



Testing simple arsenic removal methods

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MANY TUBEWELLS IN Noakhali District where the Mennonite Central Committee (MCC) Agriculture Program works have arsenic levels above the Bangladesh maximum of 0.05 mg/L. In this study, we tested an arsenic removal procedure developed by DANIDA for use in rural areas. The DANIDA method recommends using alum and potassium permanganate to coagulate the arsenic. In this study, we compared the performance of alum and ferric chloride as coagulants, both with and without an oxidant. Residual aluminum in treated water was measured when alum was used as the coagulant.

Most investigations using alum or ferric chloride as coagulants have used artificial water produced in a laboratory. (Hering et al, 1997) showed differences in removal by coagulation of As (III) and As (V) depending on the source and pH of the water.

Because of the observed differences between artificial and source waters, it is important that systems be tested using actual groundwater. We investigated removal of arsenic from actual groundwater using methods suitable for use in rural Bangladeshi households and all measurements were taken using methods suitable for field use. These methods are generally less sensitive and less precise than laboratory methods.

Arsenic is best coagulated as As (V) and most investigations of chemical coagulation methods have concluded that a pre-oxidation step must be used in order to convert As (III) into As (V). In a laboratory study of the oxidation of As (III) to As (V) in the pH range of 6-10, As (III) was immediately converted to As (V) in the presence of 1 mg/L free chlorine. In the same study, pure oxygen could not oxidize As (III) to As (V) in 1 hr, but complete oxidation of As (III) to As (V) occurred during 2 months of ambient temperature storage of synthetic groundwater (Frank and Clifford, 1986).

Two of the most commonly used precipitating agents are ferric chloride (FeCl_3) and alum or aluminum potassium sulfate. In general, ferric chloride removes 81-100% of arsenic from water while alum removes 85-92% (Legault, A. S. et al. 1993)

Few studies to determine the relative amounts of As (III) and As (V) in Bangladesh groundwater exist. Available data indicate that the median values for Bangladeshi groundwater show a ratio of roughly 50% for each species, but there was a wide range and little relationship with other measured parameters (Anonymous, 1999). A survey in Noakhali Pourashava (Anonymous, 1998a) reported that 80% of the total arsenic occurs in the form of As (III).

Materials and methods

We used commercial-grade alum purchased in a market in Dhaka. Commercial grade was used because this is the quality that would normally be available to rural Bangladeshis in the areas most affected by arsenic contamination. Reagent-grade ferric chloride from Thailand was used because commercial grade was not available in Bangladesh markets. The chemical properties of water samples were determined both before and after treatment. Groundwater samples were tested for total arsenic both before and after treatment. When comparative arsenic treatments were performed, total iron and pH were also tested. Aluminum content was determined several times, but not routinely. The data for total iron are limited because of problems with reagents that eventually had to be replaced. Initially arsenic samples were determined in duplicate, but the protocol was changed to single observations per sample when no variation was noted due to standard sampling conditions and the relative insensitivity of the field methods.

Total arsenic in water was determined using the Merck Arsenic Kit which determines both As (V) and As (III) as total arsenic. This test kit is the only one being recommended by UNICEF for use in Bangladesh (Bajracharya, 1999) because it is the only kit that meets its quality standards. The Merck kit is semi-quantitative so in the most useful range for water samples it can only determine 0.0, 0.1, or 0.5 mg/L arsenic in water. For this investigation, arsenic content was reported to the next highest value on the color chart, thus if a sample appeared to have a concentration of about 0.3 mg/L arsenic, it was reported as 0.5 mg/L.

The pH of the water samples was determined using a "Champ" Calibration-Free pH meter, produced by Hanna Instruments.

Aluminum in water was determined using a test kit manufactured by LaMotte (7864 Octet Comparator Method) employing APHA Method 306B. This method has color standards representing 0, 0.05, 0.1, 0.15, 0.2, 0.3, 0.4 and 0.5 ppm aluminum. Total iron was determined using a LaMotte Iron Test Kit (4447 Octet Comparator) which uses a bipyridal indicator and has color standards representing 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, 6.0, 8.0, and 10.0 ppm iron.

We constructed and tested the two bucket system arsenic removal system developed and promoted by DANIDA. The system consists of two vertically stacked buckets. The coagulation chemicals are mixed with the arsenic-contaminated water in the top bucket and following 2 hours of settling, the water is allowed to run through the bottom bucket which contains only sand. The total cost for construction

(excluding labor) using materials found in local markets was about US\$7.00.

Water for all tests was taken from the same well in Sonapur Village in Noakhali Pourashava. A survey of 19 wells in this area showed that the median arsenic level is 0.16 mg/L (Anonymous, 1998a).

Results and discussion

Groundwater extraction and storage system

The well from which water samples were drawn for testing water was in an MCC facility. The well has consistently tested at or above 0.1 mg/L of arsenic. Groundwater from the well was stored in an elevated concrete slab storage tank. The water was extensively oxygenated as it is pumped into the tank. Water enters the facility tank by a galvanized pipe attached to the bottom of the tank.

The period of testing was from September 1999 until May 2000. In January, we realized that the process of pumping and storing the water reduced the arsenic and iron contents. After discovering this, we routinely tested water before it entered the storage tank, although for uniformity, samples used for arsenic removal tests continued to be drawn after the storage tank. However when the process of pumping and storing reduced arsenic levels in the water to zero, water for arsenic testing and removal was taken before it entered the tank. For all arsenic

removal tests, the initial water composition was determined at least once per day for arsenic and pH. Iron content was determined for about half the samples. Tests showed a consistently high concentration (4-6 mg/L) iron in the water.

Studies have shown that it is possible to remove arsenic by oxygenation of water that is high in both arsenic and iron. For water containing 0.27 mg/L iron and 0.08 mg/L of arsenic, van den Berg (1998) found that oxygenation removed about 65% of the arsenic from the water. When iron is oxidized, it forms flocs ($Fe(OH)_3$) to which the arsenic is adsorbed.

The arsenic content of this well has been tracked for one year, although in some months there were only a few tests done because of either holidays or country-wide general strikes. The arsenic levels are shown in Figure 1.

The data shown are for months in which there was a minimum of four tests made, each on a different day. Rainfall measurements are shown for the period May, 1999 to May, 2000. It appears that the arsenic levels in this well are related to weather and specifically rainfall amounts, but is probably more related to the flow of underground water than rainfall. Although preliminary since arsenic concentrations should be monitored through at least one complete weather cycle (rainy-cool-hot-rainy), these data suggest arsenic levels are seasonally dependent. Arsenic levels can change seasonally depending upon an area's geology (Hoffbuhr, 1999).

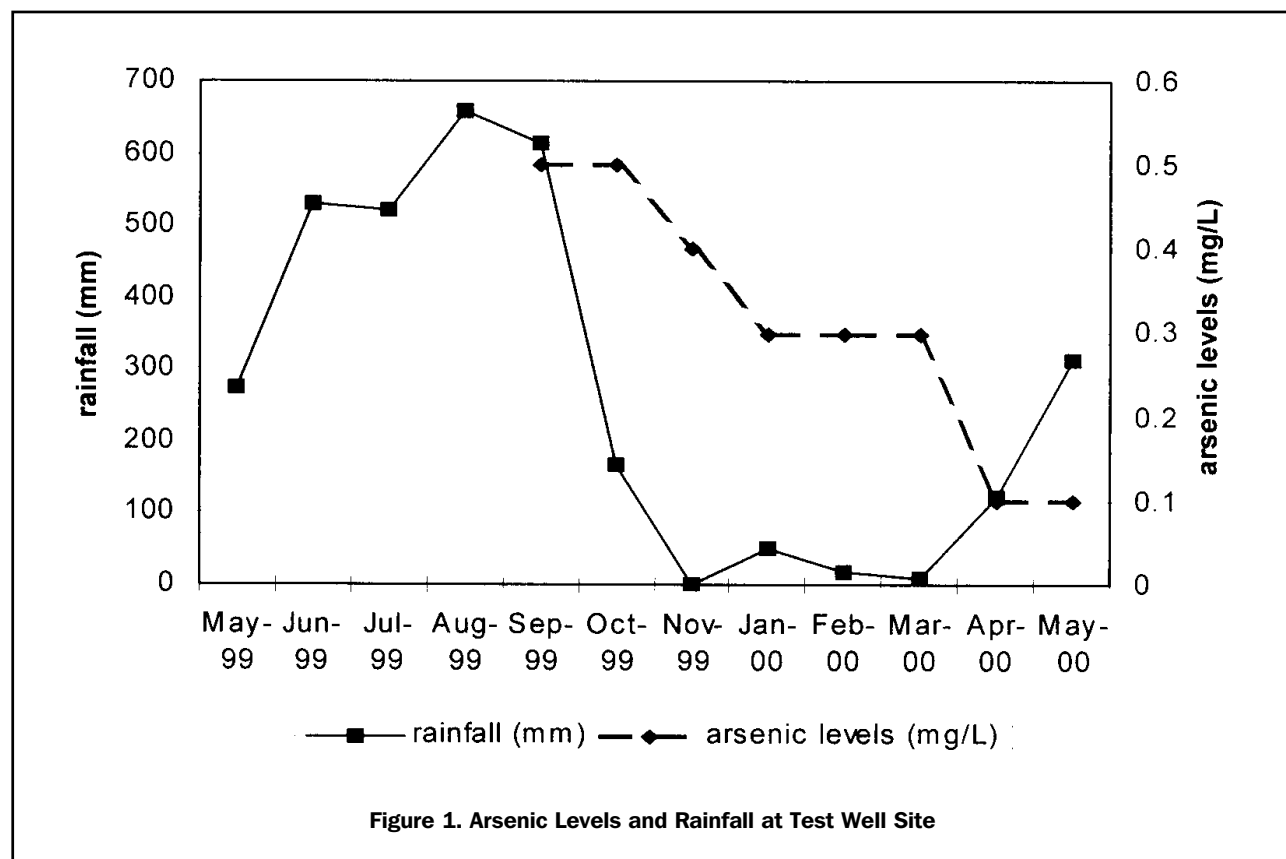


Figure 1. Arsenic Levels and Rainfall at Test Well Site

The trend in Figure 1 indicates that testing a well once does not give a complete picture of the arsenic content. The iron content of this well stayed high even during the dry season when the arsenic levels were dropping. This is consistent with observations in the Mott-MacDonald/BGS report (Anonymous, 1999). Which showed that arsenic shows no strong, overall correlation between arsenic and dissolved iron, thus iron content cannot be used to predict arsenic concentration.

Changes in arsenic concentration in the test well were consistent with changes in a well 0.5 km away. A decline from 0.5 mg/L arsenic to 0.1 mg/L in May 2000 in this well was similar to the decline in the test well (Fig. 1).

A survey of arsenic levels in Samata village in Jessore (Yokota, 1998) found that 32% (12 out of 38) had higher arsenic concentrations in the rainy season than in the dry season, while only one well had higher arsenic concentrations in the dry than in the rainy season. The remaining wells had similar arsenic concentrations in both seasons. He concluded that a fast flow of underground water delivered arsenic from elsewhere in the rainy season.

Evaluation of the DANIDA Double Bucket System

We tested the double bucket system developed by DANIDA and treating the water with 4 g alum and 0.03 g potassium permanganate in 18 liters of water. The results are shown below:

	As	Al	Fe	pH
Top (1 hrs) ^a	0.1± 0 (n=5)	0.35±0.07 (n=2)	0.5±0 (n=2)	7.7± 0.23 (n=3)
Top (2 hrs) ^b	0.07± 0.05 (n=6)	0.3±0.06 (n=5)	0.5±0 (n=2)	7.8± 0.25 (n=3)
Bottom (1) ^c	0±0 (n=4)	0.22±0.03 (n=3)		7.9± 0.26 (n=4)
^a Top (1 hrs): Tested after one hour of settling. Water allowed to settle for 1 more hour and then filtered. ^b Top (2 hrs): Tested after 2 hours settling. Sample taken before going through sand filter. ^c Bottom (1): After 2 hours settling followed by filtration through sand filter.				

The arsenic content of the untreated water was measured before chemical treatment and was in the range of 0.1-0.5 mg/L for all tests (rounded up to 0.5 mg/L). The precipitation reaction is usually complete in one hour, although in some cases it continues for the full two hours. The Merck kit gives readings as ranges so slight variations in arsenic content are not observable. It also appears that the sand filter removes most if not all of the residual arsenic. Although high, the residual aluminum meets the upper limit for aluminum content for drinking water of 0.2 mg/L set by the US and Australia.

We tested for a relationship between initial arsenic content in untreated water and aluminum content in water after treatment using the double bucket system. Water with a low initial arsenic concentration (0.1 mg/L) and also a high initial As content (0.5 mg/L) was treated with low (4 g) alum and high (10 mg/L) amounts of alum respectively. In both tests, the final arsenic content after filtration was 0.0 mg/L. For the test with low initial As, the aluminum content was 0.25 ppm after 2 hours of settling but before filtration where presumably the amount would be reduced. For the test using 10 g. of alum, the aluminum content after filtration was also 0.25 ppm. Although the final aluminum content of the water is high, it is not above the levels recommended by most regulatory agencies in the west.

We also tested the DANIDA double bucket system using 4 g. of alum without an oxidant. The results, shown below, are typical data, all taken on the same day (9/20/99).

	As	Al	pH
Initial Water Composition (mg/L)	0.5	0	8.3
After 1 hour settling	0.1	-	-
After 2 hours settling	0.1	0.3	-
Final, after filter (mg/L)	0	0.25	7.7

When either alum or ferric chloride was used as a coagulant without an oxidant, the arsenic level in the water was substantially reduced. If a sand filter was used as a final step, the water tested at 0.0 mg/L by the Merck kit. The same results were observed when using 5 g of alum alone as recommended by DANIDA-DPHE (Anonymous, 1998b). They reported that this method had a removal efficiency of 90% and that this could reduce the arsenic levels in 90% of the affected tubewells in Noakhali to less than 0.05 mg/L.

These results seem inconsistent with those from other investigations, which suggest that it is difficult to remove As (III) if it is not oxidized to As (V). DANIDA/DPHE results showed high removal of As even though 80% of the arsenic in the wells was As (III). Borho and Wilderer (1997) provide a possible explanation. They found that 80% of the As (III) (at 0.06 mg/L in solution) converted to As (V), even when stored at the recommended pH of <2.0. Trace amounts of Fe (III) were likely responsible for the conversion of As (III) to As (V) (Borho and Wilderer, 1997).

Water in our system was oxygenated as it was pumped into the tank. Available oxygen may have helped convert most of the As (III) into As (V) a process that would have been accelerated by Fe (III) since Fe (III) is also formed from Fe (II) in the presence of oxygen. The water that was used for the tests has consistently tested high in iron and visual observation has also shown that iron content is high. If the conversion described above was occurring, it would help

remove arsenic since other work (Hering, et al., 1997) has shown that close to 100% of As (V) is removed when ferric chloride with no oxidant is used. Alum when used alone removes almost no As (III) and removal is reduced as alum concentration increases (up to 120 mM).

The relatively high concentrations of aluminum that remain in the water following alum treatment have raised health concerns. Because of this, the double bucket method was evaluated with ferric chloride instead of alum as the coagulant. The following tables show typical data for one complete trial for the Double Bucket system evaluated using the chemical amounts shown.

Table 3. 4 g ferric chloride; 0.03 g permanganate (2/10/2000)			
	As	Al	pH
Initial Water Composition (mg/L)	0.5	2.0	8.3
After 1 hour settling	0.0	4.0	7.7
Final, after filter (mg/L)	0.0	0.0	7.7

Table 4. 2 g ferric chloride; 0.03 g permanganate (2/22/2000)			
	As	Fe	pH
Initial Water Composition (mg/L)	0.1	1.0	8.4
After 1 hour settling	0.0	3.0	7.7
Final, after filter (mg/L)*	-	-	-

Table 5. 1 g ferric chloride; 0.03 g permanganate (3/7/2000)			
	As	Fe	pH
Initial Water Composition (mg/L)	0.1	1.0	7.2
After 1 hour settling	0.0	3.0	7.0
Final, after filter (mg/L)*	-	-	-
* not determined since 0 mg/L arsenic reached after 1 hour			

Table 6. 0.7 g ferric chloride; 0.03 g permanganate (3/7/2000)			
	As	Fe	pH
Initial Water Composition (mg/L)	0.1	2.0	6.8
After 1 hour settling	0.1	3.0	6.8
After 4 hours settling	0.1	3.0	7.5
Final, after filter (mg/L)	0.0	0.0	7.5

Table 7. 0.7 g ferric chloride; 0.03 g permanganate (5/4/2000)			
	As	Fe	pH
Initial Water Composition (mg/L)	0.1	6.0	8.0
After 1 hour settling	0.0	6.0	7.8
After 3 hours settling	0.0	5.0	-
Final, after filter (mg/L)	0.0	0.0	7.4
Note: water used was directly from the ground because water inside facility had 0.0 mg/L arsenic.			

For any of the various amounts of ferric chloride, except 0.7 g., coagulation had finished after one hour and it appears that the sand filter would not be needed to remove excess unwanted chemicals. This is in direct contrast to precipitation with alum, which took longer and required the sand filter to bring levels of arsenic and aluminum down to acceptable levels. It appears that higher existing iron levels helped remove the arsenic faster even when small amounts of ferric chloride were added.

Conclusions

The DANIDA Double Bucket removal system effectively removes arsenic when either alum or ferric chloride is used as a coagulant. Ferric chloride will remove arsenic more completely and more quickly, but is not readily available in Bangladesh. The procedure will remove substantial amounts of arsenic without employing an oxidant such as potassium permanganate or chlorine. Arsenic can be removed from water that is high in iron if an air-oxidation step is added. Fe (III) is known to be effective for coagulating arsenic and the oxygenation step probably helps convert iron in the water from iron (II) into iron (III). Preliminary data suggest that arsenic levels in groundwater will vary depending upon the season rainfall, and probably underground water flows. Longer term data are required to confirm these relationships. These limitations notwithstanding, existing data show that testing a well only once does not necessarily give a complete picture of the arsenic content of that well.

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