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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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Abstract

This study assesses the role of competing ions in the mobilization of arsenic (As) by surface complexation modeling of the temporal variability of As in groundwater. The potential use of two different surface complexation models (SCMs), developed for ferrihydrite and goethite, has been explored to account for the temporal variation of As(III) and As(V) concentration, monitored in shallow groundwater of Bengal Basin over a period of 20 months. The SCM for ferrihydrite is the better predictor of the observed variation in both As(III) and As(V) concentrations in the study sites. Among the competing ions, PO_4^{3-} was the major competitor of As(III) and As(V) adsorption onto Fe oxyhydroxide, and the competition ability decreases in the order PO_4^{3-} >> Fe(II) > H_4SiO_4 = HCO_3^-. It is further revealed that a small change in pH can also have a significant effect on the mobility of As(III) and As(V) in the aquifers. A decrease in pH increases the concentration of As(III), whereas it decreases the As(V) concentration and vice versa. The present study suggests that the reductive dissolution of Fe oxyhydroxide alone cannot explain the observed high As concentration in groundwater of the sedimentary aquifers. This study supports the view that the reductive dissolution of Fe oxyhydroxide followed by competitive sorption reactions with the aquifer sediment are the processes responsible for As enrichment in groundwater.

Keywords: Bengal Basin; Groundwater; Arsenic mobilization; Temporal variability; Competing ions; Surface complexation modeling

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 sediment and dissolved As concentration in groundwater, which led them to emphasize the role of adsorptive equilibria in the As mobilization. Meanwhile, Kim et al. (2000), Appelo et al. (2002), and Anawar et al. (2004) claimed that the high concentration of HCO_3^- in groundwater may be responsible for the mobilization of As in Bengal Basin aquifers; however, this was not experimentally supported by Meng et al. (2000), Radu et al. (2005) and Stachowicz et al.(2007). Sometimes the adsorption of H_4SiO_4 has also been considered as a competitor of As adsorption onto Fe oxyhydroxide (Meng et al., 2000; Swedlund and Webster, 1999). Based on batch experiments involving multi-sorbate ions, Meng et al. (2002) showed that although PO_4^{3-}, HCO_3^- and H_4SiO_4 can compete with As(III) adsorption onto Fe oxyhydroxide, their effect on As(V) adsorption is very small even at high concentration and suggested that the high mobility of As in Bengal Basin aquifers is due to their combined effect. Recently, by similar experiment and subsequent modeling, Stollenwerk et al. (2007) and Stachowicz et al. (2008) again concluded that PO_4^{3-} is the major competitor for As adsorption and in the presence of significant PO_4^{3-} the competition of HCO_3^- becomes negligible. However, these contradictory conclusions are made mostly based on laboratory adsorption studies. Because of the complexity of the competitive adsorption equilibria (Stachowicz et al., 2008), so far only a very few studies (for e.g. Jessen et al., 2012; Postma et al., 2007; Swartz et al., 2004), have attempted to simulate the natural groundwater condition to assess the role of adsorptive equilibria in the As mobilization.

The objective of the present study is to fill up the gap in existing knowledge with the assessment of relative roles of different competing ions in the As mobilization by means of surface complexation modeling of the naturally occurring As enriched groundwater in the aquifer of Bengal Basin. A total of 10 piezometers have been monitored for aqueous As and other important hydrogeochemical parameters including different competing ions, over a period of 20 months. Such monitoring has provided the opportunity to assess the role of different competitive adsorption equilibria in the As mobilization processes by testing the hypothesis that temporal variation of As in groundwater of Bengal Basin is governed by the variation in concentration of competing ions. Two different surface complexation models (SCMs) have been used to test this hypothesis. The relative roles of different competing ions on the As mobilization is assessed by testing the sensitivity of the modeled aqueous As concentration towards changes in the concentration of specific competing ion.

2. Materials and methods

2.1. Piezometers installation, groundwater sampling and laboratory analysis

Based on a survey at Chakdaha Block of Nadia District, West Bengal, two sites at the village of Sahispur (Site 1; 23^{0}04'15.5"N, 088^{0}36'33.5"E) and Chakudanga (Site 2; 23^{0}04'58"N, 088^{0}38'13"E), where the concentration of As in groundwater was high and relatively low respectively, were selected for piezometers installation. At each site over an area of 25 m^2, five piezometers (well A, B, C, D and E) were installed with different screening 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: 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 groundwater samples (see Appendix for the picture of piezometer nests). Continuous sediment cores were collected during drilling of deepest piezometer (well E) at each site, using a split-spoon core barrel fitted to a PVC tube of 0.65 m length. Sediment samples were preserved in the field by flushing with N_2, followed by rubber capping at both end of the barrel.

The piezometers were sampled in 15 days intervals over a period of 20 months (December 2008 – July 2010). The regular sampling interval at both sites was interrupted once, in the month December 2009, when pumping and in-situ bio-stimulation experiments were 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-

MS, with percentage of Fe(II) and subtracting the calculated Fe(II) concentration from total Fe concentration respectively. For the samples, where percentage of Fe(II) was not measured, median percentage of Fe(II) for other samples of the corresponding well was used for the calculation of concentrations. Furthermore, the concentration of H_4SiO_4 was not measured for the monitoring samples but was measured during pumping and bio-stimulation experiment at site 1 and 2 respectively. Tto incorporate the competition effect of H_4SiO_4 on As adsorption in the simulations, the baseline value for each well, determined just before these experiments was considered for all samples of the corresponding wells.

2.2. Modeling approach

One key step during the setup of different SCMs is the selection of sorbent phase(s) to be used during simulation. An operationally defined seven-step sequential extraction of As from aquifer sediments (n = 13) together with the association of As and Fe in sediment column at both the study sites have indicated that As is mainly present in the specifically adsorbed fraction, bound to amorphous to crystalline Fe oxides (Biswas et al., submitted for publication; Neidhardt et al., 2013a, b). Similar findings have been also reported from other parts of the study area (Métral et al., 2008), Bangladesh (Swartz et al., 2004; van Geen et al., 2008), and Vietnam (Berg et al., 2008). Ferrihydrite, the major Fe oxyhydroxide mineral in oxic and slightly anoxic sediment (Stachowicz et al., 2007), has been used extensively for previous adsorption studies. Additionally, the investigations of Fe mineralogy in the reduced sediment, collected from the As-rich aquifers of Meghna and Red River flood plain have also indicated the presence of relatively crystalline goethite (Datta et al., 2009; Postma et al., 2010), which has strong affinity for As(III) and As(V) adsorption (Dixit and Hering, 2003). Recently, Jessen et al. (2012) have also pointed out that for the reduced aquifer sediment the use of SCM for goethite may be more appropriate. Thus in our simulations, we studied the SCMs for both ferrihydrite and goethite. For ferrihydrite, we used 2-pK diffuse layer SCM, as proposed by Dzombak and Morel, (1990) (hereafter referred to as D&M SCM). For goethite, the 3-plane CD-MUSIC SCM, developed by Hiemstra and van Riemsdijk, (1996) was used. Considering the fact that the purpose of the present study was not to compare between the two model parameterizations, these two different SCMs were chosen as they are thermodynamically most developed and frequently used for simulations of ion adsorption onto ferrihydrite- or goethite-containing materials. Furthermore, an underlying assumption with the selection of sorbent phases for the two models was that the adsorbing behavior of the Fe oxyhydroxides present in the aquifer sediment is well approximated by their pure synthetic analogs (Davis et al., 1998). However, it should be mentioned here that in natural reduced aquifer sediment these sorbent phases are more heterogeneous, often the complex mixture of multiple impure phases and further interact with other metal oxyhydroxides (for e.g. Mn and Al oxyhydroxides), clay minerals and organics (Hiemstra et al., 2010; Jessen et al., 2012). Thus in the aquifer the mobilization and transport behavior of As may be more complex compared to the assumption made. However, the simulation of such complexity demands further development of thermodynamic database for the surface complexation reactions of As to the natural aquifer sediment.

The sorbent contents in the two SCMs were normalized for the individual well by equilibrating the first monitoring sample of specific well, following the approach of Postma et al. (2007) (Appendix Table A.1). The sorbent content was varied until the modeled aqueous As(III) and As(V) agreed with their measured concentrations. We hypothesized that the amount of sorbent content in the sediment and total As content in the system ($As_{adsorbed}$ + $As_{dissolved}$) for a particular well remained the same over the monitoring period; only the variation in pH and concentrations of competing ions determined the extent of partitioning of As between sorbent and aqueous phase and thus the temporal variation of As in groundwater. Consequently, the sorbent content in the specific SCM and total As content in the system for a particular well were kept constant during the equilibration of all groundwater samples, collected from the same well. The total As content in the system for a particular well was calculated by adding the readily mobilizable and specifically adsorbed As content in the sediment of screen position [converted to g/L assuming the porosity and grain density of aquifer sediment as 0.3 and 2.65 g/cm^3 respectively (Jessen et al., 2012)] to the average dissolved As content in groundwater of the respective well. The readily mobilizable and specifically adsorbed pools of As in the sediment samples were extracted in the first two steps of sequentially extractions with 0.05 M $(NH_4)_2SO_4$ and 0.5 M NaH_2PO_4 respectively (Eiche et al., 2008).

The geochemical code Visual MINTEQ ver. 3.0 was used for all the simulations (Gustafsson, 2011). For the D&M SCM of ferrihydrite, the parameters were set to the default values of Visual MINTEQ, whereas the CD-MUSIC SCM for goethite was parameterized according to Jessen et al. (2012). The input concentrations for the measured groundwater components (except As) were specified as '*Total Dissolved*' in the simulations. For all groundwater samples, the value of Eh corresponding to H_3AsO_3/AsO_4 redox couple was calculated from the measured concentration of As(III) and As(V) in a separate speciation modeling exercise. Instead of field measured Eh value, this calculated Eh value was specified during simulations of both SCMs for the corresponding groundwater sample so that the ratio of modeled aqueous As(III) to As(V) would become similar to the measured value and thus the exact influence of As speciation into surface complexation reactions could be accounted. In all simulations, ferrihydrite was allowed to precipitate with log $^*K_s$ of 3.2 at 25°C (where $^*K_s = \{Fe^{3+}\}/\{H^+\}^3$). For simulations with the D&M SCM, we used the default database in Visual MINTEQ, *feo-dlm_2008.vdb*. This is based on the database of Dzombak and Morel, (1990) but with the extension of surface species for HCO_3^- (Appelo et al., 2002), H_4SiO_4 (Swedlund and Webster, 1999), and Fe(II) (Appelo et al., 2002; Liger et al., 1999) and modification of equilibrium constants for the surface reactions of PO_4^{3-} (Gustafsson, 2003) As(III) and As(V) (Gustafsson and Bhattacharya, 2007) (Appendix Table A.2). For the simulation of CD-MUSIC SCM, all the surface complexation reactions and the corresponding equilibrium constants were taken from the database prepared by Jessen et al. (2012) (for details see their Electronic Annex Table EA-1).

3. Results and discussion

3.1. General hydrogeochemistry in the aquifer at two sites

As the present study does not focus on the discussion of the detailed hydrogeochemical evolution of the aquifer, here we present only the generic overview of groundwater composition at the two sites. In the groundwater at both sites, Ca^{2+} is the predominating cation followed by Mg^{2+}, Na^+ and K^+ and HCO_3^- is the major anion followed by Cl^-. Consequently, the groundwater at both sites is Ca-Mg-HCO_3-type to Ca-HCO_3 type with circumneutral pH (Appendix Fig. A.1). The concentration of SO_4^{2-} is mostly below the detection limit (BDL) over the monitoring period, except in the well A & B at site 1. Similarly, the concentration of NO_3^- is also mostly BDL in all the wells at both sites. The concentration of most of the ionic constituents is higher at site 1 compared to site 2. The EC in groundwater follows a similar trend, being higher at site 1 (Appendix Fig. A.1). In all the wells at both sites, the concentrations of dissolved As exceeds the WHO provisional drinking guideline of 10 µg/L. Arsenic shows the highest enrichment in well C and well B at site 1 and site 2 respectively (Appendix Fig. A.2). The aquifer at both sites is reducing in nature, where the lower oxidation state of As and Fe predominates over the corresponding higher oxidation sate. In all the wells, the concentration of PO_4^{3-} shows a strong positive correlation to As (Biswas et al., submitted for publication). The hydrogeochemical evolution of the groundwater composition at the two sites has been discussed in detail elsewhere (Biswas et al., submitted for publication). The groundwater composition presented here is representative for the shallow aquifers of whole Bengal Basin (Bhattacharta et al., 2002; Biswas et al., 2012; Charlet et al., 2007; Harvey et 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

The temporal variations of As(III) and As(V) over the monitoring period are displayed in Fig. 1 and 2 respectively. Additionally, the extent of variability is statistically estimated by calculating the standard deviation of As(III) and As(V) concentration (Appendix Table A.3). In all the piezometers of both sites, the standard deviation of As(III) concentration is ≥ 10 µg/L (Appendix Table A.3), reflecting strong temporal variation.

In site 1, a general trend of As(III) enrichment was observed for well A over the monitoring period (Fig. 1). A very strong temporal variation in As(III) concentration was observed for well B and C, where the concentration respectively varied between 70.1 – 393 µg/L and 20.6 – 317 µg/L, with a standard deviation of 103 µg/L and 63.0 µg/L respectively (Appendix Table A.3). In both wells, the variation followed a cyclic trend over the monitoring period (Fig. 1). In well B, starting from the monitoring in December 2008, the As(III) concentration had been decreasing over the dry season until the end of April 2009. No considerable variation was observed in the following 7 month period up to November 2009, when regular sampling was stopped for one month for the pumping experiment (Fig. 1). When sampling was started again in January 2010, the As(III) concentration increased to close the value recorded at the beginning of monitoring in December 2008 (Fig. 1). In the following dry season period, the variation pattern was similar to the previous year. However, this time the As(III) concentration increased instantly after approaching the minimum value in May 2010 (Fig. 1). In well C, a small decrease in the As(III) concentration was also observed at the end of April 2009 (Fig. 1). However in contrast to well B, after an initial decrease,, the concentration increased back to the original value instantaneously and was then quite stable throughout the rest of the year. When the well was first sampled in 2010 after the pumping experiment, the As(III) concentration was roughly the same (Fig. 1). In the following dry period of 2010, the variation pattern was similar to that in the previous year. However, this time the decrease in concentration was very large, resulting in the lowest value observed during the whole monitoring period considering all the piezometers of site 1 (Fig. 1). The temporal variation in As(III) concentration for well D and E of site 1 did not show any specific trend (Fig. 1). Except for well A, the standard deviation of As(V) in all other wells was ≥10 µg/L, being the highest for well C (Appendix Table A.3). However, the temporal variation did not show any specific trend over the monitoring period for any well (Fig. 2).

In site 2, the highest temporal variation was observed in well A (Fig. 1), where the As(III) concentration varied between 16.8 and 127 µg/L with a standard deviation of 29.6 µg/L (Appendix Table A.3). In contrast to the variation observed in site 1, the dissolved As(III) concentration increased at the beginning of dry period, both in 2009 and 2010 and the relative enrichment in 2010 was slightly higher than in 2009. After passing through the maximum value, the concentration decreased to the lowest value around the end of the dry season and no significant variation was observed in the following monsoon period (Fig. 1). The temporal variation in As(III) concentration for other wells of site 2 did not show any specific trend over the monitoring period (Fig. 1). The standard deviation of the As(V) concentration was throughout <10 µg/L for all wells (Appendix Table A.3) and no specific trend was observed in the temporal variation also (Fig. 2). The temporal variations of total As and other aqueous parameters at the two sites over the monitoring period have been reported in Biswas et al. (submitted for publication).

3.3. Application of SCMs in predicting temporal variability of As

To investigate the role of different surface complexation reactions onto aquifer materials in the As mobilization in groundwater, we attempted to model the temporal variability in As(III) and As(V) concentrations by use of the D&M and CD-MUSIC SCMs (Fig. 1 and 2). The comparison of the model-predicted concentration with the measured value indicates that though the performance of the CD-MUSIC SCM in predicting As(III) concentration in the wells of site 1 is fairly good, the predictions of the D&M SCM are even closer to the measured trends (Fig. 1). In site 2, the As(III) concentration predicted by both D&M and CD-MUSIC SCMs closely follows the measured concentration until the end of November 2009, when the sampling was stopped for one month for the bio-stimulation experiment (Fig. 1). In the post-experiment period, the CD-MUSIC SCM largely under-predicts the As(III) concentration, whereas the concentration predicted by the D&M SCM quite closely follows the measured value to the end of the monitoring (Fig. 1).

Estimation of root mean square error (RMSE) of the logarithm of dissolved As(III) concentration was used as an indicator of the accuracy of the models. This analysis supports the above inferences. In site 1 except for well B, the values of RMSE for the D&M SCM are ≤0.10, while the values for the CD-MUSIC SCM in all the wells are >0.10 (Appendix Table A.4), indicating the better performance of the D&M SCM over the CD-MUSIC SCM in predicting the variability of As(III) concentration at our study site. Similarly in site 2, except for well A the values of RMSE for the D&M SCM are <0.10. For the CD-MUSIC SCM, the RMSE was estimated for the pre- and post-experiment period separately, to evaluate the effect of bio-stimulation experiment on the model performance. In the pre-experiment period, the RMSE values are close to that calculated for D&M SCM; however, they have increased largely in the post-experiment period (Appendix Table A.4). The poor performance of both SCMs in predicting As(III) concentration for the well B and well A of site 1 and 2 respectively (Fig. 1), might be due to the fact that for these wells the total As content in the system did not remain constant over the monitoring period as our hypothesis. The investigations by Neidhardt et al. (2014) and Neidhardt et al. (2013a) have already pointed out the possibility of seasonal vertical mixing of groundwaters with distinct As concentrations from different depths in these two wells.

For As(V), the predicted concentration by both SCMs approximately follows the scattered peaks observed in the measured concentration over the monitoring period (Fig. 2). However, the estimation of RMSE indicates that the performance of the D&M SCM is to some extent better than that of the CD-MUSIC SCM and both models provide better estimations for As(III) than for As(V) (Appendix Table A.4).

3.4. Modeled surface speciation of the aquifer sediment

An attempt was also made to investigate the extent of formation of different complexes at the surface of sorbent considered in the two SCMs, by analyzing the simulated fractional site occupancy. Well E from site 1 was selected for this investigation, based on the low estimated RMSE values for both SCMs for the prediction of As(III) concentration in groundwater (Appendix Table A.4). The surface speciation of the weak sites on Fe oxyhydroxide, as predicted by the two SCMs, fairly well resembles each other (Fig. 3). According to both SCMs, the surface complexes of PO_4^{3-} are the major adsorbing species, covering 35% and 58% of the week surface sites of ferrihydrite and goethite, respectively. For ferrihydrite, the D&M SCM further predicts that H+ and Fe(II) occupy 26 % and 14 % of the surface sites, respectively. The CD-MUSIC SCM for goethite predicts a higher adsorption of Fe(II) (22%) compared to H^+ (9%) (Fig. 3). Though HCO_3^- is the major anion in groundwater, very low to negligible site occupancy by carbonate surface complexes is estimated by both the SCMs. According to the D&M SCM they only cover 10% of the surface sites, similar to the adsorption of H_4SiO_4 species, and the CD-MUSIC SCM estimates <1% of the surface coverage to be due to the complexes of the HCO_3^- and H_4SiO_4 species (Fig. 3). Following the large predominance of As(III) concentration over As(V) in groundwater, both SCMs predict higher average concentration of As(III) surface complexes compared to As(V) complexes. The previous study by Jessen et al. (2012) also reported similar surface speciation for the Vietnam aquifer sediment by the simulation of CD-MUSIC SCM for goethite, the only difference being a higher adsorption of As(V) compared to As(III). However, the estimation by the D&M SCM for ferrihydrite in the present study significantly differs from the composition of surface complexes previously calculated by the simulation of the D&M SCM for Bangladesh (Swartz et al., 2004), and for Vietnam aquifer sediment (Jessen et al., 2012; Postma et al., 2007), where H_4SiO_4 and HCO_3^-were reported to be the major adsorbing species with a relatively low surface coverage by PO_4^{3-}. Further, in agreement with the findings of Jessen et al. (2012) the CD-MUSIC SCM predicts the binding of As(III) to goethite exclusively by the formation of the As(III)-Fe(II) ternary surface complex ($>Fe\_uniOAs(OH)_3Fe^{+0.5}$). The formation of such a complex may explain the under-prediction of As(III) concentration by the CD-MUSIC SCM in the post-bio-stimulation experiment period for the wells at site 2. It should be mentioned here that due to the bio-stimulation in the aquifer by injecting degradable organic matter, the local groundwater composition was changed drastically for several days, including an elevation in As and Fe concentration (Neidhardt et al., 2014). When the regular monitoring was started again in January 2010, the As concentration had returned to the baseline value in all five piezometers (Fig. 1), while the Fe concentration remained elevated till the end of the monitoring (Neidhardt et al., 2014).

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

In order to estimate the relative roles of competing ions and pH on the As mobilization, the sensitivity of the modeled aqueous As(III) and As(V) concentrations towards the changes in the concentration of competing ions and pH was investigated (Fig. 4). The sensitivity test was performed by the simulation of only the D&M SCM for the well E of site 1. The D&M SCM was chosen as it better predicts the temporal variation of As at both study sites over the whole monitoring period. For the sensitivity test, only the concentration of the selected parameter of interest was varied (-100% to +100%, except for pH, which was varied -5% to +5%) in the simulation, while keeping concentration of other parameters fixed to the measured value. The results indicate that in the aquifer PO_4^{3-} is the major competitor of As(III) and As(V) adsorption onto Fe oxyhydroxide (Fig. 4) and the competition ability of the different ions decreases in the order PO_4^{3-} >> Fe(II) > H_4SiO_4 = HCO_3^-. In the simulation, when dissolved concentration of PO_4^{3-} is set to zero, the modeled concentration of both As(III) and As(V) is reduced on average by 92.5%. However, a similar imposition for the concentration of Fe(II), H_4SiO_4 and HCO_3^- in the simulation only reduces the As(III) concentration by 12.2%, 7.40%, and 7.04% respectively (Table 1). Phosphate, Fe(II) and H_4SiO_4 appears to be equally effective to compete with both As(III) and As(V), while HCO_3^- competes more strongly with As(V) as compared to As(III) (Table 1). Though previous studies have concluded that Fe(II) does not affect the re-sorption of As onto residual Fe oxyhydroxide (Appelo et al., 2002; Dixit and Hering, 2006), our results indicates a small but significant competition between Fe(II) and As for adsorption sites on Fe oxyhydroxides. It is further observed that the As concentration does not vary linearly with the change in PO_4^{3-} concentration. Although, the As(III & V) concentration is reduced by 92.5% when the PO_4^{3-} concentration is set to zero in the simulation, it is increased by only 31.4% when the PO_4^{3-} concentration is doubled (Table 1). This demonstrates that in the aquifer the competition of PO_4^{3-} with As for the adsorption sites might already reach close to maximum level. In contrast, the relationships with the other competing ions are still linear (Table 1).

Some studies have also concluded that Ca^{2+} can enhance the adsorption of As(V) onto Fe oxyhydroxide significantly particularly at high pH, by reducing the surface negative charge (Stachowicz et al., 2008). In contrast, recently Saalfield and Bostick, (2010) have suggested that the adsorption of Ca^{2+} or Mg^{2+} together with HCO_3^- can increase the desorption of As(V) from ferihydrite to a greater extent compared to their individual competition. To this end a sensitivity test was performed by changing the concentrations of these ions in different combinations. The results indicate that the change in concentration of Ca^{2+} and Mg^{2+} together with HCO_3^- affect the adsorption of both As(III) and As(V) to Fe oxyhydroxide almost negligibly (Appendix Fig. A.3).

The results further indicate that the pH value also has a strong influence on the mobility of As(III) and As(V) in the aquifer by changing their concentration oppositely to each other (Fig. 4). A 5% decrease in pH increases the As(III) concentration by 65.3% and decreases the As(V) concentration by 91.2% on average, representing greater influence on the As(V) mobility. The influence on the As(V) mobility becomes even more prominent during increase of pH (Table 1). The ease of formation of the major surface complexes for As(III) and As(V) determines their different behavioral pattern towards the change in pH. In the D&M SCM, the major surface complex for As(III) and As(V) are $>Fe\_wH_2AsO_3$ and $>Fe\_wHAsO_4^-$, respectively. With a decrease of pH the formation of $>Fe\_wH_2AsO_3$ and $>Fe\_wHAsO_4^-$ complexes and consequently the adsorption of As(III) and As(V) are constrained and favored respectively. Moreover, as reflected in the modeled speciation of surface complexes formed in the D&M SCM (Fig. 3), with a decrease of pH the protonation of the weak sites would be increased making them less available for As(III) adsorption. At the same time the protonation of the weak sites reduces the surface negative charge and consequently decreases the 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.

Acknowledgements

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Table 1. Average change in modeled aqueous As(III) and As(V) concentration for the samples collected from well E of site 1 in response to the variation in pH and concentration of different competing ions. The '-' & '+' signs indicates the decrease and increase of the value 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

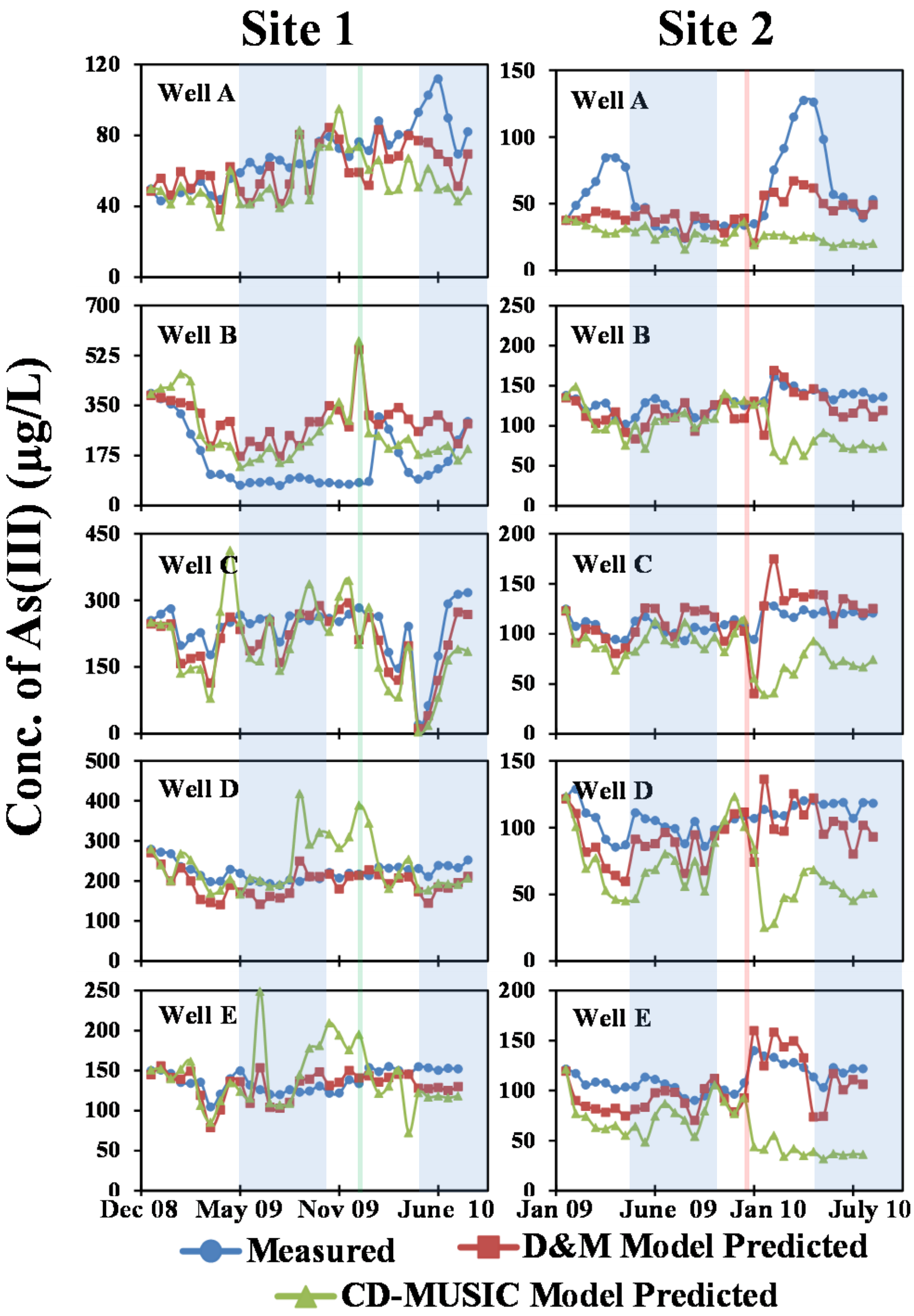

Fig. 1. Measured and predicted (with the D&M and CD-MUSIC SCMs) temporal variability in the concentration of aqueous As(III) for the piezometers of site 1 & 2. Blue-shaded area and white area in the figure represents monsoon period and dry period respectively. Green line and red line represents the time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

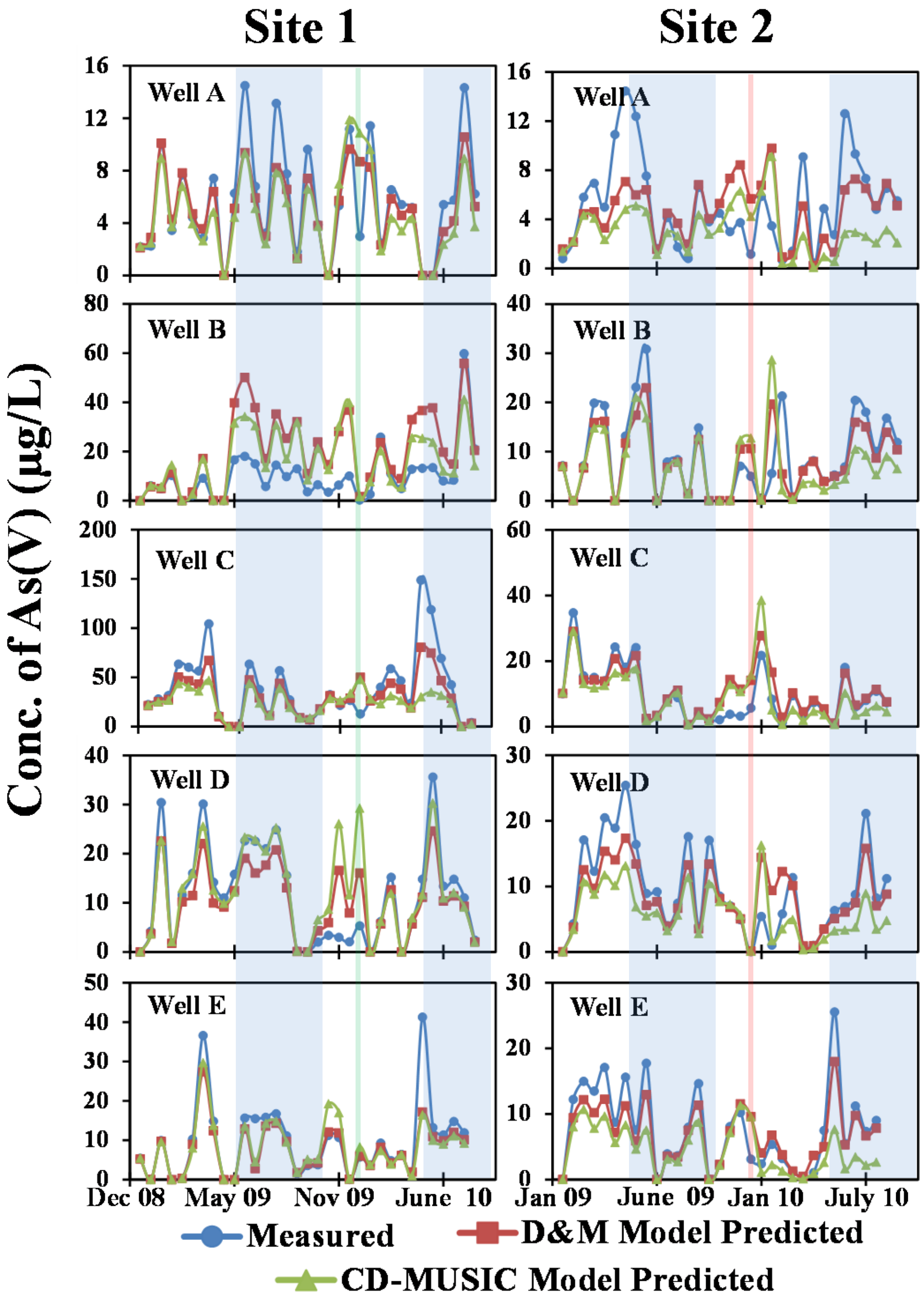

Fig. 2. Measured and predicted (with the D&M and CD-MUSIC SCMs) temporal variability in the concentration of aqueous As(V) for the piezometers of site 1 & 2. Blue-shaded area and white area in the figure represents monsoon period and dry period respectively. Green line and red line represents the time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

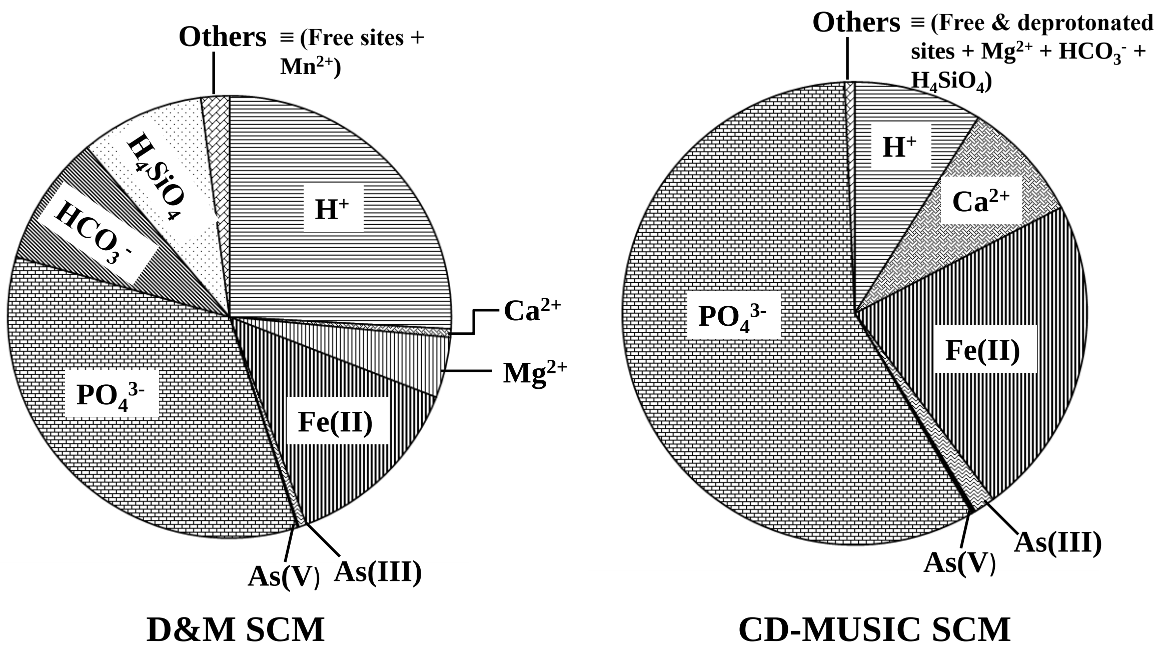

Fig. 3. The average D&M and CD-MUSIC SCMs predicted surface speciation of the weak adsorption sites, estimated by the equilibration of groundwater samples, collected from the well E of site 1. The fractional site occupancy by a component (except H^+) is calculated by adding all the surface complexes 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.

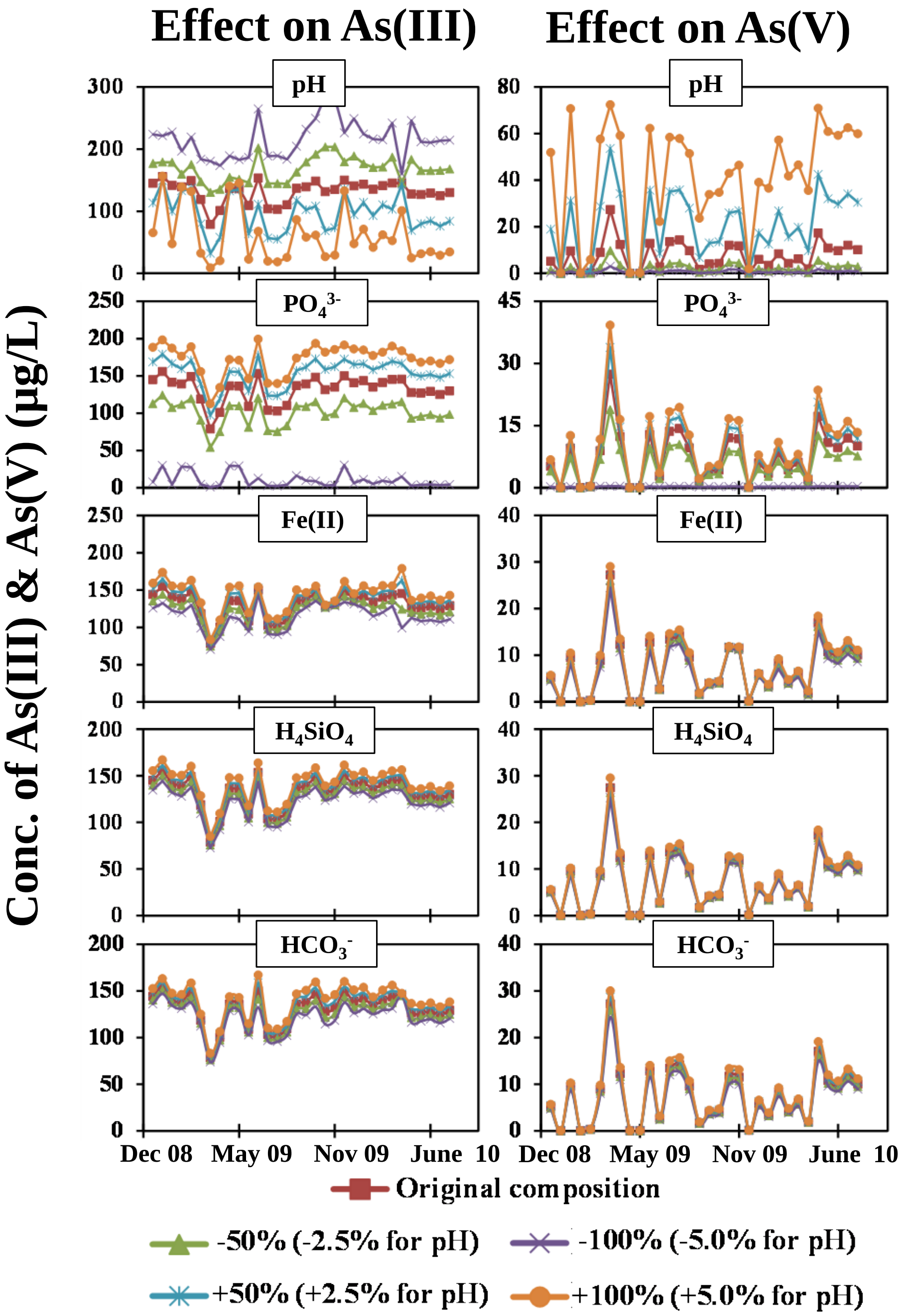

Fig. 4. Sensitivity of the modeled aqueous As(III) and As(V) concentration towards the change in pH and concentration of competing ions. A sensitivity test was performed by the simulation of the D&M SCM by equilibrating the groundwater samples of well E of site 1. In the sensitivity test only the value 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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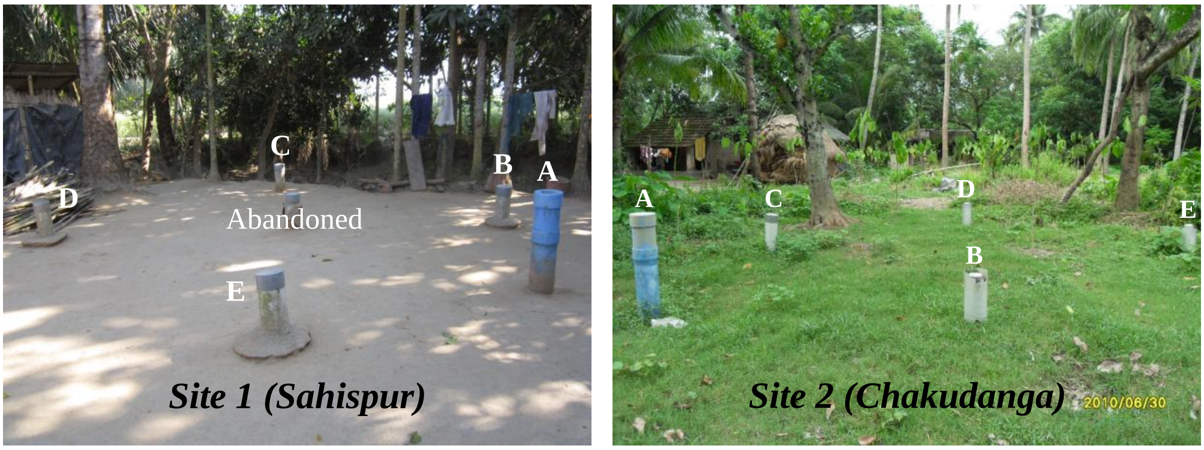
Content



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
Site 1	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
	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
Site 2	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
	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
Site 1	A	0.10	0.15	0.15	0.19
	B	0.40	0.34	0.40	0.35
	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
Site 2	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)
	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.

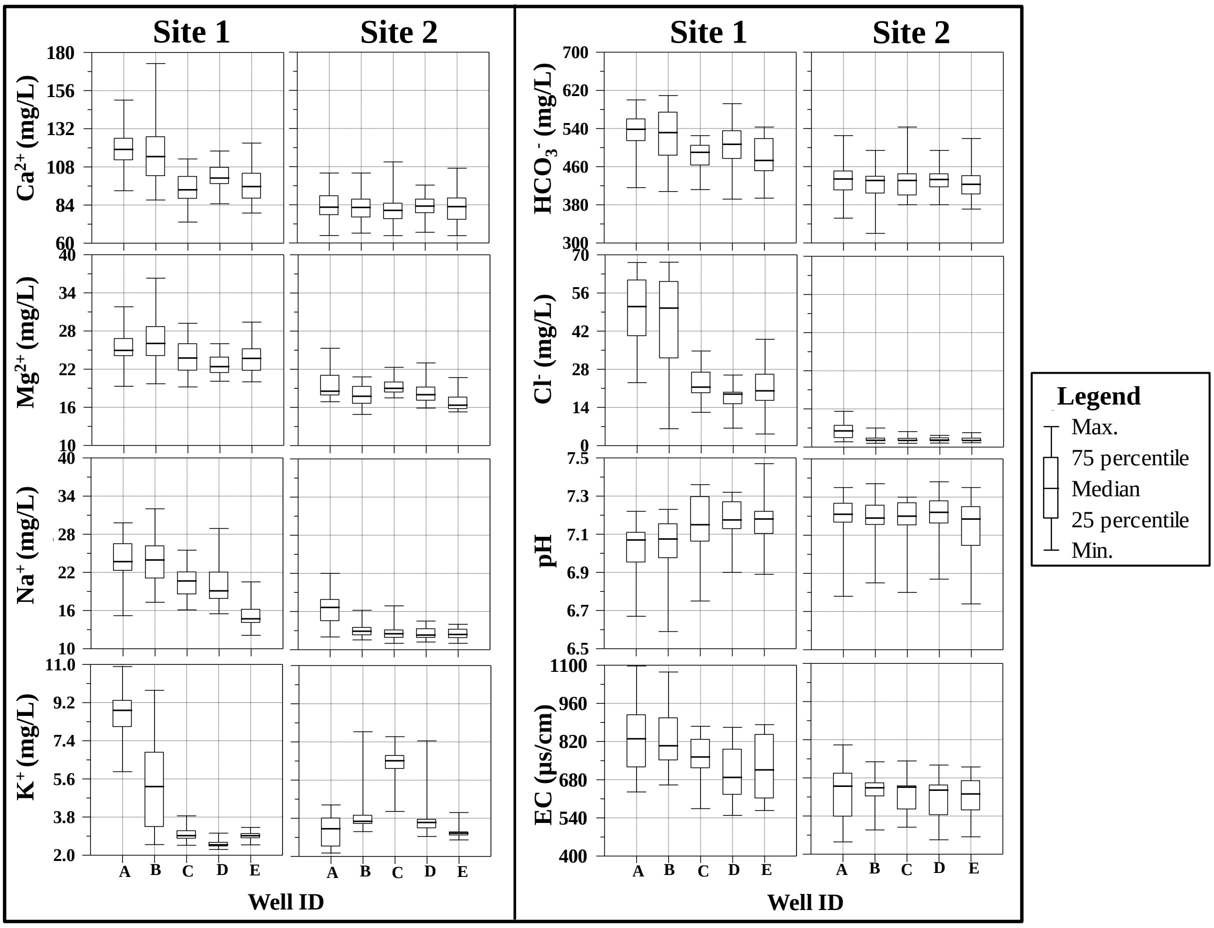


Fig. A.1. Distribution of major cations, anions, pH and electrical conductivity (EC) in the wells at two sites.

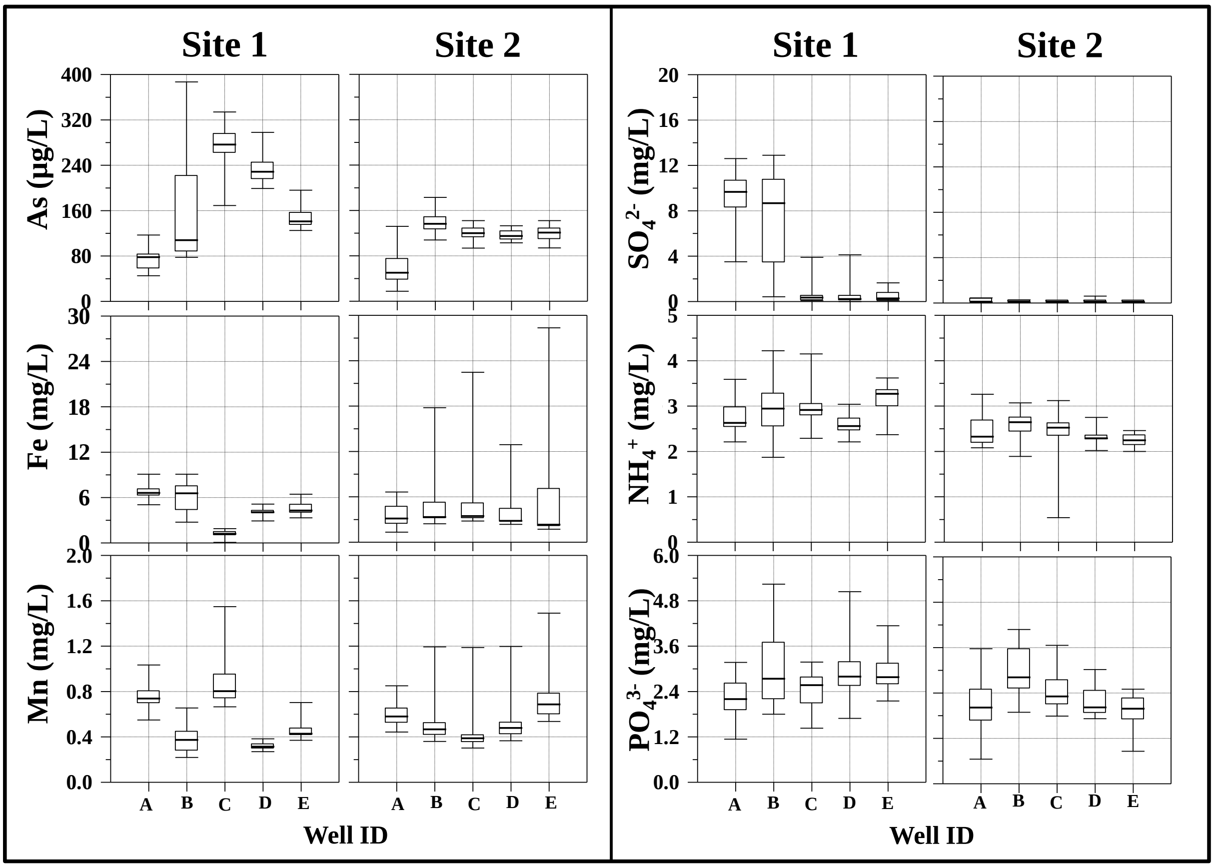


Fig. A.2. Distribution of As and other aqueous redox parameters in the wells at two sites. The legend of the Box Whisker plot is same as Fig. A.2.

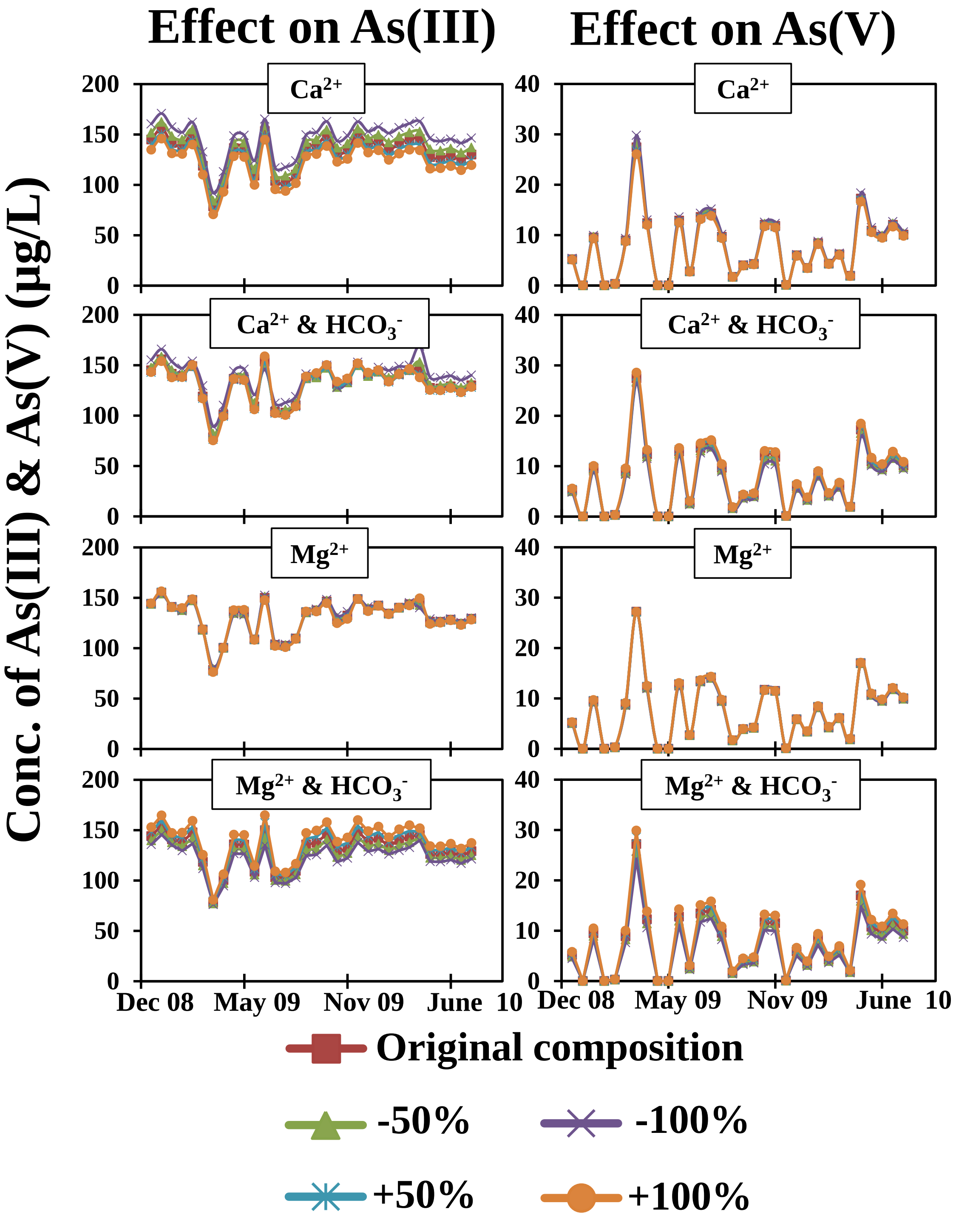


Fig. A.3. Sensitivity of the modeled aqueous As(III) and As(V) concentration towards the change in the concentration of Ca^{2+}, Mg^{2+} and HCO_3^- in different combination. A sensitivity test was performed by the simulation of only D&M SCM by equilibrating the groundwater samples of well E of site 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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