Impact of sulfate reduction on the scale of arsenic contamination in groundwater of the Mekong, Bengal and Red River deltas

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34 **Abstract**

35 Arsenic contamination of groundwater is a pressing human health issue since more than

36 a decade, with tens of millions of people worldwide being at risk of chronic arsenic

37 poisoning through the consumption of arsenic-burdened groundwater. To elucidate the

38 importance of dissolved sulfur on the scale of arsenic concentrations, we assessed the

39 composition of groundwater samples from 926 locations spanning over the floodplains

40 of three severely arsenic affected regions in Asia (Bengal-, Mekong-, Red River deltas).

41 A binary mixing model based on chloride or boron as conservative tracers implies that

42 two types of water may be regarded as end-members with respect to groundwater

43 composition in these deltas, namely surface derived water (approximated by river water)

44 and saline water identical to residual sea water. Six redox zones were distinguished by

45 comparing the model-calculated sulfate concentrations with the measured values. Only

46 one zone (denoted methanogenic) had very high average arsenic concentrations and

47 they were significantly higher than in the other zones - for all three regions and

48 regardless of applying chloride or boron as a tracer in the model. Average arsenic

49 concentrations ± standard error in the methanogenic zone were 182 ± 23 μg L^{-1} (n =

50 50%), 41 ± 6 μg L^{-1} (n = 43%), and 61 ± 20 μg L^{-1} (n = 24%) in the Mekong, Red River

51 and Bengal delta, respectively. Arsenic levels were significantly lower in the sulfate-

52 reducing and the iron-reducing zones, where averages did not exceed 23 ± 7 μg L^{-1} (n =

53 27%, zone I), 14 ± 3 μg L^{-1} (n = 48%, zone S) and 26 ± 9 μg L^{-1} (n = 64%, zone S).

54 These results suggest that a sufficient supply of sulfate inhibits the release of arsenic to

55 groundwater and that sulfate reduction may be as important as iron reduction in

56 controlling the enrichment of arsenic in groundwater.

57

1. INTRODUCTION

More than 100 million people worldwide ingest excessive amounts of arsenic through groundwater contaminated from natural geogenic sources. People in Bangladesh, India, Vietnam and Cambodia have been reported to be suffering from skin lesions and arsenicosis caused by chronic arsenic poisoning (Chowdhury et al., 2000; Smith et al., 2000; Berg et al., 2006; Buschmann et al., 2008; Polya et al., 2005, 2008; Sampson et al., 2008). Other Asian countries affected by elevated arsenic levels in drinking water resources include China (Smedley et al., 2003; Guo et al., 2008), Myanmar (Winkel et al., 2008a), Nepal (Shrestha et al., 2003), Pakistan (Nickson et al., 2005) and Sumatra, Indonesia (Winkel et al., 2008b).

It is widely accepted that reductive dissolution of sedimentary iron phases, driven by metal reducing bacteria and the presence of natural organic matter, is important with respect to arsenic mobilization (Nickson et al., 1998; McArthur et al., 2001; Berg et al., 2001; Harvey et al., 2002; Islam et al., 2004; Rowland et al., 2007). Depending on the environmental conditions, sulfur can also have an important influence on the arsenic speciation and concentration because arsenic levels are controlled by the rate of microbially mediated sulfate reduction (Jong and Parry, 2003; Kirk et al., 2004), the solubility of (arsenic) sulfide phases and/or the adsorption processes to sulfide minerals (Wolthers et al., 2003; Bostick et al., 2005; Roman-Ross et al., 2005; Keimowitz et al., 2007; Lowers et al., 2007). Solid phases such as $FeAsS$ (arsenopyrite), As_2S_3 (orpiment), AsS (realgar) or amorphous arsenic-sulfide phases are formed (O'Day et al., 2004; Kober et al., 2005; Eiche et al., 2008) and removal of arsenic by adsorption onto FeS (mackinawite) and partitioning into FeS_2 (pyrite) have been reported (Wolthers et al., 2003; Lowers et al., 2007). Therefore, the speciation and concentration of sulfur could be tightly coupled with the magnitude of dissolved arsenic.

Like arsenic, sulfur is a redox sensitive element. In its oxidized form, sulfate may precipitate as $CaSO_4$, $BaSO_4$, and other sulfate minerals (evaporite deposits (Bottrell and Newton, 2006)). An important removal process of sulfate from the ocean to marine sediments is bacterial reduction of sulfate (Bottrell and Newton, 2006). Microbially or chemically reduced to S(-II), sulfide may precipitate as MnS, FeS and FeS_2 (pyrite, slow formation) (Wilkin and Ford, 2006) or form organo-sulfur compounds (Hesterberg et al., 2001). The pyrite sulfur is assumed to be the predominant sink for bacteriogenic

92   reduced sulfur in marine sediments (Bottrell and Newton, 2006). Depending on the pH

93   value and the SO_4^{2-}/Fe(III) ratio, bacteria may favour sulfate over iron as terminal

94   electron acceptor (redox buffer) (Postma and Jakobsen, 1996). Moreover, sulfide may

95   be re-oxidized to intermediate sulfur species such as S^0, $S_2O_3^{2-}$, SO_3^{2-} which are known

96   to be microbially disproportionated, thereby decreasing the sulfide concentration and

97   retarding the follow-up processes (Habicht and Canfield, 2001). Previous studies

98   assessed the sulfur-arsenic geochemistry at various field sites (O'Day et al., 2004;

99   Zheng et al., 2004; Polizzotto et al., 2005). Jessen et al. (2008) showed dropping arsenic

100 concentrations with increasing amounts of missing sulfate (difference between

101 measured and seawater derived sulfate) in a transect tapping Holocene and Pleistocene

102 aquifers.

103

104 In our study, we provide a simple approach that defines zones of varying redox

105 conditions significantly indicative of low and high risk of arsenic enrichment in

106 groundwater. The impact of sulfur on the magnitude of dissolved arsenic is evaluated

107 over large areas, namely the Mekong, Red River and Bengal delta floodplains (Figure

108 1). By applying a binary mixing model of surface derived water (approximated by river

109 water) and residual sea water to these deltaic groundwater data sets, it can be concluded

110 that (i) saltwater identical to sea water significantly contributes to the groundwater

111 composition in these river deltas (anthropogenic impacts and rainwater seem to be

112 negligible) and (ii) reduced or precipitated sulfate (in this study called "missing sulfate")

113 together with the actual sulfate concentration play a central role in the magnitude and

114 distribution of arsenic. The model is based on either the actual chloride or boron

115 concentration (conservative tracers) and the measured sulfate and iron concentrations of

116 the groundwater.

117

118

119 **2. MATERIALS AND METHODS**

120

121 **2.1. Groundwater data sets and study areas**

122 Comprehensive groundwater data of 926 samples from the Mekong, the Red River and

123 the Bengal deltas were evaluated by the application of a binary mixing model. These

124 groundwater samples represented a broad range of chemical compositions, i.e. from

125 oxic to highly reducing and from low to high mineralization characteristics (Total

126 Dissolved Solids, TDS range: 0 - 17.9 g L^{-1}; [As]: 0 - 1340 µg L^{-1}; [Fe]: 0.1 - 55.8 mg

127 L^{-1}; [Mn]: 0 - 33.5 mg L^{-1} and [SO_4^{2-}]: 0.02 - 1020 mg L^{-1}). The Mekong delta data set

128 included 352 samples collected over areas of ≈ 6000 km^2 in Cambodia (240 samples)

129 and ≈ 2000 km^2 in Southern Vietnam (112 samples) (Buschmann et al., 2007;

130 Buschmann et al., 2008). In the model calculation of the Mekong delta, 41 samples

131 were omitted due to i) excessive salinity (E_c >3000 µS cm^{-1}, TDS >1.8 g L^{-1}) which

132 prevents the use as drinking water (Buschmann et al., 2007), and ii) to avoid skew of

133 the statistics caused by very high sulfate levels in these samples. The data from the Red

134 River delta consisted of 461 groundwater samples that were derived from a survey

135 covering an area of 11,000 km^2 (manuscript in preparation). Groundwater samples in

136 the Red River delta were collected and analyzed as described in detail elsewhere (Berg

137 et al., 2007; Berg et al., 2008). The third data set was from the British Geological

138 Survey (BGS and DPHE, 2001) and included 113 samples (with chloride analysis)

139 evenly spread over the country of Bangladesh. The BGS data comprises 3,531 samples

140 with boron measurements (no chloride analysis).

141

142 **2.2. Statistical Analysis**

143 For the redox zones established by the binary mixing model, statistical analysis of

144 variance (ANOVA) was conducted. In order to explicitly test the significance of

145 differences, pairwise comparison probabilities (*p*) were calculated for As, Fe, Mn, DOC

146 and sulfate and for each pair of zones (Mekong delta data set) using the Bonferroni

147 adjustment (http://www.statistics.com/resources/glossary/b/bonfadj.php).

148

149

150 **3. MIXING MODEL**

151 Chloride is among the most conservative of dissolved constituents in groundwater

152 (Bertin and Bourg, 1994; Hendry et al., 2000) which makes it a suitable tracer in

153 groundwater mixing models (Bourg and Bertin, 1993). In our study, the chloride

154 concentration was used as a reference for the estimation of the SO_4^{2-} concentration that

155 could be expected in the groundwater, [SO_4^{2-}]$_{theoretical}$, if (i) the groundwater consisted of

156 the same fractions of river and sea water as chloride concentrations suggest in a binary

157 mixture and (ii) SO_4^{2-} behaved as conservative as Cl^- (including the assumption of same

158 migration rates). Our calculations are based on surface derived freshwater composition,

159 where the average Cl^- concentration after infiltration of rain, lake and river water is very

160 similar to river water ($\approx$ 5.8 mg L^{-1}, (Galy and France-Lanord, 1999)), and salt water

161 identical to sea water for which the average Cl^- concentration is $\approx$ 19,500 mg L^{-1}

162 (Stumm and Morgan, 1981). The same procedure was applied with boron as a

163 conservative tracer (boron river concentration $\approx$ 6 μg L^{-1} (Buschmann et al., 2007) and

164 sea water concentration $\approx$ 4,400 μg L^{-1} (Stumm and Morgan, 1981)).

165

166 The fraction of river water infiltration (x) is based on the assumption that groundwater

167 in the selected river deltas is dominantly composed by a combination of river water and

168 (residual) sea water. It may be argued that in a monsoon dominated area, infiltration of

169 rain water should be considered as a separate supply of groundwater; however, the

170 results of the model verified the assumption of a binary mixture (surface derived water

171 and sea water). Possible anthropogenic chloride inputs were not considered in the

172 calculation. The fraction of river water (x) was calculated by equation 1 (Schreiber and

173 Mitch, 2006):

174

175 $$[Cl^-]_{actual} = x \cdot [Cl^-]_{river} + (1 - x) \cdot [Cl^-]_{sea} \qquad \text{(eq. 1)}$$
176

177 The fraction of sea water is 1-x. Based on this calculation, the theoretical sulfate

178 concentration was calculated (with x derived from equation 1) by equation 2:

179

180 $$[SO_4^{2-}]_{theoretical} = x \cdot [SO_4^{2-}]_{river} + (1 - x) \cdot [SO_4^{2-}]_{sea} \qquad \text{(eq. 2)}$$
181

182 where the average sulfate concentration in river water is $\approx$ 5 mg L^{-1} (Galy and France-

183 Lanord, 1999) and in sea water $\approx$ 2,700 mg L^{-1} (Stumm and Morgan, 1981). Similar

184 sulfate concentrations are found in the Ganges River (6.7 mg L^{-1}, (Galy and France-

185 Lanord, 1999)), the Mekong River ($\approx$ 5 mg L^{-1}, (Buschmann et al., 2007)) and in the

186 Red River (5.9 mg L^{-1}, (Berg et al., 2008)).

187

188 Our model is based on the comparison of the actual sulfate concentration and the

189 theoretical one. As the SO_4^{2-} species is not as stable and conservative as chloride, due to

190 its redox sensitivity and various complexation or precipitation processes, the actual and

191 the theoretical sulfate level may differ significantly. Firstly, three groups are classified

192 as depicted in Figure 2, namely (i) where $[SO_4^{2-}]_{actual} < [SO_4^{2-}]_{theoretical,}$ which can be

193   attributed to reduction of sulfate and precipitation processes and (ii) where $[SO_4^{2-}]_{actual}$ =

194     $[SO_4^{2-}]_{theoretical}$ (no overall SO_4^{2-} sinks) and (iii) where $[SO_4^{2-}]_{actual} > [SO_4^{2-}]_{theoretical}$

195   implying additional sources of SO_4^{2-} besides river or sea water.

196

197   Secondly, these three groups are split further: The wells where $[SO_4^{2-}]_{actual} < [SO_4^{2-}]_{theoretical}$

198     $]_{theoretical}$ were classified *sulfate-reducing* if they still had measurable SO_4^{2-} which is a

199   prerequisite for sulfate reduction (Kirk et al., 2004) or *methanogenic* if no SO_4^{2-} was

200   detectable (Figure 2). The wells with $[SO_4^{2-}]_{actual} = [SO_4^{2-}]_{theoretical}$ were classified *iron-*

201   *reducing* if the Fe concentration was > 0.2 mg L^{-1} and *neither iron- nor sulfate-reducing*

202   if Fe < 0.2 mg L^{-1}. The wells with more SO_4^{2-} than estimated were treated in the same

203   way as wells with $[SO_4^{2-}]_{actual} = [SO_4^{2-}]_{theoretical}$. The additional sulfate, however, is

204   attributed to other sources than river or sea water. Groundwater with excess sulfate and

205   *iron-reducing* conditions might possibly result from evaporation before recharge

206   (Allison and Hughes, 1978) or from transport processes along flow paths inducing

207   different transport velocities for sulfate and chloride, respectively (De Jonge and

208   Rothenberg, 2005). Groundwater with excess sulfate and *neither iron- nor sulfate-*

209   *reducing* conditions may indicate pyrite oxidation (Smedley and Edmunds, 2002). The

210   impact of anthropogenic contamination such as $SO_2(g)$, domestic waste or $CaSO_4$ in

211   plaster of house building seems to be negligible compared to the main SO_4^{2-} sources

212   from rocks and residual sea water.

213

214

215   **4. RESULTS AND DISCUSSION**

216

217   **4.1. Comparison of chloride and boron as conservative tracers**

218   Although boron is more reactive than chloride with respect to surface sorption and pH

219   sensitivity, it is often applied as a conservative tracer as well (Schreiber and Mitch, 2006).

220   The three data sets were therefore analyzed on the basis of chloride and additionally of

221   boron as conservative tracers in order to test whether the results of the binary mixing model

222   were identical. Generally, the two tracers gave the same results (Appendix Table A1) with

223   respect to average concentrations for the zones established. Only some cases differed

224   significantly in the calculated average concentrations of $[SO_4^{2-}]_{theoretical}$, with 14%, 11% and

225   3% of the data from the Bengal, the Red River and the Mekong delta, respectively. The

226 differences may be explained by variable degrees of aquifer flushing by surface derived

227 freshwater in the three deltas. Whereas the groundwater samples from the Mekong delta

228 and the Red River delta are both partly freshwater flushed and partly intruded by saline

229 water (Figures 3 a-d), the samples from Bangladesh are clearly dominated by freshwater

230 flushing (Figure 3e).

231

232 Freshwater flushing causes boron desorption due to the lower ionic strength and lower pH

233 compared to sea water (Ravenscroft and McArthur, 2004). Elevated boron concentrations

234 caused by desorption lead to higher levels of $[SO_4^{2-}]_{theoretical}$. If this is predominantly the

235 case in the Bengal delta, differences in sample attribution to redox zones are expected when

236 taking boron instead of chloride as a conservative tracer, which is confirmed by the model.

237 Apart from these exceptions where theoretical sulfate concentrations differ, both

238 conservative tracers, chloride and boron, give results that are in good agreement (Appendix

239 Table A1).

240

241 **4.2. Application of the model**

242 Average concentrations and standard errors of arsenic, iron and sulfate are shown for the

243 six redox zones, the three river deltas and the calculation based on either chloride or boron

244 in Figure 4a-c. For all three data sets analyzed, significantly higher As levels than in the

245 other zones occur in zone M under *methanogenic* conditions, accompanied by high Fe, low

246 Mn and high DOC levels (see Table 1 and Table 2 for statistical results). Average arsenic

247 concentrations ± standard error in the methanogenic zone were 182 ± 23 µg L^{-1} (n = 50%),

248 41 ± 6 µg L^{-1} (n = 43%), and 61 ± 20 µg L^{-1} (n = 24%) in the Mekong, Red River and

249 Bengal delta, respectively. Arsenic levels were significantly lower in the sulfate-reducing

250 and the iron-reducing zones, where averages did not exceed 23 ± 7 µg L^{-1} (n = 27%, zone I),

251 14 ± 3 µg L^{-1} (n = 48%, zone S) and 26 ± 9 µg L^{-1} (n = 64%, zone S). According to the

252 literature, iron-reducing conditions are often declared indicative for high levels of As due to

253 the reductive dissolution of iron(hydr)oxides and the release of surface-bound As (Nickson

254 et al., 1998; McArthur et al., 2001). In the classification here, As does not accumulate to

255 concentrations many times the WHO guideline under *iron-reducing* conditions (zones I and

256 I'), although the usual indices accompanying these conditions such as high DOC and high

257 Fe levels are confirmed (Figure 4b and Table 1). There seem to be still enough solid phase

258 hosts such as carbonates (Akai et al., 2004), silicates, sulfates and remaining

259   iron(hydr)oxides for the (re)sorption of arsenic (Roman-Ross et al., 2002; Postma et al.,

260   2007). This is in accordance with recent studies investigating the arsenic mobilization under

261   iron reducing conditions: (i) arsenic may be retained by evolving new precipitates that

262   incorporate As and iron (Bostick et al., 2004; Herbel and Fendorf, 2006), (ii) the sorption

263   density of As(III) on iron oxide phases increases with increasing $Fe_{(aq)}$ (Dixit and Hering,

264   2006) and (iii) reductive dissolution of As-bearing ferrihydrite can promote As

265   sequestration rather than desorption (Kocar et al., 2006). These laboratory studies are

266   supported by the findings of a recent field study in the area of Hanoi, Vietnam (very high

267   Fe levels accompanied by moderate As levels) (Berg et al., 2008). In Figure 5a it is shown

268   that although Fe levels under *iron-reducing* conditions are high, arsenic levels are moderate

269   on average. Field observations show that groundwater in contact with reduced (grey)

270   sediments can be low in dissolved arsenic (van Geen et al., 2008). Very high arsenic

271   concentrations (>200 µg L^{-1}, corresponding to >20 times the WHO guideline value of 10 µg

272   L^{-1}) were found predominantly in the group classified *methanogenic*. Figures 5b and 5b'

273   (extended graph) show a plot of $[SO_4^{2-}]_{actual}/[SO_4^{2-}]_{theoretical}$ versus dissolved Fe

274   concentration for a better visualization of the zones' conditions. Such a graph is a useful

275   scheme for a quick evaluation to estimate if a groundwater well is at risk of arsenic

276   contamination.

277

278   As observed in several field studies for marine and lake sediments as well as for aquifers,

279   the bacterial iron reduction seems to continue and occur simultaneously to the sulfate

280   reduction and to the methanogenesis as long as iron(III) in solids is bioavailable (Postma

281   and Jakobsen, 1996; Washington et al., 2004). Whereas iron concentrations increase in iron

282   reducing zones due to dissolution of iron(hydr)oxides, they decrease in sulfate reducing

283   zones most probably due to precipitation of FeS (Wolthers et al., 2005; Lowers et al., 2007)

284   and increase in *methanogenic* zones caused by Fe(III) reduction and the absence of further

285   sulfide generation. In the Red River delta, this effect is not observed due to very high iron

286   concentrations (see Table 1). Here, the Fe/S ratio is obviously too high for significant iron

287   removal by FeS precipitation (O'Day et al., 2004). In the *sulfate reducing* zone, arsenic

288   concentrations are at low levels probably either due to sorption to evolving amorphous

289   mackinawite, FeS (Wolthers et al., 2003) or caused by precipitation of amorphous arsenic

290   sulfide phases (Kober et al., 2005).

291

4.3 Manganese

In contrast, manganese, a second important contaminant in Asian groundwater (Wasserman et al., 2006; Buschmann et al., 2008), accumulates from under *neither iron- nor sulfate-reducing*, to *iron-reducing* and to *sulfate-reducing* conditions (see Table 1), probably caused by the higher solubility of MnS compared to FeS (Weast, 1988). Only in the late stage of *sulfate-reducing* conditions where iron becomes limited but a residual pool of dissolved sulfide is still available (HS$^-$(aq) > Fe(aq)) does Mn^{2+}(aq) precipitate and form MnS (Weast, 1988; Bottcher et al., 1998). This is confirmed by the analysis of the Mekong data: concentrations of Mn increase from redox zones N (0.7 mg L^{-1}), to I (1.0 mg L^{-1}) and peak under sulfate-reducing conditions (2.8 mg L^{-1}). They are low again under methanogenic conditions (0.7 mg L^{-1}). However, for the Bengal delta and the Red River delta, no significant trend with respect to Mn was apparent. In these two deltas, the Fe/S ratio is higher compared to the Mekong delta and Mn concentrations are smaller on average, which hinders such trends from being observed. Due to the high Fe/S ratio the situation of HS$^-$(aq) > Fe(aq) is unlikely to occur and in the competing precipitation processes of FeS and MnS, FeS precipitation will dominate.

4.4. Implications

The results of the binary mixing model applied to the comprehensive groundwater data sets of three large river deltas in South and South East Asia imply that two end-members of water types may be regarded as dominant with respect to groundwater composition: (i) surface derived freshwater (approximated by river water) and (ii) salt water identical to sea water. Samples containing more sulfate than calculated with the model amounted to 27%, 18% and 13% of the Mekong, Red River and Bengal delta samples, respectively, which is explained by additional sources such as transport processes along preferential flow paths, pyrite oxidation or evaporation before recharge (see Mixing Model in section 2). The three river deltas have several features in common, such as, e.g., river drainage from rapidly weathering mountain ranges, buried natural organic matter, young Holocene aquifers and very low basin-wide hydraulic gradients (Charlet and Polya, 2006; Amini et al., 2008; Winkel et al., 2008a). The same trends of arsenic magnitudes in the zones classified according to the mixing model are found, even though anthropogenic activities may have affected arsenic contamination due to extensive groundwater abstraction for irrigation in Bangladesh (Roberts et al., 2007), or for urban water supply in Vietnam (Berg et al., 2008), but not so in Cambodia (Polizzotto et al., 2008). The impact of rainwater and anthropogenic

326   waste has been omitted in this model. The results show, however, that their impact is

327   negligible compared to the main sulfate sources such as rock weathering and residual saline

328   water (Penny, 2006). But the fraction of sea water in the groundwater has to be considered

329   significant, with averages of 0.7%, 0.06% and 1.8% for the Mekong, the Bengal and the

330   Red River delta, respectively (medians: 0.06 ‰, 0.13 ‰ and 0.44 ‰).

331

332   The second important finding is that very high arsenic levels (>200 µg L^{-1}) are almost

333   exclusively found in the zone classified *methanogenic* (zone **M**), with 100%, 98% and 95%

334   in the Mekong, the Red River and the Bengal delta, respectively.

335

336   The results of our model show that arsenic levels are only very high if (a) there is not a lot

337   of sulfate missing (up to 10-20 mg L^{-1}) and (b) the actual sulfate level is below detection

338   limit (<0.3 mg L^{-1}). Nevertheless, the absence of sulfate alone is not a reliable indicator for

339   high arsenic levels because it may be that former high levels of sulfate were reduced and

340   arsenic may have been sequestered by processes based on sulfide. Therefore, both low

341   "missing sulfate" and low actual sulfate are important prerequisites for very high arsenic

342   levels.

343

344   Under *sulfate-reducing* conditions where sulfate is detectable (accompanied by rather low

345   Fe, DOC and ammonia compared to the *methanogenic* zone), simultaneous Fe(III)

346   reduction leads to the formation of FeS which is commonly found in equilibrium with HS$^-$

347   at neutral pH (Postma and Jakobsen, 1996). Re-adsorption and/or incorporation of

348   sediment-released arsenic onto remaining iron(hydr)oxides, mackinawite, FeS, or other

349   evolving mineral-sulfide phases can be regarded as responsible for low As levels. Thus, the

350   risk for high As levels (>200 µg L^{-1}) seems to be low even under proceeding dissolution of

351   iron(hydr)oxides because of the continuing and overall dominating sulfide production and

352   its follow-up precipitation processes. A graph of "missing sulfate" versus As levels

353   confirms this assertion: if a lot of sulfate is "missing", low arsenic concentrations are

354   present in the aqueous solution, provided that there is enough dissolved sulfate present for

355   on-going sulfate reduction (Figure 6).

356

357   When the amounts of "missing sulfate" present in the *methanogenic* and the *sulfate-*

358   *reducing* zones were compared, it was observed that "missing sulfate" levels in zone **M** (1-

359   10 mg L^{-1}) are small compared to zone **S** (10-200 mg L^{-1}). Thus both, a lot of missing

360   sulfate and ongoing sulfate reduction are important requirements for arsenic levels to

361   remain low.

362

363

364   **5. SUMMARY AND OUTLOOK**

365   On the basis of a binary mixing model, the actual sulfate level can be compared to a

366   theoretically determined one, and, using Fe concentrations in addition, be an indicator of

367   the redox environment of the corresponding groundwater and finally of the risk for high

368   arsenic levels. Application of the model to three large river delta data sets shows that both

369   low levels of calculated "missing sulfate" and low actual dissolved sulfate are prerequisites

370   that arsenic may accumulate to high levels. Thus, the reductive dissolution of

371   iron(hydr)oxides seems not the only important mechanism for the enrichment of arsenic in

372   groundwater. Our model even implies that more arsenic is released under methanogenic

373   conditions compared to iron reducing conditions. A sufficient supply of sulfate will inhibit

374   the release of arsenic to groundwater than would be expected on the basis of (often) high

375   dissolved iron. Our findings may stimulate analogous studies that establish similarities and

376   differences across the Asian region and help better understand the processes influencing the

377   magnitude of arsenic enrichment in groundwater.

378

379

387

388

389   **Appendix A. Table A1**

390   (insert Table A1 here)

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598

599 **Figures Captions**

600

601 **Figure 1.** Map of the Bengal delta and the major floodplains of Southeast Asia. The

602 investigated regions of the Mekong delta (Cambodia and Vietnam), the Red River delta

603 (Vietnam) and Bangladesh are highlighted with hatched shapes. Further arsenic affected

604 regions on this map are West Bengal, India (Chowdhury et al., 2000) and the Irrawaddy

605 delta, Myanmar (Winkel et al., 2008a). The Chao Phraya basin is at low risk (Winkel et

606 al., 2008a).

607

608 **Figure 2.** Flow chart of the six redox zones grouped according to their actual sulfate

609 concentration compared to the theoretical one.

610

611 **Figure 3.** a), b) and c) log [Na] versus log [Cl] for the Mekong, the Red River and the

612 Bengal delta data set. d) and e) log [B] versus log [Cl] for the Red River and the Bengal

613 delta. The evaluation of freshwater or saline water intrusion is based on the binary

614 mixing line (red line). The red points denote 0.01‰, 0.1‰, 1‰, 1%, 10%, 100%

615 seawater. Blue dashed lines show absolute errors of 5 mg L^{-1} Na and 3 μg L^{-1} B,

616 respectively, whereas black dashed lines show a relative error of 30%.

617

618 **Figure 4.** Average arsenic, iron and sulfate concentrations for the six zones calculated

619 with the binary mixing model (values from Table A1). Vertical lines indicate standard

620 errors. Redox zones are denoted as defined in Figure 2. See Table 2 for statistical

621 comparison.

622

623 **Figure 5.** a) Arsenic concentration versus iron concentration in the groundwater

624 samples of the Mekong delta (redox zones classified based on chloride as tracer). b) and

625 b') $[SO_4^{2-}]_{actual}$ / $[SO_4^{2-}]_{theoretical}$ versus iron concentration for visualization of the zones'

626 conditions. Note: Fe level range in b) was cut off at 3 mg L^{-1}. Zones I and I' as well as

627 zones N and N' were combined because only 27%, 13% and 18% of the Mekong,

628 Bengal and Red River Delta, respectively, had $[SO_4^{2-}]_{actual}$ > $[SO_4^{2-}]_{theoretical}$. Redox

629 zones are denoted as defined in Figure 2.

630

631 **Figure 6.** Missing sulfate versus arsenic concentrations in the Mekong delta, Red River

632 delta and Bangladesh.

633

634 **Tables**
635

636 **Table 1.** Average concentrations (arithmetic mean) and standard error of groundwater parameters of
637 the Mekong delta (n=311), the Bengal delta (Bangladesh, n=113) and the Red River delta (n=461)
638 classified according to Figure 2. Zones I and I' were combined as well as zones N and N', because
639 only 27%, 13% and 18% of the Mekong, Bengal and Red River delta, respectively, had $[SO_4^{2-}]_{actual} > [SO_4^{2-}]_{theoretical}$. Results are given for the calculation based on chloride as conservative tracer.
641 Statistical analysis of variance, ANOVA, and pairwise comparison are given in Table 2 for the
642 Mekong delta. The results for the calculation based on boron as conservative tracer are summarized
643 in Appendix A (Table A1).
644

Parameter	*Methanogenic* (zone **M**)			*Sulfate-reducing* (zone **S**)		
(unit mgL^{-1} except As in µgL^{-1})	Mekong delta (n=50%)	Bangladesh (n=24%)	Red River delta (n=43%)	Mekong delta (n=18%)	Bangladesh (n=55%)	Red River delta (n=36%)
As	182 ± 23	61 ± 20	41 ± 6	14 ± 6	26 ± 9	14 ± 3
Fe	4.10 ± 0.57	3.0 ± 0.8	15.2 ± 1.6	0.76 ± 0.28	1.5 ± 0.4	9.0 ± 1.4
SO₄	<0.3	<0.01	0.11 ± 0.01	15 ± 1.5	5.0 ± 1.5	15 ± 2.1
Mn	0.65 ± 0.21	0.62 ± 0.23	0.8 ± 0.1	2.78 ± 0.65	0.43 ± 0.07	1.0 ± 0.2
DOC	3.38 ± 0.3	no data	3.2 ± 0.20	<2.0 ± 0.37	no data	5.7 ± 0.60
NH₄-N	6.69 ± 0.8	4.6 ± 1.7	7.5 ± 1.1	2.53 ± 0.49	0.43 ± 0.20	7.7 ± 1.1
PO₄-P	0.63 ± 0.07	1.55 ± 0.31	0.51 ± 0.04	0.13 ± 0.03	1.81 ± 0.56	0.51 ± 0.08
HCO₃	317 ± 14	337 ± 36	188 ± 11	258 ± 27	244 ± 21	303 ± 24

645

Parameter	*Iron-reducing* (zone **I**)			*Neither iron- nor sulfate red.* (zone **N**)		
(unit mgL^{-1} except As in µgL^{-1})	Mekong delta (n=11%)	Bangladesh (n=9%)	Red River delta (n=12%)	Mekong delta (n=21%)	Bangladesh (n=12%)	Red River delta (n=9%)
As	23 ± 7	13 ± 11	8.5 ± 3.2	7.0 ± 2.5	3.2 ± 1.4	1.3 ± 0.4
Fe	4.34 ± 1.0	4.5 ± 3.3	9.5 ± 1.7	0.04 ± 0.01	0.06 ± 0.02	0.01 ± 0.01
SO₄	85 ± 29	37 ± 25	71 ± 16	55 ± 8	34 ± 9.5	50 ± 9
Mn	1.00 ± 0.22	0.60 ± 0.22	0.80 ± 0.10	0.70 ± 0.11	0.54 ± 0.17	0.50 ± 0.10
DOC	4.25 ± 1.68	no data	3.8 ± 0.40	1.68 ± 0.16	no data	1.9 ± 0.50
NH₄-N	2.51 ± 0.69	0.25 ± 0.25	2.5 ± 0.5	0.55 ± 0.15	0.04 ± 0.00	1.6 ± 0.5
PO₄-P	0.41 ± 0.11	0.54 ± 0.21	0.35 ± 0.08	0.11 ± 0.03	0.77 ± 0.61	0.17 ± 0.07
HCO₃	388 ± 33	153 ± 37	242 ± 23	352 ± 29	311 ± 39	247 ± 40

646
647

648 **Table 2.** Statistical analyses of variance (ANOVA) for the four redox zones described in the
649 manuscript. (Zones I and I' as well as zones N and N' were combined.) Pairwise comparison
650 probabilities (p) are given for each pair of redox zones applying the Bonferroni adjustment (Systat
651 11). P values <0.0005 are denoted 0.000. **M** = methanogenic, **S** = sulfate-reducing, **I** = iron-
652 reducing, **N** = neither iron- nor sulfate reducing.

653

654 a) Mekong Delta

Parameter	Comparison of redox zones					
	M and **S**	**M** and **I**	**M** and **N**	**S** and **I**	**S** and **N**	**I** and **N**
As (aq)	0.000	0.000	0.000	1.000	1.000	1.000
Fe (aq)	0.001	1.000	0.000	0.013	1.000	0.001
Mn (aq)	0.000	1.000	1.000	0.018	0.000	1.000
DOC	0.326	1.000	0.054	0.117	1.000	0.029
SO_4^{2-} (aq)	0.924	0.000	0.000	0.000	0.004	0.161

655

656 b) Red River Delta

Parameter	Comparison of redox zones					
	M and **S**	**M** and **I**	**M** and **N**	**S** and **I**	**S** and **N**	**I** and **N**
As (aq)	0.000	0.001	0.000	1.000	1.000	1.000
Fe (aq)	0.011	0.285	0.000	1.000	0.035	0.087
Mn (aq)	0.400	1.000	1.000	1.000	0.250	1.000
DOC	0.000	1.000	1.000	0.217	0.002	0.942
SO_4^{2-} (aq)	0.013	0.000	0.000	0.000	0.000	0.226

657

658 c) Bengal Delta

Parameter	Comparison of redox zones					
	M and **S**	**M** and **I**	**M** and **N**	**S** and **I**	**S** and **N**	**I** and **N**
As (aq)	0.243	0.497	0.112	1.000	1.000	1.000
Fe (aq)	0.725	1.000	0.234	0.246	1.000	0.085
Mn (aq)	1.000	1.000	1.000	1.000	1.000	1.000
SO_4^{2-} (aq)	1.000	0.003	0.002	0.006	0.003	1.000

659

660 **Table A1.** Concentrations of redox sensitive species (average values and standard errors) for the
661 three groundwater data sets (Mekong delta, Red River delta, Bangladesh), for the six zones
662 calculated according to the binary mixing model (M, S, I, N, I' and N'; for definition see
663 manuscript), and for the calculation based on chloride or boron as a conservative tracer.
664
665 (*) Note that the Mekong Delta data set had only 252 samples with both, chloride and
666 boron measurements.
667

Parameter	*Methanogenic* (zone **M**)					
(unit mgL^{-1} except As in μgL^{-1})	Mekong delta (*)		Bangladesh		Red River delta	
	Chloride	Boron	Chloride	Boron	Chloride	Boron
n	145	145	27	36	196	196
As	193 ± 24	193 ± 24	61 ± 20	60 ± 18	41 ± 6	41 ± 6
Fe	5.3 ± 1.0	5.3 ± 10	3.0 ± 0.8	3.4 ± 0.8	15.2 ± 1.6	15.2 ± 1.6
SO$_4$	<0.3	<0.1	<0.1	<0.1	0.1 ± 0.04	0.1 ± 0.04
Mn	0.6 ± 0.2	0.6 ± 0.2	0.6 ± 0.2	0.6 ± 0.2	0.8 ± 0.1	0.8 ± 0.1
DOC	3.3 ± 0.3	3.3 ± 0.3	no data	no data	3.2 ± 0.2	3.2 ± 0.2
HCO$_3$	321 ± 14	321 ± 14	337 ± 36	328 ± 31	188 ± 11	188 ± 11

668

Parameter	*Sulfate-reducing* (zone **S**)					
(unit mgL^{-1} except As in μgL^{-1})	Mekong delta (*)		Bangladesh		Red River delta	
	Chloride	Boron	Chloride	Boron	Chloride	Boron
n	24	36	62	42	167	152
As	7 ± 4	13 ± 5	26 ± 9	30 ± 10	14 ± 3	15 ± 4
Fe	0.5 ± 0.2	0.4 ± 0.1	1.5 ± 0.4	0.9 ± 0.2	9 ± 1.4	7.6 ± 1.3
SO$_4$	14.7 ± 3	16.6 ± 3.1	5 ± 1.5	11.1 ± 3.7	15.8 ± 2.1	30 ± 4
Mn	0.8 ± 0.3	0.6 ± 0.2	0.1 ± 0.05	0.5 ± 0.1	1.1 ± 0.2	1 ± 0.2
DOC	1.8 ± 0.5	1.8 ± 0.5	no data	no data	5.7 ± 0.6	6 ± 0.6
HCO$_3$	375 ± 57	341 ± 35	244 ± 21	308 ± 24	303 ± 23	317 ± 26

669

Parameter	*Iron-reducing* (zone **I**)					
(unit mgL^{-1} except As in μgL^{-1})	Mekong delta (*)		Bangladesh		Red River delta	
	Chloride	Boron	Chloride	Boron	Chloride	Boron
n	4	4	5	5	7	11
As	13 ± 9	9 ± 7	1 ± 0	1 ± 0	2 ± 1	10 ± 4
Fe	3.5 ± 2.7	5.2 ± 4.2	0.8 ± 0.4	1.8 ± 1.1	1.3 ± 0.4	9.7 ± 3.1
SO$_4$	7.6 ± 1.3	34 ± 10.8	7.6 ± 1	2.2 ± 0.3	10.4 ± 3.1	24 ± 17
Mn	0.5 ± 0.4	0.5 ± 0.3	0.2 ± 0.1	0.4 ± 0.1	0.8 ± 0.4	0.5 ± 0.1
DOC	0.4 ± 0.4	2.2 ± 0.8	no data	no data	3.5 ± 1.7	4 ± 1.3
HCO$_3$	348 ± 37	413 ± 35	162 ± 50	147 ± 25	212 ± 52	177 ± 29

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Parameter	*Neither iron- nor sulfate reducing* (zone **N**)					
(unit mgL^{-1} except As in μgL^{-1})	Mekong delta (*)		Bangladesh		Red River delta	
	Chloride	Boron	Chloride	Boron	Chloride	Boron
n	8	3	4	8	7	15
As	5 ± 2	5 ± 3	0 ± 0	1 ± 1	2 ± 2	0 ± 0

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Fe	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
SO₄	7.5 ± 1.3	11 ± 3.2	10 ± 1.8	5 ± 2.1	9.5 ± 2	3 ± 0.5
Mn	0.4 ± 0.2	0.2 ± 0.2	0.6 ± 0	0.5 ± 0.3	0.4 ± 0.1	0.1 ± 0
DOC	1.4 ± 0.5	4.9 ± 3.2	no data	no data	0.3 ± 0.3	0.3 ± 0.2
HCO₃	286 ± 53	394 ± 103	150 ± 44	172 ± 53	156 ± 46	84 ± 21

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Parameter	*Iron-reducing* (zone **I'**)					
(unit mgL^{-1} except As in μgL^{-1})	Mekong delta (*)		Bangladesh		Red River delta	
	Chloride	Boron	Chloride	Boron	Chloride	Boron
n	29	28	5	11	48	51
As	28 ± 8	26 ± 8	26 ± 9	2 ± 1	9 ± 4	11 ± 4
Fe	4.5 ± 1.1	4.3 ± 1.1	1.5 ± 0.4	4.6 ± 3	10.7 ± 1.9	14.9 ± 3.1
SO₄	102 ± 36	102 ± 38	5 ± 1.5	31 ± 23	80 ± 18	51 ± 17
Mn	0.8 ± 0.1	0.8 ± 0.2	0.4 ± 0.1	0.6 ± 0.2	0.8 ± 0.2	1.1 ± 0.2
DOC	3.3 ± 0.7	3 ± 0.7	no data	no data	3.8 ± 0.4	2.9 ± 0.3
HCO₃	418 ± 35	418 ± 36	244 ± 21	61 ± 12	247 ± 26	176 ± 19

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| Parameter	*Neither iron- nor sulfate reducing* (zone **N'**)					
(unit mgL^{-1} except As in μgL^{-1})	Mekong delta (*)		Bangladesh		Red River delta	
	Chloride	Boron	Chloride	Boron	Chloride	Boron
n	42	36	10	11	36	36
As	7 ± 3	3 ± 0.5	4 ± 2	2 ± 1	1 ± 0	1 ± 0
Fe	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
SO₄	82 ± 17	90 ± 20	43 ± 12	26 ± 7	58 ± 11	35 ± 5
Mn	0.8 ± 0.2	1 ± 0.2	0.5 ± 0.2	0.4 ± 0.2	0.6 ± 0.1	0.7 ± 0.2
DOC	2.1 ± 0.4	1.9 ± 0.4	no data	no data	2.3 ± 0.5	1.2 ± 0.3
HCO₃	429 ± 42	444 ± 51	376 ± 36	235 ± 44	265 ± 47	165 ± 25

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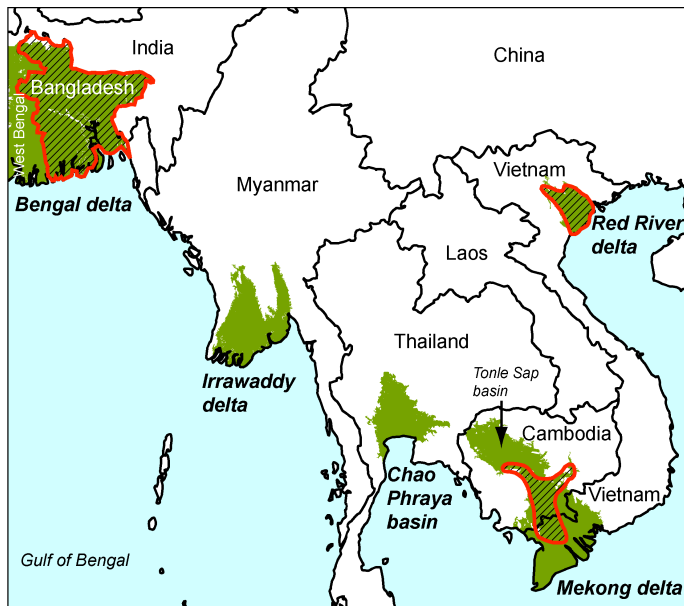
Figure 1. Map of the Bengal delta and the major floodplains of Southeast Asia. The investigated regions of the Mekong delta (Cambodia and Vietnam), the Red River delta (Vietnam) and Bangladesh are highlighted with hatched shapes. Further arsenic affected regions on this map are West Bengal, India (Chowdhury et al., 2000) and the Irrawaddy delta, Myanmar (Winkel et al., 2008a). The Chao Phraya basin is at low risk (Winkel et al., 2008a).
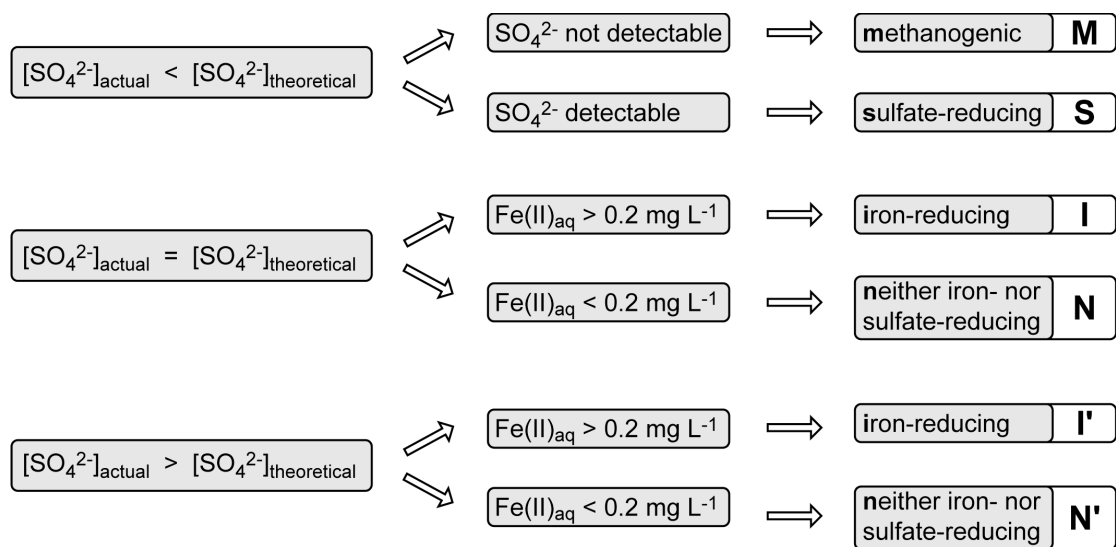
Figure 2. Flow chart of the six redox zones grouped according to their actual sulfate concentration compared to the theoretical one.
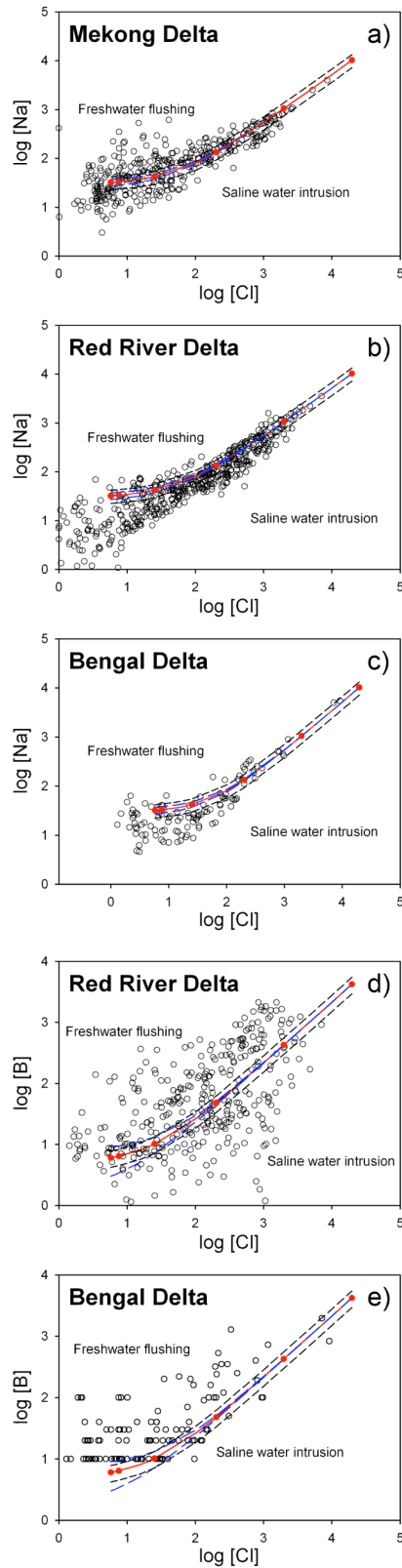
Figure 3. a), b) and c) log [Na] versus log [Cl] for the Mekong, the Red River and the Bengal delta data set. d) and e) log [B] versus log [Cl] for the Red River and the Bengal delta. The evaluation of freshwater or saline water intrusion is based on the binary mixing line (red line). The red points denote 0.01‰, 0.1‰, 1‰, 1%, 10%, 100% seawater. Blue dashed lines show absolute errors of 5 mg L^{-1} Na and 3 μg L^{-1} B, respectively, whereas black dashed lines show a relative error of 30%.
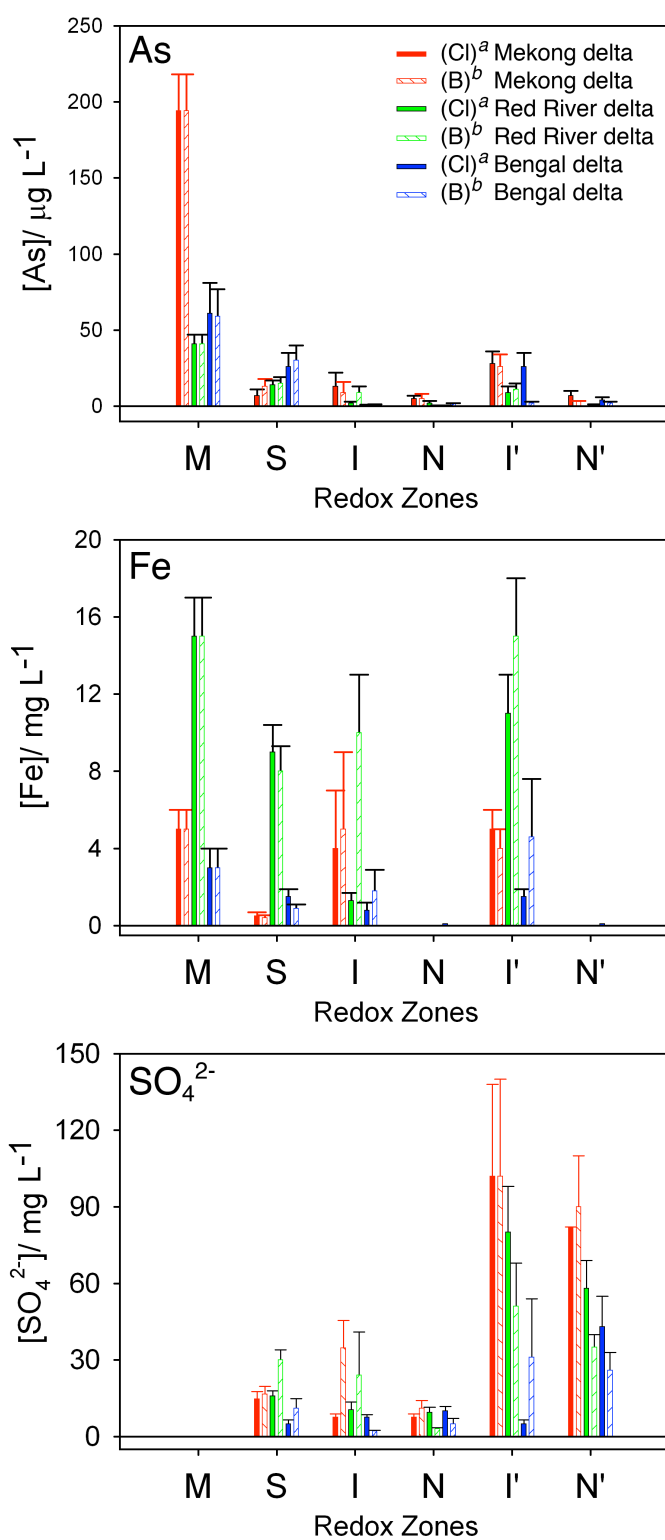
Figure 4. Average arsenic, iron and sulfate concentrations for the six zones calculated with the binary mixing model (values from Table A1). Vertical lines indicate standard errors. Redox zones are denoted as defined in Figure 2. See Table 2 for statistical comparison.
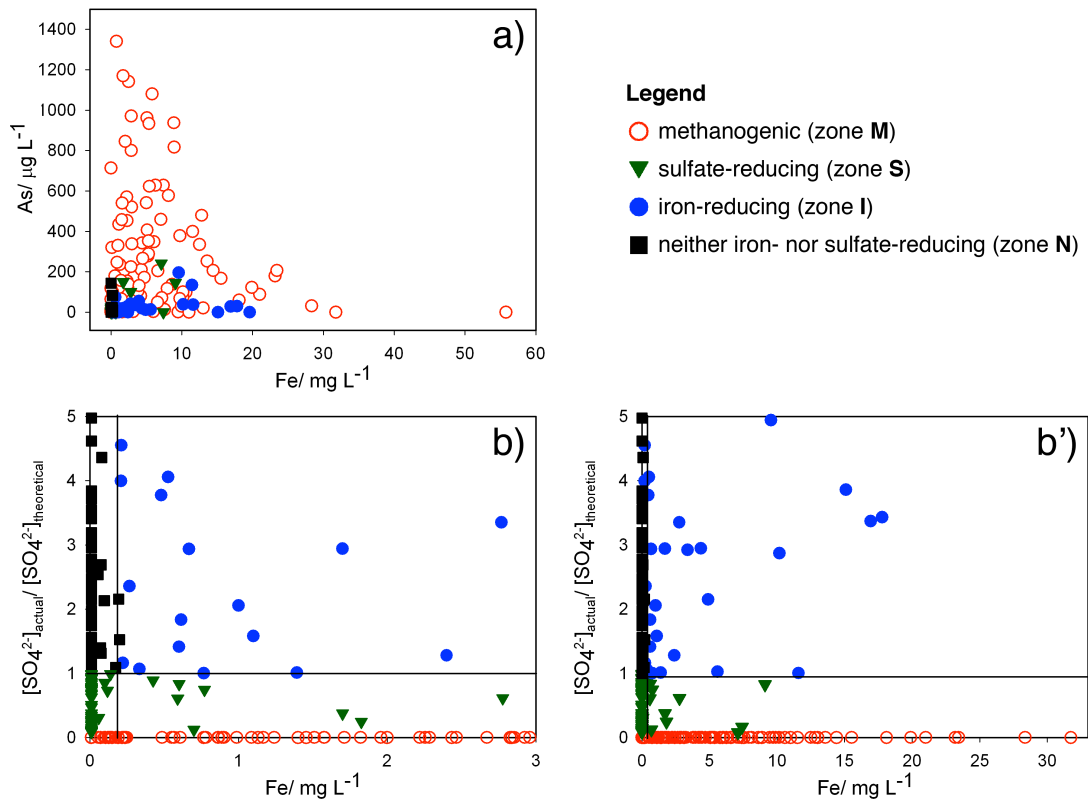
Figure 5. a) Arsenic concentration versus iron concentration in the groundwater samples of the Mekong delta (redox zones classified based on chloride as tracer). b) and b') $[SO_4^{2-}]_{actual}$ / $[SO_4^{2-}]_{theoretical}$ versus iron concentration for visualization of the zones' conditions. Note: Fe level range in b) was cut off at 3 mg L^{-1}. Zones I and I' as well as zones N and N' were combined because only 27%, 13% and 18% of the Mekong, Bengal and Red River Delta, respectively, had $[SO_4^{2-}]_{actual}$ > $[SO_4^{2-}]_{theoretical}$. Redox zones are denoted as defined in Figure 2.
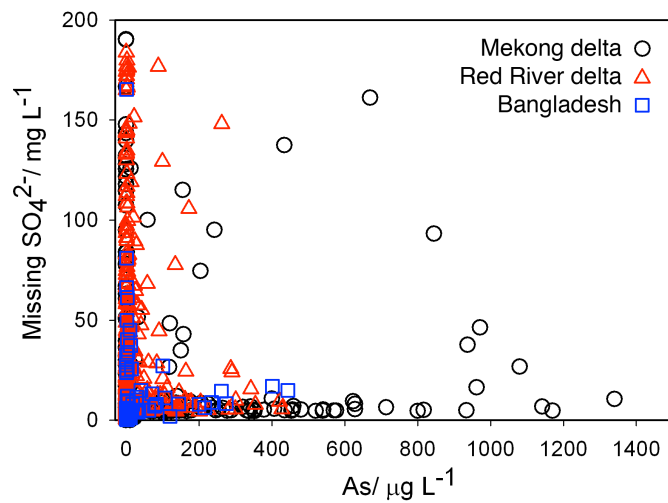
Figure 6. Missing sulfate versus arsenic concentrations in the Mekong delta, Red River delta and Bangladesh.