Scientific Research Publishing

Open Journal of Soil Science, 2022, 12, 253-294
https://www.scirp.org/journal/ojss
ISSN Online: 2162-5379
ISSN Print: 2162-5360

Agent Blue Spraying in the Mekong Delta during the Vietnam War: Fate of the Arsenic Based Herbicide Weapon Used to Destroy Rice Crop and Mangrove Forests

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How to cite this paper: Olson, K.R. and Cihacek, L. (2022) Agent Blue Spraying in the Mekong Delta during the Vietnam War: Fate of the Arsenic Based Herbicide Weapon Used to Destroy Rice Crop and Mangrove Forests. *Open Journal of Soil Science*, **12**, 253-294.
https://doi.org/10.4236/ojss.2022.127012

Received: June 28, 2022
Accepted: July 12, 2022
Published: July 15, 2022

Abstract

Agent Blue, a mixture of cacodylic acid (CH_3) As O_2H) and sodium cacodylate (C_2H_6 $AsNaO_2$), was a tactical arsenic-based herbicide used during the Vietnam War to destroy grasses and rice crops. Natural and synthetic sources of arsenic can degrade into water-soluble forms and persist in groundwater and potentially contribute to elevating As levels in drinking water. The United States Department of Defense (DOD) and United States Department of Agricultural (USDA) Operation Ranch Hand records for tactical herbicides including Agent Blue sprayed in southern Vietnam during the Vietnam War (1961-1971) are very detailed, rather complete and publicly available. The same is not true for tactical herbicides sprayed by the Republic of Vietnam (RV) during the Khai Quang program which was supported by the U.S. Army, U.S. Navy and Central Intelligence Agency (CIA) in the Mekong Delta. Agent Blue was sprayed by the RV military for three years before the official start of the American-Vietnam War. Few, if any, RV military, US Army, US Navy and CIA spray records exist from 1962 to 1965. Vietnam War veterans, historians and scholars have reported the spraying of 3.2 million liters (468,008 kg As) of Agent Blue on rice paddies and mangrove forests in the Mekong Delta and Central Highlands by the RV military with the support of the US Army, US Navy and CIA. The Institute of Medicine estimated that 3.2 million liters (468,000 kg As) were sprayed during the RV Khai Quang program. This was in addition to the U.S. Air Force's Operation Ranch Hand spraying of the tactical herbicide Agent Blue primarily by C-123 aircraft. The Operation Ranch Hand missions maintained location and quantities of her-

bicides sprayed (over 4,712,000 liters (664,392 kg As) from 1961-1971. The RV military and US military (Army and Navy) spray equipment included hand and backpack sprayers, sprayers mounted on Brown Water Navy boats, on Army track vehicles and Army land-based helicopters and helicopters based on the decks of Blue Water Navy ships. Some of these spray missions were a military secret and spray records were classified or if kept were not maintained. Agent Blue containing cacodylic acid had a short half-life and degraded to water-soluble arsenic, which was released into the surface water and/or leached into the groundwater. Once the water-soluble arsenic leached into the Vietnam Mekong Delta groundwater, the arsenic-rich water was pumped back to the surface by tens of thousands of tube wells for urban and agricultural use. The primary objectives of this research are to explore the conditions during the Vietnam War under which 1) the RV military herbicide spray program with the support of the US Navy, CIA and US Army, and 2) the US Air Force spray program during Operation Ranch Hand may have significantly contributed to the natural and anthropic As spikes found in the Mekong Delta today. The environmental impacts of Agent Blue, on the Menominee River at manufacturing sites in the United States, were studied to identify possible As remediation and mitigation strategies. The lessons previously learned at the manufacturing sites in Wisconsin and Michigan, United States can be considered and applied to the Mekong Delta to help mitigate and remediate the arsenic-rich surface water, soil, sediment and groundwater found in the Mekong Delta.

Keywords

Operation Ranch Hand, Khai Quang program, Agent Blue, Arsenic, Cacodylic Acid, North Vietnam Army, Republic of Vietnam, Democratic Republic of Vietnam, American-Vietnam War

1. Introduction

1.1. Democratic Republic of Vietnam (DRV) and the Republic of Vietnam (RV)

After the end of the First Indochina War, the nearly century-long colonial rule of the Indochina region by the French ended with a defeat in the battle of Dien Bien Phu. In July 1954, a treaty was signed at the Geneva Conference that split Vietnam (**Figure 1**) in half at the 17th North Parallel latitude line. The DRV controlled the north and the RV, with U.S. backing, controlled the south [1].

In 1959 DRV, with the objective of re-uniting the country of Vietnam, began military actions against the RV in the form of guerilla attacks. The U.S. then started to provide military assistance to "stop the spread of communism" which was called the "domino theory". Initially, the U. S. only provided technical aid and support which included tactical herbicide weapons. However, following the August of 1964 Gulf of Tonkin incident, in which U.S. destroyers off the coast of

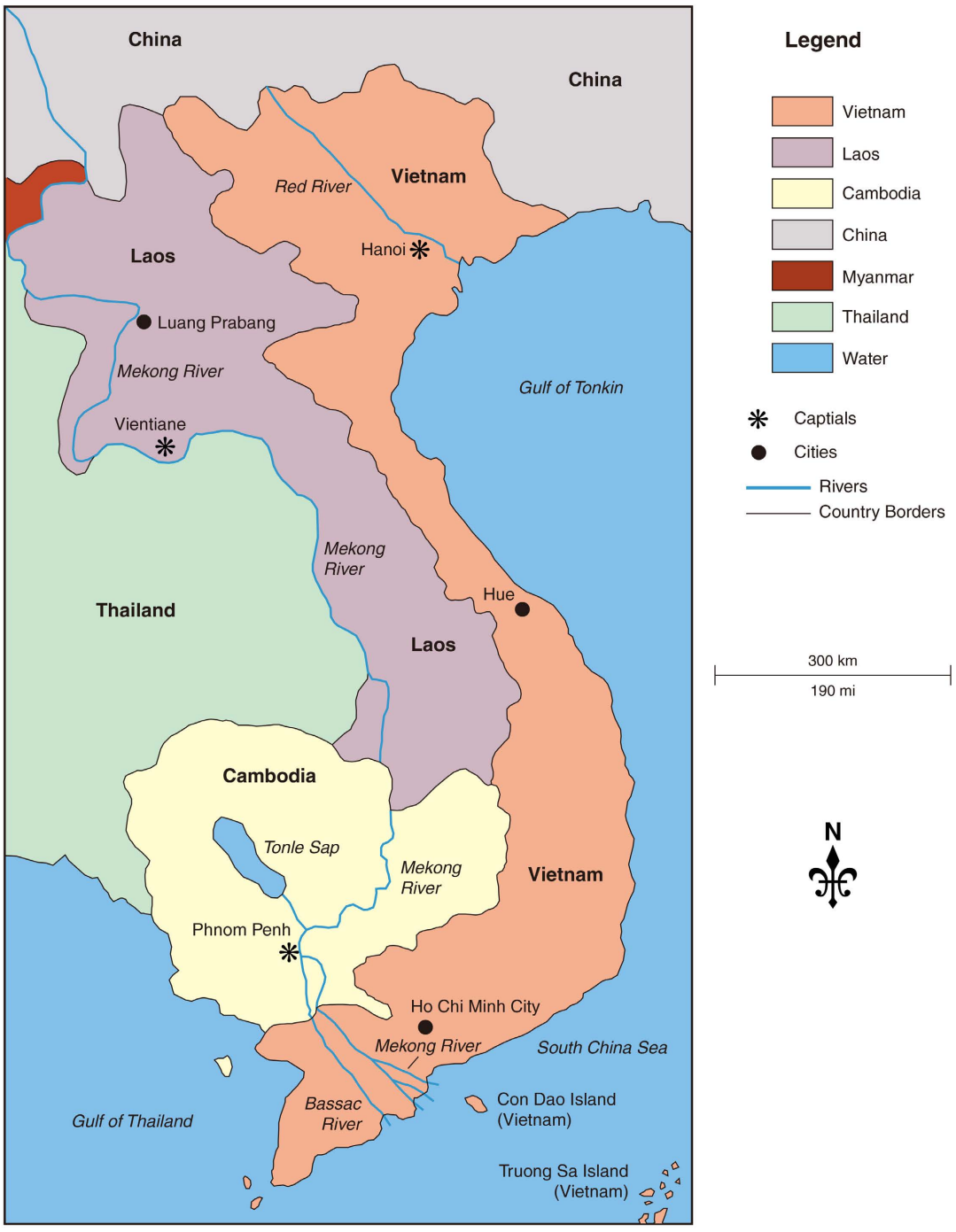

Figure 1. South East Asia countries including Vietnam. The Mekong and Bassac Rivers flow south into the Mekong Delta. Reprinted with the permission of the editor of the Open Journal of Soil Science. Map by Mic Greenberg.

Vietnam were attacked, the United States officially entered the American-Vietnam War in August 1964.

At the height of the war, there were more than 500,000 U.S. military personnel serving in southern Vietnam. During the Vietnam War, the U.S. government and military (Air Force) engaged in a controversial and aggressive chemical

warfare program, with the code name Operation Ranch Hand. The purpose was to destroy the North Vietnamese Army (NVA) bases forest cover, cultivated land and food crop supplies, from 1962 to 1971, in southern Vietnam. The U.S. Air Force Operation Ranch Hand sprayed 50 million liters of tactical herbicides across RV. In addition, the RV military, US Navy, CIA and US Army also sprayed millions of liters of tactical herbicides in southern Vietnam as part of the Khai Quang program. Four of the six herbicides, Agent Purple, Agent Pink, Agent Green and Agent Orange contained dioxin TCDD. Another tactical herbicide, Agent Blue contained arsenic and was used to destroy the NVA food supply including rice. Both dioxin TCDD and arsenic were extremely toxic to human health.

The U.S. began its withdrawal from RV in 1972 and the conflict between DRV and the U.S. ended following the Paris peace accords in January of 1973. The conflict between RV and DRV ended on April 30, 1975 after the surrender of the RV government.

1.2. North Vietnamese Army (NVA) Bases in Southern Vietnam Including Mekong Delta

Tactical herbicides, including Agent Blue and Agent Orange, were sprayed around suspected NVA areas (**Figure 2**) in southern Vietnam [1] as part of the RV Khai Quang program to improve visibility and destroy the enemy food supply [2]. The intensity of spraying was greatest in the proximity to NVA's bases that were identified by the CIA during the Vietnam War [3]. Between 1962 and 1971, the U.S. Air Force sprayed 50 million liters of six tactical herbicides [4] across the RV. In addition, the RV military, U.S. Navy and U.S. Army sprayed Agent Blue, Agent Purple and Agent Orange on the rice paddies and mangrove forests of the RV. However, the Khai Quang program spray mission was classified or operational records were not maintained. The RV military operations, with the support of the U.S. Navy and Army, contributed to elevated dioxin TCDD and arsenic levels in the Mekong Delta landscape.

It is estimated that up to 366 kg of pure dioxin TCDD and more than 1,132,400 kg of pure arsenic were sprayed and as many as 4.8 million Vietnamese civilians were exposed [3] [4] [5]. The tolerable daily dioxin TCDD intake is defined by WHO to be between 1 and 4 pg (pictograms) per kg of body weight (one pg equals 10^{-15} kg). Numerous biological and epidemiological studies have shown robust medical linkages between herbicide exposure with dioxin TCDD or arsenic and a range of health problems. Among the most comprehensive, veterans and Agent Orange research was conducted by the National Academies of Science, Engineering and Medical. This report was updated annually and led to the Agent Orange Act of 1991 [6].

The first tactical (rainbow) herbicide delivered to Tan Son Nhut Air Base, RV, in 1962, was Agent Blue. This herbicide was in powder form and then mixed with water before spraying. This process often resulted in spills of Agent Blue

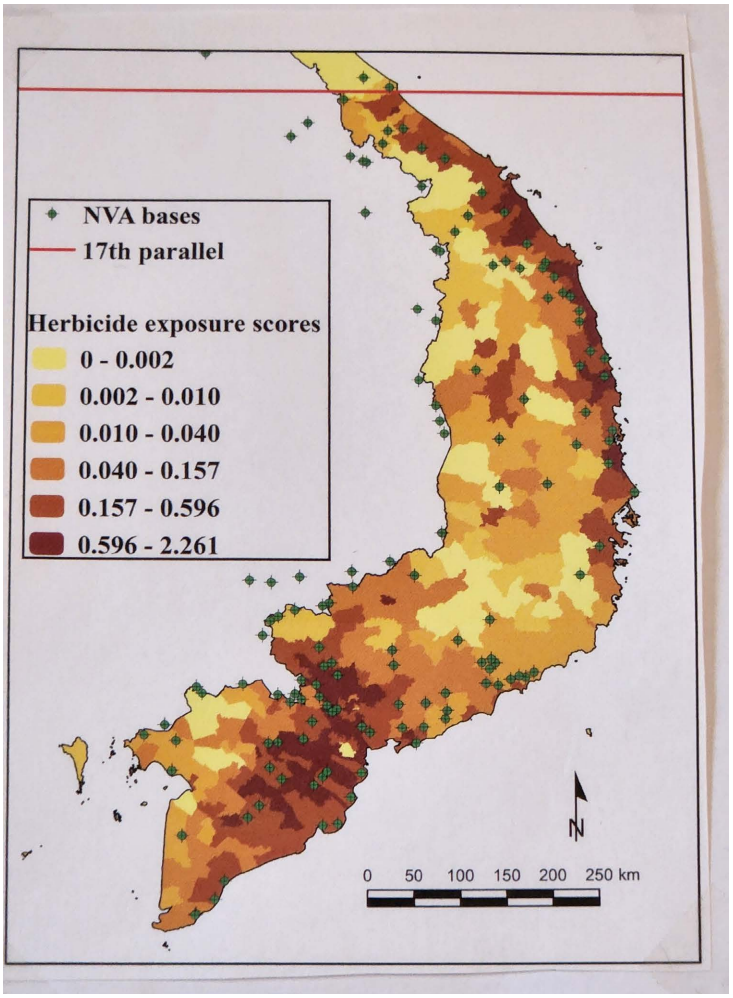

Figure 2. Distribution of herbicide exposure scores and location of North Vietnamese Army bases. The modified figure shows the distribution of herbicide exposure scores and locations of NVA bases [1] [3].

and its main ingredient cacodylic acid, both of which have short half-lives. Agent Blue and cacodylic acid were degraded to water-soluble arsenic, which has no half-life, and was released into surface water, soil and groundwater.

Records [2] indicate that 42% of the herbicide used in southern Vietnam (**Figure 2**) prior to 1965 was the herbicide Agent Blue with the active ingredient cacodylic acid-containing arsenic, selected by the RV government and military to destroy the rice crop. However, there is no publicly available RV military, Navy, CIA and Army records of the Agent Blue spray missions or identification of areas sprayed in the Mekong Delta, prior to 1965, and few records after that date. Stated RV and U.S. government and military goal, prior to 1965, was to eliminate the food supply of the NVA by destroying the southern Vietnamese rice crop in southern Vietnam just prior to harvest (**Figure 3**). Most of the rice crop was grown in the Mekong Delta and not the Central Highlands where more Operation Ranch Hand spray mission records are available. Apparently, the Agent Blue sprayed in the Mekong Delta by the RV military with the support of

Figure 3. Rice residue in dried out fields similar to the rice paddies sprayed with Agent Blue in the 1960s and 1970s. Reprinted with the permission of the editor of the Open Journal of Soil Science.

US Army, CIA and US Navy was not counted as part of the U.S. Air Forces Operation Ranch Hand mission (Air Force kept and maintained their own spray mission records). The goal of the RV Khai Quang herbicide spray program, with the support of the US Army, US Navy and CIA, was to eliminate the local food supply, defoliate the jungle, including the stream banks on the canals, waterways and rivers to prevent ambushes and to expose the NVA and their base camps (Figure 2). There were at least 26 NVA mobile base camps in the Mekong Delta. Most were located in mangrove forests surrounded by rice paddies and adjacent to waterways. Agent Orange or Agent Purple was used to defoliate the forest and Agent Blue was used to destroy the rice crop. Since it took almost two weeks for leaf drops to occur after forests were sprayed with Agent Purple, Agent Orange or Agent Blue was sometimes combined with Agent Orange to speed up the defoliation process. Agent Blue applications, spraying and subsequent burning of the rice residue (to eliminate the seeds) by the US Army resulted in the Vietnamese living in the Mekong Delta losing capacity to feed themselves and the occupying NVA soldiers.

Some of the rural Vietnamese in southern Vietnam supported the NVA soldiers while others did not. However, the NVA soldiers had weapons and could take the rice, if not freely provided by local farmers. As a result, many of the rural Vietnamese in southern Vietnam, during the 1960s, were without a stable food supply and forced to move to the slums of Saigon and/or other urban areas. Nearly 2 million Vietnamese, living in both the Mekong Delta and Central Highlands were re-located into slums of Saigon as part of a RV government Strategic Hamlet project (easier to defend the rural Vietnamese population if concentrated in urban areas or hamlets). All of the southern Vietnam rural providences lost population during the Vietnam War (1960-1975) because of

both population shifts (hamlet strategy) and civilians being killed during the war.

The US Army, Blue Water Navy and Brown Water Navy continued to spray the Mekong Delta stream banks (Figure 4) and rice paddies and mangrove forests after the U.S. government officially entered the Vietnam War in 1965. Despite the official declaration of war, Mekong Delta Agent Blue spray records were classified or not maintained. Agent Blue (arsenic), along with Agent Orange (with 2,4,5-T with unknown amounts of dioxin TCDD), were also used in combination by US Air Force as part of Operation Ranch Hand, after 1965, to defoliate the mangrove forests used by the NVA as base camps in the Mekong Delta. This deforestation exposed the stream banks and shoreline to soil erosion and destroyed the livelihoods of the local woodcutters.

The total amount of Agent Blue shipped to Vietnam was much more than the Operation Ranch Hand C-123s (Figure 5) and helicopters sprayed, according to the official Operation Ranch Hand records for the American-Vietnam War (from 1962 to 1971). This does not include the RV government's Khai Quang Program. The Agent Blue, in powder form, was mixed with water and sprayed by the RV military, with the support of US military, on NVA base camps and adjacent lands in the Central Highlands and Mekong Delta (Figure 2). The RV military, US Navy and US Army spray records were classified or not maintained.

The purpose of the RV Khai Quang program spraying was to eliminate the local food supply (primarily rice) in southern Vietnam so the rural Vietnamese could not feed themselves or the NVA soldiers. Agent Blue was applied by RV

Figure 4. Stream banks vegetation a few weeks after being sprayed with tactical herbicides. Agent Orange and other herbicides we sprayed with low and slow moving flying C-123 aircraft, by helicopters, backpack sprayers, and from Brown Water Navy boats over the Vietnam jungle and rural landscapes. Most of these herbicides had short-half lives of hours, days and a few weeks; and vegetation regrowth required additional applications. Picture taken by U.S. Army Flight Operations Specialist 4 John Crivello in 1969. Reprinted with the permission of the editor of the Open Journal of Soil Science.

Figure 5. C-123s Fairchild Provider aircraft that was used during the Vietnam War to spray tactical herbicides. Reprinted with the permission of the editor of the Open Journal of Soil Science.

soldiers, with the support of the US military, on the perimeter of the NVA base camps and adjacent lands and selectively on more populated areas of the Central Highlands and the Mekong Delta. The spray equipment used included hand and backpack sprayers (Army), sprayers on Brown Water Navy boats, from Army military vehicles (Figure 6) and from military based helicopters including those on Blue Water Navy ships. While it was easy for the U.S. Government to explain and justify the Operation Ranch Hand defoliation objective to the media and the public, it was not so easy to explain and justify why the U.S. and RV governments and militaries were eliminating the local Vietnamese food supply and starving of the rural Vietnamese living in southern Vietnam. The elimination of the local food supply by the US military was done at the request of the RV government and military to force the rural Vietnamese into hamlets, which would be easier for the RV military to defend and to prevent the feeding of the NVA.

In southern Vietnam, Agent Blue was used as a contact herbicide for grassy plant control and rice destruction. More than 4.6 million liters of Agent Blue (664,393 kg of As) and known as Phytar 560-G and manufactured at the Ansul Chemical Plant on the Menominee River (Figure 7) in Wisconsin and Michigan, was sprayed as part of the DOD and USDA herbicide program code named Operation Ranch Hand. This was in addition to the RV Khai Quang program which also sprayed Agent Blue. In total, over 7.8 million liters of Agent Blue with 1,132,400 kg of arsenic (As) were sprayed on southern Vietnam (Figure 8).

The fact that RV and U.S. militaries were eliminating the food supply of the Vietnamese living in southern Vietnam to make it easier for the RV soldiers to defend the civilians from enemy attacks, became the official reason. However, the RV and U.S. military attempts to destroy the local Vietnamese food supply

Figure 6. Ansul Chemical Plant and ship loading. Reprinted with the permission of the editor of the Open Journal of Soil Science.

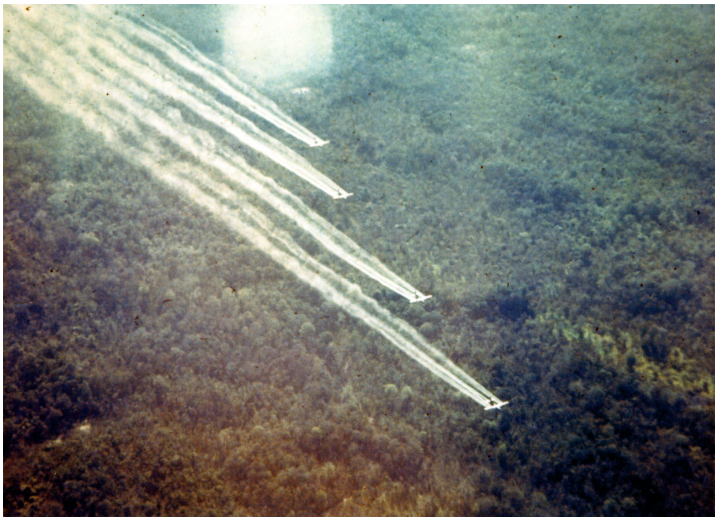

Figure 7. C-123s spraying tactical herbicides in formation over southern Vietnam in the 1960s. Reprinted with the permission of the editor of the Open Journal of Soil Science. Reprinted with the permission of the editor of the Open Journal of Soil Science.

Figure 8. Ttactical herbicides sprayed from a M113 Armored Tracked Personnel Carrier, Reprinted with the permission of the editor of the Open Journal of Soil Science.

was not considered by the media and the public to be a noble mission. Perhaps that destruction of the local food supply was part of the reason the RV military, US Army, CIA and US Navy the Khai Quang program spray records were classified or not maintained. Most of the U.S. media focus, after 1965, was on Agent Orange and the U.S. attempts to defoliate the jungle and expose the enemy (NVA).

To the credit of the US Air Force, they did keep excellent spray mission records, as part of Operation Ranch Hand; however, the total Agent Blue applied did not include the Khai Quang program Agent Blue applied and sprayed by the RV military, US Blue and Brown Water Navy, CIA and US Army. Without these spray mission records, it is hard, after 50 years, to locate the areas where Agent Blue was used to destroy the rice crop, especially in the Mekong Delta. Therefore, it is difficult (nearly impossible) to overlay the known arsenic spikes in the Mekong Delta groundwater with the spray and application mission records [3] [4] [5] of the RV military, US Navy, CIA and US Army as part of Khai Quang program.

Arsenic has no half-life and is water-soluble. Once it leaches into the groundwater it can be pumped back to the surface by hundreds of thousands of tube wells (**Figure 9**), constructed after 1975 to supply the freshwater needs of the rice paddies, and shrimp ponds and to meet the household and drinking water needs of the Vietnamese living on Mekong Delta or Central Highlands. Most of the anthropic arsenic remains in the southern Vietnam environment to this day. The primary loss of anthropic arsenic from the southern Vietnam landscape would have occurred when Agent Blue spray drifted into or was sprayed directly

Figure 9. Tube wells in the Mekong Delta. Reprinted with the permission of the editor of the Open Journal of Soil Science.

on the rivers or adjacent stream banks. Surface runoff waters, with water-soluble cacodylic acid and arsenic components, flowed into the Mekong Delta Rivers, the South China Sea or Gulf of Thailand (Figure 10). However, most of the Agent Blue was utilized to destroy the rice crops and arsenic, with no half-life, has remained in the rice paddy root zone soils and/or leached into the groundwater only to be returned to the soil surface by tube wells, for urban and agricultural use.

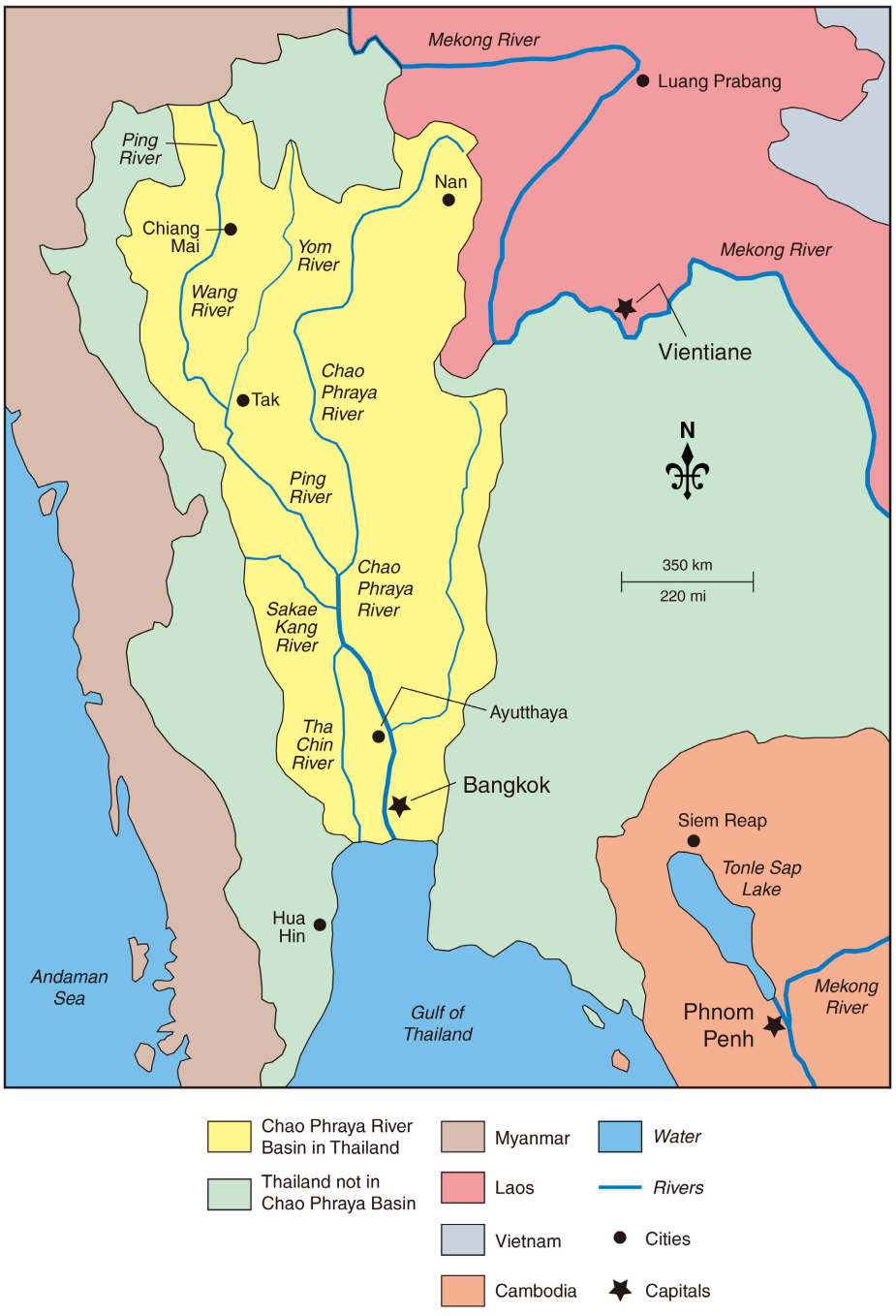

Figure 10. Chao Phraya River, tributaries, and Chao Phraya Delta. Reprinted with the permission of the editor of the Open Journal of Soil Science. Map by Mic Greenberg.

1.3. Environmental Impact of Agent Blue Manufacturing on the Menominee River in Michigan and Wisconsin (United States)

The Menominee River flows into Lake Michigan via Green Bay (Figure 11). The Ansul Chemical Company at Marinette, Wisconsin manufactured almost all of the Agent Blue, an As containing herbicide, used during the Vietnam War in the 1960s and 1970s [7]. Agent Blue was shipped via Green Bay, the Great Lakes and the St. Lawrence Seaway to the Atlantic Ocean (Figure 12). Approximately 98% of the Agent Blue used during the Vietnam War from 1962 to 1971 was manufactured at Ansul Chemical plants on the Menominee River in Michigan and Wisconsin [7]. The As contaminated surface water and sediments near Ansul manufacturing plant flowed into the Menominee River (Figure 13). The groundwater and the river bottom sediments were heavily contaminated with As, which had been released by Ansul Company from 1957 to 1977, as waste products from the manufacture of Agent Blue for the Vietnam War effort. Ocean going-ships carrying the herbicide then passed through the Panama Canal [8] and the Pacific Ocean on the way to the South China Sea (Figure 14).

In 2009, the Ansul Company operated under two consent orders for environmental mitigation; one from the Wisconsin Department of Natural Resources and another from the USEPA. In September of 2009, Ansul Company agreed to spend an estimated $28 million on:

1) Removal of 56,600 m^3 of arsenic-contaminated sediments from the Menominee River;

2) Construction of an impermeable barrier to bedrock for about 160,000 m^2 of sediment;

3) Cap or remove 17,000 m^2 of surface soils contaminated with arsenic levels above 16 - 32 ppm;

4) To pump and treat contaminated groundwater;

Figure 11. Air View of Menominee River former Ansul company chemical plant on Menominee in Marinette, Wisconsin (L) and Menominee, Michigan (R). Reprinted with the permission of the editor of the Open Journal of Soil Science.

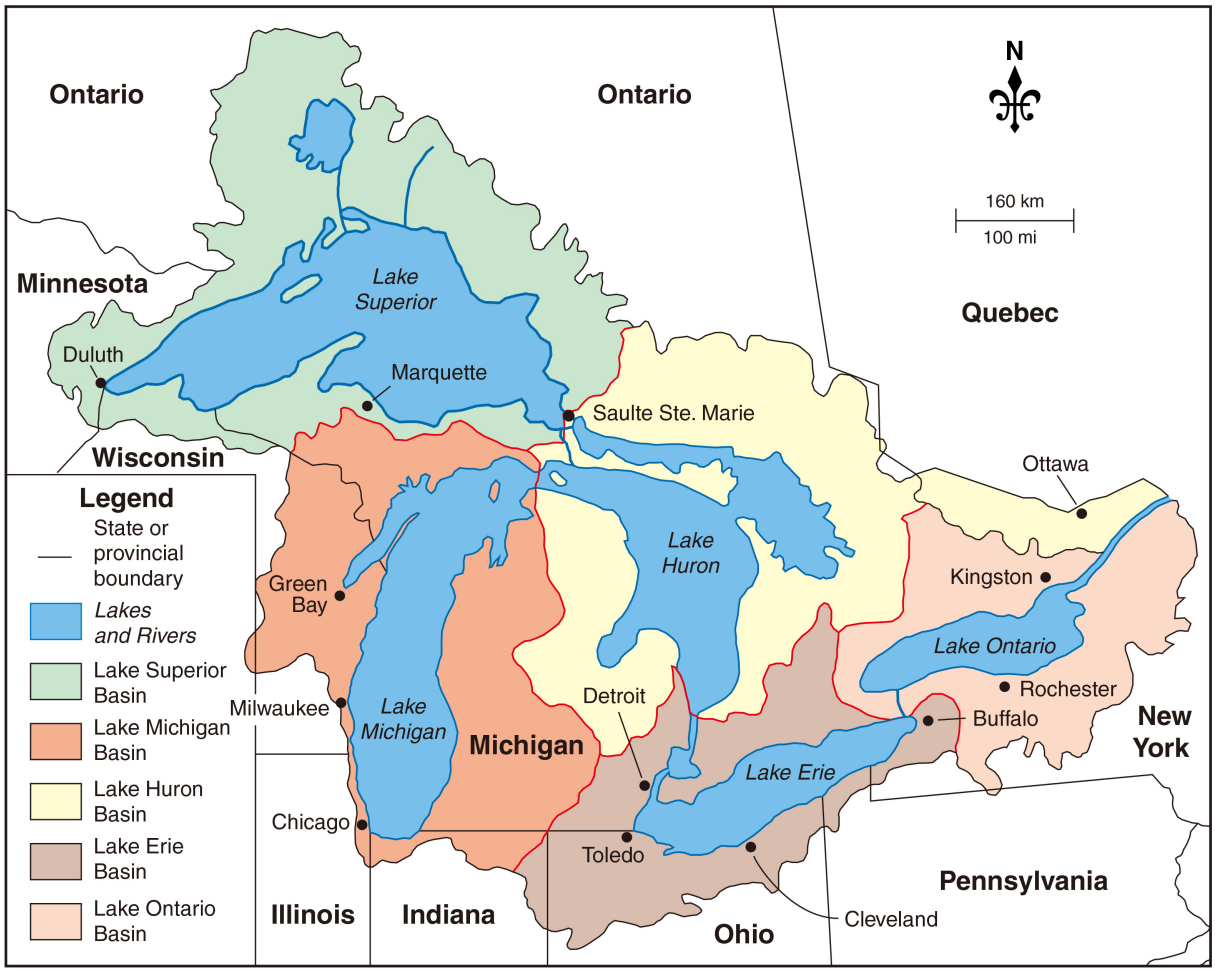

Figure 12. Map of the St. Lawrence Seaway and the Great Lakes. Reprinted with the permission of the editor of the Open Journal of Soil Science. Map by Mic Greenberg.

Figure 13. Bulk storage of raw materials, where the arsenic ash for making Agent Blue was stored at Ansul Chemical plant on Menominee River in Marinette, Wisconsin during the 1960s and 1970s. Reprinted with the permission of the editor of the Open Journal of Soil Science.

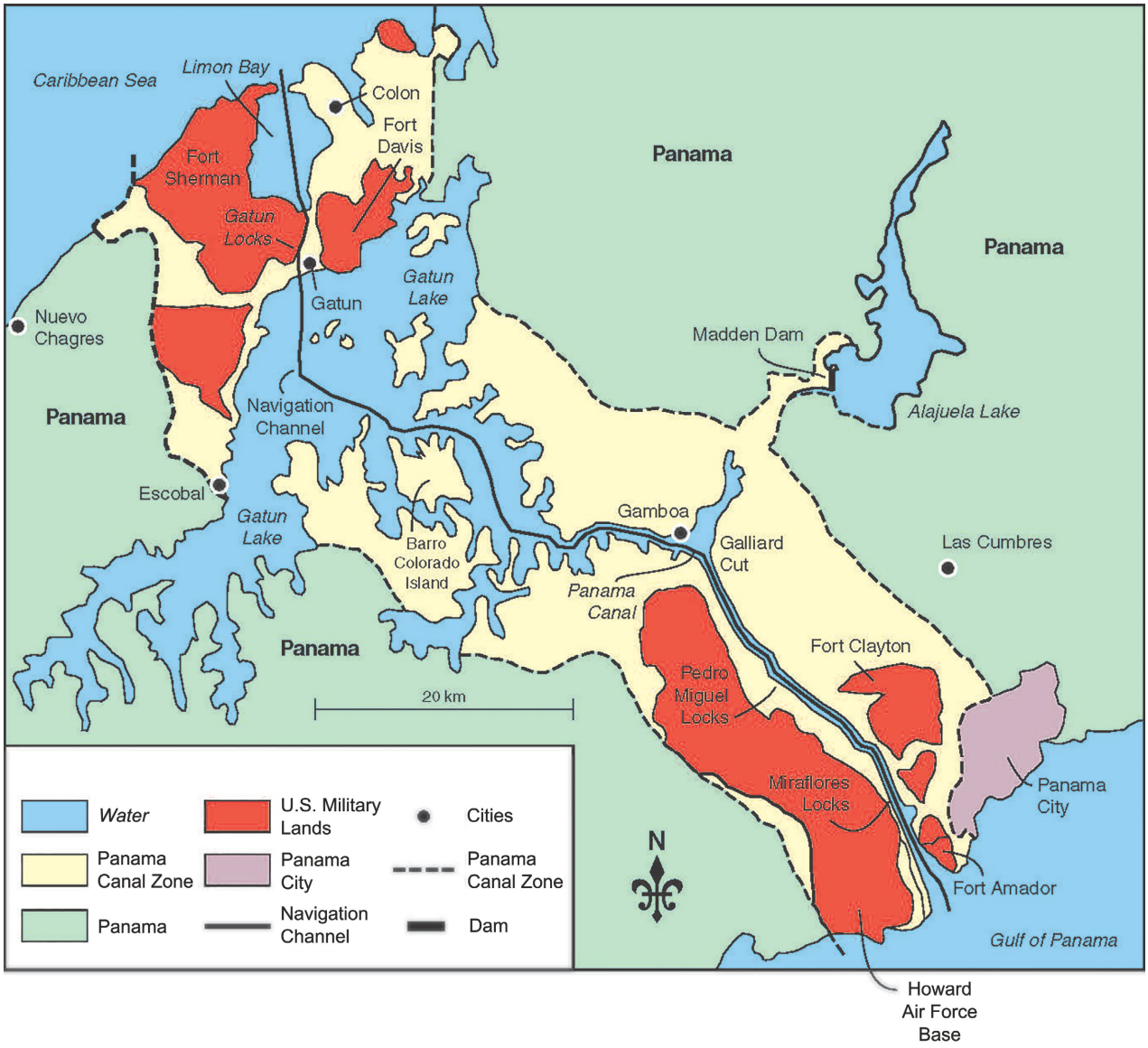

Figure 14. Panama Canal and locks. The military lands are identified and located. Reprinted with the permission of the editor of the Open Journal of Soil Science. Map by Mic Greenberg.

5) The total remediation costs were: 1976-1984, $11 million to pump and treat contaminated groundwater at the southern property border and to install a groundwater interceptor trench [7] in 1998-1999, $12.4 million to remove arsenic-contaminated sediment from the 8th Street section of the Menominee River and

6) An impermeable barrier system was installed to bedrock near the 8th Street slip and adjacent salt vault.

In 2012-2013, approximately $25 million was spent to dredge and then cap As contaminated river sediments due to an EPA order for the removal of 190,000 m^3 of sediment from the main channel. The project cleanup began in July of 2012 after Ansul (Tyco) Company hired Stevenson Environmental Services of New York as the general contractor.

1.4. Cacodylic Acid

Cacodylic acid is manufactured by reducing disodium methyl arsenate with sulfur dioxide and methylating the sodium salt to the resultant arsenomethane. The solubility in water of both the acid and sodium salt is extremely high. The chemical is non-volatile and stable in sunlight; physical and chemical properties contribute to its effects and fate in plants and soil [7].

Cacodylic acid (**Figure 15**) is a contact herbicide because it lacks mobility and only kills tissues into which the compound enters causing the chemical symptoms to appear within two days. It is less effective if rain falls within a few hours of the treatment and before the chemical induces its full effects on the plants. Sub-lethal doses induce defoliation and malformed inflorescence and fewer seeds due to incomplete destruction of the rice plants. Cacodylic acid appears to undergo little breakdown within plant tissues.

In the soil, cacodylic acid undergoes microbial degradation. The breakdown is slow under aerobic conditions but much more rapid in flooded, anaerobic soils. The ultimate environmental fate is a change to inorganic arsenate or arsenite, which are mostly bound as relatively insoluble compounds in soil. Soils naturally contain As in this form, with the average content being 5 ppm. In Southeast Asia, sodium arsenite has been applied as a pesticide in rubber plantations at high rates for over 20 years without causing any crop injury [9].

Plants absorb cacodylic acid from the soil more readily than inorganic As but the evidence suggests that crops do not suffer an injury on land which has previously been treated. Excessive rates on soils unusually rich in phosphates can cause injury to sensitive plants such as rice and peanuts due to the phosphate ion blocking the adsorption of arsenate to the soil particles causing the As to remain in the soil solution. The toxicity rating of cacodylic acid for humans is coded as three (3), or medium toxicity. Toxicological data for commercial herbicides, Ansar 160 (16.8% As) and 560 (15% As), both are similar to Agent Blue [10]. Cacodylic acid is a non-selective herbicide that kills a wide variety of herbaceous plants [11]. Acute and chronic toxicity studies in a variety of animals indicate a low to medium toxicity rating [9]. Sodium cacodylate is regarded as a Special Health Hazard by the New Jersey Department of Health and EPA. The Agency for Toxic Substances and Disease Registry states, "Arsenic cannot be destroyed once added to the environment".

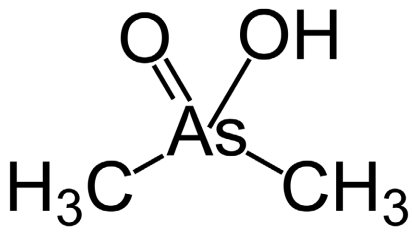

Figure 15. Formula of cacodylic acid. Reprinted with the permission of the editor of the Open Journal of Soil Science. Drew by Mic Greenberg.

1.5. Military Arsenic Contributions

During the Vietnam War Operation Ranch Hand, the project for aerial spraying of Agent Blue (**Figure 16**), contributed to the As contamination crisis in southern Vietnam [9]. In addition, the RV military (assisted by the US military unofficially), US Army and US Navy applied Agent Blue from 1962 to 1965 the program was extended until 1971 to the rice paddies in the Central Highland and the Mekong Delta. However, no official RV, Navy or Army spray records are publicly available. According to the US Department of the Army [12] [13] the primary goals, after 1965, were to clear out foliage and food crops [12] to achieve enhanced security, improve military intelligence, reduce cover for the enemy resistance [14], increase availability of the troops being used for combat and reduce US military personnel casualties.

The original intent of the RV and US military before the Vietnam War (1962-1965) was to kill rice (**Figure 3**) and other food crops as part of a Navy and Army strategy to destroy the food supply of the Vietnamese living in southern Vietnam and the NVA [14]. Agent Blue, $(CH_3)_2$ As OOH) was a mixture of two As compounds, cacodylic acid and sodium cacodylate and was the most effective of all the tactical (rainbow) herbicides for killing rice [9]. The one major tactical

Figure 16. Tacticial herbicides being sprayed by helicopter on rice paddies and mangrove forests. Reprinted with the permission of the editor of the Open Journal of Soil Science.

herbicide used for all 10 years of the war was Agent Blue. Two-thirds of Agent Blue was shipped to the 20th Ordinance Storage Depot in Saigon and the other one-third was shipped to the 551st Ordinance Storage Depot in Da Nang. Agent Blue was primarily used on crops including cereals and grains [12] [13]. Agent Blue was aerially sprayed, by rotary (helicopters) and fixed wing (C-123) aircraft (Air Force), and since it was a desiccant, it dried plants and was used in the preparation of areas for crop burning [15]. During the 10 years, land affected, primarily rice paddies, by Agent Blue totaled 400,000 ha in southern Vietnam. The primary sprayed area was near Saigon and Da Nang with over 51,000 ha of forest defoliated by spraying at least 4 times and 27 thousand hectares of mangroves mostly along the South China Sea and the Gulf of Thailand were completely destroyed [16] [17] [18].

1.6. Agent Blue, the Arsenic Based Herbicide Used to Destroy the Rice Crop

During the Vietnam War, Agent Blue was sprayed for the primary purpose of destroying rice and other food crops (**Figure 2**). As part of the RV and US government and military strategy to destroy the food supply, of both the communist insurgents and the southern Vietnamese living in rural areas, as part of the President Diem government's "Strategic Hamlet" program [7]. Agent Blue, a mixture of two As compounds, cacodylic acid (CH_3 As O_2H) and sodium cacodylate (C_2H_6 $AsNaO_2$), was the most effective of all the tactical (rainbow) herbicides in killing rice. Arsenic has been a known poison since the Middle Ages. During the Vietnam War, the US government, DOD and USDA ignored warnings of thousands of scientists of its hazards and sprayed Agent Blue on rice paddies, mangroves [9], bamboo groves (**Figure 17**) and US military base perimeter fences. This resulted in exposure to As by Vietnamese civilians, DRV communist insurgents in the Mekong Delta and the U.S. military personnel who were stationed (boots on the ground) in southern Vietnam.

Spraying and dumping of Agent Blue by RV military with the assistance of the US Navy and Army to desiccate rice plants before maturity added massive quantities of water-soluble As to the soil root zone and the surface water and groundwater of the rice paddies [7]. Southeast Asia is a region where natural occurring As in soils and sediments tends to be higher because of the occurrence of As containing geologic formations in the region [1]. The RV Khai Quang program spraying significantly added to the As load (3.2 million liters of Agent Blue (468,008 kg of As) in southern Vietnam including the Mekong Delta environment. In addition, the U.S. used an estimated 4.6 million liters (664,392 kg As) of Agent Blue herbicide, as part of Operation Ranch Hand, as a chemical (herbicide) weapon for "crop destruction and defoliation". For the last 50 years, As has been ingested by the Vietnamese living in southern Vietnam including the Mekong Delta via food and drinking water.

Water-soluble As leached into the soil root zone and into the groundwater

Figure 17. Bamboo growing in the Mekong Delta. Reprinted with the permission of the editor of the Open Journal of Soil Science.

from the frequent application of Agent Blue by the RV military with the assistance of the US Army and Navy (in addition to Operation Ranch Hand (US Air Force)) and/or was transported by the surface runoff water directly into the waterways and rivers. After the Vietnam War was over, vast amounts of natural and residual manufactured arsenic-laced groundwater were pumped from private wells (**Figure 18**) to the surface to irrigate the rice paddies, fill shrimp ponds (**Figure 19**) and meet the drinking water needs of the 20 million people living in the Mekong Delta [7]. The water-soluble As continues to cause health effects in both animals and humans. In addition, during the 1962 to 1971 period, animals and humans, absorbed As primarily through skin contact with Agent Blue in their environment [18] [19].

1.7. Impact of Agent Blue on Human Health

Arsenic toxicity and health effects are complex and the impact of Agent Blue on human health was not well known for many years. Post-Vietnam War, arsenic-based industrial wood preservatives and herbicides with cacodylic acid were used throughout the U.S. in wood products, golf course management, and cotton fields (**Figure 20**) and for desiccating agricultural crops to hasten ripening

Figure 18. Tube wells powered by solar panels. Reprinted with the permission of the editor of the Open Journal of Soil Science.

Figure 19. Shrimp farming in the Mekong Delta of Vietnam that was developed after 1975. Reprinted with the permission of the editor of the Open Journal of Soil Science.

Figure 20. Cotton fields in the United States, which were, sprayed with tactical herbicides with dioxin TCDD and/or cacodylic acid. Reprinted with the permission of the editor of the Open Journal of Soil Science.

prior to harvesting. Today, none of these herbicides are commercially available with the exception of the weed killer monosodium meta-arsenate (MSMA) for use on U.S. cotton and for control of certain golf course vegetation. The frequent use of manufactured arsenic products in industry and agriculture has resulted in human exposure by way of inhalation, contaminated drinking water, and food. Epidemiological evidence and animal studies show excessive risks of lung and skin cancers as well as delayed health effects at relatively high exposure rates [20] [21].

Agent Blue, the As based herbicide (one of the military's six tactical herbicides) was (**Figure 21**) field-tested in the United States, Puerto Rico, Canada and Thailand prior to its use in southern Vietnam. Later, Agent Blue was used at full strength during the Vietnam War. 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, and liver cancer and the arsenic is able to cross the placenta to create cancers in the fetus as well as both birth defects and childhood cancers have been linked to arsenic [21]. The effects of arsenic were delayed and can take decades to appear in humans [22]. Arsenic can cause damage to human DNA, which can adversely affect future offspring. Arsenical herbicides containing cacodylic acid as active ingredients are still being used today as weed killers and crop desiccants in some parts of the world. Less toxic formations of arsenical herbicides sold over the counter today can cause headaches, vomiting, dizziness, profuse and watery diarrhea, followed by dehydration, electrolyte imbalance, and gradual fall in blood pressure, convulsions, stupor, general paralysis, and possible death in 3 to 14 days in instances of acute poisoning [22] [23].

Cognetta *et al.* [24] found the most common manifestation of, As exposure in susceptible individuals is bilateral palmoplantar hyperkeratosis. Arsenic is one of the known causes of acquired palmoplantar keratoderma (PPK). Cognetta *et al.* [24] reported a unique case of palmoplantar hyperkeratotic lesions and numerous

Figure 21. Rainbow (tactical) herbicides identified in a chart with appropriate color striped barrels. The amount of Agent Blue listed as sprayed does not include years 1962 to 1965. Reprinted with the permission of the editor of the Open Journal of Soil Science.

squamous cell carcinoma *in situ* (SCCIS) which developed in a Vietnam veteran approximately 15 years after exposure to As during the Vietnam War. "*It is possible that exposure to Agent Blue contributed to the development of these lesions. Though a causal link between Agent Blue and skin cancer cannot be established, increased awareness of this potential exposure may prompt further study to improve our understanding of Agent Blue and its role in cutaneous oncology.*"

During the last 50 years, the Vietnamese people living in the Mekong Delta have continued to ingest and bio-accumulate As (manufactured and natural) via their drinking water and food supply. Arsenic can bio-accumulate in animals and humans as it is transported by blood to different organs in the body [25]. However, not all of the ingested As remains in the human body. The major proportion can be excreted as organic forms of As. The portion that is not excreted, is the part that bio-accumulates.

1.8. Effects of Cacodylic Acid and Arsenic on Human Health

The routes of entry of cacodylic acid into the human body are ingestion, inhalation, absorption through the skin and eye contact irritant. Cacodylic acid is more readily absorbed into the bloodstream when inhaled as an aerosol [26]. It is metabolized by the liver and bio-accumulates in and is excreted by skin, nails and hair [27]. Unlike inorganic arsenicals, dmethyl arsenic (DMAA) and monomethyl arsonic acid (MMAA) are metabolites of inorganic arsenic formed intra-cellular by most living organisms exposed to natural sources and do not bind strongly to molecules in humans. Hence, the acute toxicity seems to be less than that of the inorganic arsenicals [28]. However, recent studies of the trivalent organic arsenicals that are metabolic products of inorganic arsenic suggest they could possibly be more toxic than the parent compound [29] [30]. This includes inhibition of oxidative stress, as well as immune, endocrine, and epigenetic effects [31]. Analytical determination of arsenic poisoning can be made by examining arsenic levels in urine, hair and toenails. Kapaj and Pederson [20] found communities and individuals relying on groundwater sources for drinking water should consider a program to document arsenic levels [20].

Since arsenic poisoning of humans can occur by the gradual accumulation of small doses until the lethal levels are reached, the use of Agent Blue (during the Vietnam War) and other organic arsenicals pose a long-term danger [11]. Neurological symptoms are usually more frequent than gastro-intestinal effects over prolonged exposure to organic arsenicals [26]. Cacodylic acid may cause parathesis and/or weakness in the hands and feet [13]. Repeated skin contact may cause hyperpigmentation and keratosis. Malnourished people are more susceptible to arsenic-related skin lesions [20] [24].

2. Discussion

2.1. Anthropic Sources of Arsenic

The initial RV military and US Army, Air Force and Navy Vietnam War objec-

tive, prior to 1965, was to spray Agent Blue, the As based rice killer, on the rice paddies of the Mekong Delta and the Central Highlands to eliminate the NVA food supply. The goal, which extended until 1972, included denying food sources to the southern Vietnamese people, who were forced to move to the slums of Saigon (Strategic Hamlets) so they would not be able to feed the enemy (RVA) or themselves and could be protected in hamlets by the RV government and military.

During the last 60 years, there has been little research work on Agent Blue and its active ingredient cacodylic acid (As) even though As is lethal when significant quantities are ingested by humans over time (Figure 22). One of the reasons that the Agent Blue contribution to the high levels of As in the Mekong Deltas groundwater can not been determined is the inability of scientists, including chemists, to separate naturally occurring As from manufactured As because the end products of As reactions in the environment are the same. Attempts were made to determine if there is a significant chemical signature difference. After 50 years no known method can separate manufactured As from naturally occurring As. We do know that arsenic can exist with oxidation states of −3 (in air), 0 (in nature and is rare), +3 (in water) and +5 (in water) charges. It appears that both natural and manufactured As are water-soluble and are in the arsenite (+3) and arsenate (+5) states. In addition, there is also organic (not harmful) and inorganic (toxic) forms of As and it is known that it may be possible for chickens to convert organic As to inorganic As.

The purpose of using the herbicide Agent Blue was to desiccate and destroy narrow-leaf plants and trees (bamboo (Figure 17), grass, rice (Figure 23), and bananas (Figure 24). "Operation Ranch Hand", was military code name for spraying of herbicides by US Air Force in southern Vietnam from 1962 through

Figure 22. Urban cemetery in the Mekong Delta of Vietnam. Reprinted with the permission of the editor of the Open Journal of Soil Science.

Figure 23. Vietnamese and Montagnard rice growing in the Mekong Delta of Vietnam. Reprinted with the permission of the editor of the Open Journal of Soil Science. Reprinted with the permission of the editor of the Open Journal of Soil Science.

Figure 24. In the Mekong Delta the roots of banana, coconut and other exotic fruit trees on the river banks slow bank erosion and grow a meter or two above the water lilies, hyacinths, cresses and other wetland vegetation. Reprinted with the permission of the editor of the Open Journal of Soil Science.

1971 [26]. In this case, the widespread use of Agent Blue by the RV with the support of the US Navy and Army prior to 1965 (and later extended to 1971) was an attempt to take away the enemy's food supply by depriving them of food resources.

Agent Blue, in 208-liter barrels with a blue stripe (hence the name-Agent Blue), was sent to southern Vietnam between 1962 and 1971. The RV and US governments and militaries used an estimated 7.8 million liters of Agent Blue herbicide (1,132,400 kg of As) during US Air Forces Operation Ranch Hand and

RV Khai Quang program and applied as a chemical weapon for "crop destruction and defoliation". Agent Blue was sprayed primarily on the mangroves, rice paddies, and the surrounding forest of the Central Highlands and Mekong Delta in southern Vietnam (Figure 25). Agent Blue was also used in Laos and Cambodia, along the Ho Chi Minh trail, to kill food crops including upland rice in an attempt to deprive the North Vietnamese communist and insurgent troops of a food source. The Agent Blue was applied at the average rate of 2.831 kg As/ha to the rice paddy and forest areas. Many areas were sprayed only once while other areas received four or more applications. The forest and mangrove areas were usually sprayed at a different rate than the rice paddies (Figure 26). Unable to control the insurgent's access to their food supplies or eliminate their grassroots village support, the RV military with US military (Army and Navy) support response was simple: "If you cannot control it, kill it" [14] [32].

Agent Blue was primarily used to defoliate narrow grass vegetation or to kill food crops by desiccation. The rice plant is highly dependent on water to survive. Spraying Agent Blue on paddies can destroy approximately 60% of an entire rice paddy and leave it unsuitable for immediate re-planting do to soil sterilization. The dried rice paddy vegetation and seeds were destroyed by burning (Figure 3). Rice-killing RV military operations with assistance of the US Army and Navy also included use of specially designed rubber or plastic fuel bladders that were probably dropped from helicopters into rice paddies, which burst on

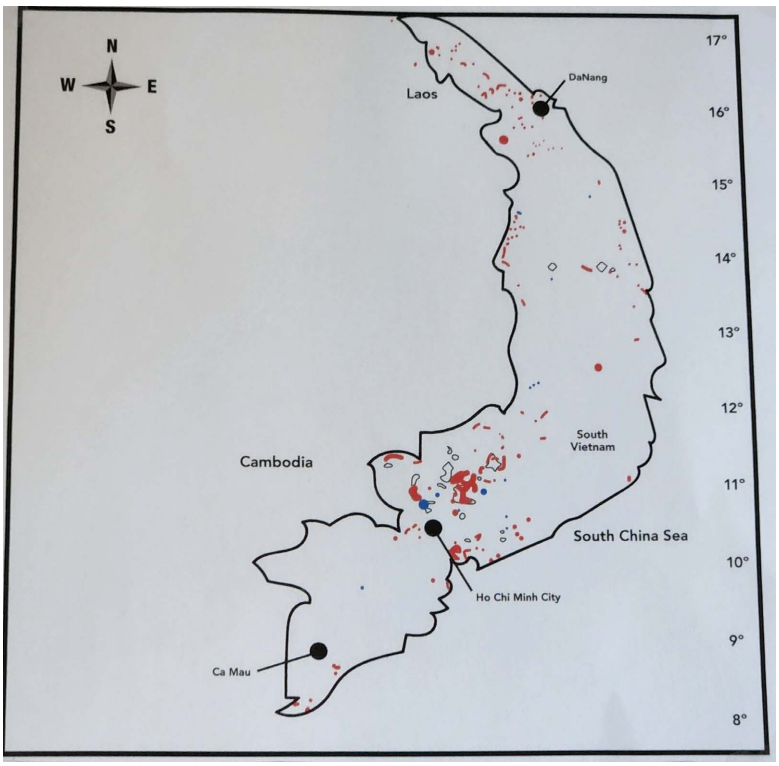

Figure 25. The locations in southern Vietnam where herbicides were sprayed (1961-1971) in volumes greater than 4800 liters. Distribution of herbicide exposure scores and location of NVA bases [1].

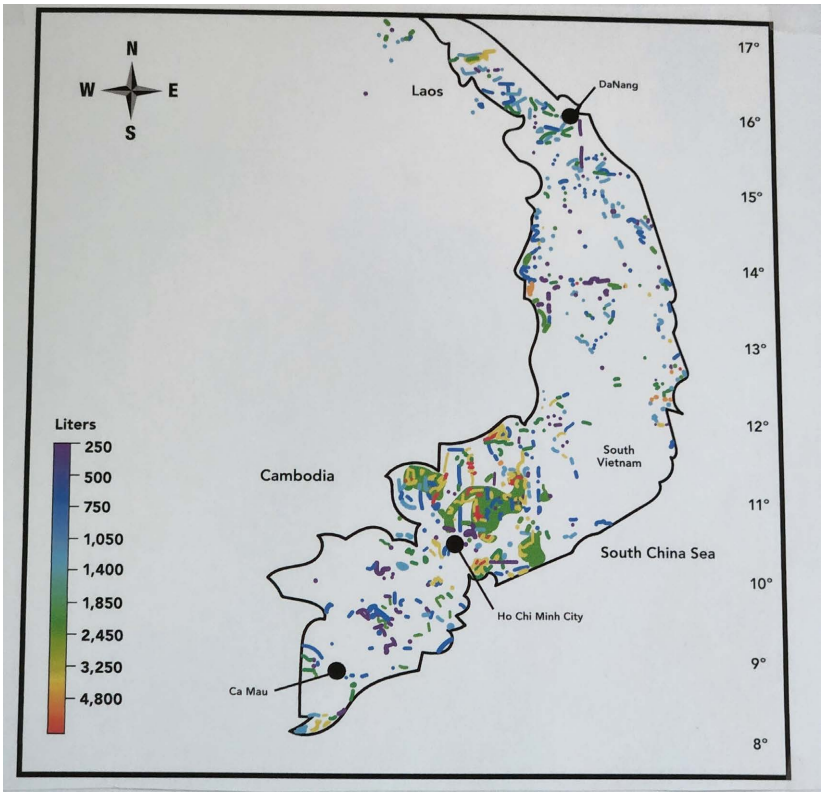

Figure 26. Volumes of herbicide, Agent Blue (cacodylic acid), sprayed by U.S. Air Force as part of Operation Ranch Hand in southern Vietnam (1962-1971) [3].

impact to release the toxic Agent Blue herbicide into the paddy waters [3]. This usually resulted in 100% of the rice crop (spraying was only 60% effective) being destroyed [3]. Bladders of Agent Blue were also dropped into the water irrigation canals, which ruptured on contact and contaminated the water in the rivers, canals and rice paddies. Arsenic-laden Agent Blue added As to the root zone, rice, water and soil. Subsequently, more recent industrial development, especially where contaminated soil has been disturbed has resulted in an increase in bio-availability of arsenicals. After the Vietnam War was over in 1975, the Vietnamese people would harvest and eat the As tainted rice (**Figure 27**), fish (**Figure 28**) and shrimp (**Figure 19**) for the next 48 years.

According to Institute of Medicine [2], over 7.8 million liters of Agent Blue herbicide (1,132,400 kg of As) was applied by the RV military with the support of the US military (Khai Quang program). This total included the US Air Force (Operation Ranch Hand) sprayed Agent Blue as a military and environmental chemical weapon for crop destruction and defoliation between 1962 and 1971 and the environmental effects of Agent Blue were understated. Spray drift affected many hectares of land adjacent to the targeted NVA bases and adjacent rice paddies. Crops were sprayed and burnt which concentrated the arsenic poison and contaminated the air with dust and smoke particulates. The Vietnamese living in southern Vietnam and US and RV military personnel had to breathe [14] As particulates. The As laced ash and dust can also be spread by wind and

Figure 27. A boat full of rice on the Mekong River. Reprinted with the permission of the editor of the Open Journal of Soil Science.

Figure 28. Fish (*pisces)* is main source of protein and income for SE Asia families. Fish and aquatic animals feeding on dioxin-contaminated sediments in rivers and lakes near former military air bases have been found to have trace amounts of dioxin TCDD 50 years later. Reprinted with the permission of the editor of the Open Journal of Soil Science.

water transport to adjacent land and to rivers and bodies of water [32]. Shallow groundwater has become the primary source for irrigation and drinking water in southern Vietnam and during the last two decades, thousands of government-subsidized shallow tube-wells were installed. Groundwater As concentrations have measured as high as 3050 ug/L. The As from Agent Blue is one of the potential sources of anthropic As hotspots. Today, Vietnamese rice is still tainted with trace amounts of inorganic As from anthropic and natural groundwater sources [33].

2.2. Red River

The groundwater of the Red River alluvial floodplain soils in Hanoi is anoxic

and rich in iron due to naturally occurring organic matter in sediment [34]. Arsenic problems are caused primarily by "tube wells", which draw water from depths of between 10 and 40 m. The wells, designed to provide safe drinking water by avoiding polluted surface waters, can bring up water from arsenic-contaminated underground aquifers [19]. The Red River valley (**Figure 29**) was not sprayed with tactical herbicides, including Agent Blue, but still has high levels of arsenic and natural or anthropic arsenic spikes.

Industrial development in Vietnam raised bio-available arsenicals to dangerous levels [35]. The arsenic contamination levels varied from 1 - 3050 ug/L with

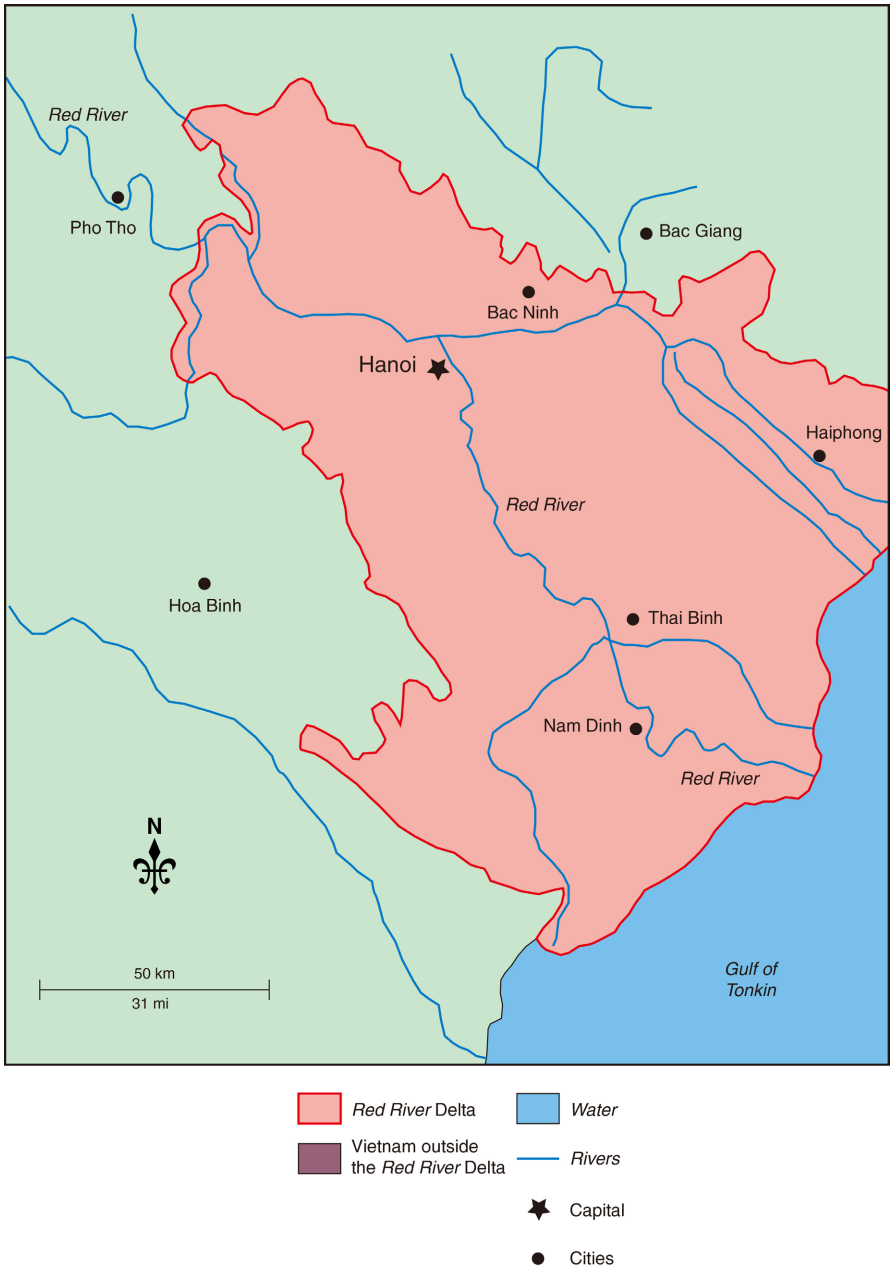

Figure 29. Red River Valley map. Reprinted with the permission of the editor of the Open Journal of Soil Science. Map by Mic Greenberg.

an average arsenic concentration of 159 ug/L in rural groundwater samples from private small-scale tube wells. In a highly affected rural area, the groundwater used for drinking water had an average concentration of 430 ug/l. Analysis of raw groundwater pumped from the lower aquifer for the Hanoi water supply yielded arsenic levels of 240 - 320 ug/L in three of eight water treatment plants and 37 - 82 ug/L in another five plants. Aeration and sand filtration applied in the treatment plants to remove iron lowered the arsenic concentration to 25 - 91 ug/L, but 50% remained above the Vietnam standard of 50 ug/L. The arsenic in the sediments may be associated with iron oxyhydroxides and released into the groundwater by reductive dissolution of iron. The oxidation of sulfide phases could also release arsenic to the groundwater, but sulfur concentrations in sediments were below 1 mg/g. The high arsenic concentrations found in the tube wells (48% above 50 ug/L and 20% above 150 ug/L) indicate that several million people consuming untreated ground water, in rural areas might be at a considerable risk of chronic arsenic poisoning [34]. According to Berg [19], "arsenic contamination levels in aquifers in Vietnam area of the same order of magnitude as in Bangladesh where tainted groundwater contributed to what a World Health Organization report called "the biggest poisoning of a population in history".

2.3. Toxicity of Agent Blue

Agent Blue contained 4.7% cacodylic acid (also known as hydroxydimethyarsinine oxide or dimethylarsenic acid – DMAA), and 26.4% sodium cacodylate as the active ingredients [36] [37]. Cacodylic acid (**Figure 15**) is a colorless, odorless, and hygroscopic crystalline solid. It was also commercially available in the form of soluble concentrates. Water solutions of cacodylic acid were sometimes blue in color [10]. Cacodylic acid is 54% arsenic [11]. Besides DMAA, another organic arsenical compound which forms the active ingredient of pesticides and herbicides used mainly for weed control is monomethylarsonic acid (MMAA). DMAA and MMAA are also metabolites of inorganic arsenic formed intra-cellular by most living organisms (animals, plants and bacteria) [38].

The routes of entry of cacodylic acid are by ingestion, inhalation, eye contact (irritant), and absorption through the skin [10]. Cacodylic acid is more readily absorbed into the bloodstream when inhaled [26]. It is metabolized by the liver and bioaccumulates in and is excreted in urine as well as by skin, nails and hair [27]. Unlike inorganic arsenicals, DMAA and MMAA do not bind strongly to molecules in humans. Hence, their acute toxicity seems to be less than that of the inorganic arsenicals [28]. However, recent studies indicate that trivalent organic arsenicals [e.g., MMA (III) and DMA (III)] that are metabolic products of inorganic arsenic could possibly be more toxic than the parent compound [29] [30].

The mechanism of toxicity of arsenic includes enzyme inhibition and oxidative stress, as well as immune, endocrine, and epigenetic effects [39] [40]. Analytical determinations of arsenic poisoning can be determined by examining arsenic levels in urine, hair and toenails. Communities and individuals relying on

groundwater sources for drinking water need to measure arsenic levels to ensure that their supplies are safe, and communities with arsenic levels greater than 5 μg/L in drinking water should consider a program to document arsenic levels in the population [20].

2.4. Republic of Vietnam (RV) Strategic Hamlet Policy

The use of tactical herbicides in southern Vietnam began as an initiative of Republic of Vietnam (RV) Vietnam President Ngo Dinh Diem. Part of the RV government's policy was to move the rural population into "strategic hamlets" that could be more easily be secured and defended than the existing villages. This also allowed the destruction of the rice crops, a potential North Vietnam Army (NVA) food source, to discourage NVA activities. President Ngo Dinh Diem 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 use on the food crops in southern Vietnam [41], 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 Quang 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) and the CIA. These 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 [14] [15]. 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 Quang Program (1962 to 1971) [2].

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 [22]. After considerable internal debate, President Kennedy gave the approval needed to use Agent Blue on 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].

2.5. Republic of Vietnam and United States Contribution of Arsenic to the Southern Vietnam and Mekong Delta Groundwater

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 [3] [4]. This was in addition to the 3.2 million liters of Agent Blue (468,008 kg As) previously sprayed or dumped by the RV military, with the support of the US military, during the Khai Quang Program [2]. The Institute of Medicine [2] estimated 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 Quang program which was assisted 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 As total available at this time [2].

Agent Blue was first delivered and used in southern Vietnam in early 1962. There are records that 42% [2] of all tactical herbicides used before 1965 was the arsenic-based Agent Blue herbicide. The RV government and military with the support of the US Army, US Navy and CIA did not document their spraying locations like the US Air Force did and make them available to the media and public. The Mekong Delta region had a complex water network of wetlands, forest vegetated stream banks, small streams and natural river distributaries of the Mekong River as well as intricate human engineering canals, dykes, and ditches used to produce paddy rice.

These drainage systems crossed the entire Mekong Delta Region. These drainage waterways were used as a navigation network and were accessible by non-motorized and motorized boats and floating platoons that were used by locals and militaries. To access and destroy the NVA base camps in the Mekong Delta and destroy rice food supply would have required the skills of water and land-based military forces including the US Army and Navy. Because there are no RV military, US Army and US Navy records of Agent Blue spraying in much of the Delta region, it is now impossible to distinguish natural from anthropogenic arsenic spikes in the Delta groundwater. However, one could surmise that arsenic based Agent Blue herbicide was one of the vegetation management tools available to the RV military, US Army and US Navy and that its use throughout the delta increased the concentration of arsenic in the Mekong Delta groundwater.

During the Vietnam War (1962-1971), herbicides were sprayed by RV and US military forces at an order of magnitude greater than amounts used for domestic weed control [12] [14]. The herbicides were stored and shipped in 208-litre bar-

rels, and named after the colored band painted on each barrel [33]. They were mostly sprayed by RV military, with the support of the US military, over the forests of southern Vietnam to kill crops in order to deprive the NVA troops of food, and to remove the vegetation cover used for concealment (**Figure 4**), making ambushes more difficult [32]. RV and US Army soldiers used mortars and grenades in an attempted to destroy rice paddies and rice stocks, but rice grains were very durable and not easily destroyed [15]. Soon, the "rice-killing operations" became more sophisticated. Rubber or plastic bladders were dropped directly into rice paddies, bursting on impact and releasing toxic herbicides including Agent Blue, and barrels of herbicides were also dropped into the water irrigating rice paddies, polluting rivers and poisoning the soil and people for many years [7]. Agent Blue was used as a contact herbicide in southern Vietnam for rapid defoliation, grassy plant control and rice destruction. Agent Blue was the agent of choice for the destruction of rice crops by the RV military with the support of the US Army and Navy.

More than 4.6 million liters of Agent Blue (also known as Phytar 560-G), were dispensed in the DOD herbicide program, according to US Air Force Operation Ranch Hand herbicide records [3] and 3.2 million liters of Agent Blue was sprayed as part of Khai Quang program [2]. Agent Blue, also applied by the RV military and the US Navy and Army worked rapidly defoliating or desiccating a wide variety of plant species of grasses and grains. It works by uncoupling phosphorylation in plants [14]. It was used in situations requiring rapid defoliation, causing browning or discoloration within one day, with maximum desiccation and leaf fall occurring within two to four weeks [14]. By starving rice plants of moisture, the enemy and millions of rice-growing villagers could be denied their most basic food source. This formed an essential part of the RV and U.S. government's "rice-killing operations" [15]. The term "Agent Blue" was first applied to cacodylic acid in powder form that was mixed with water. Cacodylic acid is a highly soluble organic arsenic compound that readily breaks down in soil [29]. It is considered to have very low toxicity for mammals [30].

The original commercial form of Agent Blue was so common and so profitable that it was among 10 toxic insecticides, fungicides and herbicides partially deregulated by the US Environmental Protection Agency (EPA) in February 2004, and specific limits on toxic residues in meat, milk, poultry and eggs were removed [31] [44] [45]. However, in 2009, the U.S. Environmental Protection Agency issued a cancellation order to eliminate and phase-out the use of organic arsenical pesticides by 2013, with one exception – monosodium methanearsonate (MSMA), a broadleaf weed herbicide for use in defoliation of cotton. Small amounts of cacodylic acid (or disodium methanearsonate) were historically applied as herbicides in cotton fields, golf courses, backyards and other areas, but its use is now prohibited under the USEPA 2009 organic arsenical product cancellation [25] [38]. Other organic arsenicals (e.g. roxarsone, arsanilic acid and its derivatives) are used as feed additives for poultry and swine to increase the rate of weight gain, improve feed efficiencies, pigmentation, and to treat and prevent

disease [14] [40] [44] [45].

The highest exposure in insecticide manufacturing was usually found at the mixing, screening, drying, bagging, and drum-filling operations (**Figure 30**). During these operations, reported arsenic concentrations in air ranged from 0.5 - 45 mg/m^3 [25]. The World Health Organization (WHO) guideline for the safety limit of arsenic is 10 μg/L in drinking water [32]. In Vietnam, the legal arsenic concentration limit is five times higher than in the WHO guidelines [31]. The groundwaters of the Red River alluvial tract in Hanoi are anoxic and rich in iron due to naturally occurring organic matter in the sediments [34]. The problems were caused largely by the "tube wells", which draw water from depths of between approximately 10 and 40 m. The wells, designed to provide safe drinking water by avoiding polluted surface waters, inadvertently tapped into arsenic laden underground aquifers [19]. The use of Agent Blue during the Vietnam War and other industrial developments caused the levels of bio-available arsenicals to spike dangerously [35]. The arsenic contamination levels varied from 1 - 3050 μg/L, with an average arsenic concentration of 159 μg/L in rural groundwater samples from private small-scale tube wells. In a highly affected rural area, the groundwater used directly as drinking water had an average concentration of 430 μg/L [44]. Analysis of raw groundwater pumped from the lower aquifer for the Hanoi water supply yielded arsenic levels of 240 - 320 μg/L in three of eight water treatment plants and 37 - 82 μg/L in another five plants. Aeration and sand filtration applied in the treatment plants to remove iron lowered the As concentrations to 25 - 91 μg/L, but 50% remained above the Vietnamese standard of 50 μg/L.

Figure 30. Re-packing herbicide barrels and recovering buried barrels leaking into the ground. Reprinted with the permission of the editor of the Open Journal of Soil Science.

During the Vietnam War (1962-1971), herbicides were sprayed by RV and US militaries at a rate of an order of magnitude greater than amounts used for domestic weed control [14] [32]. The herbicides were stored and shipped in 208-liter barrels, and named after the colored band painted on each barrel. They were mostly sprayed over the forests and rice paddies of southern Vietnam to kill the mature rice crop in order to deprive the NVA troops of food, and to remove the vegetative cover used for concealment, making ambushes more difficult [15]. Agent Blue was used as a contact herbicide in southern Vietnam for rapid defoliation, grassy plant control and rice destruction. Blue (and later Agent Blue) was the agent of choice used by the RV and U.S. militaries for the destruction of rice crops.

More than 4.6 million liters of Agent Blue (also known as Phytar 560-G), were dispensed in the Operation Ranch Hand herbicide program, according to Air Force herbicide spraying records [3]. This was in addition to 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 Quang Program (1962 to 1971). Agent Blue works by rapidly defoliating or desiccating a wide variety of plant species of grasses and grains [14]. It works by uncoupling phosphorylation in plants [32]. It was used in situations requiring rapid defoliation, causing browning or discoloration within one day, with maximum desiccation and leaf fall occurring within two to four weeks [33]. By starving rice plants of moisture, the enemy soldiers and millions of rice-growing southern Vietnamese villagers would be starved of their most basic food. This formed an essential part of the US government's "rice-killing operations" [15]. The term "Agent Blue" was first applied to cacodylic acid in powder form that was mixed with water in the field. Cacodylic acid is a highly soluble organic arsenic compound that readily breaks down in soil [36]. It was considered, at the time, to have very low toxicity for mammals [30].

Agent Blue affects plants by causing them to dry out (**Figure 3**). As rice is highly dependent on water to live, using Agent Blue on these paddies can destroy an entire field and leave it unsuitable for further planting. This is why Agent Blue was also used where food was not a factor, but the foliage was. The Communist insurgents (RVA) had an advantage while fighting in southern Vietnam because they were used to the abundance of plant life on the battlefield. The U.S. found themselves at a disadvantage and based on the precedent set by the British in Malaya [46] decided that the best retaliation would be to take the enemy's advantage away from them by removing their cover. Along roads, canals, railroads, and other transportation networks, Ranch Hand cleared several hundred yards using the herbicides to make ambushes more difficult for their enemies. In Laos, the herbicide removed the jungle canopy from the roads and trails used for infiltrating men and supplies, making them more vulnerable to attack from the air.

Although the acute and chronic effects of organic arsenicals are not as severe

as those of inorganic arsenicals, organic arsenicals still have a significant impact on human health. Additional studies many uncover more currently unproven or unknown health effects. The present public health concern to human exposure to arsenic was linked with the consumption of arsenic-rich drinking water. This is a result of the alluvial sediments on the floodplains being rich in arsenic [47] [48]. Current epidemiological and experimental studies have attempted to elucidate the specific mechanism of arsenic carcinogenicity. This has led to the question of whether it is an epigenetic carcinogen. Due to the complexity of the mechanism of toxicity on the molecular level, and because of genetic polymorphism in the human population, both options continue to remain plausible [28]. However, recent studies show that the trivalent organic arsenicals that are metabolic products of inorganic arsenic could possibly be more toxic that the parent compound [29] [30]. The mechanism of arsenic includes inhibition and oxidative stress, as well as immune, endocrine, and epigenetic effects [31].

Analytical determination of arsenic poisoning may be made by examining arsenic levels in human urine, hair and toenails. Kapaj and Pederson [20] found communities and individuals relying, on groundwater sources for drinking water, need to measure arsenic levels to ensure their water supplies are safe. Communities with arsenic levels greater than 5 ug/L in drinking water should consider a program to document arsenic levels [20].

Since arsenic poisoning of humans can occur by gradual accumulation of small doses until lethal levels are reach, the use of Agent Blue (during the Vietnam War) and other organic arsenicals pose a long-term danger [18]. Neurological symptoms are usually more frequent than gastrointestinal effects over prolonged exposure of organic arsenicals [26]. Cacodylic acid may cause paresthesia and/or weakness in the hands and feet [42]. Repeated skin contact may cause hyper pigmentation and keratosis. Malnourished people are more susceptible to arsenic-related skin lesions [20].

3. Conclusions

Agent Blue is one of the "tactical (rainbow) herbicides" that is known for its use by the RV and US militaries during the Vietnam War to destroy the rice crop. It contained a mixture of dimethylarsinic acid (also known as cacodylic acid) and its related salt, sodium cacodylate and water. Largely inspired by the British use of herbicides and defoliants during the Malayan Emergency, killing rice was a military strategy from the very start of US military involvement in Vietnam. At first, RV military and US Army soldiers attempted to blow up rice paddies and rice stocks, using mortars and hand grenades. However, grains of rice were far more durable than they understood, and were not easily destroyed. Every grain that survived was a seed to be collected and planted again.

In a report to the International War Crimes Tribunal (founded by Bertrand Russell) at the end of 1967, it was stated that: "*The U.S. soldiers discovered that rice is one of the most maddeningly difficult substances to destroy; using ther-*

mite metal grenades it is almost impossible to make it burn and, even if one succeeds in scattering the rice, this does not stop it being harvested by patient men." So, they went to a bigger and better option that would actually kill off the paddies. The purpose of Agent Blue was to destroy narrow-leaf plants and trees (grass, rice, bamboo, banana, etc.) "Operation Ranch Hand" was military code for spraying herbicides from US Air Force aircraft in Southeast Asia from 1962 through 1971. The widespread use of herbicides in Southeast Asia during the Vietnam War was a unique military operation in that it was meant to destroy the plants that provided cover. The continued use of Agent Blue, one of the "Tactical (rainbow) Herbicides", by the RV military and US Army and Navy was primarily intended as an operation to take away the enemy's advantage on the terrain as well as deprive them of food.

Between 1962 and 1971, the RV and US militaries used an estimated 76 million liters of herbicides as chemical weapons for "defoliation and crop destruction" which fell mostly on the mangrove forest of southern Vietnam, but was eventually used in Laos as well to kill crops in order to deprive NVA troops of food. It was sprayed on rice paddies and other crops by the RV military and the US Army and Navy in an attempt to deprive the NVA of the valuable crops the plants provided. Unable to control NVA access to food supplies or their grassroots village support, the RV and U.S. military response was simple: *If you cannot control it, kill it.* Agent Blue is a mixture of two arsenic-containing compounds: sodium cacodylate and cacodylic acid. Agent Blue is chemically unrelated to the more infamous Agent Orange with unknown amounts of dioxin TCDD and other herbicides used during the war.

Agent Blue affects plants by causing them to dry out. As rice is highly dependent on water to live, using Agent Blue, applied by the RV military with the support of the US Army and Navy on these paddies could destroy an entire field and leave it unsuitable for further planting by sterilizing the soil for a period of time. This is why Agent Blue was used where food was not a factor, but the foliage was. The NVA insurgents had an advantage while fighting in Vietnam because they were used to the abundance of plant life as cover on the battlefield. The RV and US militaries found themselves at a disadvantage and based on the precedent set by the British in Malaya, decided that the best retaliation would be to take the enemy's advantage away from them by removing their cover. Along roads, canals, railroads, and other transportation networks, Operation Ranch Hand cleared swaths of vegetation several hundred yards wide using herbicides to make ambushes more difficult for their enemies. In Laos, the herbicide removed the jungle canopy from the roads and trails used for infiltrating men and supplies, making them more vulnerable to attack from the air.

The introduction of Agent Blue, an As based herbicide, in 1962 and three years before the start of the American-Vietnam war into the armed conflict in Vietnam, represented an application of a new technique for modern warfare. The US military was criticized for introducing a perceived chemical warfare

agent contrary to previous international agreements. Later, the herbicides have been considered to be chemical (herbicide) weapons and in violation of the Geneva Convention. For this reason, the U.S. should collaborate to remediate the environmental problems the U.S. military left in southern Vietnam 50 or more years ago. No element of the southern Vietnam environment was more detrimental to military base defense than the plant life that flourished in over-whelming and unwanted profusion. Prior to 1962, a large and useful amount of information about vegetation control, especially woody species control, existed in American agriculture literature and within USDA. The chemicals of choice were the phenoxy and arsenical herbicides. Thus, the use of herbicides in southern Vietnam removed foliage along travel routes, defoliated areas surrounding bases and communication routes, improved visibility in heavily canopied jungle, and destroyed insurgent subsistence crops. This in a great part was an attempt by the RV government to get the rural south Vietnamese population to move to "strategic hamlets" to be more defensible but resulted in many Vietnamese moving to larger cities creating the slums of Saigon as well as to stop producing food for or that could be taken by the Communist insurgents. In effect, it also prevented the rural population from producing their own food products.

Vietnam officials remain hopeful that a research project will identify remedies in addition to placing limits on extraction of available As rich groundwater since it contributes to economic growth. Vietnamese people continue to question the role of groundwater extraction in the land subsidence [49].

Most of the As in the Mekong Delta is from natural groundwater sources. However, the use of Agent Blue by the RV military with the support of US Army and Navy started before the American-Vietnam War (1962-1965) and continued during most of the war (1965 to 1971). These other military branches (US Air Force Operation Ranch Hand) contributed an additional anthropic source of manufactured (anthropic) As. Additional anthropic sources include the burial of millions of Vietnamese since 1962 (to present) with high As levels [7], industrial sources, sewage and wastewater treatment discharge into the waterways have added to the As levels in the Mekong Delta groundwater. Arsenic does not have a half-life and once added to the Mekong Delta environment in the 1960s was not destroyed and could only be eliminated when the water-soluble arsenic was in the river water, which flowed to South China and/or the Gulf of Thailand. In addition, As can be transported in the harvested grain, volatized or incinerated and released into the air. However, most of the water-soluble arsenic was retained in the rice paddies soils and/or leached back into the groundwater. The tube wells then return the As rich groundwater to the surface for urban and agricultural uses.

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 term "Agent Blue" was first applied as cacodylic acid in power form that was mixed with water in the field by the RV military and the US Army, Navy and Air Force during the Vietnam War. Cacodylic acid is a highly soluble organic arsenic compound that readily breaks down to the soil to water-soluble arsenic. Cacodylic acid is considered to have very low toxicity for mammals. In 2009, the USEPA issued a cancellation order to eliminate and phase out the use of organic arsenical pesticides by 2013, with the exception of monosodium methanearsonate [MSMA] a broadleaf weed herbicide for use on cotton.

The highest exposure in insecticide manufacturing was usually found at the mixing, screening, drying, bagging, and drum-filling operations. During these operations, reported arsenic concentrations ranged from 0.5 - 45 mg/m^3. The World Health Organization guideline for the safety limit of arsenic is 10 *u*g/L in drinking water. In Vietnam, the legal arsenic concentration limit is five times higher than in the WHO guidelines.

The As in the sediments may be associated with iron oxyhydroxides and released into the groundwater by reductive dissolution of iron. The oxidation of sulfide phases could also release arsenic to the groundwater, but sulfur concentrations in sediments were below 1 mg/g. The high arsenic concentrations found in the tube wells (48% above 50 μg/L and 20% above 150 μg/L) indicate that several million people consuming untreated groundwater in rural areas might be at a considerable risk of chronic arsenic poisoning. According to Berg [9], arsenic contamination levels in aquifers of Vietnam are of the same order of magnitude as in Bangladesh, where tainted groundwater contributed to what a World Health Organization report called "the biggest poisoning of a population in history".

Most of the As in the Mekong Delta groundwater is from natural alluvial sediment sources and not anthropic sources. However, Operation Rand Hand (US Air Force) contributed massive amounts of Agent Blue, the As based herbicide as did the RV military, Khai Quang Program (1962 to 1971), with the support of the US military (Army and Navy), during the Vietnam War did contribute a significant total amount (over 1,132,400 kg of manufactured (anthropic)) As to the Mekong Delta landscape. Other anthropic sources include the burial of millions of Vietnamese with elevated As levels since 1962, industrial sources, smelting by-products; sewage and wastewater treatment discharges into the waterways have added to the Mekong Delta As levels in the soil and groundwater. The As spikes and levels in the Mekong Delta soils groundwater need to be mitigated [7], especially when used as a drinking water source. Arsenic in rice can be more problematic than As in fish or shrimp since it is often organic arsenic. The uptake of trace amounts of inorganic As in rice is indeed critical food security and human health issue.

Researchers have identified many anthropic sources of the As in the Mekong

Delta groundwater including industrial. However, there has been little research into the environmental impact of RV military and US Air Force use of Agent Blue and the application of over 1,132,400 kg of manufactured (anthropic) As to the Mekong Delta and Central Highland landscapes. The rice paddies on the Mekong Delta were a nearly closed system and once the water-soluble As was introduced to the rice paddy ecosystem, the As continued to exist. The only removal of anthropic As from the Mekong Delta was by runoff water from the riverbanks and direct spraying into the waterways. The As is water-soluble and would flow into the South China Sea or into the Gulf of Thailand. The As rich water in the rice paddies remained in the soil root zone or was leached into the groundwater. It is then returned to the surface, via hundreds of thousands of tube wells for urban and agriculture use. The amount of natural As in the alluvial sediments is much larger than the As amount in anthropic sources including Agent Blue spilling, spraying and dumping hotspots. However, the Agent Blue (As) hotspots, military bases, mixing areas, spills, and military spraying and dumping of Agent Blue on rice paddies (Khai Quang Program (1962 to 1971) could have contributed to some of the As spikes that have been identified through groundwater monitoring. The 1,132,400 kg of As applied by the US Air Force as part of Operation Ranch Hand and RV military's Khai Quang Program (with the support of the US Army and Navy), during the Vietnam War would have raised the As level in the Mekong groundwater.

There is still no viable chemical or physical method to separate anthropic As from natural As after 50 years. RV military, US Army and US Navy applications of Agent Blue including the amount and location records are almost non-existent so one cannot match their spray records to the Mekong Delta landscape maps. The only way to assess the significance the anthropic arsenic of the US military (including Air Force) application of Agent Blue to the Mekong Delta would be to compare the As levels and spikes in the Mekong Delta with the As levels and spikes in the Red River near Hanoi. The Red River valley was never sprayed with Agent Blue while Mekong Delta was. The objective would be to determine if As levels and frequency and magnitude of As spikes in the Mekong Delta are significantly higher than those found in the Red River valley. This would require a significant research and funding investment. At this time, it does appear that the RV military and US military application of 1,132,400 kg of manufactured (anthropic) As to the Mekong Delta and Central Highland landscapes contributed to higher As levels in the groundwater.

The more important lesson is that the As hotspots, such as in the Menominee River (United States) and the Mekong River (Vietnam), need to be cleaned up [7]. The As levels, including both natural and anthropic sources, in the groundwater of the Mekong Delta, need to be reduced to meet WHO drinking water standard (10 ug/L) prior to using as a drinking water source for the 20 million people living on the Mekong Delta. High As levels in the water used for agriculture can also contribute to the As contamination of the food supply especially rice, shrimp and fish. Some of the As can bio-accumulate in animals and hu-

mans. As levels in the Mekong Delta hotspots and groundwater need to be mitigated regardless of whether it is from anthropic Agent Blue applications and spraying, from other anthropic sources or is naturally occurring As.

To access and destroy the NVA base camps in the Mekong Delta mangrove forest and destroy the rice food supply of adjacent lands would have required the skills of water and land-based military forces including the RV military and the US Army and Navy. Because there are no official RV military, US Army or US Navy records of Agent Blue spraying (amount and location) in much of the Delta region, it is now impossible to distinguish natural from anthropogenic arsenic spikes in the Delta groundwater. However, one could surmise that arsenic based Agent Blue herbicide was one of the vegetation management tools available to the RV military, with the assistance of the US Army and US Navy. This Khai Quang program spraying of Agent Blue was in addition to the Operation Ranch Hand spraying (US Air Force) in the Mekong Delta. The combined operation and program applications of Agent Blue, an estimated total of 7.8 million liters (1,132,400 kg As), were applied to southern Vietnam from 1961 to 1971. These applications significantly increased the concentration of As in the groundwater and the need for mitigation and remediation such as that which was applied to the Ansul Chemical Plant sites and the adjacent Menominee River in Michigan and Wisconsin.

Acknowledgements

Department of Natural Resources, Office of International Programs and the Office of Research, College of Agricultural, Consumer, and Environmental Science, University of Illinois provided funding support. This research study was conducted with the support and approval of the Merry Band of Retirees Committee, which includes nine U.S. Army and Vietnam Era veterans, and four Agricultural College Professors. The study was approved for publication by the Director of the Office of Research and the Office of International Programs, ACES, University of Illinois, Urbana, Illinois.

Conflicts of Interest

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

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