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Geochemical and hydrogeological contrasts between shallow and deeper aquifers in two villages of Araihaazar, Bangladesh: Implications for deeper aquifers as drinking water sources

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Abstract—Sediment and groundwater profiles were compared in two villages of Bangladesh to understand the geochemical and hydrogeological factors that regulate dissolved As concentrations in groundwater. In both villages, fine-grained sediment layers separate shallow aquifers (< 28 m) high in As from deeper aquifers (40–90 m) containing < 10 $\mu\text{g/L}$ As. In one village (Dari), radiocarbon dating indicates deposition of the deeper aquifer sediments > 50 ka ago and a groundwater age of thousands of years. In the other village (Bay), the sediment is < 20 ka old down to 90 m and the deeper aquifer groundwater is younger, on the order of hundreds of years. The shallow aquifers in both villages that are high in As contain bomb- ^3H and bomb- ^{14}C , indicating recent recharge. The major and minor ion compositions of the shallow and deeper aquifers also differ significantly. Deeper aquifer water is of the $\text{Na}^+\text{-HCO}_3^-$ type, with relatively little dissolved NH_4^+ ($76 \pm 192 \mu\text{mol/L}$), Fe ($27 \pm 43 \mu\text{mol/L}$) and Mn ($3 \pm 2 \mu\text{mol/L}$). In contrast, shallow aquifer water is of the $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ type, with elevated concentrations of dissolved NH_4^+ ($306 \pm 355 \mu\text{mol/L}$), Fe ($191 \pm 73 \mu\text{mol/L}$), and Mn ($27 \pm 43 \mu\text{mol/L}$). In both villages, the quantity of As extractable from deeper aquifer sands with a 1 mol/L phosphate solution ($0.2 \pm 0.3 \text{ mg/kg}$, $n = 12$; $0.1 \pm 0.1 \text{ mg/kg}$, $n = 5$) is 1 order of magnitude lower than P-extractable As from shallow deposits ($1.7 \pm 1.2 \text{ mg/kg}$, $n = 9$; $1.4 \pm 2.0 \text{ mg/kg}$, $n = 11$). The differences suggest that the concentration of P-extractable As in the sediment is a factor controlling the concentration of As in groundwater. Low P-extractable As levels are observed in both deeper aquifers that are low in As, even though there is a large difference in the time of deposition of these aquifers in the two villages. The geochemical data and hydrographs presented in this study suggest that both Holocene and Pleistocene deeper aquifers that are low in As should be a viable source of drinking water as long as withdrawals do not exceed recharge rates of $\sim 1 \text{ cm/yr}$. Copyright © 2005 Elsevier Ltd

1. INTRODUCTION

Evidence of widespread poisoning from drinking groundwater elevated in arsenic (As) emerged in the mid-1980's in West Bengal, India, and in the mid-1990's in Bangladesh (Chakraborty and Saha, 1987; British Geological Survey and Department of Public Health Engineering, 1999). About 35 million people in Bangladesh, i.e. $\sim 27\%$ of the total population, are estimated to consume groundwater containing > 50 $\mu\text{g/L}$ As (the Bangladesh drinking water standard); a staggering 57 million people drink groundwater containing > 10 $\mu\text{g/L}$ As (WHO guideline value), of which $\sim 36\%$ are children younger than 15 yrs (WRI, 1998; British Geological Survey and Department of Public Health Engineering, 2001). The consequences of chronic arsenic exposure are anticipated to be a daunting public health challenge for decades to come (Smith et al., 2000; Yu et al., 2003).

Past investigations of the distribution of As in Bangladesh groundwater based on field and laboratory analyses of well waters (Chakraborti et al., 1999; British Geological Survey and Department of Public Health Engineering, 2001; <http://www.bamwsp.org/maps/maps.h6.jpg>) show distinct regional patterns and depth trends. Higher proportions of shallow wells containing > 50 $\mu\text{g/L}$ As are found in the south and southeastern parts of the country; the lowest proportions have been documented in the northwest and within the uplifted terraces of north-central Bangladesh. This regional pattern appears to be, at least in part, related to the age of the sediments. Holocene (<10 ka) alluvial and deltaic deposits generally contain groundwater elevated in As; while concentrations are very rarely elevated in older Pleistocene sediments (>40 ka). This is indicated by the very high fraction (99%) of wells deeper than 150 m containing < 50 $\mu\text{g/L}$ As (British Geological Survey and Department of Public Health Engineering, 1999). Even shallow tube wells that reach these older deposits in uplifted terraces (e.g. Barind and Madhupur tracts) yield groundwater that is systematically low in As.

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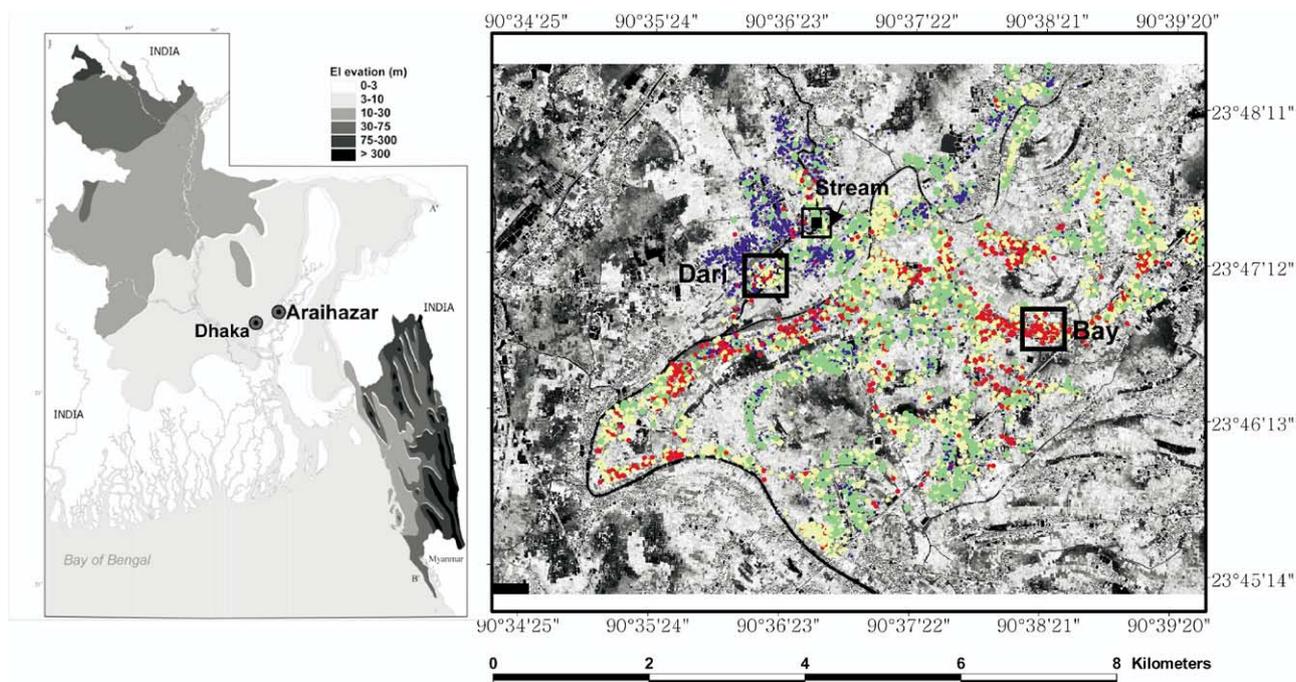


Fig. 1. The Araihaazar study area (left panel) is located in the low-lying (3–6 m elevation) Meghna River flood plain to the east of Dhaka. The right panel shows the arsenic concentration distribution (blue: $< 10 \mu\text{g/L}$, green: $10\text{--}50 \mu\text{g/L}$, yellow: $50\text{--}200 \mu\text{g/L}$, red: $200\text{--}400 \mu\text{g/L}$, dark red: $400\text{--}900 \mu\text{g/L}$) in 6000 contiguous wells sampled in a $\sim 25\text{-km}^2$ area. Also shown are the study sites in the western (Dari Satyabandi) and eastern (Baylakandi) portions of the Araihaazar study area. Location of the surface water level monitoring of a local stream is indicated by an open square, labeled “Stream.”

The origin of the association between aquifer age and groundwater As is not well understood. Redox conditions play an important role because of the strong association of As with Fe oxyhydroxides that are subject to reductive dissolution (Aggett and Kriegman, 1988; Belzile and Tessier, 1990; Bhattacharya et al., 1997; Nickson et al., 2000). Holocene deposits are generally gray in color and contain high proportions of Fe(II) in the acid-leachable Fe(II+III) fraction (British Geological Survey and Department of Public Health Engineering, 2001; Horneman et al., 2004; Swartz et al., 2004). Whether the reduced carbon that drives Holocene deposits towards reducing conditions is provided in the solid phase at the time of deposition or in the dissolved phase with recharge over time is still unclear (British Geological Survey and Department of Public Health Engineering, 2001; Harvey et al., 2002; McArthur et al., 2004). In contrast, Pleistocene deposits that are typically orange in color contain little Fe(II) in the leachable Fe fraction (Horneman et al., 2004). These are still not truly oxic aquifers, however, since groundwater associated with Pleistocene deposits rarely contains detectable dissolved oxygen and dissolved Fe concentrations can reach $\sim 1 \text{ mg/L}$ (Nickson et al., 2000; British Geological Survey and Department of Public Health Engineering, 2001; Zheng et al., 2004).

In this detailed study of sediment and groundwater properties in two villages of Araihaazar upazila, Bangladesh, we show that the amount of As that is easily mobilizable from the sediment (e.g., soluble in 1 mol/L phosphate solution near neutral pH), rather than sediment age *per se* plays an important role in regulating dissolved As concentrations. We also examine the hydrogeology of the deeper aquifers to evaluate their potential

as a source of safe drinking water. Section 2 of this paper describes the geological setting of the region where the two study sites are located as well as the methods used to collect a sediment core from each village, install monitoring wells around each site, and gather a variety of geochemical data for groundwater and sediment. This includes geochemical measurements of the oxidation-reduction potential (ORP), pH, concentrations of O_2 , NH_4^+ , Mn^{2+} , Fe^{2+} , SO_4^{2-} in groundwater, and HCl-leachable Fe(II)/Fe ratios, as well as the bulk and phosphate-extractable As content of the sediment. Section 3 provides an overview of the main results, starting with the description of vertical profiles of As in groundwater. Radiocarbon dates for several sediment intervals at both sites are presented to constrain the age of the deposits. We then document variations in hydraulic heads in the monitoring wells and estimate groundwater age using both radiocarbon and tritium. Section 4 discusses the likely factors contributing to low dissolved As concentrations in the deeper aquifers and the sustainability of these aquifers as drinking water sources. The effect of physical or chemical changes induced by enhanced pumping from deeper aquifers on As release is specifically addressed.

2. METHODS

2.1. Study Sites

Two villages were selected for detailed study based on a previous survey of As concentrations in 6000 wells within an $\sim 25 \text{ km}^2$ area of Araihaazar upazila (Fig. 1), Bangladesh, $\sim 25 \text{ km}$ east of Dhaka (van Geen et al., 2002, 2003a). The region lies between the present Meghna River floodplain to the east and much older deposits of the uplifted

Madhupur tract to the northwest (Goodbred et al., 2003). The range and depth distribution of groundwater As concentrations are very different in the existing wells of the two selected villages (see Figs. 9 and 10 in van Geen et al., 2003a). The western site (Site A) in Dari Satyabandi village (23.785°E, 90.603°N, referred to as "Dari") was chosen because As concentrations in existing shallow wells (7–20 m) vary across a wide range (< 5–800 µg/L). Overall, 53% ($n = 299$) of shallow wells within a 0.5-km² area centered on the location of the sediment core meet the Bangladesh drinking water standard of 50 µg/L for As. There are very few wells with a reported depth between 20 and 30 m in this particular village. Groundwater pumped from almost all existing wells in the 30- to 50-m depth range contains < 5 µg/L As (216 out of $n = 219$). The eastern site (Site B) in Baylakandi village (23.780°E, 90.640°N, referred to as "Bay") was chosen because groundwater from nearly all wells (155 out of $n = 162$) contains > 50 µg/L As. The depth of wells in this village ranges from 15 to 40 m and As concentrations as high as 520 µg/L were measured.

2.2. Sediment Collection

2.2.1. Coring

A split-spoon sampler made from a 0.6-m (2-ft) section of PVC pipe (ID 5 cm) was used to retrieve sediment samples in January 2001 with a drill rig operated by the Bangladesh Water Development Board, identical to that used by British Geological Survey and Department of Public Health Engineering (2001). The ends of sub-sections containing sediment were wax-sealed on site immediately after sediment color and texture were recorded. The sealed sections were shipped at ambient temperature and stored at 4°C upon their arrival at Lamont-Doherty's core repository in May, 2001. Drilling reached a depth of 91 m (300 ft) below the surface at both sites; recovery averaged $30 \pm 2\%$ and $29 \pm 2\%$ at the Dari and Bay sites, respectively.

2.2.2. Needle-Sampler

To document that geochemical properties of the core were not significantly affected by storage, fresh sediment was collected from both sites in October 2003 using a simple device that builds on the local well drilling technique (van Geen et al., 2004a). The device relies on a 46-cm-long needle piercing a silicone stopper to collect groundwater and sediment into an evacuated 100-mL tube at prescribed depth intervals, ahead of the disturbed portion of the drill hole. Both the Fe(II)/Fe ratio of the leachable iron fraction of the sediment and the amount of phosphate-extractable As on the sediment was determined on the day of collection under anaerobic conditions (see section 2.4).

2.3. Monitoring Wells

2.3.1. Installation

Eight monitoring wells were installed within 10 m of the two coring sites. Each well consists of a 1.5-m section of galvanized iron (GI) pipe at the top, a length of PVC pipe (ID 5 cm) to reach the desired depth, a 0.9-m screen made of PVC pipe with < 1-mm-wide slots, and an ~0.5-m PVC plug at the bottom to collect particles settling within the pipe without clogging the filter. Sand was poured alongside the pipe to surround the screen and prevent clogging, followed by fine-grained material until close to the surface to seal the well. The distance between the top of the GI pipe and the mid-point of the screens was measured to determine the well depths listed in Table 1. The deepest wells at both sites are equipped with hand-pumps and used extensively by the local community as a source low As water (van Geen et al., 2003b).

2.3.2. Groundwater level monitoring

Variations in groundwater level relative to the top of the GI pipe casing were measured with a Solinst Model 101 meter at bi-weekly intervals in most monitoring wells starting in February 2001, and in March and June 2002 in the remaining wells. The absolute elevation of the top of the GI pipe of one well from each site and a reference mark for monitoring the water level of a river near the Dari site were determined with differential Global Positioning System (GPS) receivers

in January 2003 with an estimated precision of ± 3 cm, using two base stations and two roving receivers (Trimble 4000SSE). GPS processing used interferometric measurements of the carrier phases of the GPS signals corrected for ionospheric delays to provide high-accuracy measurements of the measured baselines. The elevation of the top of the GI pipe of the other wells relative to the reference well from each nest of wells was determined visually within ± 1 mm by leveling with a transparent flexible tube filled with water.

2.3.3. Groundwater samples and field protocols

All analyses were performed on groundwater samples collected from the monitoring wells with a battery-driven submersible pump (Whale SuperPurger) at Dari in January 2001 and at Bay in June 2001, except for dissolved ammonia. Ammonia (NH₄⁺) was analyzed by colorimetry (Sorzano, 1969) in the field for groundwater samples collected from the same monitoring wells in January, 2003. Procedures followed to measure temperature, conductivity, pH, ORP, dissolved oxygen and alkalinity, and to speciate inorganic As by anion exchange columns in the field (Ficklin, 1983) were the same as those described by Zheng et al. (2004). Groundwater was filtered using a vacuum filter unit (Nalgene) connected to a hand-vacuum pump (Nalgene) instead of a syringe with a filter, as used in previous work (Zheng et al., 2004). By this new method, dissolved Fe, As and PO₄ concentrations were comparable in filtered and unfiltered samples, after acidification to 1% HCl. Most dissolved constituents (i.e. Ca²⁺, Mg²⁺, Na⁺, K⁺, As, Fe, Mn, PO₄³⁻ and SO₄²⁻) were measured in filtered and acidified samples. Dissolved Cl⁻ and NO₃⁻ concentrations were measured on filtered samples without acidification. Samples for ³H were collected in 250-mL glass bottles with Polyseal caps or in 1-cm-OD copper tubes crimped on the ends with stainless steel clamps (Weiss, 1968). Samples for analyses of ¹³C/¹²C and ¹⁴C/¹²C in dissolved inorganic carbon were collected in 250-mL glass bottles with Polyseal caps and were poisoned with 0.2 mL of saturated HgCl₂ (Fisher Scientific) solution.

2.3.4. Water analyses

Concentrations of dissolved As, P, Fe, Mn, S, Ca, Mg, K, Na in groundwater samples were measured by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICP-MS) by a method with a detection limit for As of ~0.1 µg/L (Cheng et al., 2004). For quality assurance, one or more of the following consistency standards were included with each run: NIST Standard Reference Material 1640 (Trace Elements in Natural Water), mineral water (Evian) spiked with trace elements, and a subset of several Bangladesh groundwater samples. Laboratory results were within 5% to 10% of certified values for As, Fe, Mn, and other dissolved ions in NIST 1640. Arsenic speciation (i.e., As[III] and As[V]) was determined by comparing concentrations of As in the groundwater and in the eluent of the anion exchange column (Ficklin, 1983) by graphite furnace atomic absorption spectrometry. Chloride and nitrate concentrations were determined by ion chromatography. Measurement precision differed for each constituent but usually was $\pm 5\%$ to 10%.

Analyses of ¹³C/¹²C and ¹⁴C/¹²C in dissolved inorganic carbon (DIC) was performed at the NOSAMS facility at Woods Hole Oceanographic Institution following standard protocols (Elder et al., 1997). Analysis of ³H in groundwater was performed on either ~40 cm³ of water collected in glass bottles or on ~16 cm³ of water collected in copper tubes using the ³He in-growth technique (Bayer et al., 1989). The precision of the ³H data is $\pm 2\%$ to 3%.

2.4. Sediment Analyses

In March 2002, sealed sections of the stored core samples were opened and sub-sampled for grain-size, hydraulic conductivity and geochemical analyses. Sediment color qualitatively appeared unchanged relative to the field observations and care was taken to sample the center of each core section. The samples were disaggregated in distilled water and washed through a 63-µm sieve to determine the sand fraction. The fraction < 63 µm was then analyzed with a particle-size analyzer (Micromeritics SediGraph 5100) to obtain continuous grain size measurements down to 0.8 µm. These same core sections and a few additional samples (total $n = 28$) were then used for the

Table 1. Aqueous parameters of monitoring wells in Dari and Bay villages, Arai hazar, Bangladesh.

Well ID	DariP1	DariP2	DariP3	DariP4	DariP5	DariP6	DariP7	DariP8	BayP7	BayP8	BayP3	BayP9	BayP4 ^b	BayP5	BayP6	BayCW2
Well depth (m)	4.1	7.1	10.2	13.2	28.8	34.6	40.7	81.5	8.1	11.1	14.2	20.3	27.9	40.1	52.7	88.5
Well elevation (m asl)	7.47	7.47	7.43	7.40	7.53	7.51	7.48		7.42	7.37	7.52	7.49	7.49	7.46	7.47	7.60
Sampling date	1/18/01	1/18/01	1/18/01	1/18/01	1/18/01	1/19/01	1/19/01	1/19/01	6/20/01	6/20/01	6/20/01	6/20/01	6/21/01	6/20/01	6/20/01	6/20/01
Total dissl. As ($\mu\text{g/L}$)	89	133	582	392	0	0	0	1	37	366	555	386	260	22	14	11
%AsIII	100	66	91	89					100	95	95	82		104	80	
Temperature ($^{\circ}\text{C}$)	26.1	26.0	26.1	26.3	26.1	26.1	26.1	26.2	25.4	25.5	25.6	25.6	25.8	25.6	25.6	26.2
Conductivity ($\mu\text{S/cm}$)	856	457	609	781	415	361	352	407	1376	1104	1093	926	898	641	496	373
pH	6.17	6.38	6.56	6.79	6.31	6.19	6.23	6.17	6.71	6.70	6.88	6.94	6.94	7.05	7.31	6.94
Alkalinity (meq/L)	6.64	3.33	5.41	7.29	2.98	2.98	2.55	2.40	9.77	7.57	8.44	8.99		6.68	5.12	4.07
ORP (mV)	-73	-72	-121	-162	39	48	48	26	-154	-147	-177	-183	-178	-171	-181	-134
DO ($\mu\text{g/L}$)	<10	<10	<10	<10	<10	<10	<10	<10	<10	15	<10	<10		<10	<10	<10
Fe $\mu\text{mol/L}$	318	82	131	213	0	1	1	5	234	149	254	206	135	111	61	11
Mn $\mu\text{mol/L}$	60	54	99	16	5	2	2	8	9	39	23	26	7	2	3	1
SO ₄ $\mu\text{mol/L}$	354	193	83	6	31	39	39	40	463	237	209	3	3	2	1	1
PO ₄ $\mu\text{mol/L}$	27	15	33	22	5	6	8	10	91	42	47	48	45	43	16	4
NH ₄ $\mu\text{mol/L}$ ^a	1048	38	403	266	0	0	0	0	14	90	79	112	699	510	21	0
NO ₃ $\mu\text{mol/L}$	0	0	0	0	0	0	0	0	84	37	0	59		0	0	0
Cl mmol/L	1.40	1.04	0.97	1.26	1.13	0.81	0.70	1.43	4.52	3.48	3.47	2.25		0.28	0.30	0.10
Na mmol/L	1.62	0.81	1.17	1.66	3.29	2.51	2.22	2.03	4.37	1.67	2.03	1.76	1.09	1.01	2.34	2.58
Mg mmol/L	0.94	0.98	1.04	1.34	0.29	0.24	0.22	0.50	2.07	1.65	1.67	1.43	0.98	1.56	0.71	0.30
K mmol/L	1.53	0.12	0.12	0.13	0.03	0.03	0.03	0.05	0.15	0.19	0.15	0.12	0.13	0.15	0.06	0.04
Ca mmol/L	1.28	1.06	1.48	1.41	0.28	0.42	0.43	0.62	2.93	3.32	2.99	2.58	2.42	1.03	0.73	0.39
$\delta^{13}\text{C-DIC}$ (‰PDB)	-13.9		-16.2		-19.2		-19.0	-19.1		-16.7				-13.9	-17.6	-19.2
¹⁴ C-DIC (FM)	1.136		1.054		0.301		0.284	0.284		1.055				0.867	0.816	0.894
³ H-H ₂ O (TU)	5.0	4.1		3.3	0.1		-0.3	0.1	3.83	3.95	3.43	1.67		-0.01	0.08	0.05

^a NH₄ was determined in Jan., 2003 in the field. Major ions and dissolved As are comparable to Jan. 2001 values reported here.

^b Na, Mg, K, Ca of Bay monitoring wells were based on samples collected on July 14, 2001.

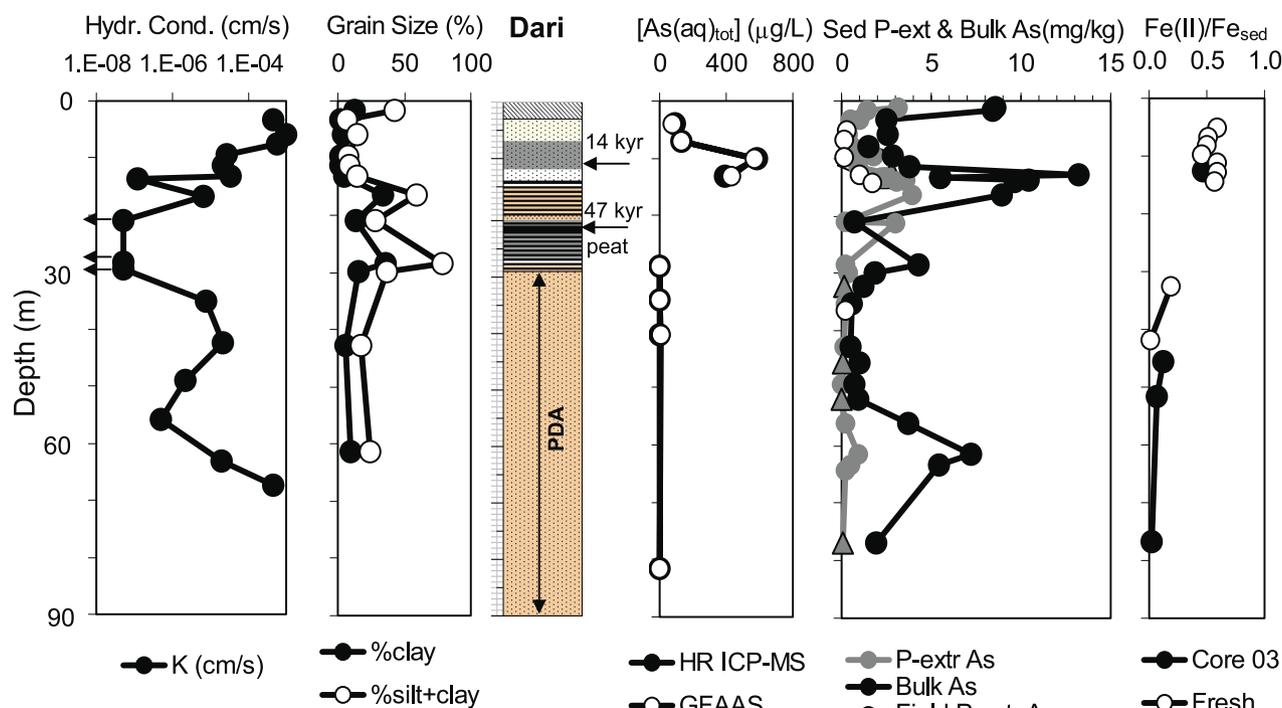


Fig. 2. Depth profiles of vertical hydraulic conductivity (K), grain size in cumulative percentages of %clay ($< 4 \mu\text{m}$), %clay with %silt ($< 63 \mu\text{m}$), color and lithologic sketches, dissolved As concentrations from the nest of monitoring wells determined by HR ICP-MS and graphite furnace atomic absorption spectrometry (GFAAS), bulk (black symbols) and the sum of first and second PO_4 extracted (gray) sediment As, and 1.2 mol/L hot HCl extracted sediment Fe(II)/Fe ratio from Dari. As concentrations are also expressed in $\mu\text{mol/L}$ units in results obtained in this study in Figs. 6 and 7. Gray triangle symbols indicate measurements made on sealed wet sediment core in September 2003. Radiocarbon ages of bulk sedimentary organic carbon, including peat, were indicated as well. Arrows pointing to the left on the hydraulic conductivity panel indicate that these are upper limits. Pleistocene deeper aquifer is abbreviated as PDA on the lithologic sketch.

vertical hydraulic conductivity measurement. A segment of undisturbed sediment of 5 cm diameter and 5 cm length was measured with the constant or falling head technique using a K-605 combination permeameter (Fetter, 1994). For a first suite of geochemical determination performed in March 2002, sediment was freeze-dried and homogenized before being subjected to various leaching procedures. In July 2003, the same core sections were sub-sampled again to repeat the same geochemical analyses on wet sediments, i.e. without freeze-drying. In September 2003, additional sealed core sections ($n = 15$) were sampled for chemical analyses of wet sediment. All samples used for bulk As determination ($n = 43$) were freeze-dried and homogenized before acid digestion.

About 20 mg of dry sediment was dissolved via the acid digestion procedure described by Zheng et al. (2003) using concentrated HF, HClO_4 and HNO_3 . Bulk As concentrations were determined by graphite furnace atomic absorption spectrometry (Perkin Elmer Analyst 800) using Pd as a matrix modifier. In parallel, ~ 1 gram of sediment was sequentially leached at room temperature using 10 mL of 1 mol/L Na_2HPO_4 (pH = 5) for 16 h and then for 24 h with a second aliquot of Na_2HPO_4 , followed by 10 mL of 1 mol/L HCl for 1 h (Keon et al., 2001). The first extraction with phosphate released 60% to 90% of the total As extracted, and $< 10\%$ additional As was typically released by the subsequent HCl extraction. In July and September 2003, the extraction solutions were purged with nitrogen and the entire procedure was conducted in a N_2 -filled glove bag. These precautions to limit oxidation of the sediment were not taken during the first batch of analyses in March 2002. Dissolved As concentrations in the extraction leachates were determined by cathodic stripping voltammetry, a method with a detection limit of $0.5 \mu\text{g/L}$ (Barra and dos Santos, 2001; He et al., 2004). The results were confirmed by re-analyzing a subset of samples for As by HR ICP-MS (section 2.3.4), which also quantified Fe and S concentrations in the leachate at the same time.

In October 2003, the P-extractable As fraction in freshly-collected slurries of sediment and groundwater was determined by adding Na_2HPO_4 and NaOH directly in the field to 100-mL needle-sampler tubes to yield a ~ 1 mol/L neutral phosphate solution. The headspace was purged with nitrogen immediately after adding the reagents and the extractions were conducted at pH ~ 7 for 24 h. The leachates from this set of extractions were all analyzed for As by HR ICP-MS.

In September 2003, wet sediment sampled from core sections collected in January 2001 was also leached in 1.2 mol/L HCl at 80°C for 30 min to determine the Fe(II)/Fe ratio of the leachable Fe fraction (Horneman et al., 2004). Iron concentrations and speciation in the leachate were determined by colorimetry with ferrozine. In October 2003, the same procedure was followed at both sites to measure the leachable Fe(II)/Fe fraction on sediment within a few hours of recovery by the needle-sampler.

3. RESULTS

3.1. Dissolved Arsenic Profiles

Dissolved As concentrations in groundwater from the monitoring wells ranged from < 1 to $570 \mu\text{g/L}$ at Dari (Fig. 2) and from 10 to $470 \mu\text{g/L}$ at Bay (Fig. 3). Concentrations increased gradually with depth in the shallow aquifers to reach maxima at ~ 13 and ~ 14 m at the Dari and Bay sites, respectively (Table 1). Groundwater from the four deeper monitoring wells at Dari (29–82 m) all contained $< 1 \mu\text{g/L}$ As (Fig. 2). This pattern is consistent with the depth distribution of As in the area surrounding the Dari site based on the numerous existing wells

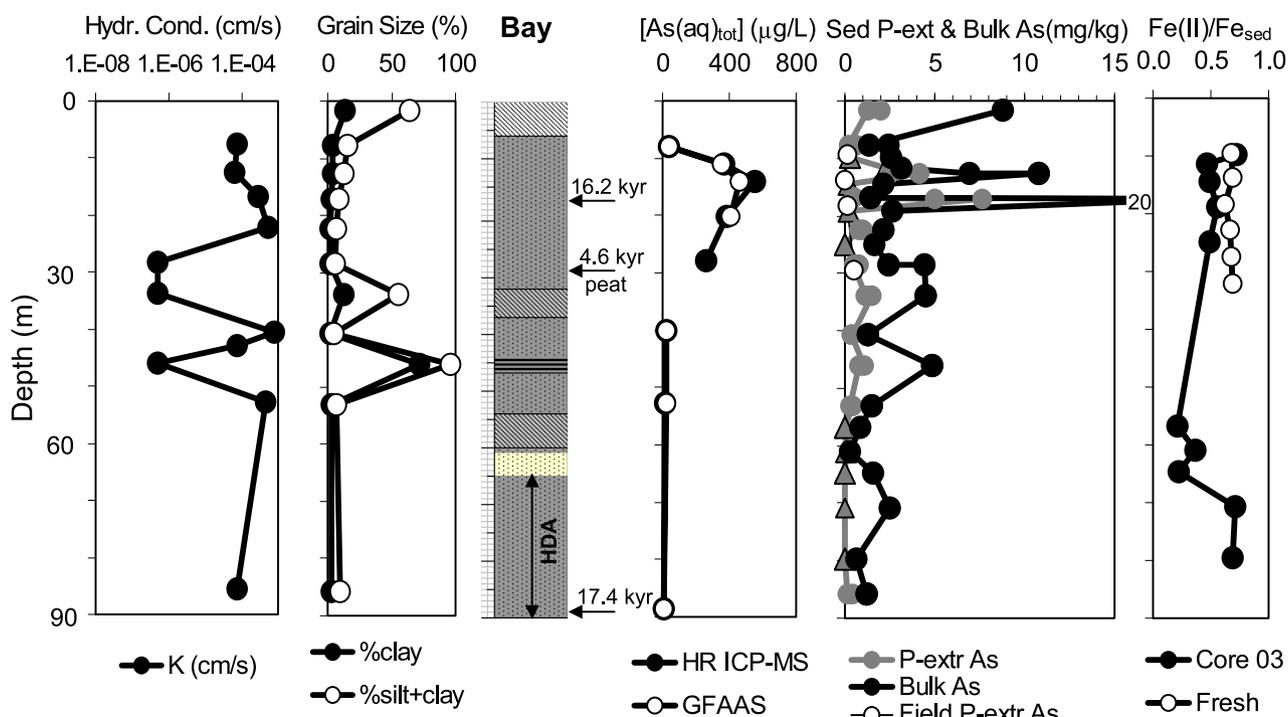


Fig. 3. Depth profiles of vertical hydraulic conductivity (K), grain size in cumulative percentages of %clay ($< 4 \mu\text{m}$), %clay with %silt ($< 63 \mu\text{m}$), color and lithologic sketches, dissolved As concentrations from the nest of monitoring wells determined by HR ICP-MS and graphite furnace atomic absorption spectrometry (GFAAS), bulk (black symbols) and the sum of first and second PO_4 extracted (gray) sediment As, and 1.2 mol/L hot HCl extracted sediment Fe(II)/Fe ratio from Bay. Triangle gray symbols indicate measurements made on sealed wet sediment core in September 2003. Radiocarbon ages of bulk sedimentary organic carbon, including a peat sample recovered in later drilling, are indicated as well. Holocene deeper aquifer is abbreviated as HDA on the lithologic sketch.

deeper than 30 m (see Fig. 9 in van Geen et al., 2003a). At Bay (Fig. 3), groundwater from the three deeper wells (40 to 88 m) contained low yet unmistakably detectable levels of As from 10 to $25 \mu\text{g/L}$. This pattern is generally consistent with the depth distribution of As in the area surrounding the Bay site since the reported depth of only 3 existing wells was > 40 m (see Fig. 10 in van Geen et al., 2003a).

3.2. Lithology and Sediment Dating

A muddy section, 15 m thick at Dari and 28 m at Bay, composed of several silt/clay sediment layers separates the upper sandy section of the shallow aquifers containing groundwater high in As from the lower sandy section of the deeper aquifers associated with lower As levels at both sites (Figs. 2 and 3). The terminology used in this study follows the classification based on the proportion of sand ($> 63 \mu\text{m}$), silt ($4\text{--}63 \mu\text{m}$) and clay ($< 4 \mu\text{m}$), where “mud” refers to a mixture of silt and clay (Folk et al., 1970). The muddy section at the Dari site contains a black peat layer at ~ 21 m depth. At the Bay site, two sandy layers permitted the installation of two monitoring wells within the silt/clay section separating high and low-As aquifers. At both sites, the shallow sandy aquifers are covered by a heterogeneous near-surface silty section.

Significant differences in sediment color between the Dari and Bay sites were recorded visually in the field. In the shallow section at the Dari site, the sediment is initially light brown and

turns gray towards the depth with maximum groundwater As concentration (Fig. 2). The deeper sandy aquifer at the Dari site is distinctly brown to orange. In contrast, the sediment from Bay is mostly gray, with the exception of a brown interval between 62 and 65 m depth within the lower sandy layer (Fig. 3).

Radiocarbon dating based on 2 peat samples constrains the depositional history at the two sites (Table 2). The radiocarbon age of the peat layer at the Dari site (Fig. 2) at 21 m depth (thickness < 10 cm, based on an X-ray image) is 46.7 ka conventional radiocarbon years before present (BP) (Stuiver and Pollack, 1977). This is near the practical limit for radiocarbon dating (Zheng et al., 2002) and indicates that the peat layer can be considered radiocarbon-dead. A peat sample recovered from 29 m depth during separate drilling at the Bay site in January 2003 yielded a much younger radiocarbon age of 4.6 ka BP (Fig. 3). This age is more accurate than bulk organic carbon ages from the site (see below). The two dated peat samples therefore suggest that the deeper aquifer sediment was deposited during the Pleistocene at Dari while the entire sediment section accumulated more recently and more rapidly at Bay.

Three bulk organic carbon radiocarbon measurements provide additional constraints on the depositional history of the two sites, even though such radiocarbon ages are likely to be biased by thousands of years because of the contribution of old

Table 2. Radiocarbon dating of sediment samples from Araihasar, Bangladesh.

Sample description	C phase	%C ^a	¹⁴ C age (yr)	FM ^b	FM (±)	δ ¹³ C (‰PDB)	NOSAMS# ^c
<i>Dari: 23.785°E, 90.603°N</i>							
Dari 36-38 ft BT, 11.4 m	TOC	0.05	13,750 ± 130	0.1801	0.0028	-23.49	OS-36317
Dari 68-70 ft BB, 21.3 m	Peat	8.60	46,700 ± 2100	0.0030	0.0008	-33.73	OS-31567
<i>Bay: 23.780°E, 90.640°N</i>							
Bay 54-56 ft BB, 17.1 m	TOC	0.14	16,200 ± 65	0.1334	0.0011	-22.75	OS-36440
Bay NS09-94 ft, 28.7 m	Peat		4,620 ± 30	0.5624	0.002	-28.36	OS-39159
Bay 280-282 ft BT, 85.8 m	TOC	0.12	17,250 ± 100	0.1167	0.0015	-26	OS-37134

^a Total combustion without pre-acidification thus includes inorganic C.

^b FM stands for fraction of modern carbon. FM of 1 indicates ¹⁴C age of 0.

^c NOSAMS# is the tracking number at the National Ocean Science Accelerator Mass-Spectrometer facility.

terrestrial carbon (Eglinton et al., 1997). The bulk organic carbon ages are used here only to place upper limits on the age of the deposits. Analysis of bulk organic carbon from 11 m depth in the upper sandy section at Dari yielded a radiocarbon age of 13.8 ka BP (Table 2). This information combined with the radiocarbon-dead peat layer underneath suggests that much of the shallow aquifer at Dari was deposited after the low-stand in sea level ~20 ka ago. At the Bay site, bulk sediment organic carbon yielded a comparable radiocarbon age of 16.2 ka BP for the shallow sandy aquifer at 17 m (Table 2). This is only ~1 ka younger than the bulk organic carbon analysis from the same site of 17.3 ka BP at a depth of 85 m. The ~12-ka older ages of bulk organic carbon compared to the peat layer confirms the strong imprint of old terrestrial organic carbon. We conclude that, in contrast to the Dari site, the entire 91-m section recovered from the Bay site was deposited after the last sea-level low stand ~20 ka ago.

3.3. Variations in Groundwater Level

The seasonal amplitude of variations in water levels is ~4 m for all monitored wells. Water levels lag precipitation linked to the summer monsoon by 1 to 2 months (Fig. 4). At the Dari site, water levels in the four shallow wells are on average 1.2 m higher than in the 4 deeper wells, and the differences vary through the seasons from -0.3 to +3.3 m (Fig. 4). The rise in water level in the shallow wells starts in early to mid March each year and precedes that of the deeper wells by up to 1 month, resulting in the largest difference water levels between the shallow and deeper aquifers in May. From February through September, water levels in the shallow wells at Dari also closely track the water level in the nearby stream that was monitored during the same period (Fig. 4). Towards the end of the dry season, the water level drop in the shallow and deeper aquifers lags the local stream by up to 2 weeks and 2 months, respectively. The lowest water levels in the shallow aquifer match the lowest river stages of the local stream closely, while the deeper aquifer matches the low stands of the regional larger rivers (e.g. Buriganga, which is located ~25 km south-west of our site, Fig. 4).

The difference in water level between shallow and deeper wells at the Bay site is not as pronounced as at Dari. The difference between the deepest of the shallow aquifer wells above the first layer of finer sediment (28 m) and the well directly below the same layer that is low in As (40 m) averages 0.15 m and ranges seasonally from -0.28 to 0.85 m. Only

water levels in the deepest well at 88 m, and to a lesser extent the next deepest well at 53 m, show water levels > ~0.5 m lower than levels recorded in shallower wells at Bay (Fig. 4). As at Dari, water levels in shallow wells at Bay generally track the level of the stream located between the two sites during the wet season and lag the stream during the dry season. None of the wells at Bay reach levels as low as the Buriganga River during the dry season.

3.4. Groundwater Dating

At both sites, groundwater from all shallow (<28 m) monitoring wells always contained detectable levels of ¹⁴C and/or ³H produced by atmospheric testing of nuclear weapons starting in the 1950s (Table 1). This indicates a groundwater age relative to recharge < 50 yr for the shallow aquifers at both sites, and considerably less at the depth of the shallowest wells containing the highest levels of these transient tracers (Fig. 5).

No well deeper than 29 m at Dari, and deeper than 40 m at Bay contained detectable levels of bomb-produced ¹⁴C and/or ³H (Table 1). This suggests a much longer residence time relative to recharge that is consistent with the significantly depleted radiocarbon content of DIC (Fig. 5). At the Dari site, the fraction of modern carbon (FM) is nearly constant with values of ~0.3 FM between 29 and 82 m depth. At the Bay site, radiocarbon DIC FM values range from 0.84 to 0.93 between 40 and 89 m depth (Fig. 5).

3.5. Sediment Geochemistry

3.5.1. Fe(II)/Fe and preservation of core samples

Fe(II)/Fe ratios in the acid-leachable Fe fraction of the sediment ranging between 0.5 and 0.7 in shallow aquifers at both the Dari and Bay sites provide a clear indication of reduction driven by the mineralization of organic matter (Figs. 2 and 3). Comparison of these measurements for sealed core samples analyzed in September, 2003 and freshly-collected sediment suggests that the leachable Fe fraction was not drastically altered by storage (Figs. 2 and 3). Considerably lower Fe(II)/Fe ratios (0.01–0.18) are observed in the deeper light brown/orange sands at the Dari site. This is consistent with a relationship between sediment color and redox conditions pointed out qualitatively by British Geological Survey and Department of Public Health Engineering (2001) and established quantitatively with Fe(II)/Fe and diffuse spectral reflectance measure-

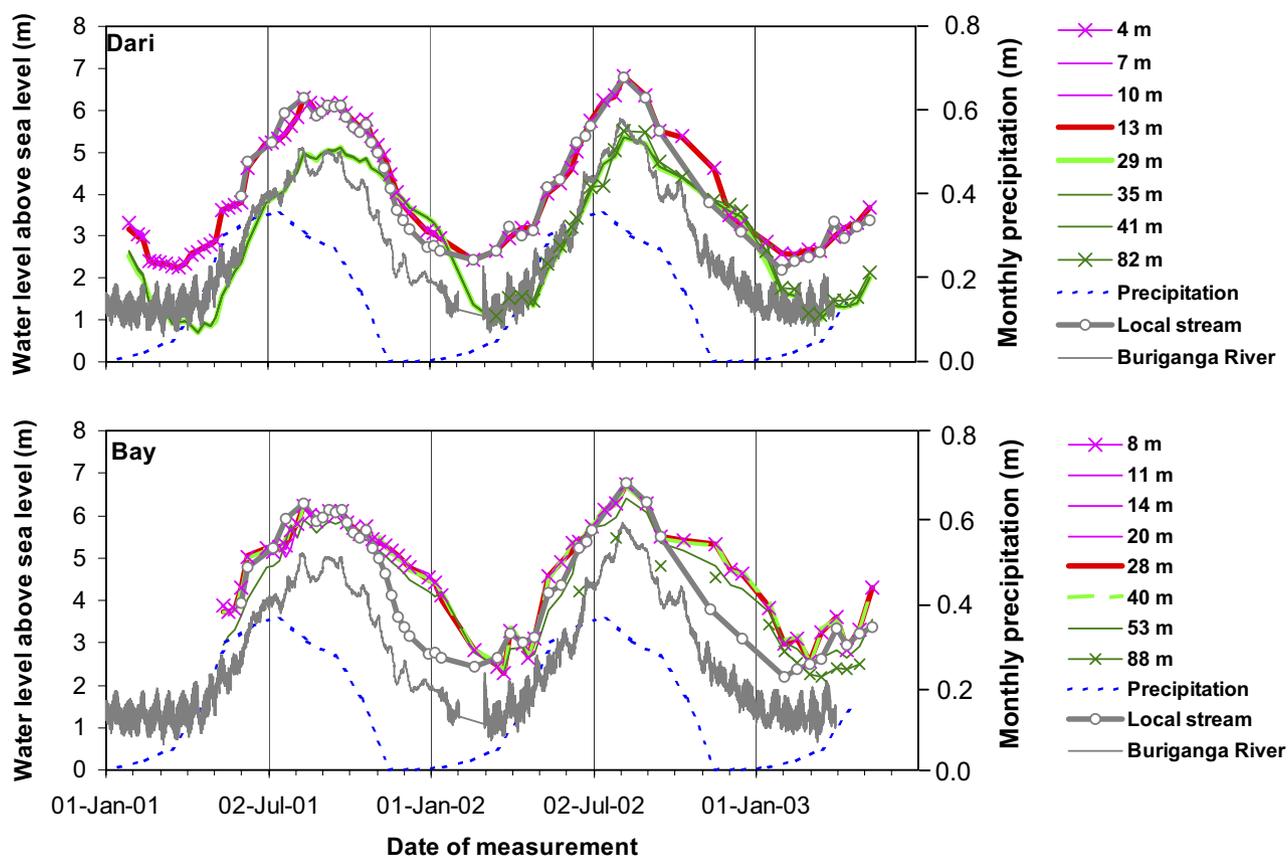


Fig. 4. Variations of water level relative to sea level in the nest of monitoring wells from both sites from January 2001 to March 2003. Also shown is the water level variation of the local stream near Dari (labeled as "Stream" in Fig. 2) from a fixed point on a bridge. The lower gray curve shows the hydrograph of the Buriganga River, ~25 km distant. All shallow monitoring wells (4, 7, 10, 13 m) show almost identical water level variation with time at Dari, so do the deeper monitoring wells (29, 35, 41, 82 m). Deeper monitoring wells show hydraulic head substantially lower than that of the shallow monitoring wells during most part of the year. At Bay, water level variations of the two deeper monitoring wells (88 m, crosses; 53 m) are different from that of the shallow wells (8, 11, 14, 20, 28 m). But the shallowest of the deeper wells (40 m, light green) shows a water level trend almost identical to the other shallow wells. The monthly precipitation data (dotted blue line) is an average based on data from a meteorological station located in Mil-barak Dhaka City from 1957 to 2001.

ments by Horneman et al. (2004). The gray color of most of the material recovered from the deeper aquifers at the Bay site indicates reducing conditions throughout the section, with the exception of a brown sand layer at 62 to 65 m depth with a lower proportion of Fe(II) in the leachable Fe fraction (Fig. 3).

3.5.2. Bulk As in the sediment

There is no simple relationship between the bulk As content of the sediment, ranging from 1 to 20 mg/kg, and the dissolved As content of groundwater in monitoring wells at the same depth (Figs. 2 and 3). The peat sample at ~21 m from Dari contained only 0.7 mg/kg bulk As. Despite differences in the age and redox state of deeper aquifer sediments at the Dari and Bay sites, their bulk As content does not differ significantly (Table 3). Three samples between 56 and 63 m depth at Dari displayed bulk As concentrations between 5 to 10 mg/kg (Fig. 2). The average bulk As content of all other deeper aquifer samples from Dari and Bay is 1.2 ± 0.7 mg/kg ($n = 13$), i.e. less than the crustal average of 2 mg/kg. The bulk As content of the heterogeneous silty layers that cap the shallow aquifers

at both sites as well as the fine-grained sediment layers underneath was variable and generally elevated (up to ~9 mg/kg).

3.5.3. P-Extractable As in the sediment

There is a significant contrast in the concentration of P-extractable As in the shallow (1–6 mg/kg) and deeper aquifers (< 0.1–1 mg/kg) at both sites (Figs. 2 and 3). There is, however, no simple correlation in P-extractable As concentrations in the shallow aquifers with groundwater As concentrations. There is also no simple correlation between P-extractable As concentrations in the shallow aquifers sands and the percentage of fine grained material (either % < 16 μm or % < 4 μm) present in the sediment (Fig. 2). In the case of extractions conducted in the laboratory with the core samples, the potential contribution of groundwater As adsorbed on the sediment during storage was not taken into account but would have been small: adsorption of 500 $\mu\text{g/L}$ As from groundwater would have contributed no more than 0.2 mg/kg to the potentially P-extractable As fraction, assuming a porosity of 40% and a sediment density of 2.5 g cm^{-3} .

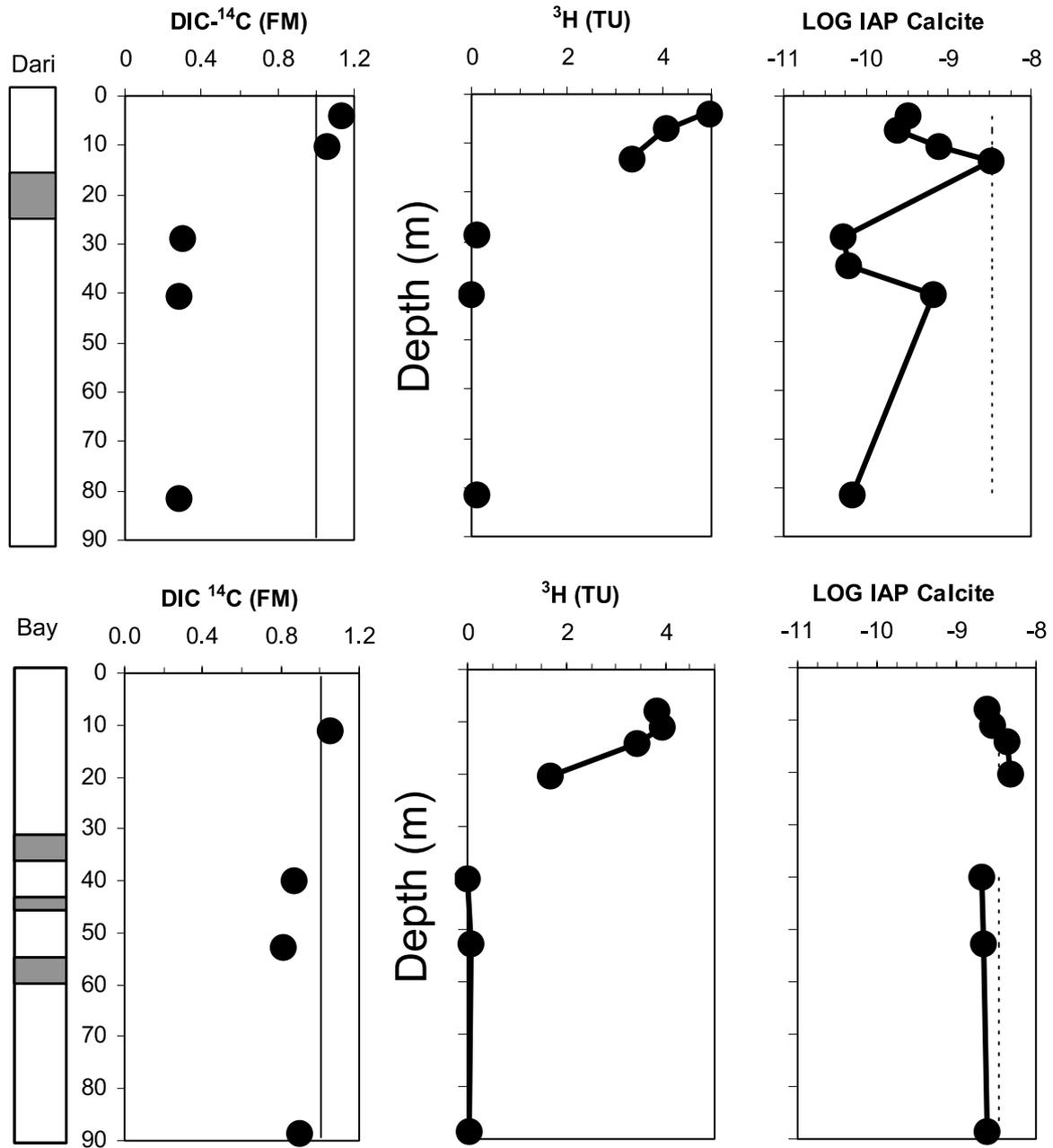


Fig. 5. Depth profiles of groundwater DIC-¹⁴C, ³H, and LOG IAP (ion activity product) compared to LOG K_{sp} of calcite (dashed line) computed using PHREEQC from western site Dari (upper panel) and eastern site Bay (lower panel). The saturation index (SI, see text) is calculated by subtracting LOG K_{sp} from LOG IAP. The sketches to the left indicate the depths of muddy sections that are poorly permeable.

Sample storage appears to have had little effect on the amount of P-extractable As in the sediment. At the Dari site, where variations in P-extractable As are not as large as at Bay, the depth trends in concentrations of P-extractable As are very similar for stored samples and sediment treated immediately after collection in October 2003. For the extractions conducted in the field, the initial content of the groundwater was taken into account to calculate the net increase in dissolved As in the needle-sampler tube caused by the addition of phosphate. The field measurements (*n* = 4) evidently did not include a sample elevated in P-extractable As at the Bay site, which is quite possible given the high

degree of spatial variability. Comparable results obtained for repeated P-extractions conducted on core samples opened in March 2002 and re-sampled and re-analyzed in July 2003 confirm that this particular As fraction is relatively insensitive to storage. Core samples opened in September 2003 (triangles, Figs. 2 and 3) also fit the depth trend obtained earlier.

3.6. Profiles of Other Dissolved Constituents

Although dissolved oxygen was not detected (i.e. < 0.01 mg/L) in any of the groundwater samples, several indicators

Table 3. Arsenic content of aquifer sediments from Bangladesh.

Sample description	Stratigraphy	Avg. groundwater As ^a ($\mu\text{g/L}$)	Avg bulk sed As (mg/kg)	Avg sed ext-As ^b (mg/kg)	Ref
<i>Aquifers with low groundwater As</i>					
Nayanganj, Araihasar, Dari deeper	Dupi Tila	<1	2.3 ± 2.2 ($n = 11$)	0.2 ± 0.3 ($n = 12$)	This study
Nayanganj, Araihasar, Bay deeper	Older Holocene	10	1.2 ± 0.9 ($n = 5$)	0.1 ± 0.1 ($n = 5$)	This study
Munshiganj, deep ^c	Dupi Tila	4	~ 1 ($n = 3$)	<0.1 ($n = 3$)	Swartz
West Bilat Haripur	Holocene?	<5		0.17 ($n = 7$)	BGS,01
Dhaka	Dupi Tila	<5		0.17 ($n = 3$)	BGS,01
Thakurgaon	Holocene alluvial fan	<5		0.15 ($n = 2$)	BGS,01
Khitta	Dupi Tila	<5		0.13 ($n = 8$)	BGS,01
Purba Fargilpur	Dupi Tila	<5		0.06 ($n = 7$)	BGS,01
<i>Aquifers with elevated groundwater As</i>					
Nayanganj, Araihasar, Dari shallow	Holocene	135	5.8 ± 4.2 ($n = 9$)	1.7 ± 1.2 ($n = 9$)	This study
Nayanganj, Araihasar, Bay shallow	Holocene	234	4.4 ± 5.0 ($n = 11$)	1.4 ± 2.0 ($n = 11$)	This study
Munshiganj, shallow ^c	Holocene	250	~ 2 ($n = 27$)	<0.1 ($n = 27$)	Swartz
Chanlai DW2	Holocene			2.53 ($n = 8$)	BGS,01
Lakshmipur piez ^d	Holocene	425	2.3 ± 1.0 ($n = 6$)	2.13 ($n = 49$)	BGS,01
West Latifpur	Holocene			1.7 ($n = 5$)	BGS,01
Ch. Nawabganj piez ^d	Holocene	268	5.8 ± 5.0 ($n = 4$)	1.57 ($n = 19$)	BGS,01
Bhimpur	Holocene			1.38 ($n = 6$)	BGS,01
Rajarampur DW1	Holocene			1.07 ($n = 16$)	BGS,01
Pirgacha	Holocene			0.85 ($n = 3$)	BGS,01
Faridpur piez ^d	Holocene	231	1.3 ± 0.5 ($n = 5$)	0.48 ($n = 43$)	BGS,01

^a Average groundwater As concentrations from existing tube wells in the area.

^b Average extractable As from sediment by phosphate (this study and Swartz) and by oxalate (BGS and DPHE, 2001).

^c Average for data in Munshiganj was based on depth profile only.

^d The three special study area reported by BGS and DPHE, 2001 where wells were installed and cores were taken.

show distinct difference in redox conditions for the aquifers tapped by the monitoring wells (Table 1). ORP values (Fig. 6) were highly negative for the four shallowest wells at the Dari site (-70 to -160 mV) and positive in the four deepest wells (30 – 40 mV). In contrast, ORP values (Fig. 7) were highly negative (-120 to -180 mV) for all eight monitoring wells at the Bay site. Dissolved Fe concentrations were elevated in the four shallow wells at the Dari site (80 – 320 $\mu\text{mol/L}$) and much lower in the four deeper wells (0.5 – 6 $\mu\text{mol/L}$). Fe concentrations were also highest in the two shallowest wells at the Bay site but declined more gradually to a minimum of 11 $\mu\text{mol/L}$ in the deepest well (Fig. 7). In the case of dissolved sulfate, concentrations also declined with depth at both sites although the lowest concentrations were observed in groundwater from the deeper wells at the Bay site rather than the Dari site. Unlike the previous observation at site Munshiganj of Harvey et al. (2002), NH_4^+ profiles do not closely resemble dissolved As profiles in Araihasar. Neglecting the very high NH_4^+ value (1048 $\mu\text{mol/L}$) at the shallowest well (4 m) at the Dari site, the ammonium and arsenic depth profiles are similar between 7 and 13 m (Fig. 6). At the Bay site, both the arsenic and ammonium have distinct peaks, but the ammonium peak at ~ 28 m is twice as deep as the arsenic maximum (Fig. 7).

There is a large difference in the major ion composition of shallow and deep aquifers. At both sites, conductivities in the deeper aquifers (382 ± 87 $\mu\text{S/cm}$; Figs. 6 and 7) are lower than in the shallow aquifers (780 ± 263 $\mu\text{S/cm}$; Figs. 6 and 7). The difference in conductivity reflects mostly differences in alkalinity (mostly HCO_3^- concentrations, but not Cl^- concentrations (Figs. 6 and 7). Deeper aquifer waters are of the Na^+ - HCO_3^- type at both sites (Figs. 6 and 7) except the 43 -m well at Bay. In contrast, shallow aquifer waters are of the Ca^{2+} - Mg^{2+} - HCO_3^- type (Figs. 6 and 7). The majority of the ground-

water samples contain very little K^+ , with exception of the shallowest (< 10 m) sample from Dari (Fig. 6). This K^+ -rich shallow groundwater also contained an anomalously high NH_4^+ level (~ 1000 $\mu\text{mol/L}$). Again unlike the observations made by Harvey et al. (2002), Ca^{2+} concentrations in shallow (< 28 m) monitoring wells in Araihasar do not vary in parallel with As concentrations.

4. DISCUSSION

4.1. Associations of As in the Solid Phase

A key finding of the present study is that P-extractable As concentrations are systematically low in sediments from the two deeper aquifers that are low in dissolved As, despite a very different depositional history at the two sites (Figs. 2 and 3). The association seems to hold also in other regions of Bangladesh and may therefore be generalizable to fluvio-deltaic sediments of the region (Table 3). At the Munshiganj site studied in detail by Harvey et al. (2002) and Swartz et al. (2004), P-extractable As concentrations were also low (< 0.1 mg/kg, $n = 3$) in deeper aquifers containing little dissolved As, and this for intervals that included gray as well as orange sands. The number of samples in their study was too small, however, to identify a systematic difference relative to the more variable and generally elevated P-extractable As concentrations ($n = 26$) in shallower gray sediment (Table 3). Whether the converse relation holds, i.e. the extent to which elevated P-extractable As in the sediment quantitatively leads to elevated As concentrations in groundwater, cannot be established based on the available data. This is in part because of the variability in P-extractable As concentrations with depth and the depth-averaging over 0.9 -m screen interval that is inevitable for

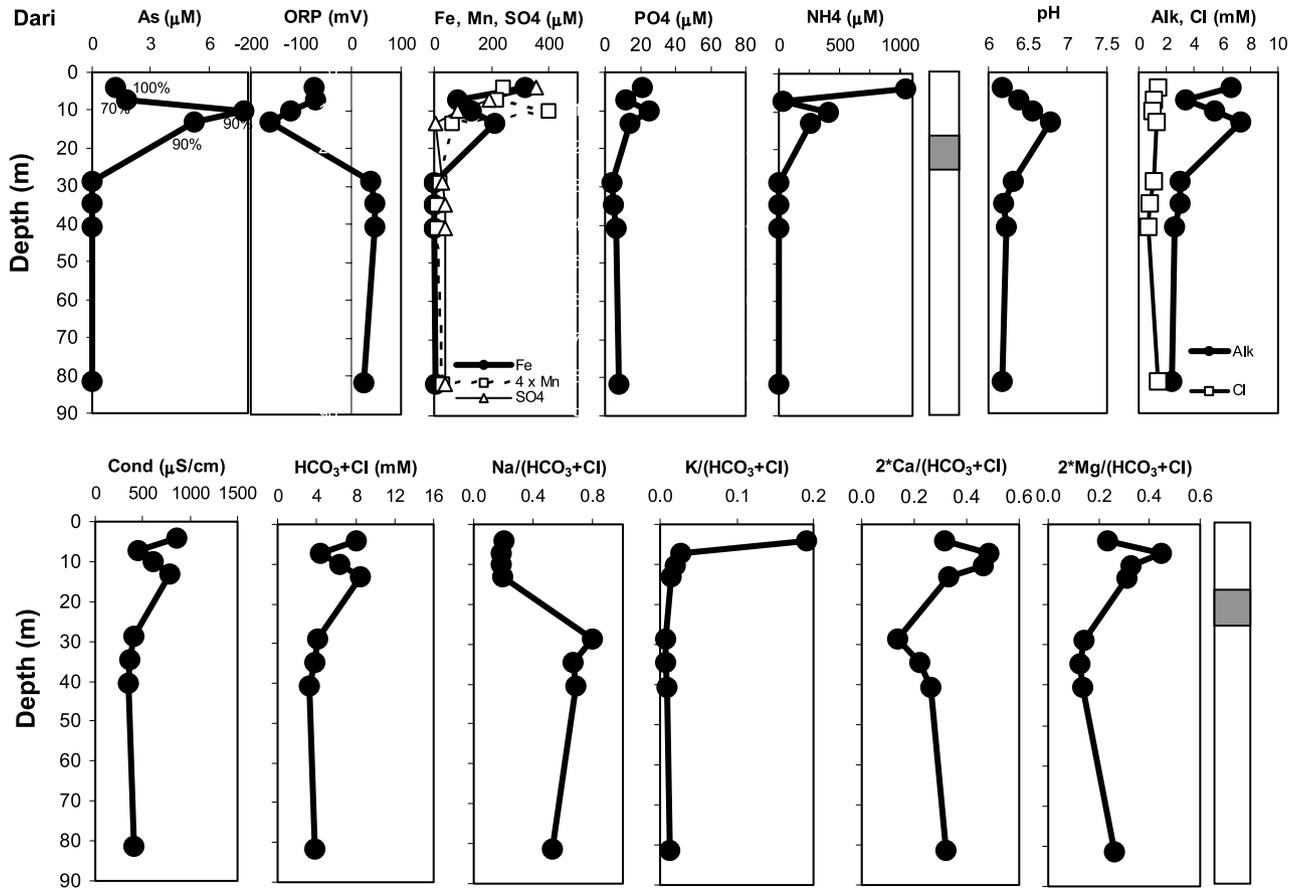


Fig. 6. Depth profiles of groundwater As, ORP, Fe, Mn, SO₄, PO₄, NH₄, pH, Alkalinity and Cl, electrical conductivity, and major ions from the nest of monitoring wells at Dari (Fig. 1). The values next to the profile indicate the percentage of arsenite based on anion exchange separation from arsenate. Brief sketches of lithologic units are included in both panels.

groundwater drawn from a monitoring well (Figs. 2 and 3). In addition, other geochemical and microbiological factors that may influence the mobility of arsenic have yet to be understood.

What is the nature of the As fraction that is released from the sediment by a 1 mol/L phosphate solution at pH 5 to 7? Phosphate has been shown to displace both arsenate and arsenite adsorbed on synthetic goethite (Keon et al., 2001). Application of phosphate fertilizer to soil in Southern Switzerland has also been shown to release As (Pfeifer et al., 2004). The relatively mild extraction suggests that the mobilizable As is bound to particle surfaces and not embedded within the crystalline structure of an insoluble mineral. Indeed, the phosphate extractions do not seem to dissolve significant amounts of Fe-oxides or Fe-sulfides: the extracts of the sediment contained < 0.1 g/kg Fe and < 10 mg/kg S, respectively. The amounts of P-extractable As from the shallow aquifer sediment dominated by sand (Figs. 2 and 3) do not correlate with the proportion of fine sediments (< 16 or < 4 µm) in these samples. We do observe a correlation between the P-extractable As content and hot HCl-leachable Fe content of shallow aquifer sediments at both sites ($R^2 = 0.42, n = 11$). The presence of mobilizable As therefore appears to be more closely related to the abundance of Fe oxyhydroxide coatings rather than grain size of aquifer solids.

A close association between As and Fe in Bangladesh sed-

iment has been demonstrated with a more aggressive reductive-dissolution procedure using oxalate (Nickson et al., 2000; British Geological Survey and Department of Public Health Engineering, 2001). An association between the sum of Mg- and P-liberated As and the sum of HCl, oxalate and Ti/citrate/EDTA liberated Fe has also been reported (Swartz et al., 2004). At the micron scale, Swartz et al. (2004) confirmed by X-ray microprobe analysis a strong association between As and Fe on the surfaces of shallow gray Bangladesh sediments. The spatial correlation between the intensity of the As- and Fe-fluorescence signals determined in this study was much weaker for a deeper sample of orange sand.

The range and average of As concentrations (up to 6 and 1.5 mg/kg, respectively, Table 3) extractable with oxalate from aquifer material associated with high As in groundwater from 8 sites in Bangladesh (see Table 11.14, British Geological Survey and Department of Public Health Engineering, 2001) is similar to that observed in shallow sediments at the Dari and Bay sites. Aquifer material from areas with generally low groundwater As concentrations also contains < 0.2 mg/kg oxalate-extractable As (see Table 11.14, British Geological Survey and Department of Public Health Engineering, 2001). The data suggest that whereas reductive-dissolution probably would have extracted significant quantities of As from Araihasar sediment as well, such a relatively aggressive treatment is not required.

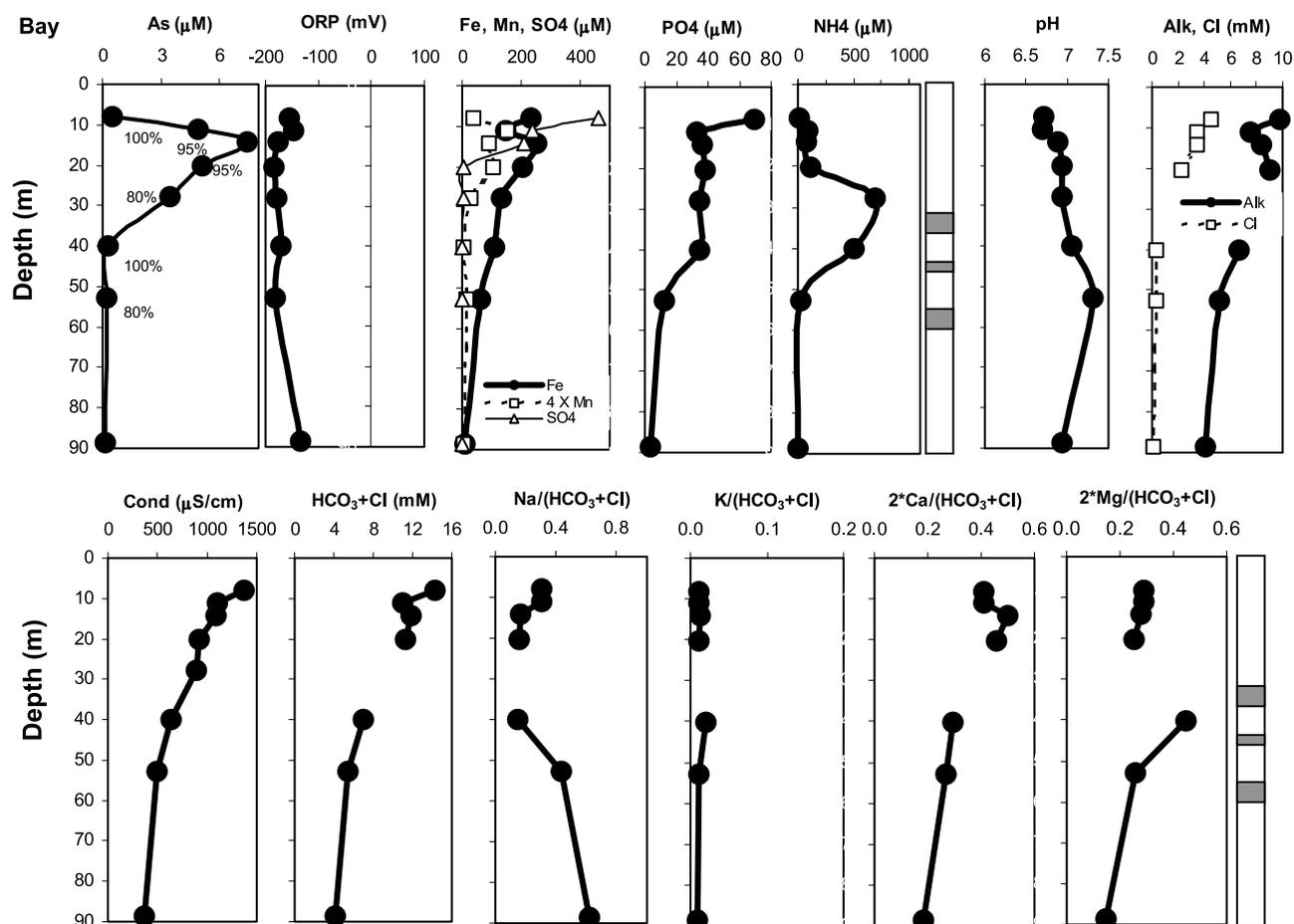


Fig. 7. Depth profiles of groundwater As, ORP, Fe, Mn, SO_4 , PO_4 , NH_4 , pH, Alkalinity and Cl, electrical conductivity, and major ions from the nest of monitoring wells at Bay. The values next to the profile indicate the percentage of arsenite based on anion exchange separation from arsenate. Brief sketches of lithologic units are included in both panels.

Displacement of As from adsorbing surfaces by P can release comparable amounts. This suggests, in turn, that As may not be uniformly distributed in various Fe oxyhydroxides phases but concentrated in accessible surface sites, as inferred from recent incubations of Bangladesh sediment (Islam et al., 2004; van Geen et al., 2004b).

The nature of the surfaces sorbing arsenic in the sediments remains elusive, although it is likely to include mixed Fe phases. The greatest amounts of P-extractable As are found in sediments with high Fe(II)/Fe ratios in the shallow aquifer (Figs. 2 and 3), suggesting that As may not be solely adsorbed to Fe(III) oxyhydroxides (Horneman et al., 2004). Dixit and Hering (2003) indeed recently showed that arsenate and arsenite bind strongly to the surfaces of a mixed Fe(II/III) phase such as magnetite. Other potential candidates are Fe(II) or mixed valence Fe(II/III) phases such as siderite (Saunders and Swann, 1992), vivianite (House, 2003), or green-rust (Randall et al., 2001).

4.2. Conditions Leading to As Mobilization

The reduction of As(V) to As(III) is frequently cited as a cause of As mobilization under reducing conditions (e.g. Ah-

mann et al., 1997). Even though 70% to 100% of dissolved As is arsenite at the Dari and Bay sites (Figs. 6 and 7), this is probably not a dominant factor leading to mobilization because it is now recognized that both As(III) and As(V) can strongly sorb to Fe oxyhydroxide phases under a wide range of conditions (Inskeep et al., 2002; Dixit and Hering, 2003). Van Geen et al. (2004b) also recently observed that oxidation of As(III) to As(V) did not preclude significant mobilization during a 2-month incubation of gray shallow sediment from Bangladesh.

Whereas the reduction of As on its own probably cannot explain widespread mobilization in Bangladesh aquifers, reductive-dissolution of the Fe oxyhydroxide sorbent has been widely invoked as a key process (Nickson et al., 1998, 2000; McArthur et al., 2001; British Geological Survey and Department of Public Health Engineering, 2001; Harvey et al., 2002; Swartz et al., 2004; Zheng et al., 2004). The same studies suggest, however, that the presence of dissolved Fe in groundwater may not be a sufficient or a necessary condition for observing elevated As concentrations in groundwater. At the Dari and Bay sites, depth profiles of dissolved As and Fe do not resemble each other in either the shallow or the deeper aquifers, even if dissolved Fe concentrations are higher in the shallow aquifers (Figs. 6 and 7). By comparing groundwater As con-

centrations and the redox state of the sediment as indicated by reflectance and Fe(II)/Fe ratios at a half-dozen sites in Arai-hazar (including Dari), Horneman et al. (2004) suggested a threshold of Fe(II)/Fe \sim 0.5 in the acid-leachable Fe fraction of the sediment below which elevated groundwater As concentrations are not observed.

Although gray sediment characterized by Fe(II)/Fe ratios of $>$ 0.5 is more likely to contain groundwater with elevated dissolved As (Horneman et al., 2004), the gray sediment from the deeper aquifer of Bay does not. At the Bay site, the 88-m well provides groundwater low in As despite an acid-leachable Fe(II)/Fe ratio well over 0.5 in sediment at the same depth (Fig. 3). Reducing conditions are confirmed by negative ORP readings (Fig. 7 and Table 1). The low concentration of P-extractable As between 60 and 90 m depth may provide an element of the puzzle. Bulk sediment As concentrations ($n = 5$) of this formation ranged from 0.3 to 2.5 mg/kg, averaging 1.2 ± 0.9 mg/kg (Table 3). This suggests that $<$ 10% of the bulk As is P-extractable for this interval (Table 3). For comparison, \sim 30% of the bulk sediment As is P-extractable in the sediments from the shallow Holocene aquifers at both sites (Table 3). Dissolved As concentrations in the deeper aquifer at Bay may therefore be low because the sorption capacity of the sediment relative to the limited amount of relatively mobile As is sufficient to prevent a large transfer to solution.

4.3. Groundwater Age in Deeper Aquifers

Potential dissolution of old calcium carbonate must be evaluated to interpret the DIC radiocarbon results in terms of groundwater ages. The carbonate concentration in the monitoring wells and the saturation index (SI) relative to calcium carbonate (Fig. 5) was calculated using PHREEQC program based on alkalinity and pH values as well as other major ion concentrations. The results show that groundwater in the monitoring wells at Dari is under-saturated with respect to calcite, with SI values ranging from -1.8 to -0.6 , with the exception of the deepest shallow well showing SI value of 0 (Fig. 5). Groundwater in the monitoring wells at Bay is closer to saturation with respect to calcite with SI values ranging from -0.1 to 0.2; the two wells with the highest level of As are supersaturated with respect to calcite (SI: 0.1–0.2; Fig. 5). Supersaturation with respect to calcite for groundwater elevated in As has been observed at a number of sites in Bangladesh, but the potential implications for As mobilization are still unclear (Swartz et al., 2004; Zheng et al., 2004).

Dissolution of old detrital carbonate could result in an overestimate of the groundwater age. A simple mass balance places an upper limit on such a potential bias. At the Dari site, if all dissolved Ca in the three deepest wells (0.3–0.6 mmol/L) originated from dissolution of radiocarbon-dead calcite ($\Delta^{14}\text{C FM} = 0$), then groundwater DIC corrected for this input would contain 0.33 to 0.38 FM in $\Delta^{14}\text{C}$. This would only reduce the radiocarbon ages of 10,000 yr by 800 to 2000 yr. For the younger waters ($\Delta^{14}\text{C FM}$ 0.89, 0.84, 0.93, Table 1) in the deeper aquifers at Bay, the bias introduced by calcite dissolution could be more significant even if the groundwater is only slightly undersaturated with respect to calcite. If all dissolved Ca in the three deepest wells at this site (0.4–1 mmol/L) originated from radiocarbon-dead calcite, then DIC of water

from these wells corrected for this input could essentially be modern ($\Delta^{14}\text{C FM} \sim 1$). The \sim 10-ka age estimate for deeper aquifer water at the Dari site is therefore robust, but the \sim 1-ka estimate at the Bay site may be an overestimate. The absence of ^3H in the deeper aquifers at the Bay sites does constrain these groundwater to be $>$ 50 yr old relative to recharge. More recent drilling in the region (e.g. Horneman et al., 2004) as well as geophysical surveys indicate greater regional continuity of the 15-m fine-grained sediment layer that separates the shallow and deep aquifer at the Dari site compared to the multiple thinner fine-grained sediment layers at the Bay site. The larger difference in hydraulic heads between shallow and deeper monitoring wells during much the year at Dari also suggests a more effective separation than at Bay (Fig. 4).

The wide spectrum of groundwater ages in deeper aquifers of Arai-hazar is consistent with observations elsewhere in Bangladesh. The radiocarbon content of DIC for a set of tritium-free deep groundwater samples drawn from depths $>$ 100 m across the country was shown to range from FM \sim 0.08 to 0.88 (Aggarwal et al., 2000). At Lakshimpur, where clay formations also separate shallow and deeper aquifers, the radiocarbon content of DIC is similar to that of the deeper aquifers at Dari (British Geological Survey and Department of Public Health Engineering, 2001). Radiocarbon data reported in the same study for Faridpur, where shallow aquifers are separated by silty formations rather than by a clay layer, also indicate considerably younger groundwater in deeper aquifers. Aggarwal et al. (2000) also report that in two deeper wells with relatively young ^{14}C ages (DIC $\Delta^{14}\text{C}$ of 0.85 FM), tritium was not detected in 1979 but became detectable in 1999. Such observations reinforce the notion that deeper aquifers with ages of thousands of years are not as influenced by processes affecting shallow aquifers than deeper aquifers with residence times of hundreds of years.

4.4. Sustainability of Withdrawals From Deeper Aquifers

The information collected at the Dari and Bay sites defines two factors that appear to play a significant role in keeping the dissolved As content of deeper aquifers low: (1) a relative small pool of easily mobilizable As, possibly the result of flushing during low sea level stands (British Geological Survey and Department of Public Health Engineering, 2001; Ravenscroft et al., 2001; McArthur et al., 2004), and (2) fine-grained deposits that separate the deeper aquifer from shallow groundwater containing elevated As concentrations. Redox conditions do not appear to play a dominant role since the deeper aquifer at the Bay site is as reducing as the shallow aquifers at Bay and Dari. This last section examines the implications of these observations for the sustainability of groundwater withdrawals from deeper aquifers, following a discussion of the hydraulics of the system. The intent is to help define an issue with important policy implications, not by any means to provide a final answer (British Geological Survey and Department of Public Health Engineering, 2001; Harvey et al., 2002; Yu et al., 2003; van Geen et al., 2002, 2003b).

4.4.1. Recharge and discharge

The hydrographs from Arai-hazar indicate that discharge pathways are distinctly different for the shallow and deeper

aquifers at Dari but probably not at Bay. The lowest water levels reached by the shallow aquifer at Dari and both the shallow and deeper aquifers at Bay during the dry season suggest discharge to the local stream (Fig. 4). Instead, the deeper aquifer at Dari appears to discharge to more distant larger rivers in the area, such as the Buriganga. Alternatively, the deeper aquifer at Dari may be within the cone of depression created by large rates of groundwater abstraction in Dhaka, ~25 km to the west. The two scenarios cannot be distinguished at the moment because long-term water level records from additional wells tapping the deeper aquifer located between the two regions are, to our knowledge, not available.

Recharge at the sites likely occurs from precipitation and surface waters and by leakage through confining beds. Hydrographs for shallow wells at both sites track the local stream throughout the onset of the wet season, whereas deeper wells at Dari again track the Buriganga River (Fig. 4). The pattern for deeper wells at Bay is more complex, with water levels at 40, 53, and 88 m intermediate between the levels of the local stream and the Buriganga (Fig. 4). The synchronous rise of precipitation, river stages, and water tables indicates effective transfers of horizontal and vertical pressure pulses throughout the system. Both precipitation and surface water bodies probably contribute to recharge during this period. A significant lag in the drop of the water table relative to the local rivers at the end of the wet season suggests continued recharge from isolated ponds while the aquifers discharge horizontally to the local rivers. The increased lag of the falling flank of the deeper aquifer at Dari likely suggests recharge from the shallow aquifer by leakage through confining beds induced by the vertical downward hydraulic gradient between them.

4.4.2. Conservative behavior of As

Assuming for now that As does not interact with deep aquifer solids in either direction, one key issue with respect to the sustainability of deep aquifers as a source of water low in As is potential vertical leakage of shallow groundwater that is elevated in As. The seasonal rise and drop of water levels in deep aquifers at the Bay and Dari sites suggest that both are replenished on a regular basis. Assuming an aquifer thickness of 50 m and a porosity of 0.3, groundwater ages of ~10,000 and ~1,000 yr for the deep aquifers at Bay and Dari correspond to long-term average recharge rates of at least 0.15 and 1.5 cm/yr, respectively. How do these rates compare to the flux of groundwater potentially leaking from the shallow to the deep aquifers? Permeameter measurements of the fine grained material yielded upper limits of the vertical hydraulic conductivity of 5×10^{-8} and 5×10^{-7} cm/s for Dari and Bay, respectively (Figs. 2 and 3). Assuming a thickness of the fine-grained layers separating shallow and deep aquifers at Dari and Bay of ~15 and 1 m, and maximum vertical hydraulic head gradients of 1 and 0.1 m, respectively, the vertical leakage rates at the two sites should be < 0.2 and 1.6 cm/yr. At both sites, the estimated maximum leakage rates from shallow to deep aquifers are therefore consistent with the recharge rates derived from radiocarbon data. Evidently, the present rate of leakage from the shallow aquifer has not resulted in a dramatic increase in As in deeper aquifers at both sites.

One source of uncertainty is the extent to which the recharge

rate could increase if groundwater abstraction from the deeper aquifers is enhanced, and whether this rate could sustain the demand of withdrawal. For a population density of 2600 persons per km² in Araihaazar (van Geen et al., 2002) and a domestic water demand of 10 L person⁻¹ d⁻¹, the withdrawal by domestic hand pumps amounts to 9600 m³/km² yr, which is equivalent to 1 cm/yr. This is, again, within the range of the estimated natural recharge rates of the deep aquifers at Bay and Dari. This suggests that a complete shift of domestic use to the deeper aquifer might be sustainable, particularly if increased withdrawal is accompanied by an increase in recharge.

The situation is very different if withdrawals due to irrigation are considered. Harvey et al. (2002) reported pumping rates for irrigation on the order of ~60 cm/yr in another region of Bangladesh. This is consistent with a requirement of ~1 m of water per growing season to irrigate rice paddies, considering that groundwater is needed only for the winter-spring crop. Under these conditions, hydraulic gradients between shallow and deeper aquifers could increase considerably and leakage of shallow groundwater elevated in As to the deeper aquifers would increase in proportion. Assuming conservative behavior of As, a massive switch of the source of water used for irrigation from predominantly shallow aquifers today to deeper aquifers in the future could therefore raise As concentrations in groundwater supplied by existing deep wells.

4.4.3. Non-Conservative behavior of As

Harvey et al. (2002) and Swartz et al. (2004) have suggested that gray sediment in shallow aquifers may have little additional capacity for As adsorption whereas deeper orange aquifer sands do. A significant difference in As binding to orange sands was also suggested by field surveys and incubations of Bangladesh aquifer material (Horneman et al., 2004; van Geen et al., 2004b). Shallow groundwater leaking into orange aquifers with a low Fe(II)/Fe ratio, such as the deep aquifer at Dari, might therefore be stripped of its As content well before it reaches the screen of a deep well. Such attenuation could be considerably weaker if, as in the case of the deep aquifer at Bay, shallow groundwater elevated in As were drawn in a more reducing aquifer composed of gray sands.

Perhaps of greater concern is the potential release of As currently stored in deeper aquifer sands through reductive-dissolution of Fe phases triggered by the penetration of electron donors in the form of dissolved organic carbon (DOC). Harvey et al. (2002) suggested this possibility based, among other observations, on the significant mobilization of As that followed the re-injection of groundwater amended with molasses in a shallow well. Laboratory incubations of shallow Bangladesh aquifer material amended with acetate have also illustrated the potential enhancement of As release in response to an input of reduced carbon (Islam et al., 2004; van Geen et al., 2004b). It is not clear to what extent such experiments are representative of what would happen if electron donors leaked into a deeper aquifer where, this and previous studies have shown, the concentration of easily mobilized As is often 1 order of magnitude lower than in shallow aquifers. Another, albeit speculative, reason such experiments may not be representative is that dissolved organic carbon penetrating from shallow aquifer

fers may no longer be labile enough to reduce Fe and mobilize As by the time a deep aquifer is reached.

The impact of leakage of electron donors into orange aquifers of Pleistocene age might be limited by an additional factor. van Geen et al. (2004b) report that the release of As from deep orange aquifer sands requires the addition of a large dose of acetate, whereas As is released spontaneously from gray sands without the addition of acetate, albeit at a slower rate. If the attenuation of As release from orange sands is due to its higher adsorption capacity, then the critical question is whether an enhanced supply of DOC could convert orange to gray sands under realistic conditions. Assuming a residence time of deeper aquifer water of 1000 yr and a DOC concentration of 12 mg/L (Harvey et al., 2002), it would take ~400,000 yr to reduce all Fe(III) to Fe(II) assuming a 1% Fe content, a porosity of 50%, and a density of the sediment of 2 g/cm³ (Zheng et al., 2004). This suggests that Fe oxyhydroxide coatings of deep orange sand grains are likely to remain in the Fe(III) state and therefore that the adsorptive capacity of this material for As would be retained over time scales relevant to policy.

5. CONCLUSIONS

This detailed geochemical and hydrological study of two sites 4 km apart in Bangladesh shows that groundwater As concentrations are lower in deeper aquifers compared to the shallow aquifers, which are presently utilized to a greater extent. The deeper aquifers in the two villages that were studied have different depositional histories (i.e., Holocene vs. Pleistocene) and different groundwater ages. Both types of deeper aquifers are reasonably well separated from the shallow groundwater. However, the deeper aquifer of Pleistocene age and the shallow aquifer are hydraulically separated to a much greater extent than the deeper aquifer of Holocene age and the shallow aquifer. The contrast is consistent with vertical differences in the geochemical properties of the groundwater, especially the radiocarbon content of DIC. A comparison with shallow aquifers containing elevated dissolved As concentrations with the deeper aquifer at both sites suggests that the concentration of easily mobilizable As present in the sediment is an important explanatory variable. It is not clear, however, to what extent and under what conditions As in the sediment is converted to such a mobilizable form.

Usage of the deeper aquifers for domestic water consumption appears to be sustainable since the recharge rate of the deeper aquifers calculated from residence times is of comparable magnitude. However, deeper aquifers should not be used for irrigation until the hydrological and chemical responses to increased withdrawals are better understood, in both the Holocene and the Pleistocene deeper aquifers.

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