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Role of competing ions in the mobilization of arsenic in groundwater of Bengal Basin: Insight from surface complexation modeling

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24   **Abstract**

25   This study assesses the role of competing ions in the mobilization of arsenic (As) by surface

26   complexation modeling of the temporal variability of As in groundwater. The potential use of

27   two different surface complexation models (SCMs), developed for ferrihydrite and goethite,

28   has been explored to account for the temporal variation of As(III) and As(V) concentration,

29   monitored in shallow groundwater of Bengal Basin over a period of 20 months. The SCM for

30   ferrihydrite is the better predictor of the observed variation in both As(III) and As(V)

31   concentrations in the study sites. Among the competing ions, PO_4^{3-} was the major competitor

32   of As(III) and As(V) adsorption onto Fe oxyhydroxide, and the competition ability decreases

33   in the order $PO_4^{3-} \gg Fe(II) > H_4SiO_4 = HCO_3^-$. It is further revealed that a small change in

34   pH can also have a significant effect on the mobility of As(III) and As(V) in the aquifers. A

35   decrease in pH increases the concentration of As(III), whereas it decreases the As(V)

36   concentration and vice versa. The present study suggests that the reductive dissolution of Fe

37   oxyhydroxide alone cannot explain the observed high As concentration in groundwater of the

38   sedimentary aquifers. This study supports the view that the reductive dissolution of Fe

39   oxyhydroxide followed by competitive sorption reactions with the aquifer sediment are the

40   processes responsible for As enrichment in groundwater.

41   *Keywords:* Bengal Basin; Groundwater; Arsenic mobilization; Temporal variability;

42   Competing ions; Surface complexation modeling

43

1. Introduction

During the last decades, the occurrence of arsenic (As) in drinking water has become a major environmental concern in many regions of the world, even in the countries of North America and Europe (Nriagu et al., 2007). Nevertheless, the problem is most severe in Bangladesh and West Bengal (jointly represents Bengal Basin), where its extent has been termed as the largest mass poisoning in human history (Smith et al., 2000).

Currently, the reductive dissolution of Fe oxyhydroxide, coupled to the microbially mediated oxidation of organic matter is the most widely accepted mechanism of As release in groundwater of the Bengal Basin (Berg et al., 2008; Bhattacharya et al., 1997; Harvey et al., 2002; Islam et al., 2004; McArthur et al., 2004; Mukherjee et al., 2008; Nath et al., 2008; Nickson et al., 1998; Polya and Charlet, 2009). Meanwhile, some studies have revealed that once As is released into groundwater, its mobility is primarily regulated by the extent of re-sorption onto the residual Fe oxyhydroxide present in the aquifer materials through formation of either inner-sphere or outer-sphere complexes (Wang and Mulligan, 2008), until adsorption sites become saturated or solid sorbents are completely dissolved (Pedersen et al., 2006; von Brömssen et al., 2008; Welch et al., 2000). In this context, competing ions such as phosphate (PO_4^{3-}), bicarbonate (HCO_3^-) and silicic acid (H_4SiO_4) might play a significant role in the mobilization of As by competing for similar adsorption sites of Fe oxyhydroxide (Sracek et al., 2004; Stollenwerk, 2003; von Brömssen et al., 2008). Nevertheless, despite its importance there is controversy regarding the relative roles of these components for As mobilization. For example, it is reported that PO_4^{3-} has a very strong affinity for adsorption sites on Fe oxyhydroxide and is a potential competitor for As adsorption in the natural environment (Acharyya et al., 1999; Dixit and Hering, 2003; Gao and Mucci, 2001; Jain and Loeppert, 2000; Manning and Goldberg, 1996). For the aquifers of Bangladesh, van Geen et al. (2008) have also found strong positive correlation between level of PO_4^{3-} exchangeable As in aquifer

69 sediment and dissolved As concentration in groundwater, which led them to emphasize the

70 role of adsorptive equilibria in the As mobilization. Meanwhile, Kim et al. (2000), Appelo et

71 al. (2002), and Anawar et al. (2004) claimed that the high concentration of HCO_3^- in

72 groundwater may be responsible for the mobilization of As in Bengal Basin aquifers;

73 however, this was not experimentally supported by Meng et al. (2000), Radu et al. (2005) and

74 Stachowicz et al.(2007). Sometimes the adsorption of H_4SiO_4 has also been considered as a

75 competitor of As adsorption onto Fe oxyhydroxide (Meng et al., 2000; Swedlund and

76 Webster, 1999). Based on batch experiments involving multi-sorbate ions, Meng et al. (2002)

77 showed that although PO_4^{3-}, HCO_3^- and H_4SiO_4 can compete with As(III) adsorption onto Fe

78 oxyhydroxide, their effect on As(V) adsorption is very small even at high concentration and

79 suggested that the high mobility of As in Bengal Basin aquifers is due to their combined

80 effect. Recently, by similar experiment and subsequent modeling, Stollenwerk et al. (2007)

81 and Stachowicz et al. (2008) again concluded that PO_4^{3-} is the major competitor for As

82 adsorption and in the presence of significant PO_4^{3-} the competition of HCO_3^- becomes

83 negligible. However, these contradictory conclusions are made mostly based on laboratory

84 adsorption studies. Because of the complexity of the competitive adsorption equilibria

85 (Stachowicz et al., 2008), so far only a very few studies (for e.g. Jessen et al., 2012; Postma et

86 al., 2007; Swartz et al., 2004), have attempted to simulate the natural groundwater condition

87 to assess the role of adsorptive equilibria in the As mobilization.

88 The objective of the present study is to fill up the gap in existing knowledge with the

89 assessment of relative roles of different competing ions in the As mobilization by means of

90 surface complexation modeling of the naturally occurring As enriched groundwater in the

91 aquifer of Bengal Basin. A total of 10 piezometers have been monitored for aqueous As and

92 other important hydrogeochemical parameters including different competing ions, over a

93 period of 20 months. Such monitoring has provided the opportunity to assess the role of

94   different competitive adsorption equilibria in the As mobilization processes by testing the

95   hypothesis that temporal variation of As in groundwater of Bengal Basin is governed by the

96   variation in concentration of competing ions. Two different surface complexation models

97   (SCMs) have been used to test this hypothesis. The relative roles of different competing ions

98   on the As mobilization is assessed by testing the sensitivity of the modeled aqueous As

99   concentration towards changes in the concentration of specific competing ion.

100   **2. Materials and methods**

101   **2.1. Piezometers installation, groundwater sampling and laboratory analysis**

102   Based on a survey at Chakdaha Block of Nadia District, West Bengal, two sites at the

103   village of Sahispur (Site 1; $23^0 04'15.5''$N, $088^0 36'33.5''$E) and Chakudanga (Site 2;

104      $23^0 04'58''$N, $088^0 38'13''$E), where the concentration of As in groundwater was high and

105   relatively low respectively, were selected for piezometers installation. At each site over an

106   area of 25 m^2, five piezometers (well A, B, C, D and E) were installed with different screening

107   positions (Site 1 – A: 12-21 m, B: 22-25 m, C: 26-29 m, D: 30-33 m and E: 34-37 m; Site – 2:

108   A: 12-21 m, B: 24-27 m, C: 30-33 m, D: 36-39 m and E: 42-45 m) to collect multi depth

109   groundwater samples (see Appendix for the picture of piezometer nests). Continuous

110   sediment cores were collected during drilling of deepest piezometer (well E) at each site,

111   using a split-spoon core barrel fitted to a PVC tube of 0.65 m length. Sediment samples were

112   preserved in the field by flushing with N_2, followed by rubber capping at both end of the

113   barrel.

114   The piezometers were sampled in 15 days intervals over a period of 20 months (December

115   2008 – July 2010). The regular sampling interval at both sites was interrupted once, in the

116   month December 2009, when pumping and in-situ bio-stimulation experiments were

117   conducted at site 1 and 2 respectively (details of the experiments and results have been

presented in Neidhardt et al. 2013a and Neidhardt et al., 2014). The sampling was resumed again from January 2010. Groundwater was sampled for the analysis of major anions, major cations and trace elements (including As), As speciation and Fe speciation with the field measurements of alkalinity (in the form of HCO_3^-), pH, redox potential (Eh), electrical conductivity (EC) and temperature (T). All the samples were filtered through 0.45 µm membrane filter (Axiva). The samples for major cations and trace elements and Fe speciation were preserved on-site with HNO_3 (1% v/v, Suprapur Merck) and HCl (12N, Suprapur Merck) respectively. The samples for the analysis of major anions were left unacidified. During sampling, the samples for As speciation were additionally passed through an cartridge (Metal Soft Centre, Highland Park, USA, Meng et al., 2001), which selectively adsorbs As(V) and the filtrate was preserved with HNO_3 for the analysis of As that represents As(III). The concentration of As(V) in the samples was determined by subtracting this As(III) from the total As. The samples for anions and Fe speciation were analyzed overnight of sampling. The anions were analyzed by a Metrohm Ion Chromatography (761 Compact IC), equipped with Metrosep Anion 1 column (No. 12007935). The percentage of Fe(II) was measured spectrophotometrically by the O-phenanthroline method (APHA, 1998). The samples for major cations and trace elements and As speciation were stored at 4 ºC until shipped (once in 8 weeks) to the Institute of Mineralogy and Geochemistry, Karlsruhe Institute of Technology for the analysis by HR-ICP-MS (VG AXIOM, VG Elemental). The analytical precision was estimated by triplicate measurements, yielding an average precision of 1.71% for As. Accuracy in the measurement was assessed by regular analysis of a certified reference solution (Trace Metals In Drinking Water, HPS), reaching to an average accuracy of 1.81% for As. The concentration of PO_4^{3-} in the samples was obtained from the elemental P concentration, as determined by HR-ICP-MS. The exact concentrations of Fe(II) and Fe(III) in the samples were calculated by multiplying total Fe concentration measured with HR-ICP-

143   MS, with percentage of Fe(II) and subtracting the calculated Fe(II) concentration from total

144   Fe concentration respectively. For the samples, where percentage of Fe(II) was not measured,

145   median percentage of Fe(II) for other samples of the corresponding well was used for the

146   calculation of concentrations. Furthermore, the concentration of H_4SiO_4 was not measured for

147   the monitoring samples but was measured during pumping and bio-stimulation experiment at

148   site 1 and 2 respectively. Tto incorporate the competition effect of H_4SiO_4 on As adsorption in

149   the simulations, the baseline value for each well, determined just before these experiments

150   was considered for all samples of the corresponding wells.

151   **2.2. Modeling approach**

152   One key step during the setup of different SCMs is the selection of sorbent phase(s) to be

153   used during simulation. An operationally defined seven-step sequential extraction of As from

154   aquifer sediments (n = 13) together with the association of As and Fe in sediment column at

155   both the study sites have indicated that As is mainly present in the specifically adsorbed

156   fraction, bound to amorphous to crystalline Fe oxides (Biswas et al., submitted for

157   publication; Neidhardt et al., 2013a, b). Similar findings have been also reported from other

158   parts of the study area (Métral et al., 2008), Bangladesh (Swartz et al., 2004; van Geen et al.,

159   2008), and Vietnam (Berg et al., 2008). Ferrihydrite, the major Fe oxyhydroxide mineral in

160   oxic and slightly anoxic sediment (Stachowicz et al., 2007), has been used extensively for

161   previous adsorption studies. Additionally, the investigations of Fe mineralogy in the reduced

162   sediment, collected from the As-rich aquifers of Meghna and Red River flood plain have also

163   indicated the presence of relatively crystalline goethite (Datta et al., 2009; Postma et al.,

164   2010), which has strong affinity for As(III) and As(V) adsorption (Dixit and Hering, 2003).

165   Recently, Jessen et al. (2012) have also pointed out that for the reduced aquifer sediment the

166   use of SCM for goethite may be more appropriate. Thus in our simulations, we studied the

167   SCMs for both ferrihydrite and goethite. For ferrihydrite, we used 2-pK diffuse layer SCM, as

168   proposed by Dzombak and Morel, (1990) (hereafter referred to as D&M SCM). For goethite,

169   the 3-plane CD-MUSIC SCM, developed by Hiemstra and van Riemsdijk, (1996) was used.

170   Considering the fact that the purpose of the present study was not to compare between the two

171   model parameterizations, these two different SCMs were chosen as they are

172   thermodynamically most developed and frequently used for simulations of ion adsorption

173   onto ferrihydrite- or goethite-containing materials. Furthermore, an underlying assumption

174   with the selection of sorbent phases for the two models was that the adsorbing behavior of the

175   Fe oxyhydroxides present in the aquifer sediment is well approximated by their pure synthetic

176   analogs (Davis et al., 1998). However, it should be mentioned here that in natural reduced

177   aquifer sediment these sorbent phases are more heterogeneous, often the complex mixture of

178   multiple impure phases and further interact with other metal oxyhydroxides (for e.g. Mn and

179   Al oxyhydroxides), clay minerals and organics (Hiemstra et al., 2010; Jessen et al., 2012).

180   Thus in the aquifer the mobilization and transport behavior of As may be more complex

181   compared to the assumption made. However, the simulation of such complexity demands

182   further development of thermodynamic database for the surface complexation reactions of As

183   to the natural aquifer sediment.

184   The sorbent contents in the two SCMs were normalized for the individual well by

185   equilibrating the first monitoring sample of specific well, following the approach of Postma et

186   al. (2007) (Appendix Table A.1). The sorbent content was varied until the modeled aqueous

187   As(III) and As(V) agreed with their measured concentrations. We hypothesized that the

188   amount of sorbent content in the sediment and total As content in the system (As $_{adsorbed}$ + As

189    $_{dissolved}$) for a particular well remained the same over the monitoring period; only the variation

190   in pH and concentrations of competing ions determined the extent of partitioning of As

191   between sorbent and aqueous phase and thus the temporal variation of As in groundwater.

192   Consequently, the sorbent content in the specific SCM and total As content in the system for a

193 particular well were kept constant during the equilibration of all groundwater samples,

194 collected from the same well. The total As content in the system for a particular well was

195 calculated by adding the readily mobilizable and specifically adsorbed As content in the

196 sediment of screen position [converted to g/L assuming the porosity and grain density of

197 aquifer sediment as 0.3 and 2.65 g/cm^3 respectively (Jessen et al., 2012)] to the average

198 dissolved As content in groundwater of the respective well. The readily mobilizable and

199 specifically adsorbed pools of As in the sediment samples were extracted in the first two steps

200 of sequentially extractions with 0.05 M $(NH_4)_2SO_4$ and 0.5 M NaH_2PO_4 respectively (Eiche et

201 al., 2008).

202 The geochemical code Visual MINTEQ ver. 3.0 was used for all the simulations

203 (Gustafsson, 2011). For the D&M SCM of ferrihydrite, the parameters were set to the default

204 values of Visual MINTEQ, whereas the CD-MUSIC SCM for goethite was parameterized

205 according to Jessen et al. (2012). The input concentrations for the measured groundwater

206 components (except As) were specified as '*Total Dissolved*' in the simulations. For all

207 groundwater samples, the value of Eh corresponding to H_3AsO_3/AsO_4 redox couple was

208 calculated from the measured concentration of As(III) and As(V) in a separate speciation

209 modeling exercise. Instead of field measured Eh value, this calculated Eh value was specified

210 during simulations of both SCMs for the corresponding groundwater sample so that the ratio

211 of modeled aqueous As(III) to As(V) would become similar to the measured value and thus

212 the exact influence of As speciation into surface complexation reactions could be accounted.

213 In all simulations, ferrihydrite was allowed to precipitate with log $*K_s$ of 3.2 at 25°C (where

214 $*K_s = \{Fe^{3+}\}/\{H^+\}^3$). For simulations with the D&M SCM, we used the default database in

215 Visual MINTEQ, *feo-dlm_2008.vdb*. This is based on the database of Dzombak and Morel,

216 (1990) but with the extension of surface species for HCO_3^- (Appelo et al., 2002), H_4SiO_4

217 (Swedlund and Webster, 1999), and Fe(II) (Appelo et al., 2002; Liger et al., 1999) and

218   modification of equilibrium constants for the surface reactions of PO_4^{3-} (Gustafsson, 2003)

219   As(III) and As(V) (Gustafsson and Bhattacharya, 2007) (Appendix Table A.2). For the

220   simulation of CD-MUSIC SCM, all the surface complexation reactions and the corresponding

221   equilibrium constants were taken from the database prepared by Jessen et al. (2012) (for

222   details see their Electronic Annex Table EA-1).

223   **3. Results and discussion**

224   **3.1. General hydrogeochemistry in the aquifer at two sites**

225   As the present study does not focus on the discussion of the detailed hydrogeochemical

226   evolution of the aquifer, here we present only the generic overview of groundwater

227   composition at the two sites. In the groundwater at both sites, Ca^{2+} is the predominating cation

228   followed by Mg^{2+}, Na^+ and K^+ and HCO_3^- is the major anion followed by Cl^-. Consequently,

229   the groundwater at both sites is Ca-Mg-HCO_3-type to Ca-HCO_3 type with circumneutral pH

230   (Appendix Fig. A.1). The concentration of SO_4^{2-} is mostly below the detection limit (BDL)

231   over the monitoring period, except in the well A & B at site 1. Similarly, the concentration of

232   NO_3^- is also mostly BDL in all the wells at both sites. The concentration of most of the ionic

233   constituents is higher at site 1 compared to site 2. The EC in groundwater follows a similar

234   trend, being higher at site 1 (Appendix Fig. A.1). In all the wells at both sites, the

235   concentrations of dissolved As exceeds the WHO provisional drinking guideline of 10 µg/L.

236   Arsenic shows the highest enrichment in well C and well B at site 1 and site 2 respectively

237   (Appendix Fig. A.2). The aquifer at both sites is reducing in nature, where the lower oxidation

238   state of As and Fe predominates over the corresponding higher oxidation sate. In all the wells,

239   the concentration of PO_4^{3-} shows a strong positive correlation to As (Biswas et al., submitted

240   for publication). The hydrogeochemical evolution of the groundwater composition at the two

241   sites has been discussed in detail elsewhere (Biswas et al., submitted for publication). The

242 groundwater composition presented here is representative for the shallow aquifers of whole

243 Bengal Basin (Bhattacharta et al., 2002; Biswas et al., 2012; Charlet et al., 2007; Harvey et

244 al., 2002; Mukherjee et al., 2008; Nath et al., 2008; Zheng et al., 2004).

3.2. Temporal variations of As(III) and As(V) in groundwater

246 The temporal variations of As(III) and As(V) over the monitoring period are displayed in

247 Fig. 1 and 2 respectively. Additionally, the extent of variability is statistically estimated by

248 calculating the standard deviation of As(III) and As(V) concentration (Appendix Table A.3).

249 In all the piezometers of both sites, the standard deviation of As(III) concentration is ≥ 10

250 µg/L (Appendix Table A.3), reflecting strong temporal variation.

251 In site 1, a general trend of As(III) enrichment was observed for well A over the monitoring

252 period (Fig. 1). A very strong temporal variation in As(III) concentration was observed for

253 well B and C, where the concentration respectively varied between 70.1 – 393 µg/L and 20.6

254 – 317 µg/L, with a standard deviation of 103 µg/L and 63.0 µg/L respectively (Appendix

255 Table A.3). In both wells, the variation followed a cyclic trend over the monitoring period

256 (Fig. 1). In well B, starting from the monitoring in December 2008, the As(III) concentration

257 had been decreasing over the dry season until the end of April 2009. No considerable

258 variation was observed in the following 7 month period up to November 2009, when regular

259 sampling was stopped for one month for the pumping experiment (Fig. 1). When sampling

260 was started again in January 2010, the As(III) concentration increased to close the value

261 recorded at the beginning of monitoring in December 2008 (Fig. 1). In the following dry

262 season period, the variation pattern was similar to the previous year. However, this time the

263 As(III) concentration increased instantly after approaching the minimum value in May 2010

264 (Fig. 1). In well C, a small decrease in the As(III) concentration was also observed at the end

265 of April 2009 (Fig. 1). However in contrast to well B, after an initial decrease,, the

266 concentration increased back to the original value instantaneously and was then quite stable

267 throughout the rest of the year. When the well was first sampled in 2010 after the pumping

268 experiment, the As(III) concentration was roughly the same (Fig. 1). In the following dry

269 period of 2010, the variation pattern was similar to that in the previous year. However, this

270 time the decrease in concentration was very large, resulting in the lowest value observed

271 during the whole monitoring period considering all the piezometers of site 1 (Fig. 1). The

272 temporal variation in As(III) concentration for well D and E of site 1 did not show any

273 specific trend (Fig. 1). Except for well A, the standard deviation of As(V) in all other wells

274 was ≥ 10 µg/L, being the highest for well C (Appendix Table A.3). However, the temporal

275 variation did not show any specific trend over the monitoring period for any well (Fig. 2).

276   In site 2, the highest temporal variation was observed in well A (Fig. 1), where the As(III)

277 concentration varied between 16.8 and 127 µg/L with a standard deviation of 29.6 µg/L

278 (Appendix Table A.3). In contrast to the variation observed in site 1, the dissolved As(III)

279 concentration increased at the beginning of dry period, both in 2009 and 2010 and the relative

280 enrichment in 2010 was slightly higher than in 2009. After passing through the maximum

281 value, the concentration decreased to the lowest value around the end of the dry season and no

282 significant variation was observed in the following monsoon period (Fig. 1). The temporal

283 variation in As(III) concentration for other wells of site 2 did not show any specific trend over

284 the monitoring period (Fig. 1). The standard deviation of the As(V) concentration was

285 throughout <10 µg/L for all wells (Appendix Table A.3) and no specific trend was observed

286 in the temporal variation also (Fig. 2). The temporal variations of total As and other aqueous

287 parameters at the two sites over the monitoring period have been reported in Biswas et al.

288 (submitted for publication).

289 **3.3. Application of SCMs in predicting temporal variability of As**

12

290   To investigate the role of different surface complexation reactions onto aquifer materials in

291   the As mobilization in groundwater, we attempted to model the temporal variability in As(III)

292   and As(V) concentrations by use of the D&M and CD-MUSIC SCMs (Fig. 1 and 2). The

293   comparison of the model-predicted concentration with the measured value indicates that

294   though the performance of the CD-MUSIC SCM in predicting As(III) concentration in the

295   wells of site 1 is fairly good, the predictions of the D&M SCM are even closer to the

296   measured trends (Fig. 1). In site 2, the As(III) concentration predicted by both D&M and CD-

297   MUSIC SCMs closely follows the measured concentration until the end of November 2009,

298   when the sampling was stopped for one month for the bio-stimulation experiment (Fig. 1). In

299   the post-experiment period, the CD-MUSIC SCM largely under-predicts the As(III)

300   concentration, whereas the concentration predicted by the D&M SCM quite closely follows

301   the measured value to the end of the monitoring (Fig. 1).

302   Estimation of root mean square error (RMSE) of the logarithm of dissolved As(III)

303   concentration was used as an indicator of the accuracy of the models. This analysis supports

304   the above inferences. In site 1 except for well B, the values of RMSE for the D&M SCM are

305   ≤0.10, while the values for the CD-MUSIC SCM in all the wells are >0.10 (Appendix Table

306   A.4), indicating the better performance of the D&M SCM over the CD-MUSIC SCM in

307   predicting the variability of As(III) concentration at our study site. Similarly in site 2, except

308   for well A the values of RMSE for the D&M SCM are <0.10. For the CD-MUSIC SCM, the

309   RMSE was estimated for the pre- and post-experiment period separately, to evaluate the effect

310   of bio-stimulation experiment on the model performance. In the pre-experiment period, the

311   RMSE values are close to that calculated for D&M SCM; however, they have increased

312   largely in the post-experiment period (Appendix Table A.4). The poor performance of both

313   SCMs in predicting As(III) concentration for the well B and well A of site 1 and 2

314   respectively (Fig. 1), might be due to the fact that for these wells the total As content in the

315   system did not remain constant over the monitoring period as our hypothesis. The

316   investigations by Neidhardt et al. (2014) and Neidhardt et al. (2013a) have already pointed out

317   the possibility of seasonal vertical mixing of groundwaters with distinct As concentrations

318   from different depths in these two wells.

319   For As(V), the predicted concentration by both SCMs approximately follows the scattered

320   peaks observed in the measured concentration over the monitoring period (Fig. 2). However,

321   the estimation of RMSE indicates that the performance of the D&M SCM is to some extent

322   better than that of the CD-MUSIC SCM and both models provide better estimations for

323   As(III) than for As(V) (Appendix Table A.4).

324   **3.4. Modeled surface speciation of the aquifer sediment**

325   An attempt was also made to investigate the extent of formation of different complexes at

326   the surface of sorbent considered in the two SCMs, by analyzing the simulated fractional site

327   occupancy. Well E from site 1 was selected for this investigation, based on the low estimated

328   RMSE values for both SCMs for the prediction of As(III) concentration in groundwater

329   (Appendix Table A.4). The surface speciation of the weak sites on Fe oxyhydroxide, as

330   predicted by the two SCMs, fairly well resembles each other (Fig. 3). According to both

331   SCMs, the surface complexes of PO_4^{3-} are the major adsorbing species, covering 35% and

332   58% of the week surface sites of ferrihydrite and goethite, respectively. For ferrihydrite, the

333   D&M SCM further predicts that H+ and Fe(II) occupy 26 % and 14 % of the surface sites,

334   respectively. The CD-MUSIC SCM for goethite predicts a higher adsorption of Fe(II) (22%)

335   compared to H^+ (9%) (Fig. 3). Though HCO_3^- is the major anion in groundwater, very low to

336   negligible site occupancy by carbonate surface complexes is estimated by both the SCMs.

337   According to the D&M SCM they only cover 10% of the surface sites, similar to the

338   adsorption of H_4SiO_4 species, and the CD-MUSIC SCM estimates <1% of the surface

339 coverage to be due to the complexes of the HCO_3^- and H_4SiO_4 species (Fig. 3). Following the

340 large predominance of As(III) concentration over As(V) in groundwater, both SCMs predict

341 higher average concentration of As(III) surface complexes compared to As(V) complexes.

342 The previous study by Jessen et al. (2012) also reported similar surface speciation for the

343 Vietnam aquifer sediment by the simulation of CD-MUSIC SCM for goethite, the only

344 difference being a higher adsorption of As(V) compared to As(III). However, the estimation

345 by the D&M SCM for ferrihydrite in the present study significantly differs from the

346 composition of surface complexes previously calculated by the simulation of the D&M SCM

347 for Bangladesh (Swartz et al., 2004), and for Vietnam aquifer sediment (Jessen et al., 2012;

348 Postma et al., 2007), where H_4SiO_4 and HCO_3^- were reported to be the major adsorbing

349 species with a relatively low surface coverage by PO_4^{3-}. Further, in agreement with the

350 findings of Jessen et al. (2012) the CD-MUSIC SCM predicts the binding of As(III) to

351 goethite exclusively by the formation of the As(III)-Fe(II) ternary surface complex

352 ($>Fe\_uniOAs(OH)_3Fe^{+0.5}$). The formation of such a complex may explain the under-

353 prediction of As(III) concentration by the CD-MUSIC SCM in the post-bio-stimulation

354 experiment period for the wells at site 2. It should be mentioned here that due to the bio-

355 stimulation in the aquifer by injecting degradable organic matter, the local groundwater

356 composition was changed drastically for several days, including an elevation in As and Fe

357 concentration (Neidhardt et al., 2014). When the regular monitoring was started again in

358 January 2010, the As concentration had returned to the baseline value in all five piezometers

359 (Fig. 1), while the Fe concentration remained elevated till the end of the monitoring

360 (Neidhardt et al., 2014).

361 **3.5. Relative roles of competing ions and pH on the mobilization of As**

362 In order to estimate the relative roles of competing ions and pH on the As mobilization, the

363 sensitivity of the modeled aqueous As(III) and As(V) concentrations towards the changes in

15

364　the concentration of competing ions and pH was investigated (Fig. 4). The sensitivity test was

365　performed by the simulation of only the D&M SCM for the well E of site 1. The D&M SCM

366　was chosen as it better predicts the temporal variation of As at both study sites over the whole

367　monitoring period. For the sensitivity test, only the concentration of the selected parameter of

368　interest was varied (-100% to +100%, except for pH, which was varied -5% to +5%) in the

369　simulation, while keeping concentration of other parameters fixed to the measured value. The

370　results indicate that in the aquifer PO_4^{3-} is the major competitor of As(III) and As(V)

371　adsorption onto Fe oxyhydroxide (Fig. 4) and the competition ability of the different ions

372　decreases in the order $PO_4^{3-} \gg Fe(II) > H_4SiO_4 = HCO_3^-$. In the simulation, when dissolved

373　concentration of PO_4^{3-} is set to zero, the modeled concentration of both As(III) and As(V) is

374　reduced on average by 92.5%. However, a similar imposition for the concentration of Fe(II),

375　H_4SiO_4 and HCO_3^- in the simulation only reduces the As(III) concentration by 12.2%, 7.40%,

376　and 7.04% respectively (Table 1). Phosphate, Fe(II) and H_4SiO_4 appears to be equally

377　effective to compete with both As(III) and As(V), while HCO_3^- competes more strongly with

378　As(V) as compared to As(III) (Table 1). Though previous studies have concluded that Fe(II)

379　does not affect the re-sorption of As onto residual Fe oxyhydroxide (Appelo et al., 2002; Dixit

380　and Hering, 2006), our results indicates a small but significant competition between Fe(II) and

381　As for adsorption sites on Fe oxyhydroxides. It is further observed that the As concentration

382　does not vary linearly with the change in PO_4^{3-} concentration. Although, the As(III & V)

383　concentration is reduced by 92.5% when the PO_4^{3-} concentration is set to zero in the

384　simulation, it is increased by only 31.4% when the PO_4^{3-} concentration is doubled (Table 1).

385　This demonstrates that in the aquifer the competition of PO_4^{3-} with As for the adsorption sites

386　might already reach close to maximum level. In contrast, the relationships with the other

387　competing ions are still linear (Table 1).

388   Some studies have also concluded that Ca^{2+} can enhance the adsorption of As(V) onto Fe

389   oxyhydroxide significantly particularly at high pH, by reducing the surface negative charge

390   (Stachowicz et al., 2008). In contrast, recently Saalfield and Bostick, (2010) have suggested

391   that the adsorption of Ca^{2+} or Mg^{2+} together with HCO_3^- can increase the desorption of As(V)

392   from ferihydrite to a greater extent compared to their individual competition. To this end a

393   sensitivity test was performed by changing the concentrations of these ions in different

394   combinations. The results indicate that the change in concentration of Ca^{2+} and Mg^{2+} together

395   with HCO_3^- affect the adsorption of both As(III) and As(V) to Fe oxyhydroxide almost

396   negligibly (Appendix Fig. A.3).

397   The results further indicate that the pH value also has a strong influence on the mobility of

398   As(III) and As(V) in the aquifer by changing their concentration oppositely to each other (Fig.

399   4). A 5% decrease in pH increases the As(III) concentration by 65.3% and decreases the

400   As(V) concentration by 91.2% on average, representing greater influence on the As(V)

401   mobility. The influence on the As(V) mobility becomes even more prominent during increase

402   of pH (Table 1). The ease of formation of the major surface complexes for As(III) and As(V)

403   determines their different behavioral pattern towards the change in pH. In the D&M SCM, the

404   major surface complex for As(III) and As(V) are $>Fe\_wH_2AsO_3$ and $>Fe\_wHAsO_4^-$,

405   respectively. With a decrease of pH the formation of $>Fe\_wH_2AsO_3$ and $>Fe\_wHAsO_4^-$

406   complexes and consequently the adsorption of As(III) and As(V) are constrained and favored

407   respectively. Moreover, as reflected in the modeled speciation of surface complexes formed in

408   the D&M SCM (Fig. 3), with a decrease of pH the protonation of the weak sites would be

409   increased making them less available for As(III) adsorption. At the same time the protonation

410   of the weak sites reduces the surface negative charge and consequently decreases the

411   electrostatic repulsion during adsorption of negatively charged oxyanions of As(V). At high

pH, this electrostatic repulsion becomes so prominent that the desorption of the oxyanions of As(V) increases drastically.

4. Conclusion

The assessment of the role of competing ions in the As mobilization processes by surface complexation modeling of the temporal variability of As in groundwater suggests that only the reductive dissolution of Fe oxyhydroxide cannot explain the observed high As concentration in the groundwater of Bengal Basin. Competitive adsorption/desorption reactions with the aquifer sediment have an important role in the As mobilization processes. In the absence of potential competition for the adsorption sites, the As released by the reductive dissolution of Fe oxyhydroxide would have been re-adsorbed onto the residual Fe phases and other sorbents present in the aquifer sediment. It appears that the reductive dissolution of Fe oxyhydroxide followed by competitive ion adsorption, mainly by PO_4^{3-}, with the aquifer sediment is the main processes responsible for As enrichment in the sedimentary aquifers of Bengal Basin.

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611

612 Table 1. Average change in modeled aqueous As(III) and As(V) concentration for the samples

613 collected from well E of site 1 in response to the variation in pH and concentration of

614 different competing ions. The '-' & '+' signs indicates the decrease and increase of the value

615 respectively.

Parameters	Change in parameters (%)	Change in conc. of As(III) (%)	Change in conc. of As(V) (%)
pH	-5.00	+65.3	-91.2
	-2.50	+28.7	-70.9
	+2.50	-28.3	+231
	+5.00	-55.5	+877
PO_4^{3-}	-100	-92.5	-92.5
	-50.0	-23.3	-23.3
	+50.0	+17.2	+17.2
	+100	+31.4	+31.4
H_4SiO_4	-100	-7.40	-7.40
	-50.0	-3.69	-3.69
	+50.0	+3.72	+3.72
	+100	+7.42	+7.42
HCO_3^-	-100	-7.04	-11.2
	-50.0	-3.53	-5.63
	+50.0	+3.55	+5.67
	+100	+7.12	+11.4
Fe(II)	-100	-12.2	-12.3
	-50.0	-5.68	-5.76
	+50.0	+5.06	+5.15
	+100	+9.61	+9.81

616

617
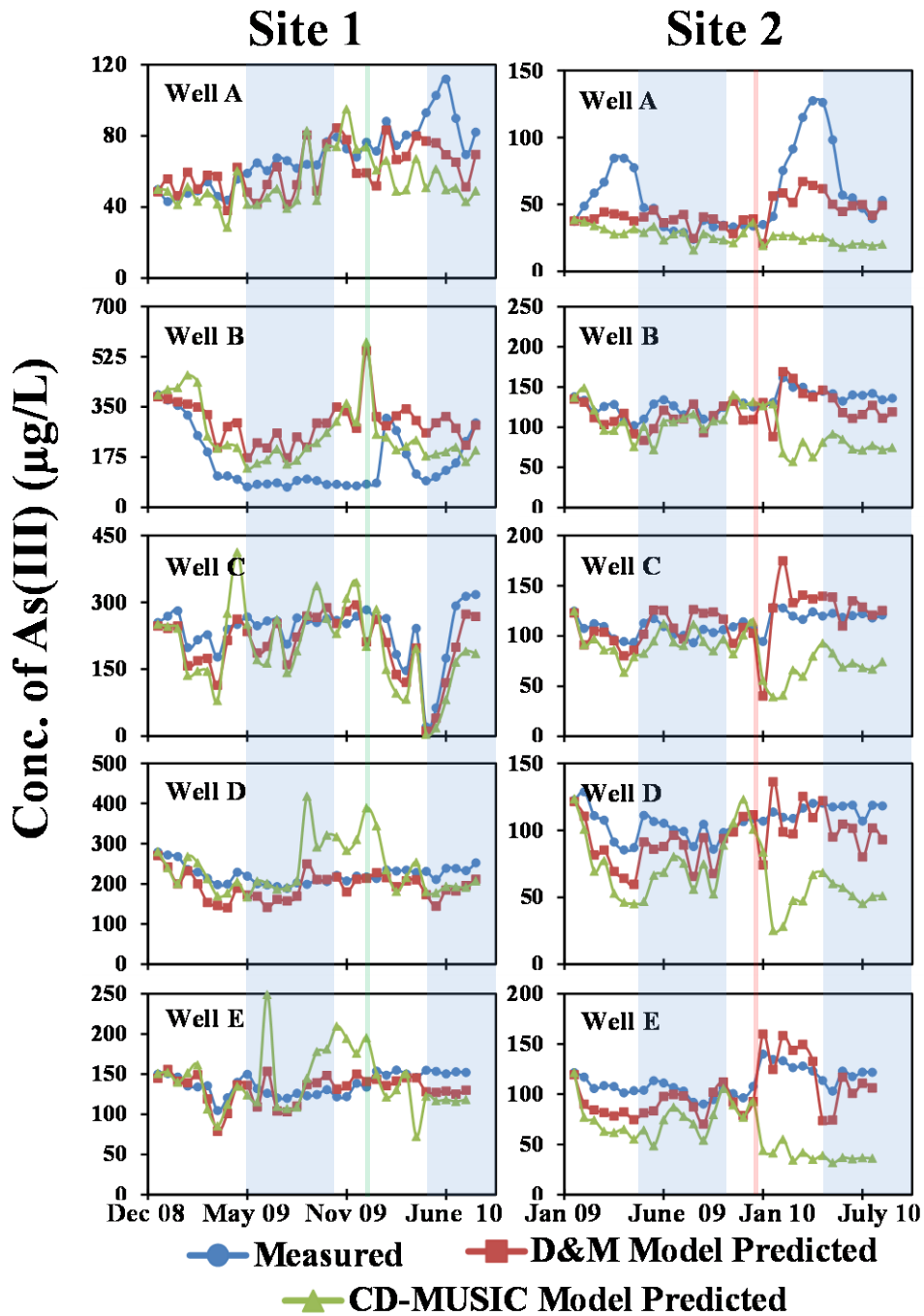
Fig. 1. Measured and predicted (with the D&M and CD-MUSIC SCMs) temporal variability in the concentration of aqueous As(III) for the piezometers of site 1 & 2. Blue-shaded area and white area in the figure represents monsoon period and dry period respectively. Green line and red line represents the time of pumping experiment at site 1 and bio-stimulation experiment at site 2 respectively.
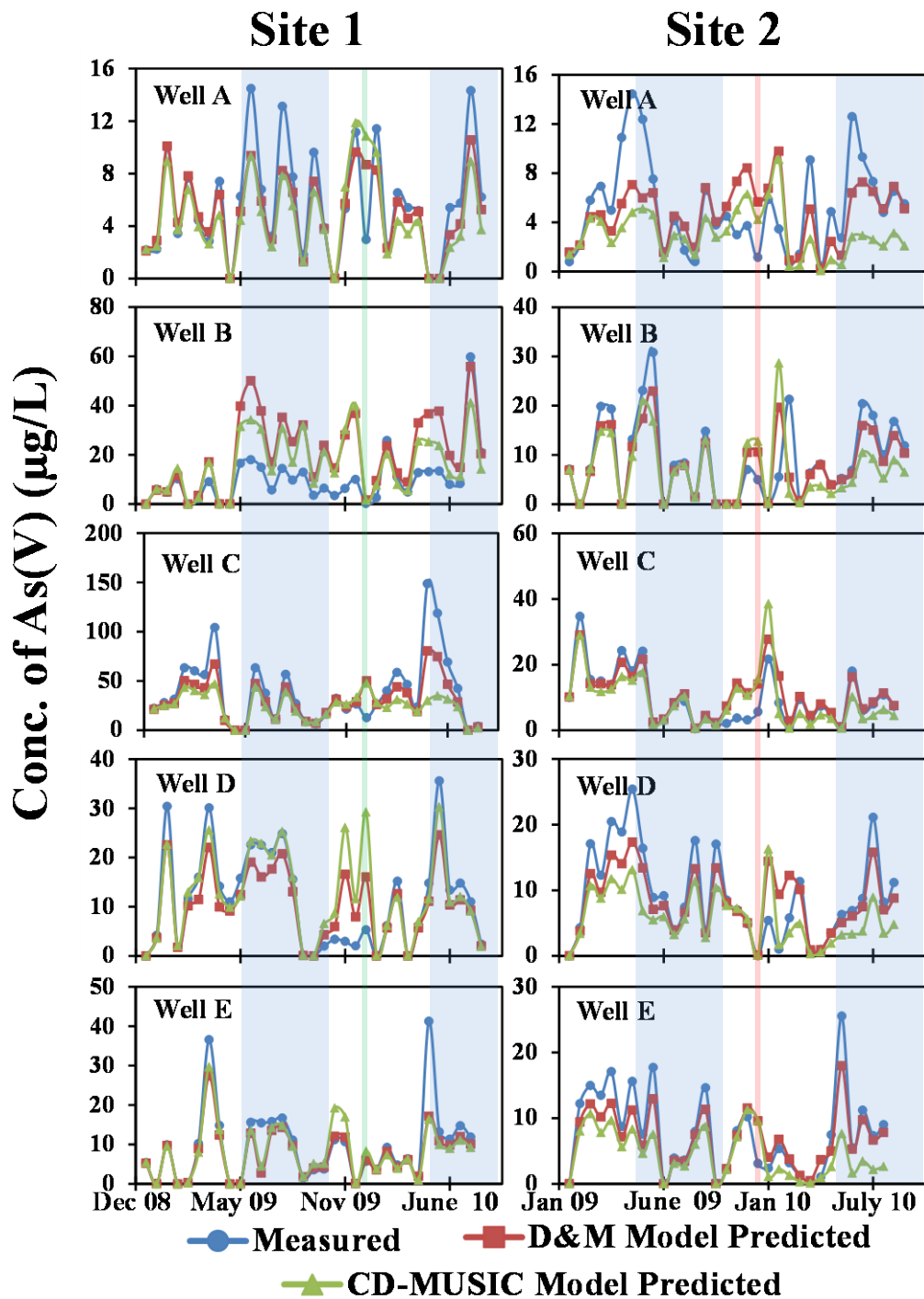
Fig. 2. Measured and predicted (with the D&M and CD-MUSIC SCMs) temporal variability in the concentration of aqueous As(V) for the piezometers of site 1 & 2. Blue-shaded area and white area in the figure represents monsoon period and dry period respectively. Green line and red line represents the time of pumping experiment at site 1 and bio-stimulation experiment at site 2 respectively.

D&M SCM
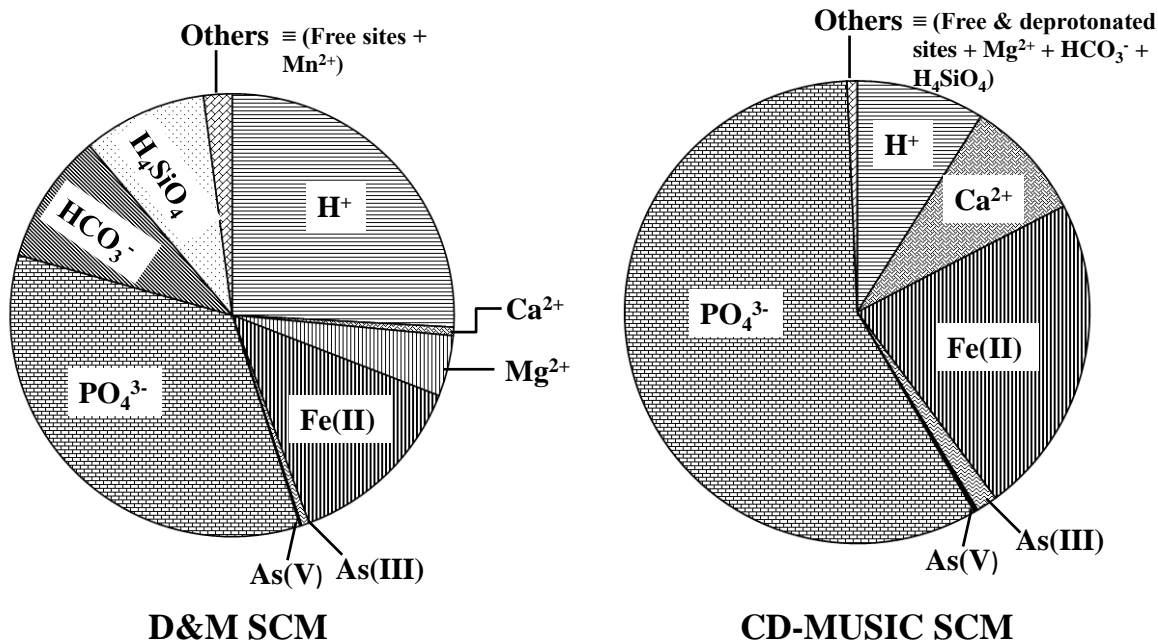
CD-MUSIC SCM

Fig. 3. The average D&M and CD-MUSIC SCMs predicted surface speciation of the weak adsorption sites, estimated by the equilibration of groundwater samples, collected from the well E of site 1. The fractional site occupancy by a component (except H^+) is calculated by adding all the surface complexes formed by the specific component with weak adsorption sites. For H^+, only the surface complex $>Fe\_OH_2^+$ and $>Fe\_OH_2^{0.5+}$ was considered for the calculation of fractional site occupancy in D&M and CD-MUSIC SCMs respectively.
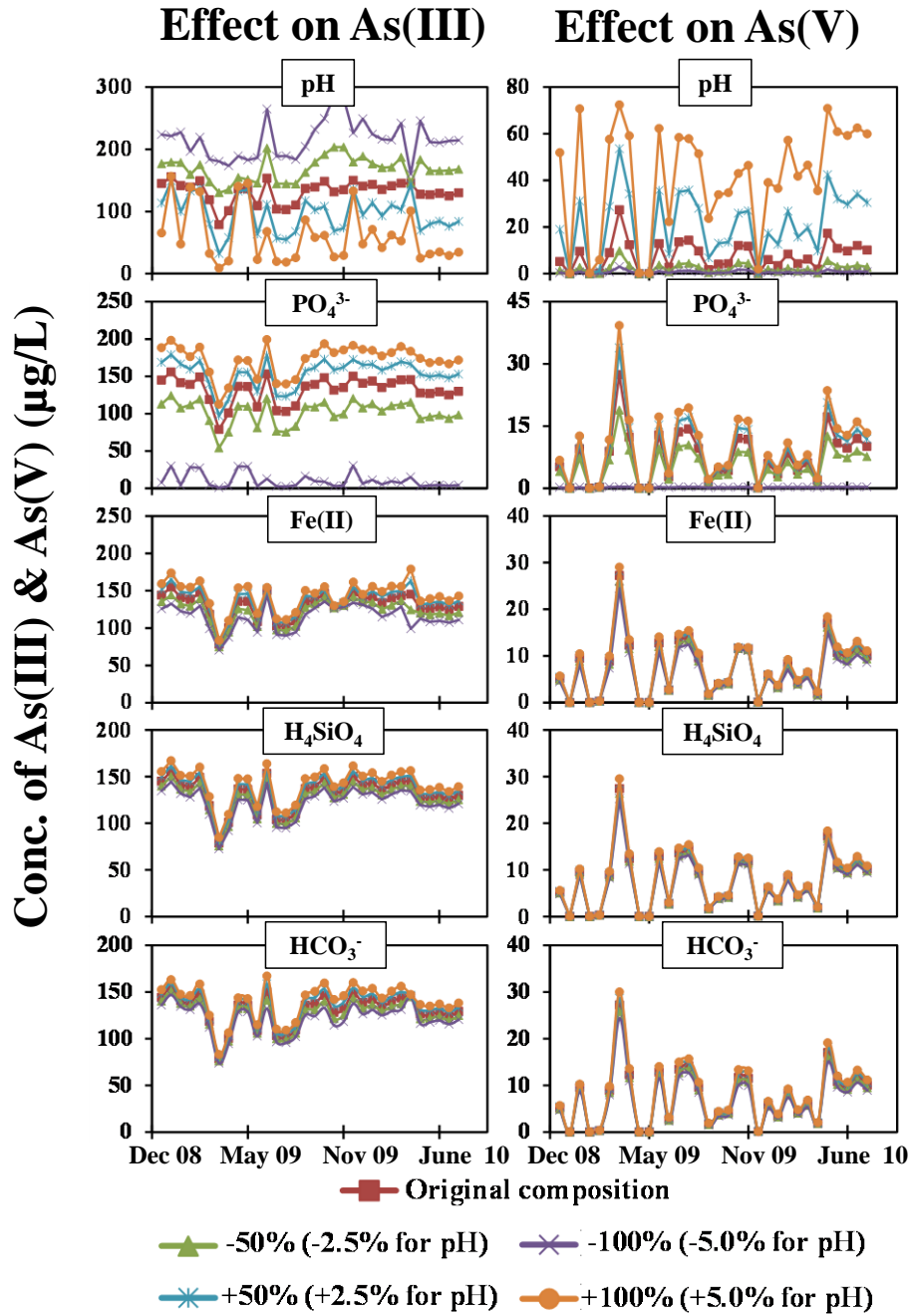
Fig. 4. Sensitivity of the modeled aqueous As(III) and As(V) concentration towards the change in pH and concentration of competing ions. A sensitivity test was performed by the simulation of the D&M SCM by equilibrating the groundwater samples of well E of site 1. In the sensitivity test only the value of selected parameter of interest was varied (-100% to +100%, except for pH, which was varied -5% to +5%), while keeping other parameters fixed to the measured value, in the simulation.

Appendix A

Role of competing ions in the mobilization of arsenic in groundwater of Bengal Basin: Insight from surface complexation modeling

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Content

Picture A.1. Picture of the piezometer nests at the two villages of Chakdaha Block, Nadia District, West Bengal, India.

Table A.1. Normalized sorbent content in each SCM for the piezometers of site 1 & 2.

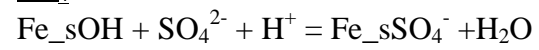| Location	Well ID	D&M SCM (g/L)	CD-MUSIC SCM (g/L)
Site 1	A	21.2	42.3
	B	4.81	10.5
	C	2.35	10.2
	D	6.72	10.2
	E	25.2	41.5
Site 2	A	16.8	49.0
	B	3.40	6.30
	C	15.0	31.0
	D	10.6	26.7
	E	6.48	19.2

Table A.2. Acid-base and surface complexation reactions and corresponding equilibrium constants used in the D&M SCM for ferrihydrite..

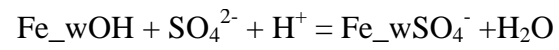| Reactions	Log K	Source
Acid-base reactions		
$>Fe\_sOH + H^+ = >Fe\_sOH_2^+$	7.29	Dzombak and Morel, 1990
$>Fe\_sOH = >Fe\_sO^-$	-8.93	Dzombak and Morel, 1990
$>Fe\_wOH + H^+ = >Fe\_wOH_2^+$	7.29	Dzombak and Morel, 1990
$>Fe\_wOH = >Fe\_wO^-$	-8.93	Dzombak and Morel, 1990
Surface Complexation reactions		
Ca^{2+}		
$>Fe\_sOH + Ca^{2+} = >Fe\_sOHCa^{2+}$	4.97	Dzombak and Morel, 1990
$>Fe\_wOH + Ca^{2+} = >Fe\_wOCa^+ + H^+$	-5.85	Dzombak and Morel, 1990
Mg^{2+}		
$>Fe\_wOH + Mg^{2+} = >Fe\_wOMg^+ + H^+$	-4.6	Dzombak and Morel, 1990
Mn2+		
$>Fe\_sOH + Mn^{2+} = >Fe\_sOMn^+ + H^+$	-0.4	Dzombak and Morel, 1990
$>Fe\_wOH + Mn^{2+} = >Fe\_wOMn^+ + H^+$	-3.5	Dzombak and Morel, 1990
Fe(II)		
$>Fe\_sOH + Fe^{2+} = >Fe\_sOFe^+ + H^+$	-0.95	Appelo et al., 2002
$>Fe\_wOH + Fe^{2+} = >Fe\_wOFe^+ + H^+$	-2.98	Liger et al., 1999
$>Fe\_wOH + Fe^{2+} + H_2O = >Fe\_wOFeOH + 2H^+$	-11.55	Liger et al., 1999
PO_4^{3-}		
$>Fe\_sOH + PO_4^{3-} + 3H^+ = >Fe\_sH_2PO_4 + H_2O$	32.08	Gustafsson, 2003
$>Fe\_wOH + PO_4^{3-} + 3H^+ = >Fe\_wH_2PO_4 + H_2O$	32.08	Gustafsson, 2003
$>Fe\_sOH + PO_4^{3-} + 2H^+ = >Fe\_sHPO_4^- + H_2O$	26.39	Gustafsson, 2003
$>Fe\_wOH + PO_4^{3-} + 2H^+ = >Fe\_wHPO_4^- + H_2O$	26.39	Gustafsson, 2003

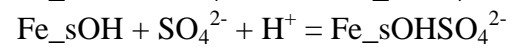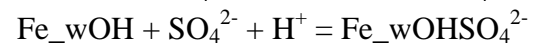|		
$>Fe\_sOH + PO_4^{3-} + H^+ = >Fe\_sPO_4^{2-} + H_2O$	20.73	Gustafsson, 2003
$>Fe\_wOH + PO_4^{3-} + H^+ = >Fe\_wPO_4^{2-} + H_2O$	20.73	Gustafsson, 2003
As(V)		
$>Fe\_sOH + AsO_4^{3-} + 3H^+ = >Fe\_sH_2AsO_4 + H_2O$	30.98	Gustafsson and Bhattacharya, 2007
$>Fe\_wOH + AsO_4^{3-} + 3H^+ = >Fe\_wH_2AsO_4 + H_2O$	30.98	Gustafsson and Bhattacharya, 2007
$>Fe\_sOH + AsO_4^{3-} + 2H^+ = >Fe\_sHAsO_4- + H_2O$	25.84	Gustafsson and Bhattacharya, 2007
$>Fe\_wOH + AsO_4^{3-} + 2H^+ = >Fe\_wHAsO_4^- + H_2O$	25.84	Gustafsson and Bhattacharya, 2007
$>Fe\_sOH + AsO_4^{3-} + H^+ = >Fe\_sAsO_42^- + H_2O$	19.5	Gustafsson and Bhattacharya, 2007
$>Fe\_wOH + AsO_4^{3-} + H^+ = >Fe\_wAsO_4^{2-} + H_2O$	19.5	Gustafsson and Bhattacharya, 2007
$>Fe\_sOH + AsO_4^{3-} = >Fe\_sOHAsO_4^{3-}$	11.92	Gustafsson and Bhattacharya, 2007
$>Fe\_wOH + AsO_4^{3-} = >Fe\_wOHAsO_4^{3-}$	11.92	Gustafsson and Bhattacharya, 2007
As(III)		
$>Fe\_sOH + H_3AsO_3 = >Fe\_sHAsO_3^- + H^+$	-2.19	Gustafsson and Bhattacharya, 2007
$>Fe\_wOH + H_3AsO_3 = >Fe\_wHAsO_3^- + H^+$	-2.19	Gustafsson and Bhattacharya, 2007
$>Fe\_sOH + H_3AsO_3 = >Fe\_sH_2AsO_3 + H_2O$	5.27	Gustafsson and Bhattacharya, 2007
$>Fe\_wOH + H_3AsO_3 = >Fe\_wH_2AsO_3 + H_2O$	5.27	Gustafsson and Bhattacharya, 2007
H_4SiO_4		
$>Fe\_sOH + H_4SiO_4 = >Fe\_sH_3SiO_4 + H_2O$	4.28	
$>Fe\_wOH + H_4SiO_4 = >Fe\_wH_3SiO_4 + H_2O$	4.28	Swedlund and Webster, 1999
$>Fe\_sOH + H_4SiO_4 = >Fe\_sH_2SiO_4^- + H^+ + H_2O$	-3.22	
$>Fe\_wOH + H_4SiO_4 = >Fe\_wH_2SiO_4^- + H^+ + H_2O$	-3.22	Swedlund and Webster, 1999
$>Fe\_sOH + H_4SiO_4 = >Fe\_sHSiO_4^{2-} + 2H^+ + H_2O$	-11.69	
$>Fe\_wOH + H_4SiO_4 = >Fe\_wHSiO_4^{2-} + 2H^+ + H_2O$	-11.69	Swedlund and Webster, 1999
HCO_3^-		
$>Fe\_sOH + CO_3^{2-} + H^+ = >Fe\_sCO_3^- + H_2O$	12.78	
$>Fe\_wOH + CO_3^{2-} + H^+ = >Fe\_wCO_3^- + H_2O$	12.78	Appelo et al., 2002
$>Fe\_sOH + CO_3^{2-} + 2H^+ = >Fe\_sHCO_3 + H_2O$	20.37	
$>Fe\_wOH + CO_3^{2-} + 2H^+ = >Fe\_wHCO_3 + H_2O$	20.37	Appelo et al., 2002

$\underline{SO_4{}^{2-}}$

$Fe\_sOH + SO_4{}^{2-} + H^+ = Fe\_sSO_4{}^- + H_2O$	7.78	
$Fe\_wOH + SO_4{}^{2-} + H^+ = Fe\_wSO_4{}^- + H_2O$	7.78	Dzombak and Morel, 1990
$Fe\_sOH + SO_4{}^{2-} + H^+ = Fe\_sOHSO_4{}^{2-}$	0.79	
$Fe\_wOH + SO_4{}^{2-} + H^+ = Fe\_wOHSO_4{}^{2-}$	0.79	Dzombak and Morel, 1990

Table A.3. Statistical summary of the temporal variation of As(III) and As(V) concentrations in the piezometers of site 1 & 2.

Location	Well ID	No. of sample	As(III) (µg/L)		As(V) (µg/L)	
			Range	Average ± Stdev	Range	Average ± Stdev
	A	33	43.0 - 112	68.5 ± 17.1	BDL - 14.5	5.70 ± 4.07
	B	33	70.1 - 393	158 ± 103	BDL - 59.8	10.0 ± 11.0
Site 1	C	33	20.6 - 317	234 ± 63.0	BDL - 149	39.0 ± 35.0
	D	33	189 -279	223 ± 22.0	BDL - 35.6	11.0 ± 10.0
	E	32	105 - 155	138 ± 14.0	BDL - 41.3	10.0 ± 10.0
	A	33	16.8 - 127	56.1 ± 29.6	0.40 - 14.4	5.20 ± 3.71
	B	33	102 - 162	130 ± 13.1	BDL - 30.8	9.10 ± 8.24
Site 2	C	32	93.2 - 128	112 ± 10.5	0.50 - 34.7	9.59 ± 8.20
	D	32	85.3 - 129	108 ± 11.4	BDL - 25.4	9.17 ± 6.86
	E	31	90.2 - 140	112 ± 13.0	BDL - 25.5	7.76 ± 6.33

Table A.4. Estimated root mean square error (RMSE) values for assessing the accuracy of fitting of the measured concentrations of As(III) and As(V) to the respective modeled concentrations, predicted by D&M and CD-MUSIC SCMs for the piezometers of two sites.

Location	Well ID	As(III)		As(V)	
		D&M Model	CD-MUSIC Model	D&M Model	CD-MUSIC Model
	A	0.10	0.15	0.15	0.19
	B	0.40	0.34	0.40	0.35
Site 1	C	0.10	0.23	0.15	0.25
	D	0.09	0.12	0.24	0.30
	E	0.06	0.12	0.24	0.25
	A	0.17	0.18(0.31)*	0.25	0.21(0.32)
	B	0.06	0.06(0.18)	0.27	0.26(0.24)
Site 2	C	0.09	0.06(0.18)	0.21	0.18(0.15)
	D	0.08	0.14(0.24)	0.28	0.22(0.20)
	E	0.09	0.14(0.32)	0.16	0.16(0.29)

*In site 2, for CD-MUSIC SCM, the RMSE values were estimated for pre- and post-bio-stimulation experiment period, to evaluate the effect of bio-stimulation experiment on the model performance. The values of RMSE for post-experiment period are given in the parenthesis.
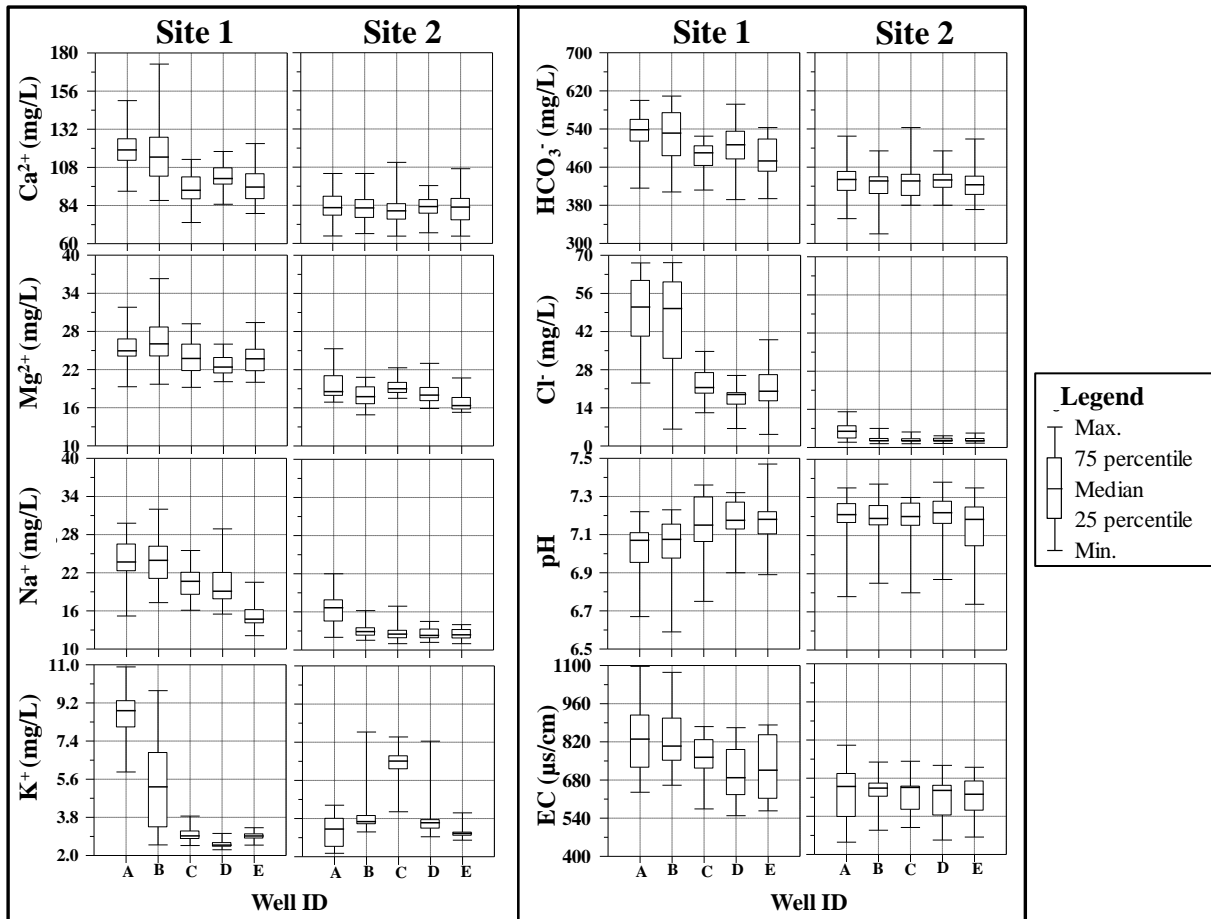
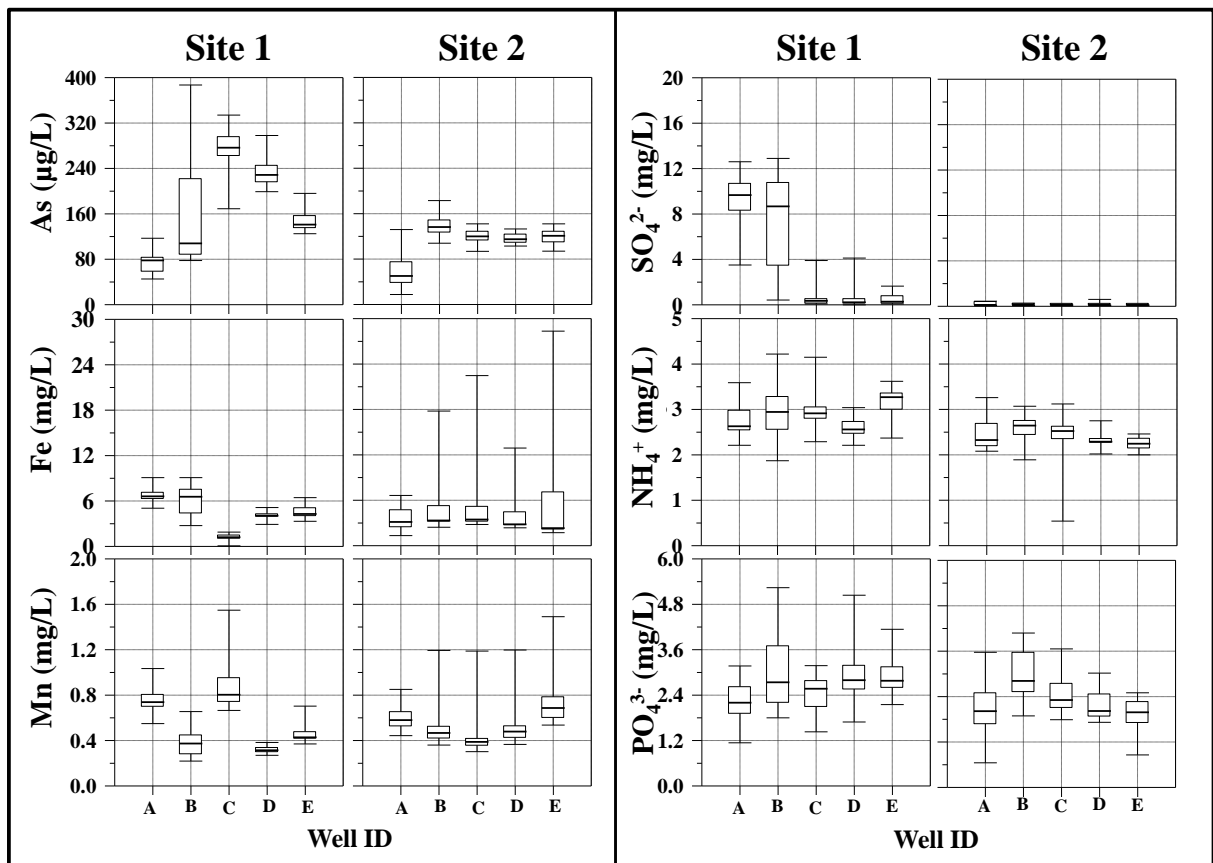*Fig. A.1. Distribution of major cations, anions, pH and electrical conductivity (EC) in the wells at two sites.*

Fig. A.2. Distribution of As and other aqueous redox parameters in the wells at two sites. The legend of the Box Whisker plot is same as Fig. A.2.
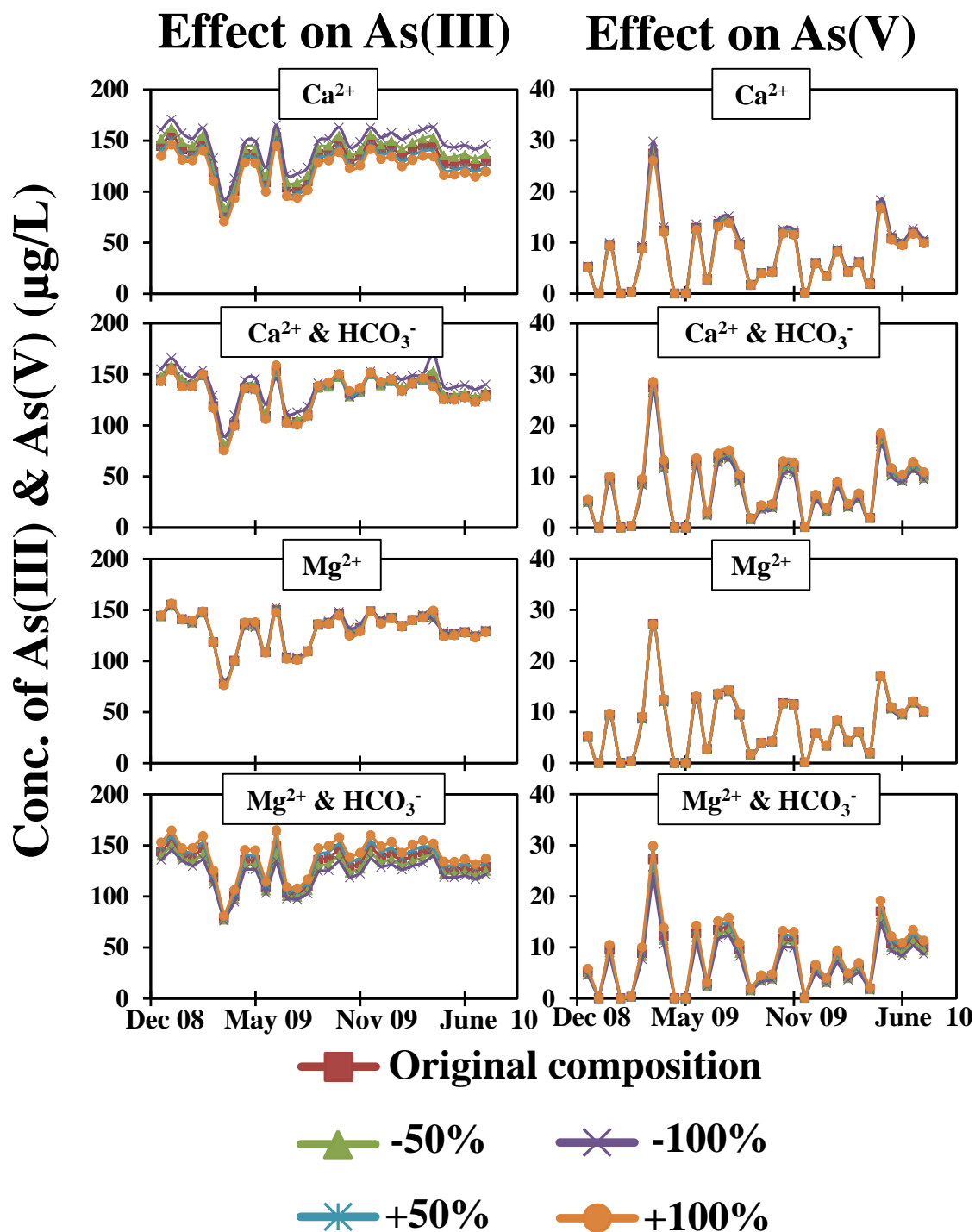
Fig. A.3. Sensitivity of the modeled aqueous As(III) and As(V) concentration towards the change in the concentration of Ca^{2+}, Mg^{2+} and HCO_3^- in different combination. A sensitivity test was performed by the simulation of only D&M SCM by equilibrating the groundwater samples of well E of site 1. In the sensitivity test only the value of selected parameter of interest was varied (-100% to +100%), while keeping other parameters fixed to the measured value, in the simulation.

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