

Performance of a Household-Level Arsenic Removal System during 4-Month Deployments in Bangladesh

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A simple arsenic removal system was used in Bangladesh by six households for 4 months to treat well water containing 190–750 $\mu\text{g/L}$ As as well as 0.4–20 mg/L Fe and 0.2–1.9 mg/L P. The system removes As from a 16-L batch of water in a bucket by filtration through a sand bed following the addition of about 1.5 g of ferric sulfate and 0.5 g of calcium hypochlorite. Arsenic concentrations in all but 1 of 72 samples of treated water were below the Bangladesh drinking water standard of 50 $\mu\text{g/L}$ for As. Approximately half of the samples also met the World Health Organization (WHO) guideline of 10 $\mu\text{g/L}$. At the two wells that did not meet the WHO guideline, observations were confirmed by additional experiments in one case ($[P] = 1.9 \text{ mg/L}$) but not in the other, suggesting that the latter household was probably not following the instructions. Observed residual As levels are consistent with predictions from a surface complexation model only if the site density is increased to 2 mol/mol of Fe. With the exception of Mn, the average concentrations of other inorganic constituents of health concern (Cr, Ni, Cu, Se, Mo, Cd, Sb, Ba, Hg, Pb, and U) in treated water were below their respective WHO guideline for drinking water.

Introduction

Groundwater has become the main source of drinking water in rural Bangladesh because surface waters are widely contaminated with human pathogens (1). The number of tube wells installed privately by households has grown exponentially since the 1970s to reach the current total of over 10 million wells (1, 2). Unfortunately, groundwater drawn from many of these is often naturally enriched in arsenic. A landmark nationwide survey (1) has shown that one-third of the existing wells yield water containing over 50 $\mu\text{g/L}$ As (the Bangladesh standard for drinking water) and two-thirds of the wells do not meet the guideline value for As of 10 $\mu\text{g/L}$ of the World Health Organization (WHO) (3). There is, therefore, an urgent need to provide rural households

throughout Bangladesh and other affected South Asian countries with access to water that is low in arsenic as well as other inorganic and microbial contaminants.

A number of approaches to mitigate the arsenic crisis have been tested in recent years. A return to surface water, which is typically low in arsenic, has been proposed but does not appear to be practical for rural Bangladesh in the short term due to the cost of water distribution from industrial-scale plants that remove microbial pathogens. Treatment of pond water at the village scale with sand filters does not meet health criteria because of insufficient removal of bacteria and the contamination of ponds with additives used for aquaculture (4). Collection of rainwater by individual households may be more promising, although the cost of storage tanks of sufficient size to last through the dry season is currently prohibitive (4). The removal of arsenic from groundwater, which generally remains microbially uncontaminated, using systems that range in capacity from household to village scale therefore continues to receive considerable attention (5–7).

The present study focuses on the performance under realistic conditions of a simple and economical arsenic removal system at the household level. In addition to 2-g packets containing ferric sulfate and calcium hypochlorite, treatment of a 16-L batch of groundwater requires only two plastic buckets, one of which with a spout mounted near the bottom, a piece of fabric, and some fine sand. After a pilot test involving seven households in 2000 (6), the so-called “bucket system” was evaluated along with eight other technologies by WS Atkins International Ltd. and BAMWSP in a project sponsored by the U.K. Department for International Development (7). The bucket system, together with six other technologies, was found to be effective in removing As from Bangladesh groundwater. Since January 2001, in collaboration with the nongovernmental organization Earth Identity Project, over 300 bucket systems have been deployed and continue to be used in several villages of Chandpur District, Bangladesh.

In the present study that involved six households from Araihaazar and Sonargaon upazila between January and May 2001, the possible causes of occasionally reduced performance of the bucket system are explored and the quality of the treated water is evaluated for a broad suite of inorganic constituents. Of the suite of 31 water inorganic constituents that were monitored throughout the deployments (Na, Mg, K, Ca, Si, P, S, Fe, Mn, Al, Li, V, Cr, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, In, Sn, Sb, Cs, Ba, Hg, Pb, Bi, U), 17 are of potential health concern, and their concentrations in drinking water are regulated by the WHO or the U.S. EPA.

Materials and Methods

Household Deployments. The participating families were from three different villages: two villages in Araihaazar, about 25 km east of Dhaka (wells 4145, 4134, and 4108 and wells 930 and 949, respectively), and one village in Sonargaon, 25 km southeast of Dhaka (well GB-125). Each household relied primarily on a single tube well for its supply of drinking and cooking water. The elevated As content of the groundwater pumped from these wells and surrounding wells had been established during previous surveys (8).

A pair of plastic buckets of ~20-L capacity, one of which had a spout mounted near the bottom, reagent packets, filter sand, and pieces of fabric were distributed to each family in January 2001. The reagent packets were prepared in the U.S. and contained a mixture of approximately 1.5 g of industrial-grade ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) and 0.5 g of calcium hy-

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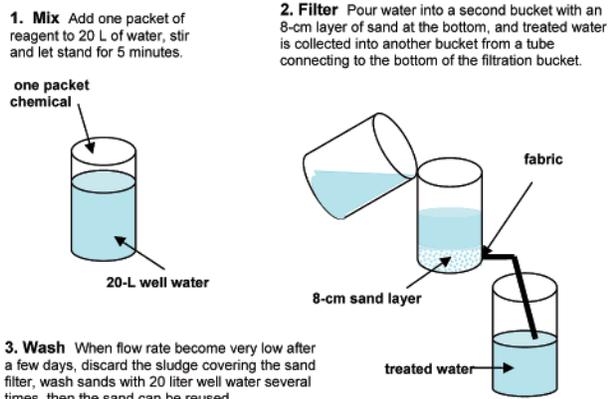


FIGURE 1. Illustration of a simple bucket system for As.

pochlorite ($\text{Ca}(\text{OCl})_2$). Fine construction sand was bought locally for the filter beds and bleached before use to eliminate possible pathogens. Well water (~16 L) is first collected in the bucket without a spout, and a packet of chemicals is added, thoroughly mixed, and allowed to react for 5–10 min (Figure 1). The water containing fresh iron oxyhydroxide flocs is then gently poured into the bucket with a spout over a ~8-cm-thick layer of sand. The fabric, folded once or twice, placed over the outlet inside the bucket prevents the loss of sand particles. When the spout is opened, the sand retains the As-bearing iron hydroxide particles as treated water drips at a rate of 0.5–2.0 L/min.

Each family was instructed to follow this procedure at least once a day during the testing period. To avoid an unacceptably low drip rate or clogging, the sand bed was resuspended in well water and washed twice a week. The families were told to discard the first 20-L batch of treated water after the sand bed had been washed. They were also asked to collect a sample of treated water for future analysis once a week, although the sampling frequency was not strictly adhered to. The treated water samples appeared to be free of visible particles and were not filtered before acidification to 1% HCl (Optima) within a few days of collection.

Additional Experiments. Similar procedures were followed in October 2003 to investigate the possible causes of systematically higher As levels in treated water from wells 949 and 4108. At well 949, three separate batches of groundwater were treated using (i) the usual amount of reagents, (ii) twice the quantities of both reagents, and (iii) twice the quantity of ferric sulfate and the usual amount of

oxidant. Effluent samples were collected once. At well 4108, groundwater was treated with (i) the usual amount of reagents, (ii) the usual amount of ferric sulfate and twice the oxidant, and (iii) twice the quantity of ferric sulfate and the standard amount of oxidant. At this well, effluent samples were collected 10 min and again 40 min after filtration started.

In these experiments, both well water and treated water were collected unfiltered and through a 0.45 μm syringe filter. As(III) was separated from As(V) by passing water through a syringe filter and (1) an SPE cartridge anion exchange column (9) in the case of well 949 and (2) a small disposable ion exchange column that retains As(V) but not As(III) marketed by Metalsoft Center, Highland Park, NJ, in the case of well 4108 (10).

Analytical Methods. All samples were analyzed by high-resolution inductively coupled plasma mass spectrometry (HR ICP-MS) on a single-collector VG Axiom for As and 31 other major and trace elements using a procedure that requires only a single dilution. The precision of the method ranges from 1% to 3% for most elements (11). Detection limits are well below the concentrations measured in the original well water and the treated water for most constituents, and well below their corresponding EPA MCLs or WHO guidelines for all elements (11).

Modeling. For comparison with the observations and to evaluate the potential effects of differences in the composition of well water, the expected removal of As was calculated with a surface-complexation model (13) using Visual MINTEQ (version 2.23, accessed February 2004, <http://www.lwr.kth.se/english/OurSoftware/Vminteq/>), the Windows version of MINTEQA2. The predictions are based on the diffuse-layer model, assuming single-layer adsorption and a specific surface area of 600 m^2/g . The most important reactions and standard adsorption constants taken from Dzombak and Morel (12) and Allison et al. (13) are listed in Table 2. The site density is the only model parameter that was allowed to deviate from the fairly standard value of 0.2 mol of sites/mol of Fe. The justification is the likely difference between adsorption on preformed iron oxyhydroxide and the process of coagulation that occurs in the bucket systems. No solids were allowed to precipitate even though the model predicts supersaturation relative to quartz (SiO_2) and calcite (CaCO_3). The kinetics of these reactions were assumed to be slow relative to those of the coagulation of iron oxyhydroxides. In the case of As, Fuller et al. (14) observed no As-bearing precipitates even for coprecipitation experiments at high As/Fe ratios. Field measurements indicate a small pH range of 6.8–7.2 for both well water and treated water; the pH was

TABLE 1. Average Concentrations of Arsenic and 12 Other Elements of Health Significance in Well Water and Treated Water Samples^a

well no.		As		Cu	Se	Mo	Cd	Sb	Ba	Hg	Pb	U	Mn
WHO guideline		50		2000	10	70	3	5	700	1	10	2	500
U.S. EPA MCL		10		1300	50				2000	2	15	30	50
		>50	>10										
GB-125	well water (3)	753		0.1	0.1	7	0.1	14	10	0.5	0.1	2.1	730
	effluent (9)	8	[0]	[3]	0.1	0.1	4	0.1	40	0.3	0.1	1.2	660
930	well water (1)	280		0.1	0.1	2	0.1	0.1	250	4.0	1	0.1	1300
	effluent (13)	5	[0]	[1]	9	0.1	4	1.2	140	0.4	0.1	0.3	1120
4134	well water (1)	275		4	0.1	2	0.1	0.2	130	0.6	3	0.2	3800
	effluent (13)	10	[0]	[5]	1	0.1	4	0.8	80	0.3	0.1	0.5	3340
4145	well water (1)	187		0.1	0.1	3	0.1	0.1	200	0.5	1	0.5	5080
	effluent (13)	10	[0]	[4]	3	0.1	2	0.1	190	0.3	0.1	0.8	4610
949	well water (1)	307		1	0.1	3	0.1	0.1	130	1.1	3	0.1	1430
	effluent (11)	23	[0]	[10]	0.1	0.1	3	0.1	80	0.3	0.1	0.4	1330
4108	well water (1)	423		3	0.1	2	0.1	0.1	120	0.8	2	0.6	4980
	effluent (13)	21	[1]	[10]	0.1	0.1	1	0.1	100	0.8	0.1	0.9	4650

^a Numbers in parentheses are the numbers of samples analyzed, while those in brackets are the numbers of samples exceeding WHO/U.S. EPA arsenic limits. Units for all are micrograms per liter.

TABLE 2. Main Reactions and Constants Used in the Model Calculations

reaction	log K
Surface Complexation Reactions	
(1) $\text{SOH} + \text{H}^+ + \exp(-F\psi_0/RT) = \text{SOH}_2^+$	7.29
(2) $\text{SOH} - \text{H}^+ - \exp(-F\psi_0/RT) = \text{SO}^-$	-8.93
(3) $\text{SOH} + \text{AsO}_4^{3-} + 3\text{H}^+ = \text{SH}_2\text{AsO}_4 + \text{H}_2\text{O}$	29.31
(4) $\text{SOH} + \text{AsO}_4^{3-} + 2\text{H}^+ - \exp(-F\psi_0/RT) = \text{SHAsO}_4^- + \text{H}_2\text{O}$	23.51
(5) $\text{SOH} + \text{AsO}_4^{3-} - 3 \exp(-F\psi_0/RT) = \text{SOHAsO}_4^{3-} + \text{H}_2\text{O}$	10.58
(6) $\text{SOH} + \text{H}_3\text{AsO}_3 = \text{SH}_2\text{AsO}_3 + \text{H}_2\text{O}$	5.41
(6) $\text{SOH} + \text{PO}_4^{3-} + 3\text{H}^+ = \text{SH}_2\text{PO}_4 + \text{H}_2\text{O}$	31.29
(7) $\text{SOH} + \text{PO}_4^{3-} + 2\text{H}^+ - \exp(-F\psi_0/RT) = \text{SHPO}_4^- + \text{H}_2\text{O}$	25.39
(8) $\text{SOH} + \text{PO}_4^{3-} + \text{H}^+ - 2 \exp(-F\psi_0/RT) = \text{SPO}_4^{2-} + \text{H}_2\text{O}$	17.72
(9) $\text{SOH} + \text{CO}_3^{2-} + \text{H}^+ - \exp(-F\psi_0/RT) = \text{SCO}_3^- + \text{H}_2\text{O}$	12.78
(10) $\text{SOH} + \text{CO}_3^{2-} + 2\text{H}^+ = \text{SCO}_3\text{H} + \text{H}_2\text{O}$	20.37
(11) $\text{SOH} + \text{H}_4\text{SiO}_4 - 2\text{H}^+ - 2 \exp(-F\psi_0/RT) = \text{SOSi}_2\text{OH}^{2-} + \text{H}_2\text{O}$	-11.69
(12) $\text{SOH} + \text{H}_4\text{SiO}_4 - \text{H}^+ - \exp(-F\psi_0/RT) = \text{SOSi}(\text{OH})_2^- + \text{H}_2\text{O}$	-3.22
(13) $\text{SOH} + \text{H}_4\text{SiO}_4 = \text{SOSi}(\text{OH}) + \text{H}_2\text{O}$	4.28
Aqueous Reactions	
(14) $\text{H}_3\text{AsO}_4 = \text{H}_2\text{AsO}_4^- + \text{H}^+$	-2.24
(15) $\text{H}_3\text{AsO}_4 = \text{HAsO}_4^{2-} + 2\text{H}^+$	-9.20
(16) $\text{H}_3\text{AsO}_4 = \text{AsO}_4^{3-} + 3\text{H}^+$	-20.70
(17) $\text{H}_3\text{AsO}_3 = \text{H}_2\text{AsO}_3^- + \text{H}^+$	-9.29

therefore fixed at 7.0 for the model calculations. Predicted removals were calculated separately for As(V) and As(III) on the basis of the composition of individual scenarios as well as an average scenario (Table 3).

Bicarbonate concentrations were not measured in water from these particular wells, but there is a rather consistent 1:1 molar relationship between Ca + Mg and HCO_3^- concentrations throughout Bangladesh (1). Bicarbonate concentrations estimated from this relationship in the six wells range from 3.7 to 8.3 μM , which is consistent with reported values (1, 6). The total concentration of iron oxyhydroxide solids was calculated from the sum of measured Fe(II) concentrations, with and without the added Fe(III). Concentrations of Ca^{2+} , SO_4^{2-} , and Cl^- take into account the addition of 1.5 g of $\text{Fe}_2(\text{SO}_4)_3$ and 0.5 g of $\text{Ca}(\text{OCl})_2$.

Results

Arsenic. Well water previously consumed by the six families contained As concentrations between 187 and 753 $\mu\text{g/L}$ (Table 1). Arsenic concentrations in the treated water were all below 50 $\mu\text{g/L}$, the Bangladesh standard, with the exception of one sample from well 4108 containing 69 $\mu\text{g/L}$ As (Figure 2 and Supporting Information table). The average As concentration in treated water for four out of six bucket systems ranged from 5 to 10 $\mu\text{g/L}$, i.e., below the WHO guideline value and

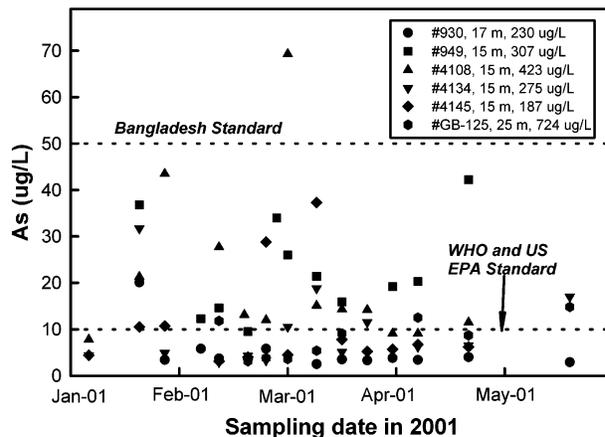


FIGURE 2. Residual As concentrations in time series effluent samples.

the revised U.S. EPA MCL (Table 1). Average As concentrations in treated water from the two remaining systems (wells 949 and 4108) were 21 and 23 $\mu\text{g/L}$, respectively. Whereas it would have been preferable if all units had consistently provided treated water that complies with WHO guidelines, these results confirm previous tests that the bucket system effectively removes inorganic As despite its simplicity (6).

Residual As concentrations in the treated water show considerable temporal variability as well as consistent differences in removal efficiency between units. At the two extremes, the units associated with wells GB-125 and 930 consistently produced water containing very little As; households using wells 949 and 4108 obtained water with generally higher and more variable As concentrations (Figure 2). For the two least performing bucket systems (wells 949 and 4108), 20 out of 44 effluent samples contained over 10 $\mu\text{g/L}$ As. Bucket systems used at wells 4134 and 4145 were intermediate in terms of performance, with 9 out of a total of 20 samples of treated water that were collected exceeding 10 $\mu\text{g/L}$. High-As “spikes” appear more frequently in effluent samples from the bucket systems that generally performed less well.

During the experiments conducted without household participation in October 2003, the residual As level of 22 $\mu\text{g/L}$ at well 949 under standard conditions was not appreciably different from the mean level during the 4-month deployment (Table 4). Filtration confirmed that As is mostly dissolved in both well water and treated water. Doubling the amount of Fe added reduced the residual As concentration to 15 $\mu\text{g/L}$; doubling the amount of both reagents only marginally reduced it further. Speciation of As in well 949 could not be determined with the ion exchange column because the high Fe content led to precipitation and, therefore, probably trapping of As in either redox state on the column. Speciation of the treated water indicates that residual As was mostly in the As(III) form.

In contrast, the performance of the bucket system at well 4108 was significantly improved in October 2003 compared

TABLE 3. Concentrations of Major Cations and Anions of Well Water Used in the Surface Complexation Model^a

well no.	[Na ⁺] (mg/L)	[Mg ²⁺] (mg/L)	[K ⁺] (mg/L)	[Ca ²⁺] (mg/L)	[Fe ²⁺] (mg/L)	[As] ($\mu\text{g/L}$)	[H ₄ SiO ₄] (mM)	[PO ₄ ³⁻] (mM)	[SO ₄ ²⁻] (mM)	[HCO ₃ ⁻] (mM)	[Cl ⁻] (mM)
4108	28.1	34.9	4.9	92.7	2.8	423	0.76	0.0059	0.46	7.5	0.4
930	18.7	29.1	4.5	89.1	20.8	280	0.73	0.0349	0.01	8.3	0.9
4145	41.5	33.7	5.8	76.4	5.3	187	0.77	0.0135	0.45	6.6	1.0
GB-125	8.4	9.2	3.1	59.4	0.4	724	0.48	0.0202	0.04	3.7	0.4
4134	17.4	21.5	6.0	53.4	8.4	275	0.84	0.0163	0.17	4.5	0.6
949	17.0	25.6	5.0	92.4	10.5	307	0.73	0.0603	0.00	8.1	0.9

^a The concentrations of bicarbonate anion are estimated from charge balance with Ca^{2+} and Mg^{2+} , whereas Cl^- is used to compensate overall charge balance.

TABLE 4. As, Fe, P, and Al Concentrations ($\mu\text{g/L}$) in Well Water and Treated Water Collected during the October 2003 Experiment

	total As			Fe		P		Al	
	UF	F	As(III)	UF	F	UF	F	UF	F
Well 4108									
well water	429		401	3120		184		24	
1 \times Fe and 1 \times OCl	3.7	3.8	3.5	25	27	23	22	27	26
1 \times Fe and 2 \times OCl	3.5	4.8	3.6	27	34	28	33	35	27
2 \times Fe and 1 \times OCl	5.7	5.7	5.1	30	32	23	29	38	39
Well 949									
well water	253	240		11200	11000	2020	1830	24	25
1 \times Fe and 1 \times OCl	22.5	19.4	17.4	27	27	17	21	25	30
2 \times Fe and 2 \times OCl	14.8	12.9	9.6	73	122	16	20	26	26
2 \times Fe and 1 \times OCl	16.5	14.6	13.6	51	52	11	14	26	22

to that of the longer deployment by the household (Table 4). Residual As concentrations of 4–6 $\mu\text{g/L}$ were consistently below the WHO guideline. Doubling the amount of Fe or the oxidant had little effect. Column separations indicated the dominance of As(III) in both well water and treated water.

Other Elements of Potential Health Concern. In addition to reducing As concentrations, the bucket systems removed almost all P and Fe initially in the groundwater, as well as some Si (Table 1). Concentrations of Cr, Ni, Sb, Hg, and Pb were also reduced in the treated water, though they are generally also very low initially in the well water. The measurements show that, on average, treated water met both WHO and U.S. EPA standards for all inorganic constituents of health concern analyzed in this study (Cr, Cu, Ni, Zn, Se, Cd, Mo, Sb, Ba, Pb, and Bi) with the exception of Mn, for which concentrations were above 500 $\mu\text{g/L}$ in both well water and treated water. In contrast to As, the bucket system did not effectively remove Mn. Treatment by even the best performing bucket systems only marginally reduced Mn concentrations from initial levels in well water that are 2–3-fold greater than the WHO guideline of 500 $\mu\text{g/L}$.

The concentration of Hg in groundwater from wells 930 and 949 exceeded both the WHO guideline and the U.S. EPA limits of 1 and 2 $\mu\text{g/L}$, respectively, but the treated water from these wells consistently met the WHO guideline value. On the other hand, the concentration of Hg in well 4108 that barely met the WHO guideline slightly increased above it in three samples of treated water (Supporting Information table). For another two elements of potential health concern, concentrations occasionally increased relative to the composition of the well water following treatment with the bucket system. U and Cd concentrations in well water met their respective WHO guideline values of 2 and 3 $\mu\text{g/L}$, but three samples of treated water from different families indicate a slight increase in U (Supporting Information table). Several samples also show an increase in Cd concentrations in treated water, and one sample of treated water from well 4134 actually exceeded the WHO guideline for Cd of 3 $\mu\text{g/L}$ while still meeting the U.S. EPA limit of 5 $\mu\text{g/L}$.

Model Predictions. The surface complexation model was first used to predict the sensitivity of the efficiency of the bucket systems to As speciation using the average major composition for the six wells. Model results are shown for As(V) or As(III) concentrations up to 1000 $\mu\text{g/L}$, assuming site density values of 0.2, 1.0, and 2.0, respectively (Figure 3). The results show that the proportion of As removed is fairly constant across a wide range of concentrations. Only at the higher site density of 2 mol of sites/mol of Fe do the predicted residual As concentrations approach the observed performance of the bucket systems. Surface site coverage with silicate, bicarbonate, and phosphate anions are the main reason for higher As residuals at the lower site density (15–18).

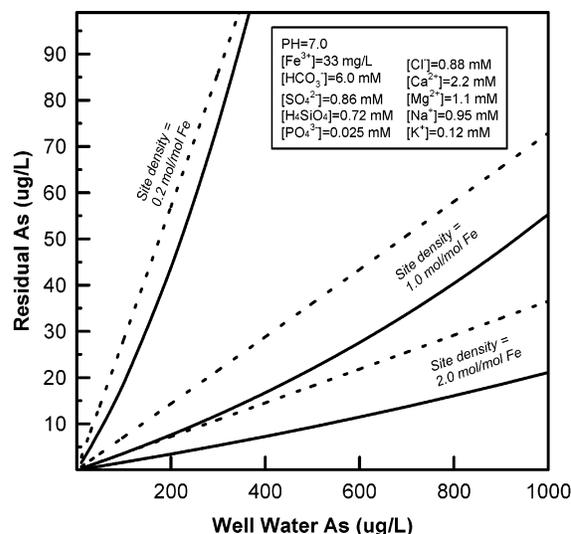


FIGURE 3. Predicted residual levels by a DLM surface complexation model in the bucket As removal system. The solid and dashed lines are for arsenate and arsenite, respectively.

The model is also used to predict residual concentrations for individual wells on the basis of the actual well water chemistry and the additions, assuming again either As(III) or As(V), and a site density of 2.0 mol/mol of Fe (Table 5 and Figure 4). The predictions are comparable to the observations, with the exception of two wells. In both cases (wells GB-125 and 4108), a residual that is considerably higher than the observations is predicted assuming the presence of As(III). Model calculations also show that the proportion of sites occupied by As (0.2–1.1%) is considerably smaller than for the competing anions phosphate (0.6–4.5%), bicarbonate (21–56%), and silicate (20–47%). Without the Fe addition, the same model predicts a much wider range in residual As concentrations (Table 5), reflecting primarily the variability of Fe(II) concentrations in well water (0.4–20.8 mg/L). Even in the best case, the predicted residual As concentration of 29 $\mu\text{g/L}$ for well 930 is higher than the 10 $\mu\text{g/L}$ WHO guideline value. In the worst case, little As removal is predicted for well GB-125.

Discussion

Efficiency of Arsenic Removal. The As content of treated water at four out of six wells typically met the WHO guideline of 10 $\mu\text{g/L}$. The performance is encouraging considering that the deployments were conducted under representative conditions and that the bucket system at well 949 still met the Bangladesh standard of 50 $\mu\text{g/L}$. The wide range of initial Fe, P, Si, and HCO_3^- concentrations does not appear to significantly influence the efficiency of As removal. The well-

TABLE 5. Predicted Residual As Levels Compared with Average Levels in Effluent Samples^a

well no.	effluent sample	avg [As] (μg/L)	Fe/As (mg/mg) after addition of 2 g of salt mixture	initial well water [As] (μg/L)	initial well water [Fe] (mg/L)	predicted residual [As] (μg/L)	
						no Fe addition	with salt addition
GB-125	As(V)	8	35	753	0.4	729	12
	As(III)					656	29
930	As(V)	5	164	280	20.8	85	7
	As(III)					29	10
4134	As(V)	10	121	275	8.4	127	11
	As(III)					67	13
4145	As(V)	10	162	187	5.3	115	12
	As(III)					67	11
949	As(V)	23/23	116	307	10.5	171	20
	As(III)					67	15
4108	As(V)	21/4	66	423	2.8	330	12
	As(III)					224	20

^a A site density of 2 mol/mol of Fe is assumed. Other parameters are listed in Table 3.

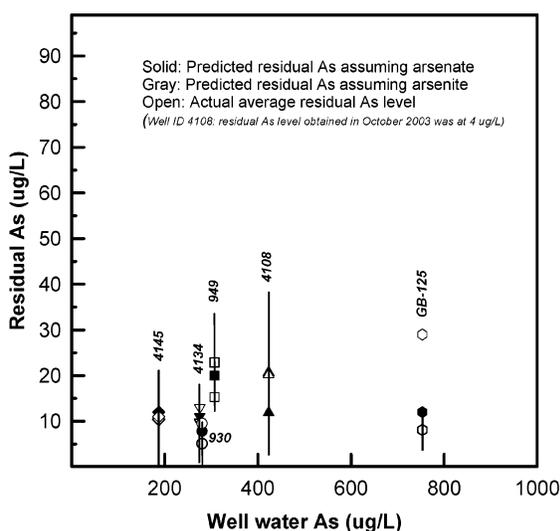


FIGURE 4. Comparison of predicted residual As levels and observed levels in effluent samples. The symbols are consistent with Figure 2. The vertical lines indicate 1 σ standard deviation from the mean of observed As concentrations in time series samples for each household. A site density of 2.0 mol/mol of Fe was used; for other parameters see Table 3, with modification by salt additions.

established competitive effects due to the adsorption of major anions are effectively minimized by the Fe addition (6, 15–18).

Comparison with Model Predictions. Predicted residual As levels approach the observations only if the typical site density of 0.2 mol/mol of Fe is increased by an order of magnitude. This is not implausible since removal in the bucket system is akin to coagulation rather than adsorption on a preformed iron oxyhydroxide surface. Site densities as high as 0.9 mol/mol of Fe have been independently inferred for Fe coagulation (19) and coprecipitation of As with Fe (14). At least in principle, one can imagine Fe(III) octahedron monomers surrounded by six As tetrahedra, forming a small complex. The proportion of As relative to Fe would decrease, however, as the clusters link to form larger colloids. The site density can be considered an adjustable parameter of a model intended mostly to estimate the sensitivity of the system to competitive interactions.

The model confirms that the addition of Fe is important to ensure effective As removal from groundwater whose composition can vary widely. As observed by Hug et al. (5), the natural Fe content of groundwater is not always suf-

ficiently high. It is not clear to what extent oxidation of As(III), typically the dominant form in Bangladesh groundwater, is critical for As removal by the bucket system. The discrepancy between observations and model predictions for As(III) at wells GB-125 and 4108 and the predominance of As(III) in the effluent suggest that conversion to As(V) is important. Another benefit of the oxidant addition may be that it promotes Fe(II) oxidation.

Variations in Performance over Time. Variations in the concentrations of dissolved Fe, P, and Al in the effluent samples provide some indication of the origin of variations in residual As concentrations over time (Figure 5). In the case of well 4145, the two highest residual As concentrations were accompanied by significantly higher Fe, P, and Al concentrations. The pattern suggests that visually undetectable sand particles may have bypassed the cloth, accompanied by iron oxyhydroxide flocs enriched in As and P that dissolved upon acidification. The pattern is less systematic for well 4134, although the two highest residual As levels are accompanied in one case by elevated Fe and in the other case by elevated As and P.

During the first 2 months of usage at well 4108, P concentrations were only a factor of 2–3 below the initial level of 0.2 mg/L in well water. Both As and P concentrations were significantly lower during the last 2 months of deployment. The bucket systems produced water with less than 10 μg/L As in October 2003 and showed little sensitivity to the quantity of Fe or oxidant added. These observations and poor removal of As and P during the first months of deployment suggest that the sand bed was not correctly maintained by the household. Either a thin layer of sand near the spout or channeling may have reduced the contact time between the water and the reactive particles. Improper handling is therefore the likely cause of residual As concentrations that were significantly higher than predicted by the model (Figure 4).

The composition of treated water from well 949 shows no clear relation between residual As and Fe, P, or Al concentrations. The well is characterized by a particularly high P concentration of ~2 mg/L, however. With the exception of one sample, over 90% of the P originally present in well water was removed during the 4-month deployments. Although the efficiency of P removal was even higher in October 2003 (~99%), residual As concentrations remained above 10 μg/L (Table 5). These observations and a somewhat lower As residual when the dosage of Fe was doubled suggest competition for iron oxyhydroxide surface sites by phosphate, whose effect was magnified by the presence of high concentrations of silicate and bicarbonate (18).

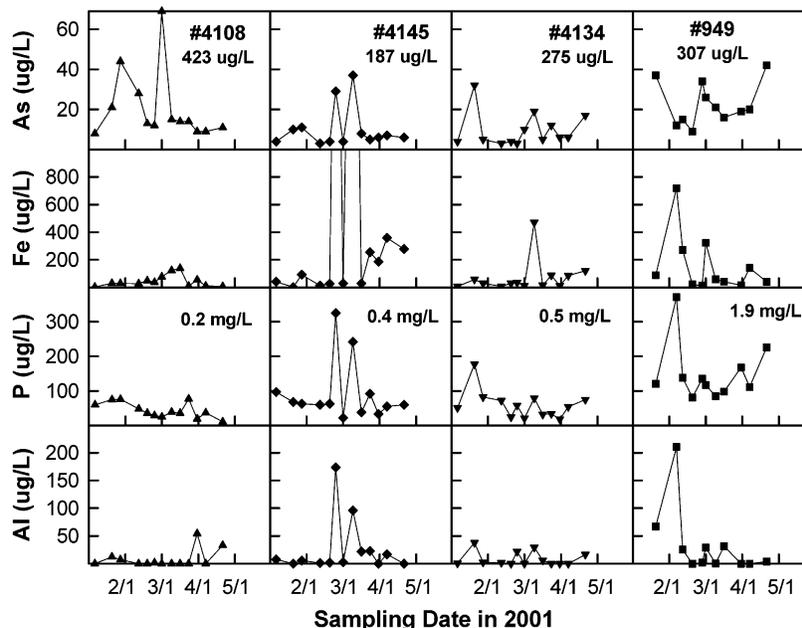


FIGURE 5. Variations of As, Fe, P, and Al concentrations in time series effluent samples. The numbers shown with well numbers are well water concentrations.

Lack of Mn Removal. The limited removal of Mn by the bucket system is a concern since BGS/DPHE (1) report that about one-third of the thousands of wells sampled throughout Bangladesh exceed the WHO guideline for Mn. Evidently, the added oxidant did not accelerate the kinetics of Mn(II) oxidation (20), or the MnO₂ particles produced by oxidation were not trapped by the sand bed. On one hand, Mn is an essential dietary element and the Mn nutritional status in Bangladesh is unknown. Moreover, in comparison to the WHO guideline for arsenic, which is based on a great deal of epidemiologic evidence from Taiwan and elsewhere, the scientific evidence for the Mn guideline is relatively weak, and is based on extrapolations from inhalation exposure in manganese-exposed workers, e.g., welders. While occupational exposure to manganese has been associated with Parkinsonism (21), long-term exposure to manganese in well water has not been associated with neurological effects (22). It is important to note, however, that some case-control studies in the U.S. have found that Parkinson's disease is more prevalent among cases consuming higher Mn groundwater than among control cases (23, 24).

Implications for Arsenic Mitigation. Thirteen inorganic constituents of potential health concern were evaluated in this study. Use of a bucket system to treat well water high in arsenic can clearly reduce household exposure to As by over an order of magnitude under realistic conditions. Equally significant is the fact that the procedure does not add other inorganic contaminants of potential health concern. Unfortunately, the bucket system in its current configuration does not appreciably lower exposure to Mn. Other inorganic constituents considered by the WHO (boron, fluoride, nitrate, and nitrite) generally meet their respective guideline values in Bangladesh groundwater (1) and are not likely to be introduced through the bucket system (7). The bucket system does require daily handling and attention to support the water consumption of a typical household, however. Households expressed their preference by abandoning the bucket system once a nearby safe well became available (2, 25). This does not mean the bucket system is not a mitigation option worth improving further for emergency deployment in the many villages of Bangladesh where no safe private or community well is currently available (1). Future efforts to improve this or similar systems should aim to reduce the

chance of channeling and leakage of particles and should explore the possibility of removing Mn.

Disposal of the orange-colored sludge produced by the systems has been cited as an obstacle preventing widespread use of the bucket system. The amount of groundwater pumped for human consumption is typically at least an order of magnitude below the withdrawals for irrigation, however. This indicates that spreading the sludge derived from usage of bucket systems in the fields surrounding a village would add much less As to the soil than prolonged irrigation with groundwater high in As (26).

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Supporting Information Available

Table showing concentrations of 31 elements in well water and an effluent water sample. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) BGS. *Arsenic Contamination of Groundwater in Bangladesh*; BGS Technical Report WC/00/19; British Geological Survey: Keyworth, U.K., 2001.
- (2) Van Geen, A.; Ahsan, H.; Horneman, A. H.; Dhar, A. H.; Zheng, Y.; Hussain, I.; Ahmed, K. M.; Gelman, A.; Stute, M.; Simpson, H. J.; Wallace, S.; Small, C.; Parvez, F.; Slavkovich, V.; LoIacono, N. J.; Becker, M.; Cheng, Z.; Momotaj, H.; Shahnewaz, M.; Seddique, A. A.; Graziano, J. H. *Bull. World Health Org.* **2002**, *80*, 732–737.
- (3) WHO. *Guidelines for Drinking-Water Quality*, 2nd ed.; World Health Organization: Geneva, Switzerland, 1996; Vol. 2.
- (4) BRAC. *Combating a deadly menace: early experiences with a community-based arsenic mitigation project in Bangladesh*;

- Bangladesh Rural Advancement Committee: Dhaka, Bangladesh, 2000.
- (5) Hug, S. J.; Canonica, L.; Wegelin, M.; Gechter, D.; von Gunten, U. *Environ. Sci. Technol.* **2001**, *35*, 2114–2121.
 - (6) Meng, X. G.; Korfiatis, G. P.; Christodoulatos, C.; Bang, S. *Water Res.* **2001**, *35*, 2805–2810.
 - (7) Sutherland, D.; Woolgar, M. *Water Supply* **2001**, *12*, 31–32.
 - (8) Van Geen, A.; Zheng, Y.; Versteeg, R.; Stute, M.; Horneman, A.; Dhar, R.; Steckler, M.; Gelman, A.; Small, C.; Ahsan, H.; Graziano, J.; Hussein, I.; Ahmed, K. M. *Water Resour. Res.* **2003**, *35*, 1140–1156.
 - (9) Le, X. C.; Yalcin, S.; Ma, M. *Environ. Sci. Technol.* **2000**, *34*, 2342–2347.
 - (10) Meng, X. G.; Wang, W. In *Book of posters of the Third International Conference on Arsenic Exposure and Health Effects: Society of Environmental Geochemistry and Health*; University of Colorado at Denver: Denver, 1998.
 - (11) Cheng, Z.; Zheng, Y.; Mortlock, R.; van Geen, A. *Environ. Sci. Technol.* Submitted for publication.
 - (12) Dzombak, D. A.; Morel, F. M. M. *Surface Complexation Modeling: Hydrous Ferric Oxide*; Wiley-Interscience: New York, 1990.
 - (13) Allison, J. D.; Brown, D. S.; Novo-Gradac, K. J. *MINTEQA2/PRODEFA2. A Geochemical assessment model for environmental systems: Version 3.0 User's Manual*; U.S. Environmental Protection Agency: Washington, DC, 1992.
 - (14) Fuller, C. C.; Davis, J. A.; Waychunas, G. A. *Geochim. Cosmochim. Acta* **1993**, *57*, 2271–2282.
 - (15) Dixit, S.; Hering, J. G. *Environ. Sci. Technol.* **2003**, *37*, 4182–4189.
 - (16) Meng, X. G.; Bang, S.; Korfiatis, G. P. *Water Res.* **2000**, *34*, 1255–1261.
 - (17) Hering, J. G.; Chen, P. Y.; Wilkie, J. A.; Elimelech, M.; Liang, S. *J. Am. Water Works Assoc.* **1996**, *88*, 155–167.
 - (18) Meng, X. G.; Korfiatis, G. P.; Bang, S.; Bang, K. W. *Toxicol. Lett.* **2002**, *133*, 103–111.
 - (19) Meng, X. G.; Letterman, R. D. *Environ. Sci. Technol.* **1993**, *27*, 970–975.
 - (20) Diem, D.; Stumm, W. *Geochim. Cosmochim. Acta* **1984**, *48*, 1571–1573.
 - (21) Gorell, J. M.; Johnson, C. C.; Rybicki, B. A.; Peterson, E. L.; Kortsha, G. X.; Brown, G. G.; Richardson, R. J. *Neurotoxicology* **1999**, *20*, 239.
 - (22) Vieregge, P.; Heinzow, B.; Korf, G.; Teichert, H. M.; Schleifenbaum, P.; Mosinger, H. U. *Can. J. Neurol. Sci.* **1995**, *22*, 286.
 - (23) Tsai, C. H.; Lo, S. K.; See, L. C.; Chen, H. Z.; Chen, R. S.; Weng, Y. H.; Chang, F. C.; Lu, S. *Clin. Neurol. Neurosurg.* **2002**, *104*, 328.
 - (24) Zorzon, M.; Capus, L.; Pellegrino, A.; Cazzato, G.; Zivadinov, R. *Acta Neurol. Scand.* **2002**, *105*, 77.
 - (25) Van Geen, A.; Ahmed, K. M.; Seddique, A. A.; Shamsudduha, M. *Bull. World Health Org.* **2003**, *82*, 632–638.
 - (26) Meharg, A. A.; Mazibur Rahman, M. *Environ. Sci. Technol.* **2003**, *37*, 229–234.

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