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Advances in Arsenic Research

**Integration of Experimental and
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Chapter 26

Removal of Arsenic from Bangladesh Groundwater with Zero-Valent Iron

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Cartridges containing zero-valent iron filings mixed with sand were tested in Bangladesh to evaluate their effectiveness in removing arsenic from groundwater. The experiments were conducted by pumping, respectively, 1830 and 1140 L of groundwater over the course of a week from two wells containing 560 and 290 µg/L As. The set-up included two cartridges connected in series for As removal, and a downstream aeration vessel followed by a nylon filter to reduce Fe concentrations in the effluent. After conditioning the cartridges for 3-4 days, As concentrations in the effluent consistently remained at or below the WHO guideline of 10 µg/L. Groundwater treatment with iron filings may therefore be a viable technology for arsenic mitigation in Bangladesh.

Dissolved arsenic concentrations in groundwater that are higher than the recommended WHO 10 µg/L guideline for drinking water have been reported in many parts of the world, notably Bangladesh, West Bengal of India, Taiwan, Argentina, Mexico as well as the United States (1-8). Poorly-understood natural processes contribute to elevated groundwater As levels across a wide range of geological settings, for example, alluvial floodplains and deltas in Bangladesh

and West Bengal, loess aquifers in Central Argentina, glacial tills in the northeastern and midwestern US, and hydrothermal systems in California and New Mexico.

The reliance on groundwater for human water supply in many parts of the world requires the development of reliable and affordable methods for removing As. One method, coined "Arsenic Remediation Technology" (AsRT, US Patent 6,387,276 B1), which is based on iron filings mixed with sand has been developed at the University of Connecticut (9). Field tests conducted in the US (Maine, and New Jersey) (10,11), Greece (12), Argentina and Switzerland (unpublished data) have demonstrated that iron filings can reduce As concentrations to below 10 µg/L for groundwaters of very different composition. The mechanisms of As removal by iron filings are only partially understood; likely processes include surface precipitation, coprecipitation, and surface complexation (9,10,13).

The present study describes the performance of two household-scale As removal units that were deployed in Bangladesh. A significant potential advantage of this approach over other methods for removing As from well water at the household-level (14,16) is that little labor would be required for routine use. The experiments were conducted as part of an interdisciplinary program to determine the causes for elevated As concentrations in Bangladesh groundwater, evaluate various mitigation options, and quantify the health impact of past exposure (<http://superfund.ciesm.columbia.edu>).

Methodology

Two units were deployed for about a week each at two different wells in January 2001. Each unit consisted of two cartridges connected in series, followed by an aeration vessel and a filtration cartridge (figure 1). The first two cartridges each contained 1.9 kg of sand and 2.4 kg of iron filings (1:1 by volume); the third cartridge contained a nylon filter. The total volume of the iron-filing/sand media in each cartridge was 2.7 L; the estimated porosity ~0.45. Iron filings were purchased from Comely-GPM, Inc. of Chicago, IL (stock number CC-1004). The silica sand was a #4 Q-Rok mined by U.S. Silica in Berkeley Springs, WV. Well water was pumped through each system at 130-150 mL/min (residence times of 8-9 minutes in the media) by a portable peristaltic pump with three heads (Masterflex). One head pumped water from the well through the first two cartridges and into the aeration vessel. The second head continuously bubbled air into the aeration vessel through a glass frit to oxidize and precipitate ferrous iron released by the filings. The third head pumped the water containing high levels of Fe-oxyhydroxide particles floccs, from the aeration vessel through the last cartridge containing a standard 5-µm nylon filter.

Samples were collected daily at the inlet of the system, the outlet of the second iron filing column (i.e. before the aeration vessel), and the outlet of the nylon filter. Temperature, pH, conductivity, the oxidation-reduction potential (ORP), and dissolved oxygen were also measured daily at the inlet and outlet with an ORION meter. All samples were acidified to 1% HCl (OPTIMA) on site. Phosphate concentrations for all samples were measured by colorimetry in the field using colorimetric molybdate-blue method (17). Samples from the inlet and outlet were analyzed for both P and Fe by inductively coupled plasma atomic emission spectrometry with coupled plasma Perkin Elmer (Optima 3300XL, instrument two months later at the University of Connecticut (UConn)). Arsenic was measured at UConn by hydride generation flame atomic adsorption spectrometry (HG-FAA) using a Perkin-Elmer Model 5100 atomic adsorption spectrometer equipped with an electrodeless discharge lamp (EPA method 6010), with detection limit at 4 µg/L. Inlet and outlet samples collected on January 11 and 18 were also analyzed by high resolution inductively coupled plasma-mass spectrometry (HR ICP-MS) in December 2001 at Lannon Doherty Earth Observatory for a broad suite of inorganic constituents (Na, Mg, Si, K, Ca, Mn, Mo, Se, Al, S, Zn, Sr, Sb, Ba, Cd, Cr, Cu, Pb, Zn, Ni and Cu), some of which are of potential health concern. The detection limit of this method for As is ~0.1 µg/L (18). The composition of the mixed iron-filing/sand mixture was also determined with HR ICP-MS after digestion with mixed H₂-HNO₃ acid.

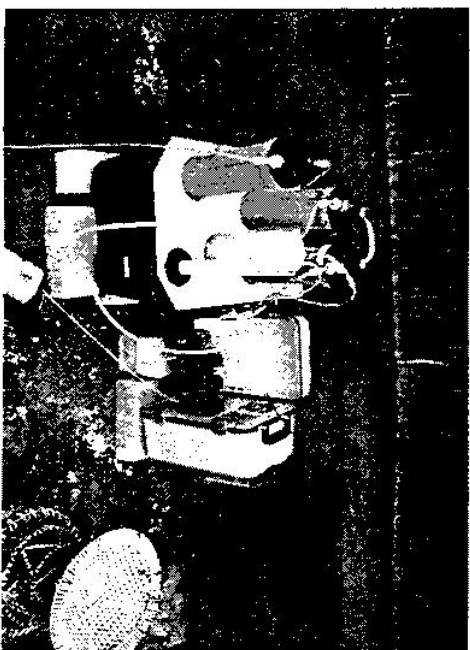


Figure 1. AsRT unit setup.

Results

The inlet As, Fe and P concentrations of the two AsRT units did not vary significantly during the deployment period (Figures 2, 3). Arsenic inflow concentrations of 560 and 290 µg/L for AsRT units A and B, respectively, were also not significantly different from concentrations obtained for the same wells (IDs 4133 and 4146) as part of a large survey conducted a year earlier (18). ORP measurements suggest that unit B was tapping a more reducing aquifer; dissolved Fe and P concentrations were significantly higher and S levels were lower compared to water at the inlet of unit A (Table I). Of all the inorganic constituents other than As that were analyzed for the inflow of both units, only Mn concentrations exceeded the corresponding WHO guideline value for drinking water of 0.5 mg/L (Table I).

AsRT units A and B treated 1,830 L and 1,140 L of well water over 8 and 6 days, respectively. During the first few days of the deployment, HG FAA and HR ICP-MS measurements indicated detectable (>4 µg/L) As in the outflow from unit A and concentrations of ~100 µg/L in the outflow from unit B (Figures 2, 3). However, both units became very effective during the second half of the deployment when As concentrations in the effluent remained consistently below 10 µg/L (Table I). Although the dissolution of iron-filing/sand media could have released many elements of potential health concern, their levels at the outlet were all below respective WHO guideline limits (Table II), with the exception of Mn (Tables I and II). Mn concentrations were reduced by about one third for both units relative to the inflow, but remained above 0.5 mg/L.

The corrosion of iron filing material releases significant quantities of Fe, which was confirmed by the orange-colored precipitate formed in the aeration vessel. Despite its simplicity, the combination of aeration and filtration effectively removed excess Fe in the solutions. Iron concentrations in the effluent were maintained below 1 mg/L, the secondary WHO criterion for Fe in drinking water which is based on taste and esthetics rather than health (Figures 2, 3). The time series data indicate that P was also removed by the AsRT units, although the removal was not as effective as for As and declined over the course of the deployments. In the case of unit A, which treated a larger volume of water than unit B, P concentrations at the intermediate sampling point (just before the aeration vessel) gradually increased to reach the level of the inflow over the course of the deployment (Figure 2). For both AsRT units, the precipitation and removal of Fe oxides contributed to the removal of As and P from the effluent.

Table I. Performance of AsRT at Two Wells in Bangladesh (January 2001)

	Unit A-4133		Unit B-4146	
	Inflow	Outflow	Inflow	Outflow
pH	6.8	7.1	7.1	7.4
Temp (°C)	23.8	21.2	24.7	22.3
Cond. (µS/cm)	653	612	724	650
DO (mg/L)	2.1	7.3	1.1	7.6
Eh (mV)	-20.9	109.8	-130.4	67.1
As (µg/L)	560	<4	290	8
Fe (mg/L)	1.2	0.4	7.2	0.4
P (µg/L)	280	130	580	96
Na (mg/L)	25	23	38	40
Mg	26	24	25	25
Si	20	15	17	13
K	9.0	8.0	6.2	6.5
Ca	81	71	65	64
Mn	6.2	5.0	3.4	2.5
S	7.4	7.1	2.4	2.6
Mn (µg/L)	4.4	9.8	6.2	7.4
Se	3.1	3.2	2.4	2.2
Al	20	18	20	17
Zn	19	18	18	18
Sr	150	270	120	160
Sb	<0.1	<0.1	<0.1	0.2
Ba	1	43	16	21
Cd	<0.1	<0.1	<0.1	<0.1
Cr	2.5	2.4	2.6	2.4
Cu	8.4	0.4	0.3	0.3
Pb	0.2	0.2	0.1	0.2
Hg	0.2	0.2	0.2	0.2
Ni	2.4	2.9	2.5	2.3
U	1.1	0.2	<0.1	<0.1

All data obtained by HR ICP-MS, except for As (HG FAA) and Fe and P (ICP-AES).

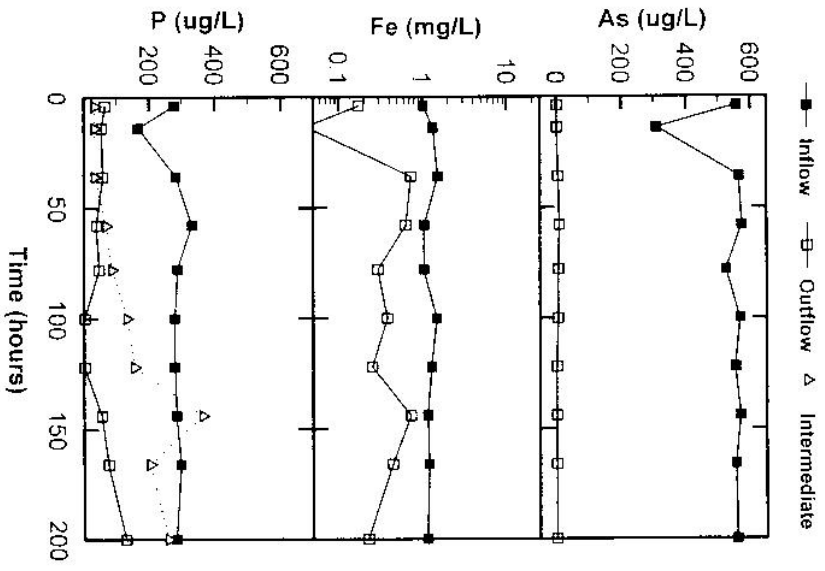


Figure 2. ASRT performance at Well 4133 in Bangladesh. Comparison of influent and effluent arsenic, iron, and phosphate concentrations.

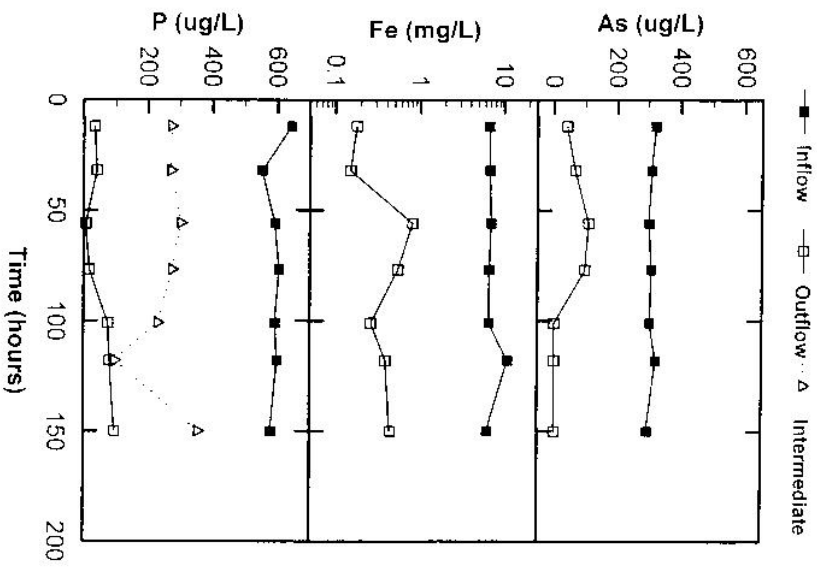


Figure 3. ASRT performance at Well 4146 in Bangladesh. Comparison of influent and effluent arsenic, iron, and phosphate concentrations.

Table II. Composition of the Iron Filings and Sand Mixture

Element	Concentration (mg/kg)	Element	Concentration (mg/kg)
Na	87	Mo	200
Mg	98	Ni	390
Si	8900	Al	78
K	107	P	213
Ca	114	S	188
As	25	Ti	86
Ba	1	V	63
Cr	870	Co	41
Cu	1240	Zn	15
Mn	3990	Fe	~50%

Discussion

A variety of methods have been developed to remove arsenic from drinking water but these are usually only effective for arsenate and required a pre-oxidation step for arsenite removal (19-22). The technologies also suffer from interferences by P in the water because of strong competition of P(V) with As(V) arsenate for surface sorption sites. In Bangladesh, arsenic is present in groundwater predominantly as As(III) (23). As observed in the past, AsRT very effectively removes both As(V) and As(III). The limited removal of P(V) at comparable concentration in the inflow suggests that AsRT may actually remove As(III) more effectively than As(V) (9, 24). One of the keys to effective As(III) removal by AsRT may therefore precisely be the relatively poor retention of P(V). This is an important feature in the case of Bangladesh since groundwater P levels are frequently an order of magnitude higher than As.

Most existing As-removal technologies cannot be applied on a wide range of scales that extends from home-based units to large scale water treatment plant and industrial waste treatment. In the case of AsRT, field tests at a landfill in Maine, U.S.A, with elevated groundwater As concentrations demonstrated a removal capacity of ~ 7 g As per kg of iron filing media (10). A larger unit deployed at the same site effectively treated 5500 L/day of groundwater for 8 months essentially without maintenance (10). The results of the deployments presented in this study show that AsRT could also be applied at the household level in rural Bangladesh.

Additional factors have to be considered for evaluating the potential for widespread use of AsRT in Bangladesh. The initial breakthrough of As from an AsRT unit has been observed in the past (10). It is probably due to the limited surface area available for arsenate and arsenite adsorption at the initial stages of the iron filing corrosion process. The rate at which this process occurs depends on the corrosiveness of the water, which may vary significantly between wells.

The implication is that proper training and monitoring of effluent water quality is required before a unit is used to produce water for human consumption. The sensitivity of the capacity of an AsRT system to potential variations in groundwater composition over time also needs to be evaluated with long-term deployments. Periodic monitoring will be required to determine when an AsRT cartridge needs to be replaced. The main complication of this technology is the significant export of iron which requires a separate removal step. Long-term deployments elsewhere suggest that clogging of Fe and sand-containing cartridges should not be a problem. Clogging significantly limits the applicability of the 3-kolshi system, which also relies on Fe filings (23). The ample supply of a reactive media, on the other hand, overcomes the problem of limited As removal when insufficient Fe is naturally present in groundwater. Another potential concern faced by all water treatment technologies is bacterial growth within the system. Although the initial setup cost of AsRT could be relatively higher than the 3-kolshi system, it is easier to maintain and can be used for much longer periods continuously (which reduces cost over the long run).

The AsRT technology is fairly unique in that it requires relatively little maintenance for a long time and is cost effective. Household-level As-removal units that require considerably more effort such as daily additions of ferric chloride, filtration through a sand bed, and periodic washing of the sand have been used by hundreds of households in Bangladesh for extended periods (14-16). Our experiments in Bangladesh suggest that an AsRT-based system similar to the ones tested could produce continuously 6 L/hour of clean water, i.e. enough to meet the drinking and cooking needs of several families. Due to the relatively low cost of iron filing and sand that can both be produced in Bangladesh, the operating and maintenance cost per unit of a household is estimated to be below US\$1 per year. In addition, the system can be scaled-up easily and can be used as a mini-water treatment plant for a group of people or a small village. Toxicity Leaching Characteristic Procedure tests (10) on the spent filter material produced As concentrations in the leachate three orders of magnitude less than the criteria, which renders the material safe for disposal in a municipal landfill in the US.

Conclusions

This pilot study demonstrates that iron filings can reduce As concentrations in Bangladesh groundwater to the level of the WHO guideline value for drinking water, without the addition of other elements of potential health concern. No reagents need to be routinely added. AsRT may become useful in areas where As-safe groundwater is not easily available.

Acknowledgements

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