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Importance of evaluating phosphate levels in tubewells in high arsenic areas of Asia

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Significant levels of naturally occurring phosphates in groundwater in some arsenic affected regions can potentially reduce removal efficiencies of some critical iron-based arsenic treatment systems that currently are among the most simple and low-cost treatment approaches.− From March-December 2007, the Massachusetts Institute of Technology (MIT), the Centre for Affordable Water and Sanitation Technology (CAWST) and LEDARS, a Bangladeshi NGO, conducted pilot testing in Bangladesh of the Kanchan Arsenic Filter. Because of the varying phosphate levels in groundwater in different districts in Bangladesh, the project also included an analysis of phosphate data from arsenic studies conducted by other organizations in high arsenic areas in Vietnam, Cambodia, West Bengal and Inner Mongolia and compared them to results from Bangladesh and Nepal.The results from the analysis indicated that the ratio of iron to phosphates in the groundwater might be a good indicator for the effectiveness of iron-based arsenic removal systems in high arsenic areas.

Introduction

Naturally occurring high arsenic levels exist in tubewells in regions of a number of countries in Asia including Bangladesh, Cambodia, China, India, Mongolia, Myanmar, Nepal and Vietnam. Arsenic treatment systems using iron-based media have been developed for use at the household level to treat groundwater used for drinking water and for cooking. Iron-based arsenic treatment systems are among the most simple, low-cost and effective treatment approaches used. A number of studies have evaluated the impact of different chemical species in groundwater on arsenic removal using iron-based media (Khan et al., 2000; BCSIR, 2003, Tyrovola et al., 2006, Roberts et al., 2004, Su and Puls, 2001). Potential interferences on removal performance include phosphates, silicates, pH, bicarbonate and possibly organic matter (Meng et al., 2002, Grafe et al., 2002 and Table 1 below). Because of their similar chemical structure to arsenic, phosphates have been identified as a potentially significant interference in a number of these studies. Phosphate and arsenate As(V) react similarly with iron oxides in the subsurface. In addition, other water quality parameters can potentially have an impact on arsenic removal efficiencies for iron-based systems (Table 1).

Moderate to high phosphates naturally occur in many of the same areas in Asia where high arsenic levels exist (Table 2). In Asia high arsenic levels in groundwater are often associated with geologically young sediments and flat low-lying areas where groundwater flow is slow. Such conditions favor the reductive dissolution of iron oxides and/or desorption of arsenic from metal oxides associated with sediments. Such conditions also often result in elevated phosphate levels by means of the same processes. Phosphate levels in shallow groundwater can be elevated because of fertilizer used for agriculture (Young and Ross, 2001). However there are differing opinions as to whether such impacts from agriculture extend deeper than a few meters or not and into the depths generally associated with high arsenic levels (Stollenwerk et al., 2007). McArthur et al. (2004) discuss the impact of phosphate loadings on arsenic levels from latrines 10 km west of Dhaka, Bangladesh. They stated that 3 wells sited within 3 meters of latrines contained arsenic concentrations of 900 ug/L while the remaining 12 wells, which were all > 15 meters from the latrines contained between 100 to 300 ug/L of arsenic. The phosphate loadings from the latrines may have competed with arsenic for adsorption sites on iron oxides resulting in increased arsenic levels.

Transport of phosphates in the subsurface likely depends on the physical and chemical properties of the aquifer (Stollenwork, 1996). For example higher pH in groundwater causes decreased sorption of phosphates on aquifer sediments. The capacity of the subsurface soils to absorb phosphates applied as fertilizers depends, in part, on the phosphate load applied. Because high phosphates are found at significant depths, the source of phosphates in such areas is believed to be caused by the same processes as those that cause high arsenic levels as noted above.

Generally the three most important additional parameters to analyse for during arsenic testing of tube-wells are: (1) total iron, (2) phosphates and (3) pH. For phosphates, the testing lab should clearly identify whether reported results are as phosphates (PO4), phosphates as P (PO4-P) or phosphorus (P). All three are acceptable but phosphate levels reported as or PO4-P as P are approximately 1/3 the concentration of PO4 reported for the same sample.

The Kanchan^{TM} arsenic filter

The Kanchan^{TM} Arsenic Filter (KAF) was developed by MIT and the Nepali NGO Environment and Public Health Organization (ENPHO). It has been extensively tested in high arsenic areas of the Terai area in Nepal. Its foundation is a biosand filter (using either plastic or concrete base) that has been modified to include a diffuser basin on the top with iron nails (see Figure 1). In the diffuser basin, 5 to 6 kg of non-galvanized nails are evenly distributed. The rust from the nails chemically interacts with the arsenic and the precipitate is filtered out in the fine sand portion of the filter. The filter is easy to use and maintain. The nails supplement

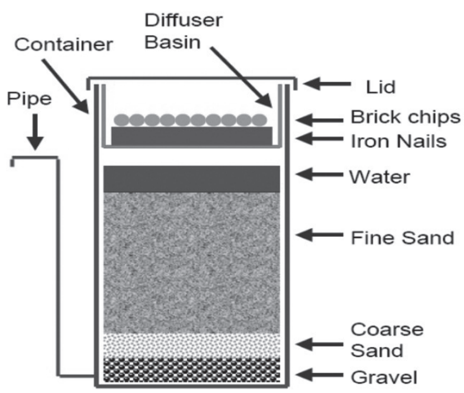

Figure 1. Kanchan^{TM} arsenic filter

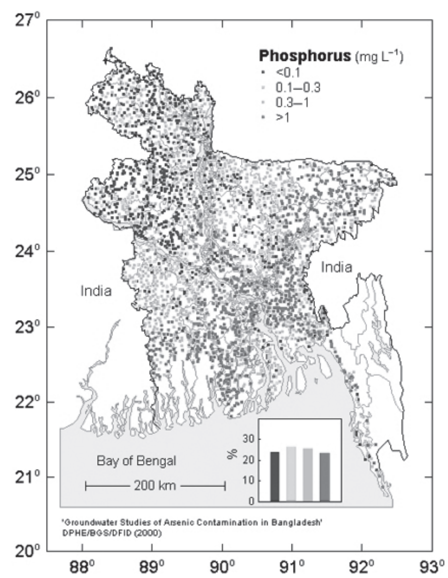

Figure 2. Phosphate levels (as P) Bangladesh (BGS & DPHE, 2001)

naturally occurring iron levels that exist in groundwater (Ngai et al., 2006). Typically, naturally occurring iron levels do not occur in sufficient concentrations or in appropriate speciation forms to adequately remove arsenic without (1) an oxidation step (initiated by the the pouring of the water into the filter) and (2) supplemental iron being added.

Findings - Phosphates by region/country in Asia

As previously noted, phosphates will compete with arsenic for adsorption sites on iron oxides. Therefore it is important to understand the levels and ratios of phosphates and iron in groundwater that will potentially be treated by adsorption systems using iron-based media. As part of the KAF pilot-testing project in Bangladesh, the authors conducted an evaluation of available arsenic studies conducted by other organizations in Asia that included groundwater analyses for phosphates. Table 2 gives average, median or range values for arsenic and phosphates from studies conducted in six Asian countries. Below are brief descriptions of the particular groundwater phosphate characteristics as they pertain to each country.

Bangladesh

Groundwater in Bangladesh has high phosphate levels in a number of districts coinciding with high arsenic levels in groundwater (Figure 2). The median concentration of phosphates (as P) in high arsenic waters (> 50 ug/L) is 1.1 mg/L as measured by BGS and DPHE (2001).

The authors conducted pilot field-testing in Bangladesh of the KAF from March-September 2007. The pilot testing was conducted to support an application for certification testing as part of the Bangladesh Environmental Testing Verification – Support for Arsenic Mitigation (BETV-SAM) program. While preliminary pilot testing results were promising, if approved for certification, extensive testing of the KAF will be conducted in a number of districts in Bangladesh with varying phosphate levels.

Nepal

Phosphate levels in Nepal are generally significantly lower than in Bangladesh averaging about 0.23 mg/L as PO_4-P (Ngai et al., 2007 and Table 2). Phosphates are generally not believed to be sufficiently elevated to interfere with the iron-based arsenic removal systems in Nepal (Ngai et al., 2007).

Cambodia

Generally phosphate levels are less than in Bangladesh and are moderately high in the high arsenic portion of Kandal Province area near Phnom Penh. Phosphates ranged from 0.001 – 3.14 mg/L as PO_4-P with an average of 0.66 mg/L as PO_4-P (Buschmann et al., 2007).

Vietnam

In the Red River Delta basin iron levels are generally very high and phosphate levels are moderately high (Berg et al., 2006). Phosphates averaged about 0.75 mg/L as PO_4-P.

West Bengal (India)

West Bengal has high arsenic levels and high phosphate levels in some wells. Phosphate levels are significant (McArthur et al. 2004). They ranged from the equivalent of about 0.3 - 2 mg/L as PO_4-P and an equivalent average of 0.4 mg/L as PO_4-P (converted from PO_4). Filters that include addition of supplemental iron, such as the KAF Arsenic Filter, would likely perform similarly as in Bangladesh but should be pilot studied.

Inner Mongolia (China)

Concentrations of phosphates are high in many of the groundwaters of the Huhhot Basin (between <1 and 1,480 μ/L) particularly in the central parts of the basin. Smedley et al. (2003) found that in shallow wells, phosphate concentrations were up to 3.1 mg/L and up to 2.9 mg/L in deep wells (deeper than 100 m). For wells with arsenic levels greater than 50 ug/L the median phosphate level is significant - approximately 1 mg/L. pH is elevated, median 7.8 in wells tested by Smedley et al. (2003). Dissolved organic carbon (DOC) concentrations are relatively high in the groundwater, up to 14.9 mg/L in the shallow wells and especially high in groundwater from the deep aquifer, up to 30.6 mg/L DOC.

Impact of Phosphates on Arsenic Removal

- Under certain conditions (high pH and/or low iron) phosphates can interfere with arsenic removal during iron-based treatment of groundwater (Meng et al., 2002; BCSIR, 2003; Tyrovola et al., 2006; Roberts et al., 2004; Su and Puls, 2001).
- Phosphates may significantly reduce adsorption of arsenic because phosphate is usually present in larger concentrations than arsenate (Table 1 and Table 2).
- The concentrations of phosphates in some areas of Asia are sufficiently high to potentially reduce removal efficiencies of some critical iron-based arsenic treatment systems that currently are among the most simple and low-cost treatment approaches (Table 2 and BCSIR, 2003).
- Extensive field-testing of five non-KAF arsenic removal technologies in Bangladesh revealed that all five technologies performed poorly in one district (Hajiganj District) that had elevated pH of 7.5-8 and phosphate levels of about 10 mg/L as PO_4 which is equivalent to approximately 3 mg/L PO_4-P and (BCSIR, 2003).
- As part of the KAF pilot study in Bangladesh, the authors decided to increase the amount of nails from 5 kg to 6 kg to address the high phosphates found in some tubewells.

Are iron to phosphate ratios a predictor of arsenic removal performance?

For the KAF, phosphate will compete with arsenic for the available adsorption sites on the iron surface, therefore, generally the higher the level of naturally occurring iron levels, the more adsorption sites are available to accommodate all of the phosphate and arsenic, thus effectively reducing the arsenic concentration in the water. Conversely the lower the levels of phosphates the better because more iron available to react with arsenic.

The individual groundwater quality data and any arsenic removal treatment data from the studies were entered into a spreadsheet for trend analysis. The iron to phosphate ratio (mg/L of influent total iron divided by mg/L of influent PO_4-P) was then determined (see Table 3). Based on that data analysis the project team has developed a hypothesis that the location specific iron to phosphate ratio in groundwater can be used to predict the adequacy of performance of iron based household arsenic treatment systems. The project team believes that the approach can be used to assess potential problems at the individual tubewell level. In addition, if sufficient groundwater quality information is available, the iron to phosphate ratio can potentially be used to predict the overall adequacy of arsenic removal in a particular district in a country. The analysis of iron to phosphate ratios for studies that included extensive data in Vietnam (Berg et al., 2006) and Bangladesh (BCSIR, 2003) indicated that high iron to phosphate ratios were associated with high percent removals of arsenic and low iron to phosphate ratios were associated with significantly reduced percent removals of arsenic. CAWST, MIT and the Institute of Technology of Cambodia (ITC), are testing the KAF with special emphasis on the impact of phosphates on removal efficiencies.

Conclusions and recommendations

- Laboratory analysis of groundwater samples from high arsenic areas in Asia should include analysis for phosphates whenever possible at least for the raw/influent water.
- A review of the data analyzed from a number of countries confirms that (a) even if the average phosphate levels in groundwater are low in a particular area of a country, a number of individual wells will have higher phosphate levels and (b) even if the average iron levels in groundwater are high in a particular area of a country (which is good for iron-based treatment), a number of individual wells will have lower iron levels. Therefore the treatment and monitoring approach used should account for the varying conditions found from well to well.
- On an individual well basis or region of a country basis, wells with low iron to phosphate ratios and/or high phosphate levels should be monitored more frequently than other wells to ensure adequate performance.
- The iron to phosphate ratio is a potential tool to predict the likelihood of effectiveness of iron-based media arsenic removal systems.
- More information is needed on arsenic removal efficiencies in a variety of different hydrogeological conditions to confirm whether the iron to phosphate ratio is a good predictor of arsenic removal performance by iron-based adsorption systems.

Table 1: Water quality parameters that can potentially reduce arsenic adsorption efficiencies

Water quality parameter	Mechanism	Comments
Phosphates	Competes with arsenic for adsorption sites on iron oxides.	Supplemental iron addition as part of treatment should provide additional iron adsorption sites, reducing impacts.
High pH	Hydroxyl ions (OH^-) compete with arsenate for adsorption sites on iron oxides (Goldberg, 2002). High pH reduces positive charge of iron oxides reducing As removal efeciencies.	In Bangladesh, the combination of high phosphates and pH > 7.5 resulted in significantly reduced removals (BCSIR, 2003). However 4 of 5 districts had pH < 7.5, reducing impacts.
Silicates	In theory, can potentially compete with arsenic for adsorption sites.	Data on impacts is conflicting. It is thought to have much less of potential impact than phosphates (Meng et al., 2002 and McArthur et al. 2004).– In an earlier round of certification testing in Bangladesh (BCSIR, 2003) silicate levels did not appear to significantly impact the performance of technologies. Technologies were certified for use in Bangladesh based on upper limits for phosphates and pH (and iron) but not silicates.
Bicarbonate	Carbonate anions can potentially compete with arsenic for adsorption sites.	Data on impacts is conflicting. Thought to have much less of potential impact than phosphates (McArthur et al., 2004).
Organic matter (dissolved organic carbon, TOC, etc.)	Occurs due to buried organic matter such as peat, organic sediments, etc. Natural organic matter is reactive towards metals (Redman et al., 2002).	Data on impacts is conflicting. Generally thought to have much less of potential impact than phosphates.

Table 2: Examples of arsenic and phosphates levels in groundwater in select areas of Asia		
Region	**Arsenic (ug/L)**	**Phosphates as P (mg/L)**
Bangladesh From BGS and DPHE (2001) data	<0.5 – 2,500	Median - 1.1 (when arsenic > 50 ppb)
Nepal From Ngai et al. (2007)	Up to 1,000	Average - 0.23
Cambodia (Kandal Province) From Buschmann et al. (2007)	1 – 1,340 Average - 233	0.001 – 3.14 Average – 0.66
Inner Mongolia (Huhhot Basin) From Smedley et al. (2003)	1 – 1,480	< 0.05 – 3.10 Average – 0.6
West Bengal From McArthur et al. (2004)	200 – 1,180	Equivalent to about 0.3 - 2 mg/L as PO_4-P Average 0.4 as PO_4-P
Vietnam (Red River Delta) From Berg et al. (2006)	9 – 382 Average - 115	Average – 0.75

Table 3: Examples of iron to phosphate ratios in groundwater in high arsenic areas of Asia		
Region	**Approximate Iron to Phosphate ratios (in groundwater) (Total Fe/ PO4-P)**	**Comments**
Inner Mongolia (Huhhot Basin) From analysis of data from Smedley et al. (2003)	1	1 is the ratio from shallow wells (< 100 m depth).– Deep tubewells have high arsenic and also very low Fe/PO4-P ratio.
Bangladesh From analysis of BGS and DPHE (2001) data	4	Iron to phosphate ratios differ significantly by district
Cambodia (Kandal Province) From analysis of data from Buschmann et al. (2007)	4	Testing of Kanchan Arsenic Filters and the impact of iron to phosphate ratios is ongoing.
West Bengal From analysis of data from McArthur et al. (2004)	9	Just north of Barasat near Kolkata
Vietnam (Red River Delta) From analysis of data from Berg et al. (2006)	18	Ratios sufficiently high to get significant arsenic removal at some wells by just aeration and sand filtration.– Supplemental iron would likely increase removal efficiency.
Nepal (Terai) From Gurung et al. (2005)	30 (Fe by AAS) 18 (Fe by field kit)	PO4 results converted to PO4-P. Ratio based on Fe results by AAS analysis. Using field test kit results Fe/PO4-P ratio would be 18.

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