554

Table S4. Batch equilibrium of As sorption to suboxic (RS39-1) and anoxic (RS39-4 and 39-6) sediments from Meghna Riverbank spiked with As(III) and As(V).

Sample ID	As(III) spiking experiment				As(V) spiking experiment			
	Added As	As in solution	As(III) in solution	Sorbed As	Added As	As in solution	As(III) in solution	Sorbed As
	µg/L			mg/kg	µg/L			mg/kg
RS39-1	0	23	25	0	0	23	25	0
	850	201	189	1273	960	209	175	1400
	1275	258	215	1828	1920	436	339	2691
	1700	356	272	2411	3840	953	890	5480
	3400	909	930	4396	7680	2251	2463	9102
	5100	1588	1328	5892				
	6800	2398	2785	7917				
RS39-4	0	63	57	0	0	63	57	0
	723	531	431	489	960	547	376	890
	1084	771	678	668	1920	1114	1058	1568
	1445	961	869	959	3840	2364	1673	2604
	2168	1421	1232	1246	7680	4855	5135	5708
	2890	2016	2019	1557				
	4335	3276	3105	1742				
	5780	4706	4596	1961				
RS39-6	0	102	86	0	0	102	86	0
	723	780	656	80	960	706	521	848
	1084	791	717	717	1920	1389		1508
	1445	982	914	889	3840	2897		2489
	2890	2320	2339	1430	7680	4872	5023	6735
	4335	3354	3350	1786				
	5780	4696	5437	2371				

Table S5. Equilibrium constants (log K) from MINTEQA2 version 4.0 database for surface complexation modeling of As, P, and carbonate with hydrous ferric oxides (HFO). Log K is same for both weak and strong sites. Surface complexation of Si is not considered because Log K value is not available in MINTEQA2 database.

Surface complexation reactions	Log K
$Hfo\_OH + H^+ = Hfo\_OH_2^+$	7.29
$Hfo\_OH = Hfo\_O- + H^+$	-8.93
$Hfo\_OH + H_3AsO_3 = Hfo\_H_2AsO_3 + H2O$	5.41
$Hfo\_OH + H_3AsO_4 = Hfo\_H_2AsO_4 + H2O$	8.61
$Hfo\_OH + H_3AsO_4 = Hfo\_HAsO_4^- + H2O + H^+$	2.81
$Hfo\_OH + H_3AsO_4 = Hfo\_OHAsO_4^{3-} + 3H^+$	-10.12
$Hfo\_OH + PO_4^{3-} + 3H^+ = Hfo\_H_2PO_4 + H_2O$	31.29
$Hfo\_OH + PO_4^{3-} + 2H^+ = Hfo\_HPO_4^- + H_2O$	25.39
$Hfo\_OH + PO_4^{3-} + H^+ = Hfo\_PO_4^- + H_2O$	17.72
$Hfo\_OH + CO_3^{2-} + H^+ = Hfo\_CO_3^- + H_2O$	12.56
$Hfo\_OH + CO_3^{2-} + 2H^+ = Hfo\_HCO_3^- + H_2O$	20.62

Table S6. Sediment As concentration (mg/kg) and speciation for RS19, 20, and 21 cores determined by 1M P-extraction and XAS; Different aliquots of the same sample were used for P-extraction and XAS.

Sample No	Latitude	Longitude	Depth m	As speciation					
				P-extraction			XAS		
				As(III)	Total As	As(III) %	As(III)	As(V)	As_2S_3
RS19-1	23º 35.011'	90º 35.149'	0.3	202	284	71	34±1%	66±1%	0±1%
RS19-3			0.9	< 1	1		36±1%	64±0%	0±1%
RS19-4			1.8	556	619	90	73±1%	27±0%	0±1%
RS19-5			4.6	3	7	52			
RS20-1	23º 35.006'	90º 35.160'	0.3	< 1	< 1		32±2%	63±1%	5±2%
RS20-4			1.8	< 1	< 1		57±1%	43±0%	0±1%
RS20-7			6.1	1	1	100	31±1%	69±1%	0±1%
RS21-1	23º 35.008'	90º 35.125'	0.3	< 1	< 1		46±1%	54±1%	0±1%
RS21-4			1.4	5	46	11	9±1%	91±1%	0±1%
RS21-7			6.7	< 1	< 1		68±1%	32±0%	0±1%

Table S7. Desorption experimental results; Homogenized composite sediment from 1.5 m to 1.8 m depth in RS19-4 was used for desorption experiment. Type I: nanopure water + kanamycin (50 mg/L), Type II: artificial groundwater + kanamycin (50 mg/L), Type III: artificial groundwater, Type IV: artificial groundwater + lactate (1 mM). Initial composition of artificial groundwater and nanopure water is shown, while initial concentrations of P and S in nanopure water are displayed in parenthesis.

Incubaton Type	Day	Supernatant (µg/L)							1.2N HCl leaching (mg/kg)							1M P extraction (mg/kg)	
		P	S	Mn	Fe	Fe(II)	As	As(III)	P	S	Mn	Fe	Fe(II)	As	As(III)	As	As(III)
Initial Conc.	0	620 (< 10)	4992 (< 100)	< 1	< 10	-	< 1	-	425	6	129	6933	3433	86	42	91	57
Type I	2	53	4540	41	1237	1202	674	571	417	2.0	107	5710	2453	71	35	88	42
	5	64	5035	42	667	703	677	152	422	1.9	117	6435	3020	69	37	81	36
	10	136	5263	62	1477	1369	677	21	412	0.5	105	5795	2622	68	33	88	20
	17	55	4839	49	729	1236	650	11	366	0.4	102	5550	2524	66	25	78	20
	30	49	5431	63	485	470	511	3	393	0.0	101	5221	2532	69	21	81	15
Type II	2	354	60117	466	< 10	<100	565	278	417	38	107	5774	2711	67	28	88	45
	5	224	51941	466	36	<100	501	23	406	31	113	6329	2926	72	35	73	37
	10	300	50466	438	1859	1569	516	23	368	43	106	5832	2933	71	29	83	27
	17	181	65873	323	120	236	468	19	417	29	107	5694	2598	68	32	89	31
	30	174	51998	246	111	137	482	<1	407	32	103	5364	2562	71	38	80	32
Type III	2	261	53663	489	18	<100	551	358	357	40	112	6183	3065	70	32	87	45
	5	222	49255	460	187	336	487	101	421	35	114	6242	2812	73	30	82	38
	10	294	53220	471	1368	1102	443	43	357	36	111	6197	3182	59	40	77	34
	17	173	50303	362	231	270	402	14	354	36	103	5533	2597	68	23	88	36
	30	122	46734	305	103	236	378	<1	403	37	103	5257	2640	71	21	79	22
Type IV	2	345	54483	484	< 10	<100	624	406	386	28	108	5757	2652	68	40	85	52
	5	187	49946	707	482	370	630	359	407	37	113	6373	3210	73	50	76	34
	10	533	48769	1470	2957	2568	3108	3609	370	33	116	6108	2879	73	28	82	28
	17	387	45836	1604	2818	3001	7498	11377	413	26	102	5998	3210	36	36	48	55
	30	708	43470	1904	7671	8629	12081	18681	408	24	99	5572	3122	23	28	36	44

*For potential causes for higher Fe(II) and As(III) than total Fe and As, see "Water Analysis" section.
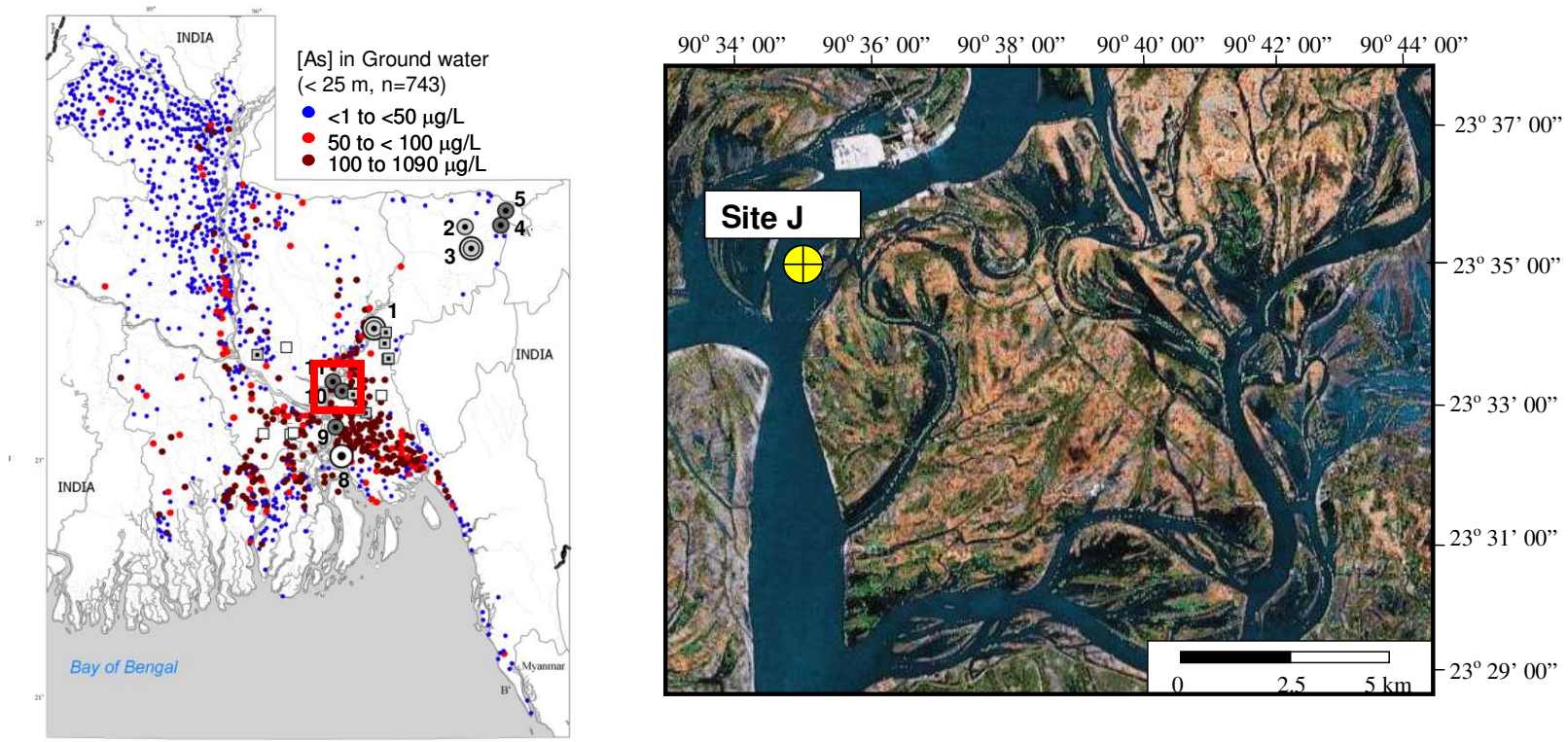
Fig. S1. Left: Map showing sediment and porewater sampling locations (red square) along Meghna Riverbank in Gazaria, Bangladesh, adopted from Datta et al (2009). Right: Sediment core RS19, 20, 21, and 34 were collected from Site J in Jan. 2006, while porewater profiles were collected from Site J in Nov. 2007.
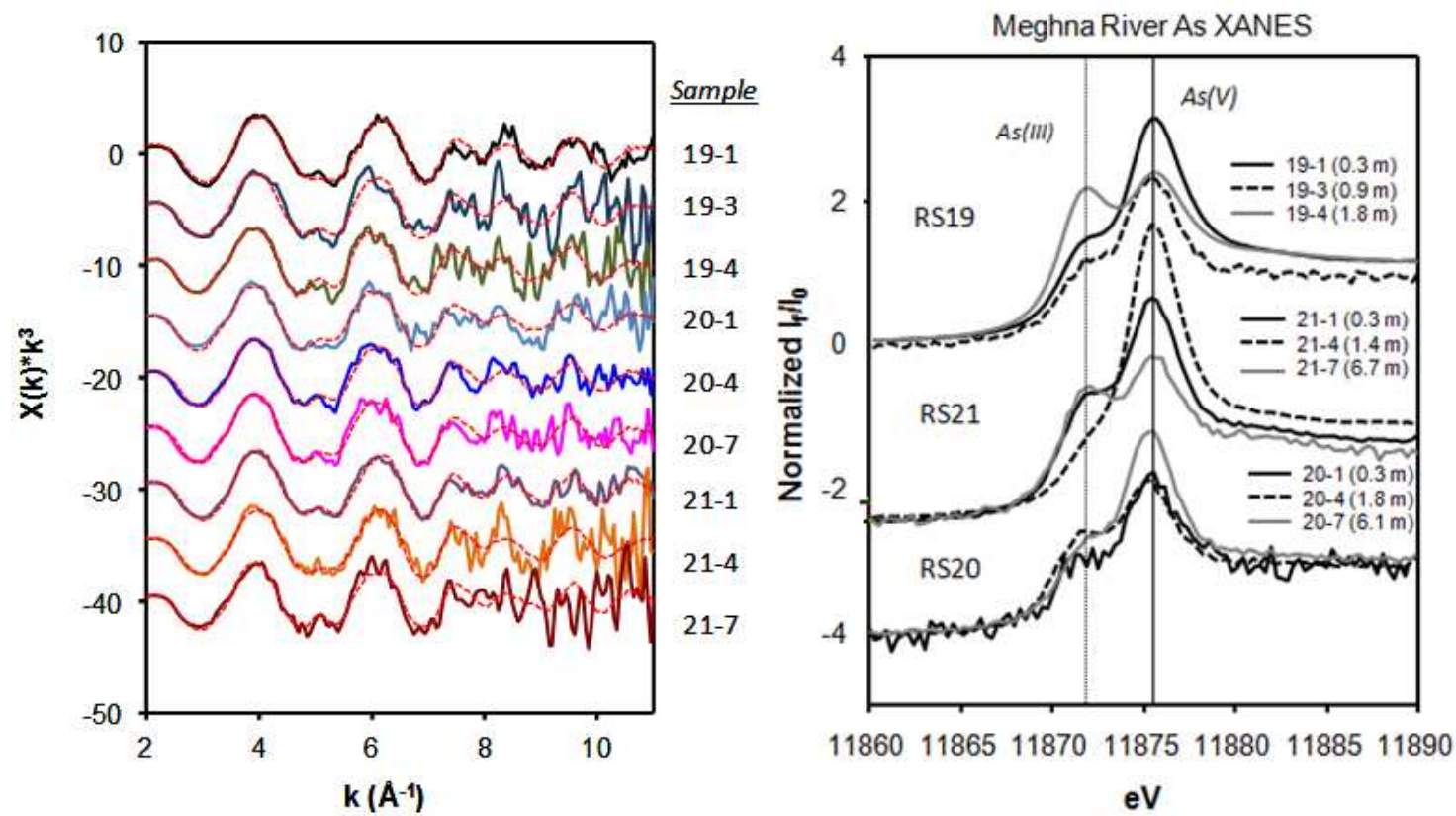
Fig. S2. Fe EXAFS (Left) and As XANES (Right) spectra for RS19, 20, and 21 sediment cores from Site J, collected in Jan. 2006.
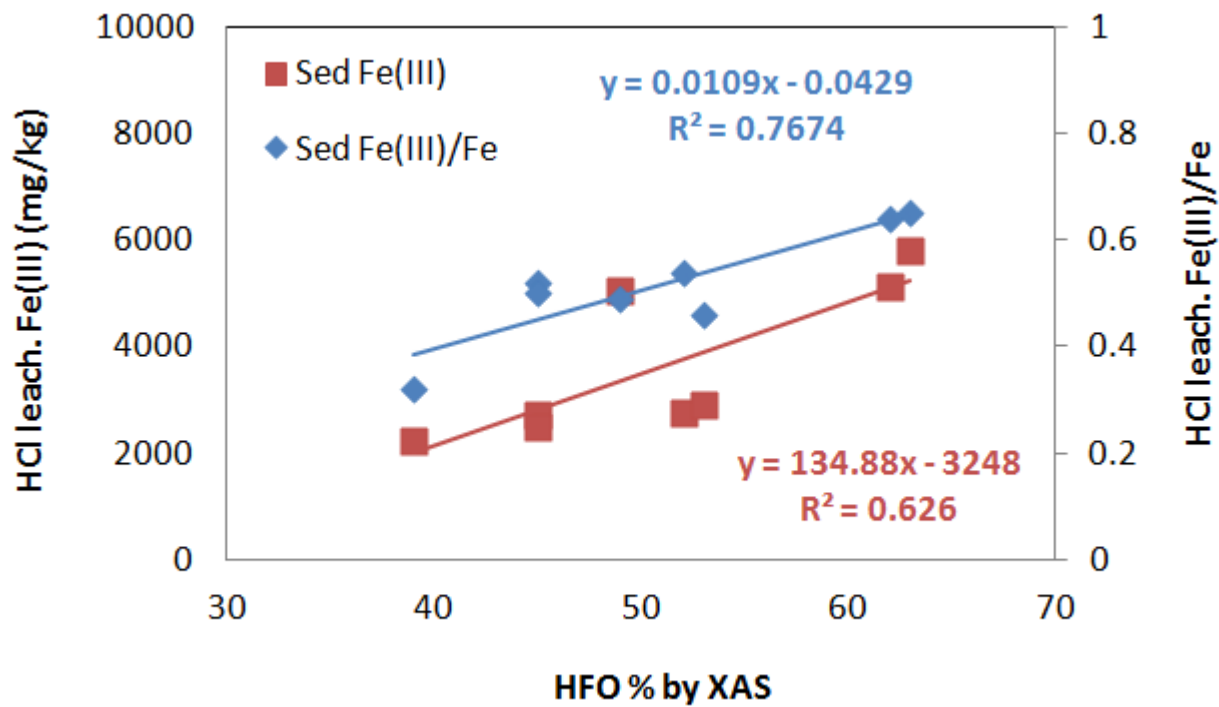
Fig. S3. Correlation between the percentage of hydrous ferric oxide (HFO) including ferrihydrite, goethite, and hematite determined by XAS and HCl leachable Fe(III) (red boxes) or Fe(III)/Fe ratio (blue diamonds).
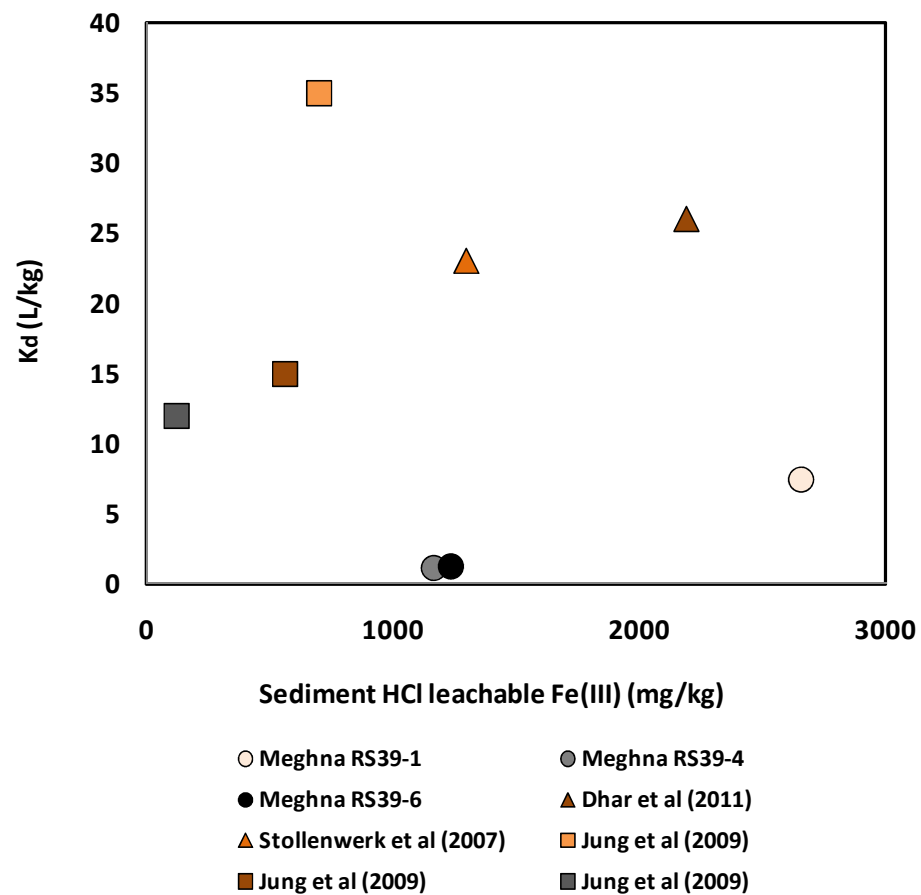
Fig. S4. HCl leachable Fe(III) concentration vs. partitioning coefficient (Kd) for As(III); HCl leachable Fe(III) concentration was determined by hot 1.2 N HCl extraction for 1 hr, except for Stollenwerk et al (2007) that used cold 0.5 N HCl extraction for 24 hrs.