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Adsorption and desorption of arsenic to aquifer sediment on the Red River floodplain at Nam Du, Vietnam

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Abstract

The adsorption of arsenic onto aquifer sediment from the Red River floodplain, Vietnam, was determined in a series of batch experiments. Due to water supply pumping, river water infiltrates into the aquifer at the field site and has leached the uppermost aquifer sediments. The leached sediments, remain anoxic but contain little reactive arsenic and iron, and are used in our experiments. The adsorption and desorption experiments were carried out by addition or removal of arsenic from the aqueous phase in sediment suspensions under strictly anoxic conditions. Also the effects of HCO_3^- , Fe(II) , PO_4 and Si on arsenic adsorption were explored. The results show much stronger adsorption of As(V) as compared to As(III), full reversibility for As(III) adsorption and less so for As(V). The presence or absence of HCO_3^- did not influence arsenic adsorption. Fe(II) enhanced As(V) sorption but did not influence the adsorption of As(III) in any way. During simultaneous adsorption of As(III) and Fe(II) , As(III) was found to be fully desorbable while Fe(II) was completely irreversibly adsorbed and clearly the two sorption processes are uncoupled. Phosphate was the only solute that significantly could displace As(III) from the sediment surface. Compiling literature data on arsenic adsorption to aquifer sediment in Vietnam and Bangladesh revealed As(III) isotherms to be almost identical regardless of the nature of the sediment or the site of sampling. In contrast, there was a large variation in As(V) adsorption isotherms between studies. A tentative conclusion is that As(III) and As(V) are not adsorbing onto the same sediment surface sites. The adsorption behavior of arsenic onto aquifer sediments and synthetic Fe-oxides is compared. Particularly, the much stronger adsorption of As(V) than of As(III) onto Red River as well as on most Bangladesh aquifer sediments, indicates that the perception that arsenic, phosphate and other species compete for the same surface sites of iron oxides in sediments with properties similar to those of, for example a synthetic goethite, probably is not correct. A simple two-component Langmuir adsorption model was constructed to quantitatively describe the reactive transport of As(III) and PO_4 in the aquifer.

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1 Introduction

Contamination of groundwater by natural arsenic (As) continues to be a major health threat for the populations living on the flood plains of the great SE Asian rivers (Ravenscroft et al., 2009; Fendorf et al., 2010). To mitigate the arsenic problem we need a quantitative understanding of the processes regulating the aqueous arsenic concentration. It is now broadly accepted that the reductive dissolution of As-containing Fe-oxides is the source of the arsenic released to the groundwater (McArthur et al., 2001; Dowling et al., 2002; Harvey et al., 2002; Swartz et al., 2004; Postma et al., 2007, 2010, 2012). The spatial distribution of arsenic thereafter becomes a function of the mobility of arsenic, which can be affected by sorption processes and also by reprecipitation of arsenic in particularly Fe(II) containing secondary precipitates (Postma et al., 2012).

Sorption of arsenic to the aquifer sediment has been investigated by different approaches. In some studies the adsorption properties are derived from determining the retardation *in situ* (Harvey et al., 2002; Radloff et al., 2011; van Geen et al., 2013,) and such studies in principle both comprise the effect of sorption and precipitation on retardation. In other studies the arsenic adsorption isotherm is determined from adsorbed As measured on the sediment, using various extraction methods, and the dissolved arsenic concentration in the groundwater (BGS and DPHE, 2001; Swartz et al., 2004; Radloff et al., 2007; van Geen et al., 2008; Nath et al., 2009; Itai et al., 2010). Still others have carried out laboratory adsorption studies where the adsorption isotherms are determined by addition of arsenic in batch experiments with aquifer sediment (Stollenwerk et al., 2007; Nath et al., 2009; Itai et al., 2010; Radloff et al., 2011). And finally BGS and DPHE (2001), Swartz et al. (2004), Appelo et al. (2002) and Postma et al. (2007) all have used the Dzombak and Morel (1990) surface complexation model for ferrihydrite to assess the partitioning of arsenic between water and sediment in particular to determine competitive effects by other anions. Stollenwerk et al. (2007) constructed a hybrid model by superimposing the results of adsorption experiments on aquifer sediments on top of the Dzombak and Morel (1990) model for ferrihydrite. Jessen et al. (2012) applied different surface complexation models on the results of a forced gradient field experiment and found that the different models yield very different results.

One of the most difficult aspects in studying the geochemical interactions between the groundwater and the aquifer sediment is to identify and separately describe the different types of processes. Normally organic matter degradation and associated redox processes, precipitation and dissolution, and adsorption-desorption reactions all occur concomitantly with the effects superimposed (Postma et al., 2007; 2012). In this respect the field setting at Nam Du on the banks of the Red River in the outskirts of Hanoi, association is unique. Because of the long-term groundwater abstraction by Hanoi water supply, river water has been infiltrating the adjacent aquifer for at least the last 20 years (van Geen et al., 2013; Norrman et al., 2008). The river water contains no arsenic and the infiltrating river water has leached the upper 10 m of aquifer sediment, to the extent that it still is anoxic but the groundwater contains very little arsenic and iron in this zone. We will use the leached aquifer sediment at 5-6 m depth to investigate the adsorption and desorption properties of the aquifer sediment for arsenic and competing species without the complications caused by

secondary precipitates. The final objective is to develop a trustworthy adsorption model for the incorporation into reactive transport models.

2 Materials and Methods

2.1 Sediment characterization

Sediment cores were taken at Nam Du on the banks of the Red River (20°58'15.50"N, 105°54'6.96"E) by using a piston corer in stainless steel coreliners and stored frozen within the coreliners. The sediment used for the adsorption and desorption experiments consists of grey fine grained sand and is from 5.6-5.85 m depth. The sediment used for the competition experiments is from 5.90-6.05 m depth and is visually similar. In this depth range the groundwater is anoxic and contains 0.15 μM As(III) and 2.25 μM Fe(II). The sediment was characterized by parallel chemical extractions at a slightly shallower (4.2-4.9 m) depth level. The results are displayed in Table 1. 0.5 M NaHCO_3 at pH 8.5 extracts desorbable ions (Hiemstra et al., 2010) and extracts 0.9 nmol/g As as well as 0.1 $\mu\text{mol/g}$ Si and P. Formic acid at pH 3 replaces the former HCl pH 3 extraction with an automatic titrator (Postma et al., 2010) and is used to dissolve carbonates and phosphates. The extracted contents (Table 1) show that the amount of secondary easily dissolvable precipitates in the sediment is small. Ferrihydrite and very poorly crystalline goethite would be extracted by ascorbic acid at pH 3 (Larsen and Postma, 2001). Table 1 reveals that only small amounts of such poorly crystalline iron oxyhydroxides, with associated arsenic, are present in these sediments in good agreement with the results of Postma et al. (2010, 2012). Better crystalline iron oxides are dissolved by the combined oxalate-ascorbate extractant (Wenzel et al., 2001). Table 1 shows that better crystalline iron oxides form the predominant iron oxide fraction and also have most arsenic associated. Postma et al. (2010) used Mössbauer spectroscopy to determine iron oxide mineralogy at a locality 30 km upstream Nam Du and showed that goethite and hematite were the predominant iron oxides while ferrihydrite was absent. Finally, HNO_3 was used to dissolve sulfides and reactive silicates. However, the extracted amounts of Fe and As were only slightly higher than those extracted by oxalate-ascorbate indicating that most reactive Fe and As is bound in crystalline iron oxides. Generally these Nam Du sediments have the same characteristics as those previously investigated on the Red River floodplain (Postma et al., 2007, 2010, 2012) but with a very low content of secondary precipitates as extracted by formic acid (Table 1). Such low contents of secondary precipitates were also measured in 3,500 year old floodplain sediments (Postma et al., 2012).

2.2 Experimental procedures

The frozen sediments were thawed and homogenized in an N_2 filled glove box. In preliminary work we used the standard $\text{N}_2:\text{H}_2$ 97:3% gas mixture with a Pd catalyst but our results showed that conditions within the glove box were not completely anoxic and led to a loss of Fe and As, thereby overestimating adsorption. To keep the atmosphere in the glove box completely anoxic, the air within the glove box was therefore in addition continuously pumped through a series of gas washing bottles, filled with a buffered Fe(II) solution inside the glove box (Jeon et al., 2004). The final washing bottle was filled with silica desiccant to reduce the moisture content of the gas inside the glove box.

Adsorption/desorption experiments were done in 100 mL septum bottles, capped by thick rubber septa, containing 50 g of wet sediment (~40 g dry sediment) by equilibrating the sediment with solutions of various composition. Preparation and subsequent handling of the bottles was done under strict anoxic conditions within the glove box. During equilibration the bottles were rotated end over end for 1-3 days. Before sampling, the bottles were centrifuged at 1400 rpm for 20 minutes. Solutions were subsequently sampled from the bottles, within the glove box, using a syringe and filtered through 0.2 μm Satorius Minisart cellulose acetate filter cartridges. Careful protocols were kept of the volumes, determined by weight, and the composition of the solutions added or removed from the bottles to calculate the amounts adsorbed or desorbed onto the sediment. To facilitate flocculation of the sediment particles, all experiments were carried out in a 50 mM NaCl matrix solution. In addition the solutions contained a buffer which was either a 10 mM NaHCO_3 or 10 mM PIPES (1,4-Piperazinediethanesulfonic acid) which has a negligible capacity to bind divalent ions. The pH of both the 10 mM NaHCO_3 + 50 mM NaCl and the 10 mM PIPES + 50 mM NaCl solutions was adjusted to 7.0, respectively by bubbling with a 5% CO_2 in N_2 gas mixture, and by addition of 2 M HCl. Small amounts of concentrated As(III), As(V), Fe(II), PO_4 and Si solutions were added stepwise to these sediment suspensions to study adsorption. For this purpose 1000 mg/L solutions were prepared using the following chemicals; As(III): AsNaO_2 , As(V): $\text{AsHNa}_2\text{O}_4 \cdot 7\text{H}_2\text{O}$, Fe(II): $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, P: KH_2PO_4 , Si: Titrisol Merck[®] standard SiCl_4 in 14% NaOH. Appropriate dilutions were prepared when needed.

The sediment samples used for determining adsorption isotherms were first leached for adsorbed and easily dissolvable ions by addition of 10 mM NaHCO_3 + 50 mM NaCl or 10 mM PIPES + 50 mM NaCl solution followed by shaking, centrifugation and removal of the supernatant solution. This procedure was repeated 7 times over a 17 days period. The concentrations in the elutant stayed close to constant in subsequent steps. In the last step the concentration ranges were As(III) 0.06-0.08 μM , and the same for total As, Fe(II) 1.8-3.6 μM , Si 0.21-0.32 mM and Ca 0.5-1.7 mM. Thereafter arsenic and iron were added stepwise to determine the adsorption isotherms. In the adsorption experiments where Fe(II) initially is present, a concentrated Fe(II)-solution was added to the sediment suspension to make the initial Fe(II) concentration close to 0.05 mM. For adsorption steps the bottles were shaken for 24 h after each addition before sampling. Desorption was studied subsequent to the adsorption isotherms by repeatedly replacing the supernatants with fresh 10 mM NaHCO_3 + 50 mM NaCl or 10 mM PIPES + 50 mM NaCl solutions, while measuring the desorbed ions. In the desorption steps, the bottles were shaken for 72 hours before sampling.

For the displacement experiments two cleaning steps with 10 mM NaHCO_3 + 50 mM NaCl were applied. In those experiments where As(III) initially is present, the sediment was leached three times with the 10 mM PIPES + 50 mM NaCl solution as described above. Thereafter a 0.6 mM As(III) solution was added in one step, corresponding to initial As(III) concentrations in the bottles in the range 28-31 μM , which after three days of shaking resulted in an aqueous As(III) concentration of 2-4 μM . Subsequently small amounts of concentrated Fe(II), P or Si solutions were added and the aqueous As(III) concentration was measured. After each addition the bottles were shaken for 72 hours before measuring.

Aqueous As(V) and As(III) were separated, within the glove box, using a disposable anion exchange cartridge at a flow rate of approximately 6 mL/min using a syringe. The cartridges contained 0.8 g aluminosilicate adsorbent that selectively adsorbs As(V) but not As(III) (Meng and Wang, 1998). Arsenite was determined as the As concentration in the water filtered through a cartridge, and As(V) was calculated as the difference between the total As and As(III) concentrations. Arsenic was measured on a PerkinElmer Elan 6100DRC ICP-MS quadrupole instrument using PerkinElmers software Elan version 3 for data collection and quantification. The detection limit was 0.01 µg/L. Fe(II), phosphate and silica were measured spectrophotometrically with ferrozine (Stookey, 1970), molybdate blue, and ammonium molybdate methods, with detection limits were 1.8, 1.1 and 0.2 µM respectively.

2.3 Geochemical modeling

Saturation calculations and surface complexation modeling were done using the code PHREEQC (Parkhurst and Appelo, 1999). For modeling surface complexation on goethite, we used the charge distribution-multisite complexation (CD MUSIC) model (Hiemstra and van Riemsdijk, 1996) with the surface complexes compiled for PHREEQC by David Kinniburgh in the code PHREEPLOT (<http://www.phreeplot.org>). The surface complexation reactions, their affinity constants and source are listed in the Electronic Annex of Jessen et al. (2012). The capacitances for the 0-1 and 1-2 planes are $C_1=0.85 \text{ F/m}^2$ and $C_2=0.75 \text{ F/m}^2$, respectively (Stachowicz et al., 2008). The model for adsorption on Pleistocene aquifer sediment from Bangladesh, by Stollenwerk et al. (2007), uses experimentally determined adsorption constants for As(III), As(V), PO_4^{3-} , and HCO_3^- , in combination with the Dzombak and Morel (1990) model for ferrihydrite for other components and for electrostatic effects. The new reactions were formulated for the Hfo_w sites (termed *Sites* in Stollenwerk et al. (2007)) and added to the PHREEQC input file overriding the standard Dzombak and Morel (1990) database.

3 Results

3.1 Adsorption As(III) and As(V)

The experiments explore the adsorption of As(III) and As(V) to the aquifer sediment by stepwise addition of arsenic. The results (Fig. 1) show that As(V) is sorbing about 6-7 times stronger to the sediment than As(III). In addition, the isotherm for As(V) adsorption is strongly convex while that for As(III) by comparison is almost linear. At the end of the adsorption experiment, desorption was measured by repeated replacement of the aqueous phase with As-free solution. For As(III) the desorption isotherm is located slightly above the adsorption isotherm, possibly indicating some kinetic delay in the As(III) release from the solid phase, but overall As(III) adsorption looks fully reversible (Fig. 1). For As(V), reversibility appear to be much lower (Fig. 1). Parallel experiments were carried out using a 10 mM NaHCO_3 or a 10 mM PIPES buffer solution, to explore the possible competitive effect of HCO_3^- . The results (Fig. 1) show no significant difference in the adsorption behavior of As(III) nor As(V) in the presence of either NaHCO_3 or PIPES, indicating that (bi)carbonate did not significantly compete with As(III) or As(V) for adsorption sites.

3.2 Interactions between Fe(II) and As sorption

Here the effect of aqueous Fe(II) on the adsorption of As(III) and As(V) is explored. First the adsorption of Fe(II) onto the sediment is measured in the absence of added As. Next the sediment is equilibrated with an Fe(II) solution and thereafter either As(III) or As(V) are added. Finally, As(III) and Fe(II) were added simultaneously to the sediment suspension.

3.2.1 Adsorption of Fe(II)—Figure 2 shows the results of Fe(II) sorption onto the sediment in 10 mM NaHCO₃ and 10 mM PIPES buffer solutions at pH 7. The combined data distribution is almost linear with a distribution coefficient, K'_d , of around 33 L/kg. In the experiments using 10 mM NaHCO₃ as buffer, the solution reaches saturation for siderite (FeCO₃) when Fe(II) exceed 13 µM and in these solutions the saturation index (SI) for siderite becomes 0.9 when dissolved Fe(II) reaches 100 µM. However, there is no significant difference in Fe(II) adsorption between solutions containing the PIPES buffer and those with the NaHCO₃ buffer. Therefore siderite is apparently not precipitating in these experiments.

3.2.2 Coadsorption As and Fe(II)—In the first series of coadsorption experiments, Fe(II) was added to the sediment suspension until the aqueous concentration was about 0.05 mM Fe(II) before arsenic was added. The results (Fig. 3) show for As(III) that the presence or absence of Fe(II) has no significant influence on the adsorption of As(III) onto the sediment. However, for As(V) the sorption isotherm in the presence of Fe(II) is significantly higher than without Fe(II) and the difference increases towards a higher As(V) concentration. It could be surmised that this difference is caused by the precipitation of ferrous arsenate. However, the solution always stays subsaturated towards symplectite (ferrous arsenate) (Johnston and Singer, 2007).

In the second approach, the solution added to the sediment contained both As(III) and Fe(II) in a molar ratio of 1:100, which corresponds more or less to what is measured in the groundwater at Nam Du. For As(III) (Fig. 4), the same adsorption isotherm was measured as in the previous experiments (Figs. 1 and 3) and the presence of Fe(II) has again no effect. And also here As(III) adsorption appears completely reversible as the desorption isotherm almost is identical to the adsorption isotherm (Fig. 4). For Fe(II) the isotherm up to 100 µM is basically the same as in Fig. 2 although the isotherm is steeper for NaHCO₃ than for the PIPES buffer, perhaps indicating that in this case some siderite may have precipitated. However, more importantly, the Fe(II) adsorption is completely irreversible, in strong contrast to As(III) (Fig. 4). Here, it is highly unlikely that the adsorbed Fe(II) has precipitated on the surfaces as FeOOH because that would immobilize As(III) as well. Overall, the adsorption and desorption of As(III) and Fe(II) on the sediment surface are clearly not coupled processes.

3.3 Competition of As(III) with Fe(II), PO₄ and Si

To investigate directly the importance of competitive effects involved in As(III) adsorption in multi-component natural groundwater systems, we have performed displacement experiments using sediment suspensions equilibrated with As(III) to initial concentrations between 2 and 4 µM. Thereafter either Fe(II), PO₄ or Si was added to the suspension and the aqueous As(III) concentration monitored. While all the previous experiments (Figs. 1-4)

were carried out on exactly the same sediment sample, the displacement experiments (Fig. 5) were carried out on similar looking sediment sample 10 cm lower in the same core.

The results (Fig. 5) show for phosphate a clear As(III) replacement effect, consisting of a strong initial As(III) increase followed by a less steep As(III) increase. In contrast, the addition of Fe(II) (Fig. 5) has no influence on the aqueous As(III) concentration which is consistent with our previous conclusion that As(III) and Fe(II) adsorption and desorption are uncoupled processes. Finally for Si, the initial sediment suspensions already contained 0.15–0.20 mM as Si continued to be released from the sediment. Further addition of Si seems to cause some replacement of As(III) from the sediment surface but the effect is not strong.

4 Discussion

4.1 Adsorption isotherms of As(III) and As(V) on aquifer sediments

Figure 6 displays a compilation of the results of arsenic adsorption experiments on sediments from arsenic contaminated aquifers from Bangladesh and Vietnam. For As(III), almost linear adsorption isotherms are obtained and the results are, except for one, surprisingly similar regardless of the sediment type, age, or the country of origin. For example the oxidized brown sediment from Bangladesh used by Stollenwerk et al. (2007) and Radloff et al. (2011) yield almost exactly the same As(III) adsorption isotherms as a reduced grey sediment from either Bangladesh (Itai et al., 2010) or those in this study from Vietnam. Much lower As(III), as well as As(V), adsorption was found in the grey sediments of Radloff et al. (2011). The adsorption experiments with As(III) were carried out in the range from pH 6.8 (Stollenwerk et al., 2007), 7.0 (this study) to 7.3–7.4 (Itai et al., 2010; Radloff et al., 2011). The data of Jung et al. (2012) was excluded because the experiments apparently were carried out under mixed As(III)/As(V) conditions (see their Table S4). The only logical explanation for why As(III) adsorption is the same for a brown oxidized sediment as for a grey reduced sediment appears to be that the adsorbent is a bulk sediment component which is ubiquitous in all systems and under all redox conditions. In support of this conclusion is the observation that As(III) adsorption is easily reversible (Fig. 1 and 4) which suggests a weak binding to an omnipresent adsorbing surface rather than strong adsorption to specific mineral surface sites. Sorption of As(V) to aquifer sediments shows much larger spread (Fig. 6). In some studies As(V) is sorbing much stronger than As(III) (this study; Stollenwerk et al., 2007), while in other studies As(V) and As(III) are sorbing about equally well (Radloff et al., 2011; Nath et al., 2009). Also As(V) sorption seems to be less reversible than As(III) sorption (Fig. 1).

A major question raised by this data compilation is how is it possible that the adsorption characteristics of As(III) and As(V) among the different sediments are so completely different (Fig. 6). Both in Stollenwerk et al. (2007), Radloff et al. (2011) and in our experiments the adsorption of As(III) and As(V) was measured separately on the same sediment. If the bulk of As(III) and As(V) aqueous species compete for the same adsorption sites on mineral surfaces, then in single sorbate systems there should be a parallel behavior for As(V) and As(III) with some sediments adsorbing both As species stronger than others. With the exception of the Radloff et al. (2011) gray sediment at 40 and 46 m, such a

behavior is not observed at all. Even though the adsorption isotherms for As(III) for all three sediments are the same (Fig. 6), the Holocene Nam Du sediment adsorbs As(V) much stronger than the Pleistocene sediment of Stollenwerk et al. (2007) which again is a much stronger adsorbant than the brown sediment of Radloff et al. (2011). Basically there appears to be no coupling between the adsorption intensity of As(III) and As(V). The only reasonable conclusion to be drawn from this observation is that As(V) and As(III) are not adsorbing onto the same mineral surfaces, or at least not to the same surface sites. A further indication that this may be the case is found in Fig. 3 showing that the presence of aqueous Fe(II) strongly affects As(V) adsorption but has no influence on As(III) adsorption. And also the difference in reversibility between Fe(II) and As(III) adsorption (Fig. 4) suggests that As(V) and Fe(II) adsorption takes place at different sites than As(III) adsorption. Finally, Itai et al. (2010) found that the K'_d for As(III) on sediment is strongly correlated to the BET surface area whilst the K'_d for As(V) is not, which also points towards a difference in adsorption sites for the two species.

4.2 Comparison of sediment sorption properties with those of pure minerals

Sorption experiments with synthetic minerals are often used as model systems to predict the behavior of trace components in natural sediments. In this section we compare the results obtained in sediment adsorption experiments with analogue experiments that use in particular synthetic Fe-oxides. The focus is here on the experimental results rather than model derived conclusions.

4.2.1 Adsorption of As(III) and As(V)—The studies of arsenic adsorption on synthetic Fe-oxides by Dixit and Hering (2003), Stachowicz et al. (2006) and Kanematsu et al. (2013) all show that the amounts of As(III) and As(V) adsorbing on hydrous ferric oxide or goethite, at pH 7 and from the same aqueous concentration, are more or less the same within a range of about 20%. Martin et al. (2014) showed, for experiments carried out with various Fe-oxides at pH 6.5, that the Langmuir maximum adsorption capacity generally was higher for As(III) as compared to As(V). However, our results for arsenic adsorption to Nam Du Holocene sediments show As(V) to adsorb 6-7 times stronger than As(III) (Fig. 1) and it is therefore hard to understand how both arsenic species can adsorb to the same Fe-oxide in the sediment. Also Stollenwerk et al. (2007) and Itai et al. (2010) found much stronger adsorption of As(V) than As(III), measured on the same sediment, while Radloff et al. (2011) found a more or less equivalent adsorption strength.

Another issue for comparison is the difference between the complete reversibility found for As(III) in contrast to the incomplete reversibility for As(V) adsorption on Nam Du sediment (Fig. 1). Also Williams et al. (2003) and Zhang and Selim (2008) observed partial irreversible adsorption for As(V) on soil sediments. Radu et al. (2005) observed for goethite coated sand a desorption recovery of 91% for As(III) as opposed to 68 % for As(V) which is more or less in line with our results. Apparently, the reversibility of As(V) and As(III) sorption shows similar features for sediments and on goethite.

Martin et al. (2014) and Goldberg (2002) reported that Al-hydroxides and clay minerals at pH 7 show much stronger adsorption for As(V) than for As(III) which is better in line with

our sediment adsorption data. Chakraborty et al. (2007; 2011) found for biotite, but not for muscovite, much stronger adsorption for As(V) than for As(III). The sandy and silty sediments of the arsenic contaminated floodplains in SE Asia are particularly rich in micas, which often constitute between 2-12% of the sediment volume both in Bangladesh (Stollenwerk et al., 2007; Shamsudduha et al., 2008; Hasan et al., 2009) as well as in the sediments of the Red River floodplain (Tran Thi Luu pers. comm.). The much stronger adsorption of As(V) as compared to As(III) on sediments found by us and in other studies may therefore point towards other adsorbants than Fe-oxides. However, both silicates and Fe-oxides are reported to adsorb arsenate as well as arsenite and why apparently different sorption sites are preferred for As(V) and As(III), in single sorbate experiments, remains unclear. If mica's and Fe-oxides are the main adsorbants in aquifer sediments then their surface properties must be very different from those of corresponding synthetic minerals. Modifications of surfaces and adsorption properties could be caused by coating with silica (Christl et al., 2012; Luxton et al., 2008; Waltham and Eick 2002) or dissolved organic matter. Martin et al. (2014) found that aluminum substitution in goethite decreased its adsorption capacity towards As(III) and As(V) by 50%.

4.2.2 The effect of bicarbonate on arsenic adsorption—The effect of bicarbonate on arsenic adsorption onto aquifer sediments from Nam Du was checked by replacing the 10 mM HCO_3 solution, corresponding to the groundwater alkalinity content, by a PIPES buffer solution of equivalent strength. The results (Figs. 1, 3 and 4) obtained with the two buffer solutions are identical and demonstrate, within the concentration range 1-10 mM HCO_3 of these aquifers, that HCO_3 does not have the capability to displace neither As(III) nor As(V) from the surface complex to any significant extent. In good agreement Stollenwerk et al. (2007) could not measure any competition between As(V) and HCO_3 for surface sites on Pleistocene aquifer sediment from Bangladesh. Gao et al. (2013) was able to leach As from Datong aquifer sediments with 8.2 mM NaHCO_3 but did attribute the effect to enhanced clay dispersion and transport of Fe-oxides with adsorbed As. Finally, Williams et al. (2003) detected only a slight negative effect of carbonate on As(V) adsorption onto Fe-oxide rich soil sediments.

For synthetic Fe-oxide systems, Meng et al. (2000) found that the presence of carbonate had a negligible effect on the removal of As(III) and As(V) by ferric hydroxide. However, Saalfeld and Bostick (2010) reported that calcium and bicarbonate in combination may displace arsenate from the surface of ferrihydrite. Stachowicz et al. (2007) investigated the effect of 10 mM bicarbonate on the adsorption of As(III) and As(V) onto goethite. For As(V), the effect of bicarbonate on As(V) sorption was very small but a significant displacement of As(III) from the goethite surface by 10 mM bicarbonate was measured at near neutral pH. Also Kanematsu et al. (2013) noted for goethite that while bicarbonate had little effect on As(V) adsorption, it reduced As(III) adsorption particularly towards lower pH. Radu et al. (2005) studied the effect of bicarbonate on arsenic sorption onto goethite coated sand in column experiments and found only a weak effect for As(V) and a slightly larger effect for As(III). Finally, Arai et al. (2004) performed adsorption experiments with hematite and the measured effects of dissolved carbonate on As(V) uptake were almost negligible.

Summarizing the available experimental evidence indicates that bicarbonate at concentrations relevant for As-contaminated aquifers has little influence on the adsorption of As(V) to either aquifer sediments nor synthetic iron oxides. However, while for As(III) no effect is seen on aquifer sediments, the results for goethite indicate that bicarbonate may significantly compete with arsenite for surface sites. The combined calcium and bicarbonate effect of Saalfield and Bostick (2010), to displace arsenate from the surface of ferrihydrite, is apparently not found for aquifer sediments because our experiments contained 0.5–1.7 mM aqueous Ca and those of Stollenwerk et al. (2007) 1.75 mM Ca and yet addition or removal of bicarbonate had no effect on the aqueous arsenic concentration.

4.2.3 Adsorption of Fe(II) on sediment and Fe-oxides—Figure 2 shows a close to linear sorption isotherm for aqueous Fe(II) to the aquifer sediment and precipitation of siderite is apparently not taking place in our experiments. Figure 4 shows Fe(II) adsorption onto the sediment to be largely irreversible. A comparison with the adsorption mechanisms of aqueous Fe(II) onto various Fe-oxides (Pedersen et al., 2005; Handler et al., 2009; Catalano et al., 2010) appears of relevance. Adsorbed on the surface of Fe-oxide, the Fe(II) ion loses an electron and turns into an Fe(III) atom incorporated in the oxide structure. The released electron is thought to migrate through the crystal and cause the reduction of an Fe(III) atom at a surface site elsewhere on the crystal which subsequently is desorbed as aqueous Fe(II). Desorption is commonly inferred by the absence of accumulating Fe(II) on the mineral surface rather than being directly observed. Whether the irreversible adsorption behavior of Fe(II) on sediment particles corresponds to sorption on Fe-oxides can only be guessed at. An alternative possibility would be the formation of a mixed Fe(II,III) phase. Conversely, the adsorption on the surface of clay minerals seems more likely to be reversible.

4.2.4 Effect of aqueous Fe(II) on Arsenic sorption—The role of Fe(II) in the adsorption of arsenic is critical because the As contaminated aquifers in SE Asia nearly always contain Fe(II) in the groundwater but at highly variable concentrations (BGS and DPHE, 2001; Winkel et al., 2011). Because Liu et al. (2001) and Hongshao and Stanforth (2001) have shown that the order of addition of the sorbates may influence sorption on Fe-oxides, we have tested different As and Fe(II) addition strategies in our sorption experiments; addition of Fe(II) before As(III) (Fig. 3), simultaneous addition of Fe(II) and As(III) (Fig. 4) and addition of Fe after sediment equilibration with As(III) (Fig. 5). The overall conclusion from these experiments (Figs. 3–5) is that the presence of aqueous Fe(II) has no effect whatsoever on the adsorption of As(III) onto Nam Du aquifer sediment. On the contrary, the clear differences in reversibility of As(III) and Fe(II) adsorption (Fig. 4) rather suggest the two processes to be uncoupled. In good agreement Dixit and Hering (2006) investigated the simultaneous adsorption of As(III) and Fe(II) on goethite and found that at a concentration of 500 μM total As(III), As(III) sorption is not affected by Fe(II) while only at 1000 μM total As(III), Fe(II) did stimulate As(III) sorption. A concentration of 500 μM total As(III) is already orders of magnitude higher than measured in SE Asian floodplain aquifers (Postma et al., 2007; Hug et al., 2008; Winkel et al., 2011). Amstaetter et al. (2010) observed rapid oxidation of As(III) to As(V) in Fe(II)-goethite systems. If such a reaction were to take place in our sediment systems, the presence of Fe(II) should cause an increase

in As adsorption because the much stronger adsorption of As(V) as compared to As(III) (Fig. 1) which is contrary to our observations (Fig. 3).

For arsenate we observed the adsorption onto sediment to be significantly increased by the presence of Fe(II). In partial agreement Catalano et al. (2011) found Fe(II) to increase As(V) sorption by 5-10% on goethite and hematite which is consistent with Fe(II) adsorption shifting the surface potential to more positive values. However, the effect observed by us is much stronger.

4.2.5 Phosphate adsorption and arsenic displacement—From our competition experiments with aquifer sediment at Nam Du, phosphate arises as by far the most effective competitor of As(III) for surface sites (Fig. 5). Likewise Stollenwerk et al. (2007) found phosphate to be the most effective competitor for As(V) in Bangladesh aquifer sediments. Also Goa et al. (2013) concluded for Datong basin sediments that competitive desorption by phosphate is the main arsenic mobilization mechanism. Finally, Williams et al. (2003) found phosphate to be very effective in displacing As(V) from Fe-oxide rich soil sediments.

Batch experiments with synthetic Fe-oxides all find phosphate to be very effective in displacing both As(III) and As(V) (Jain and Loeppert, 2000; Dixit and Hering, 2003; Stachowicz et al., 2008; Kanematsu et al., 2013). However, the reaction appears not to be a simple exchange reaction (Hongshao and Stanforth, 2001). Radu et al. (2005) carried out column experiments with displacement of As(V) from goethite coated sand, Both Stachowicz et al. (2008) and Radu et al. (2005) concluded that given the competitiveness of phosphate at neutral pH, phosphate, rather than carbonate, would be the key factor controlling the concentration of As(V) in groundwater.

4.2.6 Concluding remarks and summary—Overall a sharp contrast is noted between the voluminous literature on the adsorption of arsenic and associated species on synthetic Fe-oxides and the few studies carried out on sediments from arsenic contaminated aquifers. The much stronger adsorption of As(V) than of As(III) in Nam Du sediments as well as the Bangladesh sediments, indicates that the perception of arsenic, phosphate and other species competing for the same surface sites of iron oxides in sediments with properties similar to those of, for example a synthetic goethite, probably is not correct. Generally, silicates have a higher affinity for As(V) than for As(III) and maybe they play an important role as sediment adsorbants. On the other hand mineral surfaces in sediments may have very different properties than those of synthetic minerals. The main anion competitor for arsenic on sediment surface sites appears to be phosphate while bicarbonate has little effect. Finally aqueous Fe(II) has no influence on the adsorption of As(III) to sediments but may enhance As(V) sorption.

4.3 A competitive Langmuir adsorption model for As(III) and PO₄

Figure 5 indicates that the main competitive effect detected in our experiments is between As(III) and PO₄. We have constructed a simple dual Langmuir adsorption model where As(III) and PO₄ are competing for the same surface sites. For the adsorption reaction:

the mass action equation is: $K_s^I = \frac{[s_I]}{[s][I]}$ and the Langmuir Equation:

$$[s_I] = \frac{[s_{tot}] K_s^I [I]}{1 + K_s^I [I]} \quad (2)$$

This equation was fitted to the experimental adsorption data for phosphate (Fig. 7). These data were obtained in experiments where also some arsenite is present. However, the amount of adsorbed As(III) is only 1-10 % of the amount of adsorbed PO₄ and will therefore not influence the PO₄ isotherm very much. For PO₄ the Langmuir parameters for the data fit shown in Fig. 7 are, $K_s^{PO_4} = 2500$ L/mol and $S_{tot} = 8.4$ μmol/g. Assuming that As(III) and phosphate are adsorbing to the same sites, the same value for S_{tot} was used to fit the adsorption data for As(III). This assumption is not sensitive because the amount of As(III) sorbed is much lower than of phosphate and the As(III) isotherm is therefore nearly linear. Figure 8 shows the data and the fitted adsorption isotherm with $K^{As(III)}_s = 1500$ L/mol.

In the case of simultaneous adsorption of As(III) and PO₄ onto the same surface site, the mass balance is:

$$[s_{tot}] = [s] + [s_{As(III)}] + [s_{PO_4}] \quad (3)$$

with

$$[s_{As(III)}] = \frac{[s_{tot}] K_s^{As(III)} [H_3AsO_3]}{1 + K_s^{As(III)} [H_3AsO_3] + K_s^{PO_4} [PO_4]} \quad (4)$$

and

$$[s_{PO_4}] = \frac{[s_{tot}] K_s^{PO_4} [PO_4]}{1 + K_s^{As(III)} [H_3AsO_3] + K_s^{PO_4} [PO_4]} \quad (5)$$

The equations were used to calculate the effect of PO₄ on As(III) sorption for several PO₄ concentrations, as shown in Fig. 8, and the presence of PO₄ is seen to lower the As(III) adsorption isotherm.

The competition experiment between As(III) and phosphate (Fig. 5) was also modeled with the two-component Langmuir sorption model and the result is compared with the experimental data in Fig. 9. The experimental data shows that PO₄ addition clearly

diminishes As(III) adsorption but not by simple exchange because the amount of PO₄ that is adsorbing (Fig. 7) is much larger than the amount of As(III) that is desorbing. The model predicts the data trend correctly but somewhat underpredicts the release of As(III) upon initial addition of phosphate. A possible explanation could be that the competition experiments were carried out on a different sediment sample from the Nam Du core than the sediment used in the adsorption experiments to derive the Langmuir parameters for As(III) and the two sediments may have slightly different adsorption characteristics. However, non-Langmuir adsorption behavior at low PO₄ concentrations could also reflect some very loosely surface bound As(III) that is released upon the first PO₄ additions. The Langmuir model describes As(III) adsorption and competition with PO₄, with a minimal number of assumptions. However, it should be considered as a descriptive rather than a mechanistic model especially because phosphate could adsorb to different surface sites than As(III).

4.4 Surface complexation models to predict multi-component sorption

Surface complexation models (SCM) enable a description of multicomponent adsorption as well as of electrical charging effects. SCM models have been constructed for various synthetic Fe-oxides. These SCM for Fe-oxides have also been used to predict the mobility of arsenic in aquifers (BGS and DPHE, 2001; Appelo et al., 2002; Swartz et al., 2004; Postma et al., 2007; Jessen et al., 2012; Biswas et al., 2014). The basic assumption in using these SCM's for Fe-oxides to describe arsenic sorption to aquifer sediment, is that the sediments contain similar Fe-oxide phases that are responsible for most of the adsorption of arsenic and competing ions and that these natural Fe-oxides have similar surface properties as the synthetic minerals.

Jessen et al. (2012) tested different models on the results of a forced gradient experiment where low arsenic river water is entering a high arsenic aquifer on the Red River floodplain. The results showed the Stollenwerk et al. (2007) model to be best in predicting both the As(III) and PO₄ behavior while the CD MUSIC model (Hiemstra and van Riemsdijk, 1996; Stachowicz et al., 2006, 2007, 2008) predicted PO₄ correctly but not As(III). Worst performed the Dzombak and Morel (1990) model. Biswas et al. (2014) in modeling field data reached the opposite conclusion as the Dzombak and Morel (1990) model performed best but their model employed an extensively modified database. For the Dzombak and Morel (1990) model, Jessen et al. (2012) calculated that bicarbonate at aquifer concentrations is the main competitor to arsenite for surface sites. Because the results of the experiments presented here (Figs. 1, 3 and 4) show that bicarbonate at 10 mM has no influence on As(III) or As(V) sorption we did not further explore the Dzombak and Morel (1990) model.

For the Stollenwerk et al. (2007) and CD MUSIC ((Hiemstra and van Riemsdijk, 1996; Stachowicz et al., 2006, 2007, 2008) models we did calculate the arsenic adsorption isotherms using the maximum number of sites derived from the Langmuir isotherm for phosphate (Fig. 7) as the total number of surface sites available for adsorption. The results are included in Fig. 1 and show the calculated isotherms to be much steeper than the measured ones. Figure 5 compares our experimental data for As(III) displacement by phosphate with the predictions of the CD MUSIC and Stollenwerk et al. (2007) models.

Both models predict the As(III) displacement by phosphate reasonably well at low, and less good at higher phosphate concentrations. Figure 5 also compares the effect of Fe(II) addition on the aqueous As(III) concentration. The Stollenwerk et al. (2007) model does not predict much displacement of adsorbed As(III) by Fe(II) in agreement with the experimental data. However, the CD MUSIC model predicts a decrease in aqueous As(III) upon Fe(II) addition due to the adsorption of a combined Fe(II)-As(III) surface complex (Hiemstra and van Riemsdijk, 2007) which clearly disagrees with the experimental data. Neither does the experimental data presented in Figs. 3 and 4 provide any support for the importance of a Fe(II)-As(III) surface complex. Finally Fig. 5 compares the displacement of As(III) by Si. Both the CD MUSIC and Stollenwerk et al. (2007) models predict a weak displacement of As(III) by Si within the range of Si concentrations in the As contaminated aquifers. This effect is possibly supported by the experimental data but the effect is certainly not strong.

Our earlier conclusion that As(V) and As(III) are not adsorbing on the same sediment surface sites is at odds with all three surface complexation models. However, there is some experimental evidence for surface site heterogeneity from synthetic Fe-oxides as well. Thus Hingston et al. (1971) found for adsorption of phosphate and arsenate on goethite that some sites were specific for each adsorbant only while others were subject to competition. Jain and Loeppert (2000) investigated arsenic and phosphate adsorption of ferrihydrite and concluded that arsenate and phosphate compete for one type of sites with a moderate preference for arsenate, while other sites show a higher affinity for arsenite than phosphate.

Finally all surface complexation models enable the calculation of the competition of arsenite and arsenate for surface sites but the models are calibrated based on single sorbate data for arsenic. Direct experimental data sets for competitive adsorption of arsenate and arsenite on Fe-oxides are few. Jang and Demsey (2008) experimentally investigated competitive adsorption of arsenate and arsenite on ferrihydrite and found that they influenced each other. However, the competition as calculated by the models of Dzombak and Morel (1990) and Dixit and Hering (2003), based on single sorbate data, did not match the experimental results. In addition, Goldberg (2002) measured virtually no competition between As(V) and As(III), at a concentration of 20 μM , for adsorption on amorphous iron oxide. This arsenic concentration is already much higher than in the groundwater at our field sites. The competitive adsorption of arsenate and arsenite on Fe-oxides clearly needs more research.

4.5 Implications for arsenic contaminated aquifers

The results presented here have some important implications for the understanding of adsorption-desorption processes of arsenic in arsenic contaminated aquifers of SE Asia. The similarity of the adsorption characteristics of As(III) onto a wide range of both Holocene and Pleistocene aquifer sediments (Fig. 6), as well as the linear isotherm, suggests that the retardation of As(III) by adsorption can be described quite well by using a constant distribution coefficient, $K'_{d-\text{As(III)}}$, in the range 11-14 L/kg. The retardation, $R = 1 + K'_{d-\text{pb}}/\theta$, with sediment bulk density, $\rho_b = 1.86 \text{ kg/L}$, and porosity, $\theta = 0.3$, ranges accordingly from $R = 69$ to $R = 162$. By comparison retardation derived from field data by van Geen et al. (2013) yields $R = 16$ -20 and Radloff et al. (2011) derived from a push-pull experiment $K'_{d-} = 1$ -10 L/kg (equal to $R = 7.2$ -72). The lower retardation derived from field studies

indicates that hydrogeological heterogeneity on a small scale and inaccessibility of adsorption sites (Radloff et al., 2011) plays an important role for reactive As(III) transport in aquifers. Our experiments also indicate the adsorption process for As(III) to be highly reversible (Figs. 1 and 4) and therefore the process should from a chemical point of view proceed close to equilibrium. With respect to the competitive effect of anions, our experiments predict that only phosphate, when occurring in high concentrations like in Bangladesh (Swartz et al., 2004) may have the capability of displacing arsenite from the sediment surface sites.

While it seems possible to make some generalized prediction for As(III) adsorption, more caution is required when considering the adsorption of arsenate As(V) to aquifer sediments since the adsorption behavior of As(V) appears to depend on the sampling site, the sediment type, the groundwater Fe(II) content and the adsorption of arsenate is also less reversible. However, the adsorption of As(V) to aquifer sediment appears much stronger than for As(III). Finally, when considering the retardation of arsenic in aquifers one should also consider the arsenic present in easily dissolved secondary precipitates in the sediment (Postma et al., 2012). When arsenic is included in secondary precipitates it increases the retardation significantly. However during a push-pull experiment, like carried out by Radloff et al. (2011), the dissolution of arsenic from secondary precipitates could yield an artificially low retardation. It is also clear from our experiments that the sorption characteristics of aquifer sediments are very different from those of synthetic iron oxides and therefore reactive transport models should use sediment based adsorption data rather than SCM's for synthetic iron oxides.

References

- Amstaetter K, Borch T, Larese - Casanova P, Kappler A. Redox Transformation of Arsenic by Fe(II)-Activated Goethite (α -FeOOH). *Environ Sci Technol*. 2010; 44:102–108. [PubMed: 20039739]
- Appelo CAJ, van der Weiden MJJ, Tournassat C, Charlet L. Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environ Sci Technol*. 2002; 36:3096–3103. [PubMed: 12141489]
- Arai Y, Sparks DL, Davis JA. Effects of dissolved carbonate on arsenate adsorption and surface speciation at the hematite water interface. *Environ Sci Technol*. 2004; 38:817–824. [PubMed: 14968869]
- BGS and DPHE. Arsenic contamination of groundwater in Bangladesh. BGS Technical Report WC/00/19. Kinniburgh, DG.; Smedley, PL., editors. 2001.
- Biswas A, Gustafsson JP, Neidhardt H, Halder D, Kundu AK, Chatterjee D, Berner Z, Bhattacharya P. Role of competing ions in the mobilization of arsenic in groundwater of Bengal Basin: Insight from surface complexation modeling. *Water Res*. 2014; 55:30–39. [PubMed: 24583841]
- Catalano JG, Fenter P, Park C, Zhang Z, Rosso KM. Structure and oxidation state of hematite surfaces reacted with aqueous Fe(II) at acidic and neutral pH. *Geochim Cosmochim Acta*. 2010; 74:1498–1512.
- Catalano JG, Luo Y, Otemuyiwa B. Effect of aqueous Fe(II) on arsenate sorption on goethite and hematite. *Environ Sci Technol*. 2011; 45:8826–8833. [PubMed: 21899306]
- Chakraborty S, Wolthers M, Chatterjee D, Charlet L. Adsorption of arsenite and arsenate onto muscovite and biotite mica. *J Colloid Interf Sci*. 2007; 309:392–401.
- Chakraborty S, Bardelli F, Mullet M, Greneche J-M, Varma S, Ehrhardt J-J, Banerjee D, Charlet L. Spectroscopic studies of arsenic retention onto biotite. *Chem Geol*. 2011; 281:83–92.

- Christl I, Brechbühl Y, Graf M, Kretzschmar R. Polymerization of Silicate on Hematite Surfaces and Its Influence on Arsenic Sorption. *Environ Sci Technol*. 2012; 46:13235–13243. [PubMed: 23163533]
- Dixit S, Hering JG. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. *Environ Sci Technol*. 2003; 37:4182–4189. [PubMed: 14524451]
- Dixit S, Hering JG. Sorption of Fe(II) and As(III) on goethite in single- and dual-sorbate systems. *Chem Geol*. 2006; 228:6–15.
- Dowling CB, Poreda RJ, Basu AR, Peters SL, Aggarwal PK. Geochemical study of arsenic release mechanisms in the Bengal Basin groundwater. *Water Resour Res*. 2002; 38:1173.doi: 10.1029/2001WR000968
- Dzombak, DA.; Morel, FMM. *Surface Complexation Modeling-Hydrous Ferric Oxide*. Wiley; 1990.
- Fendorf S, Michael HA, van Geen A. Spatial and temporal variations of groundwater arsenic in south and southeast Asia. *Science*. 2010; 328:1123–1127. [PubMed: 20508123]
- Gao X, Su C, Wang Y, Hu Q. Mobility of arsenic in aquifer sediments at Datong Basin, northern China: Effect of bicarbonate and phosphate. *J Geochem Expl*. 2013; 135:93–103.
- Goldberg S. Competitive Adsorption of Arsenate and Arsenite on Oxides and Clay Minerals. *Soil Sci Soc Am J*. 2002; 66:413–421.
- Handler RM, Beard BL, Johnson CM, Scherer MM. Atom exchange between aqueous Fe(II) and goethite: An Fe isotope tracer study. *Environ Sci Technol*. 2009; 43:1102–1107. [PubMed: 19320165]
- Harvey CF, Swartz CH, Badruzzaman ABM, Keon-Blute N, Yu W, Ali A, Jay J, Beckie R, Niedan V, Brabander D, Oates PM, et al. Arsenic mobility and groundwater extraction in Bangladesh. *Science*. 2002; 298:1602–1606. [PubMed: 12446905]
- Hasan MA, von Brömssen M, Bhattacharya P, Ahmed KM, Sikder AM, Jacks G, Sracek O. Geochemistry and mineralogy of shallow alluvial aquifers in Daudkandi upazila in the Meghna flood plain. Bangladesh. *Environ Geol*. 2009; 57:499–511.
- Hiemstra T, Van Riemsdijk WH. A surface structural approach to ion adsorption: the charge distribution (CD) model. *J Colloid Interf Sci*. 1996; 179:488–508.
- Hiemstra T, van Riemsdijk WH. Adsorption and surface oxidation of Fe(II) on metal (hydr)oxides. *Geochim Cosmochim Acta*. 2007; 71:5913–5933.
- Hiemstra T, Antelo J, Rahnemaie R, Van Riemsdijk WH. Nanoparticles in natural systems I: the effective reactive surface area of the natural oxide fraction in field samples. *Geochim Cosmochim Acta*. 2010; 74:41–58.
- Hingston FJ, Posner AM, Quirk JP. Competitive adsorption of negatively charged ligands on oxide surfaces. *Discuss Faraday Soc*. 1971; 52:334–342.
- Hongshao Z, Stanforth R. Competitive adsorption of phosphate and arsenate on goethite. *Environ Sci Technol*. 2001; 35:4753–4757. [PubMed: 11775149]
- Hug SJ, Leupin OX, Berg M. Bangladesh and Vietnam: Different groundwater compositions require different approaches to arsenic mitigation. *Environ Sci Technol*. 2008; 42:6318–6323. [PubMed: 18800496]
- Itai T, Takahashi Y, Seddique AA, Maruoka T, Mitamura M. Variations in the redox state of As and Fe measured by X-ray absorption spectroscopy in aquifers of Bangladesh and their effect on As adsorption. *Appl Geochem*. 2010; 25:34–47.
- Jain A, Loeppert RH. Effect of competing anions on the adsorption of arsenate and arsenite by ferrihydrite. *J Environ Qual*. 2000; 29:1422–1430.
- Jang JH, Dempsey BA. Coadsorption of arsenic(III) and arsenic(V) onto hydrous ferric oxide: effects on abiotic oxidation of arsenic(III), extraction efficiency, model accuracy. *Environ Sci Technol*. 2008; 42:2893–2898. [PubMed: 18497140]
- Jeon BH, Dempsey BA, Royer RA, Burgos WD. Low-Temperature Oxygen Trap for Maintaining Strict Anoxic Conditions. *Jour Environ Eng*. 2004; 130:1407–1410.
- Jessen S, Postma D, Larsen F, Pham QN, Le QH, Pham TKT, Tran VL, Pham HV, Jakobsen R. Surface complexation modeling of groundwater arsenic mobility: Results of a forced gradient experiment in a Red River flood plain aquifer, Vietnam. *Geochim Cosmochim Acta*. 2012; 98:186–201.

- Johnston R, Singer PC. Solubility of symplectite (ferrous arsenate): implications for reduced groundwaters and other geochemical environments. *Soil Sci Soc Am J.* 2007; 71:101–107.
- Jung HB, Charette MA, Zheng Y. Field, laboratory, and modeling study of reactive transport of groundwater arsenic in a coastal aquifer. *Environ Sci Technol.* 2009; 43:5333–5338. [PubMed: 19708362]
- Kanematsu M, Young TM, Fukushima K, Green PG, Darby JL. Arsenic (III,V) adsorption on a goethite-based adsorbent in the presence of major co-existing ions: Modeling competitive adsorption consistent with spectroscopic and molecular evidence. *Geochim Cosmochim Acta.* 2013; 106:404–428.
- Larsen O, Postma D. Kinetics of bulk dissolution of lepidocrocite, ferrihydrite and goethite. *Geochim Cosmochim Acta.* 2001; 65:1367–1379.
- Liu F, De Cristofaro A, Violante A. Effect of pH, phosphate and oxalate on the adsorption/desorption of arsenate on/from goethite. *Soil Sci.* 2001; 166:197–208.
- Luxton TP, Eick MJ, Rimstidt DJ. The role of silicate in the adsorption/desorption of arsenite on goethite. *Chem Geol.* 2008; 252:125–135.
- Martin M, Violante A, Ajmone-Marsan F, Barberis E. Surface interactions of arsenite and arsenate on soil colloids. *Soil Sci Soc Am J.* 2014; 78:157–170.
- McArthur JM, Ravenscroft P, Safiulla S, Thirlwall MF. Arsenic in groundwater: testing pollution mechanisms for sedimentary aquifers in Bangladesh. *Water Resour Res.* 2001; 37:109–117.
- Meng, X.; Wang, W. Speciation of arsenic by disposable cartridges. *Proc Third Int Conf Arsenic Exposure and Health Effects Soc Environ Geochem and Health, Univ Colorado at Denver.* 1998.
- Meng X, Bang S, Korfiatis GP. Effects of silicate, sulfate, and carbonate on arsenic removal by ferric chloride. *Water Res.* 2000; 34:1255–1261.
- Nath B, Chakraborty S, Burnol A, Stüben D, Chatterjee D, Charlet L. Mobility of arsenic in the sub-surface environment: An integrated hydrogeochemical study and sorption model of the sandy aquifer materials. *J Hydrol.* 2009; 364:236–248.
- Norrman J, Sparrenbom CJ, Berg M, Dang DN, Pham QN, Roskvist H, Jacks G, Sigvardsson E, Baric D, Moreskog J, Harms-Ringdahl P, et al. Arsenic mobilization in a new well field for drinking water production along the Red River, Nam Du, Hanoi. *Appl Geochem.* 2008; 23:3127–3142.
- Parkhurst DL, Appelo CAJ. User's guide to PHREEQC (Version 2) – a computer program for speciation, reaction-path, 1D-transport, and inverse geochemical calculations. *USGS Water Resour Inv Rep.* 1999; 99:4259.
- Pedersen HD, Postma D, Jakobsen R, Larsen O. Fast transformation of iron oxyhydroxides by the catalytic action of aqueous Fe(II). *Geochim Cosmochim Acta.* 2005; 69:3967–3977.
- Postma D, Larsen F, Nguyen TMH, Mai TD, Pham HV, Pham QN, Jessen S. Arsenic in groundwater of the Red River floodplain, Vietnam: Controlling geochemical processes and reactive transport modeling. *Geochim Cosmochim Acta.* 2007; 71:5054–5071.
- Postma D, Jessen S, Nguyen TMH, Mai TD, Koch CB, Pham HV, Pham QN, Larsen F. Mobilization of arsenic and iron from Red River floodplain sediments, Vietnam. *Geochim Cosmochim Acta.* 2010; 74:3367–338.
- Postma D, Larsen F, Nguyen TT, Pham TKT, Jakobsen R, Pham QN, Tran VL, Pham HV, Murray AS. Groundwater arsenic concentration in Vietnam controlled by sediment age. *Nature Geoscience.* 2012; 5:656–661.
- Radloff KA, Cheng ZQ, Rahman MW, Ahmed KM, Mailloux BJ, Juhl AR, Schlosser P, van Geen A. Mobilization of arsenic during one-year incubations of grey aquifer sands from Arai-hazar, Bangladesh. *Environ Sci Technol.* 2007; 41:3639–3645. [PubMed: 17547190]
- Radloff KA, Zheng Y, Michael HA, Stute M, Bostick BC, Mihajlov I, Bounds M, Huq MR, Choudhury I, Rahman MW, Schlosser P, et al. Arsenic migration to deep groundwater in Bangladesh influenced by adsorption and water demand. *Nature Geoscience.* 2011; 4:793–798.
- Radu T, Subacz JL, Phillippi JM, Barnett MO. Effects of dissolved carbonate on arsenic adsorption and mobility. *Environ Sci Technol.* 2005; 39:7875–7882. [PubMed: 16295850]
- Ravenscroft, P.; Brammer, H.; Richards, K. *Arsenic Pollution: A Global Synthesis.* Wiley-Blackwell; 2009.

- Saalfeld SL, Bostick BC. Synergistic effect of calcium and bicarbonate in enhancing arsenate release from ferrihydrite. *Geochim Cosmochim Acta*. 2010; 74:5171–5186.
- Shamsudduha M, Uddin A, Saunders JA, Lee M-K. Quaternary stratigraphy, sediment characteristics and geochemistry of arsenic-contaminated alluvial aquifers in the Ganges–Brahmaputra floodplain in central Bangladesh. *J Contam Hydrol*. 2008; 99:112–136. [PubMed: 18502538]
- Stachowicz M, Hiemstra T, van Riemsdijk WH. Surface speciation of As(III) and As(V) in relation to charge distribution. *J Colloid Interf Sci*. 2006; 302:62–75.
- Stachowicz M, Hiemstra T, van Riemsdijk WH. Arsenic-bicarbonate interaction on goethite particles. *Environ Sci Technol*. 2007; 41:5620–5625. [PubMed: 17874764]
- Stachowicz M, Hiemstra T, van Riemsdijk WH. Multi-competitive interaction of As(III) and As(V) oxyanions with Ca^{2+} , Mg^{2+} , PO_4^{3-} and CO_3^{2-} ions on goethite. *J Colloid Interf Sci*. 2008; 320:400–414.
- Stollenwerk KG, Breit GN, Welch AH, Yount JC, Whitney JW, Forster AL, Uddin MN, Majumder RK, Ahmed N. Arsenic attenuation by oxidised sediments in Bangladesh. *Sci Total Environ*. 2007; 379:133–150. [PubMed: 17250876]
- Stookey LL. Ferrozine—A new spectrophotometric reagent for iron. *Anal Chem*. 1970; 42:779–781.
- Swartz CH, Blute NK, Badruzzaman B, Ali A, Brabander D, Jay J, Besancon J, Islam S, Hemond HF, Harvey CF. Mobility of arsenic in a Bangladesh aquifer: Inferences from geochemical profiles, leaching data, and mineralogical characterization. *Geochim Cosmochim Acta*. 2004; 68:4539–4557.
- van Geen A, Zheng Y, Goodbred S Jr, Horneman A, Aziz Z, Cheng Z, Stute M, Mailloux B, Weinman B, Hoque MA, Seddique AA, et al. Flushing history as a hydrogeological control on the regional distribution of arsenic in shallow groundwater of the Bengal Basin. *Environ Sci Technol*. 2008; 42:2283–2288. [PubMed: 18504954]
- van Geen A, Bostick BC, Pham TKT, Vi ML, Nguyen NM, Phu DM, Pham HV, Radloff K, Aziz Z, Mey JL, Stahl MO, et al. Retardation of arsenic transport through a Pleistocene aquifer. *Nature*. 2013; 501:204–207. [PubMed: 24025840]
- Waltham CA, Eick MJ. Kinetics of arsenic adsorption on goethite in the presence of sorbed silicic acid. *Soil Sci Soc Am J*. 2002; 66:818–825.
- Wenzel WW, Kirchbaumer N, Prohaska T, Stingeder G, Lombic E, Adriano DC. Arsenic fractionation in soils using an improved sequential extraction procedure. *Anal Chim Acta*. 2001; 436:309–323.
- Williams LE, Barnett MO, Kramer TA, Melville JG. Adsorption and transport of arsenic(V) in experimental subsurface systems. *J Environ Qual*. 2003; 32:841–850. [PubMed: 12809285]
- Winkel LHE, Pham TKT, Vi ML, Stengel C, Aminia M, Nguyen TH, Viet PH, Berg M. Arsenic pollution of groundwater in Vietnam exacerbated by deep aquifer exploitation for more than a century. *P Natl Acad Sci USA (PNAS)*. 2011; 108:1246–1251.
- Zhang H, Selim HM. Competitive sorption-desorption kinetics of arsenate and phosphate in soils. *Soil Sci*. 2008; 173:3–12.

Fig. 1.

Adsorption and subsequent desorption of As(III) and As(V) on Holocene aquifer sediment at Nam Du in either 10 mM NaHCO_3 or 10 mM PIPES buffer solutions with a 50 mM NaCl background. In both cases the pH was adjusted to 7.0. Adsorption and desorption isotherms were obtained by stepwise addition or removal of arsenic from the batch. The symbol legend is the same in both panels. Note the differences in scale. The lines for the CD MUSIC and Stollenwerk *et al.* (2007) models were calculated for a site density of $8.4 \mu\text{mol sites/g}$ derived from the Langmuir isotherm fit to PO_4 data, as discussed in Section 4.3.

Fig. 2.

Sorption of Fe(II) on aquifer sediments in 10 mM NaHCO_3 and 10 mM PIPES buffer solutions, both adjusted to pH 7. Two separate experiments were carried out for both NaHCO_3 and PIPES.

Fig. 3.

Adsorption of As(III) and As(V) in the presence of Fe(II). The sediment suspensions were equilibrated with 0.05 mM Fe(II) before the addition of As. For comparison, adsorption results from Fig. 1 in the absence of Fe(II) have been included. The symbol legend is the same in both panels.

Fig. 4.

Coadsorption of Fe(II) and As(III) on aquifer sediment. The As(III):Fe(II) molar ratio in the added solutions was 1:100. At the end of the adsorption experiment, desorption was measured by repeated replacement of the aqueous phase by buffer solutions without As or Fe. The two panels display As(III) and Fe(II) measurements carried out on the same aliquots.

Fig. 5.

Displacement experiments of sediment samples pre-equilibrated with As(III) to an aqueous concentration between 2 and 4 μM. Thereafter either phosphate, Fe(II) or silica was added stepwise while the aqueous As(III) concentration was monitored. For Si the initial concentration was 0.15-0.2 mM. The lines for the CD MUSIC and Stollenwerk et al. (2007) models were calculated for a site density of 8.4 μmol sites/g derived from the Langmuir isotherm fit to PO₄ data, as discussed in Section 4.3.

Fig. 6.

Comparison of the adsorption of As(III) and As(V) onto Pleistocene and Holocene aquifer sediments from Bangladesh (BD) and Vietnam(VN).

Fig. 7.

Adsorption of phosphate to aquifer sediment at pH 7. The solid line is a Langmuir fit, using Eqn. 2, corresponding to $K^{\text{PO}_4}_s = 2500 \text{ L/mol}$ and $S_{\text{tot}} = 8.4 \text{ μmol/g}$.

Fig. 8.

Adsorption of As(III) to aquifer sediment. The solid line is the Langmuir fit, using Eqn. 2, corresponding to $K^{\text{As(III)}}_s = 1500 \text{ L/mol}$ and $S_{\text{tot}} = 8.4 \mu\text{mol/g}$. The dashed lines are As(III) adsorption isotherms calculated, using Eqn. 4, in the presence of 100 and 500 $\mu\text{M PO}_4$.

Fig. 9.

Release of As(III) from aquifer sediment upon the addition of PO₄. The solid line was calculated for dual Langmuir competitive adsorption.

Table 1

Characterization of aquifer sediment by parallel chemical extraction. All extractions were carried out by shaking for 24 hours, except the HNO₃ extraction, which was done by microwave for 25 minutes. For interpretation, see text.

Sediment at Nam Du 4.2-4.9 m depth	As(III)	As(T)	Fe(II)	Fe(T)	Si	P
	nmol/g	nmol/g	μmol/g	μmol/g	μmol/g	μmol/g
0.5 M NaHCO ₃ pH 8.5	0.9	0.9	ND	0.0	0.1	0.1
0.5 M Formic acid, pH 3	0.1	0.3	0.9	2.7	1.5	0.2
0.1M Ascorbic acid, pH 3	1.0	2.6	ND	14.4	2.8	0.6
0.2M NH ₄ -oxalate + 0.1M ascorbic acid, pH 3	ND	24.6	ND	77.9	ND	ND
16N HNO ₃ (65%)	ND	29.2	ND	98.6	ND	ND