1 # Investigating arsenic speciation and mobilization in

2 # sediments with DGT and DET: a mesocosm evaluation

3 # of oxic-anoxic transitions

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12   **Abstract**

13   Mobilization of arsenic from freshwater and estuarine sediments during the transition from oxic to

14   anoxic conditions was investigated, using recently developed diffusive sampling techniques. Arsenic

15   speciation and Fe(II) concentrations were measured at high resolution (1-3 mm) with in situ diffusive

16   gradients in thin films (DGT) and diffusive equilibration in thin films (DET) techniques. Water column

17   anoxia induced Fe(II) and As(III) fluxes from the sediment. A correlation between water column Fe(II)

18   and As(III) concentrations was observed in both freshwater (r_s=0.896, p<0.001) and estuarine (r_s=0.557,

19   p<0.001) mesocosms. Porewater sampling by DGT and DET techniques confirmed that arsenic

20   mobilization was associated with the reductive dissolution of Fe(III) (hydr)oxides in the sub-oxic zone

21   of the sediment; a relationship that was visible because of the ability to measure the co-incident profiles

22   of these species using combined DGT and DET samplers. The selective measurement of As(III) and

23   total inorganic arsenic by separate DGT samplers indicated that As(III) was the primary species

24   mobilized from the solid phase to the porewater. This measurement approach effectively ruled out

25   substantial As(V) mobilization from the freshwater and estuarine sediments in this experiment. This

26   study demonstrates the capabilities of the DGT and DET techniques for investigating arsenic speciation

27   and mobilization in a range of sediment conditions.

28

Introduction

The mobilization of geogenic arsenic from sediments and soils can impact significantly on environmental and human health. Groundwater in Bangladesh and India often contains dangerously high concentrations of naturally mobilized dissolved arsenic, frequently exceeding the World Health Organization limit of 10 µg L^{-1} by one to two orders of magnitude and affecting the health of more than 46 million people.[1, 2] Arsenic mobilization during monsoonal flooding of rice paddy fields in Bangladesh has also been reported;[3] this process is integral to understanding the potential effect of arsenic contamination on rice yields. Aquatic systems such as rivers, lakes and coastal areas are also at risk from arsenic contamination via mobilization processes. For example, eutrophication-induced anoxic events in freshwater and estuarine systems have the potential to cause arsenic mobilization from the sediment to the water column.[4, 5] Understanding the processes of mobilization and sequestration in surface sediments is essential for predicting and managing potential releases into aquatic systems, hence effectively mitigating the health consequences associated with environmental arsenic contamination.

The mobility of arsenic in surface sediments is closely linked to iron biogeochemistry. Fe(III) (hydr)oxide minerals such as ferrihydrite, goethite and magnetite, formed under oxic conditions, strongly adsorb dissolved inorganic arsenic via complexation.[6] Reductive dissolution of these arsenic-bearing Fe(III) (hydr)oxides can release dissolved arsenic into the porewater and result in fluxes of arsenic to the overlying water column.[6-9] Uncertainty still exists, however, on the relative importance of arsenic speciation shifts on arsenic mobility.[10] Some research has shown that reduction of As(V) to As(III) can result in increased mobility of arsenic due to weaker adsorption of the reduced arsenic species to Fe(III) (hydr)oxide minerals.[8] However, other research has demonstrated that the affinity of As(III) for ferrihydrite and goethite minerals in the pH range typical of natural systems (pH 6-9) is similar, and sometimes greater, than that of As(V).[6] Further research is therefore needed in this area to elucidate the role of As(V) reduction on arsenic mobility.

During water-column anoxia, as a result of increased oxygen demand or high water temperatures, arsenic that is mobilized from the solid phase to the porewater can flux to the overlying water column. Closely coupled reductive dissolution of Fe(III) (hydr)oxide phases and mobilization of adsorbed arsenic has been observed in a number of studies,[11-13] although decoupling of these processes has also been reported.[14-16] Competitive adsorption of other anions, such as bicarbonate, has also been shown to liberate arsenic from Fe(III) (hydr)oxide minerals.[17-19] The mineralization of organic carbon associated with dissimilatory iron reduction produces bicarbonate,[20-22] which may further enhance the mobilization of arsenic through competition for binding sites.

Recent research by Skoog and Arias-Esquivel[23] utilized sediment mesocosm incubations to measure benthic fluxes of dissolved organic carbon, iron, manganese and phosphate during induced water column anoxia and subsequent reoxygenation. This approach proved to be valuable in indentifying the coupling of iron redox cycling with organic carbon and phosphate mobilization and sequestration. In this study, we expand upon the experimental design of Skoog and Arias-Esquivel[23] by utilizing diffusive porewater sampling techniques (diffusive gradients in thin films (DGT) and diffusive equilibration in thin films (DET)) to investigate porewater arsenic and iron in freshwater and estuarine sediment during induced anoxia and subsequent reoxygenation of the overlying water. Previous research[3] has investigated the effect of anoxia on fluxes and porewater profiles of arsenic and iron in a flooded rice paddy field; the majority of the arsenic mobilized was As(III), and porewater profiles obtained by peepers revealed coupling between iron and arsenic release from the solid to solution phase. Our study aims to examine arsenic mobilization processes in a similar way, but in a controlled mesocosm setting. This is the first time that such an experiment has been performed using mesocosms and diffusive sampling techniques (DGT and DET) to examine both the water-column and porewater chemistry of arsenic and iron under changing redox conditions.

80 Diffusive sampling techniques such as DGT and DET are important tools for investigating sediment

81 biogeochemistry. They allow the in situ measurement of a number of important porewater solutes at

82 higher spatial and temporal resolution than is possible with traditional techniques and are capable of

83 measuring co-distributions to facilitate the interpretation of mechanistic interactions.[24-29] Recently, the

84 development of a colorimetric DET technique for the measurement of Fe(II)[28] and a DGT technique

85 capable of measuring total inorganic arsenic,[30] allowed the investigation of arsenic and iron

86 biogeochemistry in freshwater, estuarine and marine sediment mesocosms.[31] The co-distributions

87 obtained with these techniques revealed coupling of reductive dissolution of Fe(III) (hydr)oxide

88 minerals with the release of dissolved arsenic into the sediment porewater, even in the presence of low

89 background arsenic porewater concentrations (<40 nmol L^{-1}). More recently, a DGT technique has been

90 reported that selectively measures As(III),[32] which when used alongside the existing DGT technique

91 for total inorganic arsenic, has the potential to provide important information on the speciation of

92 dissolved inorganic arsenic in sediment porewaters.

93

94 This study aims to demonstrate the benefits of DGT and DET sampling techniques to investigate arsenic

95 and iron biogeochemistry during sediment anoxia and subsequent reoxygenation. Combining this new

96 approach to porewater sampling with the measurement of benthic fluxes of arsenic and Fe(II), the

97 relationship between the reductive dissolution of Fe(III) (hydr)oxide minerals and the mobilization of

98 arsenic will be investigated in both freshwater and estuarine sediments. The high spatial and volumetric

99 resolution of the DGT and DET measurements, coupled with the capability of measuring co-distributed

100 Fe(II) and arsenic, will enable the mechanistic interpretation of this important process; this will serve to

101 clearly demonstrate the advantages of using this new approach for investigating arsenic biogeochemistry

102 and mobilization.

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Experimental

Reagents, materials and solutions. Deionized water (Milli-Q Element, Millipore) was used to prepare all solutions. Bisacrylamide-crosslinked polyacrylamide diffusive gels, and Metsorb and mercapto-silica binding gels, were prepared as previously described.[28, 31, 32] DGT components (including materials used to prepare DGT gels) were acid-cleaned in 10%(v/v) HNO$_3$ (AR grade, Merck) for at least 24 h and rinsed thoroughly with deionized water prior to use. All salts used to prepare solutions were AR grade or higher.

Sediment collection. Sediment was collected from two sites on the Gold Coast, Queensland, Australia: the Coomera River (freshwater) and the Gold Coast Broadwater (lower estuarine). Sediment and water from the sites were transported back to the laboratory where the sediment was sieved to <1 mm, homogenized and incubated in four 20 L mesocosms (two freshwater and two estuarine) containing approximately 13 L of sediment and 7 L of overlying water. Oxygen saturation and mixing of the overlying water was ensured by sparging with air. Mesocosms were allowed to stabilize for 3 months prior to the start of the experiment to ensure re-establishment of physicochemical profiles within the sediment. Porter and co-workers[33] recently investigated the effect of sediment sieving and homogenization on nutrient and gas fluxes and found that they returned to normal after 3 weeks of stabilization. A period of 12 weeks was chosen for this experiment to ensure that chemical profiles of arsenic and iron were re-established, as they are typically generated from the solid phase and may require a longer stabilization time.[31]

Assembly of DGT/DET samplers. Sediment DGT sampling devices were supplied by DGT Research Ltd. Probes for measuring total inorganic arsenic (Metsorb) and As(III) (mercapto-silica) were prepared as described previously.[30, 32, 34] The diffusive gel was 0.08 cm thick and was overlain by a 0.45 μm cellulose nitrate membrane (Millipore, Billerica MA) of 0.01 cm thickness to protect the probes during deployment. The combined thickness of the diffusive gel and membrane filter (0.09 cm) was used for all

6

132   DGT calculations. The diffusive gels of the mercapto-silica DGT probes were used as the DET gels for

133   the colorimetric analysis of Fe(II), allowing the measurement of Fe(II) and As(III) at the same location

134   in the sediment.

135

136   **Sediment incubations.** The experiment consisted of one control and one treatment mesocosm for both

137   the freshwater and estuarine sediment. All mesocosms were mixed using small aquarium pumps set at a

138   low flow rate (0.5 L min^{-1}) to ensure no accumulation of solutes at the sediment-water interface whilst

139   avoiding agitation of the sediment surface. The control mesocosms were sparged with air throughout the

140   experiment to ensure oxygen saturation in the overlying water. The treatment mesocosms were sealed

141   on Day 6, for a period of 11 days, with a 10 mm thick Perspex lid to exclude atmospheric oxygen and

142   allow the natural bacterial oxygen demand to induce anoxia. This duration was selected to ensure that

143   the experiment would capture significant reductive dissolution of Fe(III) (hydr)oxide mineral phases,

144   and thus allow interpretation of the mechanistic interactions between iron and arsenic mobilization. To

145   ensure no oxygen leakage, each lid was sealed in place using a waterproof polymer-based sealant (All

146   Clear, Selleys). A single sampling port, sealed with an air and watertight plastic stopper when not in

147   use, was used to take water samples and measure physicochemical parameters. Dissolved oxygen was

148   measured daily using an optical dissolved oxygen sensor (Opti-Ox, Mettler Toldeo) and pH and

149   temperature were measured daily using a combined pH/temperature sensor (FiveGo, Mettler Toledo).

150   DO was measured more frequently during days 6-7 to record the oxygen consumption during the

151   development of anoxia. During deployment of DGT/DET sediment probes in the anoxic phase of the

152   incubation, the pumps were switched off and the lids removed for no more than five minutes to

153   minimize disturbance of the anoxic conditions.

154

155   **Deployment and analysis of DGT/DET samplers.** Prior to deployment, DGT/DET probes were

156   deoxygenated overnight in 0.01 mol L^{-1} NaCl (AR Grade, Merck) for freshwater deployments and 0.7

157   mol L^{-1} NaCl for estuarine deployments, by sparging with high-purity nitrogen gas. This ensured that

158 the probes did not disturb the anoxic zone of the sediment upon deployment. In each mesocosm, a

159 Metsorb and a mercapto-silica DGT sediment probe were deployed for 48 h at three different phases

160 during the incubation: the initial oxic phase (Day 2-4), the anoxic phase (Day 15-17) and following

161 reoxygenation (Day 22-24). Upon removal of the probes, a stainless steel scalpel was used to cut out the

162 gels from the exposure window. The diffusive gel of the mercapto-silica probes was then immediately

163 analysed for Fe(II) by following the DET staining procedure of Robertson and co-workers,[28] as

164 modified by Bennett and co-workers.[35] Diffusive gels from the Metsorb probes were also analysed for

165 Fe(II) but were found to have consistently lower concentrations than the corresponding mercapto-silica

166 probes; indicating adsorption of Fe(II) by the Metsorb binding phase, and thus underestimation of the

167 porewater Fe(II) concentrations. This does not affect the Fe(II) profiles obtained from mercapto-silica

168 samplers, but is discussed further in the Supporting Information where the Metsorb data is given.

169

170 The Metsorb and mercapto-silica DGT binding gels were washed in 50 mL of deionized water for at

171 least 1 h and then sliced at 3 mm intervals. Each slice was eluted using 1 mol L^{-1} NaOH (AR Grade,

172 Chem-Supply) for Metsorb[30] and 0.01 mol L^{-1} KIO_3 (AR Grade, Univar) in 1 mol L^{-1} HNO_3 (Baseline,

173 Seastar) for mercapto-silica.[32] Eluents were diluted 20-fold and analyzed for arsenic (*m/z* 75) by

174 ICPMS (Agilent 7500a) with yttrium (*m/z* 89) as an internal standard. The ArCl (*m/z* 75) interference on

175 As (*m/z* 75) was minimized via the selective accumulation of arsenic by the DGT samplers and

176 subsequent elution in a simple matrix. This selective preconcentration by DGT in the presence of

177 interfering ions such as chloride, permits the analysis of very low porewater arsenic concentrations in

178 complex matrices.[32] The maximum relative standard deviation of internal standard counts in any single

179 run was 4.2%, indicating minimal instrument drift and that no significant matrix effects were present. A

180 certified quality control standard (High Purity Standards; NIST traceable) analyzed regularly throughout

181 each run had an average recovery of 102.3 ± 3.7%.

182

183   The average ICPMS limit of detection for arsenic (LOD; 3σ) across all analytical runs was $0.014 \pm$

184   0.008 μg L^{-1} (0.19 nmol L^{-1}) and the limit of quantification (LOQ; 10σ) was 0.045 ± 0.025 μg L^{-1} (0.60

185   nmol L^{-1}); all measured samples were above these values. The method detection limits (MDL),

186   calculated based on a 48 h deployment time, were 0.015 μg L^{-1} (0.20 nmol L^{-1}) for mercapto-silica DGT

187   and 0.035 μg L^{-1} (0.47 nmol L^{-1}) for Metsorb DGT. All mercapto-silica DGT samples were above the

188   MDL, and only 2% of Metsorb DGT samples were below the MDL. The sediment DGT measurements

189   are interpreted here as porewater concentrations, which is reasonable for those zones in which arsenic is

190   being released due to microbial reduction of Fe(III) (hydr)oxides.[36] The arsenic concentrations

191   indicated at other depths may well be an underestimation of the actual porewater concentration due to

192   the depletion of arsenic from the porewater by the sampler and resupply from the solid phase to the

193   porewater not being fully sustained.[37] Because the DGT-measured concentration is dependent on the

194   analyte resupply rate from the solid to solution phase, it is an excellent tool for investigating

195   mobilization and sequestration processes in sediment systems.[38] Conversely, DET induces minimal

196   resupply from the solid to solution phase, which means it measures the actual porewater concentration.

197   Where full resupply of analyte to the DGT samplers is expected, such as in areas of microbial iron(III)

198   reduction, the direct comparison between DET and DGT is valid, as both measurements will be

199   measuring porewater concentrations. In areas where resupply is not fully sustained, however, direct

200   comparison of the DET and DGT measured concentrations must be made carefully.

201

202   **Water-column sampling.** Water samples were collected daily for analysis of total inorganic arsenic (50

203   mL), As(III) (50 mL) and Fe(II) (5 mL; fixed immediately with ferrozine colorimetric reagent). The

204   same volume of deoxygenated (treatment mesocosms) or oxygenated (control mesocosms) freshwater or

205   seawater was added to the mesocosm to ensure a constant volume was maintained. All calculated

206   concentrations were adjusted for the dilution caused by the addition of water during the experiment. Due

207   to the high chloride concentration in the estuarine mesocosm, As(III) and total inorganic arsenic were

analyzed by solid phase extraction (SPE) because the large dilution required to measure As speciation by HPLC-ICPMS results in a loss in sensitivity that is problematic when measuring background As concentrations. Fe(II) was measured by the ferrozine colorimetric method.[39, 40] Further details of the water-column analyses are given in the supporting information.

Results and Discussion

Benthic fluxes of dissolved oxygen, Fe(II) and arsenic. Benthic fluxes were calculated based on the water column concentration measurements taken over the duration of the experiment. The concentration of dissolved oxygen in each mesocosm was measured daily. The freshwater and estuarine control mesocosms had stable dissolved oxygen concentrations for the duration of the incubation, with averages of 245 ± 4 μmol L^{-1} (7.84 mg L^{-1}) and 201 ± 2 μmol L^{-1} (6.43 mg L^{-1}), respectively. The dissolved oxygen concentrations of the treatment mesocosms, which were sealed from the atmosphere on days 6–17, decreased rapidly during the first two days (Figure S1, supplementary information). Average oxygen consumption rates during the first 30 h in the freshwater mesocosm and the first 46 h in the estuarine mesocosm were 757 ± 180 μmol m^{-2} h^{-1} and 451 ± 92 μmol m^{-2} h^{-1}, respectively (Table 1).

Table 1. Average benthic fluxes of dissolved oxygen (μmol m^{-2} h^{-1}), Fe(II) (μmol m^{-2} h^{-1}), As(III) (nmol m^{-2} h^{-1}) and As(V) (nmol m^{-2} h^{-1}) for treatment and control mesocosms during the phases of the incubation. Numbers in brackets indicate days over which the flux was calculated.

Parameter	Freshwater Treatment		Freshwater Control	Estuarine Treatment		Estuarine Control
	Oxic	Anoxic	Oxic	Oxic	Anoxic	Oxic
DO	−757 ± 180 (6-7)	-	-	−451 ± 92 (6-8)	-	-
Fe(II)	0.15 ± 0.95 (0-7)	79.0 ± 39.3 (10-16)	0.00 ± 0.69 (0-24)	−0.03 ± 0.09 (0-8)	61.3 ± 20.9 (11-17)	0.06 ± 0.31 (0-24)
As(III)	0.46 ± 0.92 (0-7)	12.5 ± 4.1 (9-11) 51.8 ± 16.3 (12-16)	−0.59 ± 3.02 (0-24)	−4.0 ± 11.6 (0-8)	14.8 ± 6.1 (9-17)	−1.75 ± 4.52 (0-24)
As(V)	0.03 ± 1.15 (0-7)	−2.6 ± 18.3 (9-16)	0.53 ± 2.98 (0-24)	1.38 ± 12.8 (0-8)	−4.23 ± 6.38 (9-17)	1.84 ± 7.48 (0-24)
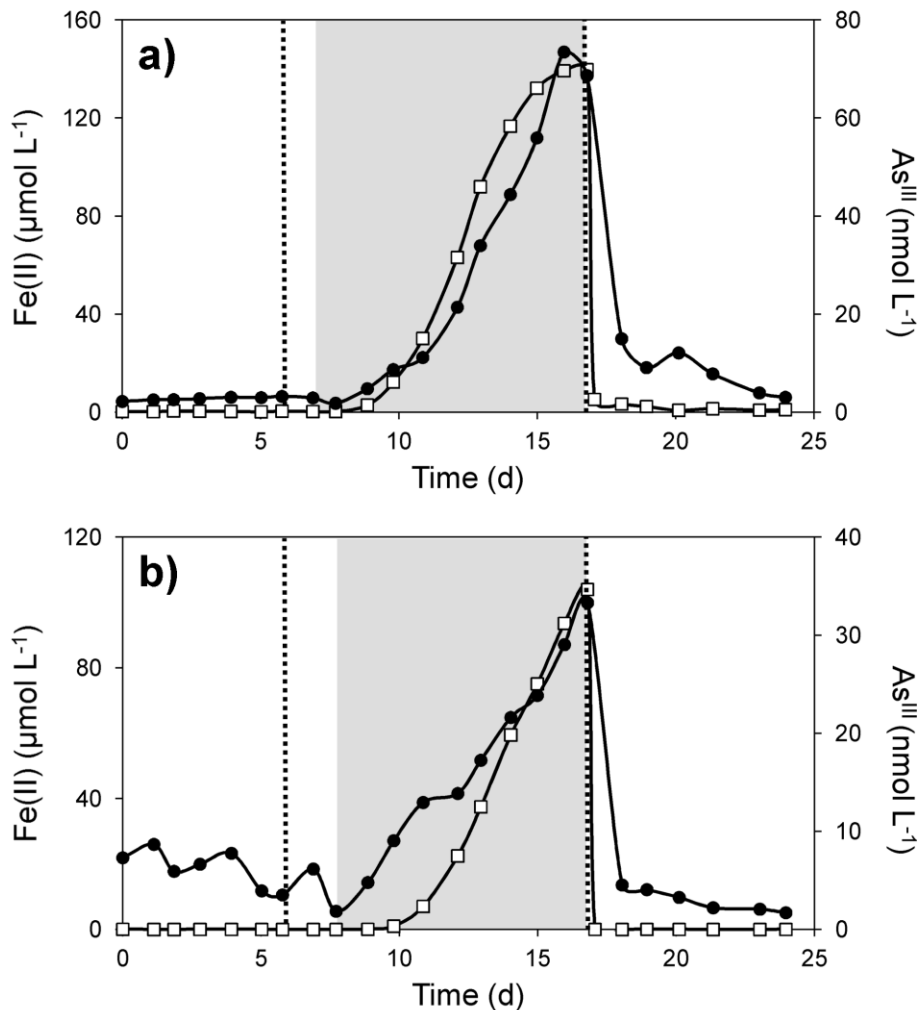
Figure 1. Fe(II) (□) and As(III) (●) water column concentrations for the freshwater (a) and estuarine (b) treatment mesocosms that developed anoxia. Dotted lines mark the exclusion from and re-exposure of the mesocosms to the atmosphere and the shaded area indicates the presence of anoxic conditions.

Both the freshwater and estuarine sediment mesocosms developed anoxic conditions during the incubation. Following atmospheric exclusion, anoxia developed in approximately 30 h for the freshwater mesocosm and 46 h for the estuarine mesocosm and was maintained for nine to ten days. Upon re-exposure of the mesocosms to the atmosphere and commencement of sparging with air, complete re-oxygenation of the water-column, measured by a return of DO to pre-anoxic levels, occurred in less than seven hours.

241   The concentration of Fe(II) in the water-column of the mesocosms was measured daily using the

242   ferrozine colorimetric method (Figure 1a, 1b). Concentrations of Fe(II) were negligible until the

243   development of anoxia, appearing after approximately 48 h of anoxic conditions in both treatment

244   mesocosms. The fluxes of Fe(II) from the sediment to the water during the anoxic phase were 79.0 $\pm$

245   39.3 μmol m^{-2} h^{-1} and 61.3 $\pm$ 20.9 μmol m^{-2} h^{-1} for the freshwater and estuarine mesocosms,

246   respectively (Table 1).

247

248   Average concentrations of As(III) in the overlying water of the control mesocosms for the duration of

249   the experiment were 2.34 $\pm$ 1.23 nmol L^{-1} and 2.94 $\pm$ 2.70 nmol L^{-1}, for the freshwater and estuarine

250   mesocosms, respectively, indicating that concentrations in the controls remained relatively stable for the

251   duration of the experiment. For treatment mesocosms, the initial concentrations of As(III) in the water

252   column (Day 0-8) were 2.71 $\pm$ 0.44 nmol L^{-1} and 5.76 $\pm$ 2.22 nmol L^{-1}, for the freshwater and estuarine

253   mesocosms, respectively. The initial higher concentration of As(III) observed in the estuarine treatment

254   mesocosm was mirrored in the estuarine control mesocosm, with a concentration of 5.61 $\pm$ 2.81

255   nmol L^{-1} for the same period. The concentration of As(III) in the treatment mesocosms increased

256   following the onset of anoxia; the flux of As(III) in the freshwater mesocosm was initially low (12.5 $\pm$

257   4.1 μmol m^{-2} h^{-1}) from day 9 to 11, but increased from day 12 to 16 to 51.8 $\pm$ 16.3 μmol m^{-2} h^{-1} (Table

258   1). The flux of As(III) in the estuarine treatment mesocosm for days 9 to 17 (14.8 $\pm$ 6.1 μmol m^{-2} h^{-1})

259   was lower compared to the overall freshwater mesocosm flux during the anoxic phase (Table 1).

260

261   Concentrations of total arsenic in the overlying water measured by Metsorb SPE, and As(V) calculated

262   by difference, are presented in the supplementary information (Figure S2) and fluxes of As(V) are

263   presented in Table 1. As(V) concentrations in the overlying water remained relatively stable over the

264   course of the incubation and exhibited no increase during the anoxic phase, as indicated by negative

265   As(V) fluxes (Table 1). This indicates that the majority of arsenic mobilized from the sediment was

266   As(III). Average concentrations of As(V) in the treatment mesocosms during the oxic and anoxic phases

12

267   of the incubation (Day 0-17) were 1.36 ± 2.53 nmol L^{-1} and 3.86 ± 2.23 nmol L^{-1}, for the freshwater and

268   estuarine mesocosms, respectively.

269

270   Following reoxygenation of the treatment mesocosms, concentrations of Fe(II), total As and As(III) in

271   the water-column dropped rapidly (Figure 1, S1 and S2). Oxidation of Fe(II) to Fe(III) and its

272   precipitation as Fe(III) (hydr)oxides would occur in the presence of oxygen, with the decrease in total

273   As and As(III) likely due to their adsorption to, or co-precipitation with, newly formed Fe(III)

274   (hydr)oxides in the water column. A slight increase in As(V) concentration (up to 12.3 nmol L^{-1}) in the

275   freshwater mesocosm, immediately following reoxygenation, indicates that some As(III) was also

276   oxidized to As(V) at this stage (Figure S2b).

277

278   There were strong and significant correlations (Spearman's rank) between water-column Fe(II) and

279   As(III) concentrations in both the freshwater (r_s=0.896, p<0.001) and estuarine (r_s=0.557, p<0.001)

280   treatment mesocosms (Figure 2). This supports the tight coupling between the reductive dissolution of

281   Fe(III) (hydr)oxide minerals and mobilization of arsenic observed in the majority of the literature.[7-9, 20]

282   No relationship was apparent between Fe(II) and As(V), indicating that any As(V) mobilized was

283   rapidly reduced to As(III) or that the majority of arsenic was mobilized as As(III). The reduction of

284   solid phase-adsorbed As(V) to As(III) under anoxic conditions has been identified as requiring further

285   investigation to determine the extent to which it contributes to arsenic mobility.[10, 41] Solid phase

286   arsenic associated with Fe(III) (hydr)oxides in the oxic sediment zone should be dominated by As(V)

287   due to the oxic conditions,[42-44] although it is possible that As(III) was also present as it was observed in

288   the water column of both sediment types throughout our incubations. Our results suggest that As(III) is

289   the primary arsenic species mobilized to the water-column. In fact, there is an initial increase of As(III)

290   in the water column without a corresponding increase of Fe(II), in both the estuarine mesocosm (Figure

291   1b). This indicates that the reduction of solid phase-adsorbed As(V) to As(III) may have mobilized

292   some arsenic prior to the major release during the reductive dissolution of Fe(III) (hydr)oxides. This is

13

293   supported by recent results from Tufano and co-workers,[41] who found that, although As(III) adsorbed

294   to Fe(III) (hydr)oxide minerals to a greater extent than As(V) (adsorption maxima 1.4 – 1.5 times higher

295   for As(III) than As(V)), it was more labile than As(V) due to the formation of a higher proportion of
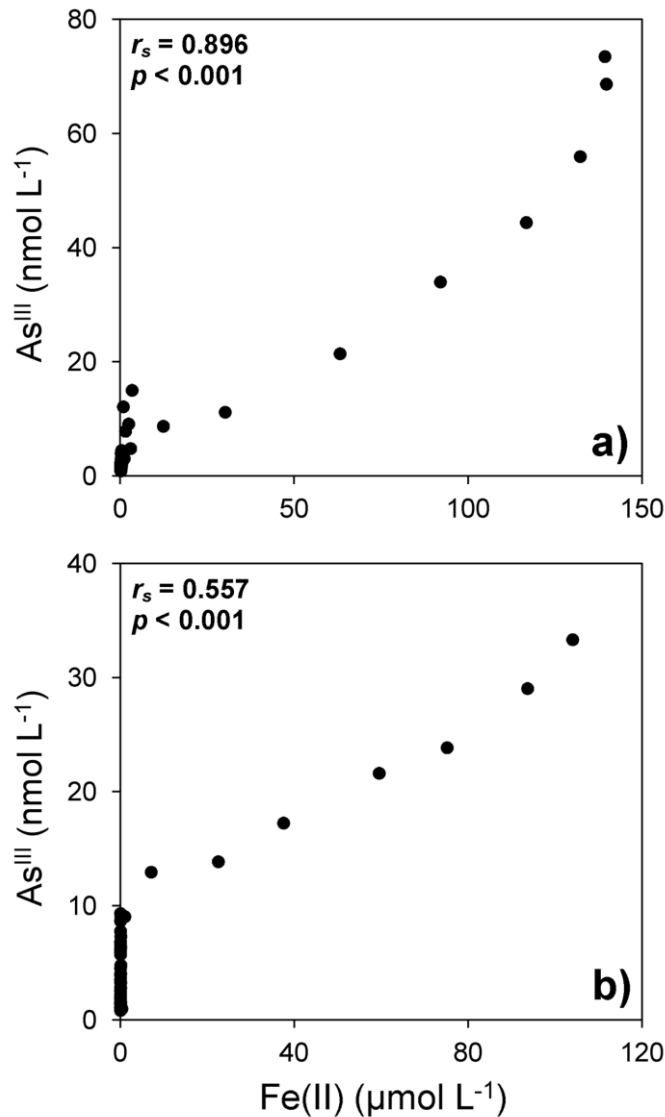
296   outer-sphere complexes.

297

298   To further investigate the effect of reductive dissolution of Fe(III) (hydr)oxides and the role of As(V)

299   reduction in arsenic mobilization, porewater profiles were measured by in situ, diffusive sampling

300   techniques capable of selectively measuring As(III) and Fe(II) co-distributions.

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302

303

Figure 2. Plot of water-column Fe(II) and As(III) concentrations for freshwater (a) and estuarine (b) mesocosms. Spearman's rank correlation analysis was done with SPSS Version 19. Data for each correlation (n=48) consists of measurements taken over the entire duration of the incubation (Day 0-24).
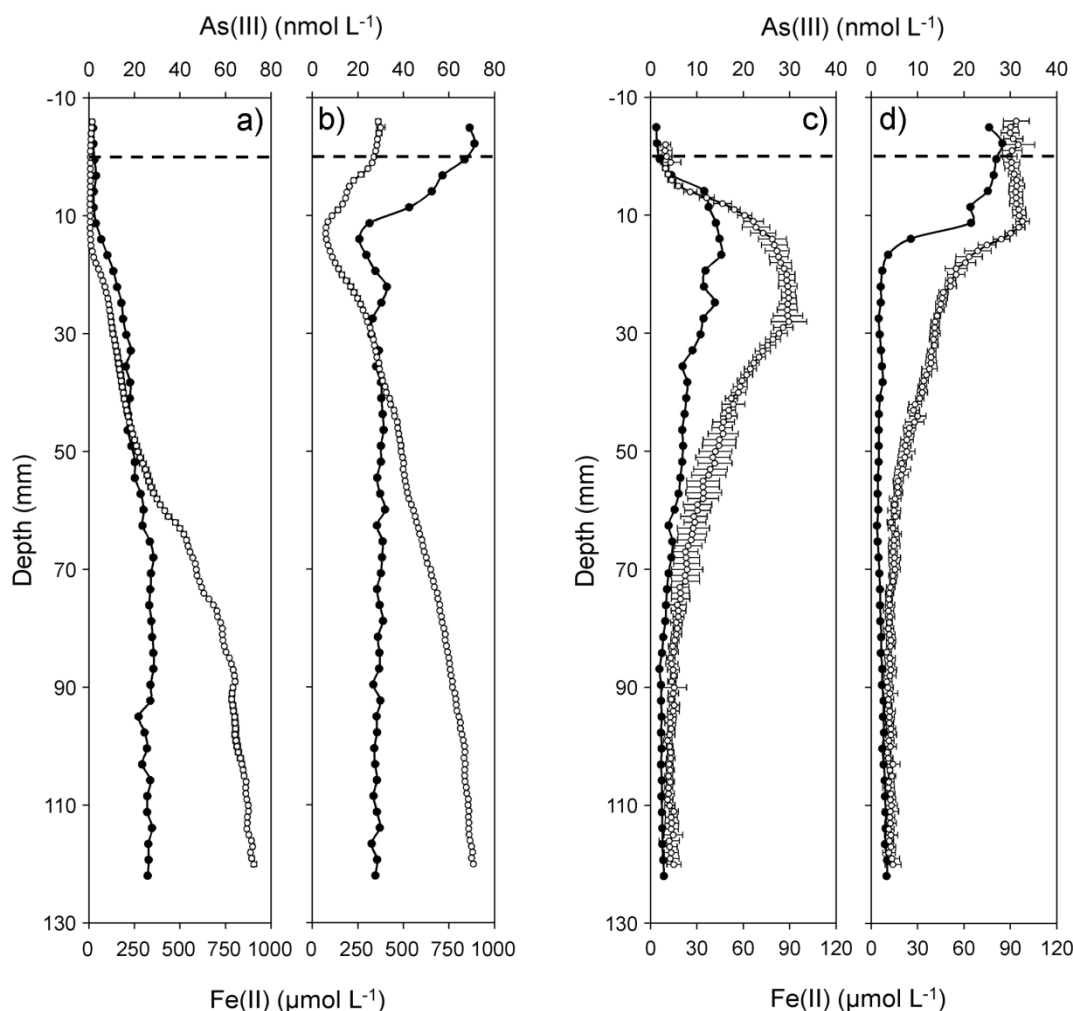
Co-distributions of porewater Fe(II) and arsenic. In situ porewater sampling of Fe(II) and As(III) by combined DET/DGT samplers allows the co-incident profiles of these analytes to be measured at the same spatial location within the sediment. Porewater profiles of Fe(II), total As and As(III) were similar in all mesocosms during the oxic phase deployment (Day 2-4; Figure S3 and S4) and in the oxygenated controls during the periods corresponding to the treatment anoxic phase deployments (Day 15-17; Figure 3 and S5) and reoxygenated phase deployments (Day 22-24; Figure 4 and S6). All profiles

315 showed sub-surface increases of Fe(II), total As and As(III) coinciding below the oxic zone of the

316 sediment, which varied from 1 – 10 mm depth. However, no flux to the overlying water was observed

317 due to the re-oxidation of Fe(II) and precipitation as Fe(III) (hydr)oxides in the surface oxidized

318 sediment, which in turn would act as a sink for dissolved arsenic diffusing from deeper sediment

319 layers.[20]

320

321 In contrast, the porewater profiles from the treatment mesocosms during the anoxic phase deployments

322 (Figure 3b and 3d) show mobilization of As(III) in the top 10-15 mm of the sediment and a flux of

323 As(III) into the overlying water. This is associated with an increase in porewater Fe(II) concentrations

324 and a flux of Fe(II) to the water-column (Table 1, Figure 1). The anoxic conditions would have favored

325 the reduction of Fe(III) (hydr)oxide minerals to Fe(II) by dissimilatory iron – reducing bacteria (DIRB),

326 resulting in the loss of the Fe(III) (hydr)oxide layer near the sediment surface and the concomitant

327 release of any adsorbed arsenic.[41] The porewater profiles of arsenic measured by Metsorb DGT

328 samplers (Figure S5, supplementary information), which are capable of accumulating both As(III) and

329 As(V), show similar profile shapes and arsenic concentrations to the As(III)-selective mercapto-silica

330 DGT profiles. Direct comparison between these two sampler types should be interpreted with caution,

331 as they were spatially separated during deployment. However, these results suggest that the majority of

332 mobilized porewater arsenic was most likely present as As(III), which is consistent with As(III) being

333 the major arsenic species accumulated in the overlying water during the anoxic phase (Figure 1a and
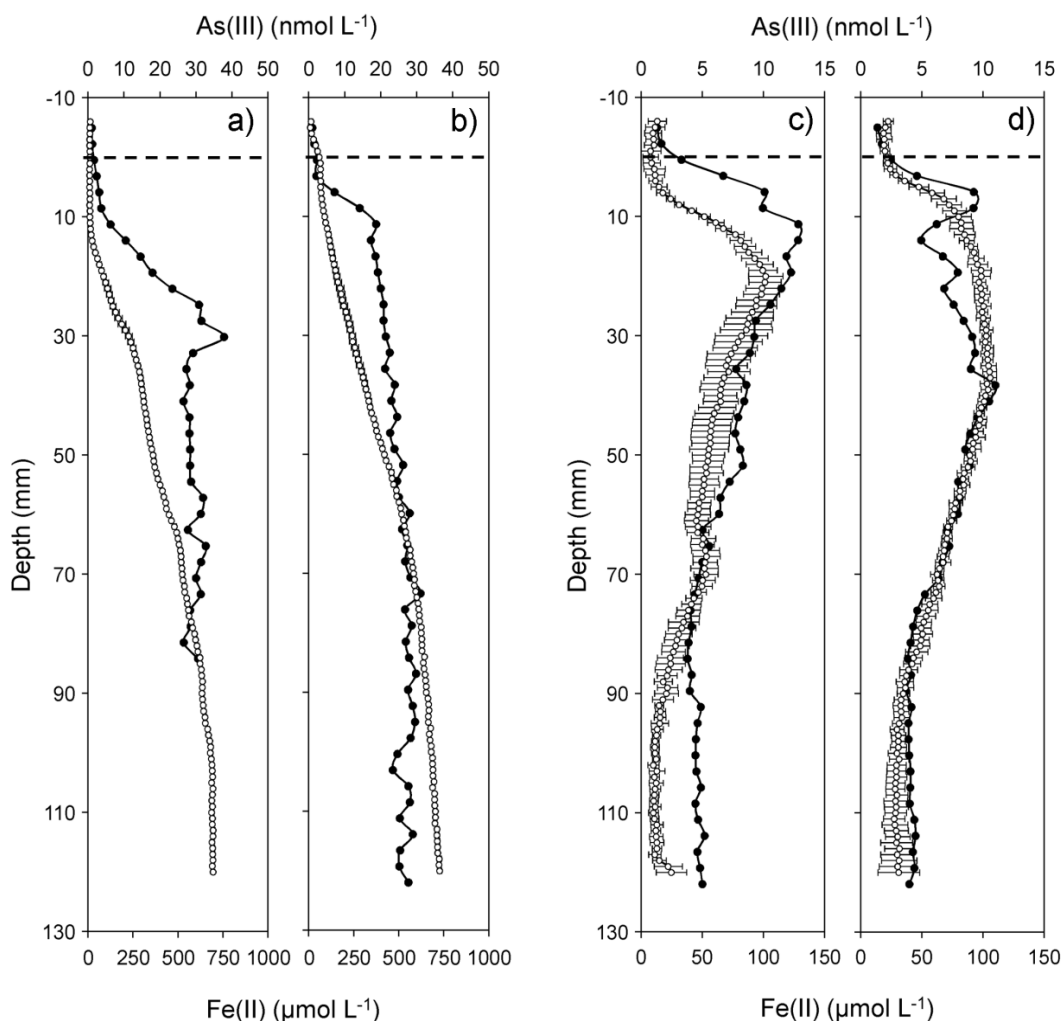
334 1b).

Figure 3. Co-distributed profiles of porewater Fe(II) (O) and As(III) (●) concentrations during anoxia, measured by colorimetric-DET and mercapto-silica DGT, respectively, for the following mesocosms: freshwater control (a), freshwater treatment (b), estuarine control (c) and estuarine treatment (d). Probes were deployed from Day 15–17 of the incubation. Error bars associated with the Fe(II) data indicate ± 1 standard deviation of the mean (n = 13).

Following reoxygenation of the treatment mesocosms the concentrations of Fe(II) and As(III) in the overlying water decreased rapidly (Figure 1). This was associated with the re-establishment of porewater profiles in the treatments somewhat similar to those in the control mesocosms, with no flux of Fe(II) or As(III) to the overlying water and the presence of increasing Fe(II) and arsenic in the suboxic zone of the sediment (Figure 4). Presumably, a layer of Fe(III) (hydr)oxide reformed on the surface and in the near-surface layer of sediment due to precipitation of Fe(III) (hydr)oxide from dissolved Fe(II) in

17

both the water-column and sediment porewater in the presence of oxygen. Porewater profiles measured

by Metsorb DGT samplers (Figure S6, supplementary information) showed similar profiles and

concentrations, although slight differences existed in the near-surface zone of the sediment. This was to

be expected when samplers are spatially separated, even in relatively homogenous sediment such as

those used in this study.

Figure 4. Co-distributed profiles of porewater Fe(II) ($\bigcirc$) and As(III) ($\bullet$) concentrations following reoxygenation, measured by colorimetric-DET and mercapto-silica DGT, respectively, for the following mesocosms: freshwater control (a), freshwater treatment (b), estuarine control (c) and estuarine treatment (d). Probes were deployed from Day 22–24 of the incubation. Some data is missing from (a) due to the gel being damaged during deployment or removal. Error bars associated with the Fe(II) data indicate ± 1 standard deviation of the mean (n = 13).

360

361   Correlations between porewater Fe(II) and As(III) in the top 20 mm of the freshwater sediment showed

362   a strong (r=0.962) and highly significant (p<0.001) relationship, confirming the coupling of reductive

363   dissolution of Fe(III) (hydr)oxide with the mobilization and release of As(III) from the sediment to the

364   overlying water. A significant correlation between Fe(II) and As(III) in the top 20 mm of the sediment

365   profiles also existed for the estuarine mesocosms (p<0.001) but the relationship was weaker (r=0.636).

366   It is interesting to note that in both Figure 3 and 4, the arsenic porewater concentration in the estuarine

367   mesocosm decreases with depth in the anoxic zone, while remaining relatively constant in the

368   freshwater mesocosm. This is likely due to the predominance of sulfate reduction in the anoxic zone of

369   the estuarine sediment, resulting in the sequestration of arsenic as sulfide and/or iron sulfide minerals.[9]

370   Conversely, sulfate reduction would be a minor pathway of organic matter mineralization in the

371   freshwater sediment and thus arsenic would remain in the aqueous phase. Correlation analysis was only

372   performed for the top 20 mm of sediment so that these additional sequestration processes did not

373   confound the investigation of the relationship between As and Fe.
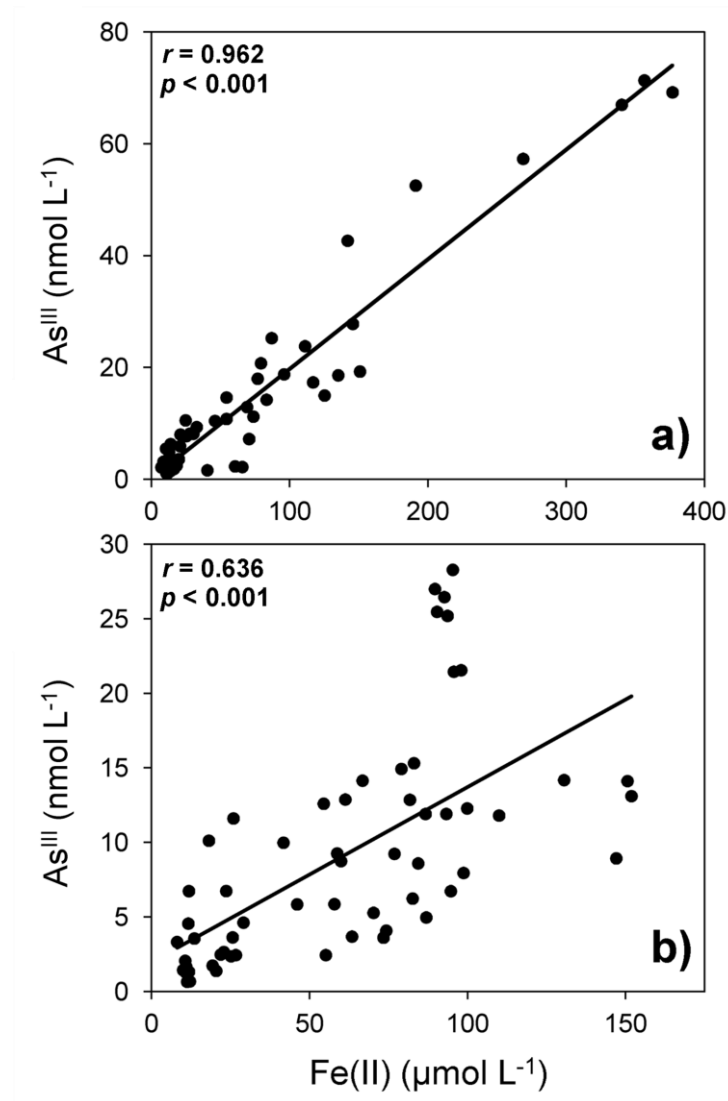
Figure 5. Correlation between porewater Fe(II) and As(III) concentrations for freshwater (a) and estuarine (b) mesocosms. Data for each correlation (n=60) consists of measurements taken from oxic and anoxic treatments from the top 20 mm of the porewater profiles.

Mechanisms of arsenic mobilization. Collectively our results support the dominant theory of reductive dissolution of Fe(III) (hydr)oxide minerals as the primary pathway for arsenic mobilization in sediments, as well as providing supporting evidence for findings that have shown that reduction of As(V) to As(III) plays a role in controlling arsenic mobility.[41, 45] The combination of water-column and sediment porewater sampling in this work suggested that As(III) was the predominant species of arsenic mobilized from the sediment during anoxia. In fact, the use of a selective As(III) porewater

385 measurement and a total As porewater measurement provides strong evidence for the absence of As(V)

386 mobilization to the porewater, suggesting that the majority of mobilized As must initially be present as

387 As(III) bound to the solid phase, or is generated in situ by reduction of As(V) to As(III) prior to release.

388 We also observed release of As(III) from the sediment to the water column prior to an increase in Fe(II),

389 indicating that As(III) mobilization was initially decoupled from Fe(III) reduction (Figures 1b).

390

391 Research in this area supports our findings. Tufano and co-workers[41] examined the effect of an iron-

392 reducing bacterium, *Shewanella* sp., which was genetically modified to be capable of either As(V)

393 reduction, Fe(III) (hydr)oxide reduction, or both, on the desorption of arsenic from Fe(III) (hydr)oxide

394 minerals. They found that treatments with exclusively arsenic-reducing *Shewanella* strains caused a

395 greater release of dissolved arsenic from ferrihydrite compared to treatments with strains of exclusively

396 iron-reducing or iron- and arsenic-reducing *Shewanella*,[41] indicating that *Shewanella* was able to

397 reduce iron-bound As(V) pools. This possibility of As(V) reduction whilst it is still adsorbed to solid

398 phase Fe(III) (hydr)oxides was also supported by Zobrist and co-workers[46] who demonstrated that

399 *Sulfurospirillum barnesii* was capable of reducing As(V) to As(III) whilst it was adsorbed onto the

400 surface of ferrihydrite, and that reductive dissolution of Fe(III) (hydr)oxides was not a necessary

401 precursor for adsorbed As(V) reduction.

402

403 However, determining the role that As(V) to As(III) reduction has in directly mobilizing arsenic is

404 complicated by the lack of solid phase speciation data and the possibility that additional processes, like

405 the competitive effects of carbonate for arsenic binding sites, may have contributed to arsenic

406 mobilization in this experiment. Further research should focus on combining the successful application

407 of the diffusive sampling techniques described in this work with the analysis of carbonate in porewaters

408 and the speciation of arsenic associated with the solid phase at different points throughout the oxic-

409 anoxic cycle. In addition, more frequent measurements throughout the oxic-anoxic transition should be

410   performed to more clearly observe the decoupling of As(III) mobilization from Fe(III) reduction in the

411   initial phases of anoxia within the sediment porewaters.

412

413   **Evaluation of diffusive sampling techniques for investigating arsenic mobility.** The mercapto-silica

414   DGT technique utilized in this study is unique in that it selectively measures As(III) at high spatial

415   resolution (~3 mm). The in situ nature of the technique, combined with the selectivity for the reduced

416   oxidation state, means that potential speciation changes associated with removing a sediment core and

417   extracting and analyzing porewater samples are entirely avoided. This is even more important when

418   considered in the context of potential oxidation of As(III) to As(V) and Fe(II) to Fe(III) during

419   porewater processing, confounding the study of redox chemistry and its relationship to arsenic mobility.

420

421   The As(III)-selective DGT technique, combined with the advantages of using homogenised mescososms

422   in a well-controlled experimental system, have allowed us to confirm some detailed aspects of As

423   mobilization. This may not have been possible with more traditional approaches to porewater sampling

424   that rely on the extraction of sediment and subsequent processing steps, each of which introduces

425   uncertainty into measurements of As speciation.

426

427   When the mercapto-silica DGT technique is combined with the colorimetric DET technique for Fe(II),

428   co-distributions of both As(III) and Fe(II) can be measured at the same spatial location within the

429   sediment, effectively eliminating artifacts associated with the heterogeneous distribution of analytes

430   within sediments and their porewaters.[27, 29] While we have used homogeneous sediments to avoid the

431   many complications of interpretation that are inevitable in heterogeneous sediments, these general

432   techniques have been demonstrated to provide highly representative measurements in heterogeneous

433   sediments too.[27, 29, 38] This is because the diffusive techniques only sample a very small volume of

434   porewater, typically on the order of tens of microliters, resulting in an extremely high volumetric

435   resolution that allows assessment and interpretation of mechanistic interactions between solutes.[47, 48]

436   These techniques can also be deployed for much shorter times than other in situ porewater samplers.[49]

437   This is in contrast to traditional porewater sampling techniques that typically extract several milliliters

438   of sample or more, which upon mixing results in the averaging of chemical profiles and the potential

439   confounding of relationships between various chemical species.[24, 28, 50] In the case of Fe(II) and arsenic,

440   the homogenization of sediment porewater extracted from cores could result in a number of artifacts: (i)

441   Fe(II) could be oxidized to Fe(III) (hydr)oxide, thus forming a sink for dissolved arsenic; (ii) As(III)

442   could be oxidized to As(V), confounding the effect of redox state on arsenic mobility; and (iii) dissolved

443   sulfide that was spatially separated in the heterogeneous sediment matrix could precipitate with Fe(II) or

444   arsenic to form insoluble sulfide minerals or chemically reduce Fe(III) (hydr)oxides resulting in

445   accumulation of both Fe(II) and previously adsorbed arsenic. The best way in which to avoid these

446   potentially confounding chemical interactions is by the use of high resolution in situ sampling methods

447   such as the DET and DGT samplers employed in this study.

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455

456   **Supporting Information Available**

457   This information is available free of charge via the Internet at http://pubs.acs.org.

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