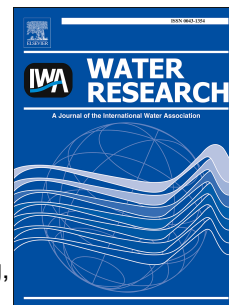


Accepted Manuscript

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PII: S0043-1354(17)30934-X

DOI: [10.1016/j.watres.2017.11.018](https://doi.org/10.1016/j.watres.2017.11.018)

Reference: WR 13348

To appear in: *Water Research*

Received Date: 24 July 2017

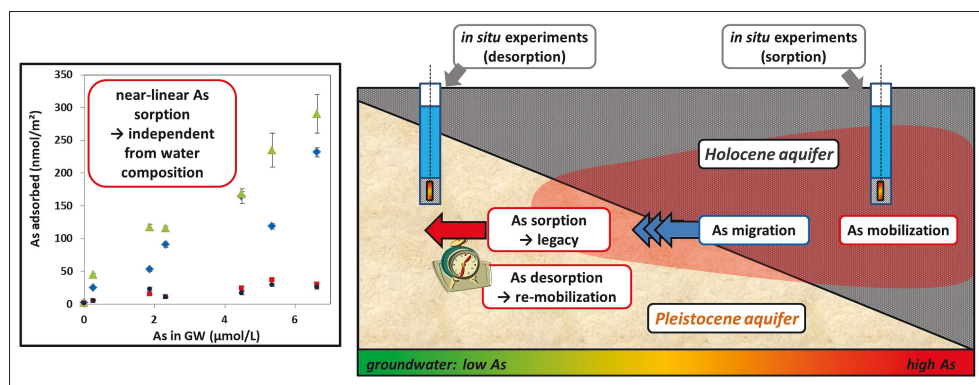
Revised Date: 2 November 2017

Accepted Date: 6 November 2017

Please cite this article as: Neidhardt, H., Winkel, L.H.E., Kaegi, R., Stengel, C., Trang, P.T.K., Lan, V.M., Viet, P.H., Berg, M., Insights into arsenic retention dynamics of pleistocene aquifer sediments by *in situ* sorption experiments, *Water Research* (2017), doi: 10.1016/j.watres.2017.11.018.

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1 **Insights into arsenic retention dynamics of Pleistocene aquifer sediments by *in situ*** 2 **sorption experiments**

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12 **Keywords**

- 13 1. Arsenic behavior
- 14 2. *In situ* sorption isotherm
- 15 3. Reducing conditions
- 16 4. Iron oxyhydroxides
- 17 5. Groundwater
- 18 6. Arsenic remobilization

Abstract

The migration of arsenic (As) enriched groundwater into Pleistocene aquifers as a consequence of extensive groundwater abstraction represents an increasing threat to the precious water resources in Asian delta regions. Pleistocene aquifer sediments are typically rich in FeIII-(hydr)oxides and are capable to adsorb high amounts of As. This results in a pronounced accumulation of As in Pleistocene aquifers, where high As groundwater infiltrates from adjacent Holocene aquifers. However, As retention by Pleistocene aquifers over long-term time scales remains largely unknown. We studied As sorption *in situ* by placing natural Pleistocene sediments and pure mineral phases directly inside groundwater monitoring wells at a study site near Hanoi (Vietnam). This *in situ* exposure allows for constant flushing of the samples with unaltered groundwater and the establishment of undisturbed sorption equilibria similar to those in local aquifer sediments, which is not readily attainable in traditional laboratory sorption experiments. The groundwaters in our experimental wells were characterized by different As concentrations (0.01 to 6.63 $\mu\text{mol/L}$) and redox states, reaching from suboxic to anoxic conditions (E_h of +159 to -4 mV). Results show that adsorption is the dominant As retention mechanism, independent from the respective groundwater chemistry (i.e. concentrations of dissolved P, HCO_3^- and Si). Whilst most of the As sorbed within the first week, sorption further increased slowly but consistently by 6-189%, respectively, within six months. Hence, the As sorption behavior of Pleistocene aquifer sediments should be determined over longer periods to avoid an underestimation of the As sorption capacity. Accompanying desorption experiments revealed that about 51% of the sorbed As was remobilized within six months when exposed to low As groundwater. We therefore conclude that a considerable proportion of the As accumulated in the aquifer sediments is prone to remobilization once the As concentrations in migrating groundwater decline. Remobilization of As should be considered in local water management plans to avoid contamination of precious groundwater resources with this As legacy.

1. Introduction

In floodplain and delta areas of South and Southeast Asia, such as the Red River Delta (RRD) in Vietnam and the Ganges-Brahmaputra-Meghna Delta in India and Bangladesh, groundwater delivered from Holocene aquifers is often highly contaminated with dissolved inorganic arsenic (As), threatening the water supplies of millions of people (Winkel et al. 2008). It is widely accepted that As is being mobilized from organic-rich sediment deposits from the Holocene age via the reductive dissolution of FeIII-(hydr)oxides (McArthur et al. 2001, Nickson et al. 1998, Postma et al. 2016b). In contrast, Pleistocene aquifers are typically characterized by low As concentrations and their exploitation currently represents the main As mitigation strategy in As-affected areas in South and Southeast Asia (Ravenscroft et al. 2014). However, most Pleistocene aquifers are hydrologically connected to overlying or adjacent Holocene aquifers and are as such prone to the migration of As-enriched groundwater when natural flow paths are altered (McArthur et al. 2016, Postma et al. 2016a, Radloff et al. 2017). There is increasing evidence that As-contaminated groundwater migrates into Pleistocene aquifers with previously low levels of As in areas of extensive pumping (Berg et al. 2008, McArthur et al. 2010, Michael and Khan 2016, van Geen et al. 2013, Winkel et al. 2011). Using numerical groundwater flow and solute transport modeling, Michael and Khan (2016) estimated that up to 30% of the deep Pleistocene aquifers in Bangladesh are vulnerable to the downward migration of high As groundwater from shallow Holocene aquifers, depending on the extent of pumping, the heterogeneity of hydraulic properties, and the sediment composition. As such, migration of high As groundwater poses a growing threat to the sustainable use of groundwater in the densely populated Asian floodplain and delta regions, especially along transition zones separating Holocene and Pleistocene aquifers without the presence of hydrologically protecting intercalated aquitard layers.

Although Pleistocene sediments exhibit a pronounced As sorption capacity due to their high contents of FeIII-(hydr)oxides (Fendorf et al. 2010), this capacity is not infinite. This results in moving fronts of dissolved As that subsequently advance into Pleistocene aquifers, as has been described at our field site, Van Phuc in the RRD (van Geen et al. 2013). Here, the lateral migration of As was estimated to be retarded by a factor of 16-20 compared to the overall groundwater flow, generating a transition zone at the boundary of a Holocene aquifer and a Pleistocene aquifer where groundwater As concentrations gradually increase from $<0.01 \mu\text{mol/L}$ to $>6.5 \mu\text{mol/L}$ when approaching the Holocene aquifer (van Geen et al. 2013). Adsorption by FeIII-(hydr)oxides is currently considered the dominating process to control As concentrations in the groundwater of Asian floodplain and delta regions

(Stollenwerk et al. 2007). It includes the surface accumulation of As via electrostatic attraction (weak attenuation) and ligand-exchange (mono- or bidentate complexes) (Müller et al. 2010). The As sorption potential is controlled by the speciation of As, the pH, the presence of competitive sorbents, the mineral composition, and the grain size distribution, which determines in turn the sediment's surface area (Itai et al. 2010). In addition, the removal of As from groundwater by precipitation and coprecipitation leads to the formation of secondary solids, such as As-sulfides or magnetite, which efficiently immobilize As via incorporation into the respective crystal lattices (Rawson et al. 2016).

So far, As sorption properties have been mainly investigated in controlled laboratory experiments using artificial groundwater solutions and synthetic Fe minerals, while only a small number of field experiments have been performed (Jessen et al. 2012, Radloff et al. 2011). Furthermore, retention of As by natural aquifer sediments is likely highly dynamic and the impact of anoxic, high As groundwater on Pleistocene sediments has to be taken into account, as it can potentially alter the aquifer sediment's As sorption capacity over time. Therefore, field experiments that are able to bridge the gap between laboratory experiments, groundwater monitoring, and reactive transport modeling are required. The aim of this study was to investigate the dynamics in the retention and remobilization of As by real Pleistocene sediments under field conditions that represent different redox states. We conducted a series of *in situ* adsorption and desorption experiments exposing Pleistocene aquifer sediment and pure synthetic FeIII-(hydr)oxides directly to natural groundwater at various locations along a gradient in redox conditions that also covers a broad range of As concentrations and other hydrochemical parameters in order to investigate changes in the As sorption behavior of our sample materials over time.

2. Materials and methods

Study area: All experiments were conducted in the village of Van Phuc near Hanoi along a transect of groundwater monitoring wells that capture a lateral gradient in As concentrations in shallow groundwater along the transition of Holocene and Pleistocene aquifer sediments (Figure S1). In the western part of Van Phuc, As concentrations remain below the World Health Organization's drinking water guideline value (10 µg/L, or 0.13 µmol/L), whereas in the eastern part, concentrations exceed 6.5 µmol/L (Eiche et al. 2008). Due to massive groundwater abstraction for the municipal water supply, huge cones of depression have formed in the aquifers below Hanoi, which alter the groundwater flow in the entire periphery, including our field site (Berg et al. 2008, Norrman et al. 2008). As a result, high

As groundwater laterally migrates from the Holocene aquifer into the adjacent Pleistocene aquifer at a rate of ~38 to ~48 m/a (van Geen et al. 2013). High As groundwater is typically associated with grey-colored channel-infill sand deposits of Holocene age, while low As groundwater is mostly associated with orange-colored Pleistocene sand that was deposited before the Holocene age (Eiche et al. 2017, Eiche et al. 2008). There is a steep rise in groundwater As concentrations of the Pleistocene aquifer in the direction of the Holocene aquifer, which is accompanied by a sharp change in the color of the aquifer sediments from orange to grey (van Geen et al. 2013). Further details regarding the aquifer architecture, sedimentation history, and the evolution of local groundwater at Van Phuc is provided elsewhere (Eiche et al. 2017, Stahl et al. 2016, van Geen et al. 2013).

Experimental approach: Our study uses the dense network of groundwater monitoring wells reported in van Geen et al. (2013) to carry out a series of *in situ* aquifer exposure experiments to investigate the retention of As by Pleistocene aquifer sediment under field conditions. We hypothesize that ongoing contact with reducing groundwater alters the As sorption capacity of the Pleistocene sediment over time, which also enables the remobilization of As. To test this hypothesis, we carried out a series of adsorption experiments as well as two accompanying desorption experiments.

Adsorption experiments: Pleistocene sediment and quartz sand coated with synthetic Fe minerals (as described below) were placed into custom-made PVC sample carriers (triplicates for the six months exposure experiments, duplicates for shorter exposure times) covered with 0.2 mm nylon mesh (Figure 1). The three different FeIII-(hydr)oxides (hematite, goethite, and two-line ferrihydrite) were selected as complementary controls to examine the stability of common Fe minerals under field conditions. For the first set of experiments conducted between April and October 2013, we used a sample holder system, which provided three slots per holder and was loaded with 4.5 g per sample replicate. For the later experiment carried out between October 2013 and April 2014, we used a second, smaller set of sample holders, which provided eight sample slots with a capacity of 0.4 g per sample replicate, to reduce the amount of limited sample material. The sample holders were connected and equipped with a weight of 300 g before their installation in local groundwater monitoring wells. The sample holders were then placed in range of the one-meter long well screenings located at 24 to 38 m below the surface (bls) (Figure S2), and positions were controlled with a borehole camera system (Witson). The well screenings were either situated in Holocene aquifer sediments where groundwater As concentrations were high (AMS-5, AMS-12, AMS-15, and VPNS-5), in Pleistocene aquifer sediments with low As groundwater (AMS-2 and AMS-4), or in Pleistocene

sediments of the transition zone where high As groundwater was present (AMS-1, AMS-11, and AMS-32; see Figures S1 and S2 for further details). The wells covered a broad range of groundwater As concentrations as well as a sharp vertical redox gradient that spans from highly to slightly reducing conditions (Figure 2, Table S1). Direct exposure at field conditions has two advantages compared to traditional laboratory sorption experiments. Firstly, there is a constant flushing with unaltered groundwater, allowing the establishment of undisturbed sorption equilibria similar to those prevailing within the local aquifer sediments. Secondly, it captures real-time variability in environmental conditions such as microbial activity or groundwater flow velocity. In laboratory experiments, it is highly challenging to reconstruct and maintain the complex composition of natural anoxic groundwater over weeks and months. Samples remained exposed for different time spans (24 hours, one week, four weeks, and six months) to investigate the fast and slow effects related to the As sorption behavior. For further details, see Figure S2.

Desorption experiments: To test how stable As retention by the Pleistocene sediment is over time, additional desorption experiments were performed. The idea was to pre-load the Pleistocene sediment and synthetic FeIII-(hydr)oxides with As and then expose the samples directly to low As groundwater at the Pleistocene aquifer as previously described. Two different approaches were used to pre-load the samples with As, which allowed us to explore the influences of aging effects on As desorption. The first desorption experiment investigated the remobilization of As from Pleistocene sediment and fresh FeIII-(hydr)oxides. Pleistocene sediment and FeIII-mineral coated sand samples were pre-loaded on-site by short-term flushing with high As groundwater from a representative well located in the Holocene aquifer close to the presumed area of As mobilization (AMS-12 with 2.32 $\mu\text{mol/L}$ As, see Figure S1). A total of 15 g per sample type was placed inside a small PP column and was connected to the hose of an electrical pump, thus preventing contact between the anoxic groundwater and air. A total volume of 15 L was percolated through each sample type at a rate of 700 mL/min. The average As concentration remained constant throughout the procedure ($2.24 \pm 0.09 \mu\text{mol/L}$, n: 15). After loading, samples were rapidly transferred into a portable glove bag where they were placed in the sample holders under a nitrogen atmosphere to avoid oxidation. Afterwards, As-loaded samples were transported under a nitrogen atmosphere to a well of the Pleistocene aquifer (AMS-2) where they were exposed *in situ* to low As groundwater (0.07 $\mu\text{mol/L}$ As) for six months.

A second desorption experiment was conducted to investigate As desorption from aged samples after six months of contact with high As and anoxic groundwater. This approach was chosen to simulate a

sudden decline in the As concentrations of migrating groundwater. For this experiment, pre-loading of the samples was achieved by *in situ* exposure to high As groundwater in well AMS-12 for six months. After recovery, sample carriers were immediately stored inside a 2L Nalgene bottle filled with fresh groundwater, which was stored under a nitrogen atmosphere in a portable glove bag and was transported to the low As well AMS-2 within 30 minutes. Here, loaded samples were kept *in situ* for six months. In both experiments, an aliquot of As pre-loaded samples (Pleistocene sediment and FeIII-mineral-coated sand) were taken to the lab to determine their respective As loadings prior to their exposure to low As groundwater.

Fig. 1. Pleistocene sediment and initial Fe mineral-coated sand samples (a), and the two types of sample carriers (b) used for the *in situ* exposure (type 1 and 2; left) and a picture of two connected sample carriers after six months of exposure (right).

Pleistocene sediment: The Pleistocene sediment used in this study originates from the low As aquifer in Van Phuc (20°55'23.74"N, 105°53'31.13"E) . It was collected as a bulk sample from 27.4 to 27.7 m bls. Details regarding the drilling and geochemical analysis are provided elsewhere (Eiche 2009, Eiche et al. 2008). In brief, the yellow-brownish sediment is composed of sand (61.9%), silt (34.2%), and some clay (3.8%), and the mineralogy is characterized by quartz, mica, feldspars, and traces of kaolinite, dolomite, hematite, and goethite. Sample material was kept frozen until it was freeze-dried under vacuum for this study, thereby minimizing the alteration effects of the sediment material. Samples were sieved to a grain-sized fraction of 0.2 to 0.5 mm, which was necessary to avoid washout of the fine fraction from the sample holders. Sieving had no notable effect on the mineralogy (see X-ray powder diffraction spectra in Figure S3), and as Fe minerals are mostly present in the form of secondary coatings equally distributed over the mineral grains (Eiche et al. 2008), the As sorption behavior of the bulk sample related to its surface area was unchanged.

Synthetic iron minerals: Hematite, goethite, and two-line ferrihydrite were first prepared from a solution of dissolved $\text{Fe}(\text{NO}_3)_3 \times 9\text{H}_2\text{O}$ (Sigma-Aldrich, p.a.) and then coated onto acid washed cristobalite grains of 0.2 to 0.4mm (Sigma-Aldrich, p.a.), according to the procedure described by Schwertmann and Cornell (2008). This grain size spectrum corresponds to the dominant sediment

grain size in the Pleistocene aquifer of Van Phuc. Hematite and goethite were chosen because they represent the predominating FeIII-(hydr)oxides in Pleistocene sediments in the RRD (Mai et al. 2014). Ferrihydrite, which is often used as a model type for weakly ordered Fe minerals in surface complexation models, was included as another important potential sink for As (Biswas et al. 2014, Stollenwerk et al. 2007). The purity of the Fe minerals was verified by powder X-ray diffraction (XRD; X'Pert Powder PRO, PANalytical, CoK α radiation, 5-95° 2 θ at 40kV and 40mA, Figure S4).

Analysis of solids: After retrieval, samples were first air dried before being transported to the laboratory. Next, samples were freeze-dried and the chemical composition was determined by inductively coupled plasma mass spectrometry (ICP-MS 7500 series, Agilent) after dissolving the Fe coatings by microwave-assisted acid digestion (ultraCLAVE IV A, MLS GmbH), in line with Environmental Protection Agency (EPA) methods 3501 and 3050. The sample material was not ground because only surface-sorbed As was targeted. The methodical detection limits (determined from acid digestion blanks, calculated for a 50 mg sample, n: 37) were 0.83 nmol/g for As and 0.32 μ mol/g for Fe. A certified reference material (sediment) was included as an internal quality control (MESS-3, NRC), yielding As concentrations of 282 \pm 7 nmol/g; n: 22 (reference value: 283 \pm 15 nmol/g). To derive the net amount of As sorbed to the Pleistocene sediment, the sediments initial extractable As content (Table S2) was subtracted from the content measured after exposure. This initial amount of As was not present in form of surface adsorbed As according to sequential extractions carried out for Pleistocene sediment samples from the same core slightly above and below (27.1, 32.4 and 38.8 m bls), which yielded no 0.5 M NaH $_2$ PO $_4$ -extractable As (Eiche 2009, Eiche et al. 2010). This finding is in agreement with the very low groundwater As concentrations (<0.02 μ mol/L) found in groundwater at depths where the Pleistocene sediment was collected.

BET and SEM analyses: The BET surface area was determined for a subset of samples via a surface area analyzer (SA3100, Beckman Coulter). Scanning electron microscope (SEM) images were recorded for a subset of samples from the adsorption experiment including all sample types (initial samples as well as samples collected after one week to six months of exposure) in order to identify potential changes of the mineral surfaces. The SEM (Nova NanoSEM230, FEI Inc., GDA detector in low vacuum mode, ETD in high vacuum) was additionally equipped with an energy dispersive x-ray fluorescence detector (Oxford EDX system, XMAX 80) that allowed us to check the elemental composition of the samples on selected regions of interest (acceleration voltage: 15kV, acquisition live time 20sec.).

Groundwater sampling and analyses: Groundwater samples were collected each time before introducing and after recovering *in situ* samples. Standard field parameters pH, oxidation-reduction potential (ORP), electrical conductivity (EC), water temperature, and O₂ content were recorded with a field multi meter system (WTW, since 2014 Hach) using a glass flow-through cell for ORP and O₂ measurements. ORP values were converted into E_h according to the manufacturer's manual. Total alkalinity (TA) was determined by a titrimetric field test kit (1.11109.0001, Merck). As soon as field parameters reached stable values, samples were filtered on-site (<0.45 µm cellulose acetate filters, Sartorius), collected into acid-washed and preconditioned sample bottles, and were either acidified with concentrated HNO₃ (cation samples) and HCl (DOC) or left untreated (anions). Samples for the determination of dissolved AsIII were collected using arsenate (AsV) restraining filter cartridges (MetalSoft Centre). Samples were transported via airplane to the Eawag laboratory in Dübendorf, Switzerland, where they were stored at 4°C until an alysis. The chemicals used were of analytical grade if not stated otherwise. Groundwater was analyzed for total concentrations of dissolved major and trace elements (ICP-MS, Agilent 7500 series), anions (IC, Dionex), and dissolved organic carbon (DOC, using a TOC 5000 A analyzer, Shimadzu). PHREEQC was used for the thermodynamic calculation of mineral saturation indices (SI) using the wateq4 database (Parkhurst and Appelo 1999).

3. Results & Discussion

3.1 Groundwater properties

Groundwater of the Holocene aquifer is characterized by a circum-neutral pH, a low E_h and a high EC and TA (see Table S1). Compared to low As groundwater typically found in the RRD (see for example Winkel et al. 2011), concentrations of dissolved As, Fe, Mn, NH₄⁺, and P are elevated, while dissolved O₂, NO₃⁻, and SO₄²⁻ remain at low levels (see Table S1). Such groundwater composition is characteristic of Holocene aquifers in South and Southeast Asia, where reducing conditions trigger the reductive dissolution of FeIII-(hydr)oxides and the mobilization of geogenic As (Nickson et al. 1998, Winkel et al. 2008). Both Fe and As in groundwater are mainly present as dissolved species, as suggested by a filtration test (see Figure S5), with 92-100% of the total As present as reduced AsIII. As previously highlighted, As migrating horizontally from the Holocene to the Pleistocene aquifer is retained by the Pleistocene sediments at the transition zone; concentrations behind this transition zone currently remain below 0.01 µmol/L (see wells AMS-2 and AMS-4). In summary, the selected monitoring wells not only reflect a pronounced gradient of As concentrations in groundwater (0.01 to

6.63 $\mu\text{mol/L}$), but also of other parameters relevant for As sorption, such as P, Si and HCO_3^- (Figure 2). In addition, redox conditions span from suboxic and mildly reducing (+159 to +112mV) to anoxic and moderately reducing (-4 to +45 mV) (Borch et al. 2010).

3.2 As sorption

Rapid sorption within one week: Figure 2 shows the amount of As sorbed to the synthetic Fe minerals and the Pleistocene sediment after one week of *in situ* exposure to groundwater wells of the Holocene and the Pleistocene aquifer. For the relatively wide range of groundwater As concentrations (0.01 to 6.63 $\mu\text{mol/L}$), the As sorption was related to the BET surface area. The initial sorption proved to be rapid, with the majority of As being sorbed within one week to the Pleistocene sediment (on average 65% as compared to contents reached after six months; see Figure 3). The same applied for the synthetic Fe minerals. The majority of As probably sorbed even within the first 24 hours, as suggested by a set of samples that was exposed for 24 hours (Figure S7) and previous As(III) sorption studies (Giménez et al. 2007). Hematite-coated sand showed the highest As sorption capacity (reaching up to 290 nmol/m^2), closely followed by ferrihydrite-coated samples (up to 232 nmol/m^2) (Figure 2). In contrast, goethite-coated sand and the Pleistocene sediment had a ten-fold lower sorption capacity (1.0 to 29.6 nmol/m^2). Hence, the As sorption capacity of Pleistocene sediment resembles that of the goethite-coated sand rather than that of hematite- or ferrihydrite-coated sand, which is in agreement with its mineralogical composition (Eiche et al. 2008).

Sorption isotherms obtained for the Pleistocene sediment as well as the three synthetic Fe mineral phases generally depict a nearly linear relationship between As sorption and groundwater concentrations, which is similar to As(III) sorption isotherms obtained in laboratory sorption experiments for Pleistocene and Holocene aquifer sediments (Mai et al. 2014). Generally, experimentally determined As(III) sorption isotherms can be fitted either by Freundlich (Itai et al. 2010) or Langmuir adsorption models, although sorption to natural aquifer sediments was shown to be linear up to a concentration of 13 $\mu\text{mol/L}$ (Mai et al. 2014). Our results also show a linear range up to the maximum concentration in groundwater of 6.63 $\mu\text{mol/L}$. In addition, As sorption appears to be independent of the groundwater composition, which is surprising since, for example, E_h (spanning from +159 to -4 mV in groundwater), pH (6.5 to 7.1), dissolved P (2.3 to 32.2 $\mu\text{mol/L}$), HCO_3^- (5.5 to 13.6 mmol/L), and Si (0.27 to 0.57 mmol/L) were previously reported to affect As sorption (Biswas et al. 2014, Stollenwerk et al. 2007).

287

288 **Fig. 2.** Observed As adsorption after one week of *in situ* exposure related to BET surface area. To compensate
289 for the loss of surface area due to dissolution of the ferrihydrite coating, Fe contents measured after exposure
290 were used to extrapolate respective BET surface areas (see Figure S6). The values below the figure summarize
291 key parameters for the groundwater of respective wells.

292

293 The partitioning of As between aquifer sediments and groundwater can also be described in a more
294 simplified way using observed distribution coefficients ($K_{d_{obs}}$), which are calculated as a ratio of sorbed
295 As (in mg/kg) and As concentration in the aqueous solution (mg/L) (Itai et al. 2010, Smedley and
296 Kinniburgh 2002). In the case of a straightforward relationship between sorbed As and groundwater
297 As, a linear adsorption isotherm results and the $K_{d_{obs}}$ defines a constant retardation factor (Smedley
298 and Kinniburgh 2002). While $K_{d_{obs}}$ values calculated for our experimental samples rapidly decrease
299 with increasing As in the lower concentration range, they are steady for As concentrations exceeding
300 2.3 μM (Figure 4). Of the synthetic FeIII-(hydr)oxides, hematite- and ferrihydrite-coated sand showed
301 the highest $K_{d_{obs}}$ values (9 to 84 L/kg and 9 to 116 L/kg, respectively), while values for goethite-coated
302 sand (1 to 67 L/kg) again remained in the range of the Pleistocene sediment (2 to 83 L/kg). However,
303 K_d values are calculated from weight-related sorption values irrespective of surface areas that
304 generally increase with smaller grain size. Since the sieving of our Pleistocene sediment prior to the
305 adsorption experiments removed the silt and clay fraction ($<0.2\text{mm}$), the BET surface area decreased
306 by a factor of 6.4 from 3.52 m^2/g to 0.55 m^2/g . We therefore extrapolated the amount of As sorbed to
307 the Pleistocene sediment samples based on this factor, assuming a linear relationship between AsIII
308 sorption and the BET surface area, as demonstrated by Itai et al. (2010) for Holocene and Pleistocene
309 sediments in Bangladesh. We then compared these extrapolated values with K_d values described in
310 literature for Pleistocene and Holocene sediments.

311

Fig. 3. Correlation between groundwater As concentrations and As sorbed. Symbols show mean As contents of the samples after *in situ* exposure to the groundwater of different wells for varying time intervals.

As a result, the $K_{d_{obs}}$ values of the Pleistocene sediment increase to values that are similar to hematite- and ferrihydrite-coated sand (see “Pleistocene sediment full grain size” in Figure 4). Batch sorption experiments using Holocene sediments from the RRD (Mai et al. 2014) and Pleistocene sediments from the Bengal Delta (Itai et al. 2010) yielded similar K_d values for AsIII in a range of 11 to 14 and 9 to 84 L/kg, respectively. Interestingly, these laboratory-derived K_d values and our *in situ*-derived $K_{d_{obs}}$ values are almost one order of magnitude higher compared to the K_d values reported by van Geen et al. (2013) for the Pleistocene aquifer of our study site in Van Phuc (1.7 to 2.1 L/kg). This estimation is based on a combination of groundwater monitoring data and a simple transport model. Radloff et al. (2017) calculated comparable K_d values (0.15 to 1.5 L/kg) for a similar Pleistocene aquifer in Bangladesh based on the outcomes of a push-pull test. It remains unknown why our *in situ* approach and laboratory batch experiments yield different K_d values compared to field data based transport modeling approaches. One plausible explanation is hydrogeological heterogeneities and the inaccessibility of adsorption sites within undisturbed aquifer sediments (Mai et al. 2014, Radloff et al. 2011). For example, Curtis et al. (2006) suggested that only around 20% of the sorption sites determined in laboratory batch experiments are effectively available for water-solid phase interactions at the field-scale. Reactive transport modeling conducted by Rathi et al. (2017) for the Pleistocene sediments we used in our experiments further suggests an even lower sorption site availability of between 5 and 20%. Without an extrapolation, $K_{d_{obs}}$ values of the Pleistocene sediment (see “Pleistocene sediment” in Figure 4) are similar to the field-derived K_d values by van Geen et al. (2013) and Itai et al. (2010). Therefore, more research is required to investigate this gap between experimentally determined As sorption behavior and data obtained from field observations in order to estimate realistic field site specific K_d values for transport modeling with reasonable efforts.

Fig. 4. $K_{d_{obs}}$ values for one week of *in situ* exposure. In the case of the Pleistocene sediment, two different group values are illustrated; the original results (grain size of 0.2 to 0.5mm), and an extrapolation for the full grain size spectrum based on the BET surface area (see methods). Note that one extremely high value (530 L/kg) was omitted (for As conc. of 0.01 $\mu\text{mol/L}$). Error bars were omitted to increase readability; see Figure 3.

Slow changes in As sorption capacity: During *in situ* exposure for four weeks to six months, the As sorption capacity of the Pleistocene sediment and synthetic Fe mineral samples partially changed over time (Figure 3, Figure S7). Before interpreting the outcomes for the Pleistocene sediment, it is beneficial to first explore changes in the synthetic FeIII-(hydr)oxides. Ferrihydrite-coated sand underwent a considerable decline in the As sorption capacity after four weeks, as illustrated in Figure 5, which presents SEM images and corresponding Fe and As concentrations before and after *in situ* exposure. The decline in As sorption was accompanied by a decrease in the Fe content and the specific surface area, indicating an almost complete removal of the ferrihydrite coating during six months of exposure. The higher standard deviations depicted for four of the ferrihydrite samples are attributed to a heterogeneous reductive dissolution of the ferrihydrite coating and the concomitant loss of adsorbed As. This assumption is supported by respective Fe contents, which show similar standard deviations for the replicates of these particular samples (see Table S3).

In contrast, goethite-coated samples showed only a slight decrease of sorbed As when exposed for four weeks to groundwater exceeding 4.5 μM , but remained steady thereafter. At the same time, a slight increase in As sorption to hematite was observed. Changes in As sorption were generally not evident at lower groundwater As concentrations, except for the ferrihydrite samples that lost their coating (see Figure 5). Unlike ferrihydrite, the total Fe contents of goethite- and hematite-coated samples reflect no clear signs of dissolution (Table S3). This could be related to differing reductive dissolution kinetics for these Fe minerals (Larsen and Postma 2001). Saturation indices calculated for Fe mineral phases based on the prevailing groundwater hydrochemistry (Table S4) suggest that weakly ordered FeIII-(hydr)oxides (i.e. ferrihydrite) are largely under-saturated, while more crystalline Fe minerals (e.g., hematite and goethite) are thermodynamically stable, as indicated by positive SI indices. Based on these observations, we concur with Jessen et al. (2012) and Postma et al. (2010) that surface complexation models applied to anoxic environments should be based on stable FeIII-(hydr)oxides rather than weakly crystalline ferrihydrite.

While the majority of As sorbed rapidly to the Pleistocene sediment within one week (Figure 3), As sorption continued slowly and increased on average by 73% (range 6-189%) after six months relative to one week exposure (Table S5). This could be related to either slow adsorption kinetics or an alteration of the mineral surfaces increasing their As sorption potentials over time. A two-stage sorption process has been previously implied by push-pull tests in Bangladesh, where 70% of AsIII

was sorbed within one day and most of the remaining amount after eight days (Radloff et al. 2011), which is in agreement with our observations. In laboratory experiments conducted by Giménez et al. (2007), AsIII reached sorption equilibria with hematite and goethite even in less than two days. In addition, a number of abiotic and biogeochemical reactions might occur when Pleistocene sediments are exposed to strongly reducing groundwater that are capable of altering the As sorption properties (Hansel et al. 2004, Islam et al. 2005). This includes precipitation and the transformation of the mineral phases (e.g., conversion of ferrihydrite into magnetite) as well as mineral dissolution reactions (Kocar et al. 2010). Electron microscopic images and EDX analysis of the synthetic FeIII-(hydr)oxide sample surfaces confirm the formation of secondary Fe mineral phases, but only for some cases and not for ferrihydrite-coated sand (Figures S8-S11). Hence, increases in the As sorption behavior of the samples are related to adsorption kinetics rather than to the formation of secondary mineral phases. However, we cannot exclude the possibility of widespread changes in the mineral surfaces at the nano-meter scale, which would exceed the spatial resolution of SEM images.

Recently, Bonte et al. (2017) demonstrated that atmospheric O₂ can penetrate the water column in monitoring wells due to thermally gradient driven convection. Assuming that O₂ diffused down to our experimental samples, this would have resulted in the oxidation of dissolved FeII and the precipitation of FeIII-(hydr)oxides as well as a partial removal of dissolved As via coprecipitation. Hence, As sorption to our *in situ* samples would have been reduced and we wouldn't have observed such a pronounced linearity between As sorption and As concentrations determined from fresh groundwater samples taken before/after removal of the experimental samples (see Figures 2 and 3). In addition, diffusion of atmospheric O₂ would also increase the redox potential within the well water, thereby preventing the reductive dissolution of ferrihydrite coatings, which clearly occurred during the four weeks and six months long exposure experiments (see Figure 5 and Figure S7). Furthermore, water level measurements showed that the water column above our experimental samples (calculated as difference between the respective water level and the position of the well screen top edge, see Figure S2) had a minimum thickness of 14.8 m. This is three meters more than the maximum water column thickness that could be penetrated by atmospheric O₂ as reported in Bonte et al. (2017). In addition, sample holders were intentionally placed in range of the well screenings as previously mentioned, allowing for a constant flushing of the samples with fresh groundwater. We therefore exclude the possibility that our experimental samples were influenced by atmospheric O₂ during the exposure experiments.

Fig. 5. SEM images of representative sample surfaces of ferrihydrite-coated sand before and after *in situ* exposure in wells AMS-1 (E_h : +45 mV) and AMS-5 (E_h : +29 mV). After six months of exposure, the samples' surfaces were strongly altered by the dissolution of the ferrihydrite coating and the accompanying loss in As sorption sites. Images recorded with GAD detector at 15.0 keV.

Implications for As sorption behavior: The *in situ* sorption experiments provide valuable insight into a number of partially counteracting processes that will occur when strongly reducing and As-enriched groundwater intrudes into Pleistocene sediments. The fast adsorption of dissolved As will take place at first, reaching near-equilibrium with the Pleistocene aquifer sediment within days. This initial adsorption phase is then followed by slower As adsorption and the alteration of associated mineral phases. If weakly ordered Fe minerals like ferrihydrite are present, they will readily adsorb As but release it again within weeks to months due to dissolution under the reducing conditions. In contrast, more crystalline Fe phases such as goethite and hematite will remain stable (at least for the mid-term), representing important sinks for sorbed As. Net changes in As sorption of the Pleistocene sediment after six months of exposure further indicate that the amount of immobilized As increases over the course of months, which is in contrast to previous assumptions that the degree of As sequestration will remain stable once Fe(III)-reducing conditions are established (Radloff et al. 2017). Because the As sorption behavior of Pleistocene sediments slowly increases over the course of months, traditional approaches to determine As retention of Pleistocene sediments, like short-termed laboratory batch sorption experiments or push-pull tests, are likely to underestimate the As retention potential of aquifer sediments.

Another key result of our *in situ* approach is that As sorption is not only linear over a wide range of As concentrations, but also independent from variations in hydrochemical groundwater properties, such as E_h , alkalinity, or concentration of dissolved P. This is in agreement with Radloff et al. (2017), who described a narrow range in the As sorption affinities of aquifer sediments in Bangladesh despite varying groundwater redox conditions. Although the reason(s) for this behavior remain to be investigated, the observed robustness of As sorption to Pleistocene sediments over a wide range of As concentrations and redox potentials implies a high transferability of the aquifer sediment sorption

behavior within the Asian delta regions. While redox potentials in high As groundwater in the Bengal Delta are similar to our experimental wells ($E_h < +100$ mV) (Smedley and Kinniburgh 2002), E_h values measured by Winkel et al. (2011) in the RRD reach down to -203 mV (median value of -65 mV, n: 504). Redox potentials reported in Buschmann et al. (2008) for the Mekong Delta in Vietnam and Cambodia even reach down to -408 mV (median of +2 mV, n: 342). To examine the potential influence of highly reducing redox conditions on our experiments, we calculated SI values for a suite of FeIII-(hydr)oxides using the groundwater data from our wells and a fixed E_h of -200 mV (Table S4b). The outcomes demonstrate that even under such highly reducing redox conditions, hematite and goethite minerals would remain over-saturated and therefore stable. Only when reducing groundwater is low in dissolved Fe (< 10 $\mu\text{mol/L}$), goethite becomes unstable. Hence, we expect that our experimental data is also transferable to highly reducing aquifer environments, where groundwater is typically enriched in both, dissolved As and Fe.

Finally, surface adsorption, rather than coprecipitation with secondary mineral phases, seems to represent the dominating As retention mechanism. Three observations support this assumption: (i) the linearity of the *in situ* sorption isotherms; (ii) SEM surface images of the synthetic Fe mineral samples that depict nearly no formation of secondary mineral phases (the formation of new minerals was only observed for a small number of surfaces of goethite- and hematite-coated grains after exposure; see Figures S10 and S11); and (iii) a pronounced remobilization potential of the Pleistocene sediment samples as described in the following.

3.3 Remobilization potential

Desorption of As: A further question we addressed in this study is to what extent sorbed As may be remobilized from the Pleistocene aquifer sediments in case the supply with As declines. This decline may be driven by either an exhaustion of the biogeochemically driven As mobilization in the area of origin or flow paths of high As groundwater that are redirected due to changes in groundwater abstraction. This question was addressed by two *in situ* desorption experiments in which samples pre-loaded with As from the Holocene aquifer were exposed for six months to low As groundwater in the Pleistocene aquifer.

The samples pre-loaded by short-term on-site flushing showed a considerably large loss of sorbed As (see Figure 6a, hematite-coated sand -63.5%; Pleistocene sediment, ferrihydrite- and goethite-coated sand nearly -100%). However, for the samples that were already pre-loaded *in situ* for six months, a

smaller fraction of sorbed As was lost (see Figure 6b, Pleistocene sediment -51.1%, goethite- and ferrihydrite-coated sand -58.8 and -64.6%, respectively), whereas hematite-coated sand only lost 3.2%. Further, despite the only mildly reducing redox conditions (E_h of +151 mV), Pleistocene sediment samples lost 21.3% (short-term flushing) and 30.0% (*in situ* loading), respectively, of their initial bulk Fe content. The loss of Fe was even more pronounced for the weakly crystalline ferrihydrite (-58.4 and -93.0%, respectively) compared to goethite (-20.1 and -24.0%,) and hematite (-7.5% and -16.5%, see Figure 6). In contrast to the other samples, hematite-coated samples received the highest initial loading of As from *in situ* exposure and not from short-term flushing (2.4 times higher As content). While 63.5% of presorbed As from short-term flushing was lost after the exposure to low As groundwater, nearly no (-3.2%) loss occurred when hematite samples were pre-loaded via six month *in situ* sorption.

Fig. 6. Net loss of As and Fe from the samples pre-loaded by short-term on-site flushing (a) and pre-loaded *in situ* for six months (b). Illustrated are As contents in the samples before (red bars) and after (blue bars) six month exposure to low As groundwater in the Pleistocene aquifer (Fh: ferrihydrite; Goe: goethite; He: hematite; Ps: Pleistocene sediment). Pleistocene sediment sample also lost a small portion of initially FeIII-(hydr)oxide associated As, which is why the value slightly exceeds 100%.

Implications for As desorption behavior: The almost fully reversible As sorption observed for the Pleistocene sediment, as well as for goethite- and ferrihydrite-coated samples that were loaded by short-term on-site flushing, points towards an equilibrium-controlled adsorption mechanism underlying the retention of As. The dissolution of As-sorbing Fe mineral coatings represents a second potential As release mechanism. However, As remobilization strongly declined in samples that had previously been exposed for six months to reducing high As groundwater, which indicates a shift to more stable binding forms.

The predominance of AsIII in the anoxic groundwater of Van Phuc (Table S1) provides an explanation for the high degree of As that was remobilized in our desorption experiments, especially when As pre-loading was achieved by short-term on-site flushing. Previous laboratory and field studies also indicate that As sorption in Asian Holocene and Pleistocene aquifers represents a reversible process (Mai et al. 2014, Radloff et al. 2017). Sorption experiments conducted by Mai et al. (2014) and Radu et al.

(2005) with natural aquifer sediments and goethite-coated sand demonstrated that AsIII sorption is mostly, but not fully reversible.

We observed such a partial reversibility also previously in batch AsIII sorption experiments carried out under N₂ atmosphere, where we used the same Pleistocene sediment as in our *in situ* experiments. Here, sediment samples were first preloaded using a 15 mmol/L NaCl solution containing 10 µmol/L AsIII as described in Rathi et al. (2017). Next, a series of four 24 hours desorption steps using 15 mmol/L NaCl was carried out, releasing a total of 22% of the presorbed As (unpublished data). By extrapolating the desorption isotherm to an As equilibrium concentration of 0.013 µmol/L, an estimated maximum of 37% of the presorbed As could be desorbed. This is only slightly higher as what we have observed in our *in situ* desorption experiments (see Figure 6).

4. Conclusions

By using an innovative *in situ* experimental approach, we verified the proposed hypothesis that enduring contact of Pleistocene aquifer sediments with reducing, high As groundwater alters the As sorption capacity over time. Whilst the majority of As sorbed quickly within one week, As sorption further rose slowly but consistently during the subsequent six months, indicating that traditional approaches (i.e., short-termed batch sorption experiments or push-pull tests) tend to underestimate the As retention of Pleistocene sediments. There are four other main outcomes from our experiments. First, As sorption to Pleistocene aquifer sediments is linear over a wide range of groundwater As concentrations (0.01 to 6.63 µmol/L) and redox states (E_h of +159 to -4 mV), implying that the findings should also be valid in many other As-troubled regions of Asia and beyond. Second, while the outcomes of our *in situ* experiments are similar to laboratory batch experiments, the calculated K_d values are one order of magnitude higher than those estimated from push-pull tests and reactive transport modeling. In order to derive realistic K_d values for transport modeling with reasonable efforts, a better understanding of these methodological differences is required. We further argue for the determination of As sorption in relation to surface areas and not on a weight-based basis in order to account for differences in grain size distribution. Lastly, although Pleistocene sediments act as an important sink for As, the *in situ* desorption experiments revealed that about 51% of the As sorbed was remobilized once concentrations in inflowing groundwater declined. The question arises if the proportion of re-mobilizable As will be different for exposures exceeding six months. Furthermore, this As legacy (i.e. As subsequently accumulated on the Pleistocene aquifer sediments) needs be taken

into account in the development of hydrological management plans, since changes in the groundwater flow directions may suddenly flush the Pleistocene aquifers with low As groundwater that will result in a considerable remobilization of As..

Acknowledgements

This work was supported by the German Research Foundation (grant number NE-1852/1-1). The authors also thank members of CETASD and the villagers of Van Phuc for their support of the fieldwork. We further thank Annick Frising, Hans Jürgen Schindler, and Bas Vriens for their analytical support as well as Emiliano Stopelli for his internal review of the manuscript.

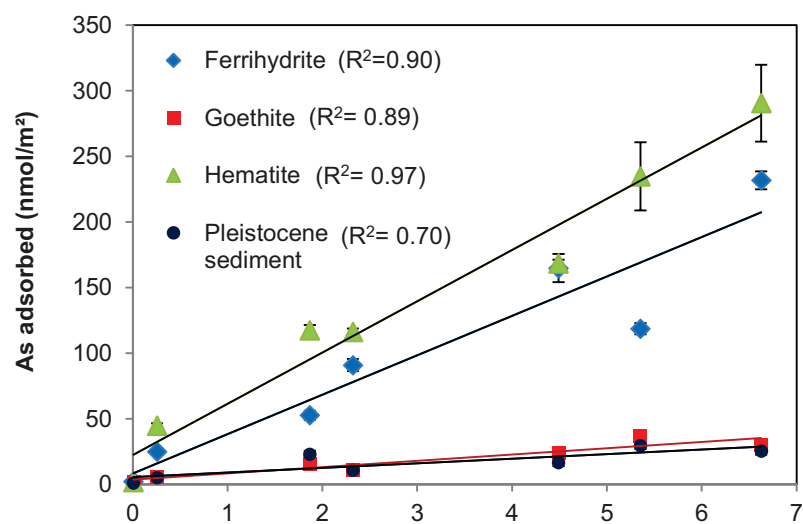
Appendix A. Supplementary data

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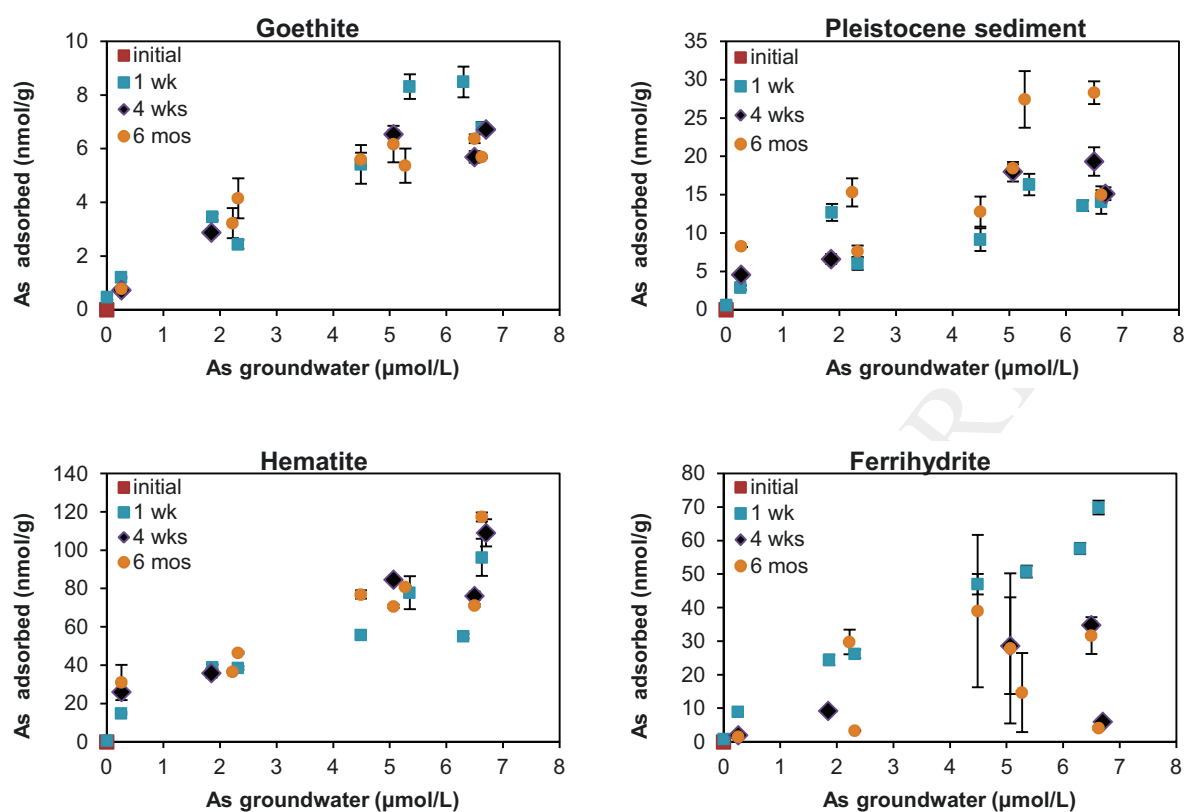
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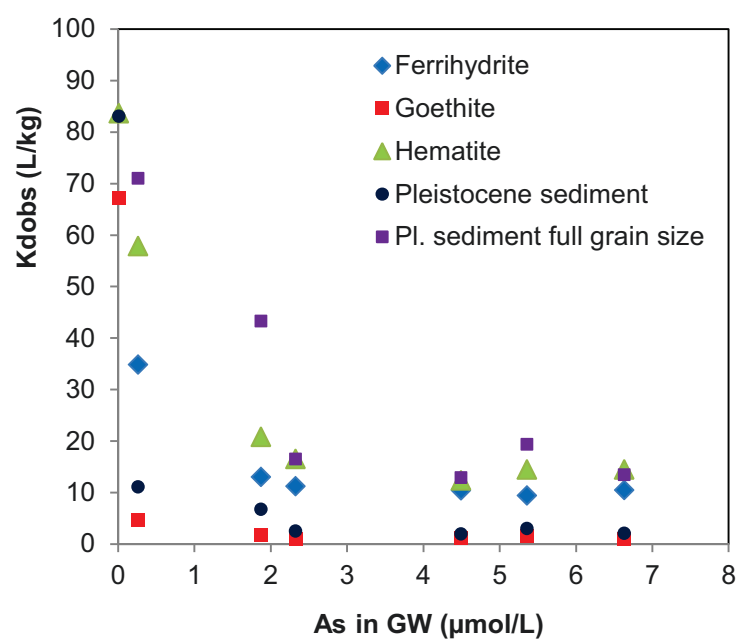
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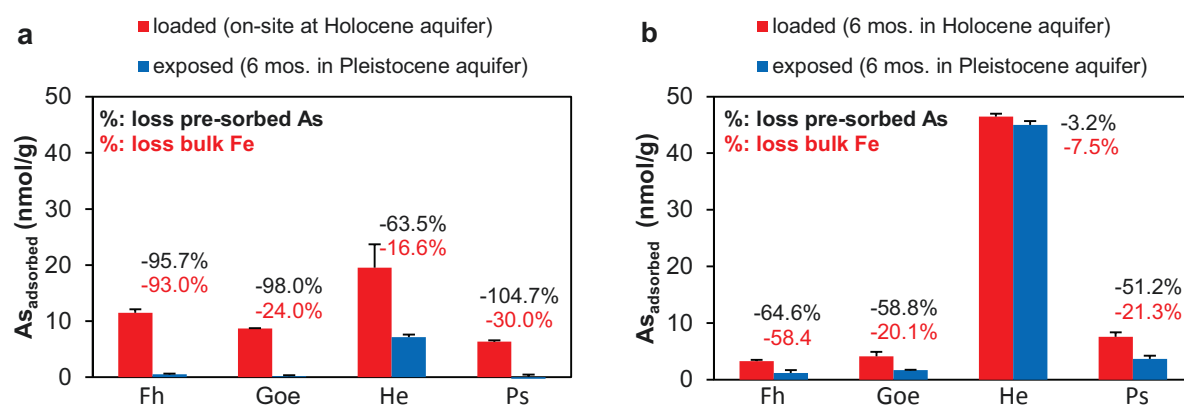


As in groundwater (µmol/L)

Well ID	AMS-4	AMS-15	AMS-32	AMS-12	AMS-5	AMS-11	AMS-1
pH	7.0	6.9	7.1	6.5	6.8	7.0	6.7
E _h (mV)	+159	+112	-4	+19	+29	+7	+45
HCO ₃ ⁻ (mmol/L)	10.1	5.51	9.70	10.8	13.6	10.5	13.4
Si (mmol/L)	0.39	0.32	0.27	0.52	0.57	0.36	0.52
Fe (mmol/L)	0.00	0.02	0.15	0.23	0.16	0.19	0.25
P (µmol/L)	3.18	2.29	25.2	29.2	32.2	22.5	19.0
As (µmol/L)	0.01	0.26	1.87	2.32	4.49	5.35	6.63



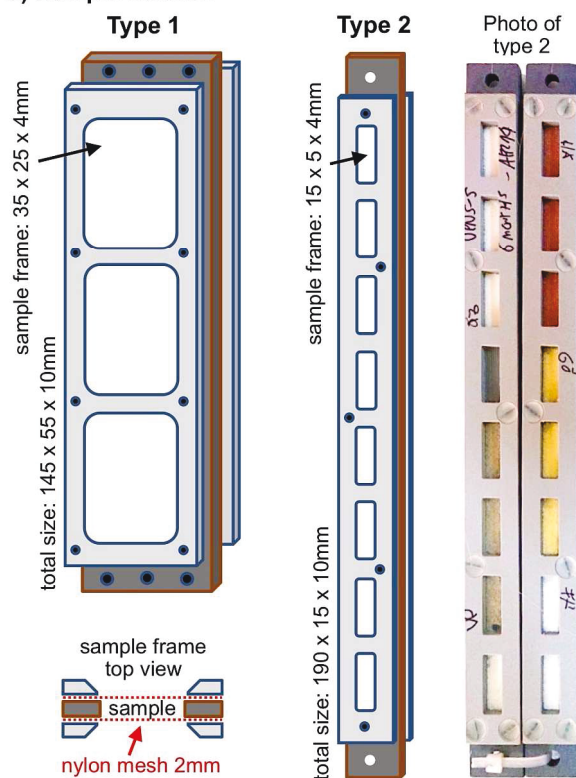


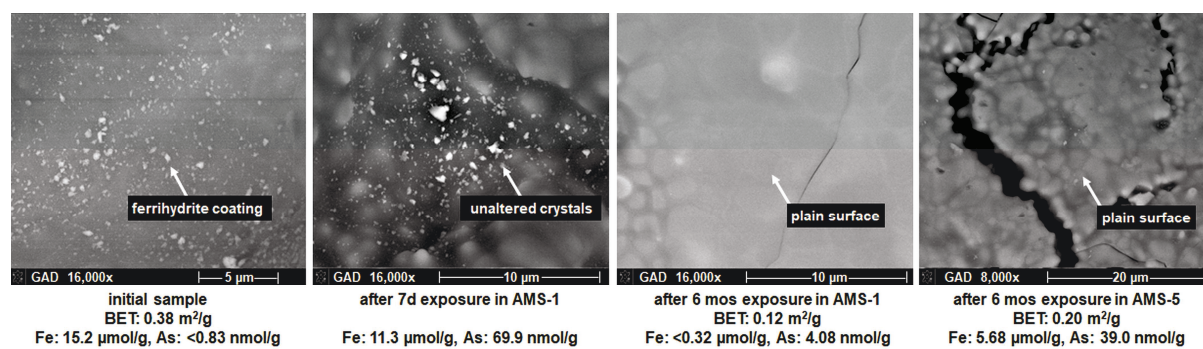


a) Samples



b) Sample holders





Highlights

- As sorption to Pleistocene sediments increased within six months *in situ* exposure
- A high proportion of As sorbed by Pleistocene aquifer sediments was remobilized
- Sorption of As by Pleistocene sediments mainly controlled by surface adsorption
- As adsorption near-linear over a wide range of As concentrations and redox states