

# Limited Temporal Variability of Arsenic Concentrations in 20 Wells Monitored for 3 Years in Araihaazar, Bangladesh

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Millions of people in Bangladesh have probably switched their water consumption to wells that meet the local standard for As in drinking water of 50  $\mu\text{g/L}$  as a result of blanket field testing throughout the country. It is therefore important to know if As concentrations in those wells could change over time. To address this issue, we report here precise groundwater As analyses for time-series samples collected from a suite of 20 tube wells containing  $\leq 50 \mu\text{g/L}$  As and ranging from 8 to 142 m in depth. For 17 out of 20 wells, the standard deviation of groundwater As concentrations was  $< 10 \mu\text{g/L}$  over the 3-year monitoring period ( $n = 24\text{--}44$  per well). Six of the 17 wells are community wells, each of which serves the needs of several hundred people in particularly affected villages. Of the three wells showing larger fluctuations in chemical composition including As, two are very shallow (8 and 10 m). Variations in As concentrations for one of these wells ( $50 \pm 32 \mu\text{g/L}$ ,  $n = 36$ ), as well as another shallow well showing smaller variations ( $48 \pm 5 \mu\text{g/L}$ ,  $n = 36$ ), appear to be coupled to seasonal precipitation and recharge linked to the monsoon. The other shallow well showing larger variations in composition indicates a worrisome and steady increase in As concentrations from 50 to 70  $\mu\text{g/L}$  ( $n = 36$ ) over 3 years. The time series of As ( $30 \pm 11 \mu\text{g/L}$ ,  $n = 24$ ) and other constituents in one deep community well (59 m) show large fluctuations that suggest entrainment of shallow groundwater through a broken PVC pipe. Even though the majority of wells that were initially safe remained so for 3 years, our results indicate that tube wells should be tested periodically.

## Introduction

Nearly half of the estimated 10 million tube wells in Bangladesh have been tested with field kits under a vast survey conducted over several years by the Bangladesh Arsenic Mitigation and Water Supply Program (BAMWSP), international agencies, and nongovernmental organizations (<http://www.bamwsp.org/>). Following the example initially set by government and aid organizations, the vast majority of these wells were installed privately in the past 10–15 years, paid for by individual households. The latest compilation of

field-kit results shows that 30% of 4.4 million wells in the 248 upazilas that are most affected by As in the country did not meet the Bangladesh standard for drinking water of 50  $\mu\text{g/L}$ . The proportion of unsafe wells is somewhat higher than the outcome of an earlier survey of 3534 wells distributed across much of the country showing, on the basis of laboratory measurements, that 25% wells exceeded 50  $\mu\text{g/L}$  (1). The difference is encouraging because the earlier survey included 496 upazilas with a low proportion of unsafe wells that were not included in the subsequent BAMWSP survey. The data confirm that the Hach field kit, as deployed by BAMWSP staff in recent years, provides a reasonably good measure of the As content of groundwater, even if the performance of the kit could be improved by increasing the reaction time (2).

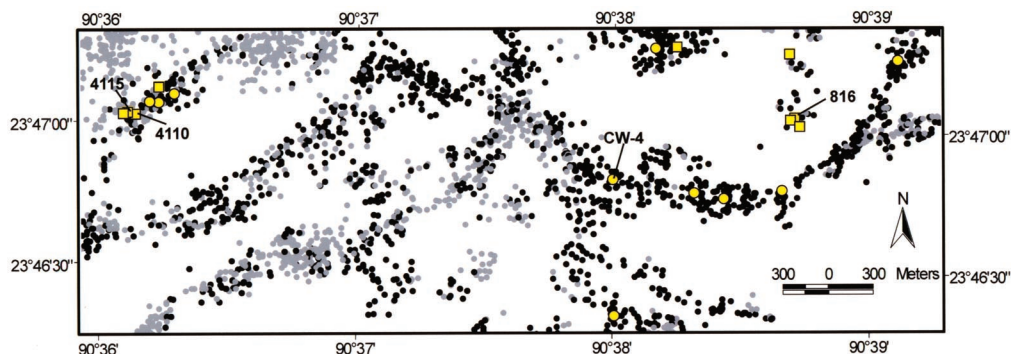
This paper focuses on the 3 million tube wells in 48700 villages distributed across the country that were declared safe on the basis of the field kit. In many villages, safe and unsafe wells frequently neighbor each other because of the highly patchy distribution of As in the shallow aquifers tapped by the vast majority of existing wells (1, 3). This mixed distribution, once recognized, provides the opportunity for many rural households with unsafe wells to lower their exposure by sharing those wells that are safe (4). This appears to have happened on a scale considerably larger than expected. In a portion of Araihaazar upazila studied for the past several years, a recent survey of 6500 households 3 years after the results from laboratory tests were communicated in 2001 has shown that two-thirds of households with unsafe wells had stopped using them for drinking and cooking (5). The majority of these households had switched to a neighboring private well that had been labeled safe. The obvious question that arises is whether presently safe wells in the proximity of other wells that are elevated in As are likely to remain sufficiently low in As as more households start using them (6).

Resampling of 344 wells in Araihaazar and comparing laboratory results for As have shown that, by and large, groundwater As concentrations did not change significantly for wells sampled 2 years apart (2). The finding is consistent with 1 year of observations for a number of wells over a range of depths in other parts of the country by BGS/DPHE (1). Other groups working in Bangladesh, West Bengal of India, and Vietnam, however, have reported worrisome indications of seasonally changing As concentrations (7, 8), or increasing As concentrations that could increase the exposure of well users without their knowledge (9). Because well-documented time series groundwater As concentrations are few and far between, a frequent sampling program was initiated in 2001 in Araihaazar for a set of 13 private and 7 community wells containing  $\leq 50 \mu\text{g/L}$  As. This paper describes the outcome of 3-years worth of high-quality concentration data for As and a suite of other groundwater constituents. The next section of the paper describes the geological setting of the 20 wells that were selected for monitoring as well as the methods used to sample and analyze groundwater for As, the major cations Ca, Mg, K, and Na, and the redox-sensitive elements P, S, Mn, and Fe. Negligible changes in groundwater As concentrations documented for 17 out of 20 wells are used in the subsequent section to demonstrate the integrity of the data. The discussion then focuses on significant fluctuations in the content of As and other constituents of groundwater pumped from the remaining three wells. The observations are used to shed new light on the still poorly understood hydrological and biogeochemical processes that regulate the As content of ground-

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**FIGURE 1.** Location map of the studied monitoring wells in Araiharzar, Bangladesh. Monitoring wells are indicated by larger gray squares and circles for depths of 0–20 and >20 m, respectively. Small dots in the background indicate other existing tube wells in the area: wells with As concentrations  $\geq 50 \mu\text{g/L}$  are represented by black dots, and those with As concentrations  $< 50 \mu\text{g/L}$  by gray dots. Four wells with notable As fluctuations over time are labeled on the map.

**TABLE 1.** Summary of Total As and Major Cations (Na + K + 2Mg + 2Ca, Molar Units) in 20 Monitoring Wells and Their Variability in Time Series Samples Collected over 3 Years<sup>a</sup>

well ID	longitude	latitude	depth (m)	year installed	no. of samples	mean As concn ( $\mu\text{g/L}$ )	mean major cation concn (meq/L)
816	90°38'38"	23°47'08"	8	1999	36	63 ± 13	7.2 ± 0.4
4110	90°36'08"	23°47'05"	10	1999	36	48 ± 5	11.8 ± 2.9
4115	90°36'06"	23°47'05"	10	1999	36	50 ± 32	16.1 ± 8.5
808	90°38'41"	23°47'19"	8	1995	35	41 ± 1	7.6 ± 0.9
823	90°38'42"	23°47'06"	10	1997	36	40 ± 3	8.7 ± 1.2
4071	90°36'14"	23°47'10"	10	1999	34	63 ± 6	8.4 ± 1.2
4101	90°36'05"	23°47'05"	10	1998	34	17 ± 1	7.3 ± 0.7
825	90°38'41"	23°47'05"	12	1997	36	64 ± 9	6.7 ± 1.1
84	90°38'43"	23°47'04"	20	1995	43	42 ± 3	4.8 ± 0.1
1651	90°38'15"	23°47'20"	20	1994	43	44 ± 5	4.7 ± 0.7
4133	90°36'14"	23°47'07"	30	2001	35	2.2 ± 1.9	3.6 ± 0.1
4146	90°36'17"	23°47'09"	30	2001	33	3.2 ± 4.6	2.9 ± 0.1
CW-1	90°36'12"	23°47'07"	40	2001	40	0.4 ± 0.3	4.4 ± 0.8
CW-4	90°38'00"	23°46'52"	60	2001	24	30 ± 11	8.0 ± 0.4
CW-6	90°38'39"	23°46'50"	60	2001	27	1.4 ± 0.6	5.4 ± 0.1
CW-3	90°38'26"	23°46'48"	60	2001	25	1.8 ± 0.3	7.2 ± 0.5
1639	90°38'10"	23°47'20"	70	2000	44	17 ± 1	6.7 ± 0.1
CW-2	90°38'19"	23°46'49"	88	2001	35	0.8 ± 0.8	4.3 ± 0.3
CW-7	90°39'06"	23°47'18"	123	2001	25	3.9 ± 0.5	4.0 ± 0.1
CW-5	90°38'01"	23°46'23"	142	2001	25	1.4 ± 1.4	3.4 ± 0.4

<sup>a</sup> All wells are divided into three groups based on well depths and As variability. They correspond to the three groups in Figure 2.

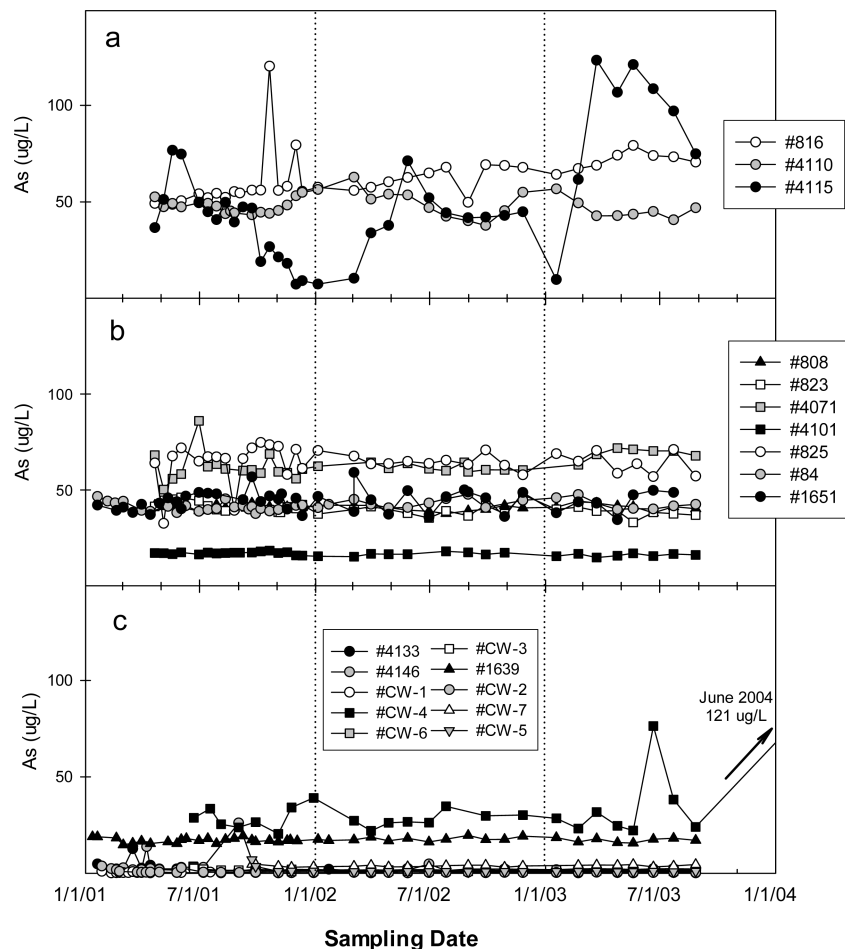
water in Bangladesh. The paper concludes with a discussion of the implications of the observations for mitigation and policy, including the documented failure of one community well.

## Methods

**Well Characteristics and Sampling.** The 20 tube wells selected for this study are all located within a 25 km<sup>2</sup> area ~30 km east of Dhaka where health, earth, and social scientists from Columbia University have been studying the groundwater As problem in partnership with Bangladeshi institutions since early 2000 (2–4, 10–16). Ten of the 13 private wells that were monitored are grouped into 2 areas in the eastern and western portions of the study area and tap relatively shallow (8–20 m) late Holocene deposits of gray sediment (14, 15) (Figure 1). A mix of high- and low-As shallow tube wells exist near wells 4115, 4110, 4101, and 4071, while wells 84, 816, 825, and 1651 are surrounded by a majority of high-As tube wells (Figure 1 and Table 1). These shallow private wells were all installed after 1994, most between 1997 and 1999. Ten deeper wells (30–142 m) that were selected are also distributed across the study area and, in most cases,

tap older aquifers of presumed Pleistocene age that are orange-brown in color (14, 15). Seven of the deeper wells were purposely installed by the program as community wells available to all surrounding households (10). A previous household survey indicated that the initial number of users of each private well ranged from 4 to 25, with an average of 11 users; the community wells typically each serve the needs of several hundred villagers (10).

Groundwater samples were collected from the hand pump every 2 weeks in the early stages of the study, and later monthly, after pumping for about 5 min to flush the well pipe. Well water was collected directly, without filtration, into 60 mL acid-leached polyethylene sampling bottles and acidified to 1% HCl (Optima, Fisher). In addition, the origin of highly variable As concentration in groundwater from CW-4 was investigated in June 2004 by collecting with a new device (16) a profile of groundwater properties from six horizons in the 8–70 m depth range. The groundwater obtained with the device, dubbed the “needle sampler”, was filtered in the field and, in addition to 10 unfiltered samples of well water collected from the pump, preserved with 1% HCl in acid-leached scintillation vials.



**FIGURE 2. Arsenic levels in time series groundwater samples collected from 20 wells around Araiharzar, Bangladesh, between 2001 and 2003: (a) well depths 8–20 m, with apparent seasonal patterns or long-term trends; (b) well depths 8–20 m, without seasonal patterns or long-term trends; (c) well depths 30 m or more.**

**Analyses.** Groundwater samples were analyzed by high-resolution inductively coupled plasma mass spectrometry (HR ICP-MS) on a single-collector VG Axiom for As and Na, Mg, K, Ca, P, S, Mn, and Fe, using a procedure that requires only a single dilution (17). The precision of the method ranges from 1% to 3% for most elements in the range of typical concentrations for groundwater. The analytical detection limit for As is  $\sim 0.1 \mu\text{g/L}$ ; the effective detection limit is closer to  $1 \mu\text{g/L}$  because a small amount of unfiltered particulate matter may occasionally increase the dissolved As concentrations upon acidification. All samples were analyzed over a period of 2 months under very similar instrumental conditions. The variability of As concentrations obtained for a consistency standard included with each run was  $320 \pm 7 \mu\text{g/L}$ , i.e.,  $\pm 2\%$  ( $n = 31$ ). Samples from the same well were analyzed within the same run to improve the precision of the time series data as much as possible.

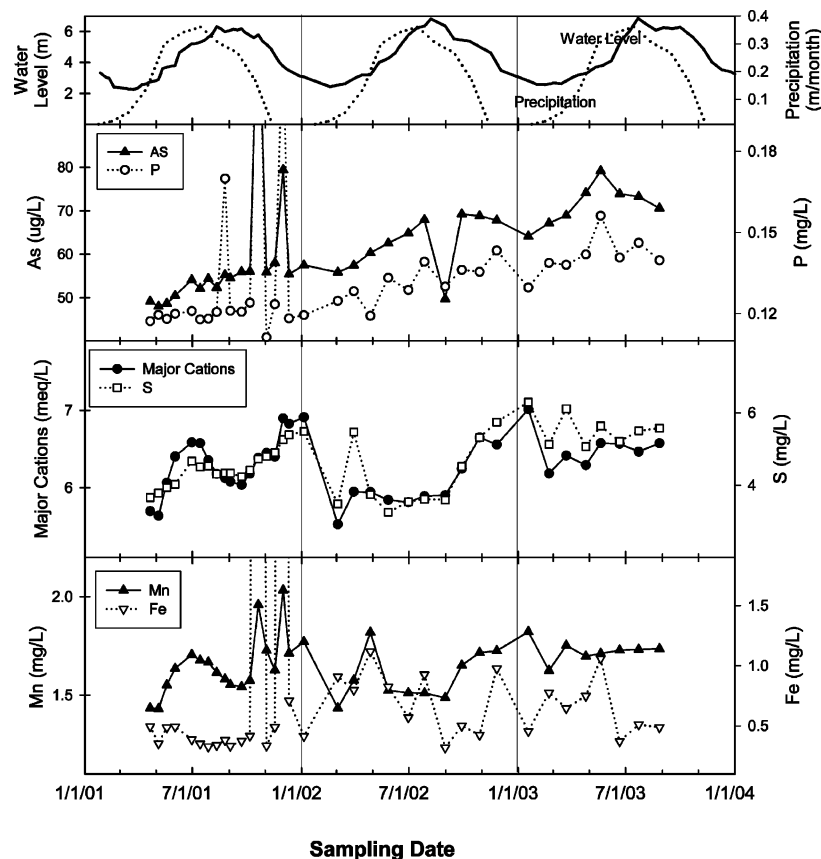
## Results

**As in Deep Wells.** In water samples collected from deep private wells 4133 and 4146, and all but one of the community wells, As concentrations remained  $< 5 \mu\text{g/L}$  throughout the 3 year monitoring period, with the exception of a handful of samples for which Fe and Al concentrations were unusually high (Figure 2 and Supporting Information; unpublished Al data). The Fe and Al data suggest that occasionally elevated As concentrations resulted from the entrainment of aquifer particles that were leached upon acidification. In deep private well 1639, the level of As was somewhat higher but also remarkably constant ( $17 \pm 1 \mu\text{g/L}$ ). In contrast, concentrations

of As in groundwater collected from CW4 fluctuated erratically between 20 and  $70 \mu\text{g/L}$  throughout the period, and rose to  $121 \mu\text{g/L}$  when the well was sampled one last time in June 2004 before it was shut down (Figure 2).

**As in Shallow Wells.** Very little change in As concentrations was detected throughout the sampling period in groundwater collected from 8 out of 10 shallow wells ( $\leq 20 \text{ m}$ ), even though average concentrations ranging from 17 to  $64 \mu\text{g/L}$  were typically higher than in deeper wells (Figure 2). The time series for the two remaining shallow wells, 816 and 4115, indicate variations in dissolved As concentrations with a standard deviation of 13 and  $32 \mu\text{g/L}$ , respectively (Table 1, Figures 3 and 4). Elevated As concentrations as high as 80– $120 \mu\text{g/L}$  were observed in May–June at well 4115, whereas in January As concentrations dropped to nearly  $20 \mu\text{g/L}$  (Figure 4). The time series data from well 816 suggest a recurrent minimum in As concentrations in January as well, but the dominant trend at this location is a distinct and, with the exception of a few outliers, gradual rise from 50 to  $70 \mu\text{g/L}$  over the course of 3 years (Figure 3). At another shallow well located within 50 m of well 4115, smaller variations in As concentrations (4110,  $48 \pm 5 \mu\text{g/L}$ ) also followed a seasonal pattern (Figure 5). The variations in groundwater As concentrations at well 4110 were several months out of phase relative to those of the two other shallow wells, however, with a peak of  $\sim 60 \mu\text{g/L}$  in December–January followed by a minimum of  $\sim 40 \mu\text{g/L}$  recorded in September–October (Figure 5).

**Major Cations.** Seasonal variations in Na, Mg, K, and Ca concentrations were considerable in some of the shallow



**FIGURE 3.** Comparison of patterns of temporal variation for well 816. The groundwater level represents measurements relative to sea level for the shallow aquifer at a nearby nest of wells (23.780°E, 90.640°N) In this and all figures hereafter, the monthly precipitation data, based on the Dhaka-PBO station, were summarized from the daily/monthly/yearly flood bulletin, Flood Forecasting and Warning Center (Rashed Chowdhury, personal communication). Information given in each panel, from top to bottom: (a) groundwater level; (b) P and As variations; (c) total major cation (molar units) and S variations; (d) Mn and Fe variations.

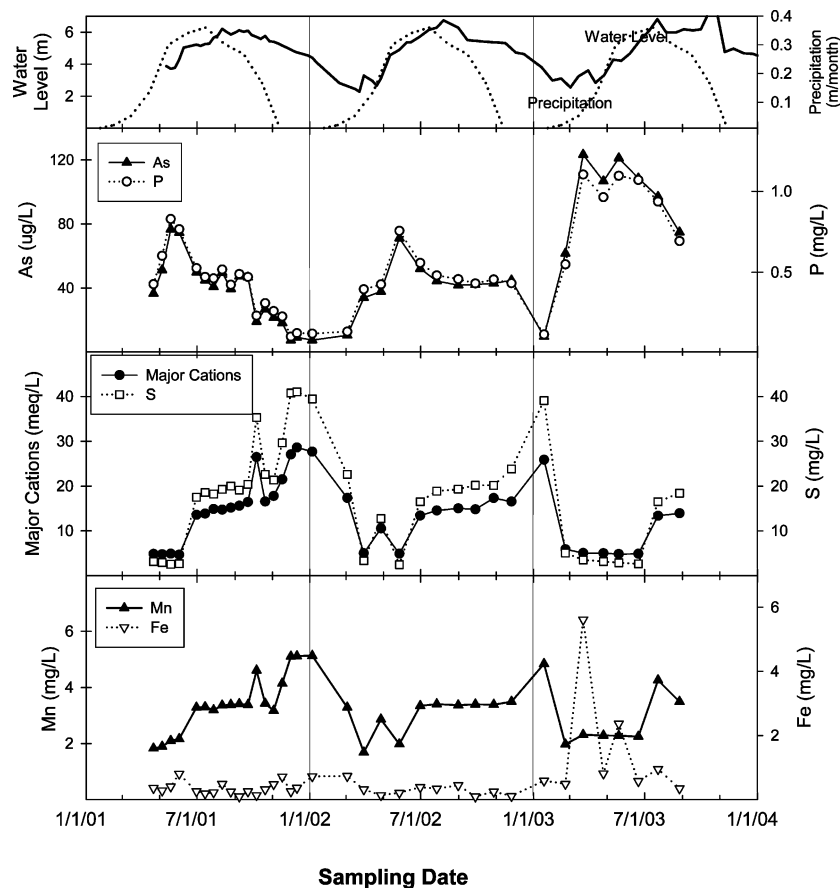
wells (e.g., 4115, 4110, 823, 4071, and 825) and are highly correlated (Supporting Information). Although the slopes of the relationships between pairs of cations differ from one well to the other (e.g., Na and Ca in Figure 6), the data can be summarized by adding molar concentrations of the four major cations, weighed by their respective charges. The combined measure should be a reflection of the concentration of total dissolved solids in the groundwater. Variations in major cation concentrations were particularly high for wells 4110 ( $12 \pm 3$  mequiv/L) and 4115 ( $16 \pm 8$  mequiv/L), some of the same wells showing a seasonal pattern of variations in As concentrations (Figures 4 and 5). In both wells, seasonal variations in major cations and As concentrations mirrored each other. The gradual decline in As concentrations at well 4115 between April and December was accompanied by a steady increase in major cation concentrations. The steep increase in As concentrations between January and May was accompanied by a rapid drop in major ion concentrations. Similarly, maxima and minima in major cation concentrations at well 4110 corresponded to minima and maxima in As concentrations, respectively (Figure 5). Even at well 816, maxima in major cation concentrations observed in December–January correspond to periods when the rise in As concentrations over 3 years was temporarily arrested (Figure 3). Major cation concentrations were generally lower in deep wells (3–7 mequiv/L) compared to shallow wells (5–16 mequiv/L) and did not show obvious changes over time (Table 1).

**Redox-Sensitive Constituents.** The concentration of several constituents of groundwater known to be sensitive to redox conditions also varied in concert with As in the shallow wells. Fluctuations in P concentrations between 0.1

and 1.2 mg/L and between 0.5 and 0.7 mg/L in wells 4115 and 4110, respectively, closely paralleled the seasonal variations in dissolved As concentrations (Figures 4 and 5). Even at well 816, there was a small but steady increase in P concentrations from 0.12 to 0.15 mg/L over the course of 3 years (Figure 3). However, the magnitude of changes in P and As concentrations was about a factor of ~2 and ~6 lower in wells 4110 and 816 compared to well 4115. P concentrations in shallow wells (0.1–0.6 mg/L) were generally higher than in deeper wells (0.1–0.2 mg/L). Temporal variations of P concentrations were not significant in the deeper wells (Supporting Information).

There were also pronounced variations in dissolved S and Mn concentrations in groundwater from the same shallow wells that exhibited the clearest variations in groundwater As. Sulfate concentrations, most likely in the form of sulfate since sulfide concentrations are typically low in Bangladesh groundwater (18), and dissolved Mn concentrations rose and fell in parallel with major cation concentrations at wells 4110, 4115, and 816 (Figures 3–5). In general, S and Mn concentrations were also higher in shallow wells than in deep wells (Supporting Information). Variations in dissolved Fe concentrations in the same shallow wells were more erratic and showed no evidence of seasonal or long-term changes related to As (Figures 3–5).

**Needle Sampler Profile.** The two shallow intervals sampled with the needle sampler near the site of CW4 indicate an increase in As concentrations with depth from 39  $\mu\text{g/L}$  at 8 m to 109  $\mu\text{g/L}$  at 15 m (Figure 7). Arsenic concentrations of ~25  $\mu\text{g/L}$  measured in the three deepest samples of the profile (60–70 m) that encompass the depth range of the filter at the bottom of CW4 were comparable to the lowest



**FIGURE 4.** Comparison of patterns of temporal variation for well 4115. The groundwater level represents measurements relative to sea level for the shallow aquifer at a nearby nest of wells (23.785°E, 90.603°N). Information given in each panel, from top to bottom: (a) groundwater level and monthly precipitation; (b) P and As variations; (c) total major cation (molar units) and S variations; (d) Mn and Fe variations.

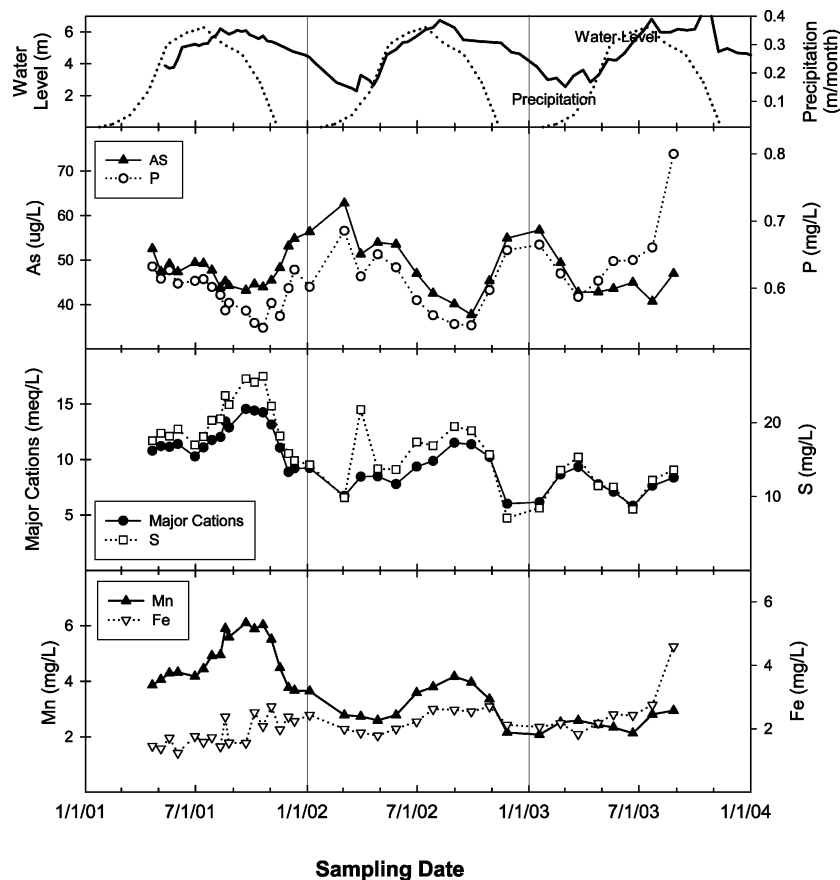
concentrations measured at the well head during the previous 3 years. With respect to As, S, and Mn, the composition of water pumped from CW4 in June 2004 was closer to that of groundwater collected at 15 m than at 60–70 m. Concentrations of Fe in water pumped from CW4 in June 2004 and during the previous 3 years, on the other hand, were significantly higher than for any interval tested with the needle sampler (Figure 7). Concentrations of P are not reported for the needle sampler because of loss by adsorption on the small amount of iron oxyhydroxides that precipitate on the syringe filter. The precipitate is visible, even when the sample tube is pressurized with nitrogen, but does not significantly affect dissolved Fe concentrations (16).

## Discussion

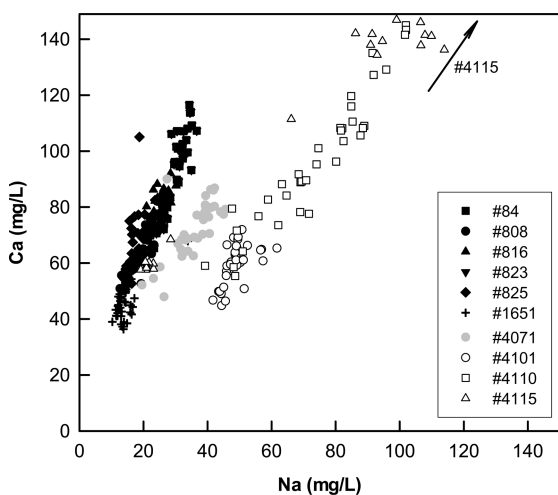
**Wells with a Constant Composition of Groundwater.** Most of the wells that were monitored, and all wells that tap aquifers deeper than 20 m (with the exception of CW4), showed little change in groundwater composition including As. As it turned out, some of these wells did not meet the Bangladesh standard for As in drinking water of 50  $\mu\text{g/L}$  (Table 1). The time series data are, however, consistent with previous measurements by graphite-furnace atomic absorption on the basis of which the wells had been classified as safe because of the larger 1 $\sigma$  uncertainty of  $\pm 12 \mu\text{g/L}$  at 50  $\mu\text{g/L}$  of this method (3). The observation that As concentrations in tube wells monitored in our study area are generally constant is similar to the outcome of shorter periods of monitoring for wells spanning a wide range of depths in other parts of Bangladesh (1). The very steady composition of groundwater in wells >20 m deep documented in the present study is consistent with a rapid drop in bomb-produced  $^3\text{H}$  concentrations at about the same

depth observed in monitoring wells from Araihasar as well as other parts of Bangladesh (1, 14, 19, 20). The trend indicates a typical groundwater age at 20 m of at least several decades, which, combined with the constant concentrations of major cations, suggests that potential fluctuations in composition linked to recharge during the monsoon are strongly attenuated at that depth. The constant composition of groundwater in 8 out of 10 shallow wells suggests that some shallow groundwater aquifers may be fairly isolated from the recharge processes as well.

**Shallow Wells with a Variable Composition of Groundwater.** In contrast to the majority of wells that were monitored, the composition of groundwater from wells 4115 and 4110, and to some extent also well 816, appears to be coupled to the annual cycle of precipitation and recharge (Figures 3–5). The observation is not entirely unexpected since variations in groundwater As concentrations in response to precipitation and recharge have been documented for other geological settings (9, 21, 22). There typically is little rainfall in our study area of central Bangladesh between November and February; precipitation then increases in March–April to peak in June–July (Figure 3). Variations in groundwater level that were recorded over the same period indicate that both shallow and deep aquifers responded to this input of freshwater, albeit with a delay of  $\sim 2$  months relative to the precipitation cycle (14). Fluctuations in the composition of groundwater at well 4115 appear to be in phase with precipitation rather than variations in groundwater level (Figure 4). The lowest As and P concentrations, and highest major cation, S, and Mn concentrations, are observed during the dry season. This is also the case for the same suite of constituents at well 816, controlling for the



**FIGURE 5.** Comparison of patterns of temporal variation in groundwater level, major cations, and redox sensitive trace elements for well 4110. The groundwater level represents measurements relative to sea level for the shallow aquifer at a nearby nest of wells (23.785°E, 90.603°N). Information given in each panel, from top to bottom: (a) groundwater level; (b) P and As variations; (c) total major cation (molar units) and S variations; (d) Mn and Fe variations.



**FIGURE 6.** Correlations of Na and Ca for time series samples collected from wells with depths  $\leq 20$  m.

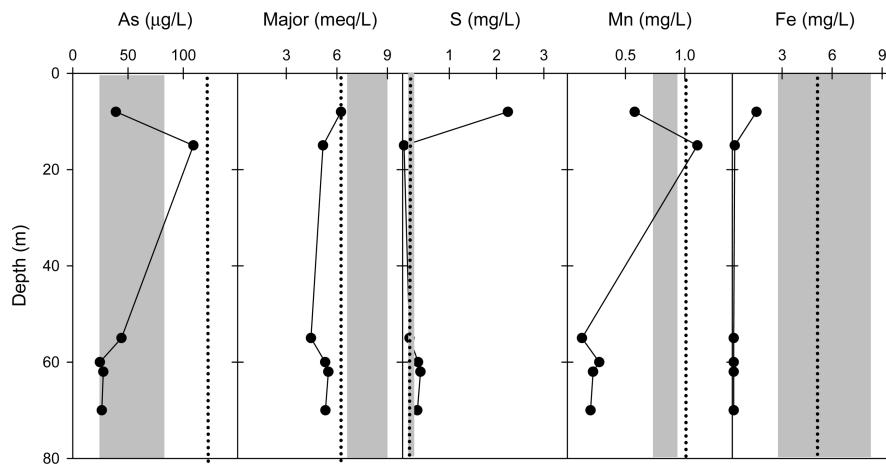
gradual rise of As concentrations over the 3-year monitoring period (Figure 3).

In contrast to the time series for well 4115, As concentrations in well 4110 are highest during the dry season and lowest during the wet season (Figure 5). The variations of As concentrations relative to that of other constituents, on the other hand, are consistent for both wells. The contrasting patterns of variations in groundwater composition over time are somewhat surprising since wells 4115 and 4110 are very close to each other, whereas well 816 is located several

kilometers to the east (Figure 1). Since precipitation and fluctuations of the water table are likely to be uniform throughout the area (14), we presently have no additional information that could help distinguish the nature of the various sites.

**Origin of Variations in Shallow Wells.** The significant seasonal variations in groundwater composition that were observed in well 4115 evoke three possible explanations, all speculative at this point. We have no plausible explanation for the opposite variations recorded at well 4110. The first focuses on fluctuations in groundwater level and takes into account the pronounced vertical gradient of As concentrations in shallow aquifers observed in many parts of Bangladesh, including Araihaazar. The second explanation is more difficult to quantify but tentatively links fluctuations in groundwater composition to flushing of the soil and the unsaturated zone by infiltration of recharge during the wet season. A third explanation ties the observed cycling of As to the potential seasonality of redox processes in shallow aquifers involving Fe and S.

Concentrations of As increase with depth in the shallow aquifers of Araihaazar by 100–700  $\mu\text{g/L}$  between 10 and 15 m depth (14, 15). In the case of wells 816 and 4115, the magnitude of seasonal variations in As concentrations observed in the three shallow wells could therefore be modulated by a vertical displacement of groundwater that is considerably smaller than the  $\sim 4$  m amplitude of changes in groundwater levels. It is difficult to predict what other changes in groundwater composition would be associated with such a shift for Mn, Fe, S, and the major cations because the concentrations of these constituents can either increase or decrease with depth in the 10–15 m range (14, 15, 23).



**FIGURE 7.** Depth profile of pore water chemical compositions near well CW4 collected using a needle sampler device. The gray bands show ranges of concentrations in CW4 between 2001 and August 2003, while the dashed lines indicate concentrations in CW4 in June 2004.

This mechanism cannot account for the changes in groundwater composition at well 4110.

During the dry season, evaporation can lead to the accumulation in soils and the unsaturated zone of solutes supplied by runoff (24). The gradual rise in major ion concentrations observed during the wet season in wells 4115 and 816 could therefore plausibly be attributed to downward flushing of these solutes as shallow aquifers are recharged locally by percolating precipitation. According to this scenario, the concomitant decrease in As and P concentrations observed during the wet season could be attributed to lower As and P concentrations in the recharge water, which is likely to be oxygenated. The pattern is consistent with an increase in S concentration over the course of the wet season that suggests an input of sulfate that temporarily dominates the loss by conversion to sulfide under reducing conditions (Figures 3–5). The pattern is not necessarily inconsistent with the parallel rise of Mn concentrations with S during the wet season since manganese oxides are reduced well before sulfate, and Mn concentrations in the unsaturated zone could therefore be elevated.

The third possible explanation brings into play instead a more closely interconnected set of interactions among As, Fe, and S in response to redox fluctuations. According to this scenario, the rise in As concentrations during the wet season could be attributed to the local dissolution of iron oxyhydroxides as conditions become more reducing, while during the dry season As is scavenged onto fresh iron oxyhydroxides. Conversely, variations in S concentrations that are out of phase with As time series may reflect the formation of iron sulfide during the wet season and reoxidation of these sulfides during the dry season. This explanation has the virtue of providing a mechanism whereby groundwater Fe concentrations are kept in check throughout the year, which matches the observations, even though the nature of the reactive Fe fraction in the particulate phase may alternate between oxyhydroxides and sulfides. The insensitivity of groundwater As concentrations to the formation of iron sulfides that is required for this scenario is consistent with past observations (25, 26).

It is unclear why groundwater As and P concentrations gradually increased over the 3 year monitoring period at well 816, especially since variations in dissolved S, Mn, and major cation concentrations fluctuated seasonally without an indication of a pronounced long-term trend (Figure 3). The systematic increase in shallow groundwater As concentrations is worrisome, and to our knowledge, no detailed time series has documented such an increase in the past. It is not known whether pumping from this well increased

significantly because surrounding households with unsafe wells switched to it.

**Variations in Groundwater Composition at CW4.** The occasionally elevated As concentrations at CW4 unfortunately resulted in excessive exposure of a number of households living nearby. Throughout the monitoring period, CW4 still supplied the best water that was available within a 50 m radius. Unlike the case of well 816, however, the cause of the degradation of water quality at CW4 can be determined with some confidence from the available data. Comparison of the time series data with the needle sampler profile shows that, with the exception of Fe, the composition of water pumped from CW4 often matched that of groundwater in the 60–70 m depth range (Figures 2 and 7). Occasional spikes in As concentrations were invariably associated with higher Fe concentrations (Supporting Information). The simplest explanation, though not necessarily the only one, is that the sections of PVC pipe used to construct the well were not properly connected to each other at fairly shallow depths. This could have led to occasional entrainment of unfiltered shallow groundwater when pumping over the 3 year monitoring period and, finally in June 2004, a worsening of the situation that led to a predominant contribution from a shallow interval. The fact that elevated Fe concentrations were observed in water pumped from CW4 even when As concentrations were relatively low suggests that the defective pipe allowed particles, clearly detectable with the naked eye in June 2004, to enter the well pipe all along. An exact location of the break in the pipe cannot be determined because of the limited depth resolution of the needle sampler profile.

**Implications for Mitigation and Policy.** From a practical perspective, the most important conclusion to draw from the data presented in this study is that groundwater As concentrations typically do not vary over time. The finding is consistent with what is known about the hydrology and geochemistry of Bangladesh aquifers (1). Poorly documented reports of highly variable groundwater concentrations, especially for deep wells, should therefore be treated with circumspection. The implications for mitigation and policy are significant because the proper installation of deep wells in thousands of affected villages in Bangladesh could provide a reliable source of safe water for years to come.

Another important lesson to learn from the observations is that concentrations of As in some wells can vary significantly over time. Understanding the origin of these fluctuations in shallow wells will require additional studies that may improve our understanding of the still elusive process of As mobilization in reducing aquifers. It would be particularly important to determine whether larger seasonal

fluctuations, or even long-term increases in groundwater As concentrations, might prevail in other areas of Bangladesh. This possibility, and the documented failure of a deep well within the relatively short monitoring period, indicate that all tube wells used as a source of water for drinking and cooking should be tested periodically for As. A testing capability provided for this purpose on a continuous basis at the village level would also serve the needs of the many households that continue to install wells (5).

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### Supporting Information Available

EXCEL tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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