Groundwater Contamination in Bangladesh: Causes, Effects, and Remediations

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I. Introduction

> About six or seven years ago blisters developed on my whole body and there was a lot of itching. A few months later, these blisters turned into black spots on my hands and legs. They itched and there was some pain. A few years later, these black spots became hard and rough. Now they have turned into sores (Chakraborti et al., 2002).

Environmental scientist Dipankar Chakraborti captures the lack of understanding among the Bangladesh population to the severity and occurrence of arsenic contamination. Though arsenic patients are generally documented from 1983 onward, surveys indicate unusual occurrences of skin lesions from 1965. One man from Calcutta reports losing six of his nine affected family members as dying to cancer from arsenic related causes (Chakraborti et. al., 2002). The discovery of arsenic in groundwater has exacerbated the health problems and shortage of sanitary water in Bangladesh. Recent studies have discovered the extent and causes of poisoning, but the government has failed to take effective measures to mitigate this growing problem. This paper addresses the causes, occurrences, and effects of arsenic contamination as well as remediations for both removal and management.

Background

Peter Gleick, of the Pacific Institute for Studies in Development and Environment, estimates than an individual needs fifty liters of sanitary water per day for drinking, cooking, sanitation, and hygiene. This minimum drinking requirement ensures the possibility of adequate health and opportunity (Gleick, 1996). However, 17% of the world's population cannot find sanitary water, two-thirds of which are in Asia. Unsanitary conditions accompany lack of sanitary water. One-million-eight-hundred-thousand people die annually from diarhhoeal diseases, 88% of which are the direct result of unsanitary water (WHO, 2004).

Undersupply of sanitary water will continue to increase in the future as the global population is expected to double. Increased urbanization will place added stress on rare resources while contributing to an increase in sewage and waste. Additionally 45% of the population in Dhaka, Bangladesh live below the poverty line (Khan and Siddique, 2000). Before the 1960s, most water came from surficial sources such as ponds. However, the poor quality of this surface water resulted in diseases such as cholera and typhoid. In the 1980s, the UN International Decade for Water Supply and Sanitation encouraged groundwater exploitation and tubewell installation in the Bengal basin, which houses 80% of the Bangladesh population (Figure 1, Caldwell et al., 2003 and Kinniburgh et al., 2003). Tubewells are simple apparatuses with a handpump sunk into the shallow subsurface for groundwater abstraction (Figure 2 and WaterAid). Some of the wells are installed by the government or NGOs, but the majority (68%) are privately installed (Hossain et al., 2005). While this reduced disease and infant mortality, an even more serious problem arose. The first problems with arsenic poisoning were recognized in 1983, but widespread recognition did not occur until the 1990s. An estimated 35 million people in Bangladesh alone are at risk for arsenic poisoning from levels defined by the World Health Organization as 10 μg/L, a value reduced from the previous guidelines of 50 μg/L. However, most Asian countries still follow the pre-1993 standard of 50 μg/L (Kinniburgh et al., 2003). Reliance on tubewells remains outstanding; ninety-four percent of the rural population relies on tubewells, and fifty percent of Bangladesh has been using these tubewells for 20 years (Caldwell et al., 2003). While arsenic contamination does not affect all tubewells, 59 of the 64 districts have some levels of arsenic contamination. There are over 10 million contaminated tubewells in Bangladesh affecting 90 to 100 million people (Hossain et al., 2005). Such high occurrences of arsenic in most of the country have prompted research into the causes of arsenic-contaminated groundwater.

II. Arsenic Occurrence

Geologic Setting and Landforms

The Bengal delta is unique in that it houses the fourth and fifth largest rivers, 2% of the world's population, imparts the greatest sediment load (1060 tons/year), and is the largest river-delta system in the world (Figure 3 and Mukherjee et al, 2009). Arsenic contamination is a widespread occurrence in Bangladesh, with the highest concentrations of arsenic in southeast Bangladesh in deltaic Holocene sediments rich in organic matter (Figure 1). The contamination is constrained geomorphically by the Bhagirthi River to the west and the Rajmahal Hills to the north (Acharyya and Shah, 2005 and Kinniburgh et al., 2003). Holocene aquifers may have between 40% and 80% of tubewells contaminated in arsenic levels above 10 μg/L (Weinman et al, 2008). In comparison to the Holocene, Pleistocene (1.8 million-Holocene) highlands and the interfluve Ganga Plain have no arsenic contamination problems (Acharrya and Shah, 2005).

Origin of Arsenic

Arsenic is a trace metalloid abundant in the earth's crust. It exists in organic forms, but the majority is in inorganic minerals such as realgar (AsS), orpiment (As_2S_3), niccolite (NiAs), cobalite (CoAsS), and arsenopyrite (FeAs). It may also come from a variety of anthropogenic sources including industrial waste, pesticides, and fossil fuel burning. There are four oxidation states, but the most common forms are arsenic (III)/arsenite, which is the reduced form, and arsenic (V)/arsenate, which is the oxidized form (Wagner et al., 2005, Singh and Pant, 2005, and Mulligan et al., 2005). The preference for either will depend on the Eh and the pH conditions of the subsurface (Driehaus, 2005 and Figure 4). Eh is the redox potential of a reaction and determines the favorable transfer of electrons; in each reaction one product will gain electrons and the other will lose electrons. pH is a measure of the hydrogen ion, which determines the acidity of the environment (Freeze and Cherry, 1979).

Weathering of the Himalayas produces the largest sediment load in the world. The Ganges-Brahmaputra-Meghna River system transports the arsenic-bearing sediment and dumps it in the flat Bengal Delta. Subsequent burial allows the more toxic reduced arsenite to accumulate in the anaerobic subsurface: the greatest concentrations of arsenic result from recent burial, between 10 and 35 meters below surface level (Wagner et al., 2005, Singh and Pant, 2005, and Mulligan et al., 2005).

Mechanism of Arsenic Release

An original hypothesis for the release of arsenic to groundwater in Bangladesh is the oxidation of pyrite. This hypothesis has an anthropogenic explanation: increased pumping for irrigation creates a greater cone of depression, drawing the water table down and consequently introducing oxygen to arsenic-rich pyrite sediments that were originally below the water table (Kinniburgh et al., 2003)

This hypothesis has been largely discounted for several reasons. Not only is pyrite found in amounts too small to account for the arsenic; it cannot account for the distribution of arsenic. The hypothesis would predict low concentrations in an area where the water table is shallow and the unsaturated zone narrow. However, the southeast of the country experiences the greatest concentrations of arsenic yet has a high water table. Similarly, if pyrite oxidation were responsible, the most affected groundwater would be in the shallow subsurface where it has a closer interface with air (Kinniburgh et al, 2003). Furthermore, oxidation of pyrite may even precipitate arsenic. Pyrite weathering by oxidation produces iron oxides, the surfaces of which may adsorb arsenic (Wagner et al., 2005).

Arsenic is generally insoluble in groundwater under oxidizing conditions. However, in the subsurface, where there is less exchange with atmospheric oxygen, a reducing environment develops. The reducing conditions release the arsenic-rich grains into solution with the groundwater (Singh and Pant, 2005, Mulligan et al., 2005). This widely accepted mechanism for arsenic release is termed the reductive dissolution of iron oxyhydroxides or hydroxides, represented by the equation:

$$CH_2O + 4Fe(OH)_3(s) + 8H^+ \rightarrow CO_2 + 4Fe^{2+} + 11H_2O$$

where CH_2O can be any organic material and the arsenic is adsorbed to the surface of iron hydroxide grains ($FE(OH)_3$). The iron hydroxide serves as an electron acceptor as microbes metabolize organic matter. The acceptance of electrons converts iron from its +3 state as an iron hydroxide to its reduced form as ferrous iron. The arsenic and iron hydroxides are therefore released from a colloidal state on a sediment grain to an aqueous state in solution with groundwater. This reaction also converts the organic carbon to inorganic carbon, and increases the pH (Sracek et al, 2005). The rate of the reaction is helpful in determining the source of arsenic. The reductive dissolution reaction occurs over thousands of years, relatively quickly in geological time (Kinniburgh et al, 2003). Therefore, it is plausible that relatively recent erosion products of the Himalayas may be reduced in present conditions.

Due to arsenic's association with the redox reaction of iron-oxyhydroxides, compounds related to the reaction can be used as a proxy for arsenic's presence (Nickson et al, 2000). Bicarbonate (HCO_3^-) is a product of iron-oxyhydroxide reduction and correlates well with arsenic:

$$4FeOOH + CH_2O + 7H_2CO_3 \rightarrow 4Fe^{2+} + 8HCO_3^- + 6H_20.$$

Bicarbonate in the subsurface derives from both carbonate dissolution and organic matter disaggregation. To distinguish between the two sources, a ratio of HCO_3^-:(Ca+Mg) is used. Calcium and Magnesium are associated with carbonate dissolution, so a ratio greater than 1 indicates the contribution of organic matter reduction (Wagner et al, 2005).

Ferrous iron is a more controversial proxy due to its involvement in other reactions, which may give a weak correlation with arsenic (Nickson et al., 2000). Other experiments indicate a good correlation of iron oxide and manganese oxides with arsenic (Sikder et al., 2005). Nitrate may also be used as a proxy for arsenic. Since microbes prefer to use nitrate or oxygen as oxygenation sources, there is no need for the microbes to reduce iron-oxyhydroxide if nitrates are present in groundwater (Nickson et al., 2000).

The reductive dissolution mechanism implies predictable settings for high arsenic concentrations. The amount of iron hydroxides is related to sediment grain size. Grain size is related to past river processes, which leave remnant landforms of predictable grain size. The grain size of the specific sediments and local topography are additional factors lending to the predictability of arsenic contamination.

Relating the mechanism of release to the type of sediment deposited

The mechanism of arsenic release explained above occurs on the surface of a detrital grain, a grain transported from the surrounding mountains. Increasing surface area leads to incorporation of more iron oxyhydroxide. Therefore, a smaller grain size will adsorb more iron oxyhydroxide. A mass of clay (<0.002 mm) will therefore have a greater potential for high arsenic concentrations than a mass of sand (2 mm-0.06 mm) (Nickson et al., 2000).

Another factor, especially prevalent in Bangladesh, that affects arsenic contamination is the hydraulic gradient of groundwater flow, which determines the rate and direction of flow and is partially a function of the surface slope. On a local scale, the profile of the water table closely follows the changes in elevation (Freeze and Cherry, 1979). Therefore, the groundwater in the steeper highlands moves with the help of gravity, whereas the Bengal delta is relatively flat (Figure 5). The hydraulic gradient is important because it determines the recharge rate and amount of flushing. Low hydraulic gradients mean that the groundwater moves very slowly and therefore has time to accumulate arsenic. High concentrations of fine sediment also contribute to long residence times since finer sediment provides less pore space for water transport. Estimations show that the shallow aquifers have very long residence times, and the groundwater may have never been flushed. A low hydraulic gradient also indicates that precipitation will reach the aquifer more slowly. There will then be less water that is oxygenated from its recent contact with the atmosphere and will contribute to reducing conditions favorable to the reductive dissolution of iron oxyhydroxide (Mukherjee et al., 2009).

Heterogeneity

Grain size is a function of energy of the transporting agent. For example, high energy rivers can transport much larger sediments than a slow-moving stream. The Bengal delta has been mainly influenced by changes in fluvial patterns in response to tectonics and sea level changes. These changes alter the underlying spatial arrangement of sedimentary layers and subsequently the deposition of finer material versus coarse material. Aquifers beneath or next to fine-grained sediment deposit tend to have higher concentrations of arsenic, whereas those beneath sand-sized sediments tend to have lower values of arsenic (Figure 6 and Weinman et al, 2008). Predicting arsenic contamination is difficult due to the extreme spatial heterogeneity with which it is found. A well 50 meters from a safe well may contain over 50 ug/L As. In order to predict patterns of arsenic concentration, it is necessary to understand the past land-forming processes and the grain sizes associated with the paleolandforms. An understanding of paleolandforms predicts grain size distribution, which may guide tubewell installers to less contaminated sites.

Himalayan building and sea level drop caused the basin switch from a marine-dominated sedimentation pattern to a fluvial pattern around 40 million years ago (Ma). This changes the sedimentary layers from fine-grained clay sediments to detrital grains. By the Pliocene (5.3-1.8 ybp), there was a significant sea level lowstand, exposing more of the basin and finalizing the transition to a terrestrial environment. This created the basin shape that serves as a dump for sediments eroding from the Himalayas and surrounding hills and shaped the depositional environment for the sediments from the Pleistocene and Holocene, into which modern contaminated tubewells draw (Mukherjee et al, 2009).

The Pleistocene highlands are composed of terraces, or former floodplains, that were created as the Ganges-Brahmaputra-Meghna (GBM) river system changed its course. They contain fewer organics and have a higher hydraulic gradient, making them less susceptible to arsenic contamination. The Holocene sediments make up the majority of the Bengal basin. They consist of the more northern features of alluvial fans in front of the Himalayas, the Tippera surface and the Sylhet basin, but the majority is the GBM flood and delta plain in the southeast portion, which is comprised of the youngest sediments and has the greatest majority of arsenic contamination (Mukherjee et al., 2009).

The same mechanics that created the paleolandforms responsible for variable sedimentation patterns are at work today. The three rivers that influence sedimentation in the delta are the Ganges, Meghna and Brahmaputra. The Ganges is predominantly meandering and for the past 250 years has been incising to the east. Contrastingly, the Brahmaputra is predominantly a braided river, which is associated with channel bars and islands. The Meghna feeds into the Brahmaputra after incorporating sediment from the Tripura hills and Sylhet basin to the north. The modern movement and energy of these rivers will be important in the future as they leave behind abandoned channels, bars, and floodplains (Mukherjee et al, 2009).

The distribution of muds and sands is explained by the path of former braided and meandering river systems. Settlement and tubewell distribution is concentrated in more highly elevated landforms in order to avoid flooding. Landforms associated with river systems include channel bars, levees, floodplains, and scroll bars. Floodplains are associated with finer sediments and therefore greater concentrations of arsenic. Channel bars of high elevation form during the monsoon flood stages when waters spill over the banks. These higher energy waters transport the coarser sands, and are thus associated with lower concentrations of arsenic. The association of arsenic with levees is less straightforward. Levees forming from meandering channels of weaker flow strength are more likely to be contaminated when compared with the levees resulting from the more energetic braided channels. Scroll bars, the remnants of active point bars, can also have varying amounts of contamination, especially since many of them are filled artificially with mud to raise their elevation above monsoonal flood levels (Figure 6 and Weinman et al, 2008).

The past river processes, affected by sea level changes and Himalayan activity, have shaped the underlying landscape. Rivers are associated with various landforms, each with a different susceptibility to arsenic concentrations. The proximity of these fluvial landforms explain the heterogeneity of arsenic occurrence, but the landforms have predictable grain sizes, and with subsurface imaging or sampling, tubewell installers can locate coarser aquifers with less contamination.

Anthropogenic contribution to arsenic contamination

Anthropogenic interference has emplaced mud caps in order to raise villages to prevent flooding. However, this increases the percentage of mud-sized particles and subsequently the occurrence of arsenic. Weinman plots arsenic concentration versus distance to sand and confirms the correlation of arsenic concentration to the thickness of the mud layer and proximity to sand units (Weinman et al., 2008).

Another anthropogenic activity contributing to arsenic contamination is groundwater used for irrigation. Irrigation water builds up the concentration in the soil, leading to an excess of arsenic past the 0.22 mg/kg dry weight maximum allowable daily limit for plants (Panaullah et al., 2008 and Huq and Naidu, 2005). Most of the arsenic is concentrated in the top 15 cm of the soil horizons where root activity predominates. Therefore, contaminated irrigation water cannot only transmit arsenic to the rice crop but can also decrease rice yield as 78-88% of the water is retained (Khan et al., 2009). Arsenic is also found in Kalmi, Amaranthus, and Arum vegetable crops in addition to rice and wheat crops (Huq and Naidu, 2005).

The WHO standard for a 130 pound person is 0.126 mg/day of inorganic As, but Bangladesh has no standard for arsenic levels in food. Arsenic ingestion through plants is less harmful than direct ingestion through drinking water, but with 0.08-0.17 mg/day through rice intake and 0.20 mg/day through water, the daily intake of arsenic of a Bangladeshi is double or triple the WHO standard. Furthermore, many Bangladeshis in rural areas are agrarian workers and consumer greater volumes of water, which if contaminated, adds additional arsenic daily intake. These estimates do not account for potential contamination of daily products from cattle that feed from rice straw, rice cooked in contaminated water, and rice straw and cattle manure used for fuel (Rahman et al., 2008 and Khan et al., 2009).

Research concerning the heterogeneity of arsenic in irrigation water is still in its infancy, but with 38% of Bangladesh employing irrigation and 1360 tons of arsenic from groundwater introduced to paddy fields, it is essential to understand the controls and effects of contaminated irrigation water (Roberts et. al., 2007). Some research shows greater concentration of crops watered by irrigation water as opposed to those watered naturally. During the monsoon season, groundwater irrigation is unnecessary, and the T. *Aman* rice crops are planted. However, *boro* rice crops, grown in the winter dry season to provide 55% of Bangladesh rice supply, rely on 18-21 irrigations per season. Fifty-four percent of irrigated groundwater derives from the more contaminated shallow tubewells at 30-60 m depth (Roberts et al., 2007 and Rahmen et. al., 2008). The reduced, more toxic speciation of arsenic predominates over the oxygenated arsenic, even at the surface. Flooding the fields, from monsoons or irrigation, prevents oxygen recharge from the atmosphere, and coupled with abundant microbial activity, creates a reduced environment. Reduction in the top soil layers causes iron oxide dissolution and releases the adsorbed arsenic. The presence of phosphates and certain organic matter may contribute to arsenic release as they compete for sorption sites (Khan et al., 2009). Phosphate, a common ingredient in fertilizers, may replace up to 77% of the adsorbed arsenic, releasing it into the groundwater. Other factors affecting the plant uptake of arsenic include the pH, the particular plant species, and clay content (Ghosh et al., 2008 and Rahmen et al., 2008).

Arsenic ingestion may be exacerbated by the low selenium intake of the Bangladesh population. Dietary selenium is ingested from plants grown in selenium-rich soils, and it naturally counteracts high arsenic intake through several mechanisms that expel or sequester arsenic. Lab analyses have reported selenium content less than 0.019 µg/g soil and arsenic content up to 32.8 µg/g soil. The standard for selenium-poor soils is less than 0.05 µg/g soil. Bangladeshi soils fall within an acceptable range for selenium; the deficiency results from the 88% of soil selenium that is insoluble and therefore unusable by plants. Since Bangladeshis obtain 80% of daily caloric intake from rice grown on local soils, the 26 µg daily intake of selenium falls far below the World Health Organization's recommended 40 µg per day value. Similarly, livestock fed from local plants produce meat and dairy that are selenium deficient. Implementing more fish into the rural population's diet may increase the natural intake of selenium, though there is currently very little supply in the rural area. Another possibility is selenium supplements, and a trial in Chandpur, Bangladesh is currently researching the effects of 200 µg supplements (Spallholz et al., 2008).

Improvements that only treat drinking water will not address the threat of arsenic contamination through irrigation; groundwater accounts for nearly 60% of the water used for irrigation. Plant contamination from irrigated groundwater contributes to the risk of arsenicosis but is largely unavoidable. Locally grown foods are a staple in Bangladesh diets, and demand for rice and produce will only increase in the future. With global population rising, the production of rice will need to increase 4 to 4.5% annually (Panaullah et al., 2008).

III. Arsenicosis

The Bangladeshi government has set lower standards of arsenic content in tubewells than those of the World Health Organization under the pretense of having an attainable goal rather than one of which the government is incapable of pursuing. However, increased levels of arsenic above the natural concentration of 1-10 µg/L for periods longer than six months may lead to arsenicosis, classified as a chronic multisystem disorder, which has a range of ailments from skin diseases to cancer (Figure 7 and Ghosh et al, 2008). Between India and Bangladesh, an estimated 60 to 100 million people are drinking contaminated water (Ng et al., 2003). A study of an area with 87% of tubewells with levels above 0.05 mg/L As documents 10% of the population as arsenicosis patients (Caldwell et al., 2003). While arsenicosis manifests globally, the majority of cases occur in Asia, especially in Bangladesh, where a quarter of the population is at risk (Ghosh et al., 2008).

Arsenicosis is associated with a progression of diseases ranging from skin lesions, internal organ damage, and even cancers of the skin, lung, bladder, liver and kidney. Risks of cancer in patients who consume arsenic levels above 50ug/L can reach up to 1 in 100 (Ng, 2003). Diagnosis of arsenicosis relies mainly on visible skin lesions including keratosis, melanosis, and cutaneous cancers (Figure 7). Some of the first signs of arsenicosis include keratosis—or thickening of the skin—on the soles and melanosis, an abnormal pigmentation. Malignant stages of arsenicosis cause the keratotic cuts to bleed or crack. The disease may manifest itself noncutaneously in respiratory ailments, neuropathy, vascular disease, cirrhosis, and edema. In the absence of skin lesions, these conditions, while not exclusive to arsenicosis, may be crucial diagnostic indicators. Where skin lesions are absent or unrelated to arsenicosis, measurements of urine, nails, and hair must be done in labs (Ghosh et al., 2008). Arsenic is detected through levels of urinary arsenic, a good indicator because as arsenic is ingested, it is converted to acids less readily incorporated into tissue and therefore more readily excreted. Hair and nails, the body's slower excretionary mechanisms, show arsenic concentrations within nine months of the test. WHO has created an algorithmic method, which allows a diagnosis with limited resources (Ghosh et al., 2008).

The diseases manifest differently in different ages, socioeconomic classes, and genders. The majority of arsenicosis patients are middle-aged, but this could be due to the long exposure time (generally 10 years) necessary for the disease to manifest. Thirty-five-million children may potentially develop arsenicosis, resulting in slower cognitive development and difficulty in school (Ghosh et al., 2008 and Nezam, 2009). Some studies have found that men have a higher risk factor for skin cancer than females at 3.0/1000 and 2.1/1000 respectively. Socioeconomic status may also exacerbate the effects of arsenic poisoning, especially in regards to a base level of health. The poor are less likely to have sufficient nutritional intake, as rice is their main sustenance. They are therefore deficient in protein, and as aforementioned, selenium due to low fish consumption (Ghosh et al., 2008).

Arsenicosis both exacerbates and is exacerbated by poverty. Arsenicosis patients with skin lesions are not only stigmatized, but their capability to work and earn a living is severely compromised. The poor are also more likely to suffer arsenicosis symptoms due to preexisting malnutrition. Chakraborti predicts that 80% of West Bengal and Bengladesh arsenicosis patients could have avoided poisoning if they had had better education and nutrition (Chakroborti et al., 2002).

Remediation for Arsenicosis

With over 38,380 cases of arsenicosis, it is surprising that there has been a generally apathetic and resigned disposition of national and local government officials (Atkins et. al., 2007). Among the general population, only 13% are aware of the extent of the consequences of arsenic poisoning (Caldwell et. al., 2006). They view it as one of the many environmental day-to-day problems and therefore continue to utilize red-labeled tubewells, which indicate contamination. The slow manifestations of arsenicosis also lure some into a false sense of security. The tubewells are an ideal social solution to domestic water supply. They allow women, the main family members responsible for gathering water, the privacy of personal wells and avoid the negative consequences of microbially contaminated surface water (Atkins et. al., 2007).

In addition to efforts to providing uncontaminated water, awareness and education dissemination are essential, especially considering the high levels of illiteracy and conservative treatment of women. Education about the disease is also especially critical in order to avoid myth that arsenicosis is contagious, which has caused social stigma and ostracism for those affected (Atkins et al., 2007). Many uneducated villagers believe arsenicosis is a curse from God or are completely ignorant of its causes (Chakraborti et al., 2002). The main sources of information on arsenicosis are the media, while the least cited sources are doctors and government officials. Public health educators must increase their role and address aspects of the disease, including causes and symptoms, as well as alternative options for water treatment and testing (Ghosh et al., 2008). Every discussion must provide education on preventative measure of arsenic-rich water consumption since there is no known cure for arsenicosis. There are ointments to ease skin lesions and thickening, but more evaluations are necessary to determine the maximum efficient dose of the salyicylic acid and urea-based ointments. The more developed lesions must be removed surgically, which is often not economically feasible. There are also medicines to alleviate symptoms associated with arsenicosis including indigestion relievers, antidepressants for neuropathy, and future research in chelating agents to reduce cancer risks (Das et al., 2008).

IV. Arsenic Removal and Remediation

Adsorption Methods

Ideal removal systems are low-cost, environmentally friendly, and produce minimal waste product. Removal agents mimic the natural process responsible for arsenic adsorption on sediment grains. Reducing conditions release the arsenic from sediment grains into groundwater, so remedies involve reprecipitating arsenic out of water, usually under oxidizing conditions. Techniques for arsenic removal involve adsorption and include coagulation/filtration, iron and manganese removal, iron oxide based adsorbents (ferric hydroxides), or ion exchange (Driehaus and Figure 3). Considerations when selecting removal techniques include charge and competitive ions. Charge is essential in removal techniques as neutral molecules cannot be effectively removed. Determining phosphate occurrence is also important because it has similar reaction characteristics to arsenic and thus serves as a competitor for adsorption with As (V) (Driehaus, 2005).

Adsorption processes involve chemical or electrostatic forces binding colloidal particles on grain surfaces of solids, namely metal oxides or hydroxides (Driehaus, 2005). Colloidal particles are the result of weathering, and their size (10-3-10-6 mm) makes surface-surface processes the predominant interaction (Freeze and Cherry, 1979). Since the Himalayas are actively building, erosion increases and produces clay-sized weathering product. Arsenic has a strong affinity for metal oxides and hydroxides, and thus most removal techniques involve arsenic adsorption to a charged metal oxide surface reaction:

1. $MOH^{2+} \rightarrow MOH + H^+$
2. $MOH \rightarrow MO^- H^+$
3. $MOH + AsO_2(OH)_2^- + H^+ \rightarrow MOAsO(OH)_2 + H_2O$

where M represents a metal such as iron or aluminum, and arsenic is in the As(V) form in the reactants and As(III) in the products. This process depends on pH of the isoelectric point, the point at which the surface of the oxide is neutral. If the pH is above this point, the surface is negative, and if it is below, the surface is positive and will strongly adsorb As (V). Therefore, adsorption processes are more efficient at low pH, or acidic conditions (Driehaus, 2005).

Most of the subsurface where arsenic occurs is under reduced conditions and therefore As (III) is the predominant form. However, most removal techniques more efficiently remove As (V), so it is therefore necessary to oxidize the arsenic (III) in order to remove it. The dissolved oxygen present in groundwater is not sufficiently fast enough to oxidize, and therefore oxidants must be applied including chlorine (the most common), ozone, permanganate, hydrogen peroxide, and manganese oxide (Singh and Pant, 2005). Permanganate and chlorine are exceptionally efficient as it takes less than a minute to oxidize arsenite (Mulligan, 2005). The dose of oxidizer is partly determined by the presence of other reduced substances with the arsenic, including organic matter, iron (II) and manganese (II).

One adsorption agent used for over 20 years is activated alumina (AA), which can remove both organic and inorganic contaminants. The process involves filtering the contaminated water over grains to which the arsenic adsorbs, creating the waste product of arsenic-loaded adsorbent. It is an especially good absorbent since it has a large surface area, but it works best with arsenate ions (Singh and Pant, 2005). Factors such as the initial pH, the time the water is in contact with the adsorbent grains, the adsorbent concentration, column height, and flow rate determine its efficiency. The process requires a pH near 6 which is buffered by mineral acids or CO_2 (Driehaus, 2005 and Singh and Pant, 2005). However, arsenate and arsenite differ in optimum pH because the pH determines the distribution of their concentrations. Arsenate adsorbs at an optimal pH of 5.8 and arsenite at 7.6 (with concentrations of 0.5 mg/L). This is based from the isoelectric point of activated aluminum. Before this point, AA exists as a positively charged surface, which reacts well with the arsenate and arsenite anions (Singh and Pant, 2005 and Figure 4). Disadvantages include the need for frequent regeneration, decreased capability after five renewals, and high volumes of waste streams (Singh and Pant, 2005 and Driehaus, 2005).

Another sorbent is Bauxsol™, a "seawater-neutralized bauxite refinery residue." The sorbent is a red mud that results from industrial residue. The Bayer process removes alumina from bauxite ores, leaving a residual red mud. The mud is then treated with seawater to neutralize its exceptionally high pH. Its high content of iron and aluminum hydroxides/oxides give it a large affinity to adsorb arsenic. Surface area can be increased with acid and heat treatment to enhance the adsorption capacity. All the raw materials for this process are inexpensive and readily available; three million tons of the mud are manufactured in Asia alone. It is therefore a viable option for arsenic removal when compared to activated aluminum, which is a more expensive treatment. Furthermore, high amounts of red mud are corrosive environmental hazards due to high concentrations of NaOH, a strong base. The waste mud is dumped into dams, the sea, or ponds, and due to its weak cohesiveness, may easily breach when used as a dam. Using Bauxsol is therefore beneficial to the environment by reducing the amount of waste from industrial processes. Although using a waste product as a removal system is economically efficient, the culture of Bangladesh may prevent the use of a waste product in water treatment (Genç-Fuhrman et al., 2005).

Sorghum Biomass, both free and immobilized, is a natural biological result of industrial or agricultural waste that is inherently capable of adsorbing metal ions. The sorghum biomass from crop waste is prepared as an arsenic adsorbent by drying, mixing, sieving and washing with HCl. The samples are treated directly from the well through the biomass column without exposure to the atmosphere. The optimal binding of arsenic to the biomass surface is at a pH near 5. An experiment run for 60 minutes at a pH of 4.5 found that the free biomass has a max adsorption of 8.43 mg/g and 6.99 mg/g with immobilized biomass. Desorption, the reverse process of adsorption, recovers the arsenic and is accomplished with the addition of HCl and successfully recovers 91% of arsenic adsorbed to the free biomass and 95% of arsenic adsorbed to immobilized biomass. Sorghum biomass is a viable option for arsenic removal because it is a natural waste product, not an environmental hazard and is low cost: $0.011/L for immobilized biomass and $0.002/L for free biomass (Gonzàlez-Acevedo et al., 2005 and Haque et al., 2005).

The coagulation/filtration technique simulates oxidized subsurface conditions. It creates the reverse conditions of those that release arsenic by precipitating the arsenic-rich iron hydroxides. The amount of coagulant is determined as a ratio to arsenic concentration based on the pH. A pH between 6 and 7 requires a ratio of 10:1 (salt:arsenic), and pH above 8 requires a 40-50:1 ratio. The arsenic-loaded hydroxide is then removed by filtration. It requires several backwashing steps, which adds a large water content to the waste sludge. The waste product is then specially treated before removal. A variation of this process is co-removal of arsenic with iron and manganese removal. The iron in the water is oxidized, precipitated, sorbs arsenic, and then filtered. This process also requires an iron: arsenic ratio of 50:1 (Driehaus, 2005).

The ion exchange method is less used because it works only in households (Driehaus, 2005). The ion exchange method passes the water through an oxidation filter and an ion-exchange filter, which removes all anions. This filter contains Purolite A-300, an anion exchange resin and works best with acidic samples. The oxidation step is therefore necessary because the method will not work with arsenite, which is most commonly in an uncharged form, H_3AsO_3. Due to competition for binding sites, sulfate in the water should be in concentrations less than 50 mg/L and total dissolved solids should not exceed 500 mg/L. Studies modeled after Bangladesh groundwater concentration (500-1600 ppb) determined that pH is the main controlling factor determining performance and is related to the ion exchange performance via the equation:

$$\text{Capacity} = 0.107834 - 0.000026C_{as} - 0.01285pH + 0.00265v + 0.0000057C_{as}pH - 0.0000053C_{as}v,$$

where v represents velocity and C_{as} represents arsenate concentration before filtration. This process is used mainly in smaller communities because it is simple to manage. However, the best disposal methods of waste products is not fully established (Mulligan et al., 2005).

The World Bank and UK Department for International Development have tested several filters that have shown 99-100% effectiveness in arsenic removal. The simplest and cheapest filter is the Sono 3-kalshi, which costs $5.00 per filter (Ghosh et. al., 2008). The filter consists of three layers; the first layer consists of coarse sand and iron filings layer, the second a finer sand and wood charcoal, and the third is the collection bucket. Ten Liters are filtered before pure water is obtained. The government has approved its use and it has been implemented in 11 districts with distributed 12,500 free filters. Besides being low-cost, the filter is environmentally safe and produces no chemical waste (Nezam, 2007).

Most of these treatments are low-cost and successfully remove arsenic. They do, however, require certain conditions, such as pH or waste removal, to be effective. Their implementation will require training from experts on use and management. With such a significant rural population, implementation will be slow and incomprehensive. The Sono filters are the easiest to use and may be a viable treatment in rural areas.

Relocation Remedies

The development of deep tubewells has been suggested as a possible alternative to the more contaminated shallow tubewells since groundwater below 800 feet is generally uncontaminated (Ghosh et. al., 2008). However, these wells must also be frequently monitored since arsenic may leak from upper layers. The effectiveness of this approach will vary between villages due to the heterogeneity of arsenic occurrence (van Geen, 2005). Deep wells may nevertheless serve as a temporary, emergency measure in especially high-contamination areas (Ghosh et. al., 2008).

Well-switching is a non-technological remediation to contaminated wells. In Araihazar, Bangladesh half of its residents had wells with high arsenic concentrations, but 95% lived within 200 m of safe wells. There are, however, socioeconomic factors that complicate this solution. The *purdah* society dictates that women may not leave their homes unaccompanied, and many wells are within private areas of a family's *baris*, located near their latrine. Despite these obstacles, well-switching is preferred to other options, such as treating or deepening a well or reverting back to surface water. Due to the high variability of arsenic concentrations, these wells identified as safe would need to be frequently tested. The small companies that install them should be equipped with field test kits to monitor any installed wells or repositioned wells (van Geen, 2002).

V. Institutional Roles in Remediation

Government Officials and Agencies

Now that tubewells are no longer considered safe sources of drinking water, measures must be taken to reverse the dependency on a technology that involves cultural aspects. Mitigation strategies require a four-fold involvement: the local and national governments, national agencies, international agencies, and local communities. The young parliamentary

Bangladesh government, however, is divided and inefficient. Since its inception in 1991, there has been hostility and lack of compromise between the two main parties: Bangladesh Nationalist Party and Awami Leage. Nevertheless, the general population remains enthused about government action, demonstrated by the 75% voter turnout. The few power-seeking corrupt officials, however, drown the majority's desire for change. Disagreement manifests in violence and hostility rather than discussion or debate. Once a party loses power, it loses its agenda, preventing any continual policy building. Opposition to policy arises from anyone who may lose power, illustrative of Bangladesh's rank as one of the most corrupt countries (Atkins et al., 2007).

Such lack of organization and accountability explains the unaccounted for management failure and a decrease in government funding. By 1990 the investment of government's development budget in water and sanitation amounted to only 1.25% (Khan and Siddique, 2000).

On top of low funding, there is general mismanagement among government sectors, especially in urban areas. The main government ministry responsible for water resource management is the Ministry of Local Government but includes involvement from the Ministries of Health and Family Welfare, Water Resources, Agriculture and Science and Technology. Administrative failures in these sectors include unaccounted for water, inability to mobilize resources, poor management and planning, and pricing and tariff policy. The water provided to urban areas is predominantly from tubewells with inadequate treatment. The amount of water provided by the Dhaka Water Supply and Sewerage Authorities (DWASA) is insufficient, leaving 40% of the city population to find their own sources of water, which usually end up as polluted surface water. The amount left unbilled is concerning, especially considering the lack of government funds already invested. Fifty-six percent of water bills were lost in a variety of technical failures, including tampered meters, lack of customer data, and false information from inspectors. Part of this is illegal connections and clientelism, but part of the mismanagement is due to an undertrained and understaffed department unable to create and meet their management goals. Management efforts are frustrated by government oversight preventing any expedient decisions and implementations (Ahmed, 2005 and Khan and Siddique, 2000).

Active remediation measures have therefore been slow. Soon after the WHO announced the arsenic crisis a major emergency, the World Bank dumped $44.4 million to create the Bangladesh Arsenic Mitigation Water Supply Project (BAMWSP) in 1997 to perform nationwide tubewell tests. Four years after its inception, only $2 million had been used for tests in only 30 of 599 thanas. The World Bank replaced this project with the Bangladesh Water Supply Programme Project in 2005 and invested $40 million more with the goal of delivering piped water to villages. The piped water would be released from either household taps, individual standpipes or shared standpipes. The population prefers the convenient treated piped water or deep wells over other remediation methods such as home treatment systems (Atkins et al., 2007).

Nongovernment Organizations

Hoping to evade the government's inefficiency, donors have turned to NGOs to pioneer development efforts. The 257 active NGOs, however, can only serve half the rural villages and suffer from similar corruption as the government with increasing competition and lack of accountability (Figure 8). Their responsibility is two-fold: to disseminate funding and implement government policy. They also lead innovation experiments for new remediation methods, such as harvesting rainwater. NGOs working alongside government agencies such as the Department of Public Health Engineering include UNICEF, Bangladesh Rural Advancement

Committee (BRAC), World Vision, Dhaka Community Hospital, and the Danish International Development Agency (DANIDA) (Atkins et al., 2007).

Community

Any effective mitigation strategy will necessarily involve the local community. Part of the Bangladesh Water Supply Programme Project delineates a Community Action Plan requiring a 10% financial contribution for piped water systems. The project also requires a 30% membership in efforts to engage community members in mitigation efforts. They also hope to engage well owners in tubewell testing in order to directly disseminate information. With 59% of men and 69% of women illiterate, such participatory programs will require active efforts of NGOs and agency employees. There is a direct correlation between the rural population's understanding of arsenic contamination and their readiness to contribute payment for piped water systems; families report willing to pay up to 0.2% of their income (Atkins et al., 2007).

Collaborative Efforts

The international community has a stake in the Bangladesh water crisis. Unsanitary water is not unique to Bangladesh; 1100 million people worldwide are without a clean water source (Pogge, 2008). Sanitary water is the foundation for a functioning community, giving citizens the capability and health to work. Successful development of a nationwide water system will set a precedent for both developing and developed countries by addressing a multifaceted problem with an interdisciplinary approach. Industrial and agricultural growth coupled with an increasing human population will both increase the demand for clean water and the potential for contamination. The need, however, is urgent, and development of a proactive plan cannot wait. In addition to arsenicosis patients, diarrhoeal disease is still a main concern in Bangladesh, accounting for 10% of child mortalities. The International Centre for Diarrhoeal Diseases and

Research hospital in Bangladesh is overwhelmed by an increase in diarrhoeal patients. They blame rising temperatures and a severe lack of safe drinking water as the culprits of the increased caseload (IRIN, 2009).

The international and private sectors can bring both technological advances as well as training and strategy in management. Thomas Pogge argues for a restructuring of the current pharmaceutical industry to incentivize research of diseases particular to the third world (Pogge, 2008). In the Bangladeshi case, however, more research is needed for affordable water treatment systems. While the problem of arsenic contamination is not unique to Bangladesh, the country will require an implementation strategy specific to its resources and needs. Most citizens prefer a piped water system delivering sanitary water to their homes. This would require a sanitation facility that treats both surface and groundwater and pumps it to individual homes. The rural community, however, may still depend on tubewells since piped water systems may be less feasible. Dissemination of treatments such as the Sono 3-kalshi filter and adsorption filters may be better options for rural villages. Any remedy will require effective collaboration between government agencies and nonprofits both to engineer piped water systems and disseminate filters. Outside experience in management and training will counter government inefficiency and help implement specific strategies (Khan and Siddique, 2000).

Pogge involves the international community with seemingly domestic problems by its association with the global trade and injustice. While the causes of arsenic contamination cannot be attributed to the international world, the failure of expedient research and remediation may reflect forces outside of Bangladesh. Currently, any political figure in power can trade or loan in his nation's name, regardless of his relationship with the country's citizens (Pogge, 2008). Bangladesh's proven corruption and failure to respond to the arsenic crisis may reflect an international lack of accountability towards its leaders, exemplified by the slow expenditure of the $44.4 million World Bank dollars. Small success in accountability measures has surprisingly come from within the Bangladesh population. The Bangladesh Environmental Lawyers' Association exposed the British Geological Survey, a part of the Natural Environment Research Council with failing to test for arsenic in their 1992 surveys. Activism and accountability from within the community align with the Bangladesh Water Supply Programme Project's efforts to involve citizen's directly affected by arsenic contamination. The particular case against the BGS may however, deter international agencies from performing tests (Atkins et al., 2007). Nevertheless, this case exemplifies the necessity of non-government operators when the government fails to hold itself accountable:

> In the absence of governmental capacity and collective political will, the duty of holding to account cross-boundary polluters and others causing environmental damage falls to a kaleidoscope of voluntary and professional activists, operating without coordination and frequently conflicting in their goals (Atkins et al., 2007).

VI. Conclusions

The groundwater contamination in Bangladesh has been considered a mass poisoning or a "slow tsunami" (Nezam, 2007). The explosion of chronic arsenic-related diseases has forced reconsideration of the haphazard installment of millions of tubewells throughout the country. Reliance on tubewells seemed like an ideal solution to societal and health problems, but high concentrations of arsenic in groundwater have shattered this panacea. The slow response of the government has fostered continual use of poisoned water sources and contributed to the slow poisoning of its citizens from chronic arsenicosis.

The natural causes and occurrences of arsenic in groundwater are of hydrogeological origin, resulting from a combination of past geologic history, subsurface redox conditions, and the delta's position as a broad flat dump for Himalayan sediments. The problem has been exacerbated by agricultural practices, malnutrition, lack of education, and capability deficits in government. Remediation efforts must now involve national and local government, international, and private sector efforts to implement affordable, proven treatments to purify groundwater and treat arsenicosis patients. The involvement of the international community is not only necessary from Bangladeshi's perspective but is crucial for the global population as sanitary water supply is essential for life.

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Figures

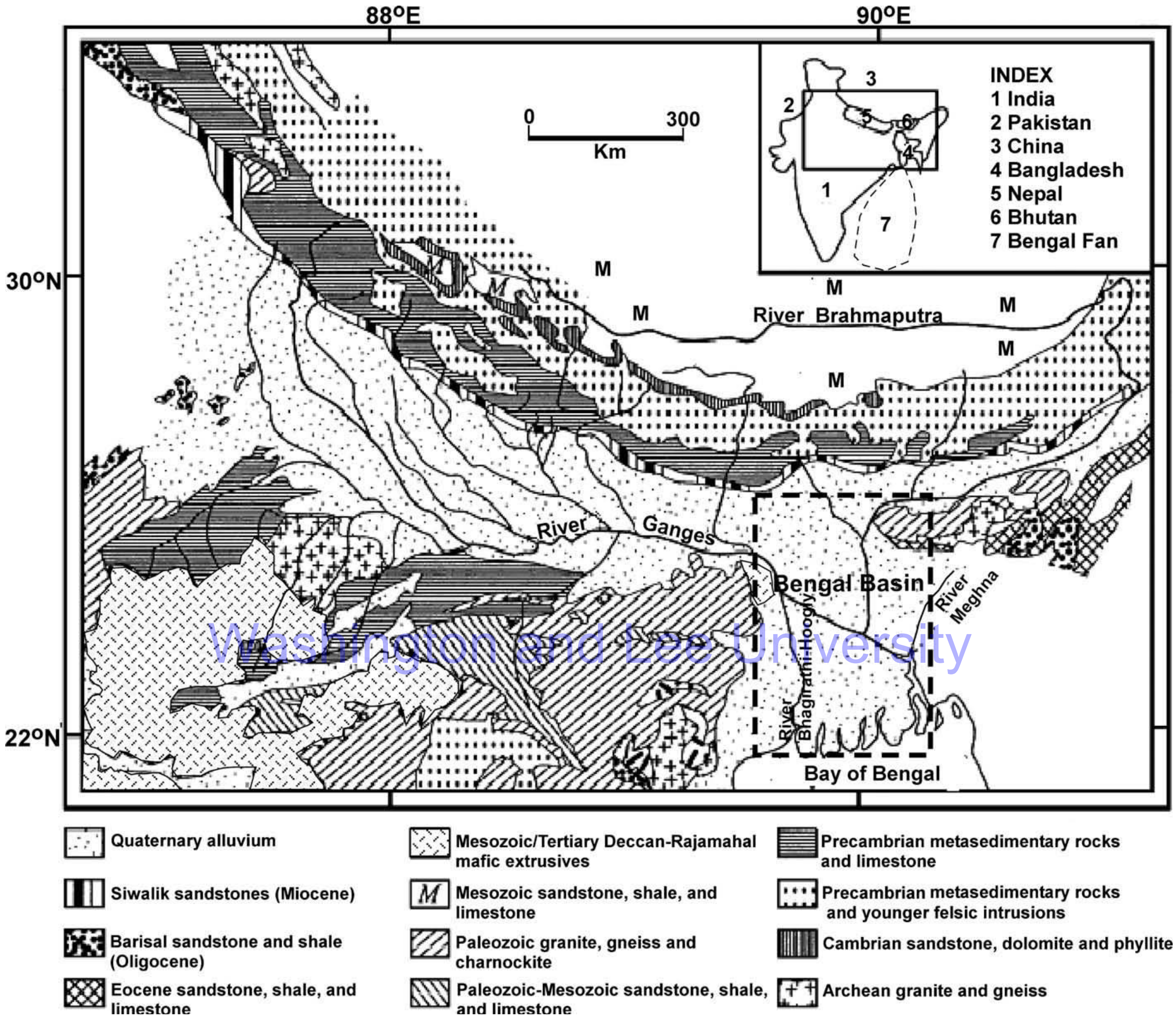
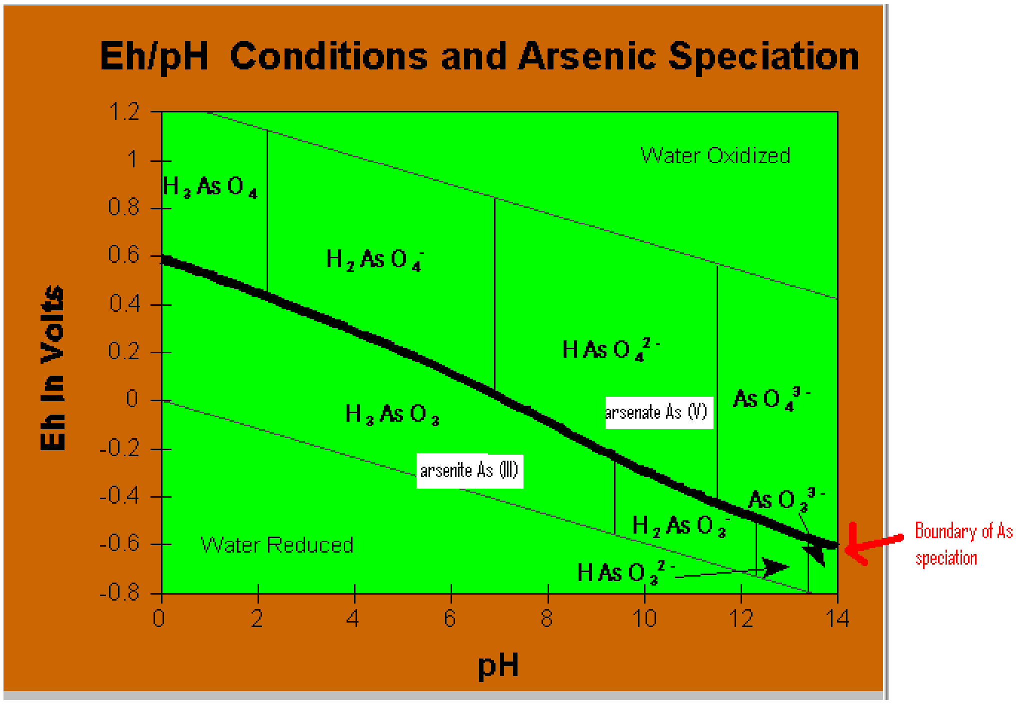


Figure 1: Indian subcontinent map. The Bengal Basin is outlined and is composed of Holocene alluvium sediments (Mukherjee et al., 2009).

Figure 2: handpump used in rural villages (WaterAid)

Figure 3: GBM river system and Bengal Delta create the largest river-delta system in the world (Figure taken from travelblog.org).



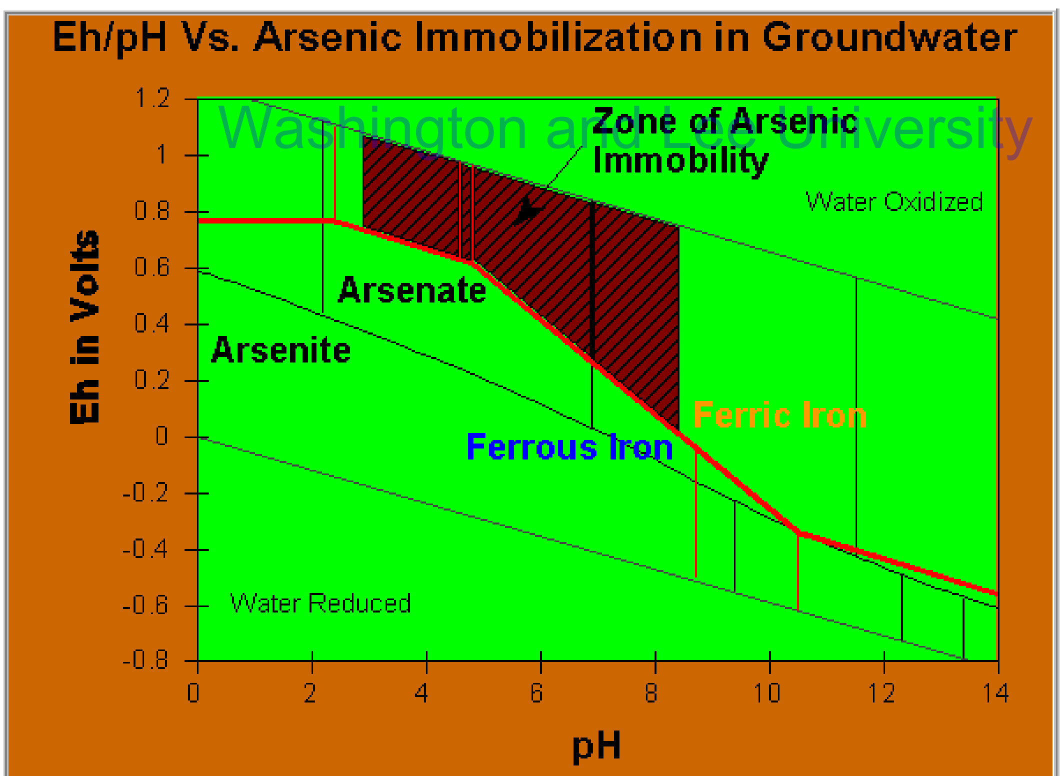


Figure 4. Arsenic Mobility in Groundwater as Controlled by the Effect of Eh/pH Conditions on the Speciation of Arsenic and Iron

Figure 4: Prevalence of Arsenite vs Arsenate depending on Eh and pH conditions and zone of arsenic immobility (Vance, 1995)

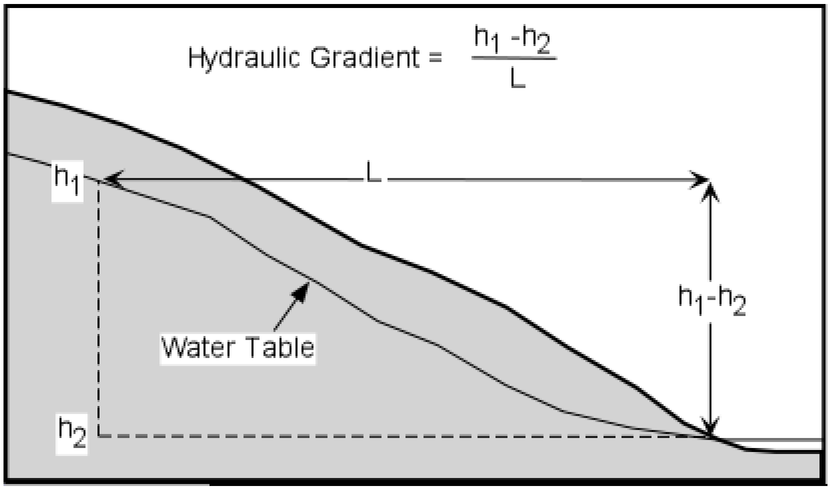


Figure 5: Hydraulic Gradient is the difference in height of the water table between two points and determines the direction and rate of groundwater flow. On a local scale, the water table closely follows the local topography (Freeze and Cherry, 1979; image taken from Tulane.edu).

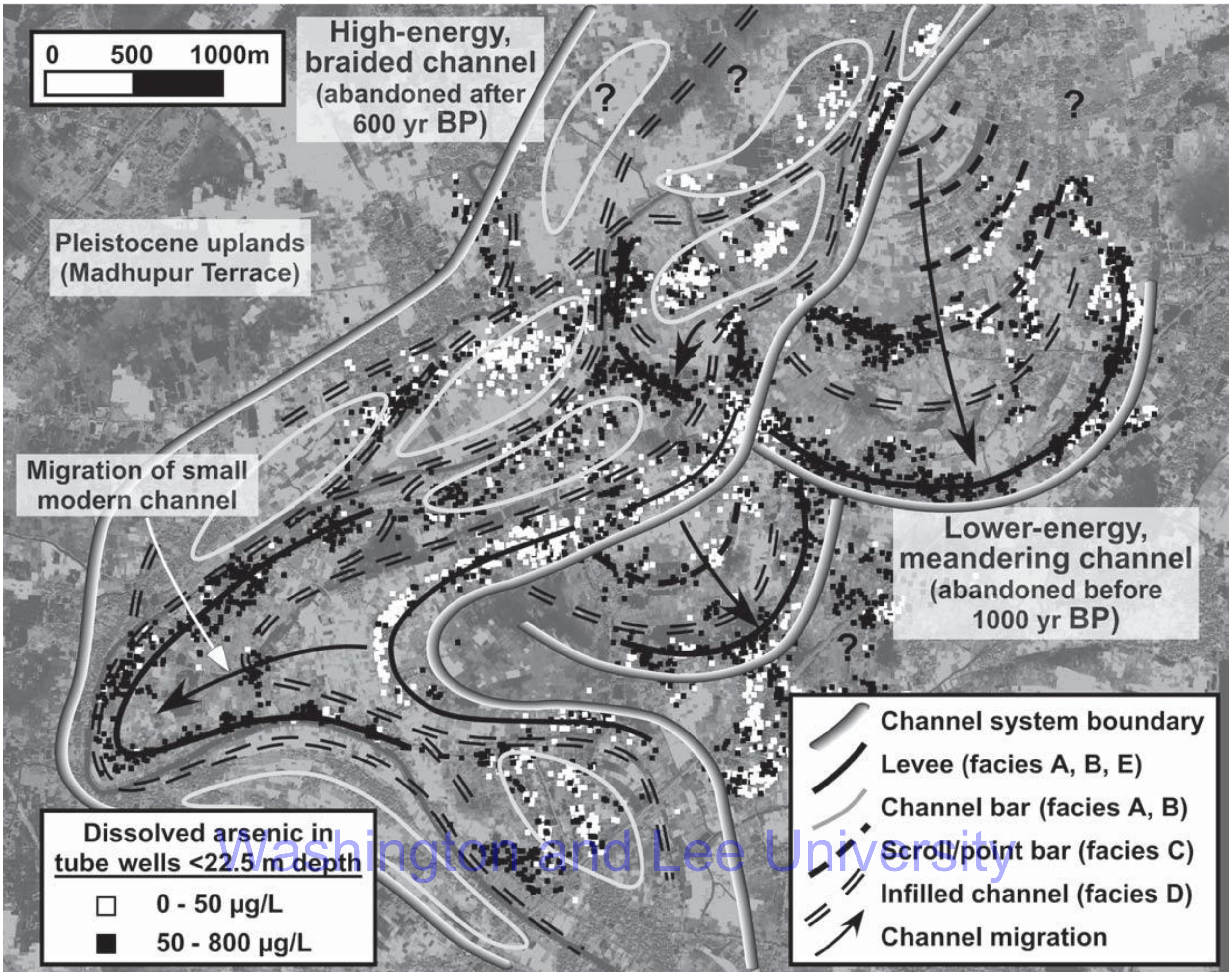


Figure 6: Map relating arsenic concentrations to landforms. High energy channels created course-grained deposits and have generally low arsenic concentrations, whereas low energy channels created fine-grained deposits and have higher arsenic concentrations (Weinman et al., 2008).

Figure 7: Arsenicosis manifestations: hyperkeratosis causing squamous cell carcinoma (Das and Sengupta, 2008)

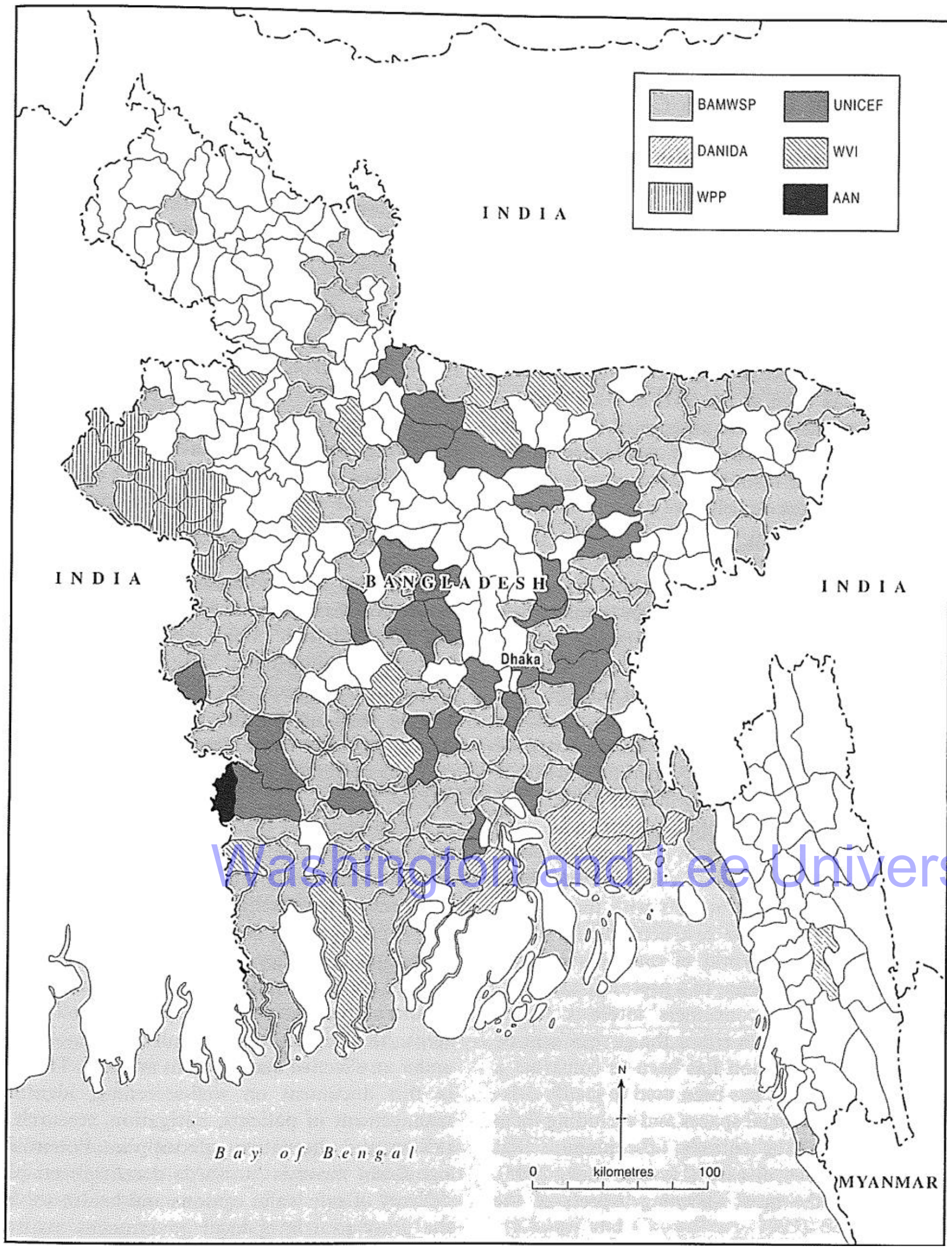


Figure 8: Locations of Agencies involved in arsenic mitigation. NGOs only reach half of the rural population, indicated by the white districts. (Atkins et al., 2007)