A transect of groundwater and sediment properties in Araihazar, Bangladesh: Further evidence of decoupling between As and Fe mobilization

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Abstract

A new sampling device was used to obtain 8 detailed profiles of groundwater and associated sediment properties to ~30 m depth in a 4 km^2 area of Bangladesh that is characterized by high spatial variability in groundwater As. Concentrations of dissolved As, Fe, and Mn ranged from <0.1 to 600 µg/L, <0.1 to 18 mg/L, and <0.1 to 4 mg/L, respectively. Voltammetric measurements conducted in the field indicate that >95% of the dissolved arsenic was As(III). The proportion of Fe(II) in the hot-leachable iron fraction of the sediment ranged from 0.2 to 0.9. The concentration of phosphate-extractable As in aquifer sands ranged from <0.1 to 1.1 mg/kg. Although the highest dissolved As concentration was measured at the site where the highest groundwater Fe and Mn concentrations were also observed, the dissolved As maximum was located several meters below the dissolved Fe and Mn maxima. Fe(II)/Fe ratios and P-extractable As concentrations in the solid phase were particularly elevated at the same site, though again the profiles of these properties did not consistently match that of groundwater As concentrations. A 500-m section composed of 5 vertical profiles confirms that whereas low As concentrations are broadly associated with low dissolved Fe and Mn concentrations, as well as low Fe(II)/Fe ratios in the solid phase, the spatial distributions of these properties in the subsurface do not follow a simple relationship. In combination with other observations from the area, the results suggest that elevated local recharge in areas where the permeability of surface soils is high prevents As from accumulating in groundwater. Conversely, dissolved As concentrations tend to be high in areas where local recharge is restricted by a surface cover of low permeability. The data demonstrate that further investigation of the mechanisms underlying As mobilization is likely to require sampling at lateral scales <1 km.
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1. Introduction

The landmark survey of groundwater pumped from thousands of tube wells in Bangladesh conducted by

DPHE/MMD/BGS (1999) and BGS/DPHE (2001) has demonstrated that the concentrations of As in aquifers throughout Bangladesh is spatially highly variable on scales of 1–100 km. The spatial variability of As in Bangladesh groundwater has led to considerable confusion about the extent of the arsenic problem, the underlying mechanisms, and the very real need for targeting aquifers that are low in arsenic as a source of drinking water and avoiding those that are not. Even after depth and broad-scale patterns associated with the geology of the country are taken into account, the average arsenic content of wells in a given village, let alone individual wells, is difficult to predict (BGS/DPHE, 2001; Yu et al., 2003; van Geen et al., 2003a; McArthur et al., 2004; Horneman et al., 2004). This observation, and the well-known spatial variability of deltaic and floodplain deposits suggest that understanding As mobilization will require consideration of vertical (Harvey et al., 2002; Swartz et al., 2004) as well as lateral processes. The goal of this study is to show that tractable changes in aquifer properties are observed if they are mapped at spatial scales < 1 km. The implication is that processes that control As concentrations in Bangladesh aquifers should probably be studied at a comparable spatial resolution.

When spatial considerations are set aside, geochemical associations between dissolved As concentrations and other properties of either the groundwater or the sediment have not been straightforward to interpret either. There is considerable scatter in the relationship between dissolved As and Fe in Bangladesh groundwater, for instance, even for samples collected within a limited region (BGS/DPHE, 2001; Zheng et al., 2004; McArthur et al., 2004; Horneman et al., 2004). Microbial reduction of As-containing iron oxyhydroxides is most widely accepted today as a key step in the mobilization of As in groundwater, but a critical question such as the origin of the electron donors that lead to iron reduction remains a matter of conjecture (Nickson et al., 1998, 2000; BGS/DPHE, 2001; Harvey et al., 2002; van Geen et al., 2003b; McArthur et al., 2004; Islam et al., 2004). It is also not clear to what extent reduction of As(V) is a requirement for mobilization or merely a by-product of a generally reducing environment (Inskeep et al., 2002; van Geen et al., 2004a). On the basis of paired tritium–helium ages and dissolved As measurements, Stute et al. (submitted for publication) recently even proposed that the recharge rate of shallow aquifers, i.e. hydrology rather than biogeochemistry, may be the primary factor controlling groundwater As concentrations in shallow Bangladesh aquifers.

Potential relationships between As concentrations and the recharge rate of groundwater are not the focus of the present study. Instead, the issue of spatial variability at the village scale is revisited by documenting subsurface patterns with a new tool, the needle-sampler, which efficiently collects paired groundwater and sediment samples through a modification of the local drilling method (van Geen et al., 2004b). Section 2 of this paper describes the geology of the area where the needle-sampler profiles were obtained. The methods used to collect and analyze groundwater and sediment samples are described in Section 3. The main results are presented in Section 4, with an emphasis on the relationship, in reality the lack thereof, between groundwater As concentrations and other properties of the groundwater and the sediment obtained with the needle-sampler. The discussion in Section 5 starts by comparing the As data collected with the needle-sampler with the distribution of As in neighboring wells to then focus on a high-resolution transect in the context of complementary studies conducted in the same area. The section concludes with an interpretation of the spatial patterns that brings into play differences in hydrology between different parts of the study area, specifically differences in local recharge that appear to be dictated by differences in the permeability of surface soils in the region.

2. Geological setting

The profiles of groundwater and sediment properties were collected within a 25 km^2 region of Araihazar upazila where the distribution of groundwater As has previously been documented by sampling and analyzing groundwater from over 6500 wells (van Geen et al., 2003a, 2005). Columbia University scientists and Bangladeshi partners have since 2000 been investigating the health effects of elevated As on a cohort of 12,000 recruited from the 70,000 inhabitants of the area (e.g. Wasserman et al., 2004). The team has also been investigating the origin of elevated groundwater As concentrations in the area and conducting an extensive mitigation program by encouraging the sharing of safe wells and installing over 50 community wells that continue to be monitored (van Geen et al., 2002, 2003c; Opar et al., in press).

Araihazar upazila straddles the present Meghna River floodplain to the southeast and much older deposits of the uplifted Madhupur tract to the northwest (BGS/DPHE, 2001; Goodbred et al., 2003; Zheng et al., 2005). Consequently, shallow wells in the northwestern portion of the previously surveyed area reach the

Pleistocene Dupi Tila Formation and supply water that is almost exclusively low in As. The majority of shallow wells southeast of this area tap thick and more recent Holocene deposits frequently associated with elevated groundwater As concentrations (van Geen et al., 2003a). Although the needle-sampler has successfully sampled Pleistocene deposits (van Geen et al., 2004b), its use is restricted in this study to document spatial variability in relatively shallow deposits (<100 ft, i.e. $<\sim 30$ m) of presumed Holocene age. Both imperial and metric units are listed throughout the paper because imperial units are more widely used in Bangladesh.

The surface morphology of the ~ 4 km^2 sub-area selected for the study is described with the help of an IKONOS satellite image that was processed to
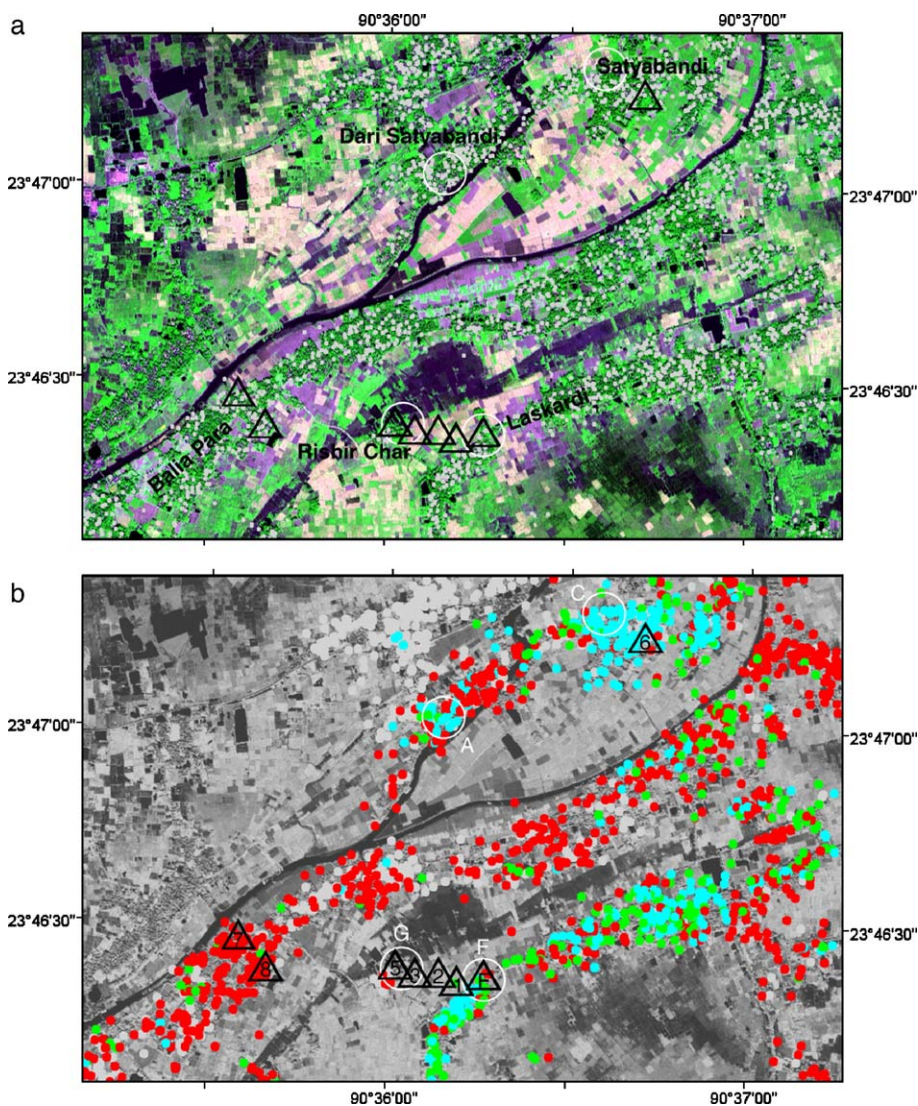

Fig. 1. a. IKONOS satellite image of the ~ 4 km^2 study area dated November 2000 that emphasizes the water content at the surface: purple streams, ponds, and irrigated rice paddies. Black triangles indicate the location of profiles obtained with the needle-sampler. Thin white circles show the location of nests of monitoring wells where the composition and age of groundwater, as well as the composition of the sediment, have previously been reported (Horneman et al., 2004; Zheng et al., 2005; Stute et al., submitted for publication). Small grey dots indicate the location of all tube wells inventoried in the area in 2000 (van Geen et al., 2003a,b,c). The names of key villages discussed in the text are also indicated. b. The same IKONOS image in grey-scale provides a background for groundwater As concentrations in wells up to 75 ft deep (22 m). Blue, green, and red circles indicate As concentrations < 10 μg/L, $10–50$ μg/L, and > 50 μg/L, respectively. Nests of monitoring wells and individual needle-sample profiles are also identified by their letter and number code, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

emphasize the presence of water from reflectance in the IR band (van Geen et al., 2003a). Two streams flowing to the southwest meet towards the center of the study area (Fig. 1a). Most shallow wells in Balia Para and other elongated villages that follow the southern bank of the southern steam are elevated in As (Fig. 1b). In contrast, most wells from Satyabandi village located in the region to the north between the two streams supply groundwater that meets the Bangladesh standard of 50 µg/L for As in drinking water, and often the WHO guideline of 10 µg/L. The satellite image also indicates a depression with high water content that lies south of the main stream. The depression runs parallel to the stream and, based on field observations, appears to be an abandoned stream channel filled with fine-grained material (Fig. 1a). The shallow wells in Laskardi village along the southern bank of this relic feature are predominantly low in As (Fig. 1b).

3. Methods

3.1. Sampling

The needle-sampler was deployed in January 2003 at 8 locations. Four closely spaced profiles (NS-1, 2, 3, and 5) were collected along a 500-m transect that extends to the west of profile NS-F collected in Laskardi village in 2002 (van Geen et al., 2004b). The western portion of the high-resolution transect reaches a small village (Rishir Char) where a limited number of existing private wells and a nest of monitoring wells indicate elevated groundwater As concentrations in the shallow aquifer (Stute et al., submitted for publication). The western-most profile of this section was collected on the margin of the abandoned stream channel north of Rishir Char. An attempt to collect a profile at another site (NS-4 in Table 1) located ~100 m west of NS-5, i.e. towards the center of the relic streambed, was unsuccessful in the sense that a nearly continuous clay layer extending to >100 ft depth (30 m) was encountered. Interspersed sand layers were observed at this location only between 40 and 60 ft depth (12–18 m). Two additional needle-sampler profiles (NS-7, 8) were collected in Balia Para village, across the abandoned stream channel, where As concentrations in existing wells are particularly elevated (Fig. 1b). For contrast, a last profile (NS-6) was collected from Satyabandi village where groundwater As concentrations are consistently very low.

The profiles of groundwater and aquifer material were collected with the first version of the needle-sampler, a simple device developed to allow drillers in Bangladesh to test groundwater before installing a well

Table 1
Location and depth range of needle-sampler profiles

Site	Latitude	Longitude	Altitude (m)	Min. depth (ft)	Max. depth (ft)
NS-F	23.7736	90.6046	7.5	16	90
NS-1	23.7733	90.6033	5.5	18	55
NS-2	23.7737	90.6025	5.5	15	55
NS-3	23.7737	90.6014	5.5	15	70
NS-4	23.7742	90.5995	4.2	50[a]	110
NS-5	23.7740	90.6005	4.2	20[a]	55
NS-6	23.7881	90.6118	–	10	55
NS-7	23.7752	90.5932	–	20	70
NS-8	23.7738	90.5945	–	15	70

Altitude refers to the height of the soil surface relative to sea-level (Zheng et al., 2005). Minimum and maximum depths are relative to the soil surface at that location.
[a] Shallower sample could not be collected because of clay layer extending from the surface.

(van Geen et al., 2004b). It consists of an evacuated sample chamber capped with a silicone stopper, a long needle and plunger assembly to transfer groundwater and sediment from a depth slightly greater than that of the drill hole to the sample chamber, and a housing unit that connects the needle and plunger assembly to the sample chamber. The device is deployed by drilling to the targeted depth using the entirely manual method that has been used to install the vast majority of the millions of wells in Bangladesh (Horneman et al., 2004). The chamber fills almost entirely with groundwater and some sediment during deployment. After filtration under nitrogen, groundwater samples were transferred to acid-cleaned scintillation vials and acidified to 1% HCl (Optima, Fisher Scientific).

The quantity of silt and sand collected in the sample chamber varied between <1 and ~50 g per deployment, depending on the size of the entry holes of the needle relative to the grain size distribution of the sampled horizon. Soon after retrieval and filtration, 0.5–1 g of sediment was scooped into scintillation vials and covered with 10 mL of trace-metal grade 1.2 N HCl to inhibit iron oxidation.

3.2. Analyses

Filtered and acidified groundwater samples were analyzed for As, Fe, Mn, and other groundwater constituents by high resolution inductively coupled plasma mass spectrometry (HR ICP-MS, Cheng et al., 2004). The effective detection limit of the method for As in unfiltered samples is ~1 µg/L; the precision is on the order of ±2% (van Geen et al., 2005). Dissolved As(III) concentrations in groundwater were also determined in

the field by cathodic stripping voltammetry (He et al., 2004). This sensitive method has a detection limit of ~0.5 µg/L and requires a solution volume of 10 mL per analysis. To reduce the volume of sample that is used and to keep the measurements within the linear range of the instrument (i.e. <190 µg/L As), groundwater collected with the needle-sampler was diluted 1:10 or 1:20 into N_2-purged electrolyte in the voltammetric vessel before analysis.

The redox state of the sediment collected with the needle-sampler was determined by measuring with ferrozine the proportion of Fe(II) in the Fe fraction that is leached in hot 1.2 N HCl (Horneman et al., 2004). To compare Fe(II)/Fe measurements quantitatively with the color of the sediment, a CM 2005d spectrophotometer (Minolta Corp., USA) was used to measure the diffuse reflectance spectrum of the collected sediment relative to a white barium sulfate plate. For convenience, the reflectance measurements were made through the polycarbonate sample tube by placing the rounded bottom directly on the instrument's aperture. The first derivative transform of the reflectance spectrum at 520 nm was calculated from these measurements (Horneman et al., 2004).

For analysis of the relatively mobile fraction of As on the sediment, ~1 g of wet sediment was leached in 5–10 ml of a N_2-purged 1 M Na_2HPO_4 (pH=5) solution for 24 h (Keon et al., 2001; Zheng et al., 2005). Dissolved As concentrations in the extraction leachate were determined by HR ICP-MS (Cheng et al., 2004). The dry weight of the sandy aquifer material used in these extractions was not determined for individual samples. Results are therefore shown on the basis of the wet weight of the slurry used for each extraction. Measurements of the water content of a subset of slurries indicate that P-extractable As concentrations can be increased by ~17% for converting to concentrations on a dry-weight basis.

4. Results

Deployment of the needle-sampler for 8 days in January 2003 yielded a total of 78 groundwater samples. For subsets of 72 and 53 samples, sediment from exactly the same horizon was analyzed for Fe(II)/Fe and P-extractable As, respectively. The highest dissolved As concentration of ~600 µg/L was observed at NS-7 in Balia Para at a depth of 45 ft (14 m). Also in Balia Para, As concentrations exceeded 200 µg/L in a total of 10 samples from NS-7 and NS-8 (Fig. 2). In contrast, As concentration between 10 and 45 ft depth (3 and 14 m) at NS-6 in Satyabandi were well below 10 µg/L in

8 samples (Fig. 2). With the exception of the deepest interval at NS-F, groundwater As concentrations along the transect that links Laskardi to Rishir Char were all below 200 µg/L. At most sites, As concentrations were lower near the soil surface and steadily increased with depth.

The correspondence between total dissolved As concentrations measured by HR ICP-MS and dissolved As(III) concentrations measured by voltammetry in Bangladesh is very good over the entire range of concentrations (Fig. 3). This confirms that most dissolved As in groundwater of this region is present as arsenite (Zheng et al., 2004, 2005). One significant advantage of voltammetry over other laboratory measurements is that the method provides rapid and sensitive determinations of As concentrations near a study site (He et al., 2004).

At the two sites with the highest groundwater As concentrations, the highest dissolved Fe concentrations (18 and 13 mg/L at NS-7 and NS-8, respectively) were observed at depth intervals well above the As maxima in the same profiles (Fig. 2). Within individual profiles of the high-resolution transect between Laskardi and Rishir Char, however, intervals of elevated As and Fe concentrations typically correspond. Dissolved Mn concentrations were generally highest in the 30–50 ft depth range (9–15 m), and with a few exceptions always exceeded 0.5 mg/L (Fig. 2). When considering all sites, there appears to be systematic relationship between dissolved As and dissolved Fe or Mn concentrations (Fig. 4). It is not clear why the relationship between dissolved As and dissolved Fe appears to be particularly weak in Araihazar compared to other areas that have been studied in some detail (Nickson et al., 1998, 2000; BGS/DPHE, 2001; McArthur et al., 2004).

As previously reported by Horneman et al. (2004), there is a general correspondence between the first-derivative transform of the reflectance at 520 nm and the Fe(II)/Fe ratio of the hot, acid-leachable Fe fraction of the sediment in Araihazar (Fig. 5). The relationship confirms that gray sediment with a flat reflectance spectrum contain a higher proportion of Fe(II) in the leachable Fe fraction and is therefore more reduced. Conversely, the leachable Fe fraction of less reduced orange to brown sediment, i.e. with a spectrum characterized by higher reflectance at long wavelengths, is dominated by Fe(III). The results reported here indicate that even when dissolved As and leachable Fe(II)/Fe are determined for groundwater and sediment from exactly the same interval, Fe(II)/Fe is a useful predictor only to the extent that Fe(II)/Fe ratios <0.4 are typically associated with low
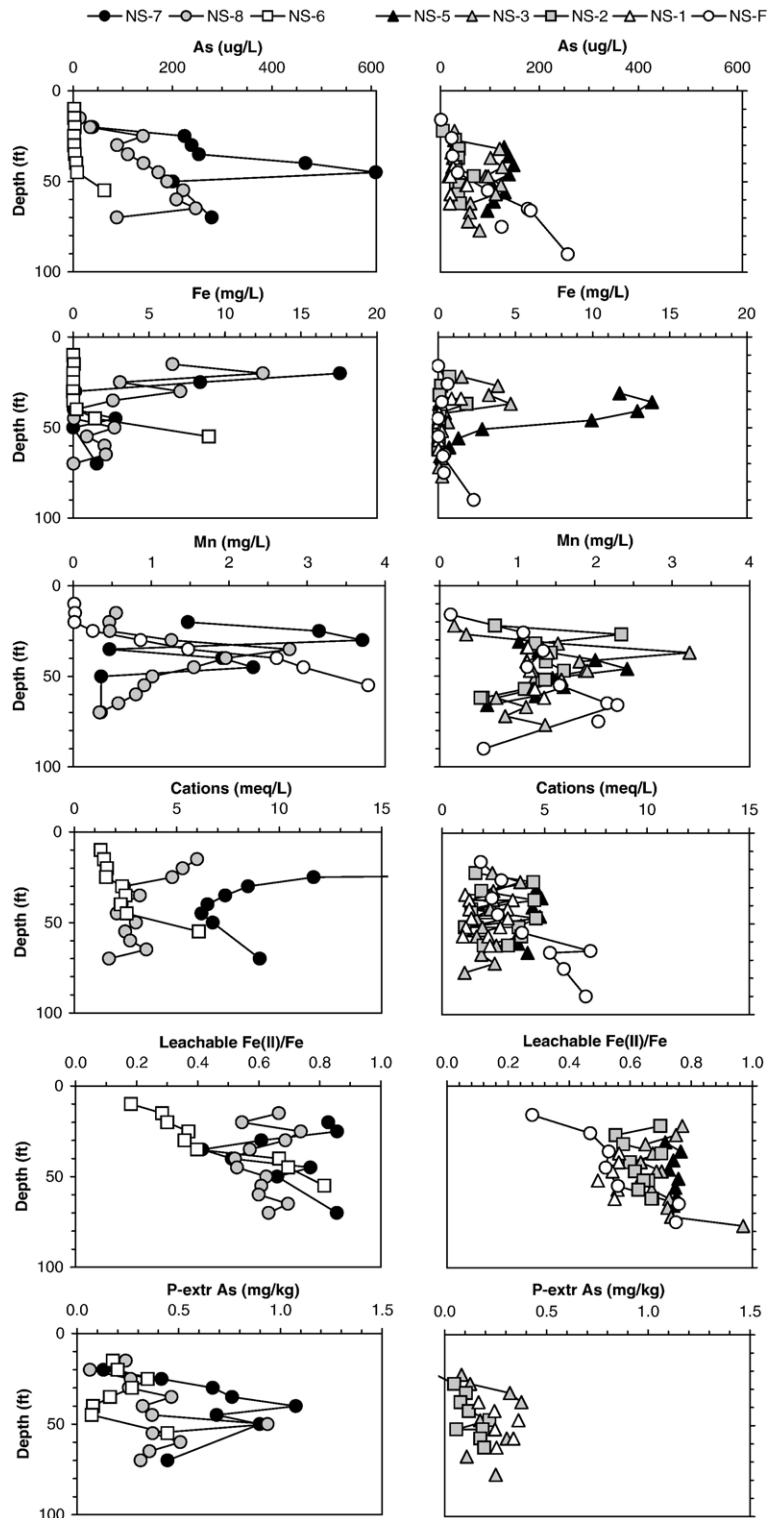
Fig. 2. Profiles of groundwater and sediment properties obtained with the needle-sampler. Data for the 5 profiles that constitute the high resolution transect between Laskardi and Rishir Char are shown in separate panels but on the same scale as for NS-6, NS-7, and NS-8. Differences in altitude were taken into account to calculate sample depths relative to the ground at NS-F (Table 1). P-extractable As concentrations are calculated relative to the wet weight of slurry taken from each sample chamber. Measurements of mobilizable As are not available at NS-F and NS-5.
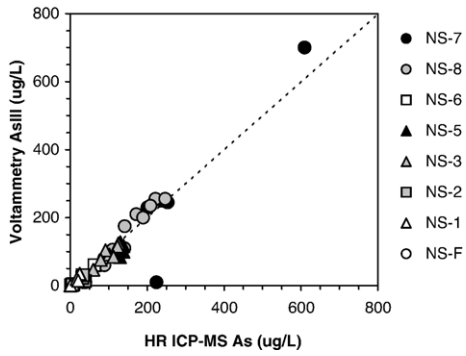
Fig. 3. Comparison of As(III) concentrations measured by voltammetry in January 2003 in Bangladesh with laboratory measurements of total dissolved As at LDEO by HR ICP-MS.
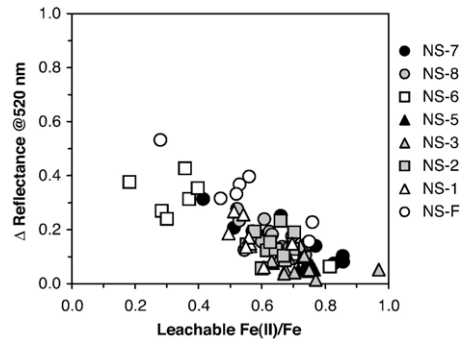

Fig. 5. Comparison of Fe(II)/Fe ratios in the acid-leachable Fe fraction of the sediment with the first-derivative transform of the spectrum reflectance at 520 nm.

As concentrations (Fig. 4). At higher Fe(II)/Fe ratios, As concentrations in the study area vary across the entire dynamic range of 1–600 µg/L.

The association between groundwater As concentrations and another property of the sediment, the concentration of P-extractable As, appears to be more
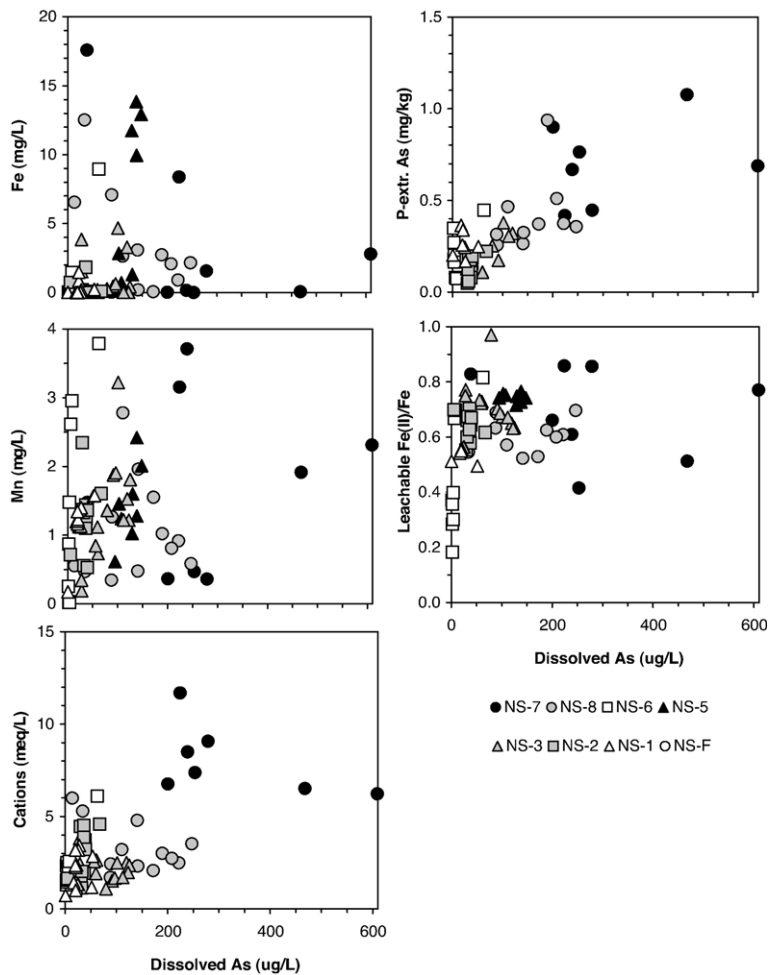

Fig. 4. Comparison of dissolved As concentrations in sample collected with the needle-sampler with other properties of the groundwater and the sediment.

systematic. Concentrations of P-extractable As in the sediment >0.4 mg/kg (Fig. 4) were observed only at the two sites where dissolved As concentrations are particularly high (NS-7 and NS-8). For horizons with P-extractable As levels <0.4 mg/kg, dissolved As concentrations were below 50 µg/L at NS-1 and NS-6 whereas they reach 200 µg/L at NS-3 and NS-8.

There is a feature of the data that appears to distinguish those sites where groundwater As concentrations are particularly high, even if the depth intervals do not necessarily correspond. This is the combined concentration of the major cations Na, Mg, Ca, and K, expressed in equivalents/L (Fig. 4), which other studies have shown to be related to the conductivity of a sample and the concentration of total dissolved solids. The concentration of major cations is particularly high (>5 meq/L) in the shallowest samples collected at NS-7 and NS-8, and also increases steadily with depth (and As concentrations) at NS-F. Major cation concentrations are <5 meq/L for all samples from the transect that extends west of Laskardi, and particularly so in the shallowest samples of NS-6 in Satyabandi (Fig. 2).

5. Discussion

5.1. Spatial patterns of groundwater As concentrations and other properties

The needle-sampler profiles of dissolved As appear to be representative of subsurface conditions reflected in the composition of groundwater pumped from surrounding wells (Table 2). Arsenic concentrations as high as 610 and 250 µg/L in Balia Para measured at NS-7 and NS-8, respectively, are consistent with the particularly high proportion of shallow private wells within 200 m of these sites in Balia Para containing >300 µg/L As (37%). At the other end of the spectrum, the very low As concentration measured in Satyabandi at NS-6 agree with the overwhelming majority of wells containing <10 µg/L As (86%). Although the number

Table 2
Proportion of shallow private wells within 200 m of needle-sample locations (%)

As (µg/L)	NS-7 and 8	NS-5	NS-F	NS-6
	(n=75)	(n=4)	(n=36)	(n=88)
≤ 10	0	0	53	86
10–50	3	0	33	7
50–100	12	0	11	2
100–300	48	75	3	3
> 300	37	25	0	1

of shallow private wells is smaller at the two ends of the high-resolution transect, the contrast in As concentrations between NS-F and NS-5 is also consistent with conditions in the villages of Laskardi and Rishir Char, respectively, even if the spectrum of As concentrations in private wells falls somewhat short of the full range spanned by NS-6 and NS-8.

Needle-sampler profiles were not collected over the 2 km distance separating Balia Para from Satyabandi, and the two villages are separated by a stream and possibly other subsurface geological features. The high-resolution transect between Laskardi and Rishir Char, however, provides a close-up view of a gradual transition between two villages with very different As concentrations in their wells. The spatial features of this transition are emphasized with a contour plot based on the 5 profiles that are ~100 m apart from each other. (Fig. 6). The contour corresponding to 50 µg/L As, the Bangladesh standard for drinking water, is crossed at a depth of 50 ft (15 m) at NS-F. Groundwater As concentrations barely reach this level at the same depth in the next two profiles to the west (NS-1, NS-2), and then actually decrease below this depth. Further west, the minimum in dissolved As content of the shallow aquifer that is located roughly mid-way between the two villages is bound by the sharp transition to NS-3 where concentrations exceed 100 µg/L from 30 to 60 ft depth (9–18 m). At the western end of the transect (NS-4), the depth range of intervals where As concentrations exceed 100 µg/L broadens to include all but the deepest sample (Fig. 6).

There is no simple relationship between groundwater As concentrations and other aquifer properties even at the ~100 m scale of the high-resolution transect. There is no pronounced east–west gradient in dissolved Mn concentrations along the transect, even if Mn concentrations are >0.1 mg/L throughout the area, consistently indicating anoxia (Fig. 6). Dissolved Fe concentrations, on the other hand, are <0.1 mg/L in 20 out of 33 samples from NS-F, NS-1, and NS-2, as opposed to only 4 out of 21 samples from NS-3 and NS-5. The pronounced plume of elevated Fe concentrations of up to 18 mg/L originating from ~30 ft depth (9 m) at NS-5 extends east to NS-3 (maximum of 15 mg/L) and to a much lesser extent also to NS-2 and NS-1 (5 and 2 mg/L, respectively). Gradual variations in the redox state of the sediment along the transect, as indicated by leachable Fe(II)/Fe ratios in the solid phase, follow the broad pattern of groundwater As concentrations along the transect fairly closely even though there is no linear correspondence. Over much of the 20 to 60 ft depth range of the profiles (6–18 m), Fe(II)/Fe ratios
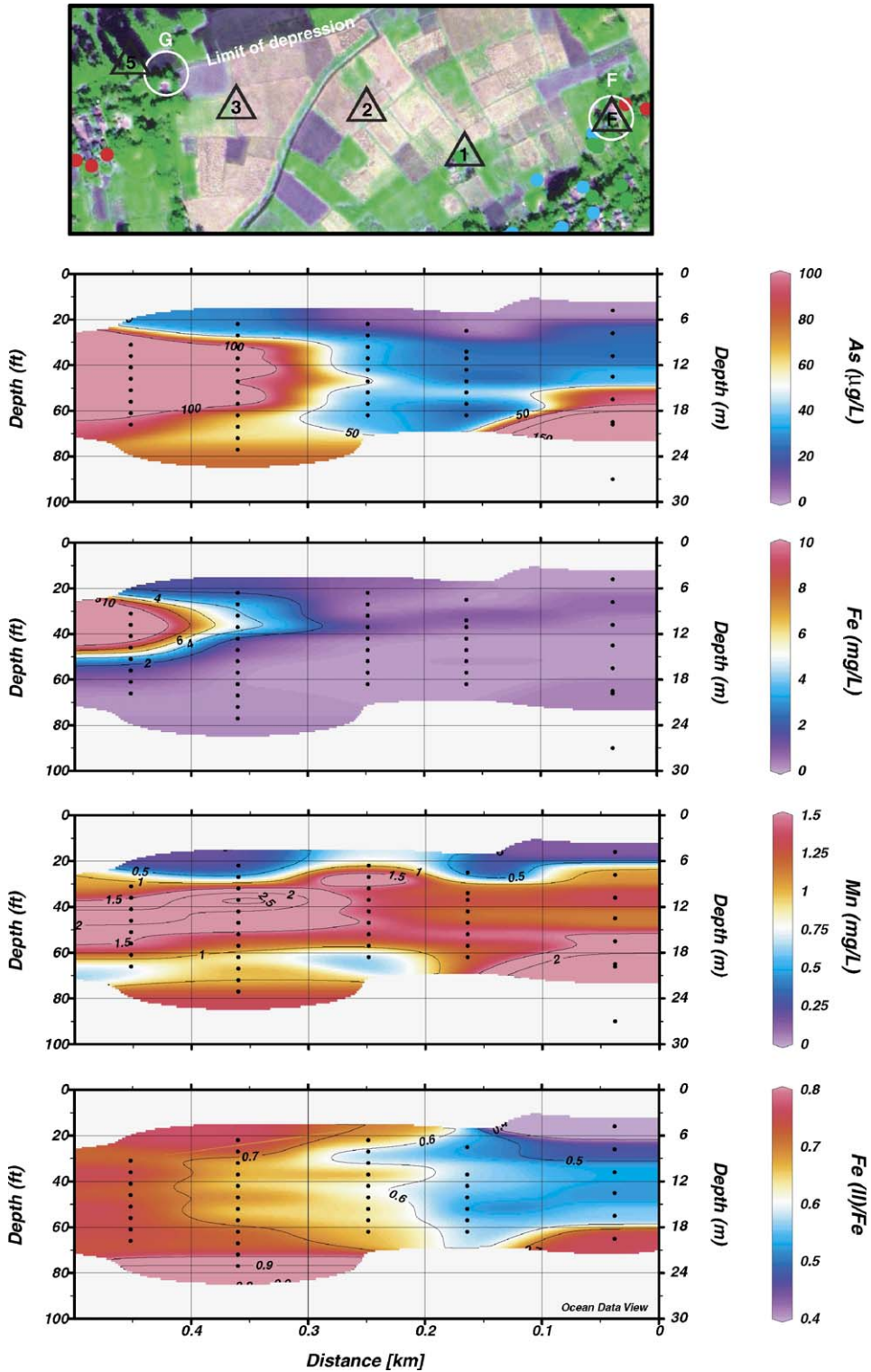
Fig. 6. Section of groundwater and sediment properties across the rice fields that separate Laskardi from Rishir Char. Rectangular shapes corresponding to individual fields that are either irrigated (purple), vegetated (green), or dry (white or pink) are easily distinguished in the satellite image. The location of needle-sample profiles of transect as well as the nests of monitoring wells at the two ends of the transect are also shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

steadily increase from ~0.5 at NS-F and NS-1 to nearly 0.8 at NS-5 (Fig. 6).

To our knowledge, no observations of groundwater and sediment composition have previously been reported for Bangladesh in relation to As at a spatial resolution that is comparable to this study. Changes in groundwater and sediment composition linked to redox gradients have been documented at high resolution for numerous contaminant plumes in other parts of the world (e.g. Christensen et al., 2000; Davis et al., 2000), and the behavior of As in response to changing redox conditions was considered explicitly in a few of these studies (Keimowitz et al., 2005). The spatial scale of observations of natural redox gradients in the subsurface, some of which with a focus on As, have typically covered much larger distances (e.g. Chapelle and McMahon, 1991; Smedley et al., 2003; Smith et al., 2003; Kirk et al., 2004). The closest analog to the work presented here is a recent study of Joypur, Ardivok, and Moyna villages in West-Bengal, India, where McArthur et al. (2004) reported that groundwater and sediment properties determined by traditional sampling methods at three locations only a few hundred meters apart were consistent with patterns of variations in groundwater As concentrations determined by sampling private wells in the area. The limited number of profiles from this area did not unambiguously demonstrate geological continuity from one site to the other, however. The three special-study areas in Bangladesh selected by BGS/DPHE (2001) also showed considerably spatial variability, but the connection to sediment properties in the shallow aquifers was not established because core material was obtained from a single site in each area only.

5.2. Comparison with other data from Araihazar

An additional source of information obtained from the same area is important for interpreting subsurface patterns of groundwater As and other aquifer properties. These are measurements of groundwater age relative to recharge obtained by the tritium–helium (^{3}H–^{3}He) dating technique for nests of monitoring wells located at NS-F, near NS-5 ("Site G"), near NS-6 ("Site C") and an additional site in Dari Satyabandi village ("Site A") (Stute et al., submitted for publication). The measurements divide the 4 sites into two distinct hydrologic regimes. Near NS-6 and at NS-F, groundwater ages increase from <1 year at ~25 ft (8 m) to ~4 years at 60 ft (18 m). At Site A and Site G, instead, groundwater is already several years old in the shallowest monitoring wells and averages 30 years at a depth of 60 ft (18 m). In the most general sense, the groundwater ages show that recharge of the shallow aquifers is more rapid in those villages fortunate enough to have low As concentrations in their wells. The high-resolution transect of profiles connecting Site F and Site G indicates that the effect on groundwater As concentrations of rapid and slow local recharge, respectively, at the two sites extends at least 100 m laterally beyond the precise location of the nests of wells where ^{3}H–^{3}He data were obtained (Fig. 6).

5.3. Implications for mechanism(s) of As accumulation in shallow groundwater

On the basis of ^{3}H–^{3}He dates for a larger portion of Araihazar upazila, Stute et al. (submitted for publication) argue that As mobilization in shallow aquifers occurs at a relatively constant rate of ~20 µg/L per year under a wide range of hydrological regimes. This hypothesis has yet to be confirmed independently by a careful series of incubations. What appears to be fairly well established is that As transfer to the dissolved phase is inhibited by the presence of Fe(III) oxyhydroxides, as indicated by either sediment color or leachable Fe(II)/Fe ratios. This appears to apply not only to the extreme case of orange Pleistocene sediment (BGS/DPHE, 2001; Zheng et al., 2005), but also for more subtle gradations of grey and brown within more recent Holocene deposits (McArthur et al., 2004; Horneman et al., 2004; van Geen et al., 2004a). The association, which could possibly be due to re-adsorption of As, is consistent with the parallel increases in groundwater As and Fe(II)/Fe in the 30–60 ft depth range (9–18 m) between Laskardi and Rishir Char (Fig. 6). For reasons that are presently unclear, the relationship breaks down at shallower depths: the dissolved As content of the two shallowest samples at NS-3 is well below 50 µg/L even though the Fe(II)/Fe ratio of aquifer material from the same depth is >0.7.

Leachable Fe(II)/Fe ratios for sediment along the high-resolution transect that show less reducing conditions at Site F compared to Site G may indicate that local recharge supplies an excess of oxidants, i.e. that the oxidizing capacity of recharged water initially containing oxygen and nitrate exceeds the reducing capacity of dissolved organic carbon. This would run counter to the mechanism of As mobilization proposed by Harvey et al. (2002), especially because groundwater is used extensively to irrigate rice paddies during winter in the fields separating Site F and Site G. We cannot, however, rule out a geological origin of the contrast in redox conditions along the high-resolution transect, such as a higher particulate organic matter content of the sediment

deposited at western section compared to the eastern section. Similarly, we cannot exclude the possibility that more reducing conditions at Site G are driven by a release of dissolved organic carbon from a thick deposit of fine-grained material capping the shallow aquifer (McArthur et al., 2004).

A different aspect of the data presented in this study provides a potential explanation for the considerable degree of decoupling between As and Fe observed in Araihazar, without necessarily invoking a radical departure from the prevailing iron-reduction hypothesis (Nickson et al., 1998, 2000; BGS/DPHE, 2001; McArthur et al., 2001, 2004). This is a consideration of the pool of As that is adsorbed and therefore potentially mobilizable, as reflected by the amount extracted with a concentrated P solution (Keon et al., 2001). P-extractable As concentrations in the solid phase are as much as an order of magnitude lower at NS-6 than at NS-8. This suggests that the transfer of particulate As from a relatively inaccessible phase to a solid form that is more mobile may under certain conditions not keep up with the rate of flushing of the certain aquifers (Zheng et al., 2005). The lower concentration of major cations at NS-6 compared to NS-8 suggest this presently hypothetical transformation of As to a more mobile form might be linked to a relatively slow, weathering-like reaction of primary minerals. A limited pool of mobilizable As might also explain why As concentrations are low in the two shallowest intervals of NS-3 despite Fe(II)/Fe ratios >0.7. At these locations, the rate of recharge of the shallowest aquifer appears to be sufficient to keep the concentration of P-mobilizable As particularly low (<0.2 mg/kg) despite of relatively reducing conditions. Overall, the subsurface patterns suggest that groundwater As concentrations are elevated only if Fe(II)/Fe>0.4 and the concentration of P-extractable As is above 0.4 mg/kg.

6. Conclusions

The main contribution of the present study is a demonstration that the concentration of As in groundwater pumped from any particular well in Bangladesh is the result of multiple and still poorly known processes. Results presented elsewhere underline the importance of local hydrology (Stute et al., submitted for publication). Given the scale of spatial variability of the moisture content of surface soils indicated by the satellite image of Araihazar, which is in turn linked to the well-known variability of the surface morphology of floodplain and deltaic environments, it is not surprising that the As

content of shallow wells varies significantly from one village to the other and even within the same village. No factor unambiguously explaining the origin of elevated As concentrations in Bangladesh groundwater has as of yet been identified, possibly because of the limited spatial resolution of previous studies. Progress on this front is likely to require targeted studies conducted with a device such as the needle-sampler that provides a large number of paired groundwater and sediment samples at a reasonable cost. Establishing causation from spatial correlations of dissolved As concentrations with other properties of Bangladesh aquifers may require yet another level of coordination of simultaneous hydrological, geochemical, and microbiological investigations.

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