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Natural and Anthropic Sources of Arsenic in the Groundwater and Soils of the Mekong Delta

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Abstract

Human exposure to arsenic (As) is primarily through drinking water and food ingestion. Arsenic is naturally present in the environment and has been known as "the king of poisons" since the Middle Ages. It is mutagenic, teratogenic, and carcinogenic and approximately 70% comes from ingested food and 29% from water. Once ingested, arsenic can bio-accumulate in the human body or be excreted. Arsenic in groundwater is a main source of As in humans and the two arsenicals most abundant in water are arsenite (+3 oxidation state) and arsenate (+5 oxidation state). In order of toxicity from the most toxic to least toxic are arsines, arsenites, arsenoxides, arsenates, pentavalent arsenicals, Arsenic compounds, and metallic arsenic. Arsenic accumulates in the body when ingested in small doses. It often takes decades before physical symptoms of As poisoning show. While As is element normally found in the human body, it is highly toxic in excess amounts. The lethal dose for rates is 48 μg/L which translates to 125 mg for a middle-aged male. The maximum safe limit for As ingestion for an average Vietnamese middle-aged male is 220 μg per day. This lethal dosage puts As in a highly toxic category in food and toxicology. Most of the As in the Mekong Delta groundwater is from natural alluvial sediment sources. Other anthropic sources include the burial of millions of Vietnamese with elevated As levels since 1962, industrial sources, smelting by-products, water treatment plants, sewage and wastewater treatment discharges into waterways have added to the Mekong Delta As levels in the soil and groundwater. However, Agent Blue, the As-based herbicide, used during the Vietnam War, did contribute a significant amount (over 1,132,400 kg of manufactured (anthropic) As) to Southern Vietnam landscape. The As spikes and levels in the Mekong Delta soils and groundwater need restoration. The

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uptake of trace amounts of As in rice is indeed a critical food security and human health issue and requires mitigation.

Keywords

Arsenic, Mekong Delta, Anthropic Arsenic, Agent Blue, Khai Hoang, Cacodylic Acid, Water Treatment Plants

1. Introduction

Arsenic toxicity is affected by organic matter content, redox potential (Eh), hydrogen potential (pH), adsorption to solid matrices, and the presence of iron and other substances. The human body cannot produce arsenic; however, As can be bio-accumulated over time if present in contaminated drinking water and the local food supply.

Sources of Arsenic in Groundwater

A natural element, As, is present in the biosphere, hydrosphere, pedosphere and atmosphere. Arsenic is the 12th most abundant in the human body, the 12th most abundant element in the earth's crust, and the 14th most abundant in seawater. There are four oxidation states of arsenic: −3, 0, +3 and +5. Elemental arsenic is characteristic of the 0 oxidation state; gaseous arsine, (AsH_3) is characteristic of the −3 oxidation state. Water-soluble arsenite is characteristic of the +3 oxidation state commonly found in reduced natural environments such as anoxic waterlogged sediments or in permanent wetlands. Water soluble arsenate is characteristic of the +5 oxidation state in well-oxidized soil systems [1]. The most readily available oxidation states for bioaccumulation are the +3 and +5 oxidation states.

Arsenic, crystalline oxides As_2O_3 and As_2O_5 are the hygroscopic and readily soluble in water and form acidic solutions. Arsenic, a weak acid and the salts called arsenates, are the most common As contaminant in groundwater that affects the Vietnamese people of the Mekong Delta (**Figure 1**). Arsenic is water soluble and almost never found in its elemental form; rather, it forms compounds called arsenicals [2]. Arsenical compounds are detected in more than 200 different minerals [3]. Arsenicals are often associated with sulfurous minerals made up of sulfur, iron, gold, silver, copper, antimony, nickel and cobalt. Arsenical contaminants commonly occur due to natural weathering of minerals or through processing and smelting of metallic ores.

The fate of As in the soil environment has several pathways including: 1) reacting with and being retained by the solid phase of the soil, 2) leached out of the soil and into groundwater and 3) taken up by plants from groundwater and accumulated in the topsoil, or 4) emitted into the atmosphere as byproducts of biological decomposition or particulate matter due to dust or smoke [4].

The Environmental Protection Agency (EPA), European Union (EU) and World

Figure 1. Borders of the Mekong Delta in Vietnam and Cambodia. Map created by Mic Greenberg.

Health Organization (WHO) all recognize As contamination as one of the major threats to human health [5] [6]. The WHO guideline for untreated water is 100 μg/L prior to being processed for consumption and 10 μg/L for processed drinking water. Ingestion includes eating food crops that grew from arsenic contaminated irrigation water, and animals that were fed with arsenic feed additives including As-enriched drinking water from groundwater tube wells.

The World Health Organization (WHO) suggests 10 μg/L is the safe drinking water standard. Many countries ignore this standard since it takes decades for people to begin to show symptoms of having been poisoned. In Vietnam, the legal arsenic concentration limits were 50 μg/L or 5 times WHO drinking water standard. However, in 2018 the drinking water standard for Vietnam was lowered to 10 μg/l. Groundwater in the Mekong Delta is already naturally high in arsenic due to As-rich clayey parent materials originating from sediments washed down from the Tibet Highlands and soil parent materials collapse and compaction when groundwater is extracted releasing As.

Zosimos in 300 AD described roasting sandarach (realgar) to obtain cloud of As (arsenic trioxide) to reduce to gray As. Arsenic is frequently used as a tool to commit murder since the symptoms of arsenic poisoning are not specific. Eventually, the Marsh test, a sensitive chemical test for its presence was developed. As a result of arsenic's potency and the ability to be used discreetly, it was used by the ruling class to eliminate their competition. Thus, As was called the "poison of kings" and the "king of poisons" [7].

Arsenic and other heavy metals are finding their way into the human food supply [8] and are known to cause neurological disorders and cancer in humans. The neurological danger is different from the cancer focus and human offspring are a very important target audience. The findings are supported by previous research [8] regarding rice consumption in the Delta and long-term impact on local Vietnamese populace.

The primary objective of this research paper is to identify the natural and anthropic sources of As and to determine ways to reduce As levels in the Mekong Delta groundwater, soils and food crops including rice. During the last 60 years, the Vietnamese people living in the Mekong Delta have bio-accumulated As from natural and anthropic (Vietnam War contamination) sources via their drinking water and food supply leading to an increasing risk of chronic poisoning over time. The primary focus of this paper is to address the high levels of As in the groundwater. An attempt will be made to determine the anthropic and natural sources of As spikes in the Mekong Delta groundwater. The anthropic sources include the 1,132,400 kg of pure As applied as Agent Blue, the As-based herbicide, by the US Air Force as part of Operation Ranch Hand and the unrecorded amount of Agent Blue applied by the RV military with the assistance of the US Army and US Navy to Southern Vietnam. During the Vietnam War from 1962 to 1971 the As was applied to 400,000 ha of land by the Republic of Vietnam and the United States militaries. The fate of the anthropic and natural As and the impact on the soils, surface water and groundwater, food supply, drinking water and human health on the Vietnamese living on the Mekong Delta will be addressed.

2. Site Location

2.1. Mekong Delta Geography and Geology

Early Quaternary and older alluvial deposits reveal the tectonic and sea level adjustments, fold and fault lines, subsidence and uplifts that characterize the evolving Mekong River [9] The Mekong River is one of the world's most diverse and unique large rivers with a flood pulse that drives an extensive and productive ecological system.

About 40 million years ago, the Mekong River precursor drained into the sea near where the Red River now flows through Hanoi, Vietnam (**Figure 2**). Over time, earthquakes and volcanic activity of the Himalayas altered the mountain drainage southward via steep gorges that appeared about 13 million years ago [10] [11]. Below this area was a wide inland sea during the Upper Mesozoic. It is likely that the Mekong River at that time flowed directly south and to the west of the Korat Upland, joining what has become the Chao Phraya River in Thailand [11]. There is evidence that subsidence in the Tonle Sap basin of Cambodia, perhaps during the last 12,000 years, drew the Mekong River eastward to its present course and flows to the South China Sea and away from its former Chao

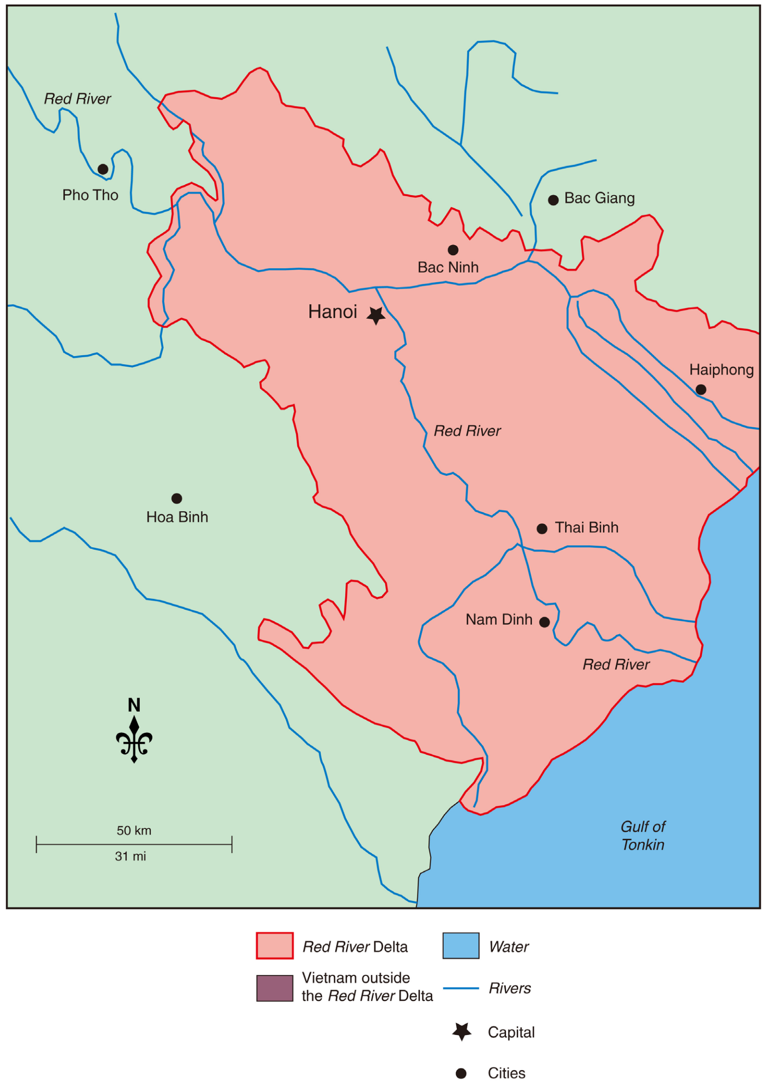

Figure 2. The Red River Valley and Delta near Hanoi and the Gulf of Tonkin. Map created by Mic Greenberg. Re-published with copyright permission from Managing Editor of OJSS.

Phraya connection and the Tonle Sap basin. The modern day Mekong River [12] carries a large supply of fluvial transported fine sediments and sands that originated in the Tibetan and Himalayan mountainous region to the Mekong Delta. These alluvial deposits have been mediated over time by glaciation, precipitation and evapotranspiration [9].

The Mekong Delta, begins near Phnom Penh, Cambodia (**Figure 1**) and extends east through Vietnam to the South China Sea. The Mekong Delta is the world's largest delta with 35% located in Cambodia and 65% in Vietnam. The 4350 km Mekong River flows south and then east into the South China Sea [10]. The Bassac River separates from the Mekong River near Phnom Penh and two rivers run parallel and east to the South China Sea. The Mekong River carries sediments and river water rich in As from the Tibet Highlands, the headwaters of the Mekong River. During the monsoon season, water flow in the Mekong

River greatly increases resulting in flooding of the lower stretches of the Mekong River. During these flooding events, floodwaters cover much of the Mekong Delta and deposited sediment, creating natural levees that migrated over time. Based on the intensity and magnitude of major flows, the natural levees can be overtopped and create midstream silt and sand bars [13].

The Mekong Delta is a flat, broad floodplain with alluvial soils (Entisols) [14], but has a "flooded" mountain region west of the Bassac River (**Figure 2**) and along the Cambodia-Vietnam border. Southern coastal dunes, along the South China Sea, are also high points above the marshlands and plains. This terrain is the result of folding by collision of Indian and Eurasian tectonic plates and tectonic uplift [13]. The Mekong River drainage system developed where the underlying geological structure is heterogeneous and active. The last glacial period ended abruptly 13,000 years ago when sea levels rose 4.5 m above present levels and the shoreline of the South China Sea reached modern day Phnom Penh, Cambodia (**Figure 3**) [13].

Figure 3. Mekong River landscape map. Re-published with copyright permission from Managing Editor of JEP. Map created by Mic Greenberg.

The Mekong Delta morphology was developed during the last 6000 to 10,000 years [9]. Eventually, the delta covered more than 62,000 km^2 of the South China Sea and developed 200 km to the east overlying the continental shelf [8]. The Mekong Delta was built up through tidal and fluvial tidal processes and was generally sheltered from the South China Sea and the Gulf of Thailand wave action [13]. However, the delta deposits were exposed to marine currents and other wave action that re-distributed the sediment to the southeast creating the Ca Mau Peninsula, a more recent, 6000 to 10,000 years old feature of the Mekong Delta. Due to the low flat topography and unconsolidated parent material of the Delta, the Mekong River has changed course many times. Riverbanks composed of unconsolidated sediments are unstable and highly erodible (**Figure 4**) [9].

2.2. Soils of the Mekong Delta

The soils of Vietnam were formed by alternating monsoon and dry seasons, sedimentation during river flooding, and intrusions of the South China Sea [14] [15] [16]. The Mekong Delta soils include Entisols, Inceptisols and Histosols (**Figure 5**) formed in the annual Mekong River and tributary fluvial deposits from the Tibet Highlands and carried by the river through the land masses of Laos, Myanmar, Thailand, Cambodia and Vietnam and into the South China Sea

Figure 4. Vietnam shore erosion along the Mekong River [37]. The house is falling into the river. Credit Line Courtesy of DTI News.

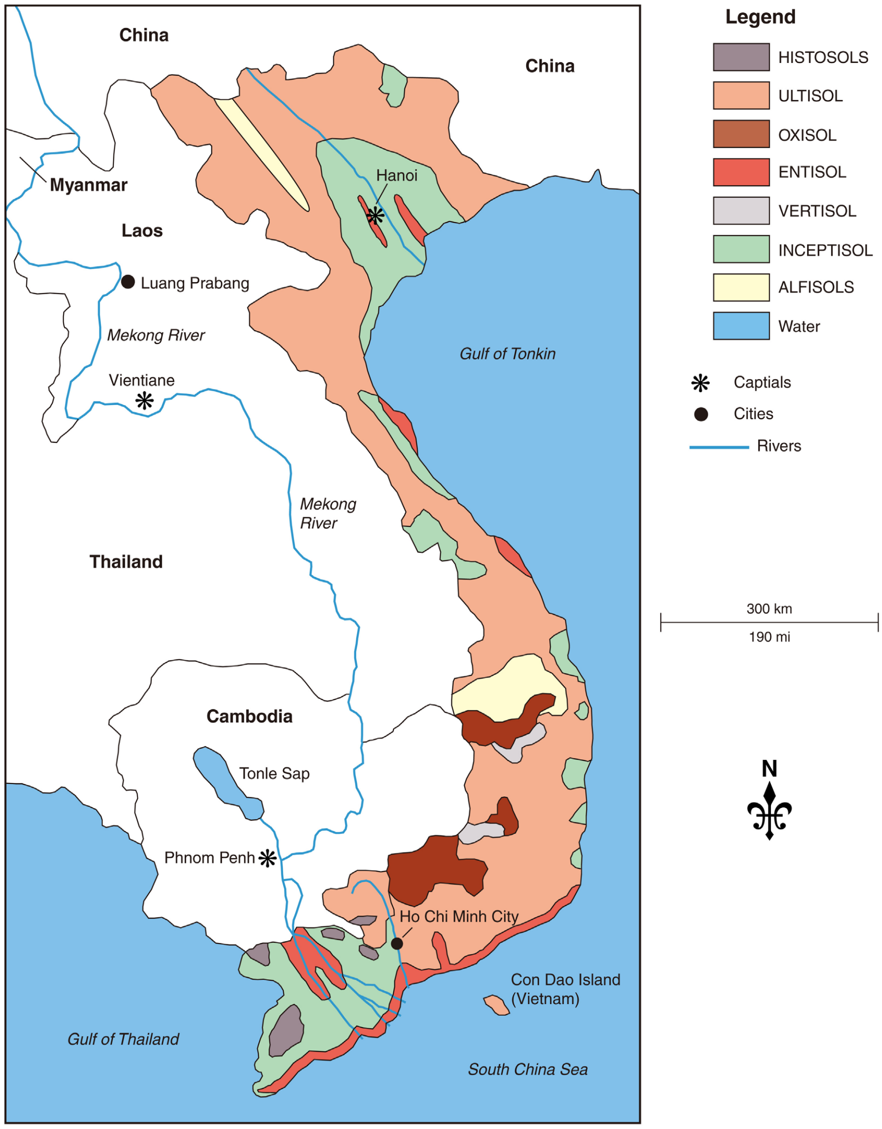

Figure 5. A soil map of Vietnam. Adapted from FAO/UNESCO Preliminary Definitions, Legend and Correlation Table for the Soil Map of the World. World Soil Resources Report No. 12; Rome: 1964. Adapted from Moormann. F. R. The Soils of the Republic of Vietnam. Saigon: Ministry of Agriculture, 1961. Map created by Mic Greenberg. Re-published with copyright permission from Managing Editor of OJSS.

(**Figure 6**). When the South China Sea covered southeast Vietnam millions of years ago, "Old Alluvium" soils (Ultisols and Oxisols) formed about 10 m above the recent floodplain deposits (Entisols) of the Mekong Delta.

2.3. Delta Wetlands and Mangrove Forests

Wetlands are distinct ecosystems where soils are seasonally or permanently water-saturated over extended periods from seasonal flooding and/or a high water table [17]. The wetlands of the Mekong Delta range from shallow freshwater depressions and ponds, backwaters of streams and rivers to vast seasonally flooded plains with melaleuca forests, rice paddies (**Figure 7** and **Figure 8**), brackish salt

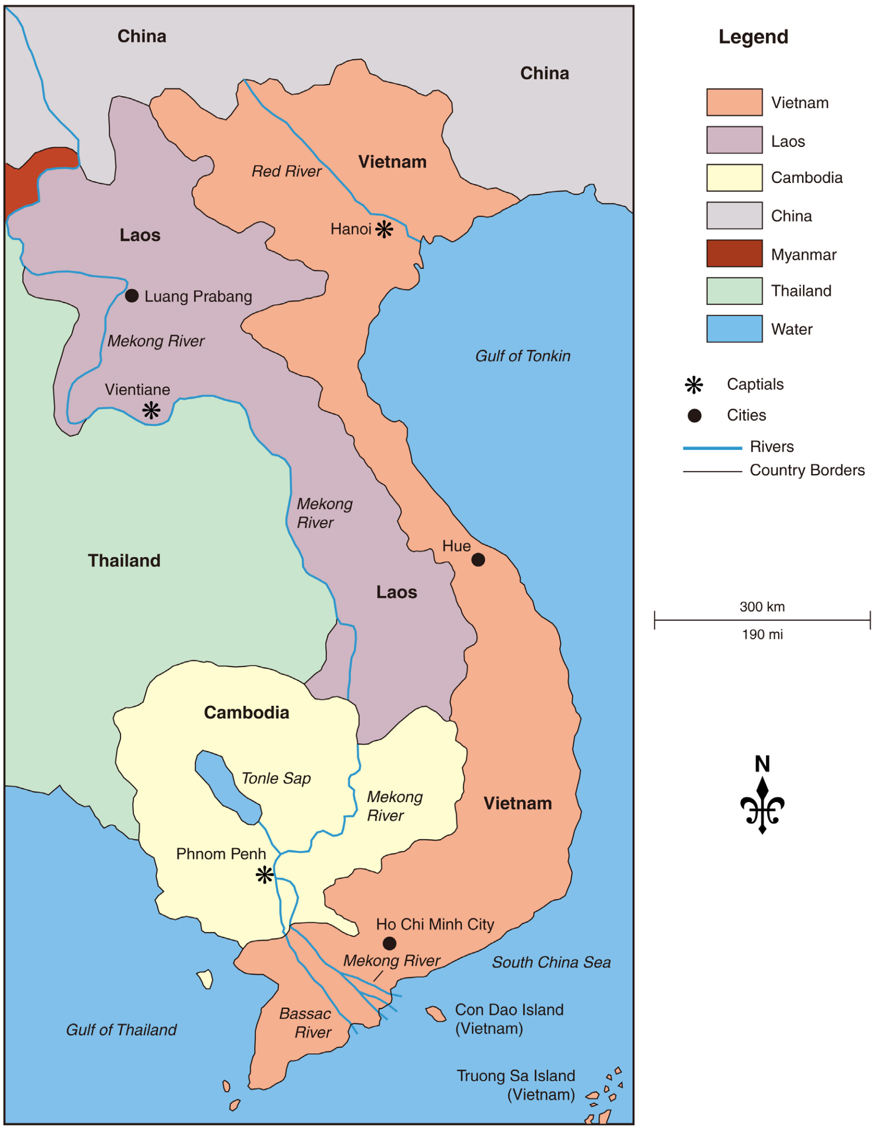

Figure 6. Mekong River from Tibet Highlands to South China Sea. Re-published with copyright permission from Managing Editor of JEP. Map created by Mic Greenberg.

Figure 7. Vietnamese and Montagnard rice growing in the Mekong Delta of Vietnam.

Figure 8. Rice paddies in the Mekong Delta. A view from Sam's mountain located near the Cambodia and Vietnam border.

marshes, mangrove swamps and tidal mudflats along the coasts, and many small offshore islands [17]. The wetland locations (**Figure 9**) in the landscape include edges of streams, rivers, and low depressions or coastal seas where precipitation and groundwater accumulated and affect the animal and plants communities, which had to adapt to permanent shallow water conditions and fluctuating wet and dry periods.

The hydrology, topography, and climate of the Mekong Delta determine whether the wetland is salt or fresh water. Flooding and rain during the wet season flush saltwater rivers (**Figure 10**), canals, and temporally replace salty waterways with fresh water. The major wetland areas occur in the Plain of Reeds located in Vietnam, freshwater wetlands located in Cambodia, and lands in the central delta both between and on both sides of the Mekong and Bassac river. Seasonally deposited sediments were carried downstream by the Bassac and Mekong rivers are fertile, and when the flooding is moderate the soils [18] in this part of the delta are not acid or saline [19]. The central delta is densely populated with settlements primarily along the river levees where the land is higher and protected from most floods. The seasonally inundated wetlands on the backside of the natural levees and away from the rivers were drained in the late 1970s by canals (**Figure 10**) and the areas became the major rice growing areas.

The delta coastal dunes (**Figure 3**) were formed by currents, tides and waves of the South China Sea from alluvial sediments and sand of the Mekong River with its nine channels. As the delta sediment deposits extended into the South China Sea, the dunes became inland ridges above the coastal wetlands. Dat Mui Nature Reserve is a delta ecosystem. Most of the original mangrove forests were

Figure 9. Picture of flooded fields from adjacent drainage ditches, waterways and Mekong River tributary.

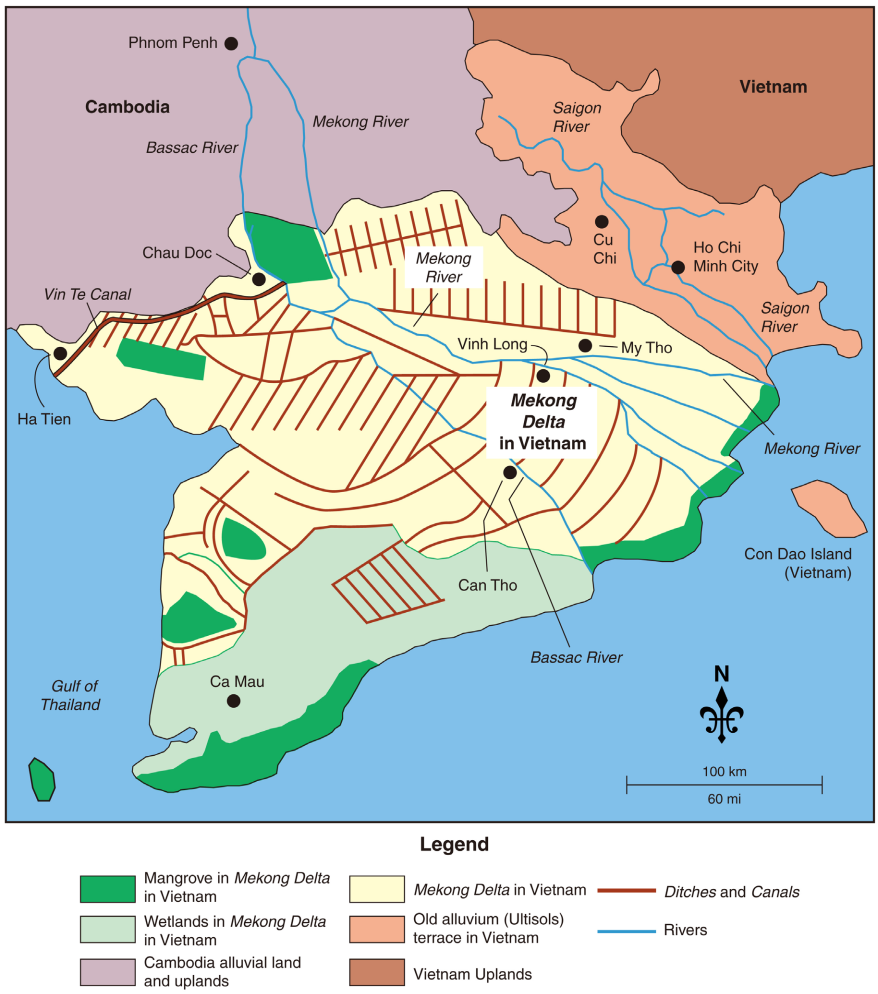

Figure 10. Mekong River and waterways and drainage ditches. Re-published with copyright permission from Managing Editor of OJSS. Map created by Mic Greenberg.

destroyed during the Vietnam War and later converted into shrimp ponds and other agricultural uses. Recently, the shrimp ponds have been phased out, and efforts are underway to revegetate coastal mudflats and inland mangrove forests.

3. Arsenic in the Mekong Delta Groundwater

3.1. Arsenic

Arsenic has an atomic number of 33 and is a chemical element, which occurs in many minerals. Arsenic and its compounds including trioxide are used in pesticides and insecticides. The herbicide use is declining due to the toxicity of As and its compounds and regulatory restrictions. Arsenic comprises about 1.5 ppm (0.00015%) of the Earth's crust and 53rd most abundant element. Typical background concentrations of arsenic are usually less than 3 ng/m^3 in the atmosphere, 100 mg/kg in the soils and 10 µg/L in freshwater.

Very few species of bacteria are able to use As compounds as respiratory metabolites. Arsenic poisoning of organisms occurs with quantities larger than needed. Arsenic contamination of groundwater is a problem that affects millions of people in the Mekong Delta and the world. The United States Environmental Protection Agency (EPA) states that all forms of As are serious risk to human health [20]. The US Agency for Toxic Substances and Disease Registry ranks arsenic No. 1 in its Hazardous Substances at Superfund sites. Arsenic is classified as a Group-A carcinogen. Synthetic arsenates are cupric hydrogen arsenate (acidic copper arsenate), calcium arsenate, and lead hydrogen arsenate. These three compounds have been used in agricultural insecticides, herbicides and poisons [8].

Historically, China was the top producer (70%) of white As followed by Morocco, Russia and Belgium. Most arsenic refinement operations in both the U.S. and Europe were closed because of environmental concerns. Unfortunately, As is often found in smelter dust from copper, gold and lead refinement processes [21].

3.2. Arsenic in the Vietnam Environment

Groundwater in Vietnam has naturally high As due to As-rich soils and geologic parent materials releasing As into groundwater. However, in the 1960s, the use of arsenic-containing herbicide (Agent Blue) during the Vietnam War and subsequent industrial developments greatly increased the levels of bio-available As in the soil and groundwater. Between the years 2000 to 2019, the Vietnam government increased the proliferation of shallow tube wells by subsidizing tube wells, and groundwater became the primary source of drinking and irrigation water in the Mekong Delta. This groundwater can contain As concentrations of up to 3050 µg/L [1] [22] [23]. Most of the As is in the +3 and +5 oxidation states, which is the most readily available form for bio-accumulation.

3.3. Natural and Geologic Sources of Arsenic

Alluvial soil layers were derived from arsenic rich sediment originating in the

Himalayas (Tibet Highlands) washed down to the Mekong Delta by rainfall and runoff. These alluvial layers of sediment have a natural abundance of As and are the primary cause of arsenicals in soil and groundwater [20].

Arsenic is released from exchangeable sites (phases) under acidic, oxic and reducing conditions. 1) Alluvial sediments have substantial amounts of As bound on exchangeable sites. The presence of co-existing ions, such as Si and DOC compete for the adsorption sites, which can be affected by variations in pH. 2) Kaolinite, muscovite and clinochlore are sources/sinks of dissolved As. 3) Peat layers in sediments contain substantial amounts of As. 4) Release of As is more extensive under acid conditions. 5) Arsenic mobility in sediments was enhanced under reducing conditions via reductive dissolution of iron-oxyhydroxides/oxides. 6) Anthropogenic activities and geochemical variations enhance the release of As from sediments into groundwater.

3.4. Arsenic Uptake by Rice Plants

Arsenic availability to rice plants is primarily influenced by soil physical and chemical properties [8]. Soils that have high As retention capacities can lead to increased As concentrations in the soil surface and decreased root and shoot lengths [21]. Arsenic interferes with plant metabolic processes, inhibiting plant growth and at high concentrations kills the plants [21]. Arsenic toxicity affects the root anatomy, root oxidizability, electrolyte leakage, water content, lipid peroxidation and damages protein, amino acids and nuclei acids, and antioxidant activities in rice. Rice plants are most sensitive to As toxicity during their early growth period. Their defense mechanisms are underdeveloped and seedling growth, roots and shoots are highly vulnerable [21]. Rice grown in flooded conditions is especially at risk from not only direct herbicide applications via aerial spray to their shoots but also from As that accumulates in rice paddy sediments and paddy waters, and can have toxic effects to current and future crops [21] [24]. Arsenic in rice paddy waters increases the concentrations of As in the rice grain, hulls and straw [24].

3.5. Arsenic Levels in Groundwater of the Mekong Delta

In Vietnam, the Mekong Delta, is one of the most densely populated regions in the world. The Vietnam Mekong Delta has an area of 39,000 km^2 with a population density of 500 people/km^2.

Approximately, 13 of the 20 million Vietnamese lack access to public water supplies and have to depend on groundwater and river water to meet the household and drinking water needs. UNICEF has encouraged the digging of private tube wells due to the pathogen-contaminated river water. Many Vietnamese have developed cholera, dysentery and other diseases. Currently, there are over 700,000 tube wells in operation in the Mekong Delta and the number is rapidly increasing. Unfortunately, much of the groundwater extracted from these shallow alluvial aquifers (less than 150 m in depth) are often enriched in

As [25].

Hoang *et al.* [26] found positive correlations between total organic carbon (TOC) and As concentration in groundwater. The wells with a high TOC content had much higher mean As concentration than did wells of low TOC. In Cambodia, the groundwater was associated in proximity to the modern major channels of the Mekong River [20]. The river water may contain an As concentration similar to the concentration in its associated aquifer. River water can contain a considerable amount of organic C originating from various wastewater sources as well as natural sources such as decaying wetland and jungle vegetation.

Huyền's [27] results showed that most of the alluvial sediments have substantial amounts of As on exchangeable sites that are easily released into solution. Leaching experiments with deionized water suggest As release is controlled by sorption-desorption reactions with clays, proton-promoted dissolution of iron, and oxidation of pyrite/organic matter. As mobility of As was enhanced under acidic conditions in presence of chloride. Seasonal drying/flooding episodes generating acid sulfate soils. Salt-water intrusion due to excessive groundwater abstraction may exacerbate the problem in the future.

3.6. Arsenic Fate in Surface Waters, Fish, Shrimp and Rice

In surface waters the arsenites and arsenates can be absorbed by algae and algae converts these water soluble and inorganic arsenite and arsenate to organic arsenic arsenosugars, arsinolipids and arsenobetanine. Fish feed on the algae and concentrate the As compounds. Due to relatively low toxicity of organic arsenicals there is little risk or concern regarding seafood. However, rice grows in flooded paddies where surface water has four inorganic arsenicals that are absorbed by the growing rice plants, which are translocated to the grain. The amount of toxic inorganic As that ends up in rice grain depends on how rich in anthropic and natural As the alluvium parent material and contamination levels in groundwaters. The Mekong Delta like most SE Asia deltas has an abundance of natural and anthropic As in both the parent material and the groundwater pumped to the surface using tube wells for the rice paddies, shrimp ponds and drinking water [27].

3.7. Toxicity of Arsenic and Effects on Human Health

There are two forms of As, organic and inorganic. Organic As is not thought to be harmful except in high doses and can be found in soil, water and food around the world. Inorganic As is not in food and water that humans ingest but is found in nature. Inorganic As is highly poisonous and is a known carcinogen [8].

Initially, it was thought that organic As would never become inorganic As. However, now there is considerable doubt. Chickens in the U.S. were given compounds with organic As in them to make the meat more plumb, redder and prevent certain chicken diseases (8). The chicken and chemical industries had insisted the As in the compounds were organic. However, the livers of chicken feed with organic As compounds were found to contain more As than the control group. Researchers concluded that organic As had been converted (transformed) into the lethal inorganic As. After a release of a 2011 peer-evaluated FDA study 89 forms of 102 As compounds which could potentially be converted from organic to inorganic As were removed from the market.

3.8. Wells and Water Pumping

After Vietnamese government opened the economy in 1986 and encouraged rice exports, the villagers used their increasing wealth to drill private wells (**Figure 11** and **Figure 12**) which strained groundwater resources. The Vietnamese also disrupted a centuries-old canal system (**Figure 10**) which favored surface irrigation. Since then, rice farming in the Mekong Delta has been replaced with more profitable shrimp farming [14]. The shrimp industry also requires groundwater to continually dilute brackish water that develops in ponds due to water evaporation to prevent shrimp yield declines. However, in the 2010s the use of groundwater for shrimp ponds has been restricted or eliminated.

Figure 11. Private well drilling operation with wells used for irrigation.

Figure 12. Private commercial well head used to irrigate crops.

Ca Mau providence is on the Delta's southern tip and is in an area where groundwater resources have been over-exploited. More than 100,000 wells have been drilled for shrimp farms (Figure 13) and rice paddies. Wells for shrimp farms and rice paddies are now no longer being drilled. In addition, the urban population of Vietnam has increased from 66 million in 1990 to 90 million in 2013 with population continuing to expand [18] [28]. Groundwater wells are being drilled deeper and pumps are bringing up increasingly saltier water (Figure 14 and Figure 15). Because the depletion of the groundwater resources results in a negative water pressure in the fresh water aquifers, saltwater is penetrating farther and farther into the Mekong Delta every year. Saltwater is heavier than freshwater and migrates both laterally and down through sediments and into shallow aquifers from above. That makes groundwater less potable and less desirable for irrigation. Salt ions also react chemically with sediments making the soil and parent material (alluvial sediments) more prone to oxidation, dispersion and compaction, and therefore results in land subsidence (Figure 15).

Figure 13. Shrimp farm in Mekong Delta of Vietnam that was developed after 1975.

Figure 14. Tubs wells with hand pump used in Mekong Delta.

Figure 15. Dried red clayey soil that was covered by salt water and then dried.

The overlying fresh water creates a head pressure holding the deeper water under pressure. As the shallower water is removed, the head pressure is reduced and the deeper water compressed by the overlying pressure will move into the space vacated by the fresh water. If the deeper water is under artesian pressure, this process will proceed more quickly. The same happens with lateral movement of seawater into a fresh water aquifer. The pumping of salt water can also contaminate fresh groundwater from below especially where the deeper aquifers have artesian characteristics [29]. Fresh water over more ancient seawater reduces head pressure on the deeper water and it can move upward through excessive pumping as the overlying head pressure is reduced. The process can take a few years, however declines in pumping create a reverse process due to surface water recharge restoring the head pressure than can take decades to achieve.

Many of the deep wells in the Mekong Delta were contaminated with As from anthropic and natural sources [22] [30] [31]. Pliocene-age aquifers as deep as 200 m can have elevated levels of anthropic and natural As [32]. Arsenic occurs in deltaic sediments throughout southern Vietnam and Southeast Asia. Solid-phase As can be released to groundwater during the microbially mediated reductive dissolution of ferric hydroxides found in river-born sediments. Seven major aquifers have been identified in the Mekong Delta. The most prominent As hotspot region, which is over 1000 km^2 in size and is 50 km southwest of Ho Chi Minh City [32].

The deep contamination of the Mekong Delta focus area is unlikely to have been caused by the shallow contamination mechanism: pumping-induced vertical migration of As or dissolved organic carbon (DOC) that triggers As release. Shallow wells are less contaminated with As than deep wells. Why? Deep pumping since the mid-1990s has resulted in hydraulic heads in deepest Pliocene-Miocene-age aquifers to decline by several meters. Head declines, in effect, are a result of a dewatering process, which induces sediment particle realignment and induces sediment compaction as water that previously supported a less organized particle arrangement in the sediments is changed by water pumping. The pumping-induced compaction is greatest in clays while sand cannot easily be compressed or compacted.

Some of the collapse is actually due to the weight of the overburden sediments compressing the underlying dewatered sediments causing the subsidence. The overburden sediments, if saturated, would be heavier that unsaturated sediments creating a downward hydraulic pressure possibly actually pressurizing the aquifer that is being pumped. If the overlying materials are kind of an aquitard, then the zone being pumped out of could actually be a sort of artesian zone depending of where the recharge area for that zone is. Wells penetrating into the aquifer could then perforate the overlying aquitard, causing pressurized As containing water to be forced up into the shallower aquifers, contaminating them. If the sediments in the older aquifers were high in natural As, the long-term saturation of the aquifer would possibly allow greater As dissolution and concentration in the waters.

Water rich in As can be expelled from compressible clays and subsequent shrinking has resulted in land subsidence [32]. Compaction due to pumping, allows dissolved As and other toxic solutes stored in the interbedded clays to be expelled from the clay surface exchange sites and into the adjacent aquifers. The solutes removed from clay sediments include DOC [33] or other competing ions that could promote As dissolution, desorption or displacement within aquifers.

3.9. Impact of Arsenic on Human Health

The Cancer Assessment Group of EPA currently puts As in the top category of cancer-causing chemicals. Arsenic, even at low doses, has been found to be responsible for lung, bladder, liver disorders and cancer. Arsenic is able to cross the placenta to create cancers in the fetus and both birth defects and childhood cancers have been linked to As. The effects of As can take decades to occur in humans. Arsenic can and does cause damage to human DNA, which adversely affects the DNA of future generations [8].

Arsenical herbicides containing cacodylic acid as active ingredients are still used today as weed killers for limited purposes. Less toxic formations of arsenical herbicides sold over the counter today can cause headaches, dizziness, and vomiting, profuse and watery diarrhea, followed by dehydration, electrolyte imbalance, and gradual fall in blood pressure, stupor, convulsions, general paralysis and possible death in 3 to 14 days [34].

3.10. Anthropogenic Sources of Arsenic

Arsenic concentrations also rise due to anthropogenic sources. Smelting of nonferrous ores create arsenic trioxides that volatilize and attach to particulate material (dust) in the atmosphere and fall out on neighboring fields and towns.

Millions of deceased Vietnamese with potentially significant levels of As in their bodies have been buried in the soil (**Figure 16**) and may have contributed to elevated As levels. Untreated As filters are dumped into landfills without liners or leaching barriers and result in As leaking back into the soil and alluvium. Mine acid drainage can lower pH and create a favorable condition for As dissolution from sediment into groundwater or speeds-up the natural release of arsenicals into the groundwater. Chemical, physical and biological methods have been used to remediate As contaminated water [27].

When plants are exposed to and take up As-contaminated groundwater, the As is retained at levels sub-lethal to the plants in the plant tissue or grain that is fed to poultry and livestock as forage and grain (**Figure 17**). The As bio-accumulates in the animals and animal products (meat, milk, eggs) that are consumed by humans. It can also pass through the animals as urine and fecal matter that then used as fertilizer, which in turn results in As levels increasing in cultivated soil and groundwater.

Figure 16. Urban cemetery in southern of Vietnam.

Figure 17. A water buffalo in rice paddy in Mekong Delta of Vietnam.

Anthropic arsenic contamination of shallow groundwater is among the most significant health threats in Southeast and East Asia deltas. An extraction of As-enriched waters from Holocene aquifers to naturally uncontaminated Pleistocene aquifers result in more than a century of groundwater abstraction. Vertical arsenic migration induced by large-scale pumping from both aquifers (**Figure 14**). Deltas most likely to be affected are where groundwater is extensively pumped to soil surface from uncontaminated aquifers underlying high As aquifers or zone.

In the Mekong Delta this includes rice paddies laced with Agent Blue, an As based rice killing herbicide, which was used during the Vietnam War. Arsenic has no half-life. The chemicals of choice were the phenoxy and arsenical (tactical) herbicides. Thus, the use of herbicides in Southern Vietnam removed foliage along travel routes, defoliated areas surrounding United States and North Vietnam bases and communication routes, improved visibility in heavily canopied jungle, and destroyed insurgent subsistence crops.

Most of the As in the Mekong Delta groundwater is from natural alluvial sediment sources. However, Agent Blue, the As based herbicide, used during the Vietnam War did contribute a significant amount (over 1,132,400 kg) of manufactured (anthropic) As to the Southern Vietnam landscape. Other anthropic sources include the burial of millions of Vietnamese with elevated As levels since 1962, industrial sources smelting by-products; wastewater and water treatment plant (**Figure 18**), intake of polluted river water, discharges into rivers, water treatment plant filter disposal in landfills have added to the Mekong Delta As levels in the soil and groundwater. The As spikes and levels in the Mekong Delta soils groundwater requires mitigation. Arsenic in rice can be more problematic than As in fish (**Figure 19**) or shrimp. The uptake of trace amounts of As in rice is indeed a critical food security and human health issue.

Figure 18. New water treatment plant on a Mekong River tributary. The goal is to supply treated river water to the villagers rather than potentially polluted and arsenic rich Mekong groundwater previously available via individual tube wells.

Figure 19. Fish (pisces) is the main source of protein and income for SE Asia families. A fish market in Ho Chi Minh City.

3.11. Republic of Vietnam and United States Military Contribution to Arsenic in the Mekong Delta Groundwater

The use of tactical herbicides in Southern Vietnam was begun as an initiative of Republic of Vietnam (RV) government. Part of the RV government's policy was to move the rural population into "strategic hamlets" that could be more easily secured and defended than the existing villages. This also allowed the destruction of the rice crops, a potential North Vietnamese Army (NVA) food source, to discourage NVA activities. The RV government insisted that Agent Blue be used to destroy the rice crop in southern Vietnam and President Kennedy finally gave the okay for testing Agent Blue on the food crops in southern Vietnam [35] [36], according to Lindsey Arison III in his report "The Herbicidal Warfare Program in Vietnam, 1961-1971". In the early 1960s the RV program known as Khai Hoang Program, was designed to make battlefield more visible by clearing foliage leaves and eliminating the food crops. This secret NVA program, from 1962 to 1965, was supported by the US military (Air Force, Army and Navy). Theses Agent Blue missions required US military handlers dressed in civilian clothing, aircraft without US military markings and if the military personnel were captured the US government would not acknowledge the crew as members of the US military [36] [37]. Most of the handlers of Agent Blue were Vietnamese and no US military warnings or safety equipment was provided. Nor were the RV military soldiers and handlers warned against drinking the water from rivers where Agent Blue was sprayed. No Vietnamese military or civilian personnel knew about the contamination or the inherent health hazards of the Agent Blue the chemical herbicide they were handling. Approximately, 3.2 million liters of Agent Blue (468,008 kg As) was sprayed or dumped by the RV military with the support of the US military during the extended Khai Hoang Program (1962 to 1971) [8] [38] [39].

President Kennedy's Joint Chiefs of Staff stated, in early 1960s, that "Care must be taken to assure that the U.S. government does not become an international target for charges of employing biological or chemical weapons". International repercussions against the United States could become significant [40] [41]. After considerable internal debate, President Kennedy gave the approval needed to use Agent Blue on Southern Vietnam food crops including rice.

On 9 January 1962 the first shipment of sodium salt of cacodylic acid and code-named "Blue" were received at Tan Son Nhut Air Base, RV. These first shipments of Blue, were in powder form and had to be mixed with water before spraying. Later shipments of Agent Blue barrels had a blue colored band painted around the centers of the 208-liter drums and designed as an identification aid for support personnel. Agent Blue was the first tactical (rainbow) herbicide used in Operation Ranch Hand, the tactical aerial spraying program in Southern Vietnam of the U.S. Air Force [42] [43].

The first recorded use of Agent Blue by the US Air Force was in November of 1962. During the next nine years 4.6 million liters (664,392 kg of As) were sprayed during Operation Ranch Hand missions [44] [45]. This was in addition to the 3.2 million liters of Agent Blue (468,008 kg As) sprayed or dumped by the RV military with the support of the US military during the Khai Hoang Program [8] [34].

The Institute of Medicine [8] [34] suggests a total of 7.8 million liters (1,132,400 kg As) of Agent Blue was applied to Southern Vietnam from 1961 to 1971. This total includes both the Agent Blue used in US Air Force Operation Ranch Hand and the Agent Blue used in the RV Khai Hoang program which was supported by the US Air Force, Army and Navy. New studies of US military flight logs suggest an even greater use of Agent Blue; however, the Agent Blue application total of 7.8 million liters (1,132,400 kg As) applied to Southern Vietnam, from 1961 to 1971, is the best available documented application total [8] [34].

3.12. Impacts of Arsenic in the Environment

Many Southeast Asia countries with deltas including Vietnam and Cambodia have geological environments that produce a high As content in groundwater. Arsenic in groundwater poses a growing health threat in the deltas of Southeast and South Asia through human consumption of naturally and anthropically contaminated groundwater. Exploitation of both shallow and deep aquifers in Southeast and South Asia caused interbedded clays to release of dissolved As or As-mobilizing solutes. As a result, deep, untreated groundwater will likely become contaminated with As.

Arsenic is naturally present in the environment and comprises 99% of human exposure to As, through ingestion of small concentrations in water and the food supply (**Figure 19** and **Figure 20**). It accumulates in the body and takes decades before any physical symptoms of As poisoning are evident. The proliferation of

Figure 20. Rice crop residual grain being hand seeded in Mekong Delta.

Vietnam government-subsidized shallow tube-wells in past 30 years, shallow groundwater has become the primary source for drinking and irrigation water in Mekong Delta. Another pathway for human exposure is inhalation of atmospheric gases and dusts. Over the past 60 years, disturbance of As contaminated soil by industrial development has maintained bio-available arsenicals in the human environment. People often begin showing symptoms of having been poisoned decades after chronic exposure.

The Mekong River Delta groundwater has As concentrations of up to 3050 μg/L [1] [22] [23], which is more than 300 times the World Health Organization (WHO) guidelines. The safe concentration of As in drinking water is 10 μg/L. The toxicity of As is related to its solubility which is affected by the pH of the environment in which it occurs. Arsenite (+3 oxidation state) is more soluble than arsenate (+5 oxidation state) at lower pH and are the most readily bioavailable oxidation states. At lower pH arsenite is more mobile and toxic.

High concentrations of As in groundwater which is often the primary drinking water source in the Mekong Delta and the source of water for agriculture production need remediation. Developing optimal treatment processes for Mekong Delta groundwater for drinking water and irrigation water is needed to reduce the As ingestion by the Vietnamese people who consume plants products, rice and vegetables produced with contaminated water and soils. The continued success of the Mekong Delta economy is dependent on agriculture.

4. Discussion

4.1. Bioremediation

The As in the groundwater is primarily of natural origin. As is release from sediment into groundwater and caused by *anoxic conditions* of the waterlogged subsurface sediments. In the Mekong River Delta, the Vietnam government undertook a massive shallow tube well drinking water program in 1980s. This program was designed to prevent drinking of bacteria—contaminated surface waters but failed to test for As in the groundwater [3]. Increased levels of As exposure increased skin cancer. Epidemiological studies suggest inorganic As exposure can increase the risk of bladder cancer. Epidemiological studies suggest a correlation between the leading causes of mortality [34] and chronic consumption of drinking water suggests, As exposure is causative in the pathogenesis of diabetes.

Bioremediation of groundwater contaminated with As aims to convert arsenite, the toxic form of arsenic to humans, to arsenate. Arsenate (+5 oxidation state) is the dominant form in surface water while arsenite (+3 oxidation state) is the dominant form in hypoxic to "anoxic" environments. Arsenite is more soluble and mobile than arsenate. Many species of bacteria can be used in groundwater remediation.

Another bioremediation strategy is to use plants that accumulate As in their tissues via phytoremediation, but the disposal of contaminated plant materials needs to be considered. Bio-remediation requires an evaluation of existing conditions. Some sites require addition of substances containing an electron acceptor while others require microbial supplementation (bio-augmentation).

4.2. Water Treatments

A successful process for removing arsenic from drinking water is to co-precipitate the dissolved As with iron or aluminum oxides. USEPA and NSF have funded several adsorptive media systems. European and Indian scientists and engineers have set up six As treatment plants in West Bengal [45]. The technology does not use any chemicals; an As is left in the insoluble form (+5 state) in the subterranean zone by recharging aerated water into the aquifer and developing an oxidation zone that supports microorganisms that oxidize As. The process does not produce any waste stream or sludge and is relatively inexpensive [34].

Another approach in the Mekong Delta is to drill 150 m or more into aquifers that have low As levels, but this approach is now contaminating the lower aquifers [46]. Klassen *et al.* [47] found deep sediment could remove As and take it out of circulation. This process is called adsorption. Arsenic adheres or bonds to surface of deep sediment (clays and silt) particles and naturally removed from groundwater. This process is however reversible and arsenic attached to soil particles can be released into the groundwater.

Magnetic separation of As at very low magnetic field gradients with high-surface area and monodisperse magnetite (Fe_3O_4) nanocrystals have been used in a point of use water purification. Fe_3O_4 nanocrystals have high specific surface area and reduce the mass waste associated with As removal from water. Chaff-based filters have been shown to reduce the As content of water to 3 μg/L. This may have applications in areas where portable water is extracted from an underground aquifer. However, the disposal of Chaff-based filters in landfills without liners can result in arsenic pollution of the groundwater.

4.3. Remediation of Arsenic in Rice

Management of contaminated water can reduce concentration of As in food supplies. Recent experiments show rice grain crops grown in soil with high As concentrations had elevated levels of As in the rice roots, leaves, grain, cooked rice, hulls, and straw [26] [38]. The flooded or wet rice production system traditionally transplants seedlings into puddled paddy fields. In this planting system, anaerobic As contaminated soil promotes increased As availability and uptake by the plant resulting in high As concentration in rice straw and grain [24] [38]. Many of Vietnam's Delta soils are high in iron oxides. Under anaerobic conditions such as flooded rice paddies, iron oxides are reduced and release inorganic As from sediments and soils making the As more available for plant use.

Water management experiments show that growing rice on raised beds with irrigated furrows between the beds rather than flooding the entire field reduces As concentration in rice primarily because of being under aerobic conditions. As is bound to iron oxides and not available for plant uptake in the soils of the beds [25]. This alternating wet and dry soil zones reduces water logging by the irrigation and reduces the amount of As released from the soil as soluble As from the irrigation waters by soil fixation which lowers the As bioaccumulation in plants [24]. Other mitigation strategies to reduce the arsenic loads in the food supply are selection of the rice cultivar and rotations with other non-rice crops with low As uptake [24] [33]. Screening of rice cultivars that do not easily uptake As and translocate into the grain reveals that root traits with higher porosity and capacity to form iron plaques that bind more As result in lower As concentration levels of translocation throughout the plant [33]. Other species that generate reactive oxygen and produce antioxidant enzymes have been found to reduce As toxicity and enhance plant resistance to bioaccumulation [48]. More research in this area is needed to identify and test crops. The different farming methods and rice cultivars used in California, Pakistan, Texas, Louisiana, and Arkansas rice production could provide useful technical guidance to help mitigate the Mekong Delta rice-arsenic problem.

5. Summary and Conclusions

Arsenic levels are naturally high in the Mekong Delta environment of Vietnam. Anthropic sources are increasing the As spikes and levels in the Mekong Delta groundwater. The human exposure to As is primarily (99%) through ingestion. Arsenic is known as the "king of poisons" and is mutagenic, teratogenic and carcinogenic. According to World Health Organization (WHO), the safe concentration level of As in drinking water is 10 μg/L. The Vietnam legal As concentration limit was 50 μg/L or five times the WHO guidelines until recently.

The American military (1962 to 1971) did contribute an additional anthropic source of manufactured As during the Vietnam War to most of Southern Vietnam including the central highlands and the Mekong Delta. Additional anthropic sources include the burial of millions of Vietnamese since 1962 with high As levels, industrial sources, water treatment, sewage and wastewater treatment discharges into the waterways, smelting, and water treatment plants have added to the As levels. Arsenic does not have a half-life and once added to the environment continues to exist. The arsenic can only be transported in the harvested grain, volatized, incinerated into the air, transported in surface water, or leached back into the groundwater only to be returned back to surface via tube-wells.

Fish and shrimp ingest significantly more arsenic than rice but it is converted to less harmful organic As that is excreted in large quantities from the human body. In contrast, the rice plant transfers the more toxic inorganic As to the grain that is consumed but is more difficult for humans to excrete. These trace As amounts can be bio-accumulated especially if you eat rice three times a day (along with some Mekong River shrimp and fish) for a lifetime.

The proliferation of Vietnam government-subsidized shallow tube wells in the 1990s to 2010s returned the As-rich groundwater to the soil surface for agricultural and urban uses. During the past 60 years of industrial development disturbance of As contaminated soils has increased the bio-available arsenicals in the environment. The high As levels in the Mekong Delta create two problems, As in the drinking water and As in the food supply, which both are in need of mitigation. Drinking water requires treatment to reduce the As levels to WHO standards. One successful process for removing As from drinking water is to co-precipitate the dissolved As with iron and aluminum oxides. Another way is through magnetic separation of As in point source water purifications. Another is to use Fe_3O_4 nanocrystals and chaff-based filters to reduce the As content of the water below WHO standards. Chaff-based filters should be incinerated rather than placed in a landfill lacking a liner.

Among the mitigation strategies to reduce the arsenic loads in the food supply are rice cultivar selections and rotations with other non-rice crops with low As uptake. The disposal of As contaminated plant materials needs to be a consideration. Many of Vietnam's Delta soils are high in iron oxides. Under anaerobic conditions such as flooded rice paddies, iron oxides are reduced and released inorganic As from sediments and soils making the As more available for plant use. This is part of the problem. Water management experiments show that growing rice on raised beds with irrigated furrow between the beds rather than flooding the entire field reduces As concentration of rice grain primarily because of the aerobic soil conditions.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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