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Temporal variability of groundwater chemistry in shallow and deep aquifers of Araihasar, Bangladesh

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ABSTRACT

Samples were collected every 2–4 weeks from a set of 37 monitoring wells over a period of 2–3 years in Araihasar, Bangladesh, to evaluate the temporal variability of groundwater composition for As and other constituents. The monitoring wells are grouped in 6 nests and span the 5–91 m depth range. Concentrations of As, Ca, Fe, K, Mg, Mn, Na, P, and S were measured by high-resolution ICPMS with a precision of 5% or better; concentrations of Cl were measured by ion chromatography. In shallow wells <30 m deep, As and P concentrations generally varied by <30%, whereas concentrations of the major ions (Na, K, Mg, Ca and Cl) and the redox-sensitive elements (Fe, Mn, and S) varied over time by up to ±90%. In wells tapping the deeper aquifers >30 m often below clay layers concentrations of groundwater As were much lower and varied by <10%. The concentrations of major cations also varied by <10% in these deep aquifers. In contrast, the concentration of redox-sensitive constituents Fe, S, and Mn in deep aquifers varied by up to 97% over time. Thus, strong decoupling between variations in As and Fe concentrations is evident in groundwaters from shallow and deep aquifers. Comparison of the time series data with groundwater ages determined by ³H/³He and ¹⁴C dating shows that large seasonal or inter-annual variations in major cation and chloride concentrations are restricted to shallow aquifers and groundwater recharged <5 years ago. There is no corresponding change in As concentrations despite having significant variations of redox sensitive constituents in these very young waters. This is attributed to chemical buffering due to rapid equilibrium between solute and solid As. At two sites where the As content of groundwater in existing shallow wells averages 102 µg/L (range: <5 to 648 µg/L; n=118) and 272 µg/L (range: 10 to 485 µg/L; n=65), respectively, a systematic long-term decline in As concentrations lends support to the notion that flushing may slowly deplete an aquifer of As. Shallow aquifer water with >5 years ³H/³He age show a constant As:P molar ratio of 9.6 over time, suggesting common mechanism of mobilization.

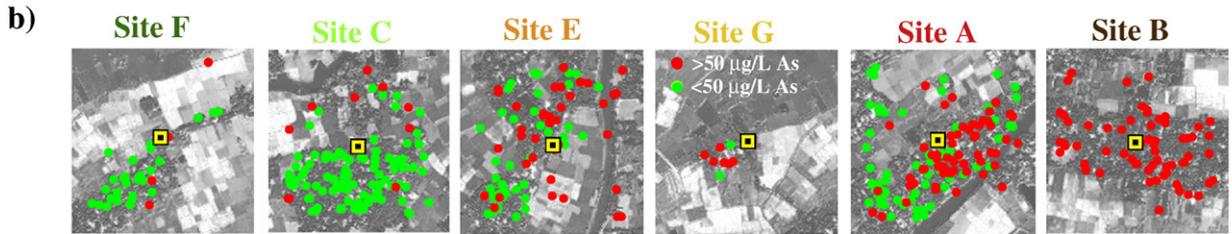
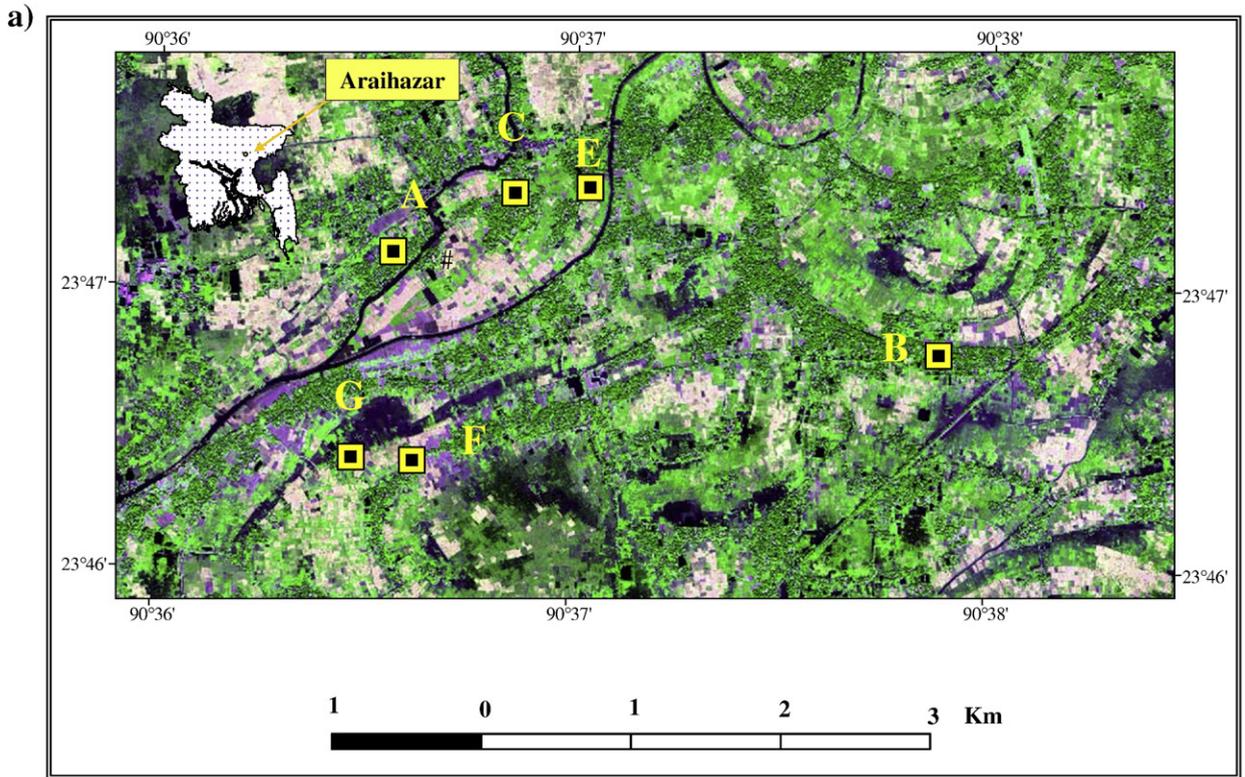
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1. Introduction

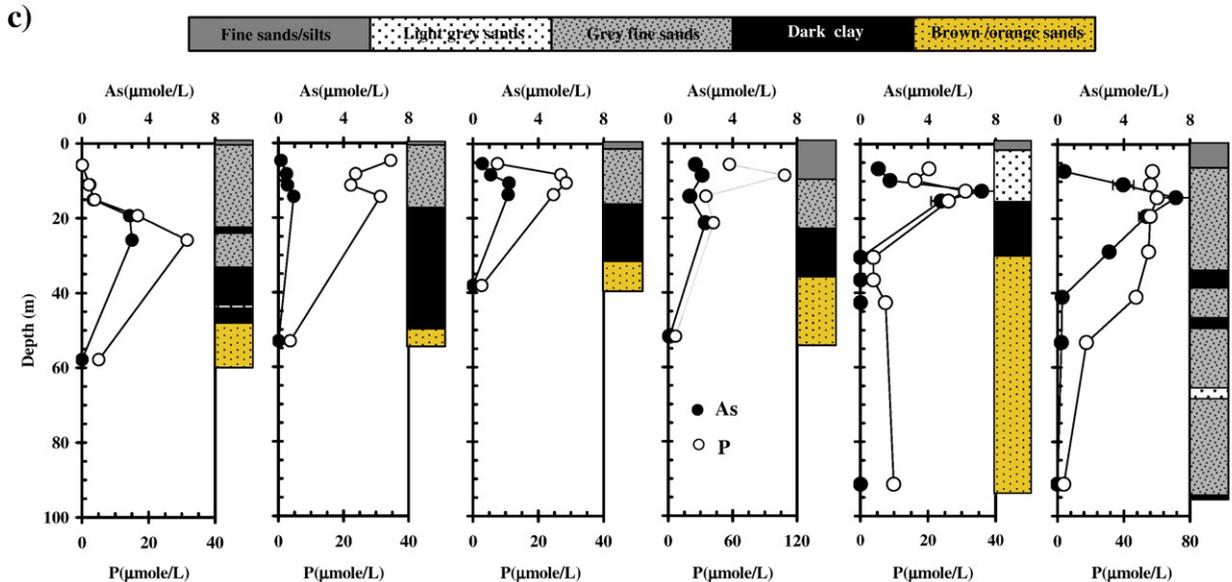
The spatial variability of groundwater As concentrations at 58 scales of 10¹ to 10⁴ m has been well documented for Holocene 59 (<10 kyr old) fluvial-deltaic aquifers of the Bengal Basin (BGS 60 and DPHE, 2001; van Geen et al., 2003; Yu et al., 2003). There 61 is growing evidence that at least part of this heterogeneity can 62 be attributed to variations in local geology and its effect on 63

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Lithology Keys



shallow groundwater flow (van Geen et al., 2006; Stute et al., 2007; Aziz et al., in revision; Weinman et al., in press). Such spatial variability naturally leads to the concern that shallow groundwater As concentration may also change over time, especially because subsurface flow is likely to be affected by large water withdrawals for irrigation in certain areas of Bangladesh (Harvey et al., 2002; Klump et al., 2006). The persisting gaps in our knowledge of the mechanisms that lead to As mobilization (Horneman et al., 2004; Zheng et al., 2004), combined with pronounced seasonal fluctuations in water levels in shallow and deep aquifers linked to the monsoon, make it particularly difficult to predict variations of groundwater As concentration over space or time. Yet, this understanding is urgently needed because a significant proportion of those shallow wells that presently meet the Bangladesh drinking water standard of 50 $\mu\text{g/L}$ are, at least temporarily, shared by villagers of Bangladesh to reduce their exposure to As and therefore reduce the likelihood of contracting a series of debilitating diseases (van Geen et al., 2002; Opar et al., 2007).

There are few high-quality time series data of groundwater As concentration from the Bengal Basin. The available data with the As concentrations ranging from 0.4 $\mu\text{g/L}$ to 64 $\mu\text{g/L}$ generally indicate little seasonality or long-term trends once very shallow (<10 m) are excluded (BGS and DPHE, 2001; Cheng et al., 2005; van Geen et al., 2005; Cheng et al., 2006; van Geen et al., 2007). On a different continent, little change in As concentration over a period of 1–20 years was also reported for 759 wells from western Nevada, USA, where concentrations range from <5 to 6200 $\mu\text{g/L}$ in a wide depth range (28 m \pm 46 m, median 16 m) (Steinmaus et al., 2005).

Besides a few very shallow (<10 m) wells monitored over several years (Cheng et al., 2005), there are other credible reports of significant changes in As concentrations in groundwater over time. A striking example was the case of a highly-contaminated private well of unreported depth at Ramnagar in West Bengal, India, that was monitored biweekly between July 1992 and June 1993 and showed occasional variations of ~30% around an average of ~2700 $\mu\text{g/L}$ (Chatterjee et al., 1995). The same group observed a long term rise in groundwater As concentration in a number of private wells in 23 villages out of 100 villages of West Bengal where initially water with low As (<50 $\mu\text{g/L}$) exceeded 50 $\mu\text{g/L}$ over time, although the data were not reported (Chakraborti et al., 2002; Chakraborti et al., 2004). Large seasonal variations of groundwater As levels were also reported in 5 monitoring wells at depths of 3–60 m in Samta village of Western Bangladesh (AAN, 1999), although the measurements of As were few and made by a less reliable method (silver dithiocarbamate spectrometry) in a local laboratory. There is more convincing evidence that As concentration declined between September–December, 1999, and May 2000 in many of the 68 wells

sampled twice in four districts of the Red River delta (Berg et al., 2001). Naturally occurring As in groundwater of Granite Falls, Washington, ranging in concentration from <10 $\mu\text{g/L}$ to 14,000 $\mu\text{g/L}$ also showed substantial temporal variability of 12–79% for 15 out of 25 private drinking water wells monitored over 12 months (Frost et al., 1993).

With the present study, we contribute to the body of groundwater monitoring data by presenting up to 3 years of bi-weekly to monthly measurements of As, P, Fe, Mg, Ca, K, Na, Mn, S, and Cl in groundwater at 6 well nests comprised of a total of 37 monitoring wells installed in Arai-hazar, Bangladesh. These observations not only fill a gap in our understanding of temporal variability in groundwater As concentrations, they also shed new light on the mechanisms of As mobilization and may help us anticipate future trends in affected areas. The monitoring wells tap aquifers from 5–91 m with a wide range of As concentrations from <5 to 600 $\mu\text{g/L}$ in an area where previous studies have documented a spectrum of hydrogeological conditions that is representative of much of the Bengal Basin (Horneman et al., 2004; Zheng et al., 2005; van Geen et al., 2006). We describe the main temporal patterns in groundwater chemistry, including long-term trends, short-term excursions, and seasonal variations in both shallow and deep aquifers. The variations in groundwater major ion composition, or mostly lack thereof, are then discussed in the context of groundwater ages.

2. Methods

2.1. Monitoring wells

The locations of the well nests were chosen to cover the spatial patterns of groundwater As concentrations established by a previous survey of 6000 wells distributed over a ~25 km² area of Arai-hazar in central Bangladesh (van Geen et al., 2003). A total of 37 monitoring wells from 5–91 m in depth were installed at 6 sites (Fig. 1a, Table 1). At each of the sites, 4 or 5 monitoring wells tapped shallow aquifers composed of Holocene alluvial deposits ranging from 15–30 m in thickness (Fig. 1c). The sites were arranged in most figures according to increasing average As concentrations of existing shallow (<30 m) wells within the 0.16 km² area centered by each of the nest of wells: 18 $\mu\text{g/L}$ (<5 to 112 $\mu\text{g/L}$) at Site F, 19 $\mu\text{g/L}$ (<5 to 143 $\mu\text{g/L}$) at Site C, 65 $\mu\text{g/L}$ (<5 to 254 $\mu\text{g/L}$) at Site E, 94 $\mu\text{g/L}$ (8 to 352 $\mu\text{g/L}$) at Site G, 102 $\mu\text{g/L}$ (<5 to 648 $\mu\text{g/L}$) at Site A, and 272 $\mu\text{g/L}$ (10 to 485 $\mu\text{g/L}$) at Site B (Fig. 1b). At all locations except for Site B, at least one monitoring well >30 m deep reached distinctly orange/brown colored sands of Pleistocene age (Fig. 1c). At Site B, grey Holocene sediments were observed even to a depth of 91 m (Zheng et al., 2005). At each site, one or several layers of fine-grained sediment separate the shallow aquifers that are elevated in As from the deep aquifers that are low in As concentration (Fig. 1c).

Fig. 1. (a) Locations of six nests of wells were plotted on an IKONOS image of Arai-hazar study area in central part of Bangladesh (inset). (b) The 400 m \times 400 m squares represent an enlarged view of the spatial distribution of As in existing wells surrounding the 6 well nests. Green and red solid circles indicate the As level <50 $\mu\text{g/L}$, and greater or equal to 50 $\mu\text{g/L}$, respectively. Sites F, C, E, G, A, and B are arranged from left to right and color coded with increasing average As concentration in the surrounding wells located in the 400 m \times 400 m squares. (c) The depth profiles of average groundwater As and P concentration for all sites. The scales for P concentration were different for Sites G and B. Error bars on As profiles showed the fluctuations over the entire monitoring period. A lithology sketch is placed next to the vertical profile at each site.

11	2.6	7.01	18	6.46±0.11	-111±22	52±9	42±3	22±2	1.6±0.7	0.6±0.50	0.6±0.56	1311±697	34±14	11±7
14	2.8	7.00	18	6.58±0.15	-114±29	36±12	70±9	31±4	2.8±0.3	0.4±0.06	0.3±0.04	773±76	33±3	23±16
53	-	7.01	18	6.38±0.15	-33±25	28±3	1±1	4±1	2.9±0.2	1.2±0.10	0.6±0.04	117±92	13±2	10±8
<i>Site E (23.790°N, 90.616°E) – Village: Hatkhola Para, multilevel wells were installed in March 2002</i>														
5	9.6	6.39	16	6.65±0.11	-40±29	34±7	43±2	8±1	4.9±0.6	0.4±0.04	0.2±0.02	48±11	17±2	232±74
8	-	6.42	16	6.73±0.12	-118±38	34±10	82±4	27±2	3.8±0.5	0.4±0.04	0.1±0.01	424±48	35±4	80±42
11	18.1	6.44	16	6.90±0.09	-140±48	35±10	166±12	29±2	4.2±0.3	0.5±0.08	0.1±0.01	392±123	33±3	2±1
14	-	6.42	16	6.82±0.13	-148±1	42±23	162±15	25±2	5.2±0.5	1.2±0.17	0.8±0.03	498±143	17±5	1±1
38	-	6.45	16	6.55±0.10	-60±39	52±19	0.3±0.02	3±0.3	5.7±0.3	2.5±0.30	1.2±0.03	56±19	5±2	<0.03±0.0
<i>Site F (23.774°N, 90.605°E) – Village: Lashkardi (Mosque), multilevel wells were installed in March and November 2002</i>														
6	0.8	7.90	21	6.18±0.12	95±92	18±2	0.2±0.02	0.1±0.1	1.6±0.3	0.2±0.06	0.2±0.06	2.4±2	2.6±1	37±25
11	-	7.87	22	6.23±0.10	10±50	21±8	35±3	2±1	1.8±0.3	0.1±0.02	0.2±0.04	63±22	31±8	24±15
15	5.3	7.81	22	6.73±0.23	-47±60	21±3	51±5	4±1	2.4±0.1	0.1±0.01	0.1±0.01	31±18	27±3	15±9
19	29.1	7.76	22	6.88±0.11	-63±55	29±6	215±19	17±3	3.7±0.3	0.3±0.02	0.04±0.00	27±16	42±2	35±4
26	-	7.74	14	7.00 0.00	-200	63	225±15	32±4	5.2±0.4	0.5±0.03	0.2±0.01	350±22	35±3	0.3±0.0 2
58	-	7.91	22	6.95±0.08	-63±23	154±8	0.3±0.02	5±0.4	12.5±1.0	11.4±0.94	9.7±0.74	5.7±2	9±0.4	9±4
<i>Site G (23.774°N, 90.601°E) – Village: Lashkardi (Bilbari), multilevel wells were installed in March 2002</i>														
6	21.4		20	6.75±0.07	-127±24	41±8	127±16	57±13	4.6±0.2	0.4±0.02	0.1±0.01	610±189	25±4	22±1
9	13.1		20	6.67±0.10	-111±38	45±11	159±13	108±23	5.2±0.3	0.4±0.02	0.1±0.01	501±66	8±2	6±4
14	26.0		20	6.93±0.08	-144±23	36±10	102±5	35±3	4.0±0.3	0.4±0.06	0.2±0.02	294±50	30±3	1±0.4
21	-		20	7.05±0.11	-163±31	42±7	173±15	42±4	4.2±0.3	0.4±0.09	0.6±0.06	194±46	28±2	2±2
52	-		20	6.85±0.09	-88±34	145±19	7±1	7±1	10.9±1	9.9±0.56	7.2±0.60	13±8	12±1	31±2

^{a3}H/³He age reported by Stute et al. (2006).

^bData based on monthly measurements from March 2004 to February 2005.

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167 2.2. Sampling and field measurements

168 Bi-weekly to monthly groundwater samples from the mon-
 169 itoring wells were collected from Jan. 2001 to Feb. 2004 at Sites

A and B, and from March 2002 to Feb. 2004 at Sites C, E, F and G. 170
 Each well was pumped for at least 15 min by a battery-driven 171
 submersible pump (Whale SuperPurger) at a rate of ~2 L/min. 172
 The 15 min of pumping allowed conductivity and temperature 173

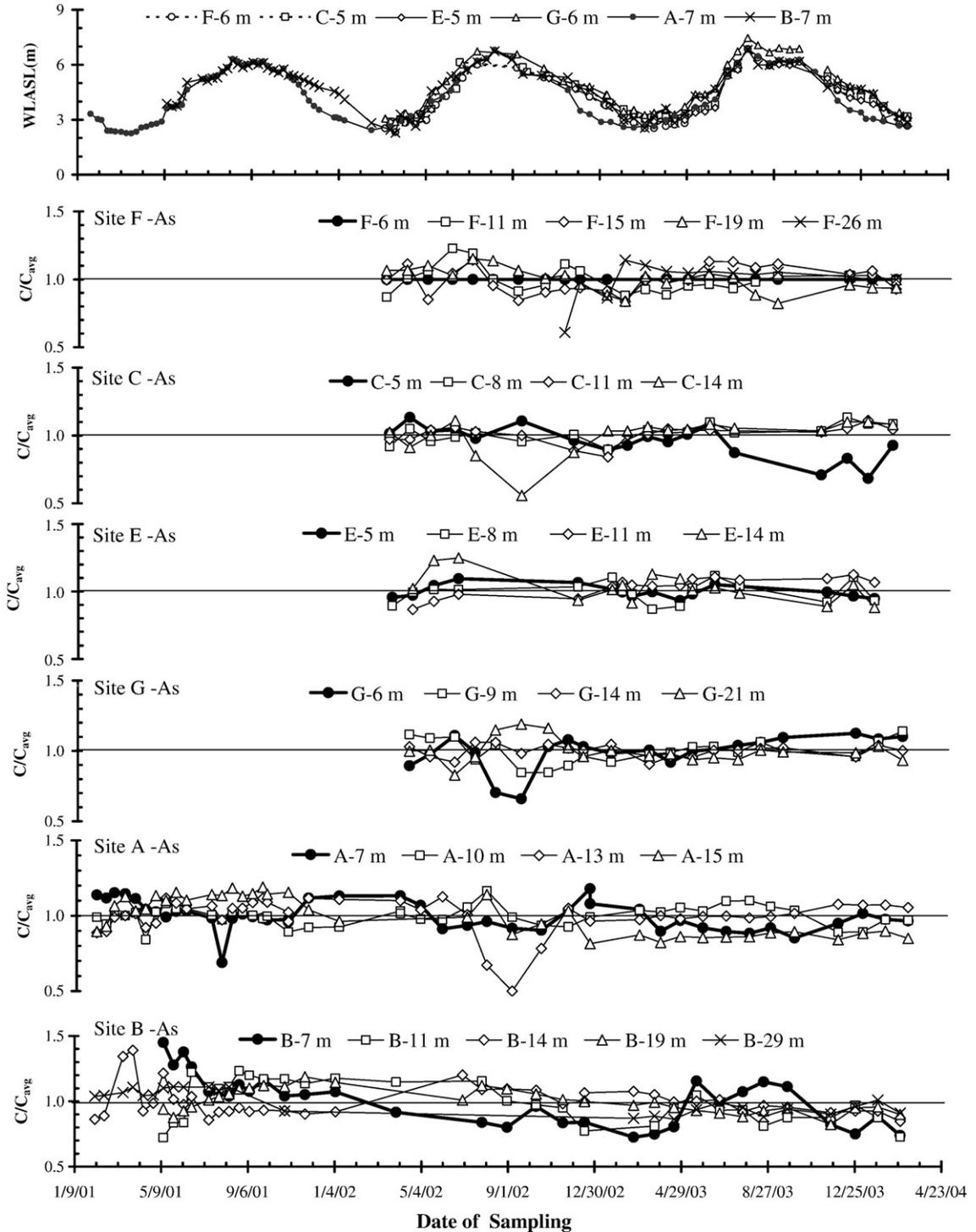


Fig. 2. Water level above sea level (WLASL) spanning the entire monitoring periods from the shallowest well of each site is shown in the upper most panel. The rest of the panels from top to bottom show in sequence, the temporal variability of As concentration in shallow aquifers for Sites F, C, E, G, A, and B. Dissolved As concentrations are plotted as the ratio (C/C_{avg}) of the concentration at the time of the sampling (C) versus the average concentration of the entire time series (C_{avg}). In each panel, the bold line always represents the shallowest well of the site.

211 readings to stabilize before sampling. Samples for As, other
 212 trace elements, and major cations were collected in 30-ml or
 213 60-ml acid-cleaned HDPE bottles and acidified to 1% HCl (Fisher

Optima) immediately after collection and without filtration. 214
 We, and others before us, have shown that the standard 215
 monitoring well screens in Bangladesh are typically sufficient to 216

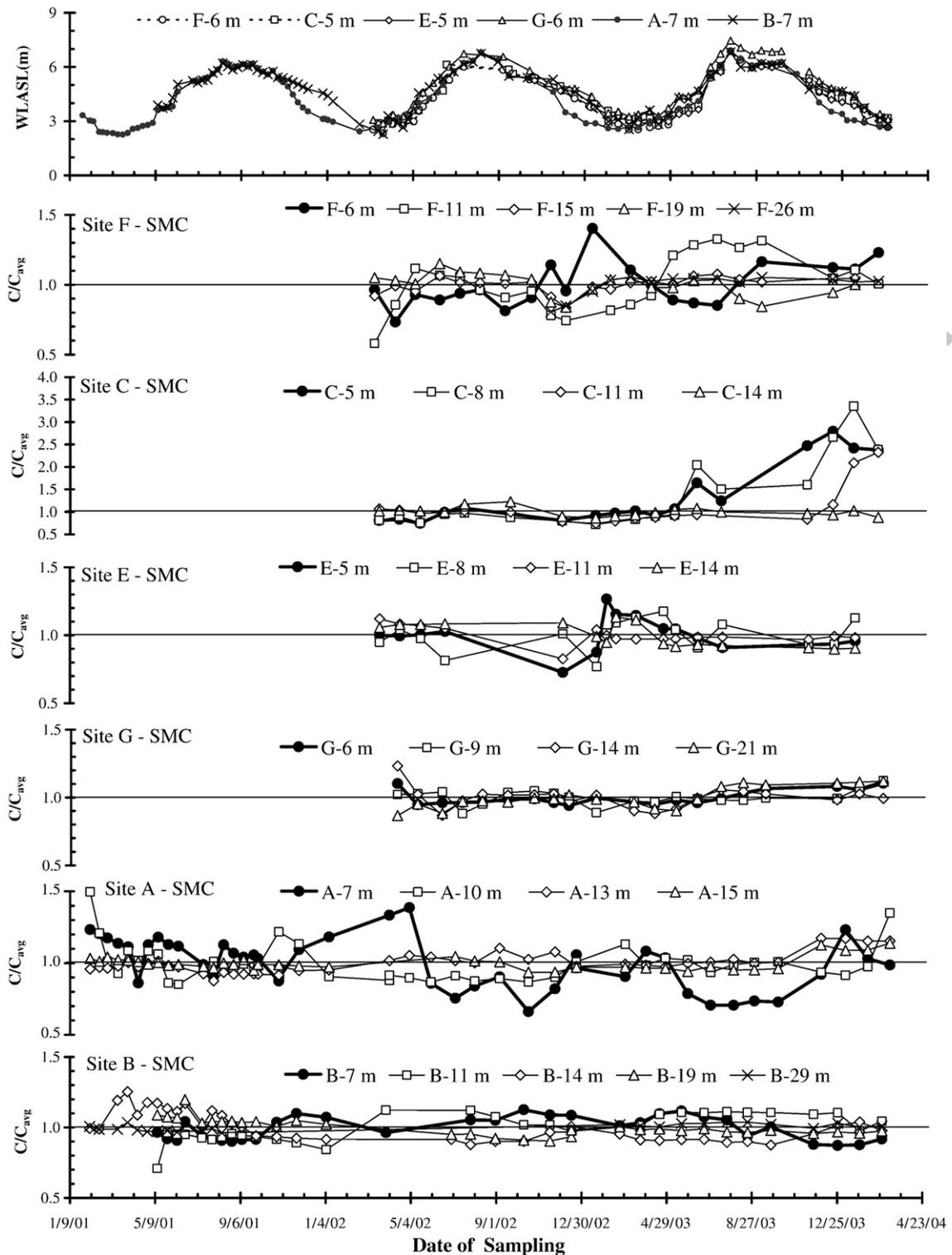


Fig. 3. Temporal variability of the sum of major cations (SMC) in shallow aquifer was shown with the groundwater level fluctuation of the shallowest well (same as in Fig. 2 panel) from top to bottom in sequence for Sites F, C, E, G, A and B. Concentrations of SMC are plotted as the ratio (C/C_{avg}) of the concentration at the time of the sampling (C) versus the average concentration of the entire time series (C_{avg}). Similar to Fig. 2, the bold line always represents the shallowest well of the site.

217 exclude particles that might dissolve upon acidification, where-
 218 as filtration can produce artifacts unless carried out under
 219 nitrogen in-line (Zheng et al., 2004). Samples for anions were
 220 collected in nanopure-washed 30 ml HDPE bottles without
 221 filtration. Starting in April, 2004, pH, ORP, temperature, and
 222 electrical conductivity of the groundwater was measured using
 223 a pH/Eh meter (Orion 210A) and a conductivity/temperature
 224 meter (Orion 105A+) with waterproof probes that were
 225 calibrated on the day of sampling. The groundwater level in
 226 each well was monitored every 1–2 weeks over the same time
 227 period using an electric water-level meter (Solinst model 101).

228 2.3. Laboratory measurements

229 Concentrations of As, P, Fe, Mn, S, Ca, Mg, K, Na and 33 other
 230 trace elements in acidified groundwater were measured at
 231 Lamont–Doherty Earth Observatory with a reproducibility
 232 typically <5% by high-resolution inductively-coupled plasma
 233 mass spectrometry (HR ICP-MS) using an Axiom single-
 234 collector instrument (Thermo Elemental, Germany) (Cheng
 235 et al., 2004). Protocols that were followed to ensure the
 236 accuracy and precision of the data included: (1) two NIST
 237 standard reference materials (1640 and 1643E, Trace element in
 238 natural water), and an internal laboratory consistency standard
 239 (LDEO tap water spiked with analyte elements) were included
 240 with each run. Results for these standards were always within
 241 5% of the certified values after calibration of the instrument
 242 with separate standards at the beginning and end of each run
 243 (Cheng et al., 2004); (2) whenever possible, time-series samples
 244 from the same well were analyzed within the same run of 30

245 samples, which usually improved the reproducibility to <3%;
 246 (3) At least 2 samples were re-analyzed between two con-
 247 secutive runs for the same well to ensure consistency between
 248 runs. Concentrations obtained for these replicates usually did
 249 not differ from each other by more than 3%.

250 Dissolved Cl^- and SO_4^{2-} concentrations in un-acidified
 251 groundwater samples were measured at Queens College by
 252 ion chromatography (IC) using a DIONEX-500 IC system,
 253 following the standard protocol of EPA method 300. Compar-
 254 ison of SO_4 data obtained by IC with total S concentrations in
 255 acidified samples obtained by HR ICP-MS showed that S
 256 quantified by HR ICP-MS was essentially all in the form of
 257 sulfate at all sites (slope of S by ICPMS versus SO_4 by IC is
 258 1.0027, R^2 : 0.9812, n =181).

259 In addition to measurement by HR ICP-MS, phosphate
 260 present in groundwater was also quantified as dissolved
 261 reactive phosphate (DRP) using molybdate-blue colorimetry,
 262 modified to determine also dissolved As (Dhar et al., 2004). A
 263 comparison of colorimetric and HR ICP-MS data indicates that
 264 not all P present in groundwater reacts with molybdate. At
 265 Sites A and B, total P concentrations in shallow (<30 m)
 266 groundwater measured by HR ICP-MS were consistently
 267 higher by 30% (R^2 =0.99, n =11) than DRP concentrations for
 268 samples collected in January 2003, suggesting that a fraction
 269 of the P could be in a non-reactive organic form (Stauffer,
 270 1980). In contrast, total P concentrations measured by HR ICP-
 271 MS were only ~10% and 5% higher than DRP concentrations in
 272 shallow groundwater from Site C and Site F, respectively, for 2
 273 sets of samples collected in Jan. 2003 and Oct. 2003 (Site C:
 274 R^2 =0.99, n =4; Site F: R^2 =0.99, n =6).

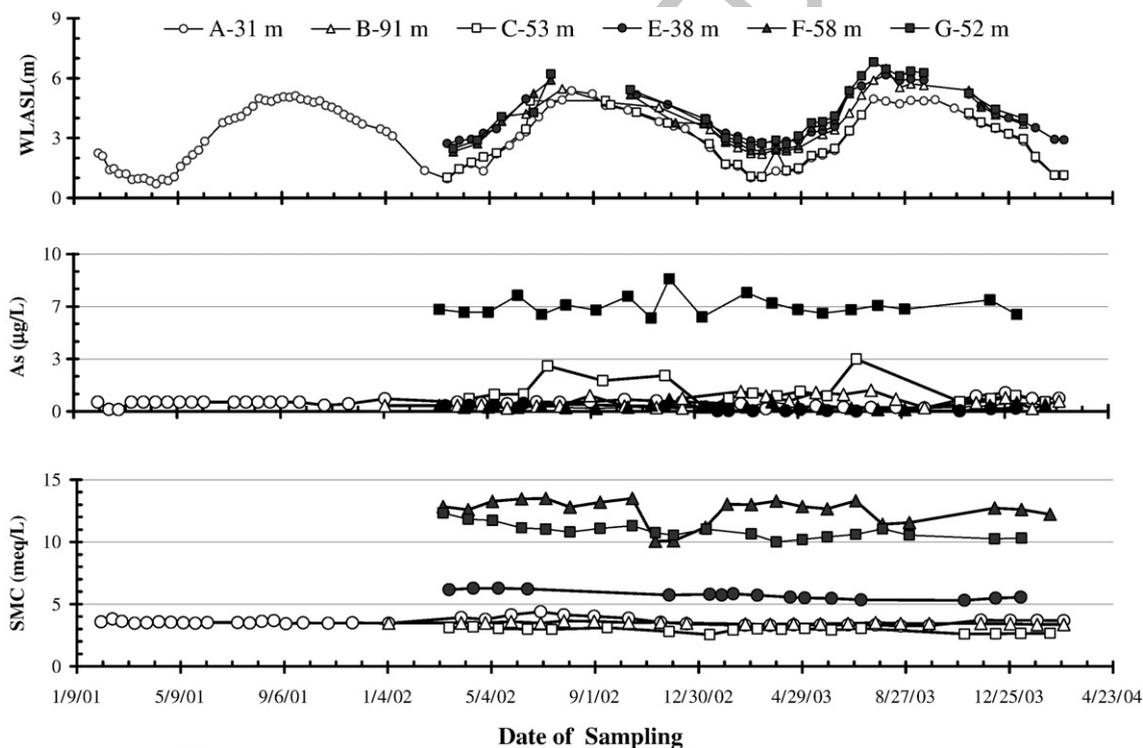


Fig. 4. The temporal variability of As and SMC in deep aquifers spanning the entire monitoring periods are shown with the water level fluctuations in deep aquifers. The upper most panel shows fluctuation of water level above sea level (WLASL) at the deep aquifer wells in six sites. Other two panels displayed the variability of As in $\mu\text{g/L}$ and SMC in meq/L at the deep aquifer wells in all sites.

275 2.4. Statistical analysis

276 The rate of increase or decrease per year in 37 shallow and
 277 deep wells was examined by performing a regression analysis
 278 of As, P and other ions concentration versus time for each well
 279 over the entire period except for C where the post summer
 280 2003 flood period was excluded (Nov. 2003 to Feb. 2004,
 281 Figs. 2 and 3) due to very large change in Na and Cl. Trends of
 282 different constituents including As, P, sum of major cations
 283 (SMC), Cl, Fe, Mn and S were considered to be statistically
 284 significant if p values were <0.05 . For most wells, the residuals
 285 were randomly and normally distributed around the linear
 286 trend line. The uncertainties in the rate of increase or decrease
 287 (e.g. the slope of regression) were expressed as 95%
 288 confidence intervals.

289 3. Results

290 The temporal data of both shallow (<30 m) and deep
 291 (>30 m) groundwater As and SMC ($2[\text{Ca}]+2[\text{Mg}]+[\text{Na}]+[\text{K}]$)
 292 are plotted as the ratio (C/C_{avg}) of the concentration at the
 293 time of the sampling (C) vs. the average concentration of
 294 the entire time series (C_{avg}) for Sites F, C, E, G, A to B (Figs. 2, 3
 295 and 4). Similar plots for other constituents are included as
 296 supplemental material. The depth profiles of variation in
 297 concentration of groundwater constituents including As, P,
 298 SMC, Cl, Fe, Mn and SO_4 are shown for both shallow and deep

aquifers of all 6 sites, with the variation expressed as percent 299
 relative standard deviation (%RSD) (Fig. 5). A statistically 300
 significant temporal trend of As concentration is observed for 301
 11 out of 37 wells in both the shallow and deep Holocene 302
 aquifer (Table 2). A decrease in As concentration over time is 303
 observed at 9 wells; an increase is recorded at only 2 wells. 304
 Correlation coefficients (R) for As trends in these wells varied 305
 from 0.5 to 0.85. The 26 wells that did not show statistically 306
 significant trends include most of the shallow and deep wells 307
 with a very low As (<10 $\mu\text{g/L}$) content (Tables 1 and 2). 308

3.1. Water levels 309

Water levels in shallow and deep monitoring wells varied 310
 seasonally from 2–3 m above sea-level (asl) during the dry 311
 season to 6–7 m asl during the wet season in both shallow and 312
 deep monitoring wells (Figs. 2, 3 and 4). Water level data for 313
 the period July–October 2003 in both shallow (Figs. 2 and 3) 314
 and deep aquifers (Fig. 4) at low-lying Sites C, E, and G were 315
 not recorded because the monitoring wells were not acces- 316
 sible due to pronounced flooding. The fluctuations in water 317
 levels tracked each other within ~ 0.3 m in all shallow (<30 m) 318
 monitoring wells over a period of 3 years. In contrast, the deep 319
 wells from the Pleistocene deep aquifer could be grouped in 320
 two categories, with water levels at fresh water Sites A and C 321
 remaining ~ 2 m below water levels at more saline water Sites 322
 E, F, and G throughout the seasonal cycle (Fig. 4). 323

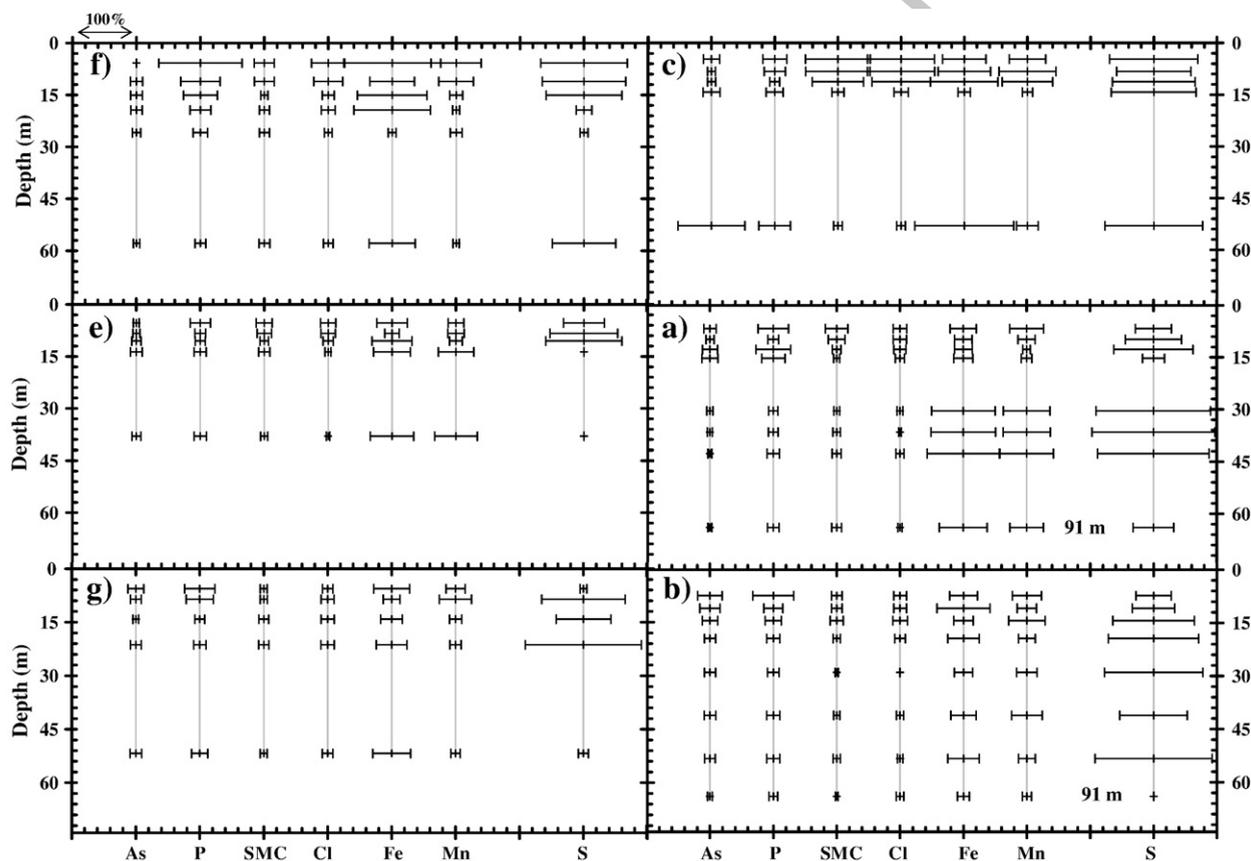


Fig. 5. Variation of As, P, SMC, Cl, Fe, Mn, S in shallow and deep aquifers of six sites are shown as %RSD. The variations of the two 91 m deep wells at Sites A and B are shown right below the 60 m depth and do not represent the actual depths of the wells.

t2.1 **Table 2**
Trends in groundwater chemistry from six well nests of 37 monitoring wells
in Araihaazar, Bangladesh

t2.2 t2.3	Depth (m)	^a As ($\mu\text{g/L yr}^{-1}$)	P ($\mu\text{molL}^{-1}\text{yr}^{-1}$)	SMC ($\text{meqL}^{-1}\text{yr}^{-1}$)	C1	Fe ($\mu\text{molL}^{-1}\text{yr}^{-1}$)	Mn	S
t2.4 t2.5	Site A							
t2.6	b7	-3±2	-2	-0.5		35	-9	-62
t2.7	10		-1				-3	27
t2.8	13		-5	0.3	0.1	15		
t2.9	b15	-34±10	-3				-1	
t2.10	30					-3	-1	10
t2.11	37			-0.7		-8		10
t2.12	43			-1.3			4	
t2.13	91							11
t2.14	Site B							
t2.15	7	-4±1.8			-0.2		-2	
t2.16	b11	-41±11	-5	0.9	0.3	171	-4	65
t2.17	14	-	7	-1.0	-0.5		-5	-86
t2.18	19	-19±12		-0.4	-0.2	94	-3	
t2.19	29	-23±8.3		0.1				
t2.20	b41	-2±0.6	-6		0.2	27		2
t2.21	53	-1±0.5		-0.2		26		-3
t2.22	91					2		
t2.23	Site C							
t2.24	5					270		
t2.25	8							
t2.26	11			-0.3	-0.2	251		
t2.27	14							
t2.28	53			-0.2	-0.1			
t2.29	Site E							
t2.30	5				-0.1		-2	
t2.31	8							
t2.32	11	19±7		-0.3	0.0	169		
t2.33	14		-8	-0.6			-7	
t2.34	38			-1.2			-3	
t2.35	Site F							
t2.36	6			0.2				-21
t2.37	11		-1	0.3				
t2.38	15					-15	2	-8
t2.39	19	-21±12		-0.2		-17		
t2.40	26			0.6	0.0			
t2.41	58				0.9			
t2.42	Site G							
t2.43	b6	14±12		0.2		-161	-4	
t2.44	9							
t2.45	14		-3		0.0	-42		
t2.46	21		-4	0.5	0.1		3	
t2.47	52			-0.8	0.9		-1	-3

^aUncertainties was shown as 95% confidence intervals.

^bWells that show the decreasing trend for [As] and [P].

^cWell that does not fall in normal probability plot blank space indicates that trend was not statistically significant (p value is >0.05).

324 3.2. Chemistry of shallow aquifers

325 3.2.1. Arsenic

326 Concentrations of As in groundwater sampled from the 26
327 shallow (<30 m) monitoring wells spanned three orders
328 of magnitude, from <1 $\mu\text{g/L}$ at F-6 m to 600 $\mu\text{g/L}$ at A-13 m and
329 B-14 m. Groundwater As concentration generally increased
330 with depth starting from the shallowest monitoring well,
331 peaks at ~15 m at Sites A, B, C and E, and at ~20 m at Sites F
332 and G, and then declined again towards the deeper part of the
333 shallow aquifer (Fig. 1c).

324.1. Trends. Overall, the temporal variability of As
325 concentration observed in the 26 shallow monitoring wells
326 was limited (Fig. 5), with a RSD <19% over a monitoring period
327 of up to 3 years (Table 1). However, linear regression of As
328 concentration as a function of time indicated that there were
329 statistically significant long-term trends ($p < 0.05$) for 11 wells
330 out of a total of 26 shallow monitoring wells (Table 2). The
331 largest decreases of -19 to -41 $\mu\text{g/L yr}^{-1}$ were observed at
332 Sites A, B and F for 5 wells containing >200 $\mu\text{g/L}$ of As. In
333 contrast, monitoring data for one well at Site E and one well at
334 Site G, both containing ~150 $\mu\text{g/L}$ of As, showed average
335 increases of +19 and +14 $\mu\text{g/L yr}^{-1}$, respectively.

336.1.2. Excursions. In addition to these long-term trends,
337 there were noteworthy reductions of ~50% of As in ground-
338 water at three different Sites: C-14 m, G-6 m and A-13 m
339 for shorter duration starting July–August 2002 (Fig. 2). By
340 November 2002, however, As concentration in all three wells
341 had returned to within 10 $\mu\text{g/L}$ of their respective long-term
342 averages. A different situation was observed during the
343 particularly severe flooding season of 2003 when, at well
344 C-5 m and only in this well, a drop from 14 to ~9 $\mu\text{g/L}$ in
345 As concentration was sustained over several months but
346 returned to 12 $\mu\text{g/L}$ by Feb.2004 (Fig. 2).

347.1.3. Seasonality. Only a single well A-7 m, the shallowest
348 at Site A, exhibited seasonal variations in groundwater As
349 concentration that were consistent from year to year (Fig. 2).
350 The amplitude of the fluctuations was on the order of ~10%
351 around a mean As concentration of 80 $\mu\text{g/L}$, with lower
352 concentrations corresponding to the wet season (May and
353 October). There may also be a connection between As
354 concentration and water level at B-7 m, but it was limited
355 to 2003 and in this case As concentration was high during the
356 wet season.

357 3.2.2. Phosphorus

358 Similar to As, concentrations of phosphorus (P) in shallow
359 groundwater spanned three orders of magnitude: from 0.11
360 ± 0.07 $\mu\text{mol/L}$ at F-6 m to 108 ± 23 $\mu\text{mol/L}$ at G-9 m (Table 1). The
361 contrast between these two monitoring wells was particularly
362 striking because they are only 400 m apart and their depths are
363 comparable (Fig. 1a). Depth profiles of groundwater P concen-
364 tration at Sites A, E, and F was broadly similar in shape to their
365 corresponding As concentration profiles, at an average atomic
366 P:As ratio of 11 ± 6 (Fig. 1c). For at least one shallow monitoring
367 well at Sites B, C, and G, groundwater P concentration exceeded
368 30 $\mu\text{mol/L}$ even though As concentration in the same well water
369 was no higher than ~100 $\mu\text{g/L}$, corresponding to a P:As molar
370 ratio of 105 ± 92 .

371.1. Trends. The fluctuations (%RSD) in groundwater
372 P concentration over time remained <32% (Fig. 5), exclud-
373 ing F-6 m where P concentration were particularly low
374 (Table 1). Statistical analyses for 9 shallow wells indicated
375 a small long-term decrease between -1 to -8 $\mu\text{mol/L yr}^{-1}$.
376 For only 4 wells (A-7 m, A-15 m, B-11 m and B-41 m), how-
377 ever, the decrease in P concentration was accompanied by
378 a detectable decline in As concentration. An increase in
379 P concentration over time of +7 $\mu\text{mol/L yr}^{-1}$ was recorded at a
380 single well B-14 m (Table 2).

394 3.2.2.2. Excursions. Along with the As concentration de-
 395 creases of ~50% observed in A-13 m, C-14 m, and G-6 m in
 396 July–August 2002, P concentration in the same shallow wells
 397 declined by up to 80% in September 2002 before returning to
 398 previous levels by November 2002. During the summer flood
 399 of 2003 that coincided with a decrease in As concentration in
 400 well C-5 m, there was instead a P concentration increase from
 401 27 to 46 $\mu\text{mol/L}$ that extended to the end of the monitoring
 402 period.

403
 404 3.2.2.3. Seasonality. Seasonal fluctuations in P concentra-
 405 tion were found in a few shallow wells and also observed to
 406 be in phase with As concentration in two shallow wells at
 407 Sites A and B. For well A-7 m, P concentrations varied between
 408 10 and 30 $\mu\text{mol/L}$ during the wet and dry season, respectively.
 409 There was also a measurable increase in P concentration
 410 during the wet season of 2003 in well B-7 m, is consistent
 411 with As fluctuation in the same year. Well F-6 m displayed
 412 seasonality in P concentration with higher values in the wet
 413 seasons, albeit around a low average of $0.1 \pm 0.1 \mu\text{mol/L}$.

414 3.2.3. Major cations and chloride

415 Expressed in equivalents, the sum of major cations (SMC),
 416 including Na^+ , K^+ , Mg^{+2} , and Ca^{+2} , in shallow (<30 m) moni-
 417 toring wells spanned an order of magnitude, from $1.6 \pm$
 418 0.7 meq/L at C-11 m to $12 \pm 1.3 \text{ meq/L}$ at B-7 m (Table 1).
 419 Chloride concentrations in shallow aquifers also spanned
 420 about an order of magnitude, from $0.040 \pm 0.004 \text{ meq/L}$ at
 421 F-19 m to $4.3 \pm 0.4 \text{ meq/L}$ at B-7 m (Table 1).

422
 423 3.2.3.1. Trends. The temporal variability of the major ion
 424 composition of shallow well water was comparable to that of
 425 As and P concentration, with %RSDs remaining below 20%,
 426 30% and 30% for SMC, Na and chloride concentrations, re-
 427 spectively (Table 1; Fig. 5). These measures of variability
 428 exclude, however, the nearly 3-fold increases in SMC and Cl
 429 concentrations in monitoring wells C-5 m, C-8 m, and C-11 m
 430 observed at the end of the wet season in 2003 (Fig. 3). Of
 431 the total of 26 shallow wells that were monitored, the SMC
 432 times-series indicated an statistically significant ($p < 0.05$)
 433 decrease of -0.24 to $-1.03 \text{ meq/L yr}^{-1}$ at 7 wells and an
 434 increase of $+0.11$ to $+0.88 \text{ meq/L yr}^{-1}$ at 8 other wells
 435 (Table 2).

436
 437 3.2.3.2. Excursions. SMC concentrations did not vary ap-
 438 preciablely in the 3 shallow wells where both As and P con-
 439 centration declined markedly for the period of several months
 440 centered on September 2002 (Figs. 2 and 3). On the other
 441 hand, a major salt pulse was observed after the summer flood
 442 of 2003 in three shallow wells at Site C, with up to 3 times
 443 higher concentrations of SMC and Cl compared to the pre-
 444 vious year (Fig. 3). Concentrations of SMC actually already
 445 started to rise in wells C-5 m and C-8 m in May 2003 and
 446 reached their highest level in November 2003 and January
 447 2004, respectively. Concentrations of SMC also eventually
 448 rose in well C-11 m, but only later in January 2004, whereas
 449 no marked change in SMC was observed throughout the
 450 period at well C-14 m. The increases in SMC reflected largely a
 451 rise in dissolved Na in groundwater, from $\sim 0.3 \text{ meq/L}$ in April
 452 2003 to maxima ranging from 2 to 7 meq/L in subsequent
 453 months. The progression of Cl concentrations over the same

period in all shallow wells at site C was similar to that of Na,
 although there was a gap in the Cl time series that extended
 from February 2002 to October 2003.

3.2.3.3. Seasonality. The concentrations of SMC in well
 A-7 m, where the clearest seasonal variations in As and
 P concentration were also detected, were low during the
 wet season and high during the dry season (Fig. 3). In
 contrast to some of the other shallow wells, these changes
 reflected primarily changes in Ca and Mg, with the sum of
 their concentrations fluctuating between 1.2 and 2.2 meq/L .
 Although the duration of sampling was relatively short at
 F-6 m, SMC and Cl both appeared to be systematically
 elevated in this well during the dry season (Fig. 3), when
 P concentration was particularly low (As concentration re-
 mained $< 0.5 \mu\text{g/L}$).

3.2.4. Iron, manganese and sulfur

Of all the constituents of groundwater that were quanti-
 fied, the concentrations of the redox-sensitive elements Fe,
 Mn and S varied the most spatially and temporally (Fig. 5
 and Table 1). Dissolved Fe concentrations spanned nearly
 three orders of magnitude, from $2.4 \pm 2 \mu\text{mol/L}$ at F-6 m to
 $1694 \pm 704 \mu\text{mol/L}$ at C-8 m (Table 1). Dissolved S concentra-
 tions also ranged over three orders of magnitude, from $0.3 \pm$
 $0.02 \mu\text{mol/L}$ at F-26 m to $677 \pm 189 \mu\text{mol/L}$ at B-7 m. Mn
 concentrations were not quite as variable and ranged from
 $2.6 \pm 1 \mu\text{mol/L}$ at F-6 m to $96 \pm 6 \mu\text{mol/L}$ at A-13 m. There was
 no consistent relationship between depth profiles of Fe or Mn
 at each site with the corresponding profiles of As or P con-
 centration. Groundwater SO_4 concentration, however, gen-
 erally decreased with depth at all sites.

3.2.4.1. Trends. There is no systematic relationship between
 trends in Fe, Mn, S, and As (Table 2).

3.2.4.2. Excursions. At Site C, three shallow wells that were
 impacted by the salt pulse during the summer 2003 flood,
 showed an increase of Fe concentration and Mn concentration
 but a decrease of SO_4 concentration after the summer (Fig. 6).
 Fe concentration increased by a factor of 2 to 4; Mn con-
 centration increased by a factor of 3 (Fig. 6). Groundwater SO_4
 concentration decreased from 129, 72 and 16 $\mu\text{mol/L}$ to very
 low values of 3, 4 and 2 $\mu\text{mol/L}$ in Feb., 2004 (Fig. 6).

3.2.4.3. Seasonality. The seasonal fluctuations in ground-
 water composition observed at well A-7 m over a 3 year
 period were systematic for As, P, SMC, Fe and Mn. In parallel
 with changes in concentration of SMC, As and P, concentra-
 tions of Fe and Mn rose during the dry season and dropped
 during the wet season. These variations were not accompa-
 nied by a consistent seasonal pattern for S in well A-7 m. In
 well F-6 m, a pronounced seasonality in groundwater con-
 stituents other than As was observed for Fe, Mn and P with
 low values found in the wet seasons.

3.3. Deep aquifers

In contrast to shallow aquifers of Araihaazar, the overall
 composition of deep (>30 m) aquifers was remarkably stable
 over time except for Fe and SO_4 concentration (Fig. 5). In a

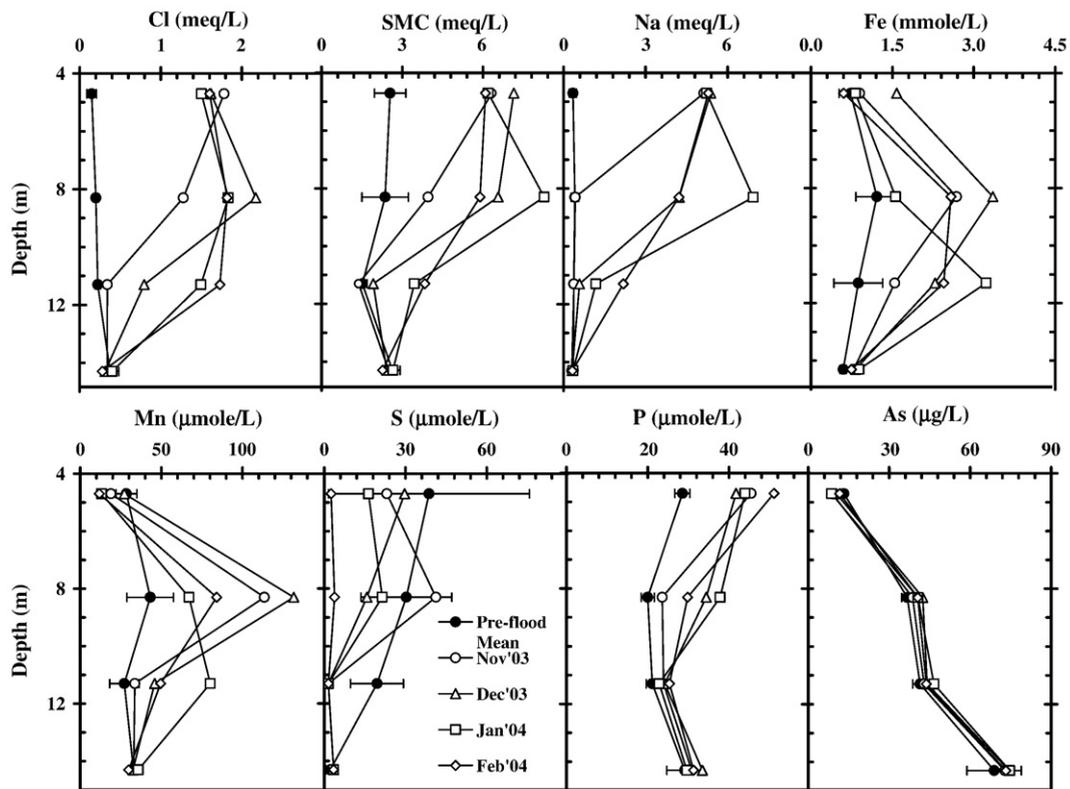


Fig. 6. Depth profiles of Cl, SMC, Na, Fe, Mn, S, P, and As of 4 shallow wells at Site C. Average pre-flood profiles were compared with 4 consecutive post-flood profiles after the flood in the summer of 2003. The black solid circles indicate the average concentration prior to the 2003 flood (March 2002 to July 2003) and error bar represents the standard deviation from the average in pre-flooding period.

sense, the time series data for the deep wells provide an independent measure of the quality of the data because all samples were collected, preserved, and analyzed in exactly the same fashion. At all but Site B (Fig. 1c), these deep wells tapped sandy aquifers with a characteristic orange-brown color that is typically associated with low sediment As concentrations (Horneman et al., 2004; Zheng et al., 2005). At Sites A, C, E, F, and G, the redox potential (ORP) of groundwater was less negative than in shallow aquifers (Table 1). Conductivity measurements and SMC data indicated that deep groundwater was fresher than in shallow aquifers at Sites A, B and C, but saltier at Sites E, F and G (Table 1). The elevated conductivity of deep groundwater at Sites E, F and G reflected primarily high concentrations of Na and Cl (Table 1).

The SMC concentration in the deepest well at all 6 sites was the most stable property measured over the monitoring period, with RSDs usually <9% (Table 1 and Fig. 5). Concentrations of As in the deepest wells at Sites A, B, C, E, and F, were stable and low at $1 \pm 0.7 \mu\text{g/L}$. The levels of As concentration were somewhat higher at B-41 m ($21 \pm 2 \mu\text{g/L}$ As), B-53 m ($17 \pm 1 \mu\text{g/L}$ As); and G-52 m ($7 \pm 0.6 \mu\text{g/L}$). There was a statistically significant decline in As concentration over time of -2 and $-1 \mu\text{g/L yr}^{-1}$ at B-41 m and B-53 m, respectively (Table 2). Concentrations of P ranged from 4 to $10 \mu\text{mol/L}$ in the deepest well from all 6 sites and varied within 30% (Fig. 5). Little systematic variation over time was observed in the deep aquifers, with the exception of a large increase in Fe and SO_4 concentration in C-53 m that

lasted from May 2002 to July 2003. In addition, there was steady rise in SO_4 concentration from <0.003 to $37 \mu\text{mol/L}$ in the deep aquifer at site A over the entire monitoring period (Table 2).

4. Discussion

4.1. Fluctuations in major ion compositions and groundwater age

Groundwater ages in deep aquifers at sites A and B are 10–1000 times higher than in the corresponding shallow aquifers of Araihaazar (Zheng et al., 2005; Stute et al., 2007). Radio-carbon ages of dissolved inorganic carbon from wells C-53 m, F-58 m, and G-52 m were $10,700 \pm 55$, 6240 ± 30 , and 3620 ± 35 years, respectively (Dhar, 2006). These observations show that the deep aquifers in Araihaazar contain groundwater that was recharged centuries to thousands of years ago.

Not surprisingly, the variability of groundwater composition for all major ion constituents that were quantified was lower (i.e., generally <10% for SMC and Cl; Table 1) than in any of the shallow aquifers. The age of deep groundwater is higher and, therefore, flow lines are likely to be longer, and dispersive mixing may have smoothed out any initial temporal fluctuations.

The shallow aquifers at the 6 sites that were monitored over a period of 2–3 years were divided into 2 groups on the basis of $^3\text{H}/^3\text{He}$ ages of groundwater collected from the same set of wells (Stute et al., 2007). In one group comprised of Sites

C and F, groundwater $^3\text{H}/^3\text{He}$ ages remain <5 years down to a depth of ~14 m, whereas $^3\text{H}/^3\text{He}$ ages already exceed 20 years at the same depth at Sites A, B, E, and G. Sites C and F are also the only 2 sites where the $^3\text{H}/^3\text{He}$ age of groundwater from the shallowest well was <1 year. The rapid recharge of shallow aquifers at Sites C and F indicated by the $^3\text{H}-^3\text{He}$ data is probably linked to the upward extension, almost to the surface, of sandy deposits at these two sites (van Geen et al., 2006; Aziz et al., in revision; Weinman et al., in press). At Sites A, B, E, and G, instead, recharge appears to be limited by the presence of a thicker layer of silt or clay that capped the local sandy aquifers. These hydrogeological constraints are used next to interpret the behavior of relatively conservative constituents of groundwater, i.e., SMC, Na, and Cl.

It is probably not a coincidence that variations in the composition of groundwater e.g. SMC, Na, and Cl, are particularly pronounced (up to 40%) and go beyond in the shallow monitoring wells at the Site C where sandy deposits extend to the surface (Fig. 3 and Table 1). What is less clear is to what extent these variations reflect vertical advection of recently recharged water, lateral motion of groundwater that is heterogeneous in composition, or a combination of both. At Site C, a progressive deepening of a front containing elevated Na and Cl levels during and following the 2003 flood is consistent with at least some vertical penetration to ~11 m (Fig. 6). At present, we cannot rule out the possibility that the changes in NaCl were due to leakage of flood water along the well casings, although that seemed unlikely given the systematic pattern of the multi-elements depth profiles obtained at different time post-flood (Fig. 6). Elevated concentrations of NaCl have previously been linked to human waste because large quantities of salt are mobilized and added to flood water in densely populated areas where sanitation is limited to pit latrines (Ahmed et al., 2004). A sizable trench (~10 m wide) that presumably could collect latrine runoff is located next to Site C and separates a vegetable field from the village.

At site F, despite similar depositional settings, the seasonal cycle of variations in Na (as SMC) and Cl concentrations is considerably muted compared to Site C and lacks the response to the 2003 flood (Fig. 3). Site F is located in a village that is built up to higher elevation than the surrounding area and has no such trench or pond next to it. This may be why Na and Cl concentrations do not vary as much as Site C.

Some fluctuations in major ion concentrations were also observed at clay/silt covered Sites A and B. The most notable variation linked to seasonal water level fluctuation was observed only in shallowest wells (Figs. 3, 5 and Table 1). The $^3\text{H}/^3\text{He}$ ages of the groundwaters from shallowest wells at these sites are also <5 years, although the groundwater age rapidly increases beyond the depth of these wells (Stute et al., 2007). Given the higher ages, and the capping of shallow aquifers around Sites A and B by relatively impermeable surface sediment, it seemed more plausible to attribute the variations in groundwater composition to lateral motion of groundwater of heterogeneous composition. In a 3-dimensional groundwater flow model developed for Araihaazar, reversal of lateral flow directions between wet-dry seasons are found, in addition to flow path oscillations driven by the seasonal variation of the groundwater table (Horneman, 2006). The oscillation and reversal of flow implies that older groundwater with different compositions can mix on seasonal

time scale without influencing the residence time. Seasonal patterns in major ion concentrations similar to the one observed in the shallowest well at Site A, though not necessarily in phase, were previously reported for two shallow existing wells in entirely different sampling locations in Araihaazar (Cheng et al., 2005). Whereas maxima and minima in major ion concentrations for shallow wells in the area often do not coincide, the seasonal pacing of the fluctuations might still be linked to variations in water level of the nearby stream (Figs. 2, 3 and 4) that in turn modulate an oscillating lateral flow field.

In contrast to the shallowest wells at Sites A, B, C, and F, fluctuations in groundwater composition were limited at G-6 m (Fig. 3). At this location, the $^3\text{H}/^3\text{He}$ age of groundwater in even the shallowest wells is >10 years (Stute et al., 2007). Variations at E-5 m, also with $^3\text{H}/^3\text{He}$ age of ~10 years, on the other hand, were comparable to Sites A and B but clearly not as stable as at G-6 m (Fig. 3).

In summary, the major ion compositions of deep aquifer groundwater is much less variable than the shallow aquifer groundwater due to a much longer residence time. Within the shallow aquifer, flooding can sometimes but not always alter major ion compositions at locations where sandy sediment extended to the surface. More importantly, fluctuation of major ion occurred on shorter time scale, and sometimes seasonal time scale, for shallow groundwater with ages >10 years, consistent with a flow regime with oscillation of horizontal flow driven by fluctuating seasonal hydraulic gradient.

4.2. Decoupling between variations in redox-sensitive constituents and As

Perhaps the greatest surprise that resulted from this study is that variations in groundwater As concentrations were considerably muted in comparison with other redox-sensitive constituents, such as Fe, Mn and SO_4 in many wells from multiple sites, including both the low-As deep aquifers and high-As shallow aquifers (Fig. 5). Considerable variations of Fe and SO_4 , and to a lesser extent Mn, were observed in the deep aquifer where major ions and As remained stable (Fig. 5). In the case of deep aquifers, such decoupling is consistent with low concentrations of mobilizable As in deep aquifer sediment (Zheng et al., 2005). In such conditions, even if microbially-mediated reduction of Fe oxyhydroxides occurred, the release of Fe could be decoupled from As due to either re-adsorption or the lack of a pool of mobilizable As in the sediment (van Geen et al., 2004).

Like the deep aquifer, the temporal patterns of concentrations of As, vs. Fe, Mn, and SO_4 can also be decoupled in shallow aquifers. One example of such decoupling is the three shallow monitoring wells (C-5 m, C-8 m and C-11 m) at sandy Site C where major ion concentrations and redox-sensitive elements were strongly affected by the 2003 flood whereas the depth profiles of As concentrations did not change (Fig. 6). Only in the shallowest well C-5 m was the concentration of As affected by the flood evident when the relative change was examined (Fig. 2), although the As level returned to pre-flood level approximately 6-months after flooding both in relative change (Fig. 2) and absolute level (Fig. 6). Whereas slight decrease in As concentration is consistent with dilution from

685 flood water, it is not what might have been expected from the
 686 dissolution of mineral oxides suggested by the rise in Fe and
 687 Mn concentrations (Fig. 6). The ability of the shallow aquifer
 688 at Site C to maintain a relative constant concentrations of
 689 groundwater As is not surprising in light of recent finding that
 690 partitioning between solute and solid As in shallow aquifer
 691 has a fairly constant coefficient based on a regional study (van
 692 Geen et al., in press). In this scenario, groundwater is rapidly
 693 equilibrated with sediment such that it is the sediment As
 694 level that controls the groundwater As concentration. Such
 695 decoupling was also evident at F-6 m (Fig. 2, Table 1) where
 696 consistently low As concentrations were observed over the
 697 monitoring period even though both major ions and redox-
 698 sensitive elements exhibited a strong seasonal pattern (data
 699 shown in Supplementary figure). What is the implication of
 700 limited temporal variation of As despite the significant varia-
 701 tion of redox sensitive ions such as Fe and Mn? Considered
 702 as a whole, not only it reinforces the notion that there is
 703 significant decoupling between the mobilization of As and the
 704 redox state of an aquifer (Horneman et al., 2004; van Geen
 705 et al., 2004; Polizzotto et al., 2005; van Geen et al., 2006),
 706 but also it supports a rapid equilibrium between solute and
 707 solid As in the aquifer (van Geen et al., in press). Finally,
 708 strong temporal decoupling between As and Fe, Mn and S in
 709 the shallow wells (5–7 m) from our sites imply that the
 710 chemical compositions of recharge water could be highly
 711 heterogeneous both spatially and highly variable temporally.

712 4.3. Trends in groundwater ~~as~~ in the shallow aquifer

713 Stute et al. (2007) have pointed out on the basis of paired
 714 measurement in groundwater from the same set of shallow
 715 monitoring wells (<20 m) that there is a surprisingly linear
 716 relationship between As concentrations and groundwater age
 717 across a wide range of settings (Table 1). It is noted that the
 718 deepest wells of most sites including A-15 m, B-19 m, E-14 m,
 719 F-19 m, G-14 m are affected by mixing, therefore were not
 720 included in regression analysis (Stute et al., 2007). The
 721 simplest interpretation of this linear relationship is that the
 722 release rate of As is relatively constant at $\sim 20 \mu\text{g/L/year}$ in the
 723 shallow aquifers of Araihasar. This rate appears to be in-
 724 sensitive to, and therefore decoupled from, the redox state of
 725 the aquifer. This steady release of As under a wide range of
 726 conditions is consistent with the observation that concentra-
 727 tions of major ions or redox-sensitive constituents are
 728 not necessarily linked to variations in dissolved As temporally.
 729 Taken together, these observations imply that the spatial
 730 heterogeneity of As concentration in shallow aquifers is
 731 considerably less than that of major ions or redox-sensitive
 732 constituents in groundwater. However, the reasons for the
 733 inferred heterogeneity in major ion and redox sensitive
 734 constituents relative to As remain unclear.

735 If groundwater As concentrations remain constant over
 736 time, then a steady rate of As release (e.g. source) would
 737 require that As is either discharged from the aquifer or
 738 immobilized (e.g. sink) to sediment for maintaining a steady
 739 state. If groundwater As increases over time, then there must
 740 be a surplus of As, or vice versa if groundwater As decreases
 741 over time. We recognize that our time series data span only 2
 742 to 3 years and it may therefore be premature to draw any firm
 743 conclusions. But, systematic differences of trends are ob-

744 served at different sites. At Sites F and C where sandy sed-
 745 iment extends to surface, there is little trend in groundwater
 746 As (Table 2), suggesting no net loss or gain of As. Although
 747 F-19 m showed a decline of $21 \pm 12 \mu\text{g/L yr}^{-1}$, it was below a
 748 silty layer with lower hydraulic conductivity and thus prob-
 749 ably more akin to old meander environment at Sites A and
 750 B (Fig. 1a). Clay/silt covered Sites A and B located in old-
 751 er meanders >6000 years old (Weinman et al., in press)
 752 showed a systematic decline over time of groundwater As in
 753 6 out of 9 shallow wells (Table 2). This implies that such
 754 settings presently experience a net loss of As. Similarly clay/
 755 silt surface cover Sites E and G located in a young flood plain
 756 <4000 years old (Weinman et al., in press) showed increase
 757 of As over time in 2 out of 8 shallow wells. This implies that
 758 such setting has a net gain of As.

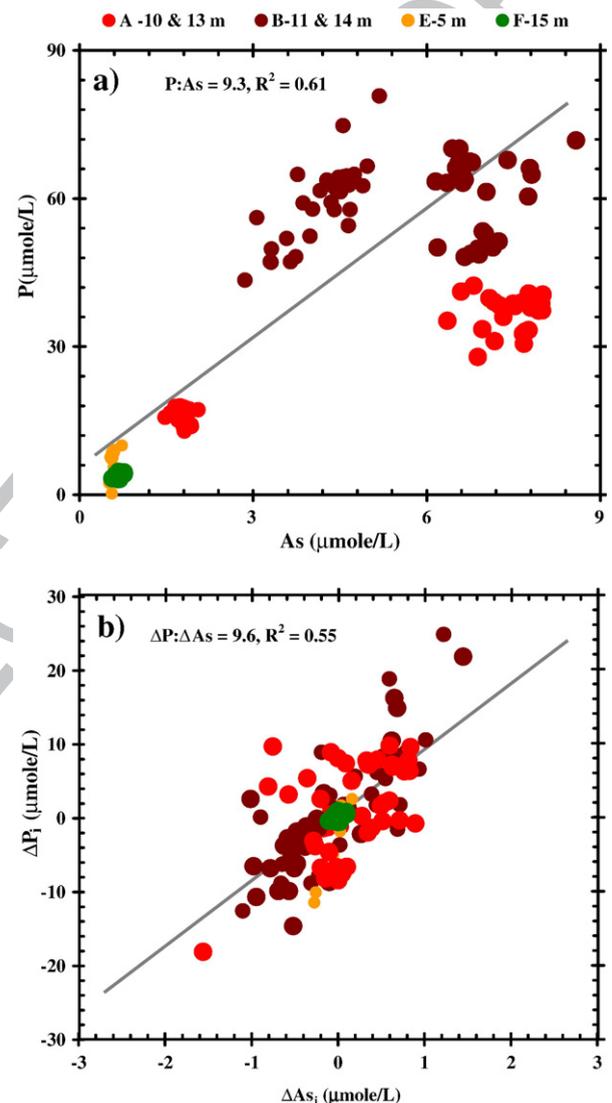


Fig. 7. a) Concentrations of groundwater P vs. As for the shallow monitoring wells with $^3\text{H}/^3\text{He}$ ages of >5 years. The data are included for the entire time period (2–3 years). b) The deviation of P concentration above or below the mean value ($\Delta P_i = P_i - P_{\text{avg}}$) vs. the deviation of As concentration ($\Delta As_i = As_i - As_{\text{avg}}$) of the same wells as in panel a).

759 Why does some aquifer system gain As, some lose As
760 and yet some with no net change? The reasons for much of
761 this remain unclear, but sites with net loss of As located on
762 older meanders is consistent with the notion that flushing
763 over time may gradually decrease the inventory of As in the
764 Holocene aquifer but that process will take thousands of years
765 if not longer (McArthur et al., 2001; Stute et al., 2007; van
766 Geen et al., in press). The increasing trends observed in Sites E
767 and G suggest that near surface mobilization and subsequent
768 transport (Polizzotto et al., 2005) may have provided a fresh
769 source of As to the aquifer in very young flood plain.

770 4.4. Coupled and decoupled behavior of P and As

771 Arsenic in its oxidized form is a chemical analog for phos-
772 phate. For this reason, parallel behaviors or interactions be-
773 tween these two constituents are frequently invoked. Arsenic
774 in aquifers of Araihaazar, however, is predominantly present
775 in groundwater in the As(III) form (Zheng et al., 2004). In
776 older groundwater (>5 years), As was observed to be co-
777 variance of P in time series data (Fig. 7). When the deviation
778 of P from the average P concentrations over time (ΔP) was
779 plotted over the deviation of As from the average As con-
780 centrations over time (ΔAs), a ΔP : ΔAs atomic ratio of 9.6
781 was found ($R^2=0.55$, $n=181$, Fig. 7b), nearly identical to the
782 ratio (9.3) established independently by using P:As ratio
783 in these wells directly (Fig. 7a). Together these suggest a
784 similar release mechanism for As and P in the older (>5 years)
785 shallow groundwaters.

786 Why then is there more P relative to As in relatively young
787 (<5 yr) shallow groundwaters? P concentrations are high not
788 only in young water at sandy Site C (but not F), but also in
789 young water tapped by the shallowest well at Sites A and B
790 (Table 1). One possibility is that P is supplied from surface
791 water recharge whereas As is not. For instance, P concentra-
792 tions increased by $\sim 20 \mu\text{mol/L}$ at both C-5 m and C-8 m after
793 the 2003 flood (Fig. 6). These observations confirm that As
794 was probably not derived from recharged water but that P
795 was. Alternatively, the increase of P post-flood at both C-5 m
796 and C-8 m result from chemical reactions that liberate P from
797 sediment, but those reactions did not influence As level.

798 5. Conclusions

799 Groundwater age is a key variable influencing the tem-
800 poral variability of groundwater chemistry in shallow Holo-
801 cene aquifers and deeper aquifers of Araihaazar. The principal
802 findings of the study are:

- 803 • In shallow and young (<3.5 years) groundwater, the var-
804 iability of As concentrations over 2–3 years is much more
805 muted when compared to that of major ions and redox
806 sensitive constituents. The decoupling between As and
807 redox sensitive constituents under such conditions reflects
808 the greater availability and mobility of Fe in the shallow
809 sediment compared to As.
- 810 • The concentration of As in shallow and older groundwater
811 (>3.5 years) as well as deep groundwater in deeper aquifers
812 that is thousands of years old, is stable over time despite
813 having considerable variability of redox sensitive constitu-
814 ents. The reason for the decoupling remains unclear but

may result from relatively constant solute to solid As par- 815
titioning observed in Bangladesh. 816

- Trends in groundwater As concentration over the entire 817
monitoring period of 2–3 years may be governed by sed- 818
iment geology and its effect on the groundwater flow 819
regime. Older sedimentary aquifers (6000–10,000 years) 820
is experiencing a net loss of As, consistent with gradual 821
flushing of As from the aquifer. 822

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Appendix A. Supplementary data 827

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