

A LABORATORY ASSESSMENT OF
BIOSAND/KANCHAN ARSENIC WATER FILTERS

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ABSTRACT

A laboratory assessment of BioSand/KAnchan arsenic water filters

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According to the United Nations Children's Fund (UNICEF), 768 million people around the world do not have access to safe and clean drinking water. In southern Asia more than 140 million people drink arsenic-contaminated groundwater, which is causing massive arsenic poisoning. NGO's, governmental, and international agencies are trying to reduce the impact of this tragedy using immediate health care interventions, and creating affordable water treatment techniques. The Kanchan arsenic filter (KAF) is a small-scale, slow sand filter adapted for household use. The KAF has an added layer of non-galvanized iron nails as a source of ferric hydroxide, which adsorbs arsenic to its surface and form aggregates that can then be filtered by the column of sand and gravel. The KAF performance in the field has been demonstrated by one study to be 85 to 98% effective in removing arsenic from contaminated water (Ngai et al. 2007); however, another study showed that the KAF was relatively ineffective at treating arsenic contaminated water with average removals fluctuating between 39.4 and 74.9% (Chiew et al. 2009). The issue with these field studies is the use of field kits to test for arsenic, which is imprecise. This laboratory assessment used ICP-MS (Inductively Coupled Plasma-Mass Spectrometry), which is the best analytical technique available for measuring trace metals in the water. The results dispelled the uncertainties about KAF performance in term of arsenic removal. This study also showed that the KAF can effectively reduce very high levels of arsenic (2500 ppb) to below the accepted level of arsenic in drinking water (10 ppb). The origin of arsenic, its distribution in the world, its effect on human health, and evaluation of affordable arsenic removal techniques will be explored in this research. Creating affordable, and effective arsenic removal technologies is not enough for a successful adaptation of the technique by the affected communities. Many factors need to be taken into consideration while promoting arsenic mitigation programs such as, the economic, geographic, cultural and social specificities of the concerned communities are discussed in this paper.

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LITERATURE REVIEW

"It is an uncanny thought that this lurking poison (arsenic) is everywhere about us, ready to gain unsuspected entrance to our bodies from the food we eat, the water we drink and the air we breathe" Karl Vogel, 1928.

Water covers 71% of Earth's surface, and makes up, 50 to 65% of an adult human body.

Water is one of the most important elements on Earth; it has many distinct properties that are vital for the proliferation of life. Unfortunately the distribution of this vital element is very uneven. Many countries have water availability issues, coupled with high rates of water contamination.

Water is necessary for life; nevertheless, about 768 million people around the world do not have access to safe, clean drinking water (UNICEF and WHO 2013), and 2.5 billion people live without proper sanitation, which increases the risk of contamination of accessible water (UNICEF 2013). West (2006) suggested that water contamination is the world's single largest cause of deaths and diseases, accounting for more than 14,000 deaths daily.

Surface water and groundwater are usually managed as two different water resources (Winter 1999); however, groundwater usually feeds surface water sources and vice-versa. This means that contaminants can also be transported between these two main water resources. Based on their origin, water contaminants can be placed in two categories (EPA Clean Water Act 1972): point source pollutants, which are contaminants that pollute a water resource from a single, identifiable source (e.g., discharge from a sewers, a factory, storm drains, etc), and nonpoint sources that are contaminants that are not

derived from single point sources (e.g., nitrogen compounds from fertilizers, and arsenic contaminants from natural rock formations or mining).

The focus of this literature review is on arsenic water contamination, as it is one of the major water contaminants in the world. This paper will explore the history of arsenic use, the process of arsenic water contamination through both natural and anthropogenic contaminations, the chemistry and origin of arsenic and its effects of arsenic on human health. Finally, ways to treat arsenic water contamination in developing countries will be discussed.

A GLANCE AT ARSENIC HISTORY

Arsenic was first discovered in 1250 by Albertus Magnus, the greatest German philosopher and theologian of the Middle Ages (Emsley 2001). Intentional and accidental arsenic poisoning was suspected to be behind the death of many prominent people throughout history, such as George III of Great Britain, and Napoleon Bonaparte (Worthington 2010). According to the Agency for Toxic Substances and Disease Registry, arsenic was used in medicine until the 1970s (ATSDR 2007). In 1786 a solution of potassium arsenite was discovered and used as a treatment for various diseases such as malaria, asthma, eczema, and syphilis. By 1910 a new arsenic-based medicine called Salvarsan was introduced to treat syphilis until penicillin became more prevalent in the 1940s (Hughes et al. 2011)

CHEMISTRY OF ARSENIC

Arsenic is a tasteless, odorless element that is toxic at levels above 10 parts per billion (ppb) (EPA 2006). Its presence and toxicity, even at high levels in the water, are

impossible to detect without expensive water analysis, which makes it extremely dangerous.

Arsenic is an element possessing metallic properties in an inferior degree it is considered a metalloid or semi-metallic element in the periodic table, with the symbol "As" and atomic number 33. Depending on the degree of oxidation, arsenic exists in four oxidation forms or valence states (-3, 0, +3, and +5). Under reducing conditions, arsenite and AsIII predominate, and under oxygenated conditions arsenate and AsV predominate (IARC 2004). This semi-metal occurs in many minerals, often in conjunction with sulfur and metals. As with most elements, arsenic often forms chemical compounds (pure chemical substances of two or more chemical elements). From a toxicology perspective, arsenic compounds are classified as three major types: inorganic, organic, and arsine gas (arsenic and hydrogen). Many organic arsenic compounds are very well known, as several were developed for chemical warfare during World War I (Girard 2010). The inorganic compounds of arsenic are of interest in this review because they explain its occurrence in water. Inorganic compounds of arsenic can form colorless, odorless, crystalline oxides (As_2O_3), commonly called white arsenic, and As_2O_5 , a weak hygroscopic (absorbs moisture from the air) acid that is readily soluble in water. Arsenates (salts) are found in an inorganic form that represents the basis of arsenic groundwater contamination. Certain arsenates are heavily used as agricultural insecticides and poisons that through leaching contribute to groundwater contamination.

The ORIGIN OF ARSENIC

Arsenic and arsenic compounds in the environment originate either from natural Earth deposits or from anthropogenic activities. Arsenic is a natural element in soils, rocks, air,

plants, animals, and water. Natural activities such as erosion, forest fires, and volcanism or human actions release arsenic into the environment.

Anthropogenic activities such as mining, agriculture and industry are responsible for the spread of arsenic water and soil contamination. In the U.S, 90% of industrial arsenic is used as a wood preservative, but it is also used in paints, semi-conductors, drugs, metals, dyes, and even soaps. Activities like the combustion of coal and copper smelting also contribute to arsenic release to the environment (EPA 2013). Furthermore, high levels of arsenic are also leached into the environment from certain fertilizers and animal feeding operations.

Arsenic exists in different forms at different concentrations depending on the host type (water, air, soil or rocks). The concern in this literature review is arsenic in water, but because most arsenic in water originates from other sources, we should also explore the different arsenic hosts. Arsenic is the 53rd most abundant element in the Earth's crust at 1.5 ppm (part per million). Soil contains 1 to 10 ppm, which is similar to the range found in sediments except where contaminated by industry or agricultural activity (Plant et al. 2004). In contrast seawater has only 1.6 ppb of arsenic on average (Emsley 2001).

The arsenic form of concern in this paper is arsenate, which makes up approximately 60% of natural arsenic. The remaining components of the global arsenic pool include about 20% as sulphides and sulfosalts, and 20% as arsenides, arsenites, oxides, alloys and polymorphs of elemental arsenic (Smedley and Kinniburgh 2002). Arsenic concentrations of more than 10^8 ppb have been reported in sulphide minerals and up to $7.6 \cdot 10^8$ ppb in iron oxides (Smedley and Kinniburgh 2002). Arsenic is incorporated into primary rock-forming minerals only to a certain extent; many igneous and

metamorphic rocks have average arsenic concentrations of 1-10 10^3 ppb. Similar concentrations are found in carbonate minerals and carbonate rocks (Plant et al. 2004). In sedimentary rocks, arsenic concentrations are more variable, depending on the sedimentation rate and the source of the sedimentary material. In sedimentary rocks arsenic is most concentrated in clays and other fine-grained sediments. The average concentration of arsenic in shale is an order of magnitude greater than in sandstones, limestones and carbonate rocks. Arsenic is strongly linked to oxides of iron, aluminium and manganese, as well as some clays, leading to its enrichment in ferromanganese nodules and magnesium and iron deposits. This fact is used in many water filters that are arsenic efficient (Plant et al. 2004). Alluvial sands, glacial till and lake sediments typically contain <1-15 10^3 ppb arsenic (Plant et al. 2004). The highest sedimentary arsenic concentrations (20-200 10^3 ppb) are typically found in organic-rich and sulphide-rich shales, sedimentary ironstones, phosphatic rocks, and some coals (Smedley and Kinniburgh 2002)

ARSENIC HISTORY AND PRODUCTION

Historically, the USA has been the largest arsenic consumer in the world. Prior to 2004, arsenic trioxide represented 90% of the total consumed arsenic because of its heavy use in the manufacture of wood preservatives. By 2007, the consumption of arsenic for wood preservation had declined by 50% (U.S Geological Survey 2008). For commercial and industrial reasons white arsenic (As_2O_3 an inorganic compound of arsenic) is heavily produced by several countries (Figure 1). In 2005, China produced 50% of the world share of white arsenic followed by Chile, Peru, and Morocco (U.S Geological Survey

2008). For environmental reasons, white arsenic production mostly ceased in the U.S and Europe (Schtone 2008).

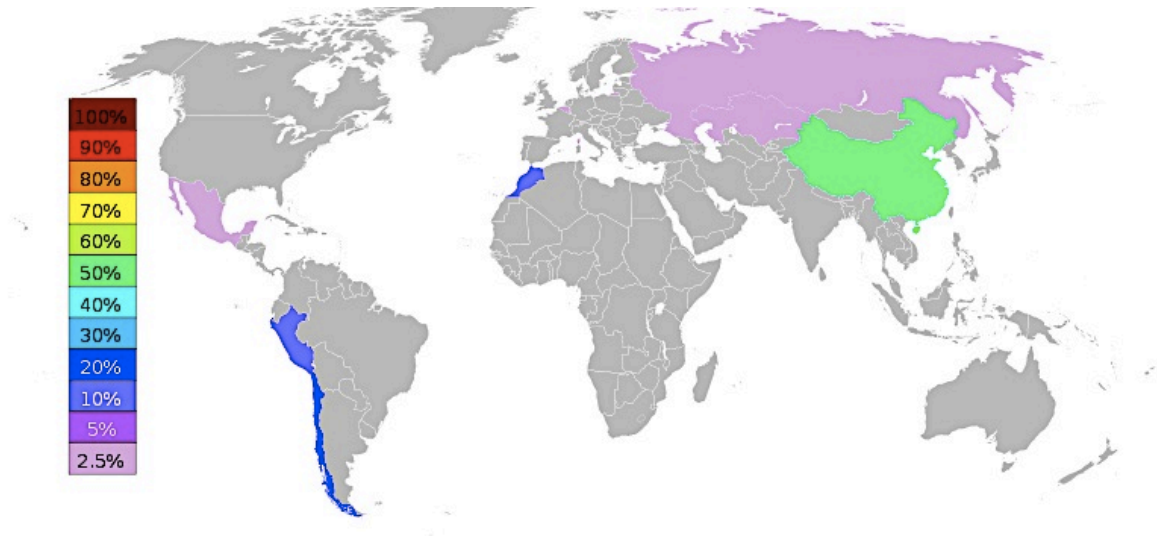


Figure 1: Arsenic production based on USGS Commodity report (2007)

ARSENIC IN WATER

The concentrations of arsenic in most groundwater sources is <10 ppb and often below the detection limit of routine analytical methods (Plant et al. 2004). The physicochemical conditions favoring arsenic mobilization in aquifers are variable, complex and poorly understood, although some of the key factors leading to high groundwater arsenic concentrations are known. Mobilization can occur under strongly reducing conditions where arsenic, mainly as As(III), is released by desorption from, and/or dissolution of, iron oxides. Immobilization under reducing conditions is also possible. Some sulphate-reducing micro-organisms can respire As(V) leading to the formation of an As_2S_3 precipitate. Some immobilization of arsenic may also occur if iron sulphides are formed (Plant et al. 2004).

ARSENIC WATER CONTAMINATION THROUGHOUT THE WORLD

High concentrations of naturally occurring arsenic are found in oxidizing conditions where groundwater pH values are high (Smedley and Kinniburgh 2002). The high-arsenic groundwater hot spots are usually in arid or semi-arid regions where groundwater salinity is also high. Evaporation has been suggested to be an important additional cause of arsenic accumulation in some arid areas (Welch and Lico 1998). High concentrations of arsenic have also been found in groundwater in areas of bedrock on sites of mining activities. Arsenic concentrations of up to 5000 ppb have been found in groundwater associated with the former tin-mining activity in the Ron Phibun area of peninsular Thailand, the source most likely being oxidized arsenopyrite (FeAsS) (Plant et al. 2004).

ARSENIC CONCENTRATION GUIDELINES

The standards for maximum concentrations of arsenic in drinking water have been declining since the high toxicity of arsenic has become obvious. The 1903 report of the Royal Commission on Arsenic Poisoning in the UK set a standard of 150 ppb. In 1942, the US Public Health Service set a drinking water standard of 50 ppb for interstate water carriers. The World Health Organization (WHO) guideline for arsenic in drinking water was reduced from 50 ppb to a provisional value of 10 ppb in 1993. Most western countries have adopted this lower limit in their current drinking water standards (Yamamura. 2003); however, most arsenic-affected developing countries still operate at the 50 ppb standard due to a lack of adequate testing facilities and economic limitations. On January 23, 2006, U.S EPA (Environmental Protection Agency) set the arsenic standard for drinking water at 10 parts per billion (ppb) which is equivalent to 9.98859 µg/l; however this value is not always met in many places in within the U.S (Figure 2).

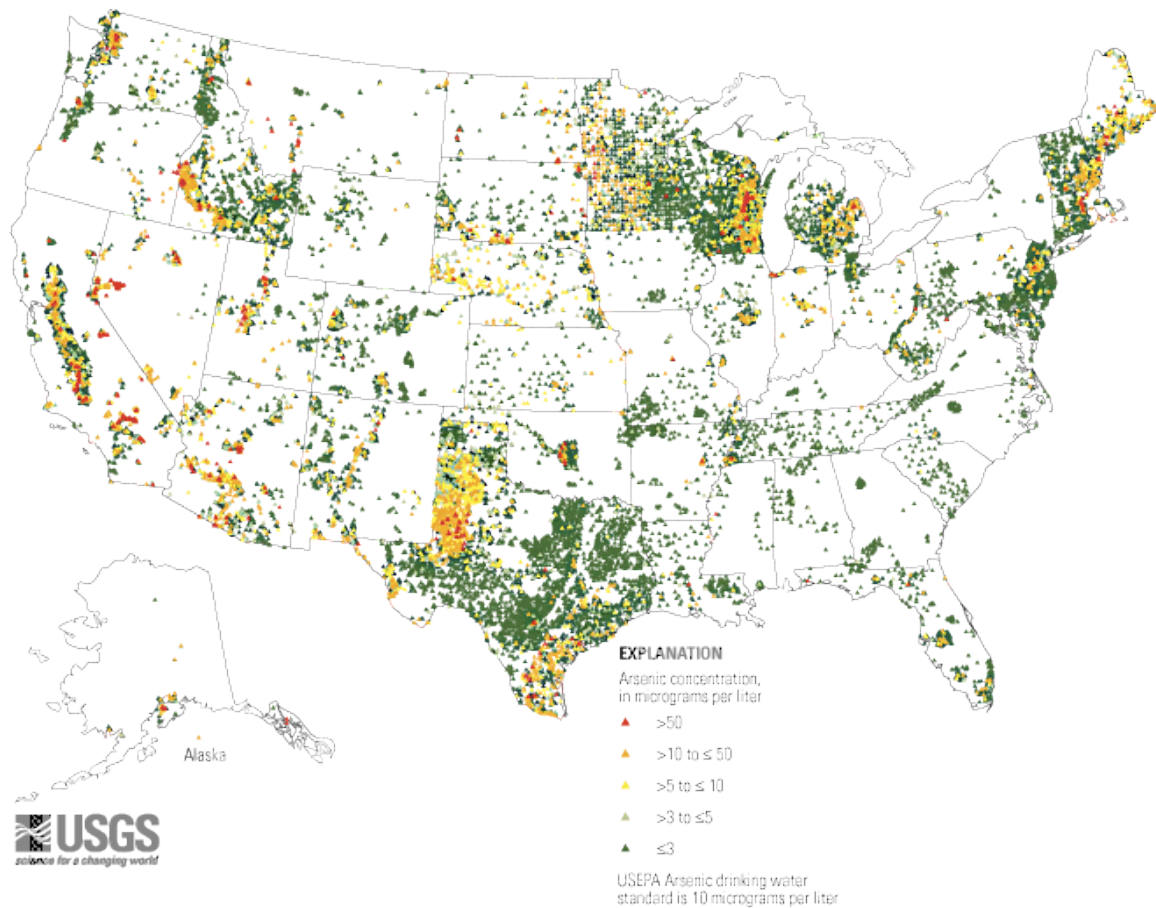


Figure 2: Distribution of arsenic concentrations in the U.S (Ayotte 2011)

Concentrations of arsenic are usually higher in ground water than surface water sources (EPA 2008). The increasing demand on drinking water increases the use of groundwater, which is highly susceptible to arsenic contamination. In many places in the world the only drinking water source is groundwater. As the volume of groundwater decreases due to human consumption, the inputs of arsenic into the groundwater remain the same. This means that the arsenic concentration in groundwater is continually increasing by release from rock formations and other sources (Smedley et al 2001).

The U.S EPA has detected several arsenic hot spots (greater concentrations than 10 ppb) within the United States. It appears that western states have the highest levels of arsenic contamination, followed by parts of the Midwest and New England whose arsenic

levels are greater than the EPA's standard of 10 ppb. There are many other arsenic hot spots around the world (Figure 3). The distribution of hot spots depends on variations in geology and Earth crust constituents.

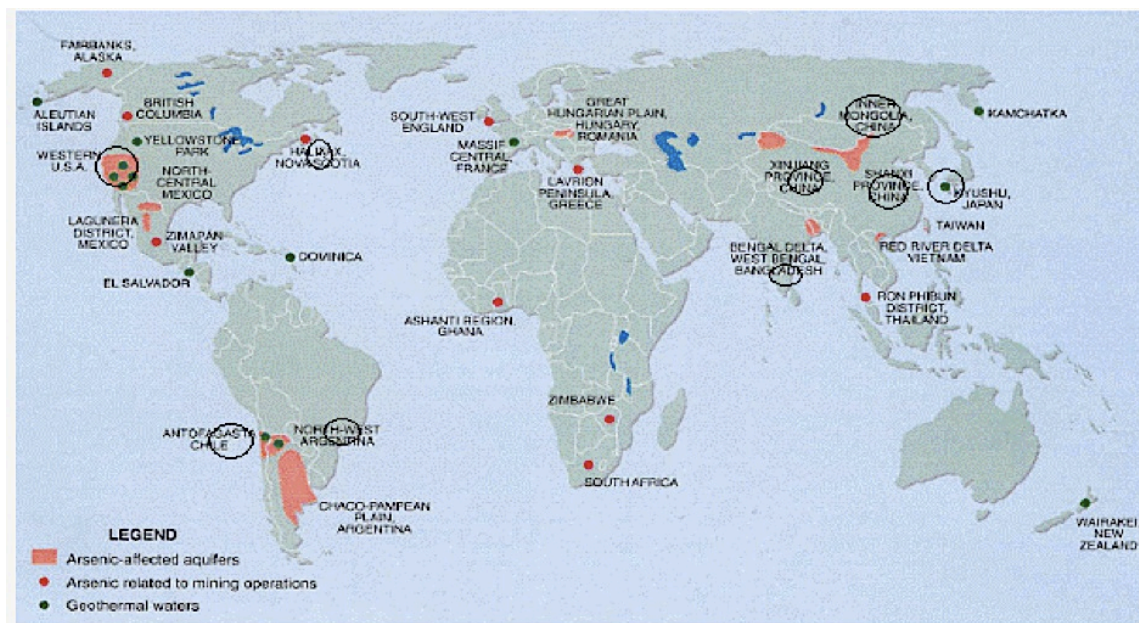


Figure 3: Arsenic-affected aquifers in the world (Smedley et al. 2002)

ARSENIC EFFECTS ON HUMAN HEALTH

Chronic arsenic exposure is linked to a range of dose-dependent conditions, including cancers of the skin, bladder, kidney and lung, as well as skin lesions, arterial hypertension and cardiovascular disease, pulmonary disease, peripheral vascular disease, diabetes mellitus and neuropathy.

The extent of arsenic poisoning depends on the dose and duration of exposure, interactions of arsenic with other dietary elements, and the age and sex of the individual. The toxicity of arsenic, and arsenic compounds, depend on the inorganic or organic form, valence state (oxidation), solubility, physical state, purity, and rates of absorption and

elimination (Agency for Toxic Substances and Disease Registry 2007). The toxicity of arsenic compounds varies significantly, with the highest toxicity for the inorganic trivalent compounds, followed by the organic trivalent compounds. The lowest toxicity arsenic compounds are the organic pentavalent compounds and elemental arsenic (Gorby 1988).

Exposure to arsenic may cause both short-term and long-term health problems. Short exposure or acute effects can occur within hours or days of intense exposure. Long-term or chronic effects occur over many years of exposure. Long-term exposure has been linked to cancer of the bladder, lungs, skin, kidneys, nasal passages, liver and prostate (US. Department of Public Health 2008). Short-term exposure to high doses of arsenic can cause other adverse health effects, but such effects are unlikely to occur from U.S. public water supplies that are in compliance with the arsenic standard. Unfortunately in many places around the world public water supplies are either very inefficient or almost absent. This means that long-term exposure is usually the case, due to a lack of early arsenic detection in the water, or the absence of appropriate water treatment.

CASE STUDIES OF ARSENIC WATER CONTAMINATION

Ground-water arsenic contamination is a global issue. Many nations, including Argentina, Chile, China, India, Mexico, Taiwan, Thailand, the United States and Bangladesh suffer from this threat. In this section a list of case studies from some of these countries will be discussed.

Bangladesh

Bangladesh suffers from the largest groundwater arsenic contamination in the world (Figure 4). Between 35 million and 77 million inhabitants of Bangladesh are at risk of

arsenic contamination (Khan et al. 1997) which is higher than any other known environmental disaster. It is even greater than the Chernobyl, Ukraine disaster in 1986, which affected millions of people. Over 60% of the groundwater in Bangladesh contains naturally occurring arsenic, with concentrations often much higher than 10 ppb, (Jian 2012)

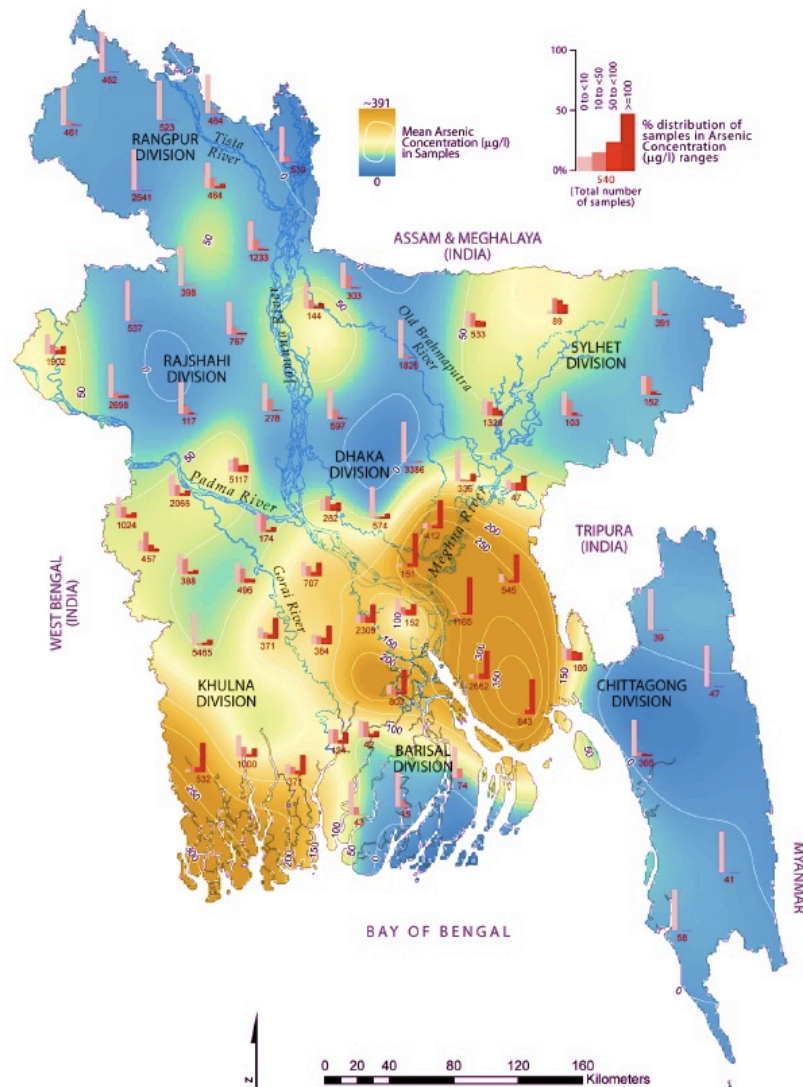


Figure 4: Arsenic concentrations in groundwater including all 64 affected districts in Bangladesh (Jian 2012)

About 20 years ago, surface water in Bangladesh was contaminated with microorganisms that caused a significant increase in disease and mortality among infants and children. This contamination of mostly stagnant pond surface waters pushed the

United Nations Children's Fund (UNICEF) and the Department of Public Health Engineering during the 1970's to look for alternative sources of drinking water (Chowdhury 2004). Groundwater was the perfect alternative, and presumably a "safe" source of drinking water at the time. Shallow wells were installed all over the country at depths of usually less than 200 m. By the 1980s the UNICEF initiative of well installation decreased due to the massive installation of tube-wells by the private sector (Chowdhury 2004, UNICEF 1999). Millions of tube-wells were installed following only the most rudimentary of water testing procedures, if any (Chowdhury. 2004). These tests did not include tests for arsenic, as it was not recognized as a problem in the water supply (Chowdhury 2004). The 1997 UNICEF country report indicated that Bangladesh had surpassed its goals of providing 80% of the population with access to safe drinking water, a rare success story in the otherwise impoverished nation.

In 1983 the School of Tropical Medicine in Calcutta, India identified the first cases of arsenic-induced diseases and symptoms. The first patients were originally from west Bengal. By 1987, many other cases that came from the same region were identified, and the cause of their contamination was linked to their primary drinking-water sources: tube-wells. However arsenic water contamination was not confirmed in Bangladesh until 1993 (Khan et al. 1997, Chowdhury 2004). Tube-wells have been used in Bangladesh since the 1940s, although arsenic water contamination has only recently come to light. This can be explained by the fact that groundwater sources have been heavily over-used, mainly for agriculture, over the past 20 years, which increased the arsenic concentration in the water by a process of accumulation and oxidation. Arsenic was released by oxidation of arsenic pyrite naturally present in the alluvial sediments. As aquifers were

drawn down, atmospheric oxygen was able to reach the aquifers, and release the arsenic in the water (McArthur 2001).

In 1997 the government of Bangladesh created a project to evaluate the extent of the arsenic problem. About 62 % of the 32,651 tube-wells sampled had arsenic concentrations greater than 100 ppb, which was twice as high as the safe drinking limit of 50 ppb set by the country (Quamruzzam et al. 1999).

Many studies have been conducted in Bangladesh to evaluate the effects of arsenic contamination on human health. The results were dramatic. In one study, of the 1,630 adults and children examined, 57.5% of them had skin lesions due to arsenic poisoning (Dhar et al. 1997, Petrushevki et al. 2007). A report from the World Bank has estimated that 20 million inhabitants of Bangladesh may be drinking arsenic-contaminated water and are at high risk of severe arsenic poisoning (Flanagan et al. 2012). More studies are needed to have a better estimation of the real extent of the arsenic contamination in Bangladesh.

Taiwan

A large-scale study conducted in Taiwan showed that the average concentration of arsenic in water was about 500 ppb. The study also showed that by the age of 60 more than 1 in 10 people developed skin cancer due to arsenic poisoning (Tseng et al. 1968, Chen et al. 2003). Dramatic increases in mortality from internal cancers have also been reported in Taiwan. Studies have been able to tie these cancers to exposures to high arsenic concentrations on the order of 800 ppb (Chen et al 1988).

South America

Arsenic has also been an issue in South America with reported arsenic contamination in

countries like Argentina and Chile. In northern Chile, 5 to 10% of deaths caused by internal cancers were attributed to arsenic water contamination. The average exposures were on the order of 500 ppb. After many years of remediation efforts, the mortality rate slightly decreased; however, it continued for 40 years after the highest exposures began (Smith et al. 1992, Ferreccio et al. 2000). A study conducted in the region of Cordoba, Argentina, found that the population was at high risk of bladder and lung cancer because of arsenic concentrations at an average of 178 ppb (Hopenhayn-Rich et al. 1998). In general, in most locations, higher the arsenic concentrations, the higher are the risks of cancer.

ARSENIC EXPOSURE INTERVENTION

In many places around the world, access to groundwater or surface water is a luxury, and standard water testing procedures before consumption are not a common practice. This makes arsenic poisoning a huge threat to many people, especially because arsenic is a tasteless and odorless element that is hard to detect in water without appropriate testing and analysis. Responses to arsenic water contamination in many regions of the world usually start after diagnosis of the first signs of arsenic poisoning (Chowdhury 2004). Chowdhury, A. M. R. (2004). ARSENIC CRISIS. *Scientific American*. Developing countries usually face many economic difficulties that make resolving public health problems a challenge. Often their health systems are not adequate to face a crisis of this magnitude and external aid is much needed in these regions.

Responses to arsenic contamination are straightforward: provide arsenic free-water. However, with limited resources this is a long-term and difficult solution. Immediate responses are often in the form of health care for the patients, including

vitamin supplements, topical lotions and treatment of infections. Immediate responses in some cases also involve the introduction of water treatment solutions (Smith et al. 2000). Defective communication and transportation systems within developing countries create even more obstacles for community intervention programs. For these reasons providing affordable arsenic removal technologies at the point of use in areas with no alternative drinking water is the best intervention that can be provided.

ARSENIC WATER TREATMENT MECHANISMS

Before this literature review expands on affordable water treatment solutions for arsenic, it is necessary to examine the available mechanisms, chemistry, and processes of arsenic removal from water. There are many available treatment technologies for arsenic removal. Technologies described in this literature review are categorized into three broad categories: precipitative processes, adsorption processes, and ion exchange processes. Several treatment techniques discussed here may be technically feasible, but their cost may be prohibitive. Most of these technologies can be reduced in scale and conveniently applied at household and community levels for the removal of arsenic from contaminated tube well water. Following this discussion I will focus on affordable arsenic removal technologies.

Precipitative processes:

Coagulation/Filtration

Coagulation/filtration (C/F) is a treatment process by which the physical or chemical properties of dissolved colloidal (solution with particles in between 1 and 1000 nanometers) or suspended matter are altered to form agglomerations that can be settled

out of a solution by gravity, and can be removed by filtration. Coagulants in the dissolved colloidal solution have the capacity to change the surface charge properties of the solids suspended in the solution, which allow them to bond to each other and form agglomerations of particles into a flocculated precipitate (Pirnie 1999). In either case, the final products are larger particles, or flocs, which are more readily filtered or settled under the influence of gravity (Pirnie 1999). This process is used in most of the arsenic treatments systems that will be described later in the literature review.

Coagulation Assisted Microfiltration

The coagulation process removes arsenic effectively by using clotting factors. In this process microfiltration is used as a membrane separation process to remove coagulates, particulates, turbidity, and microorganisms. In coagulation-assisted microfiltration technology, microfiltration is used in a manner similar to a conventional gravity filter (Muilenberg 1997).

Iron/Manganese Oxidation

Oxidation is the loss of electrons or an increase in oxidation state by a molecule, atom or, ion. Oxidation reactions are commonly associated with the formation of oxides from oxygen molecules. Iron/Manganese (Fe/Mn) oxidation is commonly used by facilities treating groundwater. The oxidation process used to remove iron and manganese leads to the formation of hydroxides that combine with the soluble arsenic, which can then be removed by precipitation or adsorption reactions (adsorption will be explained later in the literature review).

Arsenic removal during iron precipitation is fairly efficient (Edwards 1994).

Removal of 2002 ppb of iron achieved a 92.5 percent removal of As(V) from a 10 ppb

As(V) initial concentration by adsorption alone. Even removal of 1001 ppb of iron resulted in the removal of 83 percent of As(V) arsenic from an initial concentration of 22 ppb of As(V) (Edwards 1994). Indeed, field studies of iron removal have indicated that this treatment can feasibly remove 3003 ppb of arsenic. However, the removal efficiencies achieved by iron removal are not as high nor as consistent as those realized by activated alumina or ion exchange. Even so, the advantage of iron removal is that there is no chemical use. Note, however, that arsenic removal during manganese precipitation is relatively ineffective when compared to iron even when removal by both adsorption and co-precipitation are considered. For instance, the use of iron removal is more efficient than using manganese removal (Edwards 1994).

Iron oxidation will make more sense with the following example. Research on oxidation filtration technologies has primarily been related to greensand filtration. Considerable arsenic removal has been demonstrated using greensand filtration (Subramanian et al. 1997). The active material in "greensand" is glauconite, a green, iron-rich, clay-like mineral that has ion exchange properties. Glauconite often occurs in nature as small pellets mixed with other sand particles, giving a green color to the sand. The glauconite sand is treated with potassium permanganate (KMnO_4) in order to coat it with a layer of manganese oxides. The principle behind this arsenic removal includes oxidation, ion exchange, and adsorption. Arsenic compounds displace species from the manganese oxide (presumably OH^- and H_2O), becoming bound to the greensand surface through an ion exchange process. The oxidative nature of the manganese surface converts As(III) to As(V) and As(V) is adsorbed to the surface. As a result of the transfer of electrons and adsorption of As(V), reduced manganese (MnII) is released from the

surface (Subramanian et al. 1997). The effectiveness of greensand filtration for arsenic removal depends on the water quality. Close attention needs to be focused on the water source and its composition. For example, a water that is iron-rich is much more efficient and has no need for more iron to be added to the water for the oxidation (Pirnie 1999)

Lime Softening

Lime softening is used as an arsenic removal technique, although this is not why it is listed in this paper. Lime softening uses many chemicals and requires close attention to the water chemical balance, which is not something that people in remote villages can do. Also this technique requires neutralization of the pH with carbon dioxide before the water is ready for consumption (Pirnie 1999). The reason why lime softening is mentioned is because hardness is an issue when using other affordable arsenic removal processes such as iron oxidation. In such cases softening is required as a pre-treatment to optimize arsenic removal. Hardness blocks the oxidation process and does not allow the iron to bond with arsenic and form a precipitate.

Hardness is predominantly caused by calcium and magnesium compounds in solution. Lime softening (LS) removes this hardness by creating a shift in the carbonate equilibrium. The addition of lime to water raises the pH. Bicarbonate is converted to carbonate as the pH increases, and as a result, calcium is precipitated as calcium carbonate. Soda ash (sodium carbonate) is added if insufficient bicarbonate is present in the water to reduce the hardness to the desired level. Usually the groundwater pH in the affected areas in Bangladesh, India, and Nepal is about 6.9, which does not require softening (Jiang et al. 2012).

ADSORPTIVE PROCESSES

Activated Alumina

Activated alumina is an adsorbent used in packed beds to remove arsenic (also used to remove fluoride, selenium, beryllium, and natural organic matter). It might be pointed out in this context that adsorption is the adhesion of atoms, ions, or molecules from a gas or a liquid, or dissolved solid to a surface. This process consists of the creation of a film of the adsorbate on the surface of the adsorbent. This is different than absorption; absorption involves the whole volume of the material while adsorption is a surface-based process.

Activated alumina (AA) is a physical/chemical process by which ions in the Feed water are adsorbed to the oxidized AA surface. Feed water, or pre-oxidation water, is a pH adjustment that may be necessary to increase arsenic removal. For example the oxidation of As(III) to As(V) can increase the effectiveness of arsenic removal, because (AA) is more effective at removing As(V) than As(III).

AA is considered an adsorption process, although the chemical reactions involved are actually an exchange of ions (American Water Works Association, 1990). Activated alumina is prepared through dehydration of aluminum hydroxide $\text{Al}(\text{OH})_3$ at high temperatures (Clifford and Lin 1995). AA is used in packed beds to remove contaminants such as fluoride, arsenic, selenium, and silica, where contaminated water is continuously passed through the bed to remove contaminants. The contaminant ions are exchanged with the surface hydroxides on the alumina. When adsorption sites on the AA surface become filled, the bed must be cleaned. AA media can encounter a reduction of the number of adsorption sites thus decreasing removal effectiveness; when the media become clogged with suspended solids present in the contaminated water a backwash is

necessary to remove the solids. This can be done through a sequence of rinsing with regenerant, flushing with water, and neutralizing with acid. The regenerant is a strong base, typically sodium hydroxide; the neutralizer is a strong acid, typically sulfuric acid.

Many studies have shown that AA is an effective treatment technique for arsenic removal. Factors such as pH, arsenic oxidation state, competing ions, empty bed contact time (EBCT), and regeneration have significant effects on the removals achieved with AA, which makes it deficient and complicated.

Ion Exchange

Ion exchange (IX) is a physical/chemical process by which an ion on the surface of a solid phase is exchanged for an ion in the feed water (pre-oxidized water). This solid phase is typically a synthetic resin, which has been chosen to preferentially adsorb the particular contaminant of concern. To accomplish this exchange of ions, contaminated water is continuously passed through a bed of ion exchange resin beads in a down-flow or up-flow mode until the resin is exhausted. Exhaustion occurs when all sites on the resin beads have been filled by contaminant ions. At this point, the bed is regenerated by rinsing the IX column with a concentrated solution of ions initially exchanged from the resin. The number of bed volumes that can be treated before exhaustion varies with resin type and influent water quality. Important considerations in the applicability of the IX process for removal of a contaminant include water quality parameters such as pH, competing ions, resin type, alkalinity, and influent arsenic concentration.

AFFORDABLE ARSENIC REMOVAL TECHNOLOGIES

Most of countries that suffer from arsenic water contamination are developing countries with limited resources and so simple, low cost processes are needed. Affordable arsenic

removal techniques clearly provide short-term solutions, especially in remote areas where arsenic concentrations are high. Nevertheless, the effectiveness of these technologies in the long run is critically dependent on both the willingness and the ability of the local communities to accept, operate, and maintain the technologies.

During the last 2-3 years many small-scale arsenic removal technologies have been developed, field-tested and used in research programs in Bangladesh and India. This coming section presents a short review of these technologies with the intention to update the technological development in arsenic removal, and understand the problems, prospects and limitations of different treatment processes as alternative water treatment options.

Electrocoagulation/ECAR

The arsenic water contamination crisis pushed many scientists and organizations to develop cost-effective and efficient arsenic treatment technologies. Electrocoagulation has been suggested as an alternative to chemical coagulation in pollutant removal from raw water. This technology removes contaminants that are hard to remove by filtration or chemical treatment systems. Electrocoagulation is a two-phase process. An electrical charge is applied to the water, followed by the coagulation, which is the process of changing the particles surface charge, allowing suspended matter to form agglomerates with the charged particle's, which then can be easily filtered (Rodrigues et al 2007).

ElectroChemical Arsenic Remediation (ECAR) is an adapted version of the electrocoagulation that has been developed to respond to a large-scale need for clean water. In ECAR, oxidation of an iron anode produces hydrous ferric oxide or Fe(III) in arsenic-contaminated water. Arsenic then combines coagulation with the Fe(III) to form a

floc, or aggregate, that can be easily separated from the water via filtration (Robert et al. 2004). An ECAR 100 liter batch prototype has been designed. It comprises a cylindrical tank for dosing and mixing connected to a sedimentation tank for coagulation and sedimentation (solid/solution separation). This system uses a voltage of $<3V$ across the electrodes (Figure 5) (Addy et al. 2011).

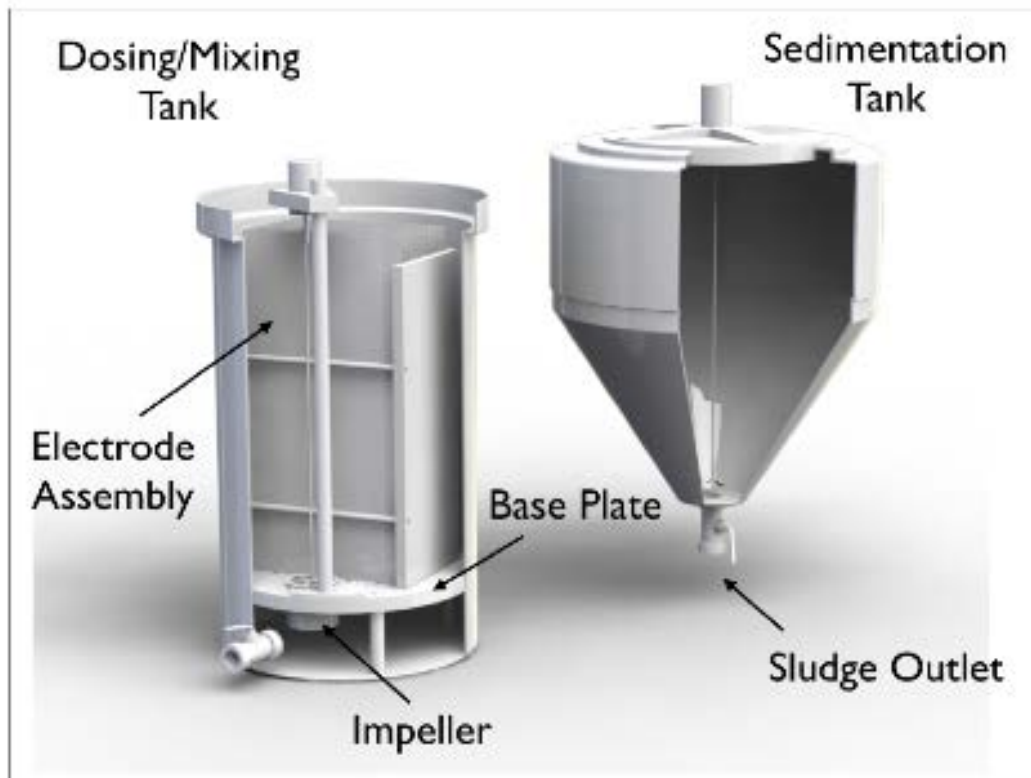


Figure 5: ECAR 100-liter batch prototype (Addy et al, 2011)

ECAR treatment has been successful in reducing initial arsenic concentrations, ranging from 93 to 760 $\mu\text{g/L}$ to the levels required by the World Health Organization, 10 $\mu\text{g/L}$ (Addy et al. 2011).

ECAR is a promising treatment method with many advantages. It includes no use of chemical coagulation, low maintenance, is of a fairly small system size, and has low sludge production. The estimated cost of this method is US \$1.13 per capita/year, or US

\$7.93 per family/year, assuming 7 people per family (Addy et al. 2011). Note that eight American dollars are equal to 621.44 Bangladeshi Taka and according to the International Monetary Fund; the per capita income in Bangladesh is estimated to be US \$2,100, which makes the cost of this method somewhat affordable. However the energy infrastructure is quite small in Bangladesh and neighboring countries. According to the World Bank (2011), only 59.6 % of the Bangladesh population has access to electricity. This percentage is even lower in rural areas, which makes the use of ECAR systems a challenge because of the necessity of a power supply.

Amal Arsenic Filter

In 1996, Water For People (WFP) an NGO based in Colorado USA, offered a \$10,000 grant to the Bengal Engineering College (India) to conduct a laboratory study to select an appropriate, and affordable arsenic-removal technology to reduce the tremendous arsenic poisoning of rural west Bengal. The fruit of this collaboration was the Amal Arsenic Filter named after Dr Amal Datta one of the first project investigators (Elangovan. 2006).

This filtration method is based on activated alumina (described earlier in the literature review). The filter is made of a tall stainless steel tube. A hand water pump gets the water to the top of the filter where it falls through a splash plate. At this stage As (III) is oxidized to As (V) to optimize the activated alumina process. The water then passes through the alumina granules, then through a column of gravel, before it is collected by a tap at the base of the unit (Figures 6 A and 6 B).

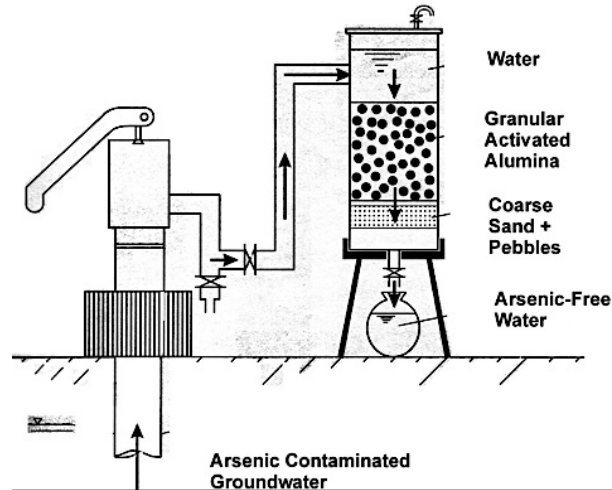


Figure 6 A: Diagram of the Amal Filter (source: the Bengal Engineering College)



Figure 6 B: An Amal filter with the sludge pit to the left and the pump to the right (source: Bengal Engineering College)

The Amal Arsenic Filter can also use iron flocs instead of activated alumina granules. The iron bonds to the arsenic and forms aggregates, which can be filtered by the rest of the filter's components. The disadvantage of the Amal filter technology is that either using iron flocs or activated alumina granules, the filter clogs often. For a filter using iron flocs a backwashing is required every 3 to 4 days depending on the use

frequency. A filter using activated alumina reaches saturation less often. After 6 to 8 months the arsenic levels in the output water rise above the acceptable limit. This requires a filter wash using an alkali solution (NaOH), which needs to be brought back to the appropriate pH using an acid solution (HCl). During this procedure there is no need for removing the alumina granules (Rosenblum et al. 1984).

Overall this technique provides a higher volume of clean water than other techniques, which is more adapted to a community level not a household setting. It is very well-understood and reliable. The filter meets the desired water requirements for arsenic removal; however, there are many inconveniences to the filter such as the use of chemicals, periodic backwashing to remove accumulated solids, the need to monitor the filter to watch for bacterial growth in the cartridges. Also the system pressure and flow rate require regular checks to verify the effectiveness of the backwashing (Jurenka 2010).

Bucket Treatment Unit

The Bangladesh Department of Public Health Engineering, DPHE-Danida Project, has developed the Bucket Treatment Unit (BTU). This treatment technique is based on the principles of coagulation, co-precipitation, and adsorption processes. The BTU is made of 2 units, “buckets” each of 20 L capacity, placed one above the other. The first bucket is designated for mixing the contaminated water with chemicals (200 mg/L aluminum sulfate + 2 mg/L of potassium permanganate) vigorously for 30 to 60 seconds, then gently for 90 seconds to allow the coagulation. The mix is then ready for precipitation for 1 to 2 hours. Afterwards the water from the first bucket is drained to the lower bucket by a plastic pipe. The lower bucket is used to collect the water and filter it through the layer of sand at the bottom of it. This design was developed by the DPHE-Danida project in

Bangladesh (Figure 7 A), which conducted a field study to evaluate the filter's effectiveness. A rapid assessment showed mixed results; in rural areas the filter failed in reducing the arsenic concentration to below the limit of 50 ppb due to inappropriate mixing and fluctuations in the water pH in different regions. However laboratory experiments demonstrated excellent results (Sarkar et al. 2000).

For better field performance, the Bangladesh University of Engineering and Technology used a different design (Figure 7 B), and chemical mix: 100 mg/L of ferric chloride and 1.4 mg/L of potassium permanganate for oxidation. With this modification the results were between 20 and 37 ppb.

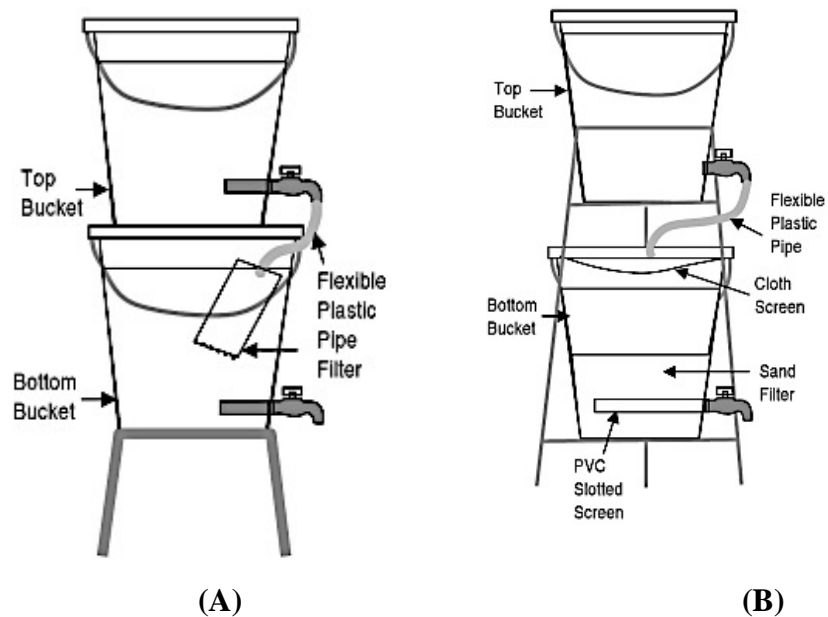


Figure 7: Diagram of the Bucket Treatment Unit (A): DPHE-Danida project design, (B) Bangladesh University of Engineering and Technology design

Three Pitcher Method

The Three-Pitcher Method is locally known in Bangladesh as the 3-Kalshi method, which is an affordable technique made with locally available materials. Kalshi is a traditional

clay water reservoir that 80% of people in Bangladesh use to store drinking water (Khan et al. 2000). In this set up, the three Kalshis are placed one above the other. Each kalshi's capacity is about 18 L. The top Kalshi contains 3 kg of non-galvanized iron chips and 2 kg of coarse sand. The second Kalshi contains 1 kg of wood charcoal and 2 kg of fine sand. The bottom Kalshi has a small hole plugged with 10% Polyester cloth, and it is used to collect the filtered water (Figure 8). This method is based on iron oxidation explained earlier in the paper, and does not requires the use of chemicals. Arsenic is removed through a formation of co-precipitates, and by adsorption onto ferric hydroxide solids. Studies showed that the filter is capable of reducing an initial arsenic concentration of 1160 ppb to bellow the detection limit of 10 ppb (Khan et al. 2000). The disadvantage of this method is that the cloth in the bottom kalshi needs to be renewed often in order to maintain the flow rate.

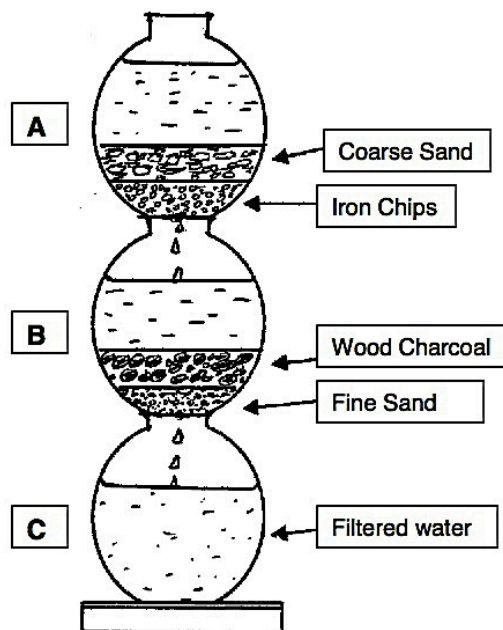


Figure 8: A diagram of the three Kalshi filter (Khan et al, 2000)

Biosand Arsenic water filter (Kanchan filter)

The Kanchan arsenic filter is a version of a BioSand filter and one of the best and most affordable technologies available to-date. The Kanchan filter went through a series of developments to get to its recent design. The following is a history of the filter.

BioSand filters are a type of slow sand filter. The first documented use of the slow sand filter goes back to 1804, in Scotland (Huisman et al. 1974). Two decades later James Simpson refined this method for the first treated public water supply in the world in London 1829 (Huisman et al. 1974). Slow sand filters are used to treat raw water, and are typically 1 to 2 meters deep, with a rectangular or cylindrical shape. The flow rate of the filter is determined by the filter's size. The mechanism of this filter is very simple; the sand itself plays a double role: a substrate for a complex biological film that develops naturally after a few days of installation on the surface of the sand, and a physical barrier that helps trap/filter suspended matter in the water.

In late 1980s Dr. David Manz from the University of Calgary, Canada adapted slow sand filters for household use (Duke et al. 2006). The BioSand filter is a slow sand filter on a household scale and just like the slow sand filter removes pathogens and suspended solids from water through a combination of biological and physical process. This process takes place in a column of sand and gravel (Figure 9).

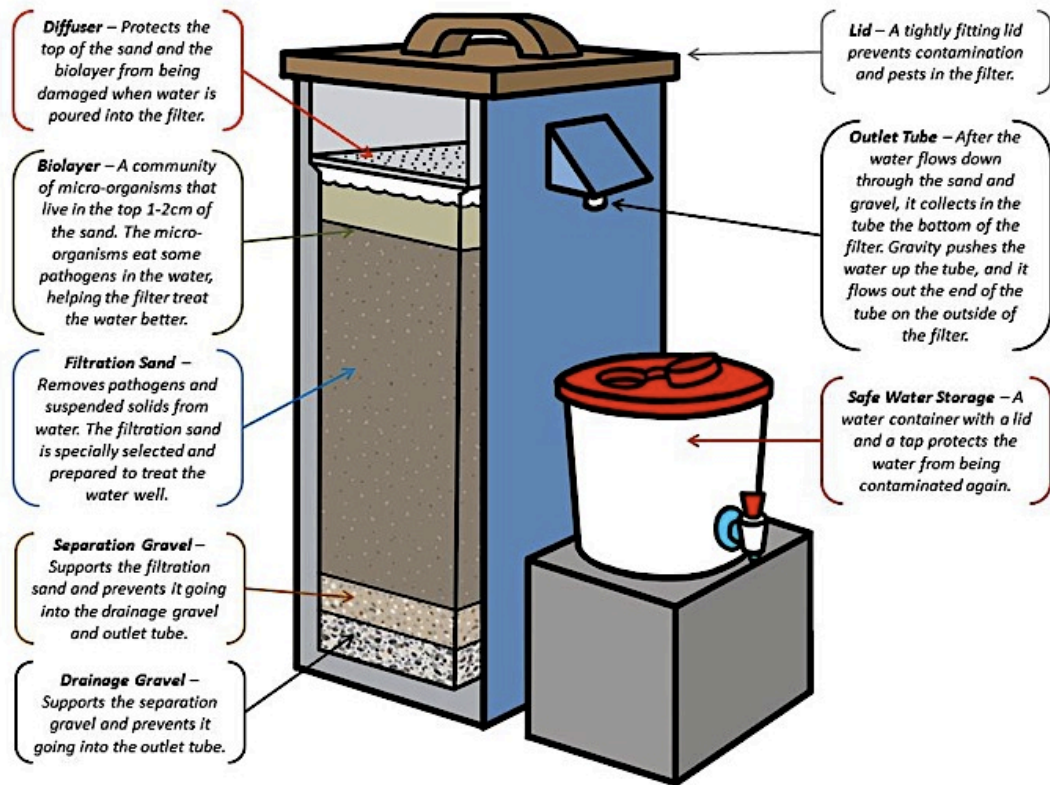


Figure 9: Diagram of a Biosand Filter (BSF) (Centre for affordable Water and Sanitation Technology)

The biological and physical treatment processes include: adsorption of bacteria by the sand, predation (the bio-layer eliminates some pathogens), and trapping (some pathogens get stuck in the sand column) (Figure 10).

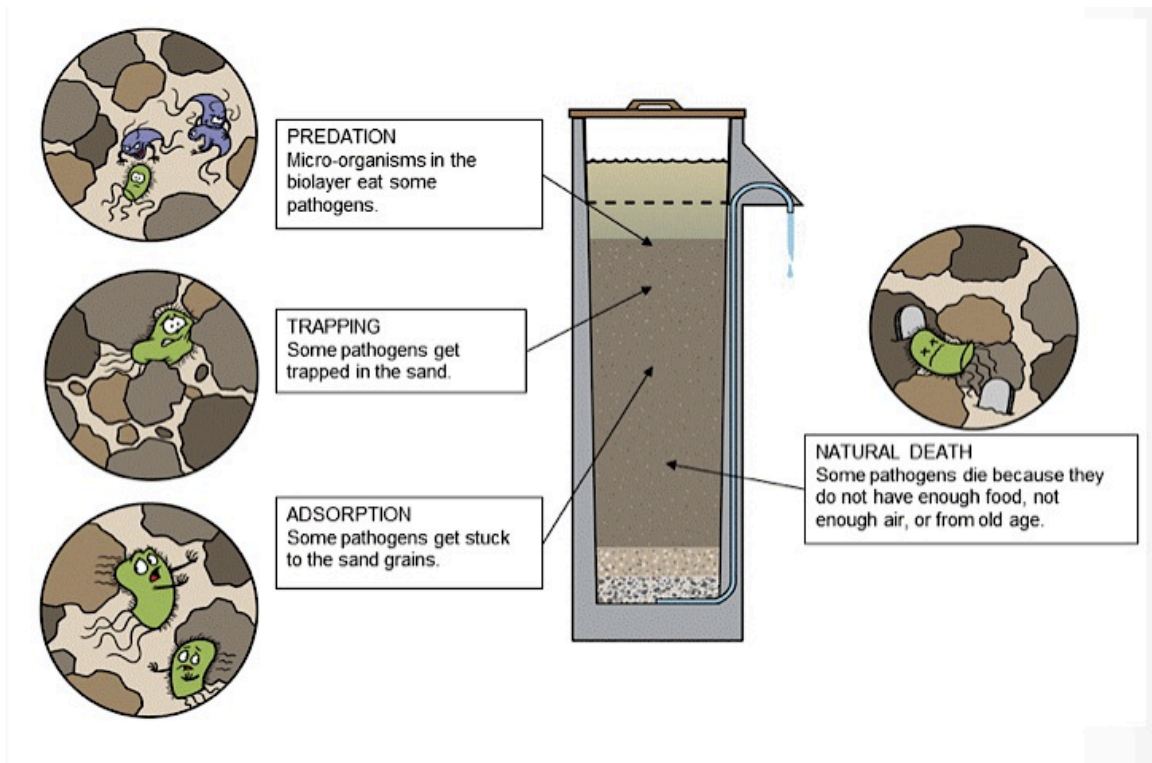


Figure 10: Diagram explaining the biological and physical treatments of BSF (CWAST 2013)

The BioSand Filter (BSF) has been the subject of extensive research. Studies have demonstrated that BSFs can treat up to 100% of worms and protozoa, up to 98.5% of bacteria, and between 70 to 99% of viruses, depending on their size. The filter is also effective in reducing turbidity by 95%, as well as iron concentrations by 95% (Stauber et al. 2006). However, the filter is not effective at treating dissolved contaminants in the water, including arsenic.

A US university (the Massachusetts Institute of Technology), a non-governmental organization in Nepal, and the Nepalese Public Health Organization designed the Kanchan Filter (KAF) after 5 years of laboratory and field research (Ngai et al. 2007). The KAF is an adaptation of the bioSand filter (BSF) with the capacity to treat arsenic

from contaminated water.

The mechanisms of arsenic removal are iron oxidation and adsorption. At the very top layer of the BSF a layer of non-galvanized nails was added (Figure 11). When the nails are exposed to air and water they rust quickly, producing ferric hydroxide, which is a perfect adsorbent for arsenic. When an effluent of contaminated water comes in contact with the ferric hydroxide (rust), the rust acts like a magnet and adsorbs the arsenic. The arsenic-loaded iron particles (flocs) are filtered by the sand column. The arsenic is not dissolved anymore, but forms particles with the ferric hydroxide that are big enough to become stuck in the sand column.

The effectiveness of KAF in removing arsenic has shown various results. A field study conducted by Ngai et al. (2007) showed that the KAF is 85 to 98% effective in removing arsenic from contaminated water. However another study demonstrated that the KAF is relatively ineffective in treating arsenic-contaminated water, and showed an average arsenic removal of between 39.4 and 74.9% (Chiew et al. 2009). This discrepancy has been attributed to the low iron concentration leached from the iron nails, and high influent in the water. Also the highest concentration of arsenic contaminated water that has been tested was about 900 ppb, which is lower than concentrations found in some wells in Bangladesh and Nepal.

The contrast in studies related to the KAF effectiveness, and also an attempt to test the highest concentration that the filter can effectively reduce to the accepted EPA level (10 ppb) will be the subject of this thesis.

ARTICLE MANUSCRIPT

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A laboratory assessment of BioSand/Kanchan arsenic water filters

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ABSTRACT

In Southern Asia more than 140 million people drink arsenic-contaminated groundwater, which represents a massive poisoning event with even greater health impacts than the Chernobyl, Ukraine disaster in 1986. Non-governmental organizations and international agencies have tried to reduce the impact of the tragedy by immediate health care interventions, and by creating affordable water treatment techniques.

The Kanchan arsenic filter (KAF) is a small-scale, slow sand filter adapted for household use. The KAF has an added layer of non-galvanized iron nails as a source of ferric hydroxide, which binds to the arsenic and forms an aggregate that can be then filtered by the column of sand and gravel. Research differs about the effectiveness of the KAF. Some research has demonstrated high performance of the KAF under field conditions, while other research has pointed out the defectiveness of the filters. The issue with field studies is that many field tests use quick chemical kits that are imprecise. This laboratory assessment used ICP-MS (Inductively Coupled Plasma-Mass Spectrometry), which is highly effective at measuring trace metals in water. The results dispelled the uncertainties about the KAF performance by reducing arsenic levels up to 2500 parts per billion to below 10 ppb, the acceptable level for drinking water.

Key words: Kanchan filter, arsenic water contamination, affordable water treatment technique.

Introduction

Over one billion people worldwide lack access to drinking water resources, and many more lack access to safe water as defined by the World Health Organization (WHO) in its Guidelines for Drinking Water Quality (2004). In Southern Asia alone over 140 million people drink arsenic-contaminated groundwater. Most countries that suffer from arsenic water contamination are developing countries with limited resources, making water treatment techniques with low costs and simple processes highly needed.

Affordable arsenic removal techniques clearly provide short-term solutions, especially in remote areas where arsenic concentrations are high. Nevertheless, the effectiveness of these technologies in the long run is critically dependent on both the willingness and the ability of the local communities to accept, operate, and maintain the technologies.

During the last decade many small-scale arsenic removal technologies have been developed, field-tested and used in research programs in Bangladesh and India. In the late 1980s, Dr. David Manz from the University of Calgary, Canada adapted slow sand filters for household use (Duke et al. 2006). The BioSand filter is a slow sand filter on a household scale and just like larger slow sand filters, it removes pathogens and suspended solids from water through a combination of biological and physical process, which take place in a column of sand and gravel (Figure 1). The Massachusetts Institute Of Technology (MIT), non-governmental organizations in Nepal, and the Environment and Public Health Organization (ENPHO) designed the Kanchan Filter (KAF) after 5 years of laboratory and field research (Ngai et al. 2007). The KAF is an adaptation of a BioSand filter (BSF) with the capacity to remove arsenic from contaminated water. The

mechanisms of arsenic removal are iron oxidation and adsorption. The KAF has an added layer of non-galvanized iron nails (Figure 1) that, once exposed to air and water, rusts quickly, and produces ferric hydroxide, which is a perfect adsorbent for arsenic. When an effluent of contaminated water comes in contact with the ferric hydroxide (rust), the rust acts like a magnet and adsorbs the arsenic. The arsenic-loaded iron particles (aggregates) settle and are filtered by the sand column. The arsenic is no longer dissolved, but instead forms particles with the ferric hydroxide that are big enough to be captured in the sand column.

Testing is a key component of any arsenic mitigation program. It is more difficult to test for arsenic than for other water contaminants, because of its chemical properties; however, there are various available methods to test for arsenic in the lab and in the field. The most common field testing methods are based on arsenic reduction to arsine gas, which then reacts with other chemicals on the test paper, or indicator tube to produce color change. With the regard to laboratory testing many techniques are used. These range from low to high sophistication and cost: Anodic Stripping Voltammetry, Graphite Furnace Atomic Adsorption Spectrometry (GF-AAS), Flame AAS, to Inductively Coupled Plasma Mass Spectrometry (ICP-MS). We chose ICP-MS for this laboratory evaluation.

The advantage of using field kits is the large number of samples that can be tested in a short period of time, which is perfect for a preliminary testing of new areas to have an estimation of the water toxicity. Field kits are also easy to use, which is important in the affected communities. Nevertheless, the overall accuracy of field tests is lower than the laboratory tests, because of the large margin of errors of the kits and also because of

the potential for human error reading the results. On the other hand laboratory testing has the advantage of being more accurate and can build a longer-term capacity for general water quality monitoring, but requires a longer testing period, complicated-costly equipment, and trained staff, and technicians. The appropriate testing tool can be determined by the purpose of the testing. For example testing to find out if the water is toxic or not in a remote area, a field test is the best to use; for a testing the capacity of a filter in treating arsenic it is best to use a laboratory technique because of the high precision of such tools.

The purpose of this study was to evaluate the performance of the KAF in a laboratory set up, by testing for the highest concentration that the filter can reduce to an acceptable level of arsenic in the water (below 10 ppb).

Methods

The KAF manufacturing procedure

The Kanchan filter (KAF) was designed to be an affordable treatment method that can be entirely built with locally available materials and in collaboration with a local population that can be easily trained. The KAF consists of a column of gravel, sand, and a layer of non-galvanized iron nails. Friendly Water For the World, a not-for-profit NGO based in Olympia (WA, USA) provided six concrete filter molds for this study. The molds were transported to The Evergreen State College laboratory (Olympia, WA) where the experiment took place. The filters were then filled with gravel and sand as shown in Figure 2-1.

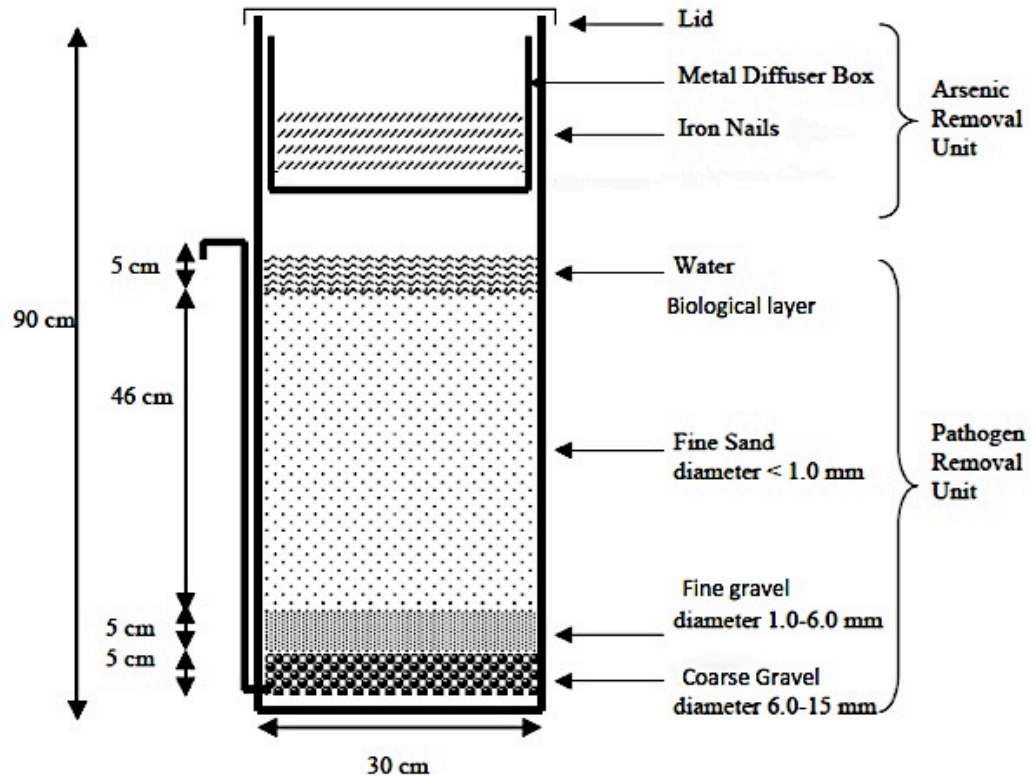


Figure 1: Cross-section of the Kanchan Arsenic Filter. The widths of each layer are as used in the experiment

The gravel was sifted with a sieve to make sure it was all the same size then washed vigorously multiple times until there was no turbidity in the water. We made sure that there were no biological remains in the gravel or the sand.

The first layer of coarse gravel was compacted and leveled before the second layer of smaller gravel was compacted and leveled. After the gravel was in place one and a half buckets of water were poured into the filter. It is necessary to have water in the filter before the sand goes in to avoid any air pockets in the filter. The sand layer is 5 cm below the water outlet level to allow the establishment of the bio-layer. The sand used for this experiment is commercially available for its use in industrial filtration products especially as pool filter sand. After the sand was in place and leveled, a metal diffuser was then

added to hold the 4.5 kg of non-galvanized iron nails and also to protect the bio-film layer from being disturbed every time water is added. At this stage all the constituents of the filter are in place and the filter is ready for “ripening”. The ripening time is the time needed for the biofilm to grow to maturity. It can take from a day to several weeks according to the water temperature and chemistry. A study conducted by Bellamy et al. (1985) showed that a new sand column could filter up to 85% of the bacteria in the contaminated water. As the sand gets microbially conditioned, the pathogen removal capacity increases up to 99% (Bellamy et al, 1985). .

Experimental set up

After two days of the installation, the KAF filters were ready for use; however we allowed the filters to ripen for 60 days between the installation and the arsenic testing. During that period the filters were flushed with tap water every other day to avoid an overgrowth of the biofilm clogging of the filter. Before using the KAF we checked the distribution of the iron nails to make sure they were distributed evenly and that there were no big gaps in between the nails to ensure even contact with the effluent water.

Six filters were installed, five were used as experimental units and one was used as a control. Solutions of arsenic-contaminated water were poured through the experimental filters with pause times of at least 4 to 6 hours between each concentration. Tap water (6 L) was used for the control at each trial, Kanchan filtered water samples were then collected and analyzed by an Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Perkin-Elmer ELAN 9000 version 3.3).

Filters	Description
Filter 1 (control)	No Iron Nails or arsenic tap water added
Filter 2, 3, 4, 5, 6	Added 4.5 kg of non galvanized iron nails to the filter, and increasing arsenic concentration of arsenic to the tap water filtered by the 5 filters

Table 1: Description of the lab experiment filter arrangements

Analytical method and instrumentation

This study focused on measuring the arsenic concentration in the water filtered by the KAF. In addition, the iron concentration was measured to make sure that there was no excess of iron in the water from the iron nails. All analytical measurements were based on the EPA requirements for determination of trace elements in waters and wastes by ICP-MS, method 200.8.

Contaminated water preparation

Since this is an evaluation of KAF performance under laboratory conditions, and also because we did not have access to naturally arsenic-contaminated water, the effluent was made up by mixing 6 liters of tap water with increasing arsenic concentrations (Table 2).

Amount of arsenic (ml) added to 6 liter of tap water	Arsenic concentration (ppb) in the contaminated water before filtration
20 (10 ppm solution of As)	33.33
30	50
60	100
120	200
2.4 (1000 ppm stock solution)	400
4.8	800
6	1000
9	1500
12	2000
15	2500

Table 2: Quantities of arsenic added to 6 L of tap water to make up the contaminated water concentrations listed in the right column

As Table 2 shows, 2000 ppb was the highest concentration that was run through all five filters. Because of laboratory limitations the 2500 ppb concentration was run only through filter number 2. The 2000-2500 ppb concentrations were chosen as the highest concentrations we tested for because they are some of the highest concentrations naturally occurring in the field.

Sample collection protocol

After the same concentration of the effluent (contaminated water) was run through the 5 filters, samples were collected in 100 ml polypropylene bottles directly from the filter's faucet/outlet after 10 to 15 min of flowing water.

Only an average of 9.5 ml of the collected water were used to prepare the sample for ICP-MS analysis according to the detailed procedure attached in appendix A. The sample was filtered through a 0.45 μm filter (vacuum filtration) to eliminate any solid particles in the sample. The samples were then brought to 10 ml with 0.3366 g of internal standard (Gallium) and 0.2 g of 50% nitric acid. All glassware used in this experiment was acid washed for an average of 24 hours in a 4-mole nitric acid bath in order to eliminate contamination.

Sample analysis: Reagents and standards

Before the first sample was run, a series of laboratory preparations were done according to the EPA (Environmental Protection Agency) requirement in method 200.8. Five standards were prepared to make a standard curve (Table 3). The way the ICP-MS determines how much arsenic and iron there are in the samples is by comparing the counts measured for the selected isotope (arsenic and iron) to an external calibration

curve that was generated for that element. The calibration standards or external standards are presented in Table 3. Arsenic 10 ppb and 1000 ppb are respectively the lowest and the highest concentrations I used for the calibration curve, with 10 ppb being the accepted concentration limit for arsenic in drinking water. For details of the preparation of standards refer to appendix A.

External standards contained iron concentrations as low as 300 ppb (the safe concentration of Fe in drinking water) and the highest was 6000 ppb (the heights concentration found to be leached from the filters).

External Standard	Final As concentration (ppb) in autosampler tube	Final Fe concentration (ppb) in autosampler tube
Standard A	10	300
Standard B	50	1000
Standard C	100	3000
Standard D	500	4000
Standard E	1000	6000

Table 3: Concentrations of Arsenic and Iron in the 5 external standards

Statistical analysis

The effectiveness of the KAF in reducing arsenic concentration in contaminated water was assessed by analyzing the laboratory data using a simple regression between the arsenic concentration before and after filtration. Data from all 5 filters were compared by analysis of covariance using JMP software.

Results

Arsenic removal

The raw data as measured by the ICP-MS are presented in Table 4 and summarized in Figures 3 and 4. The table shows that the KAF percentage effectiveness ranges from 89% to 99.9% corresponding to initial arsenic concentrations from 50 to 2000 ppb respectively.

Arsenic concentration Pre Filtration	Filter 1 (control)	Filter2	Filter3	Filter4	Filter5	Filter6	% Effectiveness	Mean
50	2.547	5.666	4.689	7.22	4.966	4.84	89.0	5.4762
100	3.278	3.558					96.442	3.278
200	3.724	3.124	2.456	2.515	2.57	2.214	98.7	2.5758
400	3.791	3.556	2.571	2.144	2.36	2.507	99.4	2.6276
1000	3.762	3.94	3.108	2.654	2.577	2.675	99.7	2.9908
1500	3.672	3.889	3.117	1.86	2.7	1.169	99.8	2.547
2000	5.445	7.019	2.111	1.637	2.205	2.375	99.9	3.0694
2500	5.584	7.236					99.6	5.584

Table 4: Arsenic concentration before and after filtration in the 6 filters

Figure 2 shows that post-filtration concentrations for all five filters combined were below the 1:1 line of concentrations prior filtration. The 1:1 line shows that for all the concentrations that the filters were tested for were reduced to almost zero.

The statistical regression results presented in Figure 3 shows that the average of post-filtration concentrations for all 5 filters combined were reduced to below 10 ppb, and there was no significant increase in post filtration concentrations based on the severity of the arsenic contamination.

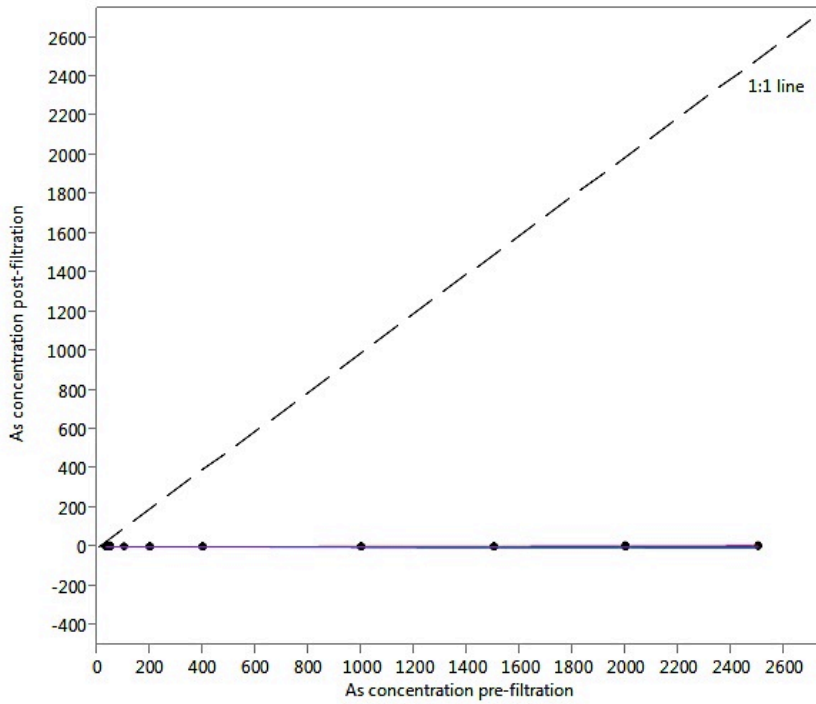


Figure 2: 1:1 line of concentrations pre and post-filtration of all 6 filters combined

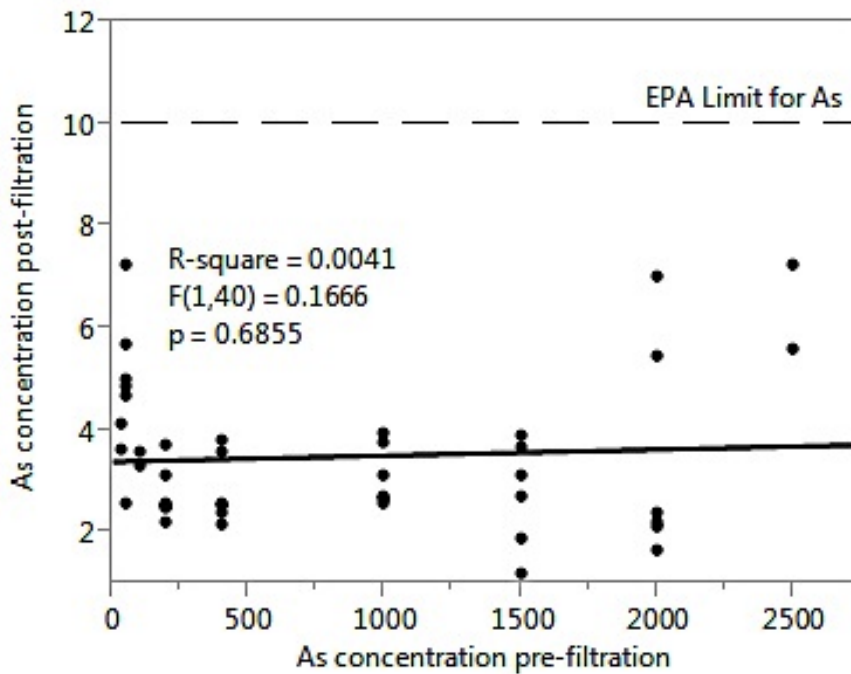


Figure 3: Average arsenic concentrations post-filtration regressed against pre-filtration concentrations for all 6 filters combined

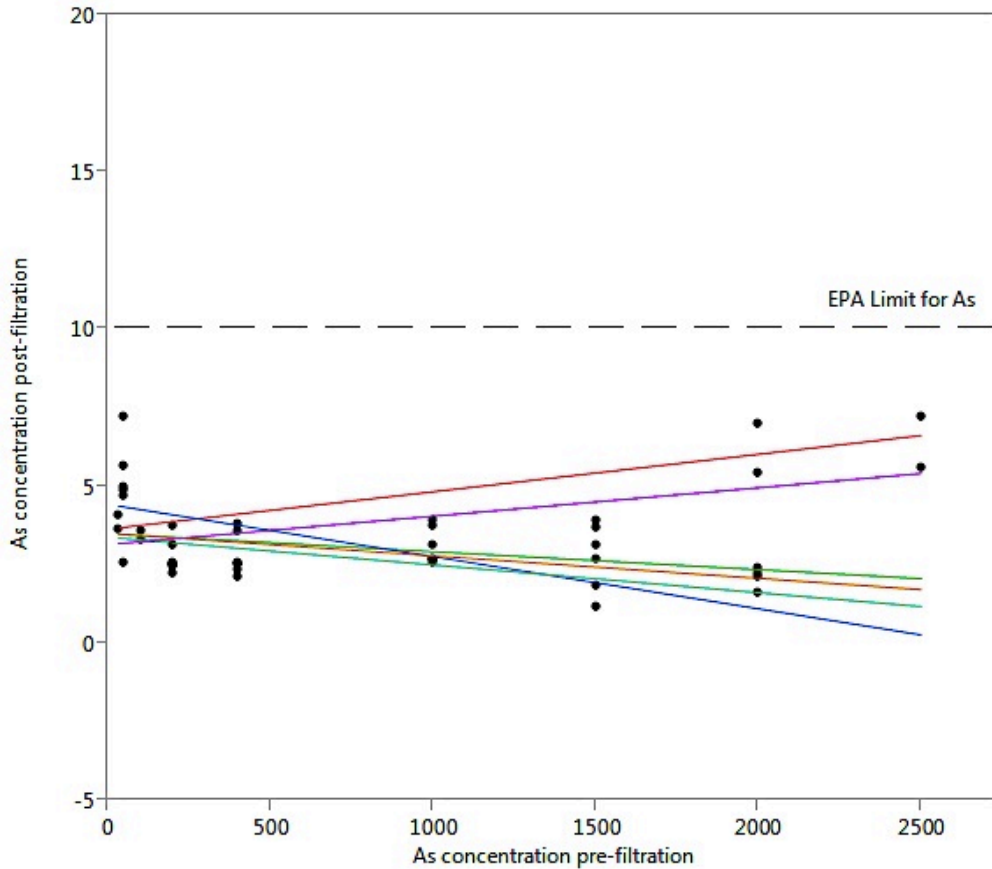


Figure 4: Arsenic concentrations after filtration regressed against pre-filtration concentrations for all 6 filters separately

The analysis of covariance (ANCOVA) of the row data showed slight differences in terms of how each filter reacted to increasing arsenic concentrations. Filter number 2 showed a slightly lower capacity in reducing arsenic concentration in contaminated water. The rest of the filters showed a similar trend in reducing arsenic concentration; however, there were no statistically significant differences among filters (Figure 4).

Flow rate

Filter	Flow rate on 5/10/14 In minutes	Flow rate on 7/15/14 In minutes
1	41	42
2	44	48
3	50	56
4	48	52
5	60	66
6	65	70

Table 5: Flow rate of 6 filters at the beginning and the end of the study

The Flow rate of 6 liters of tap water was measured twice: at the beginning and the end of this study. The flow rate of effluent during filtration is presented in Table 4. Measuring flow rate was important in this study to account for any possible decrease or increase in the flow, which could affect the filters' performances in term of the duration of contaminated water contact with the ferric hydroxide on the non-galvanized nails. The outflow rate for the first measurement did not significantly decrease throughout the experiment and was only an average of 4 minutes faster than the second measurement.

Discussion

The outcome of this research was beyond our best expectations, considering the high concentrations that the filters were able to reduce to below 10 ppb. These results revealed excellent performance of the KAF under laboratory conditions. The filters were able to reduce 2000 ppb to an average of 3.06 ppb, with an effectiveness that ranged between 89 and 99.9 ppb. Knowing that the allowed arsenic concentration in drinking water where the filter is already in use is 50 ppb, the KAF is providing safe water that meets the even

more strict limits of 10 ppb of arsenic level in drinking water.

The KAF effectiveness in removing arsenic in the field has shown various results. A field study at the Massachusetts Institute of Technology conducted by Ngai et al. (2007) showed that the KAF is 85 to 98% effective in removing arsenic from contaminated water (Ngai et al. 2007; Makhan Maharjana et al., 2009). However, another study demonstrated that the KAF was relatively ineffective in treating arsenic-contaminated water. In this study the average arsenic removal fluctuated between 39.4 and 74.9% (Chiew et al. 2009). These results were attributed to the low iron concentration leached from the iron nails, and high arsenic concentration in the water. The highest concentration of arsenic tested in both these previous studies was 900 ppb, which is lower than concentrations found in some wells in Bangladesh and Nepal.

Filter number one was used as a control, with no added iron nails or arsenic to account for any arsenic that might already exist in tap water, and/or the material used to build the filter. To further investigate the origin of the average arsenic values measured in filter 1 (3.9 ppb), I made a separate analysis of the tap water that revealed a value of 1.143 ppb which is consistent with the value of 1.001 ppb given by the official website of the city of Olympia. This shows that the additional arsenic in filter number 1 might have leached from the sand and gravel used to manufacture it, and/or it might be due to the instrument (ICP-MS) detection limit.

It is not statistically significant, but filter number 2 had a slightly lower rate in reducing the initial arsenic concentration compared to the other filters. This could be explained by the fact that filter 2 had the one of the highest flow rates compared to the rest of the filters and may not have allowed the same period of contact with the ferric

hydroxide on the surface of the non-galvanized nails, which was the issue with the study that showed low KAF effectiveness. A proper installation of the filter is critical to its performance. For example the amount of iron added to the filter determine the amount of ferric hydroxide available for arsenic adsorption in the contaminated water, and an appropriate installation of the sand and gravel layers determines the flow rate and thus the contact period with the ferric hydroxide.

The range of arsenic concentrations (10 ppb to 1000 ppb) used for the standard curve was higher than the range of arsenic concentrations in the filtered water (all less than 10 ppb). For further research the standard curve need to reflect the range of the expected concentrations in the samples.

It was observed that all five filters have higher performance for medium to high concentrations (100 to 1500ppb) than very low concentrations (50ppb and lower); however this was not statistically significant, and can be subject of further research. A possible theory that again needs further research is that high abundance of arsenic in the water coupled with abundance of ferric hydroxide can lead to a formation of bigger molecules that can be filtered more efficiently by the column of sand and gravel. This is in contrast to low arsenic concentrations that may forms aggregates not big enough to be trapped in the column of sand and gravel of the filter. This could be the subject of further research.

Water hardness is a factor that also needs to be considered in this study. The City of Olympia's drinking water is considered "slightly hard" at 55-60 milligrams per liter (mg/L) (City of Olympia 2014). This might have affected the filters' arsenic removal capacity. Hardness blocks the oxidation process and does not allow the iron to bond with

arsenic and form the aggregates that can then be filtered by the column of sand and gravel. Usually the groundwater pH in the affected areas in Bangladesh, India, and Nepal is about 6.9, (Jiang et al. 2012), which might suggest that the filters would have a better performance in these areas

The filters have not been used regularly and the amount of water run through them (6 to 23 liters daily) is lower than it would be under field use. Also the pause time allowed for the filter in other studies is lower than the pause time in this study, which might be a possible reason why the filters were highly effective.

Conclusion

This evaluation of the effectiveness of Kanchan Arsenic Filters (KAF) has shown high performance of the filters under laboratory conditions. This research also shows that arsenic in contaminated water can be removed by a simple filtration technique using available material without having to use chemicals or electricity, which are the weaknesses of other available arsenic removal methods. Due to lack of time and resources, the study did not examine the relative arsenic removal efficiency over long time scales. A long-term study is needed to further investigate the performance under heavy and frequent use of the filter, which would better replicate the conditions of field use.

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DISCUSSION & BROADER IMPACTS

An estimated 130 million people are potentially exposed to arsenic in drinking water at concentrations above 10 ppb. This number might increase as new regions are further tested. While some countries such as Bangladesh, India, and China are at an advanced stage in their arsenic mitigation programs, other countries are still in the early stages and need collaborative assistance to overcome this deadly issue. Even though lessons learned and the experience gained from ongoing mitigation programs are being used as a guide for countries at an early stage of the mitigation process, careful attention needs to be brought to the specificities of each receiving community. Many health issues are the direct results of arsenic contamination. These issues are translated into more complex and indirect economic and social effects. Finding ways to attenuate the disastrous effects of arsenic contamination is critical for the healthy development of affected communities, and depends on the social, economic, and cultural structure of these communities.

Technical performance, social acceptability, and economic affordability were the criteria of a survey done in Nepal, which revealed that the KAF is the best among the available arsenic removal techniques (Maharjan et al. 2009). Proving its effectiveness for high concentrations of arsenic up to 2500 ppb will help its acceptance in new communities. However ongoing support and education on effective use of the KAF are still needed to implement and determine the benefits and estimate the value of using the KAF for further introduction to new communities (Serafini 2005). This is necessary because it is the most efficient way to convince the rural people in affected areas to change their beliefs and current water drinking practices. Interviews revealed beliefs such as “I have been drinking this water for many years and I have never been sick” or “This

filter is expensive, and I cannot afford it” (Serafini 2005). Arsenic water contamination combined with the poor financial situation of local populations, and their lack of awareness of the dangers of drinking toxic water creates a very complex situation. To solve this complexity a holistic program needs to specifically address social, economic, and cultural aspects of the targeted communities.

SOCIAL & CULTURAL IMPLICATIONS

Social problems always restrict the continuous and sustainable use of new arsenic removal methods (Maharjan et al. 2009). During the past decade, because of illiteracy, many villagers in Bangladesh and Nepal confused skin lesions caused by arsenic poisoning with leprosy, which the villagers consider a contagious and lethal disease (Alam et al. 2002). This led many people with arsenic skin lesions to hide their symptoms to avoid being excluded from the community. When family members noticed the symptoms, they tended to avoid direct contact with the affected person. The exclusion response can even go as far as not allowing the sufferers to appear in public. Children did not attend school, adults did not attend cultural or religious events, and workers lost their jobs. Often when an employee loses a job, no other local employer will provide them with alternative jobs (Alam et al. 2002). This has caused a significant drop in Bangladesh and Nepal economy.

Women and children are usually the most affected population in the community (Alam et al. 2002) because they are physically susceptible to arsenic poisoning and are socially vulnerable. In poor rural households, adult females are undernourished and vulnerable to disease. If a woman shows symptoms of arsenosis, the best-case scenario is that the husband will send her to her parents’ house to be treated. In most cases the

husband seeks a divorce. As a result women and their children find themselves with no place in the society, which increases the poverty level in the community. Parents with affected young women have no chance of marrying their daughters without offering an enormous dowry, which is already a difficult social problem to be further complicated with the arsenic issue (Alam et al. 2002).

ECONOMIC IMPLICATIONS

Flanagan et al. (2012), estimated that US \$12.5 billion was the economic loss undergone by Bangladesh in 2009 due to arsenic contamination. This loss was calculated by measuring the productivity of per capita gross domestic product (GDP). The loss in GDP attributed to death does not reflect health costs and other costs to society. For example life expectancy in the US is higher than in Bangladesh; however any loss of life in Bangladesh would translate into greater reduction of lifetime productivity. This is because the time people spend working in Bangladesh is higher than in the US, thus the calculated GDP loss underestimates the full economic burden. This economic load is expected to increase when better treatment methods will prolong the lives of people with chronic arsenic poisoning. The latency period related to arsenic-related diseases lasts for several decades after exposure. In best conditions the latency period and exposure are expected to be completely eliminated by 2030, as arsenic exposure of fetus need to be considered as well. If about 90 million of children are born between 2000 and 2030, 1 to 5 million of their deaths will be attributed to exposure to arsenic concentrations above the Bangladeshi national level of 50 ppb (Flanagan et al. 2012). Failure in sustaining arsenic mitigation programs can result in disastrous deaths among the exposed population. These

predictions were based on qualitative and semi-quantitative analysis, which present serious factor to consider for future mitigation and evaluation programs.

As mentioned earlier, social and cultural behavior has resulted in a massive loss of jobs that in turn affected the economic situation of the country. In Bangladesh alone between 20 million and 45 million people are exposed to arsenic concentrations above 50 ppb, according to a national water quality survey conducted in 2009 (Flanagan et al 2012). Based on a local study in Bangladesh, concentrations above 50 ppb are responsible for 24,000 adult deaths in the country annually (Flanagan et al. 2012). Continuing losses in productivity could result of loss of \$1.1 billion US over the next 20 years in Bangladesh. Supplying safe drinking water is not only a health emergency, but also an economic imperative. Providing safe water solutions for a village of 50 people per water point would cost about 44 to 49 million US dollars depending on the choice of arsenic removal unit (Flanagan et al 2012). A KAF costs about \$20 US dollars and is sufficient for about 20 people (Ngai 2006). This is a very affordable safe water solution that would reduce economic losses and prevent the potential economic disaster in Bangladesh in absence of water treatment units.

The KAF is a slow filter, and it needs to be cleaned periodically, but it has high performance and is highly affordable. Many organizations are working on providing clean water programs to affected communities; however, more programs are needed. Friendly Water For the World (FWFW), is a non-profit organization based in Olympia WA, with the mission of expanding access to low-cost clean water technologies and information about sanitation and health to people in need. FWFW also focuses on empowering people to take charge of their water quality, through explicit trainings that

provides useful skills on how to build the BioSand filters and maintain them. The trainings also create opportunities for small enterprises to start manufacturing filters that benefit the community as a whole. These enterprises create job opportunities and bring the community together around one shared benefit despite sometimes religious and ethnic differences.

Dedicated and well-organized volunteers run FWWF, people who do not hesitate to travel to different countries in order to provide the necessary trainings and identify new communities in need of safe drinking water. The organization is active in Kenya, India, Uganda, and Burundi and it is looking to expand its program to other countries. For this reason FWWF provided 6 BioSand filters for this research to evaluate their effectiveness in treating arsenic before they consider expanding their services to arsenic-contaminated regions. The results of this thesis exceeded our highest expectations and the FWWF is now considering a mitigation program in arsenic-contaminated regions.

ARSENIC MITIGATION PROGRAMS

There are many NGO's, agencies, and international institutions that are looking for affordable arsenic removal techniques. However, a vital part of the implementation of these techniques is missing. Knowledge and acceptance of the arsenic contamination issue among the affected communities is a key component to a successful introduction of arsenic removal methods into the communities. A study of the benefited community needs to be implemented even before the product design. Potential users need to be aware of the scope of the problem and the benefits of arsenic removal.

Reports have shown differences in terms of the best method to approach arsenic water treatment. The arsenic removal method depends on water availability, and the needs and cultures of the affected communities. Thus it is necessary to do a preliminary investigation before the introduction of the arsenic removal method, or at least an ample presentation of the method to convince people to use it and maintain it for a sustainable health benefits. According to the UNICEF, removing arsenic from drinking water is the last option for providing clean drinking water because it is technically challenging, it is difficult to ensure the proper operation and maintenance of the removal units, and because of the cost of acquiring and maintaining the units. The UNICEF report stated that the best options for alternative safe drinking water is a combination of water sources and technologies. Furthermore the most common option is the use of household rainwater harvesting during the rainy season and shared boreholes during the dry season.

There are two types of mitigation programs, programs that provide prevention, and others that provides solutions for arsenic contamination. To prevent further exposure to arsenic poisoning, the Bangladeshi government developed a program to screen all contaminated tube wells and the degree of contamination. Tube wells of higher than 50 ppb were painted in red and less that 50 ppb with green. People were advised to drink safe water after any available treatment or from alternative sources, such as rainwater and surface water after the use of disinfectant. With no or very limited education programs coupled with very limited safe water alternatives, people continued drinking contaminated from what is available and easy to access. In the region of Comilla in Bangladesh, access to clean water decreased from 93% in 2007 to 83% in 2009. This can be attributed to the continual installation of new shallow contaminated tube wells, and

most importantly to the fact that memories of arsenic awareness-raising programs have begun to fade. Past achievement can be lost if arsenic mitigation efforts are not sustained.

On another hand, social acceptability and sustainability are crucial factors to be considered when choosing any mitigation strategy. The greatest improvement in access to clean water was achieved among the poorest populations, for their eagerness to accept anything that could improve their health situation. On another hand, middle class populations have less acceptability to simple arsenic removal technologies. They do not show a continuous use of the introduced simple arsenic removal methods as they look at it as going back to the use of rudimentary methods, and want more sophisticated technologies even if they cannot really afford it.

ARSENIC-LADEN WASTE

Co-precipitation of arsenic and iron hydroxide in an arsenic removal unit produces a certain quantity of sludge containing a good amount of arsenic. Arsenic-laden waste is an inconvenient factor to most arsenic removal technologies including the KAF. Arsenic-laden waste is almost as important as arsenic removal from drinking water because of its hazardous potential to be recycled back to drinking water sources. During the arsenic removal process, about 5 to 7 Kg of arsenic have been found per m³ of sludge generated, which is classified hazardous by the US EPA.

According to Center for Affordable Water and Sanitation Technology (CAWST), the KAF lifespan is 30+ years depending on the water condition: arsenic concentrations, suspended solids and other contaminants. Furthermore, based on the surface contact of the nails, the nails may need to be replaced every 2 to 3 years (once arsenic binds to ferric

hydroxide it cannot be separated again). Thus every 30+ years the filter will need to be replaced and the old ones are potentially arsenic-laden waste that needs to be disposed of. The KAf has relatively lower arsenic-laden waste than other arsenic removal methods because of the size and the lifespan of the filter.

Banerjee and Chakraborty (2005) found a suitable solution for disposal and stabilization of arsenic-bearing sludge. They used the sludge to produce briquettes, cement sand-mortar and concrete, by mixing up to 10,18, and 40% of volume respectively with the other common ingredients. The final product was found to be leaching less than 0.2 g/m^3 as required by the Ministry of Environmental & Forest, Government of India.

In another study arsenic-laden sludge has been mixed with concrete and packed into roadways to minimize its mobilization and leaching. The concrete was then crushed to particles $< 9.5 \text{ mm}$ diameter prepared and analyzed by ICP-MS. The results showed levels well below US EPA regulatory limits (Addy et al. 2011). This Concrete stabilization has been tested on ECAR arsenic-laden sludge for a landfill disposal in the US (ElectroChemical Arsenic Remediation, described in the literature review of this thesis). In developing countries this might be a luxury that cannot be afforded. Many arsenic technological solutions have been found to be successful; however, the safe disposal of the sludge produced by its treatment still remains a challenging problem to be sorted out for developing countries.

CONCLUSION

The research explored in this thesis was designed to verify the effectiveness of the Kanchan Arsenic Filter (KAF). Here we show that the KAF is effective at reducing arsenic concentrations of 2000-2500 ppb to below 10 ppb. The KAF fits the needs of the majority of arsenic-affected communities. It employs simple technology, uses no electricity, and can be built with locally available and inexpensive materials.

Raising awareness and building capacity is not a task that one entity alone can do to help attenuate the amplitude of the arsenic disaster. The approach needs to be holistic and include partnerships with local NGO's, micro-financial institutions, and local village groups. This is the best strategy to be part of the social network to get the people's trust and engagement faster. Women play the important role as water caretakers so promotional campaigns that target women have a better chance to be well-received. Education to increase awareness of arsenic contamination as well as changes in traditional drinking, sanitation and hygiene practices are vital to attain behavior changes and to optimize mitigation programs.

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APPENDIX A: METHODS

Trace Metal Analysis of arsenic contaminated water by ICP-MS

Experimental set up

My experiment is an attempt to answer the question: *What is the laboratory performance of the Kanshan Arsenic Filters (KAF) in treating arsenic in drinking water?*

I'm testing for the highest concentration that the filters can effectively reduce to the safe concentration of arsenic in drinking water (10ppb) according to the EPA (2012). The highest concentration I'm testing for is 2500 ppb (Ngai et al 2003).

The contaminated water will be made, by mixing 6 liters of tap water with increasing arsenic concentration, as it will follow in table (1). The contaminated water will be poured into the filters and then a sample will be collected and analyzed by ICP-MS.

Because iron is added to the filters (non-galvanized nails), I'm also going to test for Fe concentration in the filtered water, my lowest concentration is 300ppb (the safe concentration of Fe in drinking water) and the highest is 6000ppb (the heights concentration found to be leached from the filters).

Replicates and controls (6 KAFs total):

- One control (no arsenic added for all the trials)
- Five replicates that each will run the same increasing As concentration

Section 1: Equipment and glassware

Glassware/material	Size	Quantity
Micropipette	100-1000 μ L	1
Box pipette tips	100-1000 μ L	1
Filter paper	45 μ m	102
Analytical balance		1

Vacuum filtration system (Buchner funnel, tubing, disposable dropper)	Filter flask (100ml wide mouth)	8
Thermometer	50-100°C	1
PP bottle	125mL	24
PP bottle	1 L	6
ICP-MS autosampler tubes	50ml	360
ICP-MS autosampler tubes	10 ml	20
Ribbed watch glasses	(to fit 50mL beaker)	4
Beakers	50mL	12
Volumetric flasks	100 mL	10
Graduated cylinders	1000 mL	6
	2000 ml	6
Volumetric flask	1000 mL	6
Bottles	10 ml	6
Volumetric pipette	1ml	10
	2 ml	10
	5 ml	10
	10 ml	10
	15 ml	10
	25 ml	10
Bucket	12 L	6

box of Polyethylene gloves	small	1

PS: it's recommended that sampler, sample bottles, filtration system, acidification vials, tubing need to be a Teflon PFA or Teflon FEP.

Section 2: Contaminated water preparation

The filters were found to be effective in removing arsenic with a range of 87% to 96% (mean = 93%) Figure.2 (Ngai, 2003). The highest concentration tested for was about 900 ppb and the lowest is 200ppb (Ngai, 2003). However in other regions the highest concentration in aquifers was found to be over 2000 ppb. This is why the highest arsenic concentration used in this research is 2500 ppb.

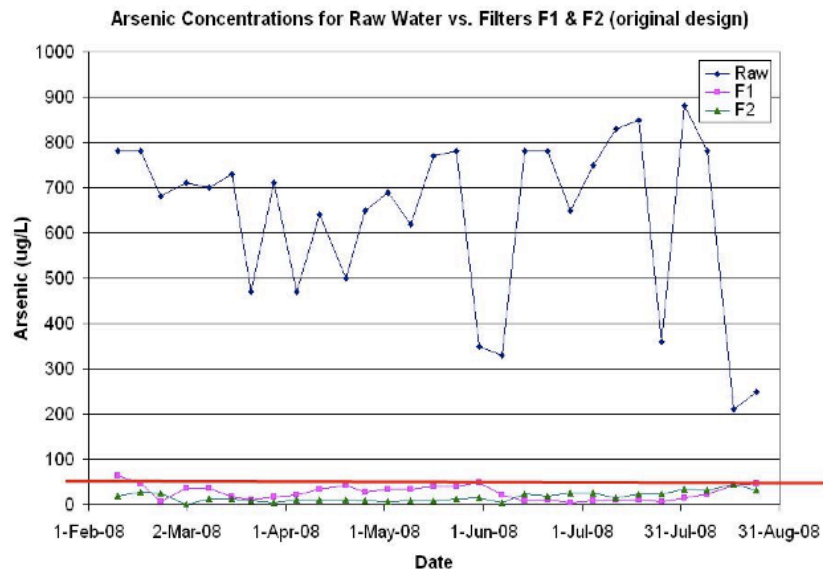


Figure 2. Arsenic removal effectiveness

Source: Ngai, 200

Amount of arsenic (ml) added to 6 liter of tap water	Arsenic concentration (ppb) in the contaminated water before filtration
20 (10 ppm solution of As)	33.33
30	50
60	100
120	200
2.4 (1000 ppm stock solution)	400
4.8	800
6	1000
9	1500
12	2000
15	2500

Table1: Preparation of 6 liters (~ 3 gallons ~) of contaminated water

Section 3 - Acid Wash Procedure:

*All equipment coming into direct contact with sample will be acid-washed

3.1 - 4M nitric acid bath

Add a 2.50 l acid bath container to 7.5 l of DI water (use a 1L graduated cylinder)

3.2 - Acid wash procedure

1. Inspect glass for cracks, damage
2. Inspect gloves for damage before wearing
3. Rinse all equipment first in hot soapy water, then DI rinse.
4. Ensure that all rubber components removed.
5. Using gloves, apron, face shield, and goggles, add equipment to acid washtub.
6. Ensure that there is enough room in acid washtub, and that no overflow occurs.
7. Ensure that equipment remains submerged

8. When acid washing is complete, remove equipment from tub to a small bin, being careful not to spill acid.
9. Rinse equipment three times in DI water, put in a big container with a lid and allow drying if possible.

Section 4: Sample collection

- Rinse a 100 ml bottle 3 times with the sample from the Kanchan Arsenic Filters
- Collect 100 ml from each of the 6 filters

Section 5- Reagent Preparation

Reagents stock solutions needed:

2.50 l of 70% HNO₃ stock solution
200 ml of 1000 ppm As stock solution
60 ml of 1000 ppm Ga stock solution
10 ml of 1000 ppm Fe stock solution

5.1- 1% Nitric Acid prep

1. Add 15.00 mL **70% trace metals HNO₃** to 1000 mL volumetric flask
2. Dilute quantitatively with DI Water to a final volume of 1000 mL, and transfer to 1000ml polypropylene (pp) bottle.

5.2- 50 % Nitric Acid prep

1. Add 71.43 g (50ml + 21.4307g) 70% trace metals HNO₃ to 100 ml volumetric flask (I changed the volume here to 100ml because I don't need a whole 1000ml of 50% HNO₃, but I'm not sure if I can measure the value I have here)
2. Dilute quantitatively with DI Water to a final volume of 100mL, and transfer to 100ml

polypropylene (pp) bottle.

5.3 - Internal standard intermediate

I'm using Ga as an internal standard for both As and Fe. The final concentration of internal standard in all solutions is 40 ppb.

To prepare an intermediate internal standard solution Ga 1999.1907 ppb add:

- 0.2001g of 1000 ppm stock solution of internal standard to 100.0908 g volumetric flask

Stock Solution	Volume of stock added to intermediate	Concentration internal standard in intermediate
Ga 1000 ppm	0.2 g (1.9991g)	2000 ppb (1999.1907ppb)

Table 2. Internal standard dilution (I'm using the same internal Standard for both As and Fe)

Section 6: External standard prep

External Standard	Final As concentration (ppb) in autosampler tube	Final Fe concentration (ppb) in autosampler tube
Standard A	10	300
Standard B	50	1000
Standard C	100	3000
Standard D	500	4000
Standard E	1000	6000

Table2: external standards final concentration in autosampler tubes.

6.1- As and Fe stock solution dilutions: Intermediate solutions

1. Arsenic 1 ppm Solution used for Standards A, B, C, and D:

Prepare 1 ppm As external standard intermediate from 1000 ppm stock solutions by adding 0.1 g As stock to a 100 ml volumetric flask. Dilute to 100 g quantitatively with 1% trace metals HNO₃ and transfer to 125 ml PP bottle. (This is the standard intermediate: diluted from the original stock)

2. Arsenic 2 ppm solution used for standard E:

Prepare 2 ppm As external standard intermediate from 1000 ppm stock solutions by adding 0.2 g Fe stock to a 1 L volumetric flask. Dilute to 100 g quantitatively with 1% trace metals HNO₃ and transfer to 125ml PP bottle

3. Iron 10 ppm solution used for Standards A, B, and C:

Prepare 10 ppm Fe external standard intermediate from 1000ppm stock solutions by adding 1 g Fe stock to a 100 ml volumetric flask. Dilute to 100 g quantitatively with 1% trace metals HNO₃ and transfer to 100 ml PP bottle

4. Iron 100 ppm solution used for standards D and E:

Prepare 100 ppm Fe external standard intermediate from 1000 ppm stock solutions by adding 10.00 ml Fe stock to a 1L volumetric flask. Dilute to 100ml quantitatively with 1% trace metals HNO₃ and transfer to 100ml PP bottle

6.2- Standard curve

1. Prepare standard E by adding:

- 25.0001 g of 2.0007 ppm As external standard intermediate

- 3.00001 g of 100 ppm Fe external standard intermediate to 50ml autosampler tube, recording weight.

- 1.0122 g of 2000 ppb internal standard intermediate, record weight (39.9817 is final Ga in the std)

- Dilute to 50.0026 gr with 19g of 1% trace metals HNO₃

2. Prepare standard D by adding:

- 25.0004 g of 1.0005ppm As external standard intermediate
- 2.0005 g of 100ppm Fe external standard intermediate to 50ml autosampler tube
- 1.0007 g of 2000ppb internal standard intermediate, record weight
- Dilute to 50.001gr with 22g of 1% trace metals HNO₃

3. Prepare standard C by adding:

- 5.00004 g of 10005ppm As external standard
- 15.0058 g of 10ppm Fe external standard intermediate to 50ml autosampler tube recording weight.
- 1.0002g of 2000ppb internal standard intermediate, record weight
- Dilute to 50.0025 gr with 29g of 1% trace metals HNO₃

4. Prepare standard B by adding:

- 2.5001 g of 1ppm As external standard intermediate
- 5.0053 g of 10ppm Fe external standard intermediate to 50ml autosampler tube
- 1.0415g of 2000ppb internal standard intermediate, record weight
- Dilute to 50.0046 gr with 41.5 of 1% trace metals HNO₃

5. Prepare standard A by:

First make another intermediate solution: 10.0017 gr external standard intermediate 1.0007ppm to 125ml PP bottle, recording weight. Dilute to 100.0014g with 1% trace metals HNO₃.

- 5.0000 g from this 100ppb As intermediate solution
- 1.5005 g of 10ppm Fe external standard intermediate to 50ml autosampler tube
- 1.0004g of 2000ppb internal standard intermediate, recording weight
- Dilute to 50g with 42.5ml of 1% trace metals HNO₃.

Section 7 - QC solution prep

As QC

1. Add 0.1014 g (0.1014g) of As 1000ppm stock solutions (Using a different stock than those used for external standards) to 100 ml (100.0011g) volumetric flask. Dilute to 1000ml with 1% trace metals HNO₃ and transfer to 100ml PP bottle.
2. To prepare 110ppb QC, add 5.5005 g (5.4531g) of this 1000 ppb intermediate to a 50 ml autosampler tube, recording weight (50.0193g). Add 1.0003g of 2000 ppb internal standard intermediate, record weight, and dilute to 50ml (50.0026g) with 1% trace metals HNO₃.

Fe QC

To prepare 3000 ppb QC, add 0.1503 g of 1003 ppm different stock solution of Fe, to a 50 g (50.0116) autosampler tube, recording weight. Add 1.0008 ml of 200 ppb internal standard intermediate, record weight, and dilute to 50ml with 1% trace metals HNO₃.

Section 3 - Sample filtration for ICP-MS (please note that this a microfiltration to eliminate any possible particles due to the KAF filtration)

1. 6 samples collected (bioSand filtered)
2. Filter by a 0.45 μ m filter through a vacuum filtration system
3. Place in sampling pp bottles different than the ones where the sample was collected

Section 8 - Sample and Blank Preparation

8.1: Sample preparation

1. Add 9.00 g of sample
2. Add 0.50 g internal standard from a 2000 ppb intermediate solution to each

- sample and replicate autosampler tube,
3. Dilute to 10 g with 0.20 g of 50% trace metals HNO₃, and record weight

8.2: Blank preparation

8.2.1: Method blank

Add 0.2003 g internal standard from intermediate solution to method blank autosampler tube and record weight. Add 1.2004 gr method blank to autosampler tube, record weight, and dilute to 10g with DI water (~1% HNO₃ matrix)

8.2.2: Subtraction blank preparation

Add 0.2007 g internal standard from intermediate solution to subtraction blank autosampler tube and record weight. Dilute to 9.8030g with **1% trace metals HNO₃**. (~1% HNO₃ matrix)

Section 9 - Cleanup

1. Following use all stock solution disposed of in metals waste containers.
2. Acid spills neutralized and disposed of in trash.
3. All equipment and glassware coming in contact with chemicals washed thoroughly in hot soapy water and DI rinse.
4. Filter paper, gloves, micropipette tips, and other disposables in trash.
5. The filters will be returned to the organization that donated them for research.
6. The after filtration water will be tested to make sure it's below 10ppb then it can be disposed in the sink. If the concentration is above 10ppm. The water might be re-filtered to lower the concentration to the acceptable level, if not it will be evaporated to reduce the volume, then put in labeled waste container for shipping

Section 10: Run list

Initial run list:

- Rinse blank
- Subtraction blank
- Standards (low to high): A, B, C, D, and E
- Rinse blank
- QC
- Run the sample
- QC

Final run list:

- Rinse blank
- Subtraction blank
- Standards (low to high): A, B, C, D, and E
- Rinse blank
- QC
- Run all 6 samples
- QC
- Run an other set of 6 samples (Different KAF filtration)
- QC

References:

1. United States Environmental Protection Agency; EPA method METHOD 200.8 DETERMINATION OF TRACE ELEMENTS IN WATERS AND WASTES BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY
2. United States Environmental Protection Agency; EPA method 3050B -ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS; Revision 2, 1996; (accessed May 29, 2013).
3. *Ngai, T., & Walewijk, S. (2003). The arsenic biosand filter (ABF) project: Design of an appropriate household drinking water filter for rural Nepal. Massachusetts Institute of Technology. Cambridge, USA*