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Arsenic Contamination in Groundwater in Vietnam

An Overview and Analysis of Historical, Cultural, Economic, and Political Parameters in the Success of Various Mitigation Options

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ABSTRACT

Although arsenic is naturally present in the environment, 99% of human exposure to arsenic is through ingestion. Throughout history, arsenic is known as "the king of poisons"; it is mutagenic, carcinogenic, and teratogenic. Even in smaller concentrations, it accumulates in the body and takes decades before any physical symptoms of arsenic poisoning shows. According to the World Health Organization (WHO), the safe concentration of arsenic in drinking water is 10 µg/L. However, this limit is often times ignored until it is decades too late and people begin showing symptoms of having been poisoned.

This is the current situation for Vietnam, whose legal arsenic concentration limit is 50 µg/L, five times higher than the WHO guidelines. Groundwater in Vietnam was already naturally high in arsenic due to arsenic-rich soils releasing arsenic into groundwater. Then, in the past half century, with the use of arsenic-laden herbicides dispersed during the Vietnam War and subsequent industrial developments, the levels of bio-available arsenicals has dangerously spiked. With the proliferation of government-subsidized shallow tube-wells in the past two decades, shallow groundwater has become the primary source for drinking and irrigation water in Vietnam. This is a frightening trend, because this groundwater has arsenic concentrations up to 3050 µg/L, primarily in the +3 and +5 oxidation states, the most readily available oxidation states for bioaccumulation.

This thesis argues that measures must be taken immediately to remedy the high concentration of arsenic in groundwater, which in Vietnam is the primary and, in some cases, the sole source of water for domestic consumption and agricultural production. Although there are numerous technologies available for treating arsenic in groundwater, not all of them are

suited for Vietnam. By analyzing the historical, cultural, economic, and political parameters of Vietnam, several optimal treatments of groundwater for drinking water emerged as most recommended, a classification that is based on their local suitability, social acceptability, financial feasibility, and governmental support. Further research on irrigation water treatment is proposed due to the need for sustainable crop production, the safe ingestion of rice and vegetables, and the continued growth of Vietnam's economy, which is heavily dependent on agriculture.

BACKGROUND

What Is Arsenic?

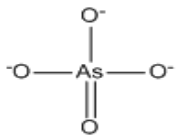
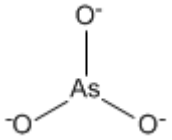
Arsenic is a natural element present in the atmosphere, pedosphere, hydrosphere and biosphere. It is the twentieth most abundant element in the earth's crust, fourteenth most abundant in seawater, and twelfth most abundant in the human body. There are four oxidation states of Arsenic: -3, 0, +3, +5. Gaseous arsine, in the form of AsH_3, is characteristic of the -3 oxidation state; elemental arsenic is characteristic of the 0 oxidation state; arsenite is characteristic of the +3 oxidation state; and arsenate is characteristic of the +5 oxidation state (Nguyen, 2008). Arsenic is water soluble and is almost never in its elemental form, rather, it forms compounds; these compounds are called arsenicals (Wang and Mai, 2004). From a geochemical standpoint, arsenicals are often associated with sulphurous minerals made up of sulphur, iron, gold, silver, copper, antimony, nickel, and cobalt; it is detected in more than 200 different minerals (Lievremont, *et al.*, 2009).

Toxicity of Arsenic and Effects on Human Health

Although arsenic is the twelfth most abundant element in the human body, it is highly toxic in any excess amounts. Arsenic is known as the "King of Poisons" and is mutagenic, carcinogenic, and teratogenic (Altug, 2003). An elemental arsenic concentration of 48 µg/L is the lethal dose for rats, which roughly translates to 125 mg lethal dosage for an average middle-age male (Altug, 2003 and Ahuja, 2008). This lethal dosage places arsenic in a highly toxic category in toxicology and food. Its toxicity is dependent on hydrogen potential (pH), redox potential (Eh), organic matter content, adsorption to solid matrices, and the presence of

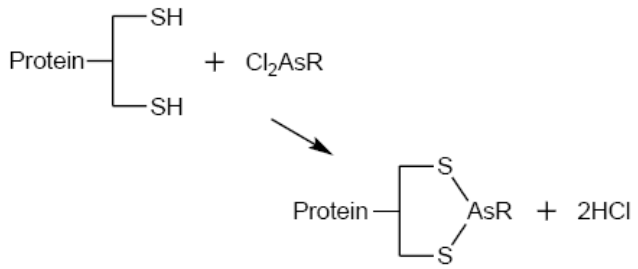
other substances, such as iron and magnesium. Arsenic cannot be produced by the human body; instead, 99% of human exposure to arsenic is through ingestion: 70% is from food and 29% is from water (Harte, *et al.*, 1991). Once ingested, arsenic continues to bio-accumulate in the body (Nguyen, 2008). The toxicity of arsenicals to living species is ranked as follows from most toxic to least: arsines, arsenites, arsenoxides, arsenates, pentavalent arsenicals, arsonium compounds, metallic arsenic (Wang and Mai, 2004). Because arsenic in groundwater is the main source of harm for humans, this thesis will focus on two arsenicals that are most abundant and toxic – arsenite and arsenate. Table 1 models these two arsenicals.

Table 1: Structure of Arsenate and Arsenite

	Arsenate	Arsenite
		
MW (g/mol):	138.9	122.9

The European Union (EU), World Health Organization (WHO), and Environmental Protection Agency (EPA) all recognize arsenic contamination as one of the major threats to human health, ranking it the second among top priorities in safety control (Brammer and Ravenscroft, 2009). The WHO guideline for safe levels of arsenic ingestion is a concentration of 10µg/L in drinking water and a limit of 100 µg/L in untreated water prior to being processed for consumption. The maximum safe limit of arsenic ingestion for an average middle-aged male is 220 µg per day (Ahuja, *et al.*, 2008). The term ingestion, as used here, includes drinking water from groundwater wells, and eating crops that grew from arsenic-infested irrigation water and animals that were fed food with arsenic additives.

The Cancer Assessment Group of the EPA puts arsenic in the top category for cancer-causing chemicals (Harte, *et al.,* 1991). It is no surprise that at even low concentrations, arsenic is responsible for lung, bladder, liver and skin cancers. Both arsenite and arsenate inhibit the energy-linked functions of mitochondria in the human cell. Arsenite compounds have an affinity to sulfhydryl groups in proteins and cause deactivation of enzymes. In addition, arsenite is re-absorbed faster in biological systems then arsenate. Arsenate competes with phosphate in cell reactions and uncouples oxidative phosphorylation so the high-energy bonds of adenosine triphosphate are not preserved (Bissen and Frimmel, 2003). Both of these chemicals ultimately cause birth defects in babies by infiltrating the placenta and creating cancers. At slightly higher concentrations, arsenic causes neurological damage, severe gastrointestinal disorders, impairment to bone marrow function, peripheral nerve effects, cardiovascular changes, painful neuritis of the upper and lower limbs, severe gastrointestinal damage, and other neurological abnormalities (Nguyen, 2008 and Harte, *et al.*, 1991). When arsenic enters the body, it inhibits more than 200 enzymes in human cells and binds to proteins in various mechanisms. For example, it can bind to the sulfydrylgroups of enzymes and induce functional impairments, chelate or complex thiol groups, serve as a structural analogue of the phosphate ion, interfere with the oxidative phosphorylation process, inhibit energy metabolism of cells, and replace phosphate in the DNA double helix, partially explaining the mutagenic, carcinogenic and teratogenic effects. In the body, arsines, arsenites, and arsenates undergo rapid hydrolysis with ATP and any other high-energy bond (Lievremont, 2009 and Laparra, 2009). Reaction 1 shows an example of bonding between arsenicals and proteins.



Reaction 1:

Proteins with sulfur containing groups react with arsenite to form products that cause biological malfunction.

(Wang and Mai, 2004)

One common visual symptom from approximately ten years of arsenic exposure at a concentration of 50µg/L is noncancerous skin lesions - pigmentation and warts, and can develop into arsenicosis, chronic arsenic poisoning. A notable and graphic disease from arsenicosis is the Blackfoot Disease (BFD), an endemic peripheral vascular disease.

Image 1:

Blackfoot Disease from approximately ten years of drinking 50 µg/L of arsenic contaminated groundwater

Sources of Arsenic in Groundwater

There are four primary fates of arsenic in soil environment. The first fate is that it reacts with and becomes retained by the solid phase of soil. The second fate is that it is volatilized into the atmosphere from biological transformation. The third fate is that it is leached out of the soil and into groundwater. The last fate is that it is taken up by plants from groundwater and groundwater accumulation of arsenic in top soil (Naidu, 2008). The last two fates, both directly affecting groundwater, are most worrisome as it greatly increases human ingestion of arsenic, and both relate to arsenic in groundwater.

Natural Sources

Arsenicals, in varying concentrations, are natural in the environment. The arsenical form is dependent upon pH, Eh, organic matter content, adsorption to solid matrices and the presence of other substances, such as iron and magnesium. There are two layers of soil that produces the abundance of arsenic and are the primary natural causes of arsenicals in soil and groundwater (Berg, *et al.*, 2006). These two levels are the sediment from the Holocene period loosely overlaying the sediment from the late Pleistocene period. The Holocene sediment layer, usually with a depth between 20 to 120 meters, could be as deep as 250 meters. It is the arsenic rich top layer that is more susceptible of weathering and groundwater flow. The Pleistocene sediment layer lies underneath the Holocene sediment layer and is rich in organic matter, has a low pH, and a lot of acid sulfate and pyrite, creating it a favorable reducing condition to release arsenic from the Holocene sediment (Nguyen, 2008).

Another natural source of arsenic is from the most abundant arsenical, arsenopyrite (FeAsS). Arsenopyrite is formed under high temperature in the earth's crust and has a concentration of above 100,000 µg/L of arsenic. It is unstable under aerobic conditions, so it oxidizes to iron oxides and releases arsenic into groundwater. Other notable arsenicals with the similar chemical properties are orpiment (As_2S_3) and realgar (AsS) (Liang, *et al.*, 2009). Arsenic can act as water-insoluble metal forming oxides and chlorides or as nonmetal forming acids (Wang and Mai, 2004). Arsenicals undergo cycles of oxidation-reduction, precipitation-solubilization, and adsorption-desorption processes alongside biological mechanisms. Some other geochemical causes of arsenic in groundwater and sediment include the dissolution of $Fe(OH)_3$ and desorption of arsenic under reducing conditions, oxidative decomposition of FeS_2

containing arsenic or desorption of arsenic from $FE(OH)_3$ due to decrease in pH under oxidizing condition. These arsenicals can also be liberated into groundwater when microbial degradation, through oxidation or reduction, of organic matter reduces ferric iron into the soluble ferrous form, where it is readily available for plant absorption. Figure 1 shows a generalized geochemical cycle of arsenic.

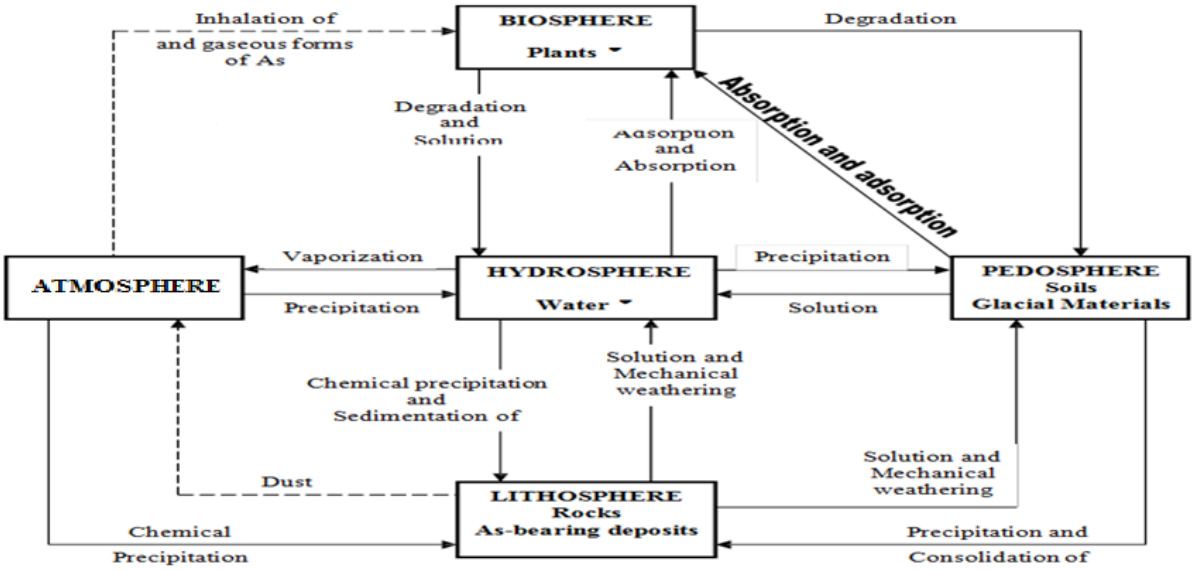


Figure 1: Generalized Geochemical Cycle of Arsenic
(as cited in Nguyen, 2008)

In alluvial or deltaic environments, analysis show that more than 70 wt% of arsenic in groundwater is associated with iron hydroxides in reducing conditions and is easily mobilized under redox conditions. (Nguyen, 2008)

Anthropogenic Sources

Arsenic concentrations are quickly rising due to anthropogenic sources. Smelting of nonferrous ores create arsenic trioxide that escapes into the atmosphere and then settles on neighboring fields and towns (Wang and Mai, 2004). Untreated arsenic filters are dumped into

landfills, leaking the arsenic back into the soil, albeit to different locations (Hug, *et al.*, 2008). Mine acid drainage lowers pH, creating even more favorable conditions for arsenic extraction from sediment to groundwater and speeds up the natural process--releasing arsenicals into groundwater (Reedy, *et al.*, 2007). When plants absorb the arsenic-contaminated groundwater, they retain the arsenic; when these plants are fed to poultry and livestock, the arsenic ascends the food chain and bioaccumulates. In addition to the arsenic laden crops fed to livestock, organic arsenic species are also added as a growth promoter in poultry and pigs (Naidu, 2006). The fecal matter of these affected livestock is then used as fertilizer, resulting in spiked levels of arsenic concentration in farming soil and groundwater (Laparra, 2005).

Arsenicals were also extensively used as herbicides, pesticides, and fungicides. Lead arsenate was often used as pesticides on fruit orchards, can accumulate up to 360 mg/kg in dry soil (Laparra, 2005). Sodium arsenite, a widely used fungicide before 2001, was the only known fungicide available for protecting grapevines from excoriosis (Lievremont, *et al.*, 2009). The extensive usage of arsenic based pest control resulted in a substantial accumulation of arsenic in soil. Electronics, pharmaceuticals, and ammunition factories also release large amounts of arsenicals into the environment through waste water and disposed products that leak arsenicals into the ground at dump sites (Reedy, 2007). At timber sites, timber is treated with a mixture of copper, chromium, and arsenic (CCA), and has been measured to have soil with arsenic concentration up to 10,000 µg/L (Naidu, 2006). The residence time of arsenicals in soil is in the magnitude of hundreds of years, as they are less interrupted by groundwater flow and can bind with iron (hydr)oxide as seen in layers of rocks from the Pleistocene era (Berg, *et al.*,

2006). Therefore, the accumulation of these arsenicals is dangerous and the problem is permanent.

WHY VIETNAM?

Additional Sources of Arsenic in Groundwater

In addition to the previously listed global sources of arsenic, Vietnam has even more sources of arsenic contamination that greatly affects arsenic levels in groundwater. These sources pose even higher dangers for all inhabitants in Vietnam.

Natural Sources

The soil layers in Vietnam, like most of South-East Asia, derive its sediments from the Himalayas washed down to the Mekong and Red River deltas from rainfall. The resulting arsenic rich sediment is absorbed to neo-formed iron oxides (Jessen, 2009). In addition, Vietnam's soil is conducive to the natural release of arsenic into groundwater. It has a thick Holocene period sediment layer of up to 50 meters deep with the overlying Pleistocene sediment composing of acid sulfate and pyrite, creating a reducing environment for arsenicals to release into the groundwater. In the Mekong Delta, there is also arsenious shale that release arsenicals into the groundwater as well (Nguyen, 2008).

Anthropogenic Sources – The Vietnam War

In addition to these natural causes, the Vietnam War's "Operation Ranch Hand" also greatly contributed to the arsenic contamination crisis in Vietnam. Operation Ranch Hand was a United States military project for aerial spraying of herbicides in southern Vietnam. The goal

was to clear out crops and foliage to achieve enhanced security, improve military intelligence, reduce cover for enemy resistance, increase availability of troops used for combat and reduce United States personnel casualties (Department of the Army, 1971).

Image 2: U.S. C-123 aircraft sprayed defoliant along powerlines in southern Vietnam in early August 1963

Between the first test in Kontum base in southern Vietnam in August 10, 1961 and October 1971, multiple chemicals were shipped to and sprayed over Vietnam (Young and Gegigani, 1988 and Nakamura, 2007). One major chemical used for all ten years of the war was Agent Blue; 65% of Agent Blue used was shipped to the 20th Ordinance Storage Depot in Saigon, and the other 35% was shipped to the 551th Ordinance Storage Depot in Da Nang. Agent Blue primarily targeted crops, especially cereals and grains (Department of the Army, 1971). The chemical was aerially sprayed by jets and since it is a desiccant, it dried plants, and prepared the areas for mass crop burning (Young, 1982).

To make things worse, the Department of Army's "Field Manual: Tactical Employment of Herbicides" recommended that the drums containing Agent Blue were to be washed out with water and left for the soil to absorb. Within those ten years, land damage from Agent Blue totaled two million hectares in southern Vietnam, primarily near Saigon and Da Nang, with over fifty-one thousand hectares of forest defoliated at least four times and twenty-seven thousand hectares of mangrove completely destroyed (Pham, 1995).

The Ansul Company produced Agent Blue, labeled as Phytar 560 G. The product consists of 4.7% cacodylic acid (hydroxydimethyarsine oxide), 26.4% sodium cacodylate (sodium dimethylarsinic acid), 3.4% surfactant, 5.5% sodium chloride, 0.5% antifoam agent, and 59.5% water (Kotchmar, *et al.*, 1970). Thus arsenicals compose 31.1% of Agent Blue, 15.4% of which is elemental arsenic, in the form of +5 oxidation state arsenical. This means that 4.8% of Agent Blue is an arsenical with similar properties to arsenate. This also means it reacts and bioaccumulates just like arsenate. Figure 2 below is the chemical structure of Cacodylic Acid and Sodium Cacodylate.

Cacodylic Acid Sodium Cacodylate

Figure 2: Chemical Structure of arsenic-containing active chemicals in Phytar 560 G

A study done by Watson, *et al.*, in 1976 demonstrated that life expectancies of non-targeted animals from Agent Blue were reduced to less than ten percent of the unexposed population. The lethal concentration of Agent Blue for rats is 3.5 µg/L.

The HERBS collection, the most thorough data repository of herbicide usage during the Vietnam War, documented that 4,712,920 liters of Agent Blue were sprayed in Southern Vietnam (Young and Gegigani, 1988 and Nakamura, 2007). This means that the total amount of arsenical sprayed onto crop lands was 235,820.2 liters. It was documented that in the early 1980's, soldiers with prolonged exposure to Agent Blue developed a garlic odor in their breath; this is one of the common noticeable symptom of arsenic poisoning (Worden, 2010). Later, research shows that the human liver absorbs 40% of the cacodylic acid into the body (Hearing in the Veterans' Affairs House of Representatives, 1980); the high bioaccumulation of arsenicals in the body and extreme addiction of arsenicals is detrimental to crops and human health.

So dangerous was the use of Agent Blue that Operation Ranch Hand received little to no publicity. President Kennedy's Joint Chief of Staff stated that "care must be taken to assure that the United States does not become the target for charges of employing chemical or biological warfare. International repercussions against the United States could be most serious." (Nakamura, 2007). So, when the program was first introduced, it was known as the "Khai Quang" Program, a southern Vietnamese program that requested the help of America to clear out foliage and make the battlefield more visible. Agent Blue missions required members to wear civilian clothing, fly aircrafts without USAF markings, and stipulated that, if captured, the US government would not acknowledge the crew as members of the US Military. There were no warnings to the soldiers handling Agent Blue, who were primarily Vietnamese, against

drinking from the rivers where Agent Blue was sprayed. (Young and Gegigani, 1988 and Nakamura, 2007). Agent Blue is also known to deteriorate the bins which held them and break down to bioavailable forms within three months, infiltrating the groundwater and entering the food chain with ease. Thus, the secrecy surrounding the use of Agent Blue meant no Vietnamese civilians or military personnel knew, or know today, about the contamination or inherent health hazards of the chemicals that they were prolifically using (Nakamura, 2007).

Other Anthropogenic Sources

Although it is a large source, Agent Blue was not the only source of human introduced arsenicals into Vietnam's groundwater. Since the late 1900's, Vietnamese farmers have used arsenicals such as monosodium methane arsenate (MSMA), disodium methane arsenate (DSMA), and cacodylic acid as pest control for crops in rural areas. These additions of arsenic into food sources resulted in an inevitable uptake of arsenic in plants, animals, and eventually, humans.

Urban areas have also seen an increase in arsenic use in the past three decades. In the city, with the mass movement toward city life in the past decade, slums dump their refuse into nearby rivers (Nguyen and Leaf, 1996). These refuse flows into the river and are deposited in the alluvial deltas – the Mekong and Red River Deltas – creating an organic reducing condition that promotes the release of arsenicals in the Holocene Era layer to groundwater. Although the release of arsenic from the Holocene period is natural, the exponential increase in this release is due to human causation, creating an even heavier concentration of arsenic in groundwater. It is this groundwater that is, then, used in well extractions for irrigation and drinking water.

Current Situation of Arsenic Contamination in Vietnam

In Vietnam, two main rivers serve as primary water source for agriculture and, since the 1980s, groundwater near these rivers are the main source of drinking water for inhabitants (Barker, 2004 and Hoang, *et al.*, 2010). They are the Red River Delta in North Vietnam and the Mekong Delta in Southern Vietnam. Figure 3 shows a map of the concentration of arsenic contamination in Vietnam.

Figure 3: Distribution of arsenic contamination in South East Asia, showing the contamination in the Mekong Delta and Red River.

There are three primary irrigation methods for agriculture in Vietnam. In the Red River Delta, large pumping systems are dominant, covering hundreds of hectares with dikes and upstream reservoir control. In the Mekong Delta, two different methods are employed: individual pumping for drainage and irrigation and tube-well irrigation. Tube-well irrigation is using water wells that transport water in which a long 100 – 200 mm wide stainless steel pipe is

drilled into the underground aquifers and the lower end is fitted with a strainer and a pump to lift water to the top for irrigation (Sonou, 1996). Figure 4 shows a schematic of how shallow tube-well irrigation works.

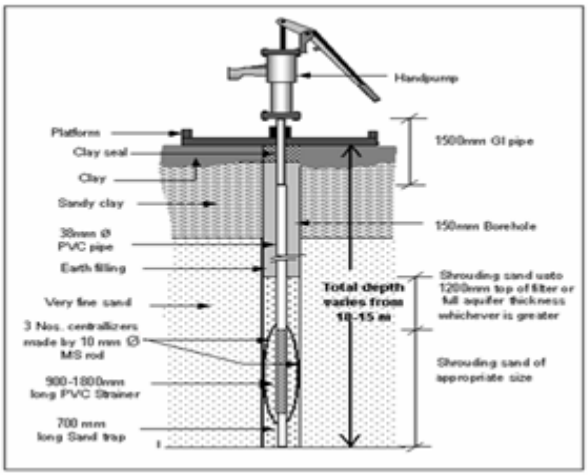


Figure 4: Schematic of Shallow-Tube-Well Irrigation

In the Mekong Delta, thirty-five million people rely on groundwater as their primary source of drinking water and approximately 17 million people rely on it for agricultural production. In the Red River area, there is an estimated 10 million people who depend on it to irrigate their fields and to fill their wells with water (Jessen, 2009 and Nguyen, 2008) and 65% of these wells exceed the WHO limit of 50 µg/L, which is already considered five times too unsafe for ingestion by the WHO guidelines (Winkel and Pham, 2011). For both rivers, water demand is above one million m^3/day in 2010, and approximately 90% of the groundwater that is abstracted is used for irrigation via tube-well water transport (Brammer and Ravenscroft, 2009, Castano and Sanz, 2009, and Hoang, *et al.*, 2010). In the case of Hanoi, near the Red River Delta, the abstraction of groundwater for irrigation has lead to a groundwater level decrease of 10 meters to 20 meters below sea level in wells, causing subsidence.

The extensive use of groundwater for crops and drinking water is a huge issue because these two river systems have extremely high concentrations of arsenite and arsenate. In the Red River Valley, arsenic levels in several groundwater wells exceed 3050 µg/L and average at 430 µg/L (Nguyen, 2008). In the Mekong Delta, more than 40% of tube wells had greater than 100 µg/L of arsenic, with a range up to 1610 µg/L (Hug, 2008 and Nguyen, 2008). These concentrations are at levels more than 300% higher than safe limits as determined by WHO. In addition to this arsenic contaminated irrigation water, farmers apply over 20,000 tons of arsenical pesticides annually without protective eyewear, shoes or masks, creating an even higher exposure to the poisonous arsenic (Pham, 1995).

Vietnam has a population of approximately 90 million people. For the 22% of Vietnamese living in cities, 50% of who reside in Saigon, Hanoi, and Hai Phong, safe drinking water is also a major problem (Pham, 1995). In Saigon alone, 129 out of 329 water-production companies failed to reach required standards on water quality and fifty-three of those companies were forced to close. Most private producers in Hanoi also failed to meet regulations on environmental sanitation. (Look at Vietnam, 2009). This means that millions of people are drinking water believing it to be safe, even though it is not. Over one million of these people are currently suffering from chronic arsenic poisoning (Berg, 2002).

These dangerous levels of contamination not only manifest in groundwater and drinking water, but are also evident in Vietnamese foodstuffs, where different plants have different sensitivity to arsenic from its phytotoxicity levels. Some plants with high phytotoxicity levels are beans, soybeans, rice, spinach, peas, green beans, other legumes, onions, cucumbers, and alfalfa (Naidu, 2006). Unfortunately, rice, one of the most arsenic-absorbent crops, is the

principle irrigated crop in Vietnam, and serves as the staple diet, alongside fish and vegetables. In the flooded rice paddies, the anaerobic conditions favor arsenic in the form of arsenite (Brammer, 2009). Arsenite in groundwater and sediment is the most readily available form of arsenical to plant roots, where bioaccumulation goes from roots to stem, leaf, and lastly, grain (Brammer and Ravencroft, 2009). According to the World Health Organization, the safe limit for a sixty kilogram adult who consumes about 450 grams of rice with a concentration of .11 µg/L arsenic a day and who drinks 4 liters of water with a concentration of 10 µg/L of arsenic a day ingests 130 µg of arsenic daily. This means that the provisional tolerable weekly intake is 15 µg of arsenic a week per kilogram of body weight (Agusa, *et al.*, 2009). This number drastically multiplies when the allowed arsenic concentration of safe drinking water in Vietnam is 50 µg/L, not the 10 µg/L limit from the WHO guidelines. On top of the too-high limit of arsenic, actual concentration of arsenic in rice and drinking water more than triples even the Vietnamese unsafe limits. In South-East Asia, arsenic concentrations in raw rice grains were measured up to 1.8 µg/L and in local groundwater concentrations reached 4,700 µg/L. When cooked, the rice had arsenic concentrations up to 4.21 µg/L. This meant that over 92% of the population had daily intake of arsenic estimated well over the guideline values (Agusa, *et al.*, 2009). The average concentration of arsenicals in vegetables was 2.38 µg/L. Fish and poultry that consume plant feed accumulate arsenic as well, and maintain a higher concentration of arsenic than in vegetables (Zavala, 2008). Being the top of the food chain, the bioaccumulation in the rice, vegetables, and meat in humans is detrimental. In 2009, Agusa, *et al.* collected human hair in the suburbs of Hanoi, and measured a concentration up to 2.77 µg/L of arsenic. In other South-East Asian countries with comparable concentration of arsenic in groundwater

and similar diets, Zavala and Duxbury found 164 µg/L of arsenic in urine samples. Agusa, *et al.*, concludes that there was a positive significant correlation between inorganic arsenic intake and human urine. It also proved that the concentration is higher in children than adults, especially for males. In both of these studies, the concentration of arsenic retained by the human body is much higher than the WHO safe limits and both studies concluded that there is a significant positive correlation between arsenic concentration in groundwater and urine.

Physical symptoms of arsenic poisoning takes over a decade to become apparent; in the case of Vietnam, it has taken thirty years from when the popular installation of tube-wells and irrigation systems became popular methods of securing water in 1980s for the symptoms to show. Although there is a base of natural arsenic contamination in groundwater due to natural geochemical sources, the primary source of the contamination problem for Vietnam is anthropogenic. This spike of arsenic in groundwater must be quickly remedied, especially since it affects a large portion of the population.

Economic, Political, and Cultural Parameters of Vietnam

To prescribe an effective and successful treatment of arsenic contamination in Vietnam, many different factors must be taken into consideration. These factors include Vietnam's economy, Communist political state, and culture. Thus, the optimal treatments must fit within the feasibility and boundaries of each parameter.

Economic Parameters

In 1986, the Sixth Party Congress initiated an economic reform called "Đổi Mới," known in the United States as "Renovations" (Nguyen and Leaf, 1996). This economic reform shifted Vietnam's economy from a centrally planned economy to one that is market oriented, with a focus on foreign investment. Since then, Vietnam and the United States have created many pacts to keep a strong import-export relation. In 2001, the Bilateral Trade Agreement (BTA) was created, and expanded Vietnam's export from USD $2.91 billion in 2002 to USD $17.9 billion in 2010. In December 2006, the United States granted Vietnam unconditional Normal Trade Relations (NTR) status, and in 2007, the United States signed a Trade and Investment Framework Agreement (TIFA) with Vietnam. Since 2008, the United States and Vietnam are negotiating a Bilateral Investment Treaty (BIT). After the new economic measures were implemented, Vietnam's economy boomed, becoming one of the world's fastest growing economies, with an average 8% Gross Domestic Product (GDP) growth from 1990 to 1997; and 6.78% to the end of 2010. Vietnam's current GDP is USD $102 billion. Per capita income rose from USD $220 in 1994 to USD $1,168 in 2010.

The new economy created a new urban landscape. The "Renovations" reform initiated a new type of housing, called "Popular Housing." These popular housing are built in unfavorable physical locations - over old graveyards and dumpsters, and next to polluted canals. Thus, they become segregated slums for low socio-economic families. Because these families lack the income and resources to buy clean water, they use the water from the canal to bathe and drink. Most of them also use the canals as a dumping ground for their refuse. (Nguyen and Leaf, 1996). These Popular Housing are usually located in large cities near the Mekong and Red River

Deltas, thus the canal water leads to the main deltas and create a highly organic environment for release of arsenic. In addition to using these canals as a sewage pipes, 95% of the inhabitants drink groundwater from wells that are drilled right next to the canals. The groundwater is highly polluted, creating anaerobic conditions favorable for release arsenic to groundwater. Due to their economic circumstances, inhabitants cannot buy purified water because they barely make half the income needed for daily sustenance. In these areas, the government must take into account the physical housing segregation caused by the economy and the conditions of the urban poor to provide subsidies for safe drinking water to "Popular Housing" inhabitants.

The new treaties with the US also created a large impact on agriculture in rural areas. 60% of Vietnam's labor force is in agriculture, and thus, rural unemployment remained low, at 2.27% in 2010 (Barker, 2004 and U.S. Department of State, 2011). This is approximately half of the unemployment rate of urban cities in Vietnam. This is not surprising; in 1989, 42% of Vietnam's exports are from agriculture. Even in 2010, after heavy industrialization and the introduction of a strong textile industry became more prominent, 21% of Vietnam's exports are still from agriculture. Together, Vietnam's exports totaled USD $17.9 billion by the end of 2010, meaning that USD $3.76 billion in exports was from agriculture, mostly in rice and coffee exports. Currently, Vietnam is the second largest international exporter of rice, exporting over 31,394 tons per year (Nguyen and Popkin, 2003). The strong impact of rice as an export in Vietnam is detrimental to global human health. Since the irrigation water for rice paddies creates a large bioaccumulation of arsenic, any rice exported from Vietnam would have unsafe levels of arsenic for ingestion. From an export and GDP standpoint, Vietnam's economy heavily

relies on rice. Rice is currently accumulating extreme amounts of arsenic from groundwater. Thus, the need for immediate treatment of arsenic contaminated groundwater to achieve safe arsenic levels in rice is dire to both the survival of Vietnam's economy and all who eat that exported rice.

Political Parameters

The Communist Party still dominates Vietnam's government. The political structure of the nation includes three branches. The executive branch includes the president, who serves as the head of state and the chair of the National Defense and Security Council; and the prime minister, who heads the Cabinet of Ministry and Commissions. The legislative branch is the National Assembly, made up of 493 representatives, led primarily by the people and serves the people. In this branch, there is a Party Congress, headed by a Politburo, the General Secretary. This congress determines the governmental policies and its implementation. The judicial branch includes the Supreme People's Court and the Prosecutorial Supreme People's Procuracy (U.S. Department of State, 2011).

The government has established that water management in agriculture is an important national issue. The Vietnamese Water Law of 1999 and the National Water Resources Council of June 2000 established basin-level committees to oversee the management and allocation of water in the Red River Delta, Mekong Delta, and the Dong Nai basin. In November 2002, the Ministry of National Resources and Environment (MONRE) was established with part of its mission to oversee usage and development of water resources (Mai, 2003). Despite all these

committees, the government does not actually have a strong impact in agriculture. Annually, the government only spends 0.1% of its USD $102 billion GDP on research and development in agricultural water management (Barker, 2004). This is much less than the 5% spent for developed countries and 1% for many other developing countries with much lower GPD. In addition to the lack of research and development, the government also has indirect taxes for industrial protection that often times create a huge burden on the agriculture sector (Barker, 2004). The agriculture sector is receiving governmental support that is proportionally much less than its contribution to the Vietnamese economy. For a country of over 6% annual economic growth to be spending 0.1% of the amount of GDP on research and development for its primary export is both unsustainable and an economic blunder. Vietnamese citizens need to push for more spending in agricultural irrigation and quality research and development.

Cultural Parameters

Currently, Vietnam has a population of approximately 90 million people with an annual population growth rate of 1.077%; of the population, 94% is literate (U.S. Department of State, 2011). Approximately 68.4 million people live near agriculture land and 13.7 million of those people live in Hanoi and Saigon (Le, 2009). This means that awareness of the arsenic contamination issue could be spread through pamphlets and other text media, especially in congregated cities like Hanoi and Saigon.

Over 12 million hectares of land in Vietnam is cultivated. Despite the vast expanse of agricultural land, individual farms in Vietnam are small, averaging two and half acres each (U.S.

Department of State, 2011). The primary source of irrigation for these farms, in the last two decades, is through pumping of shallow groundwater near the Red River and Mekong Deltas. Below is a table that shows a drastic increase of pumps between 1991 and 1999.

Table 2: Number of pumps by region in Vietnam (Barker, 2004)

Region	1991 (in thousands)	1999 (in thousands)	1991-1999 (%/yr)
Red River Delta	12.11	25.99	10.02
Northeast	4.68	57.88	36.96
Northwest	0.08	.49	25.23
North Central Coast	4.11	9.66	11.29
South Central Coast	8.83	38.41	20.17
Central Highlands	4.50	44.96	33.34
Northeast South	76.16	258.22	16.49
Mekong River Delta	92.83	357.72	18.37
Whole Country	203.29	793.33	18.58

In 2002, the government also decided that the water belongs to the people, and thus, the people have the right to exploit or use resources as needed without regulation or quality control (Barker, 2004). This means that people do not know if the water they are using is safe, so they do not know the danger of arsenic contamination in their water and do not press the government to remedy the issue.

These farms, with their unregulated water use, provided the rapid economic growth for Vietnam. However, the rapid growth is incongruent with the high malnutrition in the rural poor in Vietnam. Vietnam's rate of malnourished children is 46%, which is almost double that of the world average and over twice as high as the East Asian countries' average (Nguyen and Popkin, 2003). With such conditions, Vietnam is a country that still needs a lot of development, management, and regulation of its resources.

Parameters and Ideal Treatment of Arsenic Contamination in Vietnam

Vietnam's parameters are very unique. In the country, the majority of the population congregates around agricultural land near rivers, primarily the Mekong and Red River Deltas. These two deltas are very high in arsenic concentration. Even so, they serve as the main source of water, both for drinking and irrigation, for the inhabitants.

It is a country with extremely high economic growth in the last two decades, yet there is a sharp distinction between the richest and poorest quintile, categorized as making an annual income of less than USD $58.17, less than half the minimum annual income of USD $156 to make ends meet in Vietnam (Lao Dong, 2000). The poorest quintile only accounted for 5.6% of total income while the top 20% accounted for 49.3% of total income in 2006 (Oxford Analytica, 2008). Standard of living for the rural poor is also lacking behind other developing nations. In addition to this, the government is spending 0.1% of GDP on research and development of irrigation water. This means that there is barely any money being spent on ensuring that

groundwater used for drinking and irrigation is at a safe level; and none is spent on educating the citizenry.

Available Solutions and Its Feasibility for Vietnam

Arsenicals in groundwater affect health in two main ways. First, it is used as the primary source of drinking water, where the water is directly ingested. The second pathway is through a crop-animal-man food chain, where the crops are irrigated with contaminated groundwater; crops absorb the arsenicals, and it goes up the food chain to when humans eat the arsenical-laden food. The first step in mitigation would be to record current concentrations of arsenic in groundwater at various key locations near villages and farms surrounding the Mekong and Red River Deltas. There are several methods to measure concentration of arsenic in groundwater. They are divided into two categories: on-site and in lab methods. Quick, affordable, and accurate on-site analysis is usually preferable because it takes less time and does not require large costly initial investments in laboratories or space for those laboratories. However, care must be taken in choosing a suitable method. Accurate and reliable results require that the instrument's limit of detection be ten-fold lower than the critical threshold value of concern (Ahuja, *et al.*, 2008). For example, using an instrument to measure at least10 µg/L arsenic would require an instrument's limit of detection to be 1 µg/L. Two favorable options are:

- Colorimetric Principle for On-Site Field Testing Kit: this method reduces arsenite or arsenate to arsine gas under acidic conditions with the addition of zinc power and measures the intensity of color used for quantification of arsenic in groundwater within a few hours. Photo 2 shows a colorimetric testing kit with the scale

concentrations by coloring of the testing paper. The cost of the kit varies depending on the specific kit's limit of detection, ranging from USD $18 to $150 per 100 tests. (Ahuja, *et al.*, 2008).

- Electroanalysis: This low running-cost method also employs reducing or oxidizing arsenic species to measure concentration of different species of arsenic in the water. The method takes approximately an hour and has a much lower detection limit than the Colorimetric Testing Kit. It only requires a nanoliter amount for testing, but is less sensitive than the colorimetric principle (Naidu, 2006).

Image 3: Colorimetric testing kit

For laboratory methods of arsenic detection, the most cost-efficient, accurate and quick method of analysis employs High Performance Liquid Chromatography (HPLC). This machine analyzes direct water samples, requiring no derivatization steps. It is also easily coupled with other machines to provide accurate results and speciation of arsenic in groundwater (Naidu, 2006).

Mitigation of Groundwater for Drinking Purposes

It is impractical to filter water for both irrigation and drinking purposes to the same standard, especially because it requires too much investment, cost of maintenance, and engineering. Up until today, most research has been focused on treating groundwater for drinking purposes. Vietnam, too, has been directing its efforts to treat drinking water. Eight major well-fields are operated by water treatment facilities, processing half a million cubic meters a day. Urban water treatment plants exclusively exploit lower aquifers between thirty and seventy meters deep while private tube-wells predominantly pump from the upper aquifer at twelve to forty-five meters deep. Unfortunately, the mitigation efforts of these treatment plants still leave water at arsenic concentrations up to 91 µg/L, almost double Vietnam's standards and more than nine times higher than the WHO guidelines (Naidu, 2006). A large portion of the problem in a one-for-all solution is that the soil composition and concentration of arsenic is different at different locations, and the solution must be customized per location to best treat the water. Therefore, more research must be done to help mitigate groundwater.

Luckily, there has been a lot of international research completed on arsenic mitigations that target different concentrations of arsenic. These treatments range from local attempts that are fairly affordable to extremely efficient but costly machinery. Most of the mitigation methods, however, only apply to drinking water, as it is too expensive to use on the large amount needed for irrigation water; therefore, it will be the focus of this section. Below is a chart comparing several successful and financially feasible mitigation options for Vietnam.

Table 3: Arsenic Treatments of Groundwater for Drinking Water (Naidu, *et al.*, 2006 and Ajuha, 2008)

Technology	Advantages	Disadvantages	Cost (USD)
Alcan Enhanced Activated Alumina: based on adsorption process	– High As removal efficiency – More known in community – Available to both community and household level – No chemical addition – Provides >3600 L/12 hours for >100 families	– pH sensitive – high possibility of media getting fouled or clogged by precipitated iron – regeneration of saturated alumina is required once column is totally saturated – activated alumina efficiency decreases after regeneration	– Community unit: $170 + $220 for filter (up to 80,000 L) – Household Unit for 5 people with filter: $34 for 11,000 L – Replacement filter for household unit: $14 per 11,000 L – Annual cost/person for community unit: $3.03 – Annual cost/person for household filter: $3.40
Three KolshiPitcher Filter (aka *Sono Three Kolshi Filter*): based on indigenous filtration process	– High As removal efficiency – More known in the community – Produces 40L/12 hrs – Filter uses sand, iron fillings, charcoal and brick chips – all found locally – Can be manufactured at the community level	– Filter media requires regular cleaning to prevent bacteriological contamination – May get clogged if excess iron is present in the feed water	– Unit: $6.00 – Replacement of Kolshi including iron fillings and coarse sand: $1.10 – Annual cost/ person: $2.08 if filter is replaced every three months
SONO Filter	– High As removal efficiency for water up to 300 µg/L [As] – Decently known in the community – All filter materials are local – Filter lasts up to 5 years – Spent material is non-toxic – Produces 80 L/ day, enough for a family of 5	– Not as successful with extremely high concentrations of arsenic – Regular cleaning is required to prevent bacteriological contamination	– Unit with filter: $40 – Filter replacement: $40 per 5 years – Annual Cost/ person: $1.60
Community Based Wellhead Arsenic Removal Unit	– High As Removal Efficiency up to 500 µg/L [As] – Available at community level – Serves 1,000 people for up to 2 years	– Filter requires some chemical additions during regenerative and new media processes – Used filter creates a solid arsenic-laden sludge that needs to be	– Unit cost with filter: $1,276 for two years – Regeneration filter cost: $638 – Annual cost/ person: $0.64

	– Adsorption medium from exhausted units can be regenerated	stored on a coarse sand filter. People must be encouraged to regenerate the filters instead of disposing them to keep waste to a minimum	
Stevens Institute Technology: based on coagulation ,filtra tion, and adsorption process	– High As removal efficiency – Decently known in the community – Produces 169 L/ 12 hours (adequate for 25 people)	– Chemical addition required – May not remove adequately when [As] is above 500 µg/L – Sand bag used for filtration must be washed twice a week to prevent clogging by flocs – Structure is not robust	– Installation cost: $35 – Chemical cost: $3.50 – Annual cost/ person: $1.82 if chemical is replaced once every four months
Shapla As removal filter: a household filter using iron-coated brick dust as an adsorption medium	– High As removal efficiency – Decently known in the community – All filter materials are local	– Regular cleaning of filter material is essential to prevent bacteriological contamination – Is slower to produce water	– Unit cost with media: $6.50 – 1 kg of replacement media: $1.72 – Annual cost/person: $1.99 if uses 2 kg of replacement media annually
Pond Sand Filter (PSF)	– Popular source for coast areas with a permanent year-round pond – Produces enough water for 50 families, depending on pond size – Can remove pathogens as well – Locally trained mason can construct PSF	– Need to be near permanent pond – Pond must be free from cattle bathing and fish culture using chemical fertilizers – Needs a locally trained caretaker	– Installation cost: $400 – 500 – Initial cost/person: $1.60 – Annual maintenance cost after first year/person: $0.40
Rainwater Harvesting System (RWHS)	– Water quality is very good – Effective for communities near coastal areas with salinity problems – Suitable for tin-roof houses; alternative arrangements can be made by using polythene or thick clothes to collect water	– Shortage of water in dry season – Mineral-free water may taste different initially and produce a mineral deficiency among malnourished people – Catchment area and storage tank needs to be kept clean for water standards	– 3,200 L tank: $150 – 500 L earthen tank: $10 – Investment cost/person: $2.00 for 500 L tank and $4.36 for 3,200 L tank

	– Has potential to be accepted by community		
Dug Wells	– Usually As safe – Well accepted by community – Sanitary protected dug wells (sealing the well-top with airtight concrete slab and water drawn by installation of manually operated hand pump, an air entry pipe is installed and connected with well rings) is microbiologically safe – Produces water for 30 families	– Cannot be installed all over the country, only suitable for certain areas with specific soil conditions – Cannot be installed all through the year; dry season especially prior to monsoon is ideal time for construction	– Installation cost: $300 – 500 – Investment cost/person: $2.00 - $3.33
Deep Tube wells	– As safe up to date (when water table is still high enough that arsenic still primarily congregates on top soil layer) – Well accepted in the community – Water can be abstracted using a manually operated hand pump – Can produce water for 50 families	– Deep aquifer cannot exist all over the country – Potential to be affected with As if not installed correctly or if area has a low water table	– Installation cost: $750 – Investment cost/ person: $3.00

* Appendix I show schematics for each of these treatment methods.

<u>Mitigation of Groundwater for Irrigation and Crops</u>

There has been little research done to filter irrigation water, especially since there is a large amount of water to handle. Much more emphasis must be placed on researching viable and sustainable methods of mitigating irrigation water to control arsenic intake of crops, and by the food chain, animals and man through food. One mitigation effort is the use of hyperaccumulator plants, primarily break ferns (Pteris vittata), ornamental arum in dry soils

and green and blue algae in rice paddies, to absorb arsenic in top soils. These ferns and arum can take up to several years' input of arsenic in groundwater while the algae also serve as a fertilizer to the soil (Ahuja, 2008 and Brammer, 2009). These catch-plants are usually planted as a short term catch crop before rice is planted. However, there is no safe method yet to dispose these ferns (Brammer, 2009). A second method, perhaps a more desperate and quick method, is to remove the ten to fifteen centimeters of top soil, where arsenic accumulation is worst, and then add manure or compost, or grow jute or deep-rooting legumes to restore soil fertility. Again, the problem lies in this method in that there is no place to relocate the contaminated top soil (Brammer, 2009).

A different approach to the arsenic in crops dilemma is to alter the way food is cooked. For example, peeling vegetables, where large percentage of the arsenic resides, before cooking, or parboiling arsenic contaminated rice with an excess of water to reduce the arsenic concentration in the rice and vegetables lowers consumption of arsenic by a third (Brammer, 2009). For farmers who can afford it, growing cereals, which absorb less arsenic, in the dry season, and grow rice during rainy season, where less arsenic contaminated groundwater needs to be used as irrigation in the paddy fields , is also a feasible option (Brammer, 2009).

The current mitigation methods employed in Vietnam today to purify irrigation are simply not enough; they are only temporary measures to delay arsenic poisoning. The removed top soil is not disposed very far away and in rainy season, the arsenic will simply leach back to groundwater in the fields. These crops could have such high level of arsenic that peeling them or parboiling them would still leave double or triple the amount of recommended arsenic

intake. More research must be done to provide sustainable long-term solutions to mitigate arsenic in irrigation water.

Recommendations for Action to Remedy Arsenic Contamination

The combat against arsenic contamination in groundwater in Vietnam requires more than technology and available treatment options. It requires a greater effort to educate the citizens, extensive research to customize the best treatment options for each troubled area, and multiple changes in laws and government implementation.

Firstly, there is a large research gap that must be fulfilled to successfully mitigate arsenic in groundwater in Vietnam for crop production. This means finding management options to prevent and mitigate arsenic contamination of agricultural lands, conducting more research on the exact risks of arsenic in water and fodder of livestock and other food products to find out at what concentration is actually safe for livestock to consume, and figuring out what crop rotation is best at different areas to absorb as little arsenic as possible.

Secondly, there needs to be a country wide measure of arsenic concentrations in drinking water in every town and every city. These concentrations of arsenic, matched up with the average income and living style of the surrounding population, must be taken into account in picking a customized drinking and cooking water treatment method suitable for the said population. This project can be taken on by the Vietnamese government, UNICEF, the World Health Organization, or a combination of all, but it must be done as soon as possible and as

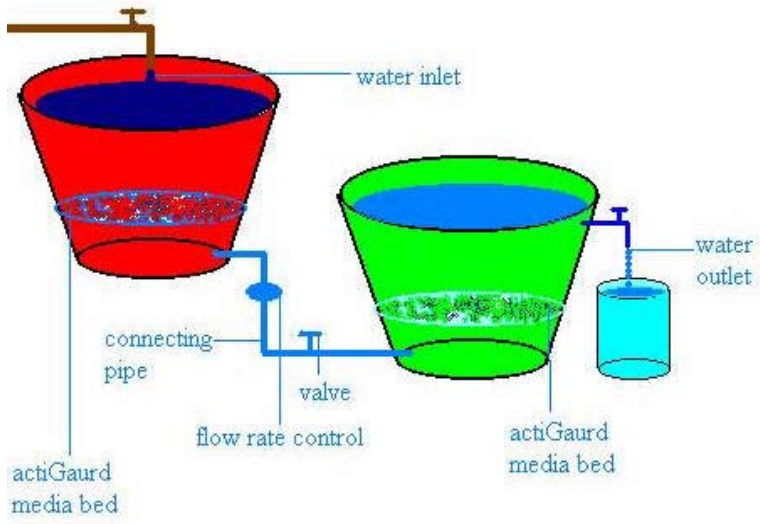
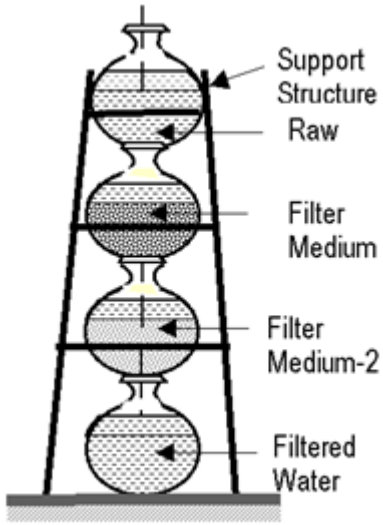
quickly as possible to provide a successful arsenic mitigation process that will be financially and culturally accepted by the population.

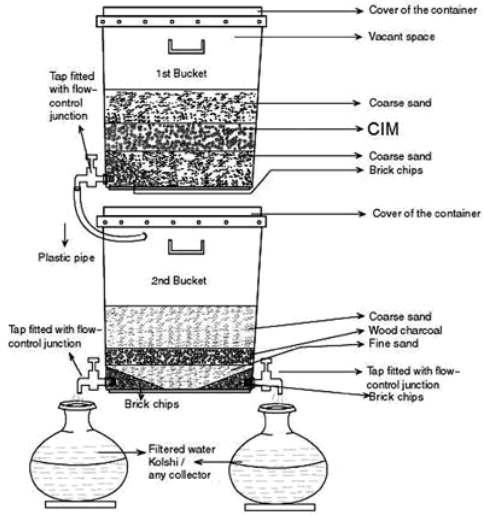
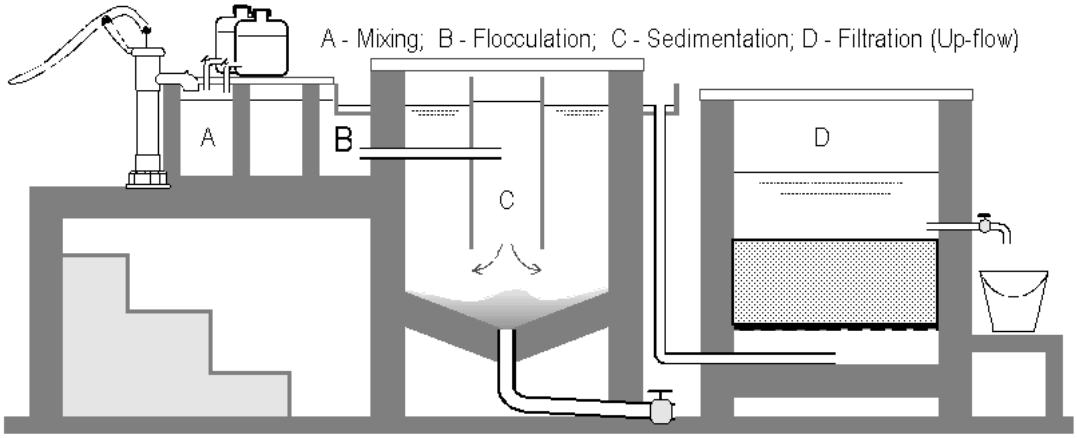
Third, the government needs to place emphasis on educating the population of the dangers of arsenic in groundwater near their homes, in their drinking water, and through their skin as they wade through the paddy fields to tend their crops. This will encompass agencies such as the National Water Resources Council publishing pamphlets, fliers, and putting notices on their websites to alert residents that they should take action or accept the new mitigation efforts in their town to filter their drinking and cooking water. They should be informed on why it is important to pay the extra cost for safe water. The extra cost primarily applies to the rural areas, since they do not have access to pre-purified bottled water. For the urban population, information on bottled water companies and their standards should be published to the public.

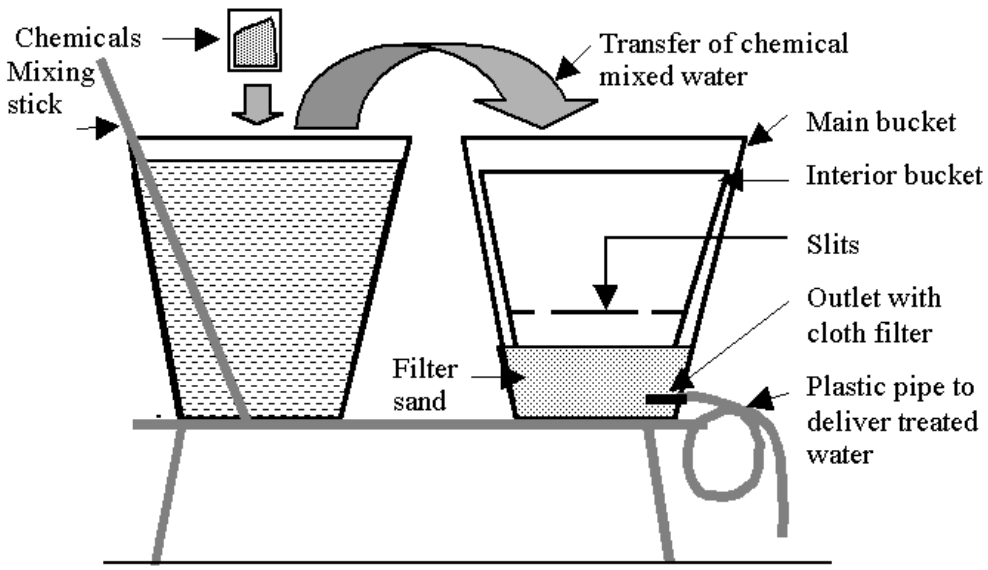
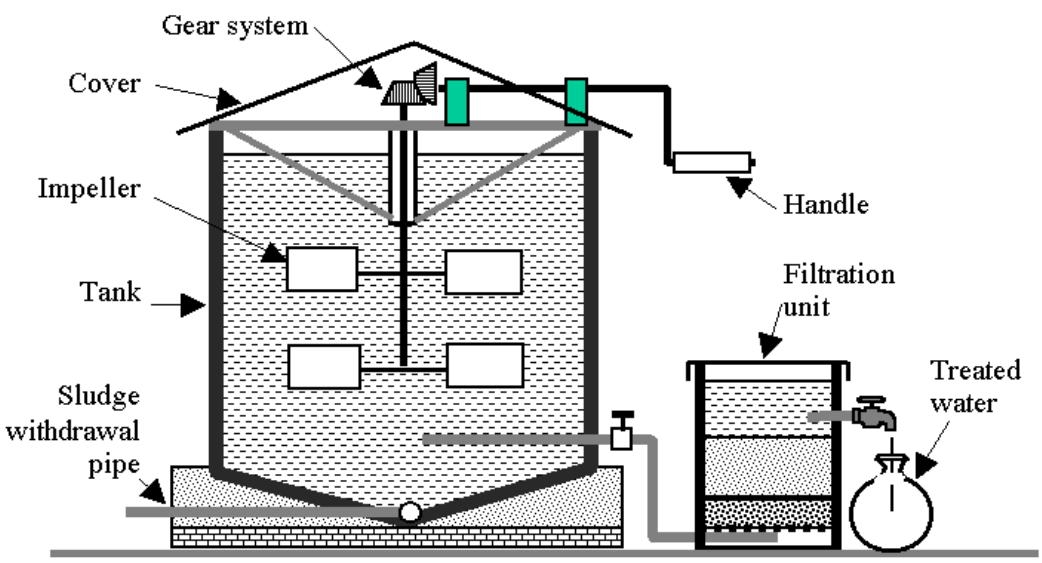
Finally, the Vietnamese government must change the legal safe arsenic concentration from the current 50 µg/L to 10 µg/L. As research shows, consuming water at a concentration of 50 µg/L is still too high for human health. To accompany this change would be for the government to change its priority to enforcing the implementation of laws via agencies and to subsidize water purification systems in areas where the population cannot afford to do so. The government must also vehemently enforce the quality standards on water bottling companies and other water filtration companies, as the population is falsely believing that the water they purchase is safe for drinking. This could be accomplished by requiring the companies to place a quality seal on their bottles and have annual reviews from the government.

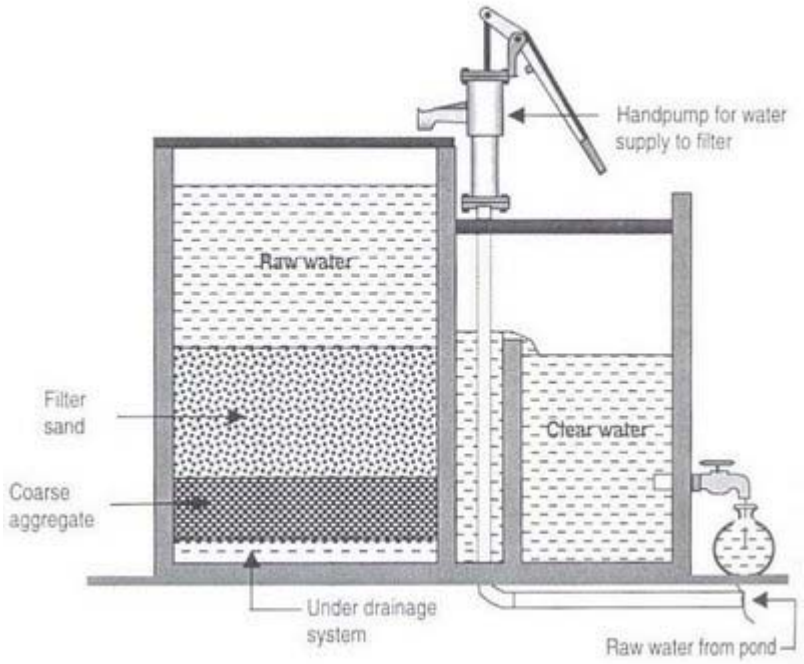
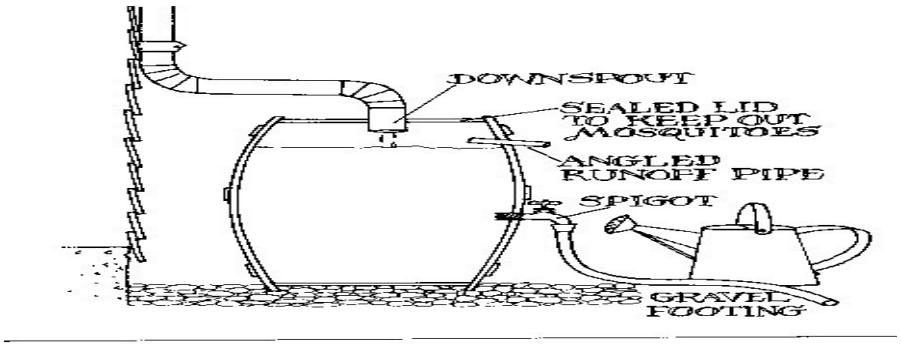
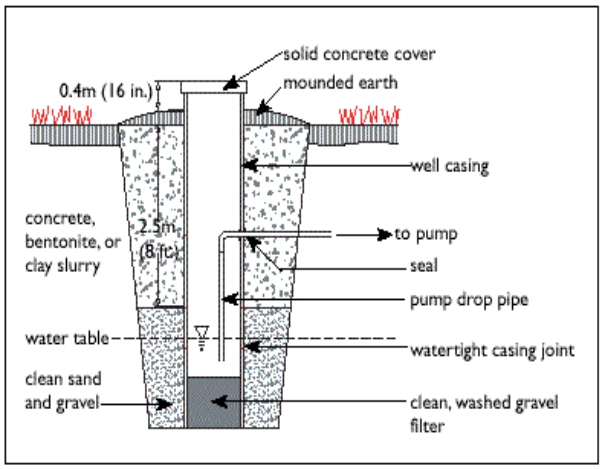
Although the above steps are listed sequentially to show the different areas that need attention, all of this must happen simultaneously. The problem has reached a critical point where waiting around for the research to be done, for the laws to change and agencies to be set up for implementation, and educating the public of the danger one after another is not fast enough, powerful enough, or successful enough. This is a crisis that impacts every person in Vietnam and even people who eat the rice from Vietnam. Action must be taken immediately to mitigate further arsenic poisoning in Vietnam.

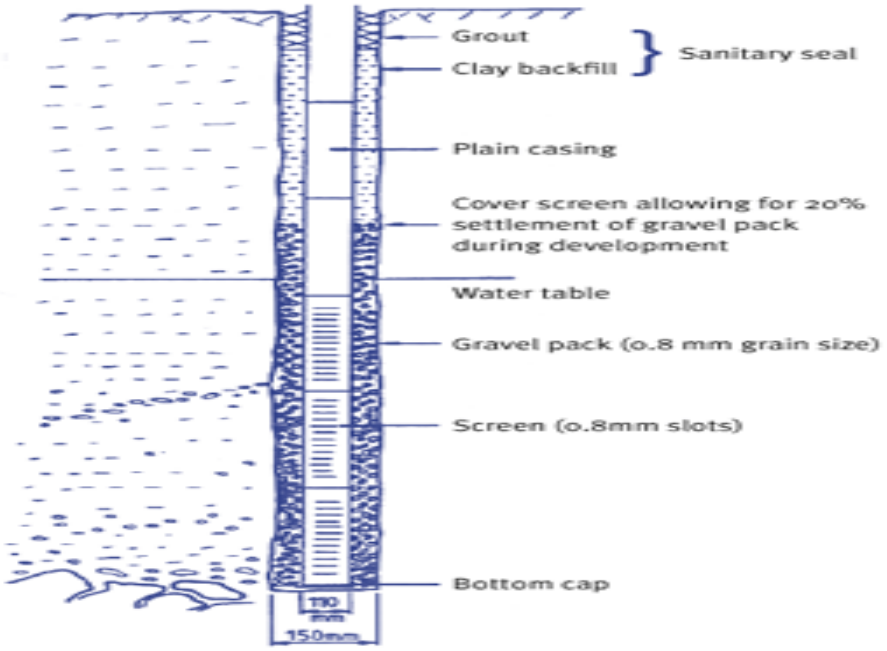
Appendix I: Schematics of Various Treatment Technologies (Sambou and Wilson, 2008)

Alcan Enhanced Activated Alumina Filter	
Three Kolshi Pitcher Filter	

SONO Filter	
Community Based Wellhead Arsenic Removal Unit	

Stevens Institute Technology Arsenic Removal Unit	
Shapla Arsenic Removal Filter	

Pond Sand Filter (PSF)	
Rainwater Harvesting System (RWHS)	
Dug Wells	

Deep Tube Wells	

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