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Evidence of decoupling between arsenic and phosphate in shallow groundwater of Bangladesh and potential implications

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ABSTRACT

Reductive dissolution of iron oxyhydroxides and reduction of arsenic are often invoked as leading causes of high dissolved As levels in shallow groundwater of Bangladesh. The second of these assumptions is questioned here by comparing the behavior As and phosphate (P), a structural analog for As (V) which also adsorbs strongly to Fe oxyhydroxides but is not subject to reduction. The first line of evidence is provided by a detailed groundwater time-series spanning two years for three wells in the 6–9 m depth range showing removal of As(III) from shallow groundwater during the monsoon without of loss of P. The data indicate a loss of ~90% of the dissolved As from groundwater in the intermediate well relative to a level of 3 μmol/L As predicted by conservative mixing between groundwater sampled from the shallower and the deeper well. In contrast, P concentrations of ~30 μmol/L in the intermediate well closely match the prediction from conservative mixing. Reduction therefore appears to inhibit the release of As to groundwater at this site relative to P instead of enhancing it. A re-analysis of existing groundwater As and P data from across the country provides a broader context for this finding and confirms that, without reduction, elevated concentrations of As would probably be even more widespread in shallow aquifers of Bangladesh. Without providing definite proof, X-ray absorption spectroscopy of sediment from the time-series site and elsewhere suggests that the loss of As from groundwater may be coupled to precipitation of As sulfide. Further study is needed to assess the implications of these observations for shallow aquifers that have been subjected to increased withdrawals for irrigation in recent decades.

1. Introduction

The presence of arsenopyrite in shallow sediment of the Bengal basin was initially interpreted as an indication that elevated groundwater As concentrations, known by then to be widespread in the region, were attributable at least in part to oxidation caused by enhanced recharge due to irrigation pumping (Chowdhury et al., 1999). Subsequent studies showed that this was unlikely because elevated As levels were associated with low sulfate levels instead of the other way around (BGS/DPHE, 2001; Harvey et al., 2002). Over the past decade, much of the attention has focused instead on reductive dissolution of iron oxyhydroxides and an enhanced supply of reactive organic carbon that might promote the release of As to groundwater (e.g. Fendorf et al., 2010).

In comparison, less attention has been paid to the still potentially important role of As-sulfur interactions. This may be in part because such interactions could plausibly affect groundwater As in opposite ways and would therefore be difficult to disentangle. On one hand, the reduction of sulfur supplied by recent recharge or organic matter in the sediment could lead to the formation of insoluble As sulfides or the sequestration of As in iron sulfide phases (O'Day et al., 2004; Kirk et al., 2004; Lowers et al., 2007; Hery et al., 2010; Kocar et al., 2010; Xie et al., 2015). Without direct evidence from sediment analysis but on the basis of an extensive set of groundwater data, Buschmann and Berg (2009) made a convincing case that sulfate reduction had an inhibiting effect on the release of As to groundwater in South and Southeast Asia. In a field experiment in shallow aquifer of Bangladesh, the

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injection of molasses and sulfate resulted in a temporary reduction of As concentrations in groundwater (Saunders et al., 2008). On the other hand, the presence of sulfide has also been shown to enhance the release of As from sediments through the formation of As-sulfide complexes in solution, although primarily in laboratory studies (Keimowitz et al., 2007; Kocar et al., 2010; Burton et al., 2013).

In order to shed some light on the roles of Fe and S, as well As reduction to As(III), in controlling groundwater As concentrations in reducing aquifers, we follow a somewhat different approach in the present study by tracking the behavior of As and phosphate P(V), its structural analog in the oxidized state. This is done first on the basis of a detailed time series of these and other groundwater constituents across a redox interface in a village of Bangladesh and, subsequently, through the re-analysis of a previous landmark survey of the entire country. Synchrotron spectroscopy was also applied to sediment from the time-series site in attempt to identify As-sulfide phases but the outcome is ambiguous. The paper concludes by pointing out why further study is needed in order to predict the future evolution of As concentrations in reducing aquifers whose hydrology is being modified by pumping.

2. Methods

2.1. Study site

Time-series data were obtained from three monitoring wells installed in the village of Dari Satyabandi in central Bangladesh (Fig. 1). The vertical distribution of As in the shallow aquifer of Dari Satyabandi is representative of the initial rise in concentrations with depth observed throughout the impacted portions of the Bengal Basin (BGS/DPHE, 2001; Harvey et al., 2002; van Geen et al., 2003). Sixty percent of shallow wells (<10 m) sampled in the village do not meet the WHO guideline for As in drinking water of 10 μg L^{-1} (0.13 μmol L^{-1}), and 90% exceed this value at >20 m depth (Fig. 2). Repeated sampling in Dari Satyabandi has shown that concentrations of As in groundwater at any given location increase consistently with depth and typically do not vary much over time (Cheng et al., 2005; Dhar et al., 2008). The vertical distribution of As in groundwater in the village is consistent with the presence of a sizeable clay layer that inhibits local recharge (Aziz et al., 2008). One documented exception is shallow household well #4115 where seasonal fluctuations in As concentrations ranged from 0.13 to 1.6 μmol L^{-1} over a 3-year period (Cheng et al., 2005). Three new ~4-cm diameter PVC monitoring wells were installed within 2 m of this household well in January 2005 using the local “hand-flapper” method. The 0.9-m (3 ft) wells screen made of finely slotted PVC were centered on depths of 6, 7.5, and 9 m, respectively. The surficial clay layer extends to less than 3 m depth at this particular site. It is also located within 50 m of a local stream and may be therefore be more sensitive to surface forcing than the northern portion of the same village (Fig. 1).

2.2. Water sampling and field measurements

From January 2005 through December 2006, groundwater was sampled from the new monitoring wells with a submersible pump every two weeks after the well volume was flushed approximately 10 times using a submersible pump at a flow rate of 15 L/min. At the time of each sampling, groundwater levels were measured manually using a Solinst (Georgetown, Ontario, Canada) Model 102 m. Groundwater conductivity, oxidation-reduction potential (ORP),

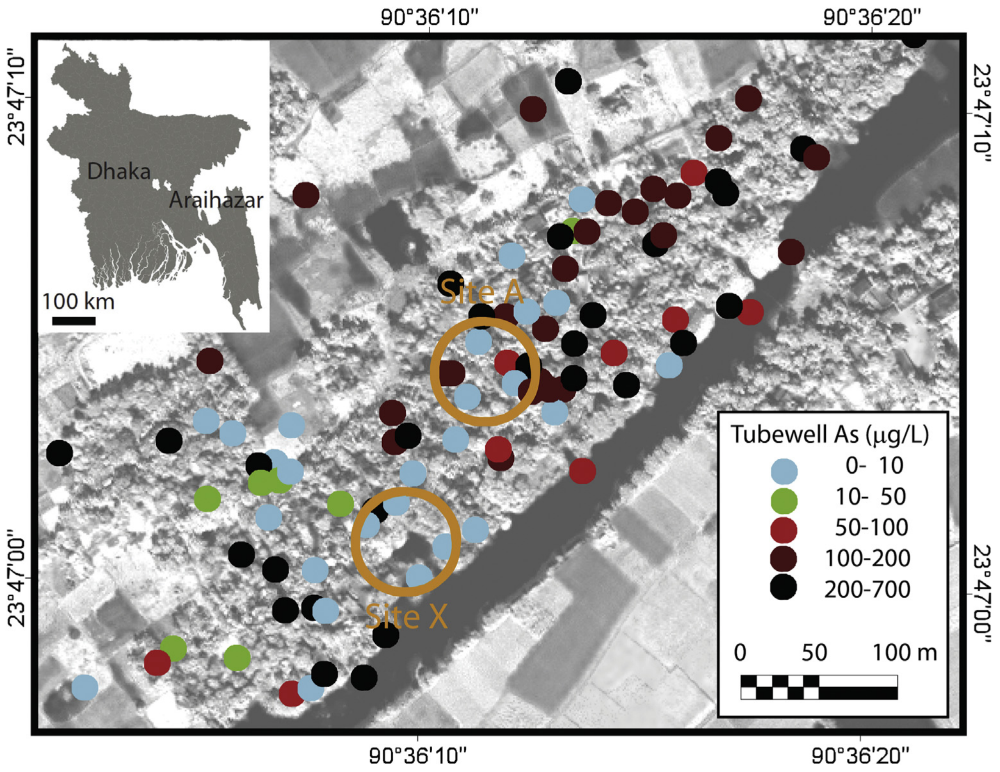

Fig. 1. Map of As concentrations in shallow tubewells of Dari Satyabandi. IKONOS satellite image of the study area showing in dark grey the local stream passing through the area and the location of wells <20 m deep along its northern bank. The color-coded circles show the As content and location of 99 wells within the village in the 9–20 m depth range. Shown in orange are the location of the three monitoring wells (Site X) and that of additional vertical profiles shown in Fig. 2. The inset shows the location of the site relative to Dhaka. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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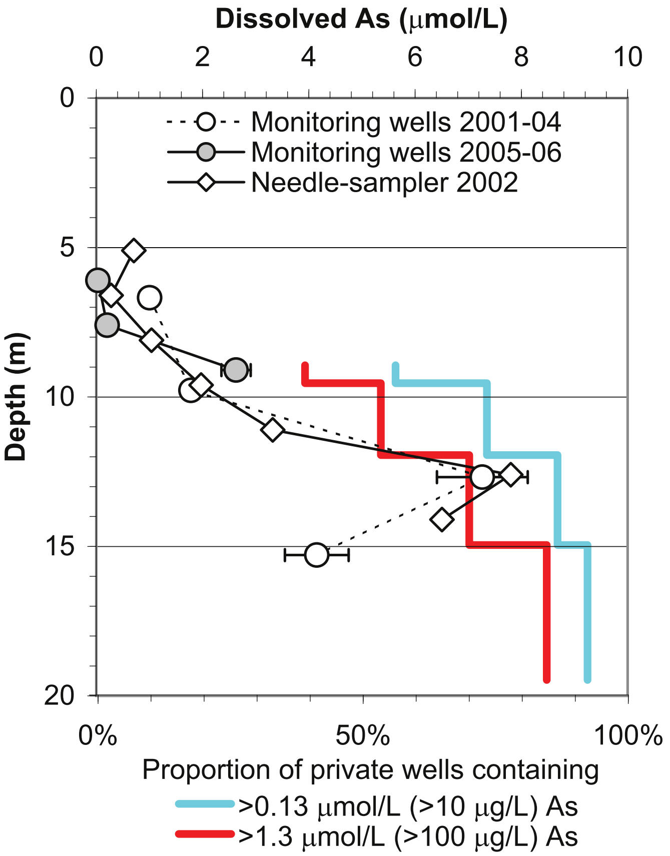

Fig. 2. Vertical distribution of dissolved As in groundwater of Dari Satyabandi. The figures combines results from a survey of household wells conducted in 2000 (van Geen et al., 2003), a set of monitoring wells installed in 2001 (Dhar et al., 2008), a needle-sampler profile collected in 2002 (van Geen et al., 2004), and the three shallow wells monitored for this study.

and pH were measured with a YSI 556 multiparameter probe mounted on a flow-through cell (YSI 5083) and were recorded after the readings stabilized. The probes were calibrated according to the manufacturer's specifications at the beginning of each sampling day. Without filtration to reduce the likelihood of artefacts (Zheng et al., 2005), one aliquot of groundwater was collected in acid-cleaned 20 mL scintillations vials and acidified to 1% high-purity HCl (Optima) and another in 20 mL scintillation vials rinsed with MQ water. Arsenic speciation was determined by passing an additional aliquot of groundwater in the field through a disposable ion exchange cartridge (Metal Soft Center, Highland Park, NJ, USA) that retains As(V) but not As(III). The difference between total As and As(III) passing through the column subsequently measured in the laboratory is assumed to be As(V). During a portion of the sampling period, groundwater was analyzed using a field kit for dissolved oxygen with a detection limit of approximately 0.05 mg/L (http://www.chemetrics.com/). In January 2008, groundwater was analyzed immediately after collection for dissolved sulfide species by cathodic stripping voltammetry using an Eco Chemie µAutolab voltammetric apparatus (Brinkmann Instruments, Westbury, NY, USA) equipped with a Metrohm 663VA electrode stand (He et al., 2002). The voltammetric measurements placed an upper limit of <0.05 µmol L^{-1} on dissolved sulfide concentrations on this occasion.

2.3. Sediment sampling and field measurements

In January 2005, aquifer sands collected at six intervals between 3 and 10 m depth was analyzed for labile properties while installing the deepest of the monitoring wells. Unexposed sediment was collected using a needle-sample device and kept in the dark and under groundwater after flushing the headspace of the needle-sampler tube with nitrogen. On the evening of sampling, the sediment was treated with two different extractions: (1) 50 mg of sediment in 10 mL of hot 10% HCl leach for 30 min and (2) 1 g of sediment in 10 mL of N_2-purged 1 M NaH_2PO_4 solution (pH~5) at room temperature for 24 h. The acid leachate was analyzed on the evening of collection for dissolved Fe(II) and Fe(III) by colorimetry using ferrozine, as an indication of the redox state of reactive Fe oxides (Horneman et al., 2004). The phosphate extracts were passed through a 0.4 µm syringe filter after 24 h and later analyzed in the laboratory as an indication of the concentration of exchangeable As in the sediment (Keon et al., 2001; Zheng et al., 2005).

In January and June 2008, fresh sediment was collected again, this time with a hammer-driven 7/8-inch core sampler from AMS (American Falls, Idaho, USA. Part no. 424.45), and placed immediately under anaerobic conditions for shipping. The fresh sediment was placed in a N_2-flushed anaerobic box (Becton–Dickinson No. 260672) containing pouches that generate H_2 and consume O_2 with a catalyst (Becton–Dickinson No. 260678), along with oxygen monitoring strips (Becton–Dickinson Diagnostic Systems No. 270504). Within one week of collection, the samples were transferred to another anaerobic chamber, excess water was poured off, and an equal volume of pure glycerol was added to the wet sediments to prevent oxidation during analysis. Glycerol prevents microbial activity and slows oxidation by limiting diffusion into the sediments during storage and analysis. The glycerol-impregnated samples were analyzed within one week. The combination of rapid analysis and glycerol is important to prevent oxidation of reduced species, and thus to accurately assess the oxidation state of Fe and As in sediments. Even synthetic mackinawite preserved in this way is not oxidized after storage for 3 months (B. C. B., unpublished data). The diffuse spectral reflectance of fresh wash borings was collected at 0.3 m (1 ft) intervals and measured on the evening of collection using a hand-held Minolta 2500d spectrometer (Horneman et al., 2004).

2.4. Laboratory analyses

Concentrations of As, Fe, Mn, S, Na, Mg, Ca, and K in acidified groundwater were measured at LDEO with a Thermo-Elemental Axiom single-collector high resolution inductively coupled plasma mass spectrometer (Cheng et al., 2004), with a detection for As on the order of 0.1 µg/L. Both sets of leachates obtained from fresh sediment in Bangladesh in 2005 were also analyzed for As by HR ICP-MS. Concentrations of chloride (Cl) and sulfate (SO_4) in unacified groundwater were measured on a Dionex DX-100 ion chromatograph. Inductively coupled plasma optical emission spectroscopy (Thermo Intrepid II XSP with radial optics) was used to determine the bulk elemental composition of the sediment by acid digestion.

2.5. Sediment digestions

Subsamples of sediments (about 500 mg) were dried, weighed, and digested using 30 mL reverse aqua regia, a 3:1 mix of trace element grade HNO_3 and HCl in acid-washed Teflon beakers. Digestions were heated at 80 °C in an aluminum block and evaporated until dry. Digested samples were then dissolved in a 5% trace

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element grade nitric acid matrix for analysis. All element emissions were optimized prior to analyses and three point calibration curves were generated for each element from multi-element NIST-traceable standards (High Purity Standards, Charleston, SC). Periodic blanks and quality controls were run to check for instrument drift. An internal standard of Sc, Y, and In was run in-line to track and correct for plasma condition changes. All measurements were made in triplicate using both the UV and visible spectra. Spectral interferences from major elements (Fe, Al, Ca, Mg, Na, and K) were calculated by analyses of high purity standards. Interferences from these major elements on trace elements were accounted for prior to quantitation when necessary, although in most cases interference-free lines were used for quantitation. This method is effective to determine total metal concentrations in soils and sediments (Chen and Ma, 2001), had detection limits of 5–20 μg/L for most elements (7 μg/L for As), and typical accuracy and precision of ±5% based on measurements with standard reference materials (lab standards, and NIST soil 2710a) digested in the same manner. These detection limits correlate to about 1 mg/kg in the solid phase after accounting for the extraction masses and volumes, dilution, and measurement.

2.6. Synchrotron measurements

Synchrotron X-ray absorption spectroscopy (XAS) for As and Fe was performed on beamline 11–2 at the Stanford Synchrotron Radiation Laboratory in California using sediment samples preserved in glycerol. A 30-element Ge detector was used to collect fluorescence data. Sample slits for measurement configuration were 1 mm by 10 mm. The monochromator crystal reflection used was Si(220) with phi angle of 90°. Fe X-ray absorption near-edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS) spectra were collected from −235 to 900 eV about the Fe K edge. Arsenic XANES spectra were collected from −235 to 425 about the As K edge. Scans were calibrated by setting Fe foil edge inflection to 7112 and sodium arsenate edge inflection to 11,874.0 eV.

Microprobe X-ray fluorescence (μXRF) was used to determine the distribution and association of As, Fe and other elements in preserved sediments. X-ray microprobe images were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline 2–3, which uses Kirkpatrick-Baez focusing optics. The samples were prepared by mounting a thin film of unconsolidated sediment grains on Kapton tape. XRF spectra were collected using a focused incident beam (2 μm nominal beam size) at 13,000 eV by continuously rastering the beam across the sample every 5 μm, and measuring the XRF spectrum for 250 μs at each point. Microprobe XANES (μXANES) spectra were collected at selected points identified in μXRF maps based on their As and Fe concentrations. At each point, the As fluorescence was maximized within the $5 \times 5\ \mu m^2$ XRF pixel, and the As XANES spectra were collected as described above using 0.3 eV energy spacing. This method can identify and speciate As in hotspots even in samples with low (<10 mg/kg) bulk As concentrations.

2.7. X-ray absorption spectroscopy data processing

All data averaging, normalization, and linear combination fitting was done with SIXPack software (Webb, 2005). Spectra were normalized with linear pre-edge and quadratic post absorption edge functions prior to fitting. Resultant normalized XANES data were compared to a library of standards. Fitting yielded the fraction of each model compound of the given element within each sample. These fractions can be converted to final sediment concentrations by multiplying by analyzed total solid concentrations, from total digestion followed by ICP-OES analysis.

Arsenic XANES fits were performed on normalized spectra using an energy range of 11,865–11,888 eV. Arsenate and arsenite adsorbed on ferrihydrite (100 g As/kg ferrihydrite, pH 7) were used to represent adsorbed As(V) and As(III), and orpiment (As_2S_3) was used to model arsenic sulfides. Orpiment and realgar (AsS) have similar XANES spectra and are thus not easily differentiated using XANES. Arsenopyrite (FeAsS), which contains As(-I), was also used in fitting but was not required to fit any spectra.

Iron EXAFS and XANES spectra analyzed using daa ranges of 2–12 $Å^{-1}$ and 7105–7140 eV respectively. XANES fitting is somewhat less specific to mineralogy than EXAFS fitting, but is a more direct means of assessing oxidation state because it is less sensitive to differences in structure. Fe XANES fits first were performed using the standards goethite (FeOOH), hematite (Fe_2O_3), and ferrihydrite ($Fe(OH)_3$), biotite (ferrous silicate, representative of silicate contribution to spectrum), fresh ferrous carbonate ($FeCO_3$, representative of non-sulfide Fe(II), magnetite (Fe_3O_4) and machinawite (FeS)). The resulting fits were then used as input fit parameters for Fe EXAFS spectral fitting. For Fe EXAFS fitting, normalized Fe EXAFS spectra were converted to k-weighted chi functions fit with reference spectra similar to XANES fitting using a fixed E_0 of 7124 eV. The same standards were used in Fe EXAFS fitting as were used in XANES fitting. Other reference spectra were also considered (including pyrite, horneblende, other ferrous and ferric silicates, etc.); these spectra generally were not required to fit unknown spectra. In this case, XANES and EXAFS fits produced similar results with one major exception—EXAFS fitting consistently overestimated the fraction of ferrihydrite and FeS relative to XANES fits, and produced unstable magnetite component fits. Although the reasons for this are not completely clear, they probably result from the fact that a limited number of representative standards are being used to represent complicated mineral assemblages. Differences in the crystallinity of mineral reference materials and those present in these materials also could influence linear combination fitting. For example, ferrihydrite EXAFS fits are representative of poorly crystalline Fe(IIII) oxyhydroxides with limited Fe—Fe shells, and can be confused with less crystalline forms of goethite or other phases.

The estimated errors in least-squares fitting are determined using SixPack software, which calculates error based on fit quality, spectrum noise levels, and reference spectrum characteristics (e.g., noise, similarity to other reference materials). These errors are commonly a few percent or better for As XANES fits, and 5–7% for most Fe minerals (using XANES or EXAFS fitting algorithms) using the spectral combinations used for Fe fits. These combined errors also compared with those estimated using based on comparisons of fits of known mixtures, which account for fitting error (usually small) and systematic errors (for example in background fitting, due to self-absorption etc.) that can be important when model compounds are used to represent complex mixtures. In the case of known mixtures, the accuracy of fits depends on the quality of reference spectra (they should be noise “free”, well calibrated, free of self-absorption etc.), the extent to which spectra are differentiated, and spectral processing. In the case of As, the sharp edges of each arsenic compound is separated by 2–3 eV, which is large enough to calculate As fractions of these species very accurately. In known mixtures, the fractions of As species are typically fit to within 3–4% of known ratios based on fits of spectra of mixtures containing equimolar mixtures of arsenite, arsenate, and arsenic sulfide. In the case of Fe reference materials, the linear combination fitting of EXAFS spectra is somewhat less accurate since many of the spectra are similar over a large k-range. In fits of mixtures of iron oxides, fractions of each could generally be determined within about 7–8% (O'Day et al., 2004), although Fe(II) minerals, silicates and sulfides have more distinct spectra and can usually be

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determined within 4–5% or better.

2.8. Microprobe X-ray fluorescence data processing

Each map represents a single mapping scan. Within that map, regions of interest (ROIs) were defined for a number of elements, including As, Fe, Si, S, K, Ca, Mn, Ti, Cu, and Zn, and the integrated counts for each used to estimate elemental abundance. While counts are proportional to concentration, it is difficult to determine accurate concentrations from this method without standardization. Therefore, we present all data as normalized counts using 250 ms counting times. Since grain mounts are of variable thickness, sample absorbance ($\log I_0/I_1$) was used to estimate sample thickness. The effect of variable thickness on elemental abundance can influence element correlations; this effect is accounted for by normalizing counts using absorbance; however, this normalization did not affect overall elemental correlations and is not used in the presented data.

Microprobe XANES (μXANES) were collected to examine the As speciation of specific locations within μXRF maps. These locations were selected based on the intensity of As fluorescence (proportional to As concentration). At these points the As fluorescence was maximized by rastering the beam within a $5 \times 5\ \mu m^2$ area identified in the XRF map. This was necessary to account for sample movement but more importantly to ensure that the signal is maximized given that the beam size was smaller than the pixel size and thus a considerable fraction of a given pixel was not sampled (thus the map contains a minimum As concentration). The XANES spectrum was obtained using a constant data spacing (0.3 eV) and collected from 11,800 to 12,000 eV. Two spectra were usually averaged together to yield the resulting spectrum and the spectra were processed as described previously. In an ideal case, the pixels are sufficiently small that only a single mineral phase is contained within the sampled location; so linear combination fitting is not required. However, adsorbed As may be found as both As(III)_ and As(V).

3. Results

3.1. Temporal variations in groundwater composition

Groundwater levels in Dari Satyabandi vary in response to the monsoon from 5 m below the ground surface during the dry season to 1 m below ground during the wet season (Fig. 3a). Occasionally, most recently in 2003, the village is entirely flooded by the nearby stream during part of the monsoon. Over the 2-year monitoring period, As concentrations remained low and relatively constant at the shallowest monitoring well ($0.04 \pm 0.03\ \mu mol\ L^{-1}$; n = 46 at 6 m) and two orders of magnitude higher and also essentially constant at the deepest well ($3.0 \pm 0.3\ \mu mol\ L^{-1}$; n = 46 at 9 m) (Fig. 3b). A modest but well-defined seasonal signal was recorded at the intermediate well in both years, with As concentration increasing three fold between October–March ($0.09 \pm 0.04\ \mu mol\ L^{-1}$; n = 24 at 7.5 m) and April–September ($0.3 \pm 0.1\ \mu mol\ L^{-1}$; n = 24). Concentrations of dissolved phosphate (P) also increase sharply with depth at the site but much wider seasonal fluctuations spanning the range of concentrations of the shallowest and deepest well were recorded in the intermediate well (Fig. 3c).

Variations of As and P concentrations in the intermediate well could in principle result from either the seasonal displacement of sharp geochemical gradients at this location, exchange between the groundwater and sediment, or some combination thereof. To quantify the effect of vertical displacement, we rely on dissolved Cl which, in contrast to As and P, is elevated in shallow groundwater and depleted at depth (Fig. 3d). Chloride does not interact with the sediment and therefore should be a reliable indicator of the contribution of shallower and deeper groundwater at the intermediate well. The data show that Cl concentrations in the intermediate well roughly match the composition of groundwater in the shallow well in the middle of the dry season and that of the deeper well during most of the wet season (Fig. 3d). This indicates that there is little groundwater mixing, with the exception of the seasonal transitions when Cl concentrations are intermediate between the shallower and deeper end member. The concentration of other weakly adsorbing ions, SO_4 and Na, at the intermediate well also alternate seasonally between levels measured during the sampling period in the shallow and the deep well (Fig. 3e, k). Variations in the proportions of shallower and deeper groundwater at the depth of the intermediate well are consistent with the seasonal reversals in vertical and lateral head gradients at the site (Fig. 3g). Vertical displacement of chemical gradients as the groundwater level varies seasonally therefore exerts a strong control on the composition of groundwater at the intermediate well for several of the monitored constituents.

If As and P behaved conservatively like Cl, SO_4, or Na, seasonal fluctuations corresponding to the full range of As and P concentrations between the shallowest and deepest well would be expected. This is precisely what is observed in the case of P (Fig. 3c) but not for As. Significantly lower concentrations of dissolved As relatively to those predicted based on Cl (Fig. 3b) unambiguously indicate a transfer of As from groundwater to aquifer sands at the depth of the intermediate well.

3.2. Impact of redox conditions

Groundwater and sediment data indicate conditions that become increasingly reducing with depth at the study site. Dissolved Fe concentrations, indicative of Fe(III) reduction to Fe(II), are low in the shallow monitoring well, but reach ~100 mM in the two deeper monitoring wells (Fig. 3f). Solid phase Fe speciation determined by XAS (Fig. 4b), the Fe(II)/Fe ratio in the acid-leachable fraction of the sediment, as well as diffuse spectral reflectance data (Fig. 4c) are all consistent with increasing conversion from Fe(III) to Fe(II) minerals with depth. The redox gradient is evidently maintained by consumption of oxidants throughout the monitored depth range that is countered by occasional inputs from above of oxygen (Fig. 3i), and possibly nitrate (which was not measured). The sharp increase in groundwater As concentration over the same interval could be interpreted as another illustration of the traditional view that reductive dissolution of As-enriched Fe oxyhydroxide coatings on aquifer sands triggers the release of As to groundwater. Under this scenario, the loss of As at intermediate depth during the wet season as deeper groundwater is displaced upwards would be attributed to adsorption onto residual or newly formed Fe oxyhydroxides. This mechanism can be ruled out because of the essentially conservative behavior of P in the intermediate well (Fig. 3c). Although adsorption onto Fe oxyhydroxides also would be effective at removing P from groundwater given its well-documented strong affinity (BGS/DPHE, 2001; Dixit and Hering, 2003), such adsorption sites evidently play little to no role in controlling the partitioning of P under conditions prevailing at the depth of the intermediate well.

Column separations conducted in the field indicate that the reduced As(III) species dominates over As(V) in groundwater and that the average proportion of As(III) increases with depth throughout the year from 77 ± 11 to 73 ± 26 and 94 ± 5% As(III) at 6, 7.5, and 9 m, respectively. Even if the affinities of As(V) and As(III) for adsorption sites on Fe oxhydroxides are comparable but not necessarily identical (Dixit and Hering, 2003; Tufano et al., 2008),

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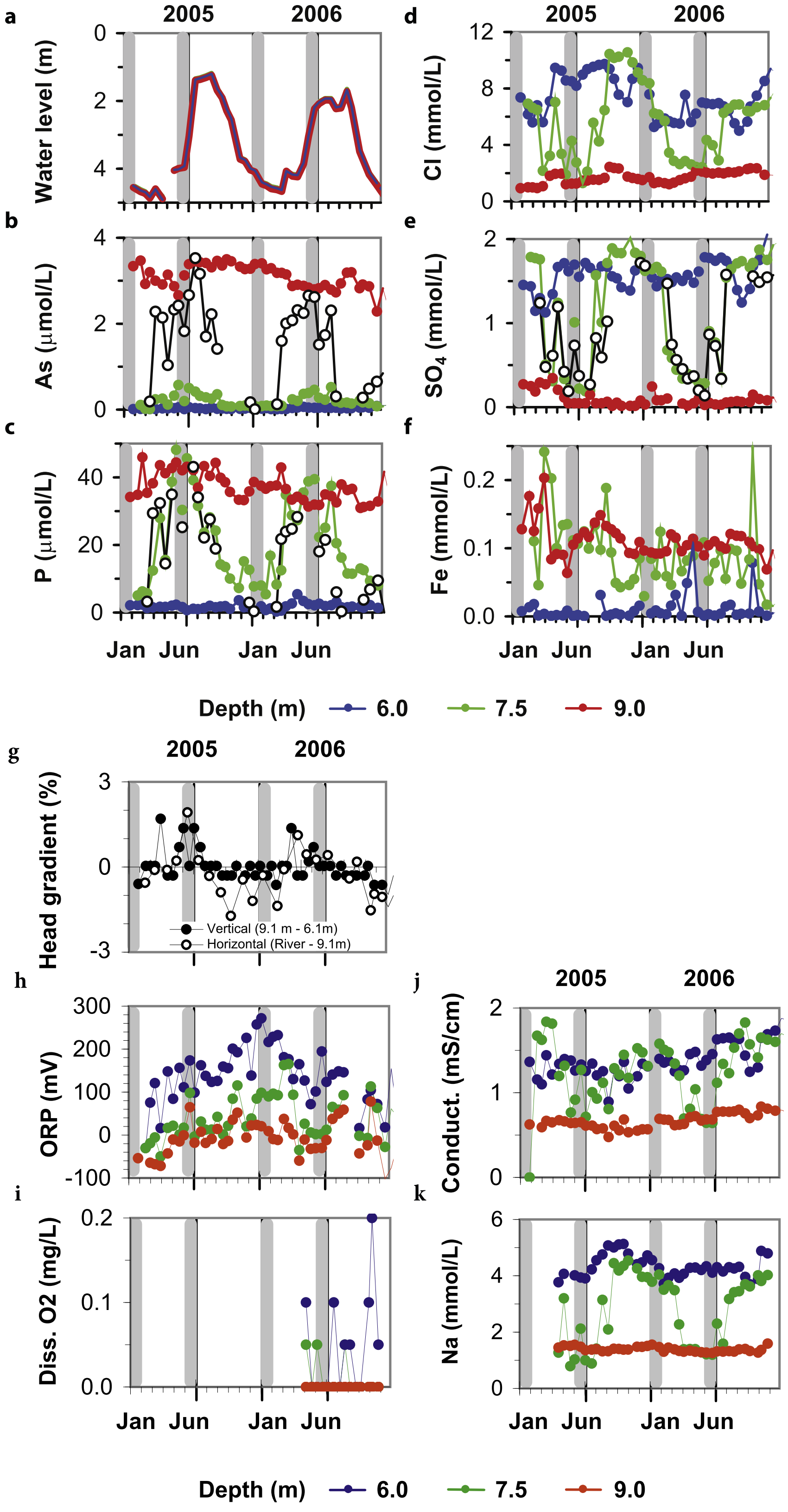

Fig. 3. Two years of monitoring data from tube wells installed at 6–9 m depth range in Dari Satyabandi. Variations in (a) water level below the ground surface and variations in the concentrations of dissolved (b) arsenic, (c) phosphate, (d) chloride, (e) sulfate, and (f) iron in groundwater. Also shown as black open circles and lines are As and P concentrations at the intermediate well predicted from chloride and assuming conservative mixing of groundwater from the shallower and deeper well. The prediction is occasionally missing when either As, P, or Cl concentrations at the intermediate well fall outside the range spanned by the shallower and deeper well. Grey vertical bars indicate when solid phase speciation data were obtained in 2008. Also shown are (g) variations in relative hydraulic head measured vertically between the deepest and the shallowest monitoring well and horizontally between the stream flowing ~50 m southeast of the study site and the deepest monitoring well (Fig. 1). The hydraulic head differences indicate lateral recharge of stream into the shallow aquifer accompanied by upward flow at the onset of the monsoon, followed by downward flow and discharge into the stream during the dry season. Variations in (h)

the loss of considerable As from groundwater in the absence of any detectable loss of P at the depth of the intermediate well during the monsoon cannot be attributed to adsorption. The implication is that As supplied from deeper groundwater is lost from groundwater by a different process.

3.3. *Speciation of As in the sediment*

The speciation of As in the sediment provided by XAS provides some constraints on the mechanism of As removal from groundwater. The sediment profiles obtained by XANES indicate a marked shift from predominantly As(V) at the depth of shallowest well to mostly As(III) at the depth of the deepest monitoring well (Fig. 4e, f; Fig. 5). The pattern in As speciation parallels the redox depth gradient indicated by the solid phase Fe speciation data and dissolved Fe data. The data indicate an increase from <10% in January to >50% in June in the proportion of sediment As bound to sulfides at the depth of the intermediate well (Fig. 4g). Even at the depth with the greatest As sulfide contribution, however, the corresponding peak in the XANES spectrum is poorly defined. In addition, for reasons that are presently unclear, As sulfides were not detected within the same depth range in January (Fig. 4g).

Elemental mapping of the sediment by μXRF indicates 10–50 μm-sized regions of concentrated As through the 4–9 m depth range (Fig. 6). In shallow sediments, these high-As zones are clearly associated with regions of Fe enrichment, as would be expected of As(V/III) adsorbed on Fe oxides. However, within intermediate depth sediments, these As hot-spots do not appear to be associated with portions of the sediment enriched in Fe, indicating that another As phase is present. This additional As phase appears to be As sulfide on the basis of μXANES of several As hot-spots, although the spectra are noisy and the evidence remains therefore ambiguous (Fig. 6). Arsenopyrite is highly reduced As(-I) and thus has an adsorption edge that is shifted relative to those of realgar and orpiment, which have formal oxidation states of As(II) and As(III) but nearly equivalent effective oxidation states. The available data do not indicate the presence of detectable (>5%) levels of arsenopyrite and cannot distinguish realgar from orpiment.

4. Discussion

4.1. *The impact of perturbations on As in groundwater*

Early concerns that groundwater As concentrations in shallow aquifers of the Bengal basin might systematically be increasing over time have been never been confirmed (Sengupta et al., 2006; Ravenscroft et al., 2006). However, long-term trends in As concentrations, both increases and decreases, have been documented over a period of 8 years for a number of wells within a relatively small region of West Bengal, India (McArthur et al., 2010). Some shorter time series have shown significant seasonal variability in groundwater composition, particularly in shallow aquifers, but by and large variations in groundwater As have been much more limited (BGS/DPHE, 2001; Cheng et al., 2005; Dhar et al., 2008; Bhattacharya et al., 2011; Planar-Friedrich et al., 2012; Neidhardt et al., 2013; Radloff et al., this volume). Only for large perturbations induced by local pumping in the vicinity of a spatial gradient have larger variations in groundwater As concentrations been reported (McArthur et al., 2010; Jessen et al., 2012; Neidhardt et al., 2013). The muted response of As concentrations relative to other groundwater constituents reported in the present study over a period of two years is therefore consistent with previous findings. The characteristic buffering of As concentrations in the face of groundwater movement has been attributed to adsorptive exchange with a large pool residing on aquifer sands (Dhar et al., 2008; Radloff et al., this volume). A contributing explanation that limits variations in groundwater As concentrations suggested by the present study is the formation of sulfides across a sharp redox-interface that dampens the effect of a vertical displacement in the concentration gradient.

4.2. *Broader evidence of divergent As and P behavior*

The groundwater time series provides a clear indication of As removal from groundwater relative to the structural analog P for As(V). The evidence is from one site only and was observed within a limited depth interval. An obvious question is whether the divergence between As and P behavior occurs elsewhere. In order to address this issue, we turn to groundwater As and P data from a country-wide survey conducted in 1999 and, more specifically, the subset of 1509 wells that were reported as $\leq$30 m deep (BGS/DPHE, 2001). The underlying assumption of this analysis is that P levels in groundwater increase primarily in response to reductive dissolution of Fe and, that in the absence of presumed sulfide formation, As is released to groundwater by the same process. In agreement with the traditional Fe reduction hypothesis, the country-wide data show that the proportion of low-As wells decreases while P concentrations increase whenever S levels are <0.2 μmol L^{-1} (Fig. 7). Using admittedly somewhat arbitrary thresholds, a two-dimensional histogram of As concentrations as a function of sulfate and phosphate concentrations was constructed. The impact of divergent As and P behavior in shallow Bangladesh aquifers is estimated by combining the four categories of tubewells containing >6.4 μmol L^{-1} P and >0.021 mmol L^{-1} SO_4, dubbed the high-S/high-P group (shaded blue), and comparing them to the two combined categories with >6.4 μmol l^{-1} P and <0.021 mmol l^{-1} SO_4, the low-S/high-P group (shaded pink). Wells containing <6.4 μmol L^{-1} P (no color) are assumed to be predominantly low in As regardless of the formation of As sulfides because of insufficient reductive dissolution of Fe oxyhydroxides.

The re-analysis shows that for 84% of the 335 wells in the high-S/high-P group, As levels do not exceed 1.3 μmol L^{-1} (100 μg L^{-1}), which is ten times the WHO guideline for As in drinking water. This holds for only 53% of the 553 wells in the low-S/high-P group. From the difference between the two groups, we estimate that concentrations of As would exceed 1.3 μmol L^{-1} for an additional 105 out 335 wells in the high-S/high-P group. The total of 105 wells, 2.9% of the total of 3543 wells sampled across the country (total population 160 million), corresponds to a total of approximately 5 million fewer villagers exposed to less than 10-times the WHO guideline for As in drinking water due to the divergent behavior of As and P, assuming that the sampling was random with respect to depth. The population protected by the loss of As relative to P in Bangladesh is in reality probably considerably larger because the country-wide sampling was biased towards wells installed by the Department of Public Health Engineering that are often considerably deeper than the much more numerous privately installed tubewells.

Buschmann and Berg (2009) also inferred from groundwater data that the release of As under reducing conditions was

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Oxidation-reduction potential measured with a platinum electrode (i) dissolved oxygen measured with a CheMET field kit, (j) electrical conductivity measured with the YSI probe, and (k) concentrations of sodium measured by HR ICP-MS at the three shallow monitoring wells. The shallow groundwater at the study site occasionally smells of sulfide, but this is typically not the case for the majority of wells in Bangladesh (they would not be so popular otherwise).

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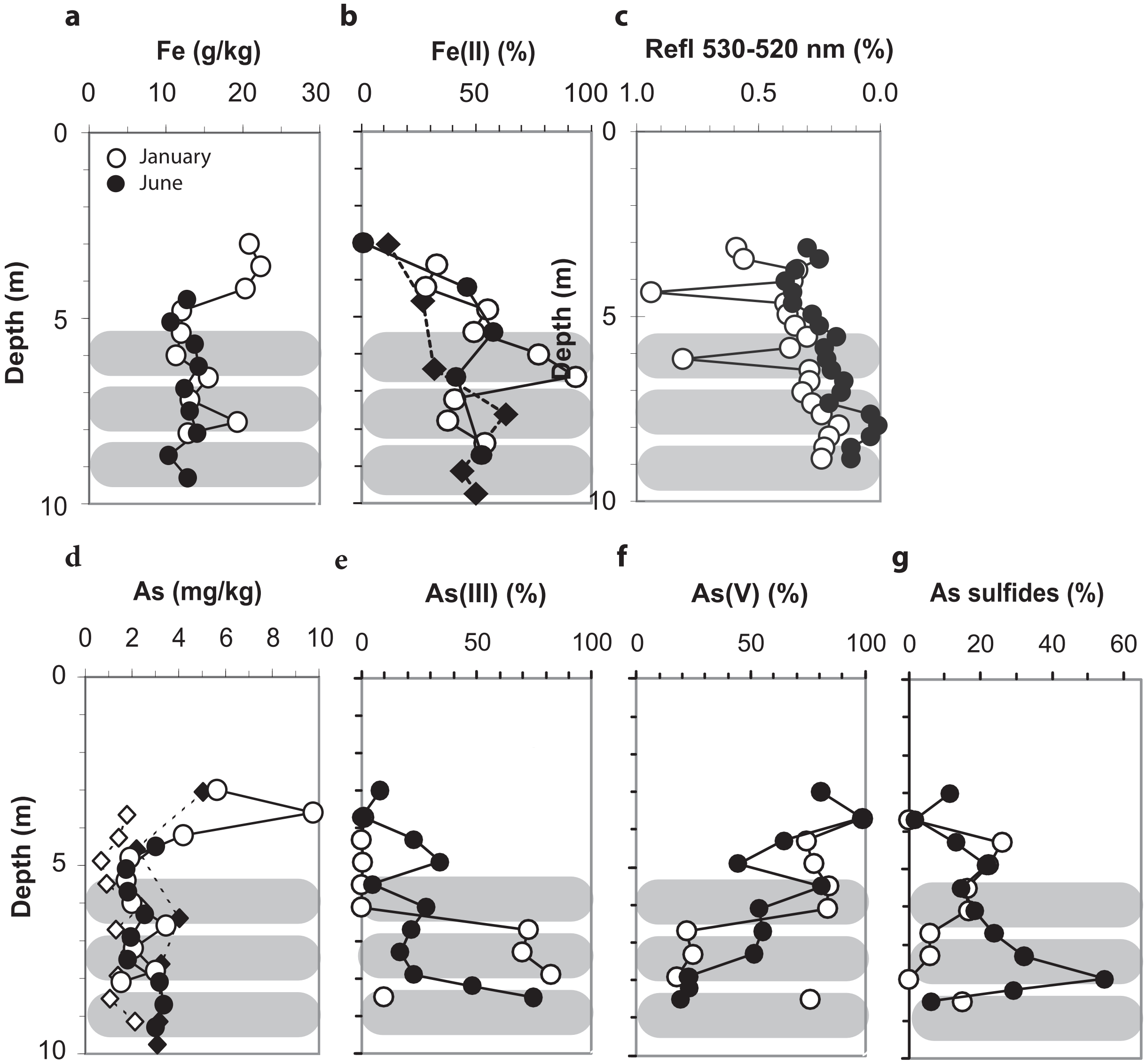

Fig. 4. Vertical profiles of sediment properties collected at the monitoring site in January and June 2008: (a) concentration of total Fe; (b) proportion of Fe(II) in iron oxyhydroxides determined by XAS for 2008 samples and, indicated by solid diamonds, Fe(II)/Fe ratios in the acid-leachable fraction measured in the sediment in January 2005; (c) difference in sediment reflectance between 530 and 520 nm, used here as an indicator of the degree of reduction of Fe oxyhydroxides (Horneman et al., 2004); (d) concentration of total As and proportions of (e) arsenite, (f) arsenate, and (g) As sulfides measured by XANES. Grey horizontal bars indicate the depth range of the screens at each of the three monitoring wells.

suppressed by SO_4 reduction in a significant fraction of a large set of groundwater samples from Vietnam, Cambodia, and Bangladesh. Their work identified SO_4 reducing conditions based on a number of indirect measures and reflected primarily groundwaters containing residual seawater and brines that are typically located much deeper than the interval studied here.

4.3. Uncertainties in the attribution of As loss to sulfide formation

The formation of As sulfides in reducing aquifers has been invoked previously as a way of inhibiting the release of As to groundwater on the basis of field data for either groundwater or sediment (Polizzotto et al., 2005; Lowers et al., 2007; Kirk et al., 2004; Buschmann and Berg, 2009). The present study attempted to link the *in situ* formation of As sulfides to an observed decrease in dissolved As concentrations in a natural setting. The loss of ~2 μmol l^{-1} As from groundwater documented between the dry and the wet season corresponds to an accumulation of only 0.014 mg/kg as As-sulfides in the sediment, assuming a porosity of 0.2 and a sediment density of 2.65 g cm^{-3}. Even if As was lost from 2 to 4 pore volumes of water as the chemical gradient shifts upwards in conjunction with the rise in the water table, an increase in concentration of 0.03–0.06 mg/kg would be hard to detect after one year against a variable background of 1–3 mg/kg in total As with the same depth interval (Fig. 4d). The loss of As from groundwater process appears to be irreversible, at least on a seasonal time scale, because no increase in dissolved As was observed in the intermediate well during the dry season. The build-up of As in the sediment would have to last over several decades to markedly affect the total concentration of As in the sediment, and even longer if sediment deposition or a systematic shift in the average depth of groundwater were to displace the locus of As precipitation. For reasons that are presently unclear, however, no clearly defined build-up of As concentrations is detected within the reaction zone at the study site. In addition, a contribution of detrital orpiment and arsenopyrite eroded from the Himalayas cannot be ruled out

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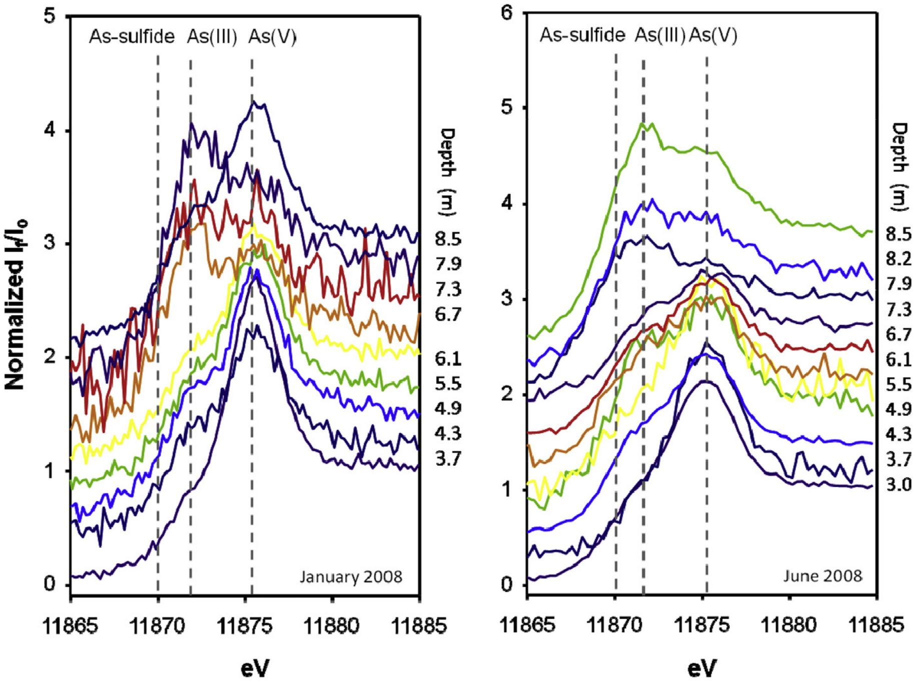

Fig. 5. XANES spectra for 9 and 11 preserved sediment samples collected at the study site in January and June 2008, respectively. FeAsS was not detected in any of these samples. The spectra are offset vertically relative to each other for clarity.

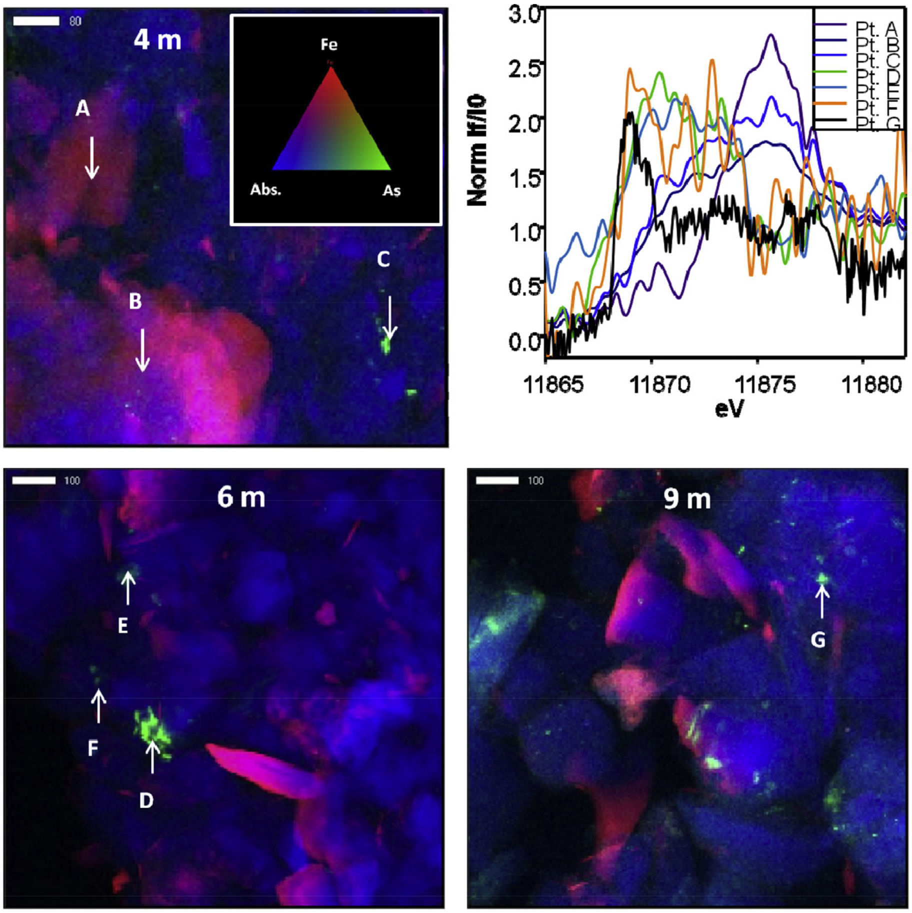

Fig. 6. Micro-scale distribution of As and Fe in sediment from 3 depths at the study site based on micro-fluorescence mapping. Also shown are micro-XANES data indicative of As speciation data at 7 selected points. The three colors indicate Fe and As counts, which are proportional to concentration, and absorbance ($-\log(I/I_0)$, a measure of the sample thickness at a given pixel. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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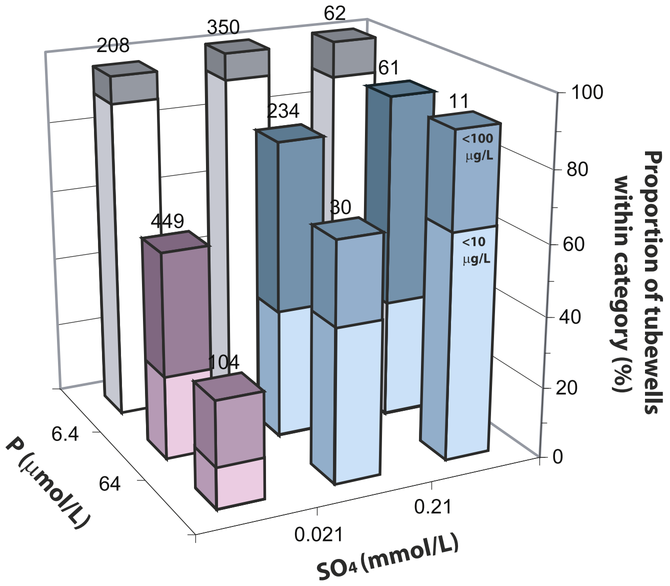

Fig. 7. Histogram of As concentrations as a function of sulfate and phosphate concentrations in shallow groundwater of Bangladesh. The compilation is based on 1509 wells that are $\leq$30 m deep (BGS/DPHE, 2001). The height of the white columns indicates the proportion of wells within a given P and SO_4^{2-} range containing $\leq$0.13 µmol L^{-1} As (10 µg/L); the sum of white and grey columns show the proportion of wells with $\leq$1.3 µmol/L As (100 µg/L). The total number of wells within each range of P and SO_4^{2-} concentrations is indicated at the top of each column.

(Polizzotto et al., 2005; Lowers et al., 2007).

The seemingly conservative behavior of SO_4 at the intermediate well is not inconsistent with the formation of As sulfide because a corresponding ~µmol/L loss would not be detected against mmol/L background sulfate levels (Fig. 3e). Thermodynamic constraints are of limited value given the current uncertainty in As solution speciation for sulfidic solution (Helz et al., 1995; O'Day et al., 2004; Planer-Friedrich et al., 2010). In addition, fine-scale heterogeneity in sulfide concentrations of the type observed in sediments elsewhere (Widerlund and Davison, 2007) could produce locally higher sulfide levels and therefore the precipitation of As-sulfide minerals. The available sediment data therefore do not rule out the formation of As sulfides at the study site, even if the lack of direct evidence is a clear limitation.

4.4. *Implications for the distribution of As and its future evolution*

There is little doubt that the reduction of Fe oxyhydroxides is a key step contributing to the release of As to reducing groundwater across South and Southeast Asia (Fendorf et al., 2010). The observations from Dari Satyabandi, complemented by the re-analysis of country-wide groundwater data indicate, however, that low concentrations of As in shallow aquifers could incorrectly be attributed to insufficient reduction of Fe oxydroxides in certain areas of Bangladesh because the mitigating role of S is not taken into account. The initial removal of As from groundwater in the form of sulfides could be a key step leading to the formation of more resilient phases such as arsenopyrite that have been observed elsewhere at greater depth (Lowers et al., 2007).

Trapping of As as sulfides in shallow aquifers could also have significant implications for the impact of large volume pumping for irrigation or industry. It has been proposed that As might have been released to groundwater as a consequence of irrigation pumping because of an induced influx of reactive organic matter promoting the reductive dissolution of Fe oxyhydroxides (Harvey et al., 2002; Neumann et al., 2010). In the Munshinganj area of Bangladesh where data have been collected to evaluate this hypothesis, dissolved S levels are highest at 5 m depth and decline steadily to a minimum at the depth of the subsurface As maximum at 30 m (Harvey et al., 2002). This suggests that the formation of sulfides might be suppressing the release of As to groundwater above 30 m depth. If recharge of this depth interval has been enhanced by a combination of irrigation pumping and the digging of ponds over the past several decades (Klump et al., 2006; Neumann et al., 2010), the possibility that the resulting enhanced supply of S lowered As concentrations from even higher levels above today's maximum instead of producing the subsurface maximum cannot be ruled out.

5. Conclusions

The time-series data presented in this study point to a divergence in the behavior of As and P upon release to groundwater by the reductive dissolution of Fe oxyhydroxides. The finding appears to be relevant to shallow reducing aquifers across Bangladesh. The divergence is attributed to reduction of As followed by the precipitation of As sulfides, although the evidence from the sediment that this process occurs at the time-series is ambiguous. The impact of irrigation pumping on the balance of reductants and oxidants supplied by recharge and, consequently, on the distribution of As in shallow aquifers is a complex issue that requires further study and must take into account the role of sulfur.

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