Supporting information (SI)

Arsenic dynamics in mangrove sediments: the Sundarbans, Bangladesh-Part 1

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Contents

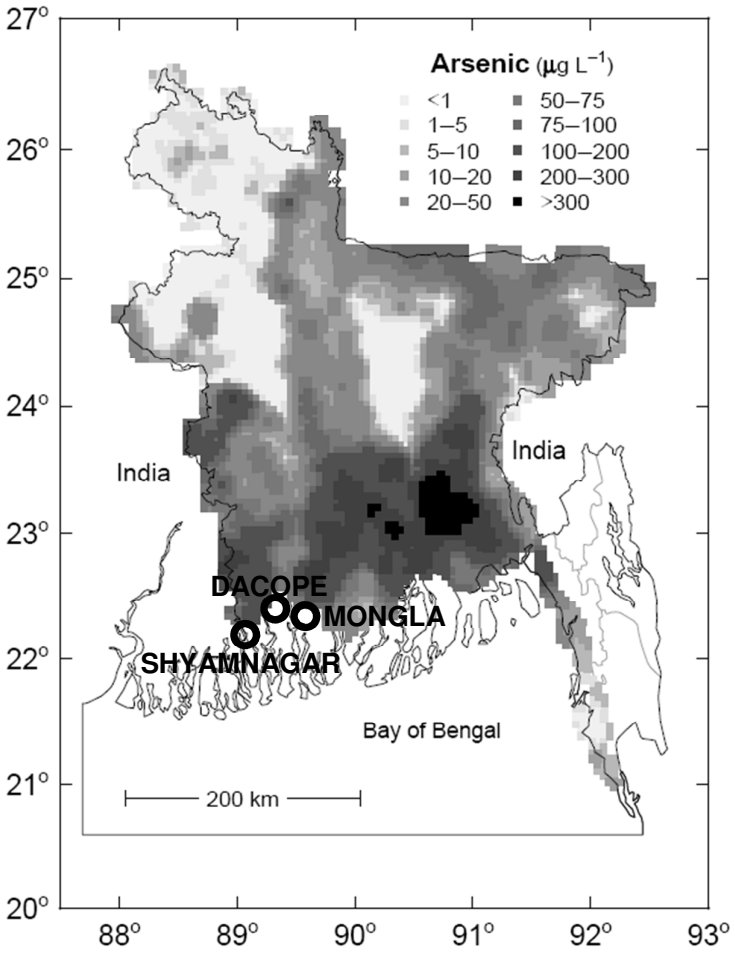


Figure SI 1. Core sampling locations in the Sundarbans overlain with the DPHE-BGS-DFID groundwater As map of Bangladesh (1).

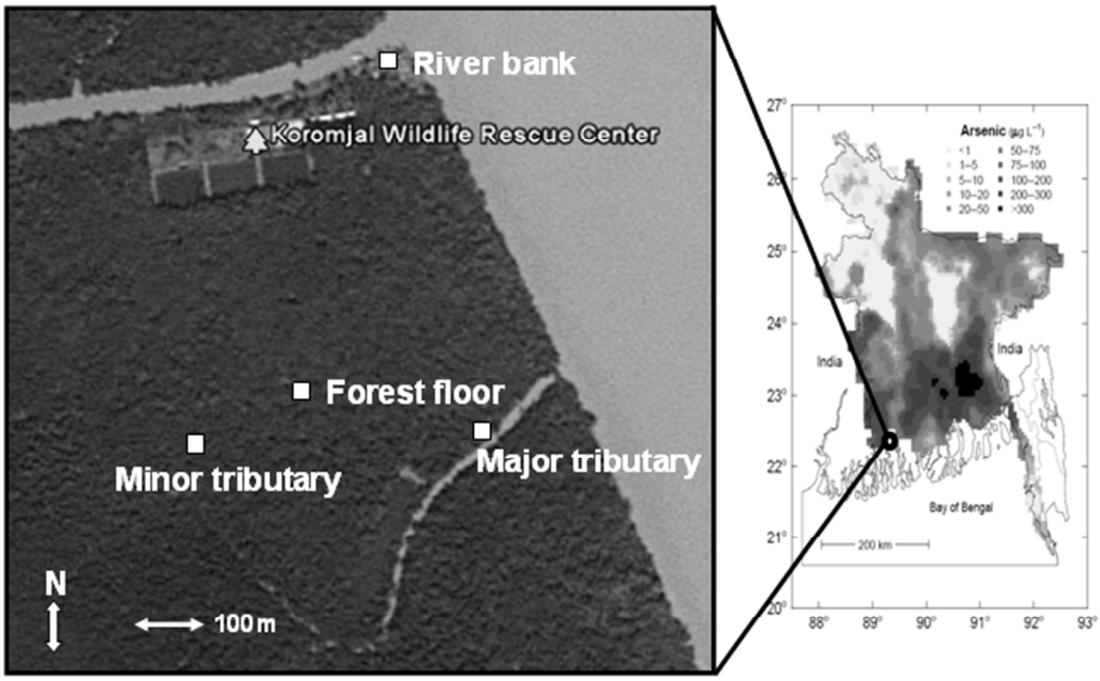


Figure SI 2. Sampling sites at Koromjal are denoted by squares. Koromjal, the Sundarbans is further pointed on the groundwater As map of Bangladesh published by the DPHE-BGS-DFID (1). Unshaded Sundarbans and some hilly districts of Bangladesh indicate unavailability of data.

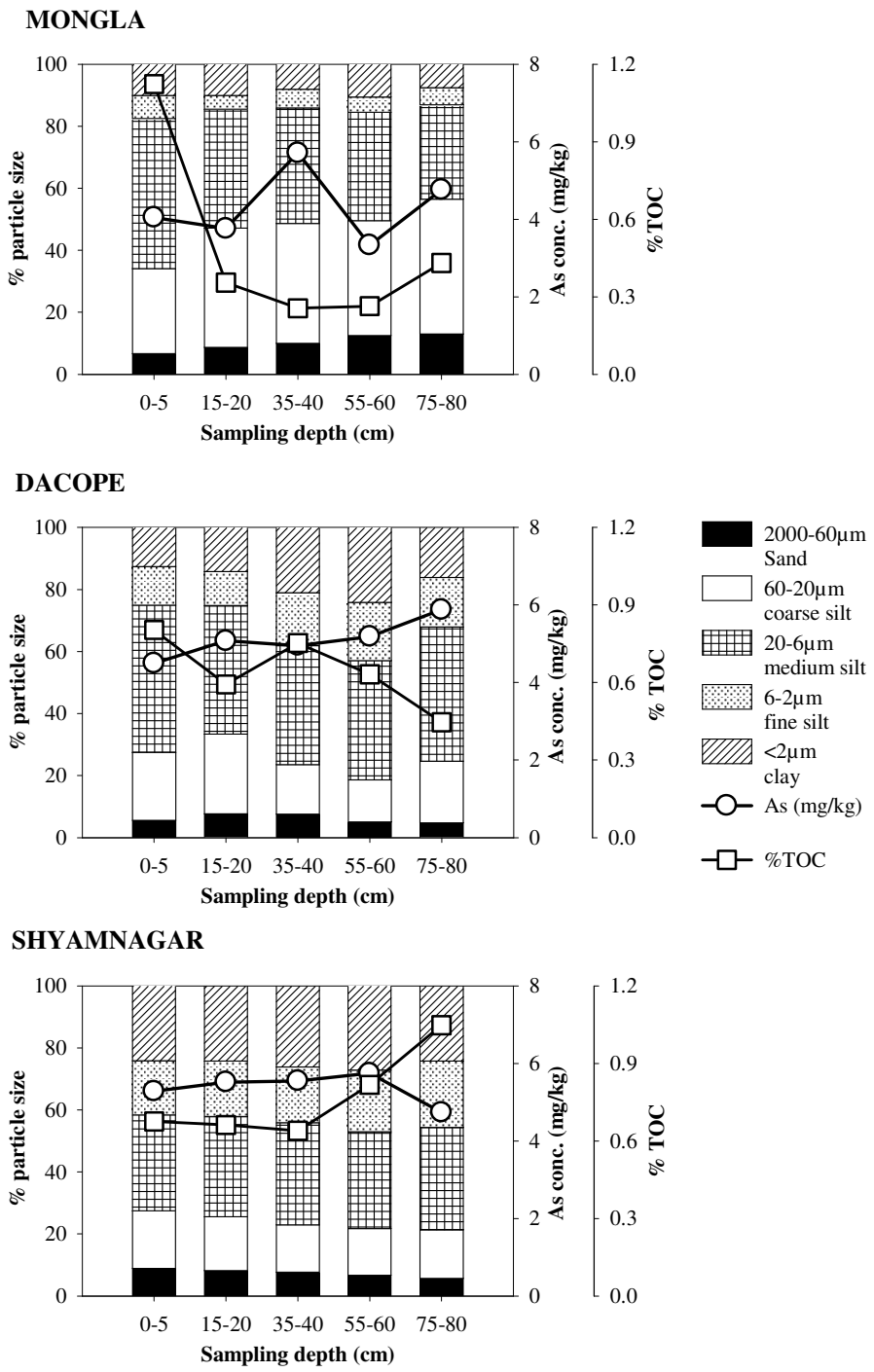


Figure SI 3. Particle size analysis of Mongla, Dacope and Shyamnagar core sediments plotted as stacked bars, overlain with total As and TOC concentration for each sediment core slice.

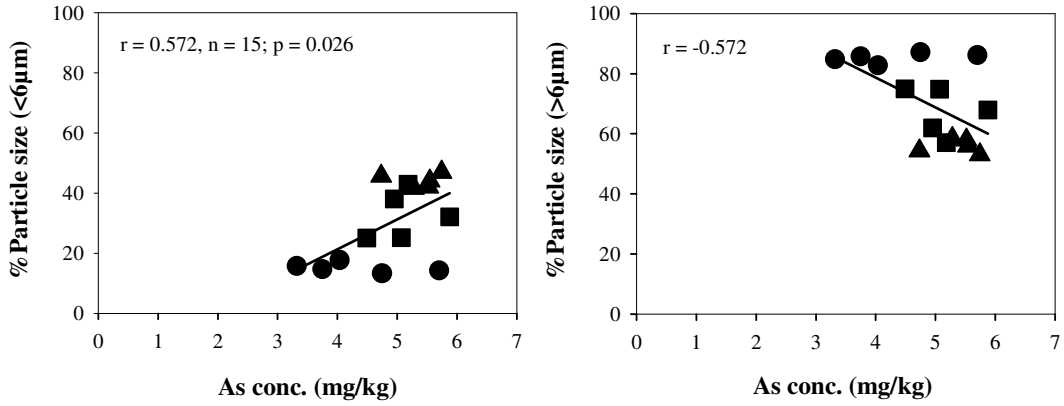


Figure SI 4. Regression plots showing relation between particle size and total As. Closed circle, square and triangle represent Mongla, Dacope and Shyamnagar sediments respectively.

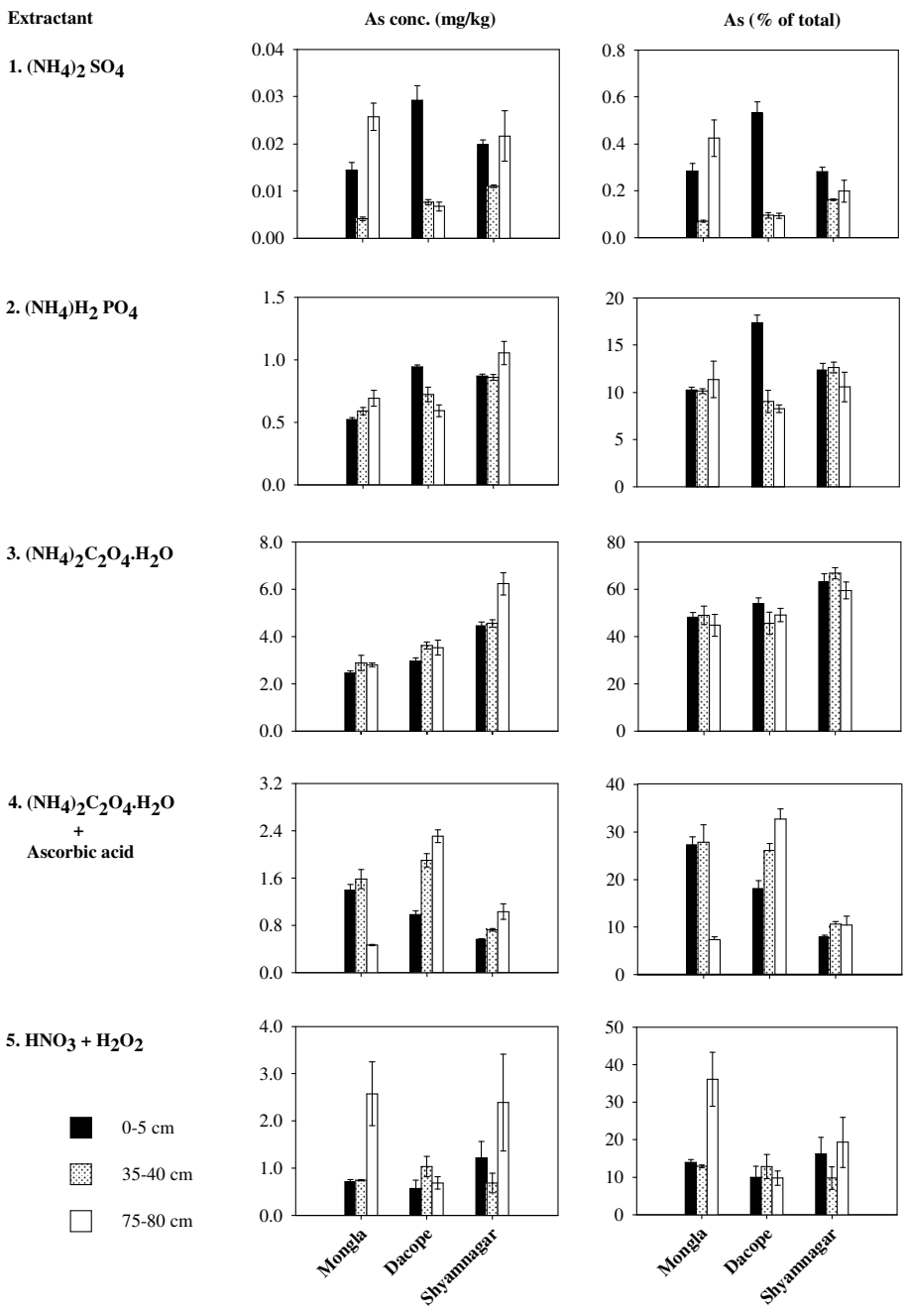


Figure SI 5. Sequentially extracted different fractions of As in Mongla, Dacope and Shyamnagar sediments with their percentage of total As. Data are mean values and ± SE (n = 6).

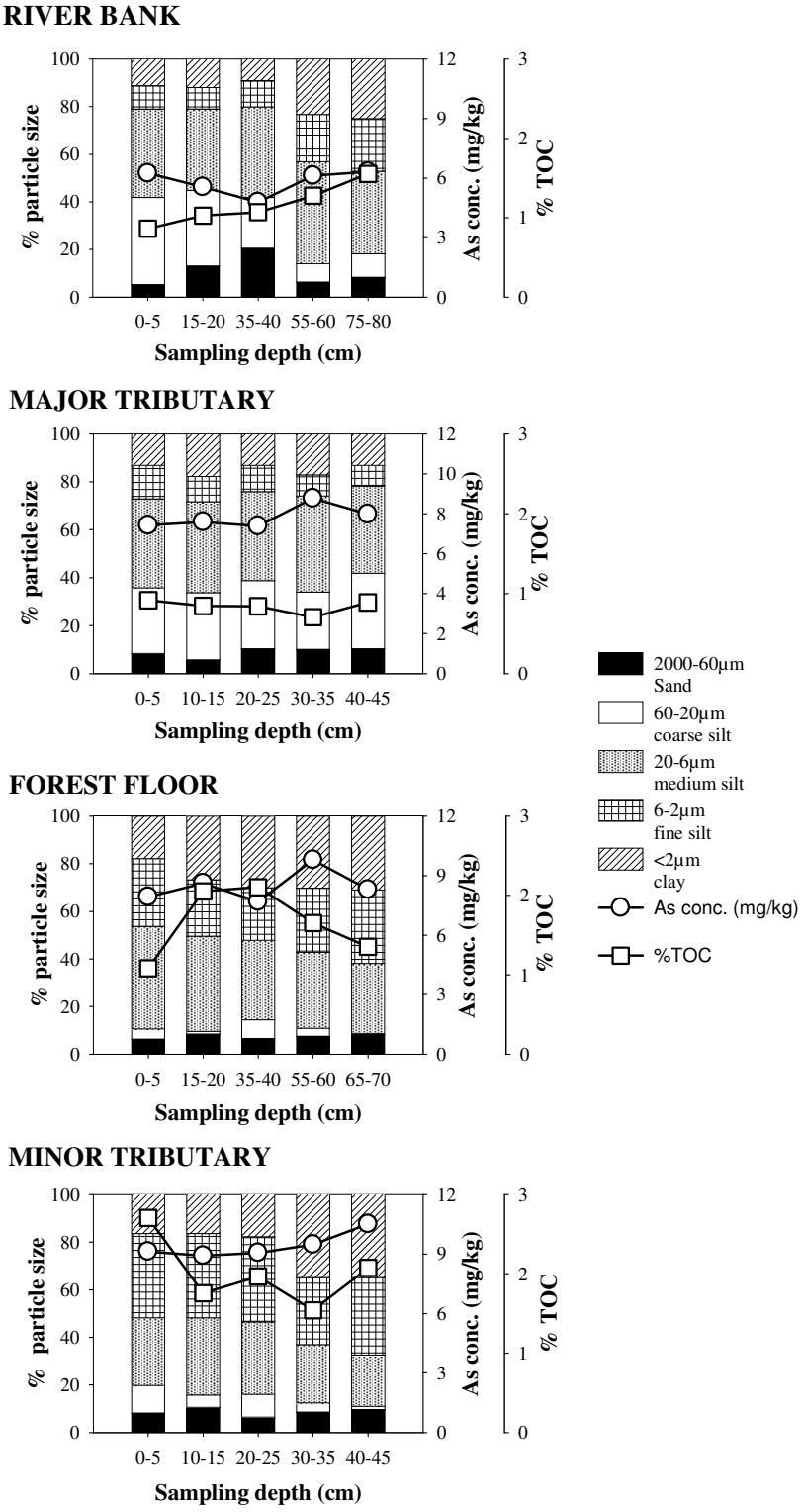
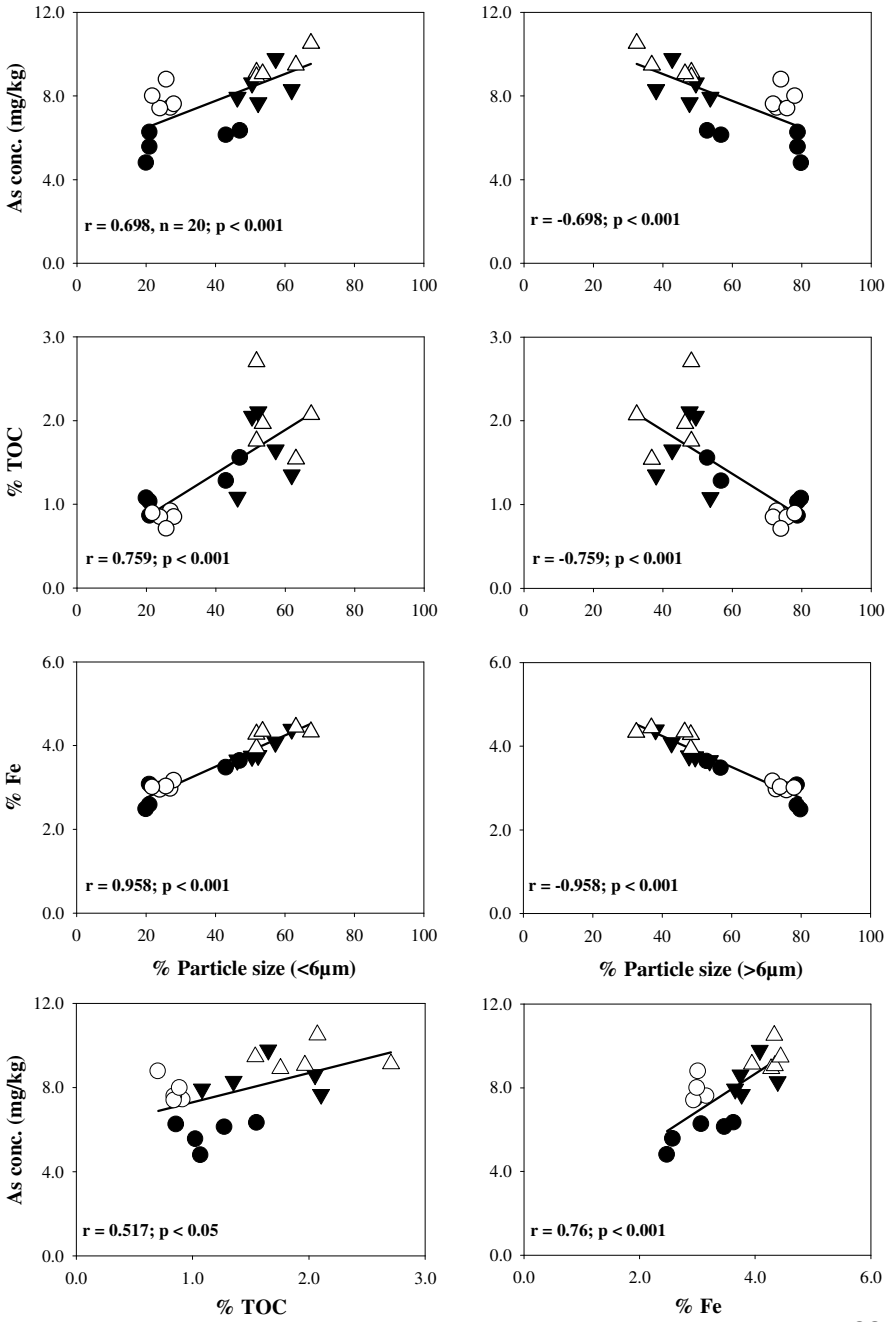


Figure SI 6. Particle size percentage overlain with TOC and total As in sediments of 4 different cites at Koromjal.



94

95 Figure SI 7. Regression plots showing relations between particle size percentage,
96 total As, TOC and total Fe from sediments. Closed circle represent river bank
97 sediments, open circle represent major tributary sediment, closed triangle down
98 represent forest floor sediment, open triangle up represent minor tributary sediment.

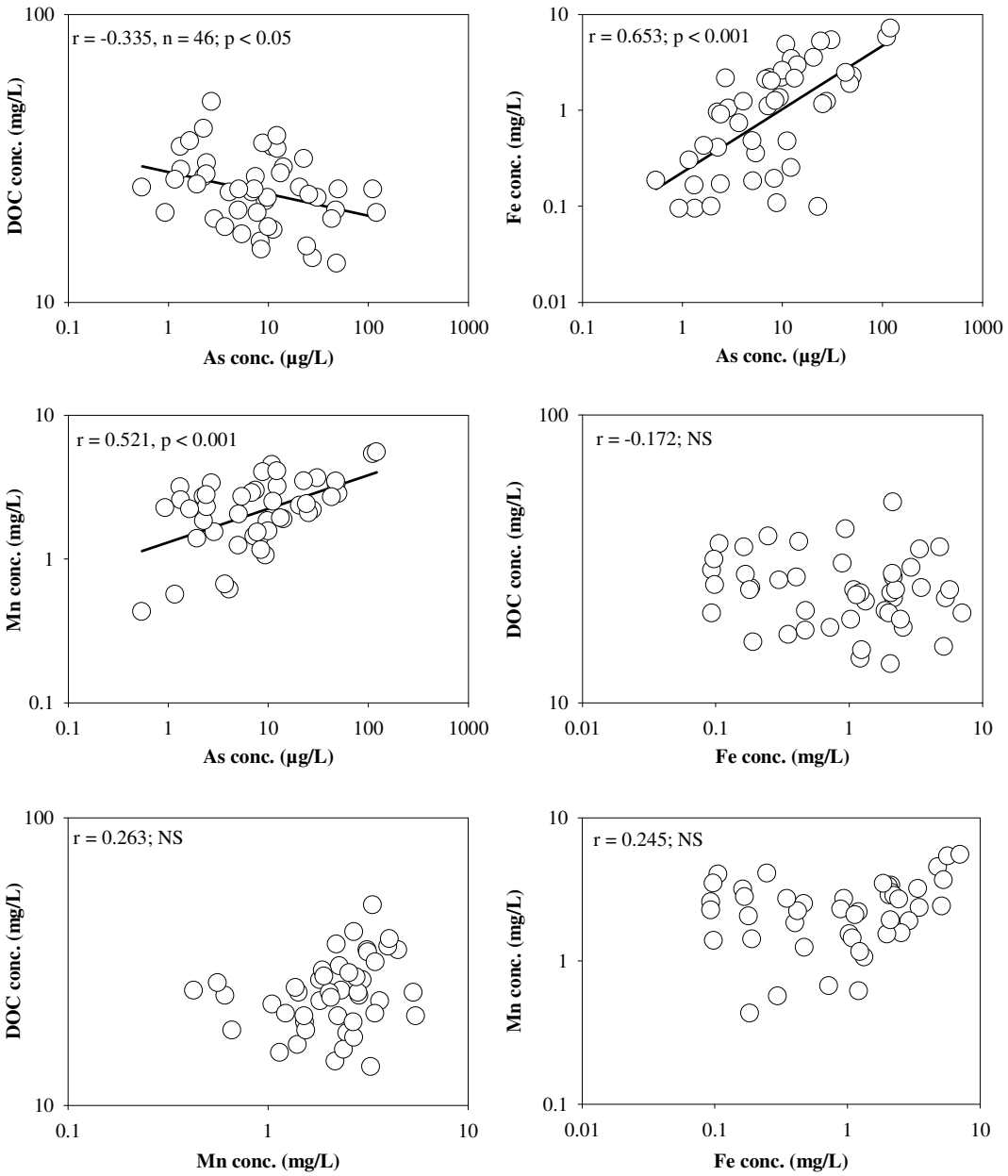


Figure SI 8. Correlation between porewater As, DOC, Fe and Mn at Koromjal. NS = not significant.

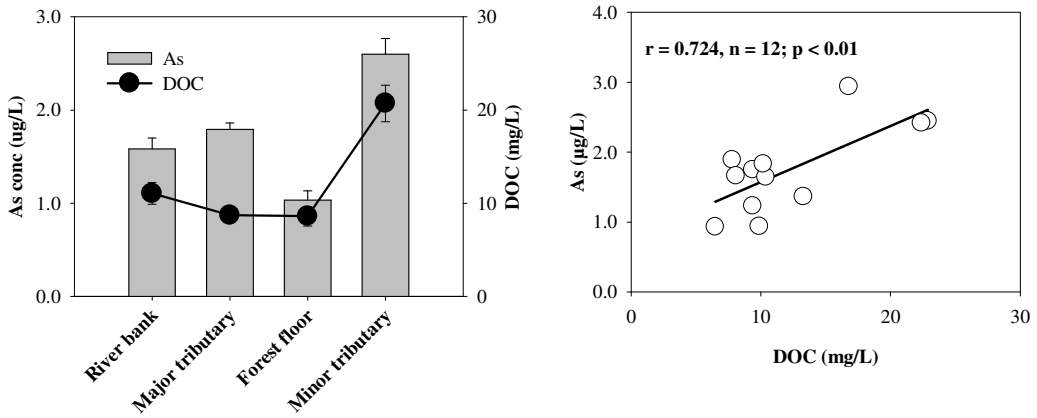


Figure SI 9. Total As and DOC in surface water collected from 4 sites at Koromjal on 19 December, 2009. Data are means and ± SE (n = 3).

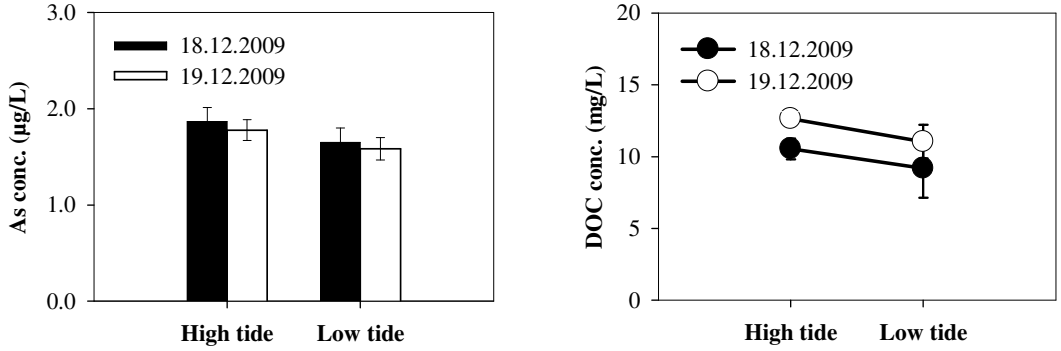
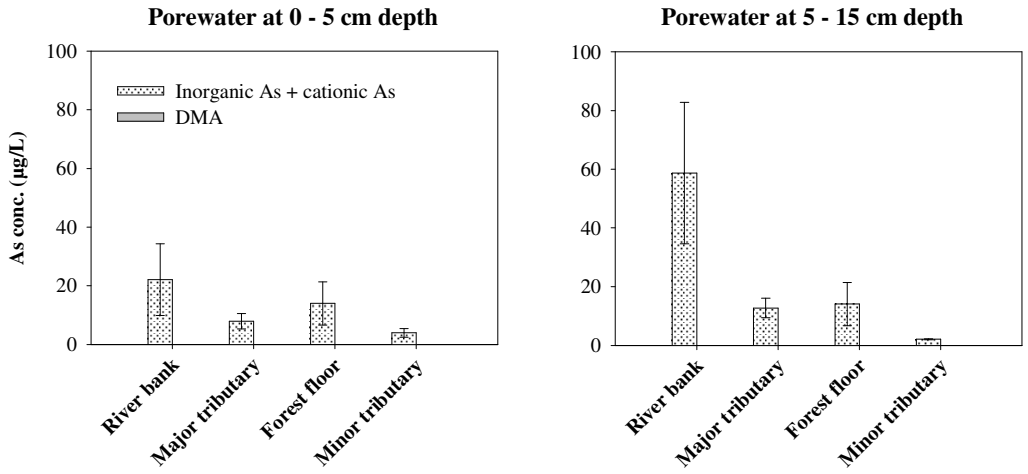


Figure SI 10. Arsenic and DOC in tidal seawater collected from Koromjal, the Sundarbans, Bangladesh. Data are means and ± SE (n = 3).



122 Figure SI. 11. Arsenic speciation in porewater collected from 4 sites at Koromjal on

123 18 December 2009. Data are means and ± SE (n = 3).

124

125

Table SI 1. Correlation matrix of elemental concentrations in Mongla, Dacope and Shyamnagar core sediments. Each site had 3 replicate samples as described in Materials and Methods. Cell contents are first Pearson correlation and below P-value. Significant (P<0.05) relationships are shown in bold.

MONGLA	Depth (cm)	As (mg/kg)	TOC (%)	TIC (%)	TN (%)	C:N	Fe (%)	Mn (mg/kg)
As	0.007							
(mg/kg)	0.970							
TOC	**-0.532**	-0.047						
(%)	**0.002**	0.797						
TIC	0.309	-0.098	**-0.401**					
(%)	0.086	0.592	**0.023**					
TN	**-0.568**	0.250	**0.839**	-0.245				
(%)	**0.001**	0.167	**0.001**	0.175				
C:N	0.243	0.214	-0.329	0.179	**-0.662**			
	0.180	0.240	0.066	0.326	**0.001**			
Fe	-0.122	0.323	**0.385**	-0.169	0.198	-0.147		
(%)	0.507	0.072	**0.030**	0.354	0.276	0.421		
Mn	0.031	**0.578**	0.111	-0.148	-0.063	0.072	**0.560**	
(mg/kg)	0.867	**0.001**	0.547	0.418	0.731	0.695	**0.001**	
P	-0.053	**-0.370**	-0.035	-0.192	0.159	-0.228	**-0.552**	**-0.411**
(mg/kg)	0.775	**0.037**	0.851	0.293	0.384	0.210	**0.001**	**0.019**
DACOPE								
As	**0.517**							
(mg/kg)	**0.002**							
TOC	**-0.621**	**-0.409**						
(%)	**0.000**	0.020						
TIC	**-0.616**	**-0.589**	0.036					
(%)	**0.001**	**0.001**	0.847					
TN	0.099	0.036	**0.460**	**-0.443**				
(%)	0.588	0.843	**0.008**	**0.011**				
C:N	**-0.591**	**-0.445**	0.080	**0.739**	**-0.780**			
	0.001	**0.011**	0.664	**0.001**	**0.001**			
Fe	**0.599**	**0.775**	-0.191	**-0.845**	**0.363**	**-0.688**		
(%)	0.000	0.000	0.296	**0.001**	**0.041**	**0.001**		
Mn	0.242	**0.726**	-0.341	-0.299	-0.081	-0.218	**0.527**	
(mg/kg)	0.182	**0.001**	0.056	0.096	0.658	0.231	**0.002**	
P	-0.172	-0.158	-0.030	0.304	-0.082	0.203	-0.181	0.090
(mg/kg)	0.346	0.388	0.870	0.091	0.656	0.264	0.321	0.623
SHYAMNAGAR								
As	-0.014							
(mg/kg)	0.942							
TOC	0.338	-0.144						
(%)	0.670	0.449						
TIC	**-0.595**	-0.253	-0.307					
(%)	**0.001**	0.176	0.098					
TN	-0.055	0.240	0.272	-0.159				
(%)	0.772	0.201	0.146	0.403				
C:N	-0.091	-0.340	0.207	**0.390**	**-0.732**			
	0.632	0.066	0.273	**0.033**	**0.001**			
Fe	-0.164	**0.744**	-0.311	-0.010	0.052	-0.141		
(%)	0.386	**0.001**	0.095	0.960	0.785	0.457		
Mn	**-0.757**	0.177	**-0.428**	0.347	-0.099	0.092	**0.400**	
(mg/kg)	**0.001**	0.350	**0.018**	0.061	0.601	0.628	**0.029**	
P	-0.095	0.311	-0.330	0.127	0.216	**-0.364**	0.292	0.086
(mg/kg)	0.617	0.095	0.075	0.502	0.251	**0.048**	0.117	0.652

Table SI 2. Sediments settled on synthetic turf after two tidal cycles at Koromjal. Data are means and ± SE (n = 3).

Sediment deposits	As (mg/kg)	Fe (%)	Mn (mg/kg)	TOC (%)	TIC (%)
River bank	7.3 ± 0.3	2.5 ± 0.04	541 ± 8	0.61 ± 0.02	0.72 ± 0.02
Forest floor	13.1 ± 1.0	4.1 ± 0.1	884 ± 13	2.08 ± 0.1	0.70 ± 0.1

Table SI 3. Correlation matrix of elemental concentrations at Koromjal core sediments. Each site had 3 replicate samples as described in Materials and Methods. Cell contents are first Pearson correlation and below P- value. Significant (P<0.05) relationships are shown in bold.

River bank	Depth (cm)	As (mg/kg)	TOC (%)	TIC (%)	Fe (%)	
As (mg/kg)	0.164 0.544					
% TOC	**0.751** **0.001**	0.011 0.969				
% TIC	**-0.706** **0.002**	0.113 0.676	**-0.921** **0.001**			
% Fe	**0.764** **0.001**	**0.522** **0.038**	**0.678** **0.004**	-0.447 0.082		
% Mn	**-0.841** **0.001**	-0.132 0.627	-0.512 0.969	**0.516** **0.041**	**-0.546** **0.029**	
Major tributary						
As (mg/kg)	0.437 0.206					
% TOC	-0.135 0.709	-0.212 0.557				
% TIC	0.383 0.274	0.281 0.432	**-0.852** **0.002**			
% Fe	-0.195 0.590	0.192 0.595	-0.178 0.623	0.221 0.539		
% Mn	**-0.799** **0.006**	-0.230 0.523	0.188 0.603	-0.300 0.400	0.410 0.240	
Forest floor						
As (mg/kg)	**0.567** 0.035					
% TOC	0.234 0.421	0.235 0.418				
% TIC	-0.327 0.254	-0.286 0.321	-0.431 0.124			
% Fe	**0.885** **0.001**	**0.557** **0.038**	-0.027 0.927	-0.385 0.174		
% Mn	**-0.906** **0.001**	**-0.581** **0.029**	-0.240 0.408	0.204 0.485	**-0.803** **0.001**	
Minor tributary						
As (mg/kg)	0.458 0.184					
% TOC	0.067 0.855	0.458 0.184				
% TIC	-0.129 0.721	-0.471 0.169	**-0.675** **0.032**			
% Fe	0.237 0.51	-0.536 0.110	**-0.840** 0.002	0.612 0.060		
% Mn	**-0.832** **0.003**	-0.543 0.105	-0.263 0.462	0.262 0.464	0.087 0.811	

Text SI Additional methods

Aristar® reagents were used throughout, supplied by BDH (Poole, Dorset, UK), along with high purity 18.2 MΩ cm water (Milli-Q®).

Sediment core slices were oven dried at 60 ℃ for 24 h and then sediment was ground, sieved (2 mm), and digested with HNO_3 and H_2O_2 at 120 ℃ on a block digester (**Error! Reference source not found.**). Soil certified reference material (CRM) (NCS-ZC-73007), spikes and sample blanks were included in each digestion batch of 40 samples with randomization as part of the quality control. Total As (m/z 75) and Indium (In)(m/z 115) analysis was determined by ICP-MS (Agilent technologies 7500, Tokyo, Japan); the instrument was tuned for the monitoring of m/z 75 (As) and m/z 77 and 82 (Selenium) (m/z 77 and m/z 78 while collision cell was used) to check ArCl interferences. Indium (10 µg/L) was run as internal standard. Standards were prepared from 1000 mg/L ICP-MS grade multi-element stock solutions with appropriate ranges (0 - 50 µg/L). Corrections were not required for polyatomic $Ar^{40}Cl^{35}$ interferences on m/z 75. Total Fe and Mn analysis was conducted by flame-atomic absorption spectrophotometry (Perkin Elmer AAnalyst 300), calibrated with appropriate standards and change in sensitivity of the instrument checked every 12 samples. A subset of samples were digested for total P analysis using a sulphuric acid,/lithium sulphate,/hydrogen peroxide mixture in 84:2.4:70 ratio, with total P determined by flow injection colourimetry (FIAstar 5000 Analyzer, FOSS Tecator, Sweden). A further subset of sediments was ball-milled (Retsch, Germany) and analyzed for total carbon (TC), total organic carbon (TOC)

185 and total nitrogen (TN) by flash combustion (NA 1500 Series 2, Fisons Instruments,
186 UK).

187

188 Porewater, surface water and tidal seawater samples were analyzed for As using
189 ICP-MS as mentioned previously. Porewaters collected on 18 December, 2009 were
190 characterized for As speciation using an anion exchange HPLC (PRP X-100,
191 Hamilton, Switzerland) coupled to ICP-MS Agilent 7500c with 6.6 mM phosphate
192 buffer (pH = 6.2).

193

194 Arsenic in DGT was determined by ICP-MS (Thermo Elemental X7). The
195 concentration of labile As trapped by DGT ($^{As}C_{DGT}$) was calculated using equation [i].

196

197 $$^{As}C_{DGT} = M \times \Delta g/(D \times A \times t) \quad --- \quad --- \quad --- \quad [i]$$

198

199 Where M is the mass of As in the binding (ferrihydrite) gel, Δg is the thickness of the
200 diffusive gel (0.08 cm) plus the thickness of the filter membrane (0.014 cm), A is the
201 surface area (2.54 cm^2), t is the deployment time (24 h), and D is the temperature
202 corrected diffusion coefficient of As in the gel (**Error! Reference source not**
203 **found.**). $^{As}C_{DGT}$ was compared with porewater As concentrations collected on the
204 same day.

205

206 DOC in water samples was analyzed by LabTOC-Aqueous Carbon Analyzer (PPM
207 Ltd., UK) with necessary dilutions for porewaters. Total Fe and Mn in water samples
208 were analysed by flame-AAS with appropriate dilutions. Fe and Mn concentrations in
209 porewater were well above the limit of detection (LOD) but all surface water and tidal
210 seawater fell below the LOD.

211

212 ***Statistics***

213 All statistical analysis was performed using general linear modeling (GLM) using
214 Minitab v.15 English (State College, PA).

215

216 ***Rhizon samplers***

217 Rhizosphere Research Products, Dolderstraat 62, NL-6706, JG Wageningen, The
218 Netherlands

219

220 *Sediment particle size analysis*

221 A subset of sections from each core profile were selected for particle size analysis.
222 Sediment (25 g) was mixed with 1 L of deionized water with 5 mL dispersant (mixture
223 of sodium polyphosphate and sodium carbonate, buffered at pH 8.3). A hydrometer
224 (g/L. T: 68 °F Zeal, Soil Hydrometer No.2/7243 ASTM. 152H, 0 - 60) was inserted
225 into the suspension and readings were recorded at 46 s, 6 min 51 s, 76 min and 11.5
226 h with corresponding temperature (^{o}C) reading to determine particles within the
227 equivalent spherical diameter (e.s.d.) ranges of 2000 - 60 µm (sand), 60 - 20 µm

228 (coarse silt), 20 - 6 µm (medium silt), 6 - 2 µm (fine silt) and < 2 µm (clay),
229 respectively (**Error! Reference source not found.**). Particle size analysis of tidally
230 deposited sediment could not be conducted due to the small sample size obtained.

231

232 *Sequential extraction*

233 Arsenic fractionation study of sediments was conducted following a published
234 method (**Error! Reference source not found.**) using 0.05 M ammonium sulphate
235 $(NH_4)_2SO_4$, 0.05 M ammonium dihydrogen phosphate $(NH_4)H_2PO_4$, 0.2 M
236 ammonium-oxalate, 0.02 M; pH 3.25 ammonium-oxalate buffer + 0.1 M ascorbic acid
237 and finally microwave digestion with HNO_3 following the procedures as described by
238 Adomako et al. (4). Extractants collected after five consecutive extractions
239 represents (I) non-specifically adsorbed As, (II) specifically adsorbed As, (III)
240 amorphous and poorly-crystalline hydrous oxides bound As, (IV) crystalline hydrous
241 oxides bound As, and (V) residual As. Soil extracts were collected in 50 mL
242 centrifuge tubes and centrifuged at 1720 x g for 10 minutes and the supernatant
243 carefully decanted into 50 mL tube and stored at 20 ℃ for analysis. Soil extracts
244 were treated with 20 % potassium iodide (KI) solution (20 % KI, 10 % ascorbic acid
245 and 20 % HCl) about 30 minutes prior to analysis for reduction of arsenate (AsV) into
246 arsenite (AsIII) and AsIII in extracts were determined by a Hydride generator Atomic
247 Absorption Spectrophotometer (HG-AAS) using matrix match AsIII standards.
248 Sample spikes (10 µg/L) and blanks were run with each analytical batch.

249

250 **References**

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4. Adomako, E.; Solaiman, A. R. M.; Williams, P. N.; Deacon, C. M.; Meharg, A. A. Enhanced transfer of arsenic to grain for Bangladesh grown rice compared to US and EU. *Environ. Int.* **2009**, *35*, 476-479.