

Review and Analysis: Agent Blue, the Arsenic Based Herbicide, Used during the Second Indochina and Vietnam Wars to Destroy the Rice Crop

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Abstract

The Republic of Vietnam and the United States (US) militaries began destroying food crops (rice) in November of 1962, primarily via aerial applications in the Mekong Delta and Central Highlands of South Vietnam. Spraying of Agent Blue on mangrove forests and rice paddies just before rice harvest time resulted in the destruction of the standing crop and rendered the land contaminated with arsenic (As). Agent Blue (cacodylic acid, $C_2H_7AsO_2$) was the most effective of all the Rainbow herbicides in killing rice and grasses. Manufacturing of cacodylic acid began in the late 1950s in the US at the Ansul Company chemical plant in Marinette, Wisconsin and Menominee, Michigan. During the Vietnam War, ocean-going ships were loaded with 208-liter Agent Blue barrels and shipped via the St. Lawrence Seaway to the coast of South Vietnam. Arsenic (As) is a naturally occurring element that is found throughout SE Asia deltas, including the Mekong Delta. Arsenic-contaminated rice and groundwater are growing concerns as neither naturally occurring arsenic nor anthropic arsenic has a half-life and cannot be destroyed. Water-soluble arsenic primarily leaches into the soil root zone and the groundwater. The As in the contaminated rice paddy soil, sediment and water are taken up by fish, shrimp or crop vegetation and trace amounts can end up in the food supply (rice grain) or be bioaccumulated by the fish, shrimp and birds, which, when eaten, are bioaccumulated in the Vietnamese people. This research reinforces the urgent need for mitigation of arsenic exposure from drinking water and food grown in flooded rice production systems. The uptake of trace amounts

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

Keywords

Arsenic, Mekong Delta, Agent Blue, Rice, Agricultural Herbicides, Chemical Weapons

1. Introduction

Use of Agent Blue as a Chemical Weapon for Food Denial during the Vietnam War

For over 50 years, US news about chemical warfare during the American-Vietnam War has been dominated by the story of Agent Orange and its devastating impacts. During the Vietnam War period, however, another diabolical concoction called Agent Blue was also used extensively in Vietnam. This arsenic-based herbicide was used to destroy the rice crop, and the public knew little about the previous use of Agent Blue in both wars. The first known media pick-up of the Agent Blue (arsenic based) being used in the Mekong Delta for crop destruction in May of 1964. Jim G. Lucas, a Scripps-Howard staff reporter, submitted an article that was published as an editorial in the Washington Post on May 26, 1964. The next news reference to this chemical weapon was a letter to the editor sent by Arthur H. Westing in 1971 and published by the New York Times under the headline “*Agent Blue’ in Vietnam.*”

These two blips of attention to tactical herbicide Agent Blue were not followed up until 44 years later, when Loana Hoylman published an article, “*Today’s Blue Arsenic in the Environment,*” in a 2014 issue of Veteran magazine, published by Vietnam Veterans of America. Finally, in 2020, Kenneth R. Olson and Larry Cihacek published the first refereed journal article on the topic, “*The Fate of Agent Blue, the Arsenic Based Herbicide, Used in South Vietnam during the Vietnam War*” in the Open Journal of Soil Science.

Using new primary source data, the 2020 article reconstructed the paper trail of those “*Made in America*” chemical weapons and developed an updated chemical research framework. International news media started paying attention. Mike Tharp, a member of the Merry Band of Retirees, our group of military veterans working on this issue, wrote articles that Asia Times published. Mike died in 2023, apparently from his exposure to dioxin TCDD and/or arsenic while stationed at Bien Hoa Air Force base in Vietnam during the Vietnam War.

The question remains: “*How can this secret use of Agent Blue to destroy civilian food (rice) sources and agricultural production sites have gone uncovered by US news organizations for 50 years?*” It’s an important question. Let’s sketch this hidden chemical warfare and its current impact. In the beginning, Agent Blue was sprayed by the Republic of Vietnam military for three years before the 1965 official

start of the United States' Vietnam War. Vietnam War veterans, historians and scholars have collected information on the spraying 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 (containing 468,000 kilograms of arsenic) were sprayed during the Republic of Vietnam's Khai Huang (food denial) program.

This was in addition to the US Air Force's Operation Ranch Hand spraying of Agent Blue primarily from C-123 aircraft. Operation Ranch Hand maintained records of the locations and quantities of herbicides sprayed (over 4,712,000 liters containing 664,392 kilograms of arsenic) from 1961-1971. The Institute of Medicine estimated that, in total, 7.8 million liters (1,132,400 kilograms of arsenic) of Agent Blue were applied to the southern Vietnam landscape from 1962 to 1971. This total includes both the 1962 to 1965 RV Khai Huang program, done by the RV military with the assistance of the CIA, US Army and US Navy, and the part of the total Agent Blue applied by US Air Force Operation Ranch Hand from 1962 to 1971.

This is a mind-boggling amount of highly toxic chemicals to be sprayed over the Mekong Delta's rice fields, which were a prime rice growing region in Vietnam, for a decade. So, what has happened to all these chemical warfare agents during the last 60 years? Since this chemical warfare began, the southern Vietnam environment and Vietnamese living in the Mekong Delta have bio-accumulated arsenic from both natural and anthropic sources via their drinking water (groundwater from tube wells) and food supply, which has increased their risk of chronic poisoning over time. Arsenic is water soluble, has no half-life, and is toxic. Put another way, its poison keeps on poisoning forever.

This paper's synthesis and analysis of publications and records will document the contributions of the South Vietnamese government and the United States military to arsenic levels, and it will describe arsenic's present-day persistence in the Vietnam Mekong Delta groundwater. Here's a one-sentence preview of the findings: As both the Vietnamese rice farmers and US military personnel who were exposed to Agent Blue can attest, poisoning the water you drink or the local food you eat is not a good idea.

2. Study Site—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 [1]-[3]. The Mekong Delta (**Figure 1**) soils include Entisols, Inceptisols and Histosols (**Figure 2**) 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. 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 (**Figure 3**).



Figure 1. Borders of the Mekong Delta in Vietnam and Cambodia. Map created by Mic Greenberg. Re-published with copyright permission from Managing Editor of OJSS.

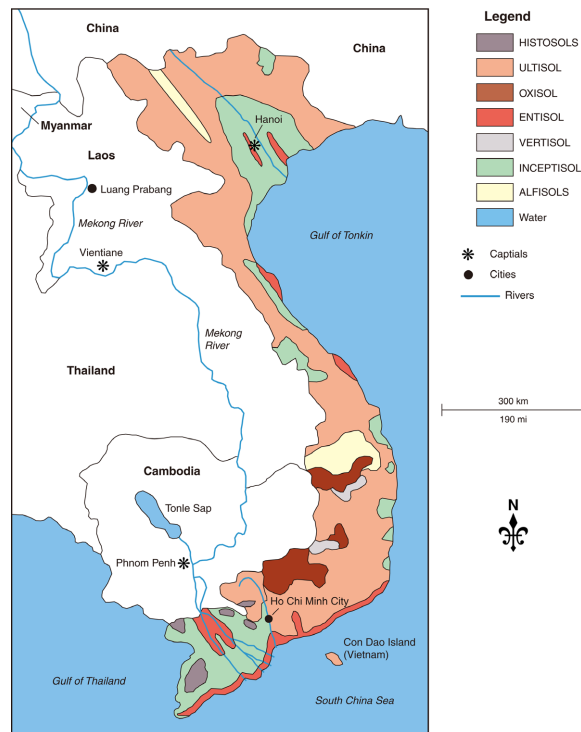


Figure 2. A soil map of Vietnam. Adapted from FAO/UNESCO Preliminary Definitions, Legend and Correlation Table for the Soil Map of the World. World Soil Resources Report No. 12; Rome: 1964. Adapted from Moormann, F. R. The Soils of the Republic of Vietnam. Saigon: Ministry of Agriculture, 1961. Map created by Mic Greenberg. Re-published with copyright permission from Managing Editor of OJSS.



Figure 3. As the Mekong and Bassac Rivers flow south, through the Mekong Delta they water a diverse landscape bringing freshwater to the lowlands around the flooded mountains; to saltwater river regions in the wet season; and sediment loads that replenish the fertility of rice fields. Coastal dunes along the South China Sea are high points in the landscape. Farmers in the uplands of Vietnam grow coffee, rubber, fruit and nut trees. Map by Mic Greenberg. Published with the copyright permission from Editor of Open Journal of Environmental Protection.

3. Findings

3.1. How United States Agricultural Herbicides Became Military and Environmental Chemical Weapons: Historical and Residual Effects

Discoveries in Charles Darwin's laboratory led to modern herbicides [4]. Darwin discovered the internal mechanism that directed plants to grow toward sunlight and sources of water. Scientists in Europe and America later called this mechanism a plant's hormone response system. Administrators and scientists, including Dr. Ezra J. Kraus, the Head of the Botany Department at the University of Chicago and a plant physiologist (Figure 4), suggested on the eve of WWII that weed killers had significant military value as chemical weapons. Dr. Kraus obtained access to a synthetic chemical, 2,4-D, and found that when the chemical was absorbed

through the leaves of plants, it destroyed a plant's hormones. After exposure, the plant experienced rapid and uncontrolled growth, and then the leaves shriveled, died and fell off. Dr. Kraus obtained funding for his Department of Botany research program from Department of Defense (DOD) during World War II (WWII). Camp Detrick (Biological Weapons Laboratory) (Figure 5) scientists later obtained samples of newly created 2,4,5-T, which contained unknown amounts of the by-product dioxin TCDD. In the 1950s and 1960s, Fort Detrick military scientists formulated the herbicide Agent Orange, which was a 50 - 50 mixture of 2,4-D and 2,4,5-T. These dual-purpose herbicides were used by DOD and USDA. American and European farmers in the 1940s used 2,4-D and 2,4,5-T to eliminate weeds from pastureland and cropland. After WWII, synthetic herbicides (and pesticides) development continued in tandem with production of synthetic fertilizers and breeding of high-yield plant varieties. These new agricultural products were then shipped worldwide to increase crop yields, as part of the Green Revolution. This new system of agricultural technologies was intended to eliminate global starvation and increase food security by increasing field and farm crop yields. In contrast, the goal of military use of herbicides, as chemical weapons, was to defoliate jungle forests and destroy food crops as a strategy to win battles and wars. The primary objective of this research study [4] was to describe how agricultural herbicides became tactical chemical weapons. A current assessment will address the environmental impacts of military and environmental chemical weapons on the United States and Vietnam ecosystems and need for additional dioxin TCDD hotspot clean-up efforts.



Figure 4. Ezra Kraus, the father of herbicide (chemical) weapons, in his laboratory at the University of Chicago. Photo Credit: University of Chicago Library, University of Photographic Archive, Hanna Holbord Gray Special Collections. Individual groups, Informal 5, apfi-03586. Re-published with copyright permission from Managing Editor of OJSS.



Figure 5. Fort Detrick Biological Weapons laboratory headquarters in Maryland. Photo Credit: YouTube. Photograph courtesy of Andrew Dutton. Re-published with copyright permission from Managing Editor of OJSS.

3.2. The Fate of Agent Blue, the Arsenic Based Herbicide, Used in South Vietnam during the Vietnam War

The destruction of the South Vietnamese rice (*Oryza sativa* L) crop (**Figure 6**) using an arsenic-based herbicide known as Agent Blue during the American Vietnam War (1965-1972) was not a secret; however, it received little media attention in the United States [5]. The Republic of Vietnam and the United States (US) militaries began destroying food crops (rice) in November of 1962, primarily via aerial applications in the Mekong Delta and Central Highlands of South Vietnam. Spraying of Agent Blue on 100,000 ha of mangrove forests and about 300,000 ha of rice paddies just before rice harvest time resulted in the destruction of the standing crop and rendered the land contaminated with arsenic (As). Six Rainbow herbicides, commonly called Agent Orange, Agent Green, Agent Pink, Agent Purple, Agent White, and Agent Blue, were sprayed on wetlands, rice paddies, forests, mangroves, bamboo and military base perimeter fences (**Figure 7**) to defoliate jungle vegetation, reveal guerilla hiding places and destroy the food supply of enemy troops. South Vietnamese farmers, US and Republic of Vietnam military personnel, and communist insurgents were exposed to these herbicides with immediate and longer-term impacts on personal health, civilian household food security and population-wide famine. Agent Blue (**Figure 8**) (cacodylic acid, $C_2H_7AsO_2$) was the most effective of all the Rainbow herbicides in killing rice and grasses. Manufacturing of cacodylic acid began in the late 1950s in the US at the Ansul Company chemical plant in Marinette, Wisconsin and Menominee, Michigan (**Figure 9**). During the Vietnam War, ocean going ships were loaded with 208-liter Agent Blue barrels and shipped via the St. Lawrence Seaway to the coast of South Vietnam. Arsenic (As) is a naturally occurring element that is found throughout SE Asia deltas, including the Mekong Delta. Today arsenic contaminated rice and groundwater are growing concerns as neither naturally occurring arsenic nor anthropic arsenic has a half-life and cannot be destroyed. Anthropic arsenic has remained in the Mekong Delta environment for the last 60 years and added to persistent As contamination in water supplies, sediments

and soils. Water soluble arsenic primarily leaches into the soil root zone and the groundwater or is carried by floodwater into adjacent waterways or volatilized under anaerobic rice paddy conditions as gaseous arsine. The health of 15 million Vietnamese people living in the Mekong Delta is at risk from the combination of manufactured and natural As in drinking water and food supply. The As in the contaminated rice paddy soil, sediment and water is up taken by fish, shrimp (Figure 10) or by crop vegetation and trace amounts can end up in the food supply (rice grain) or be bioaccumulated by the fish (Figure 11), shrimp and birds which when eaten were bioaccumulated in the Vietnamese people. It should also be noted that As can be excreted by animals and humans. It is urgent that elevated As concentrations in water supplies and agricultural products be identified and mitigated through better run-off control and groundwater management; improved rice genetics and alternate crop selections; shifts in crop management associated with tillage, fertilization and phosphorus use; and systematic monitoring of food and drinking water.



Figure 6. Vietnamese and Montagnard rice growing in the Mekong Delta of Vietnam. Irrigated rice. Published with the copyright permission from Editor of Open Journal of Soil Science.



Figure 7. The defoliated perimeter of an airbase fence after being sprayed with Agent Orange in the 1960s. Credit Line: Picture taken by US Army Flight Operations Specialist 4 John Crivello in 1969. Reprinted with the permission of the editor of the Open Journal of Soil Science.

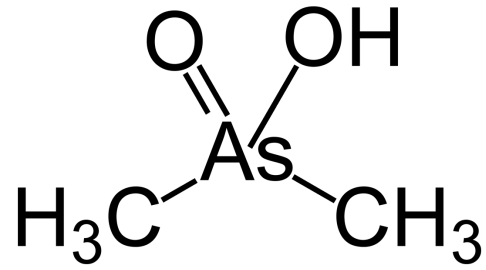


Figure 8. Cacodylic acid chemical formula. Drawing by Mic Greenberg. Published with the copyright permission from Editor of Open Journal of Soil Science.



Figure 9. Aerial view of the former Ansul company chemical plant on Menominee River in Marinette, Wisconsin (L) and Menominee, Michigan (R). The Menominee River flows into Green Bay. Published with copyright permission from Editor of Open Journal of Soil Science.



Figure 10. Shrimp farm in Mekong Delta of Vietnam that was developed after 1975. Re-published with copyright permission from Managing Editor of OJSS.



Figure 11. Fish (pisces) is the main source of protein and income for SE Asia families. A fish market in Ho Chi Minh City. Re-published with copyright permission from Managing Editor of OJSS.

3.3. Fate of Arsenic Applied to Canal Shipping Lane Vegetation and United States Military Base Grounds in the Panama Canal Zone

The opening of the Panama Canal in 1913 (**Figure 12**) increased the availability of internationally traded goods and transformed ocean-shipping by shortening travel time between the Atlantic Ocean and Pacific Ocean [6]. The canal sparked the growth of port authorities and increased ship tonnage on both coasts of Panama. Since the construction of the Panama Canal, in the 1910s, pesticides, herbicides and chemicals, including arsenic, have been essential for controlling wetland vegetation, including hyacinth, which blocked rivers, lakes, and the canal as well as managing mosquitoes. Pesticides and chemicals flowed into Lake Gatun (reservoir) either attached to sediment or in solution during the monsoon season. Lake Gatun (**Figure 13**) was the drinking water source for most of the people living in the Panama Canal Zone. The United States military base commanders had the ability to order and use cacodylic acid (arsenic based) from the Naval Depot Supply Federal and Stock Catalog and the later Federal Supply Catalog on the military base grounds in the Panama Canal Zone. Cacodylic acid was shipped to Panama Canal Zone ports, including Balboa and Cristobal, and distributed to the military bases by rail or truck. The objective of this study [6] was to determine the fate of arsenic: 1) applied between 1914 and 1935 to Panama Canal shipping lane hyacinth and other wetland vegetation and 2) cacodylic acid (arsenic) sprayed from 1948 to 1999 on the US military base grounds in the Panama Canal Zone.

3.4. 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

Agent Blue, a mixture of cacodylic acid ($C_2H_7AsO_2$) and sodium cacodylate ($C_2H_6AsNaO_2$), was a tactical arsenic-based herbicide used during the Vietnam

War to destroy grasses and rice crops [7]. 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 (Figure 14) for tactical herbicides including Agent Blue sprayed in southern Vietnam during the Vietnam War (1961-1971) are very detailed, rather complete and publicly available [8]. The same is not true for tactical herbicides sprayed by the Republic of Vietnam (RV) during the Khai Huang program which was supported by the US Army, US 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,

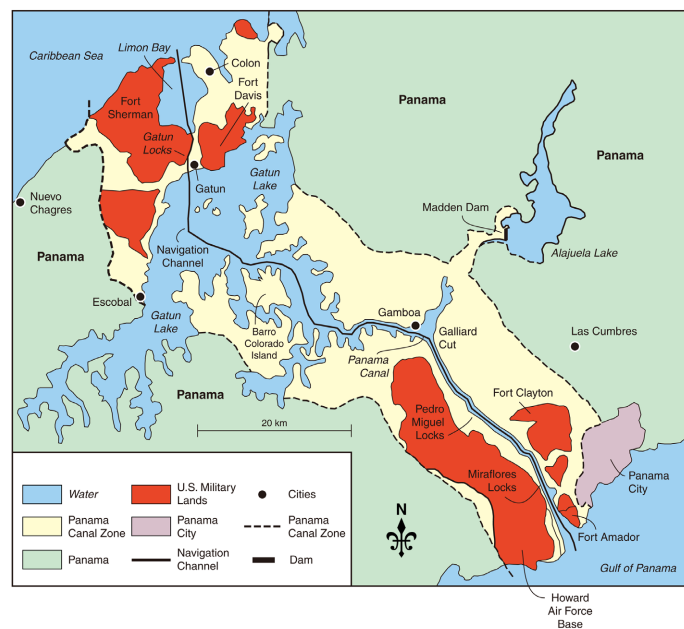


Figure 12. Panama Canal Zone map showing the Panama Canal, Lake Gatun, military bases and Panama City. Published with the copyright permission from Editor of Open Journal of Soil Science.



Figure 13. Lake Gatun. The source of drinking water in the Panama Canal Zone. Published with the copyright permission from Editor of Open Journal of Soil Science.



Figure 14. The Republic of Vietnam and United States printed correspondence is kept at Vietnam War Archive number 2 in Ho Chi Minh City. Reprinted with the permission of the editor of the Open Journal of Soil Science.

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 [9] estimated that 3.2 million liters (468,000 kg As) were sprayed during the RV Khai Huang program. This was in addition to the US Air Force's Operation Ranch Hand spraying of the tactical herbicide Agent Blue primarily by C-123 aircraft (Figure 15). Operation Ranch Hand maintained location and quantities of herbicides 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 (Figure 16) and helicopters based on the decks of Blue Water Navy ships. Some of these spray missions (Figure 17) 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 (Figure 18) for urban and agricultural use. The primary objectives of this research [7] were 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.



Figure 15. 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. Photo credit: Picture courtesy of Jim Lang.

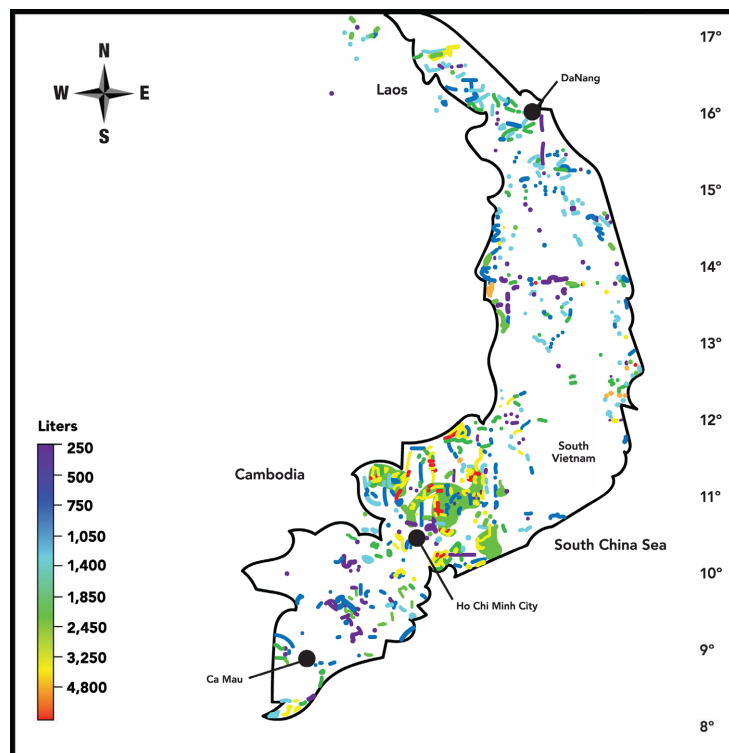


Figure 16. Volumes of herbicides Agent Blue (cacodylic acid, $C_2H_7AsO_2$) sprayed by US military forces in RVN (South Vietnam). Reprinted with the permission of the editor of the Open Journal of Soil Science.



Figure 17. Tactical herbicides being sprayed by a helicopter on mangrove forests. Reprinted with the permission of the editor of the Open Journal of Soil Science.



Figure 18. Tube wells in the Mekong Delta. Reprinted with the permission of the editor of the Open Journal of Soil Science.

3.5. Saigon River Valley: A Navigation, Trade, Mitigation, Invasion, Liberation, and Unification Pathway

The Saigon River is in southern Vietnam with headwaters starting in southeastern Cambodia [10]. The river flows southeast for about 225 km to the South China Sea. Most readers of Vietnam's history know about the American-Vietnam War (1965-1973). However, centuries before that time, Vietnam fought with the Chinese, the Khmers, the Chams and the Mongols. The history of Vietnam begins in

the Red River Delta, where farmers first cultivated rice. A millennium of struggle against the Chinese then followed. The Saigon River Valley was the pathway used by the North Vietnamese Army (NVA) to get from the Ho Chi Minh Trail in Cambodia to Saigon during the 1968 Tet Offensive. The NVA dug Cu Chi and Iron Triangle soil tunnels near Cu Chi in the Old Alluvium terrace to hide from American Forces and Air Force bombers. In 1962, the Tan Son Nhut Air Force base on the northern edge of Saigon received the first shipments of Agent Blue, the arsenic-based herbicide, used to destroy the rice crop. The most dioxin TCDD and arsenic contaminated site in Vietnam was Bien Hoa Air Force base on the Saigon River, just 30 km northeast of Ho Chi Minh City. The adjacent Bien Hoa City has a population of over 800,000. The Port of Ho Chi Minh City is the most significant river port in Vietnam and Southeast Asia. The river is navigable by ships which draft up to 9 m. Vietnam only became a united country in the 19th century. Its independence was soon affected by French colonialism and then the destructive American intervention in the Vietnam War. The Vietnam War Archive no. 2 in Ho Chi Minh City houses residual correspondence between the Republic of Vietnam (RV) President Diem's administration and US President Kennedy's administration related to the Khai Huang program (hamlet strategy). In addition, the archive contains some of the tactical herbicide spray records of the RV military for the Mekong Delta. The primary objective of this study [10] was to document the role that the Saigon River Valley played in modern warfare. The Saigon River Valley was used as a navigation, trade, invasion, liberation and unification pathway. The Vietnamese people have survived centuries of stormy, troubled times and their power of character has served them well.

3.6. Agent Blue: A Secret Military and Environmental Chemical Weapon Used for Food Denial in South Vietnam during the Vietnam Civil War (1962-1965)

Olson [11] noted that *“the use of tactical herbicides in Southern Vietnam was begun in 1961 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 the early 1960s the RV program known as Khai Huang RV Program was designed to eliminate food crops. 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 RV during the Khai Huang program which was supported by the US Army, US Navy, and*

Central Intelligence Agency (CIA) in the Mekong Delta. During the Vietnam Civil War, Agent Blue, in powder form, was shipped to Port Saigon, via the Saigon River, and transported to the Tan Son Nhut Air Force base during the Vietnam Civil War. After the official start of the American-Vietnam War (1965-1973), the tactical herbicides were re-routed to Bien Hoa Air Force base (1965 to 1971)."

"Agent Blue was sprayed by the RV military for three years before the official start of the American-Vietnam War in 1965. Few, if any, RV military, US Army, US Navy, and CIA spray records exist from 1962 to 1965. 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. DoD has consistently claimed that United States spraying of Agent Blue was done in the Central Highlands and not in Mekong Delta so there were no records or very few spray records available for the delta for the entire 10-year period (1962-1971) to be found. It is a known fact that the goal of the South Vietnamese government (RV) and military was to eliminate the North Vietnam Army (NVA) and Viet Cong (VC) food supply and to implement the Hamlet strategy. Most of the rice was produced in the Mekong Delta not the Central Highlands, which does have Operation Ranch Hand Agent Blue spray records. The US government, CIA, and military records were either not kept or they were not maintained. The additional RV spray program, from 1962 to 1965, is supported by the documented mass migration from rural South Vietnam to hamlets or to Saigon slums. However, Vietnam War Archive no. 2 in Ho Chi Minh City may have the spray records of the RV military, assisted by the US Navy, US Army, and CIA to implement the hamlet strategy and these records need to be electronically preserved. Vietnamese correspondence between President Diem's administration and the President Kennedy administration is shelved in loose binders at the Vietnam War Archive number 2 in Ho Chi Minh City (personal observation during an October 2022 visit to Archive number 2)" [11].

During the last 60 years, the southern Vietnam environment and Vietnamese living in the Mekong Delta have bio-accumulated arsenic from natural and anthropic (Vietnam Civil War (1962-1965)) sources via their drinking water (groundwater from tube wells) and food supply leading to an increasing risk of chronic poisoning over time [12]. A synthesis and analysis of publications and records is presented to document the Republic of Vietnam (RV), the official name of the South Vietnam Government, and the United States (US) military's contribution to arsenic levels and toxic spikes in the Vietnam Mekong Delta groundwater. During the Vietnam

Civil War, Agent Blue, in powder form, was shipped to Port Saigon, via the Saigon River, and transported to the Tan Son Nhut Air Force base (Figure 19) during the Vietnam Civil War. After the official start of the American-Vietnam War (1965-1973) the tactical herbicides were re-routed to Bien Hoa Air Force (Figure 20) base (1965 to 1971). Approximately 3.2 million liters of Agent Blue (468,008 kg As) was sprayed or dumped by the RV military with the assistance and support of the Central Intelligence (CIA), US Army and US Navy, during the 1962-1965 Khai Huang (Hamlet) Program. A portion of an additional 4.6 million liters of Agent Blue (664,392 kg of As) was sprayed between 1962 and 1965 by the US Air Force as part of Operation Ranch Hand and prior to the official start of the American-Vietnam War in August 1964. Operation Ranch Hand began in 1962 and ended in 1971. The Institute of Medicine estimated a total of 7.8 million liters (1,132,400 kg As) of Agent Blue was applied to southern Vietnam landscape (Figure 21) from 1962 to 1971. This total includes both the 1962 to 1965 RV Khai Huang program with the assistance of the CIA, US Army and US Navy, and the total Agent Blue applied by US Air Force Operation Ranch Hand from 1962 to 1971. The primary objective of this study [12] was to document how Agent Blue, the arsenic-based herbicide, became a secret US military and environmental chemical weapon used by the RV and US militaries in southern Vietnam during the Vietnam Civil War years (1962-1965). This assessment found that the anthropic arsenic, including Agent Blue, added a toxic burden to the Mekong Delta soils, surface water, groundwater, drinking water, food supply, and human health. However, there are missing details regarding political decisions and a full accounting of the geographic locations sprayed and amount of Agent Blue used. Vietnam War Archives have paper correspondence and RV herbicide spray records (Figure 22) that shed greater light on this period. These records are over 50 years old and need to be electronically scanned, stored, and made available for additional historical analyses.



Figure 19. Tan Son Nhut Air Force base museum in Ho Chi Minh City. Reprinted with the permission of the editor of the Open Journal of Soil Science.



Figure 20. Picture of active Bien Hoa Air Force Base taken in the 1960s during the Vietnam War. Credit line: Photograph courtesy of Vietnam War Commemoration.



Figure 21. Agent Orange and other color-coded herbicides were sprayed by low flying aircraft over the Vietnam jungle and rural landscapes and subject to small arms fire from the ground. Most these herbicides had short-half lives of hours, days and a few weeks; and vegetation regrowth required additional applications. Picture taken by US Army Flight Operations Specialist 4 John Crivello in 1969. Reprinted with permission from Editor of Open Journal of Soil Science.

3.7. Natural and Anthropogenic Sources of Arsenic in the Groundwater and Soils of the Mekong Delta

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 [13]. 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



Figure 22. Tactical herbicides sprayed from a M113 Armored Tracked Personnel Carrier, Reprinted with the permission of the editor of the Open Journal of Soil Science.

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 $\mu\text{g}/\text{L}$ 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 (**Figure 23**) with elevated As levels since 1962, industrial sources, smelting by-products, water treatment plants (**Figure 24**), 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 [12]. The As spikes and levels in the Mekong Delta soils and groundwater need restoration. The uptake of trace amounts of As in rice is indeed a critical food security and human health issue and requires mitigation. The uptake of trace amounts of As in rice is indeed a critical food security and human health issue and requires mitigation.

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 nano-crystals 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.



Figure 23. Urban cemetery in southern of Vietnam. Reprinted with the permission of the editor of the Open Journal of Soil Science.



Figure 24. 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. Reprinted with the permission of the editor of the Open Journal of Soil Science.

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.

4. Results—The Secret Toxic Legacies of Chemical Warfare: Agent Blue Use during the 2nd Indochina and Vietnam Wars in Laos, Cambodia, and Vietnam (1961 to 1971)

During the 2nd Indochina War which started in 1959, the United States Central Intelligence Agency (CIA), Air America, and the Air Force waged a secret and unconventional air war in Laos (**Figure 25**) from Udorn Air Force base located in Thailand and across the Mekong River from Vientiane, Laos [11]. Starting in 1961, four years before the official start of the American-Vietnam War, Agent Blue, the arsenic-based herbicide used to kill rice and other food crops, was used extensively in Laos, Vietnam and to a lesser extent in Cambodia. During the secret 2nd Indochina War and the Vietnam Civil War, the public knew little about the use of Agent Blue. After the official start of the American-Vietnam War in 1965, the United States media news reports, about chemical warfare were dominated by the story of Agent Orange and its devastating impacts. The public knew very little about the previous use of Agent Blue in both wars. The first known media pick up of the Agent Blue (arsenic based) and Agent Pink, Agent Green, and Agent Purple (all three contain 2,4,5-T and unknown amounts of dioxin TCDD) was in May of 1964. Jim G. Lucas, a Scripps-Howard staff reporter submitted an article that was published as an editorial in the Washington Post on May 26, 1964. The next news reference to this chemical weapon was a Letter to the Editor published in the New York Times titled “Agent Blue” in Vietnam by Arthur H. Westing in 1971. The use of herbicides, including Agent Blue in Laos during the 2nd Indochina War, was kept a secret until 1982, when a draft of Buckingham's study of Operation Ranch Hand was made public.

Much about the US war effort in Laos is still classified. In a 2014 issue of the VVA Veteran magazine, Loana Hoylman published an article on “*Today's Blue Arsenic in the Environment*”. The first refereed journal article on this topic, “*The Fate of Agent Blue, the Arsenic-Based Herbicide, Used in South Vietnam during the Vietnam War*” was published in 2020 in the Open Journal of Soil Science by Kenneth R. Olson and Larry Cihacek [5]. In 2021, the Asia Times (print), CounterPunch (print), Chemistry World (print) and VietnamVeteran-News (radio podcast) picked up the Agent Blue story. During the early 2020s, Olson published six additional refereed journal articles [4] on Agent Blue, cac-

odylic acid, and arsenic. The primary objective was to determine why no major news organization in the United States, including the New York Times and Washington Post, have never investigated Agent Blue use during the 2nd Indo-China and Vietnam Wars? Why did the use of Agent Blue story, used to destroy Laotian and South Vietnamese civilian food (rice) sources and production sites, received only very limited coverage by US print media news organizations during the last 64 years?

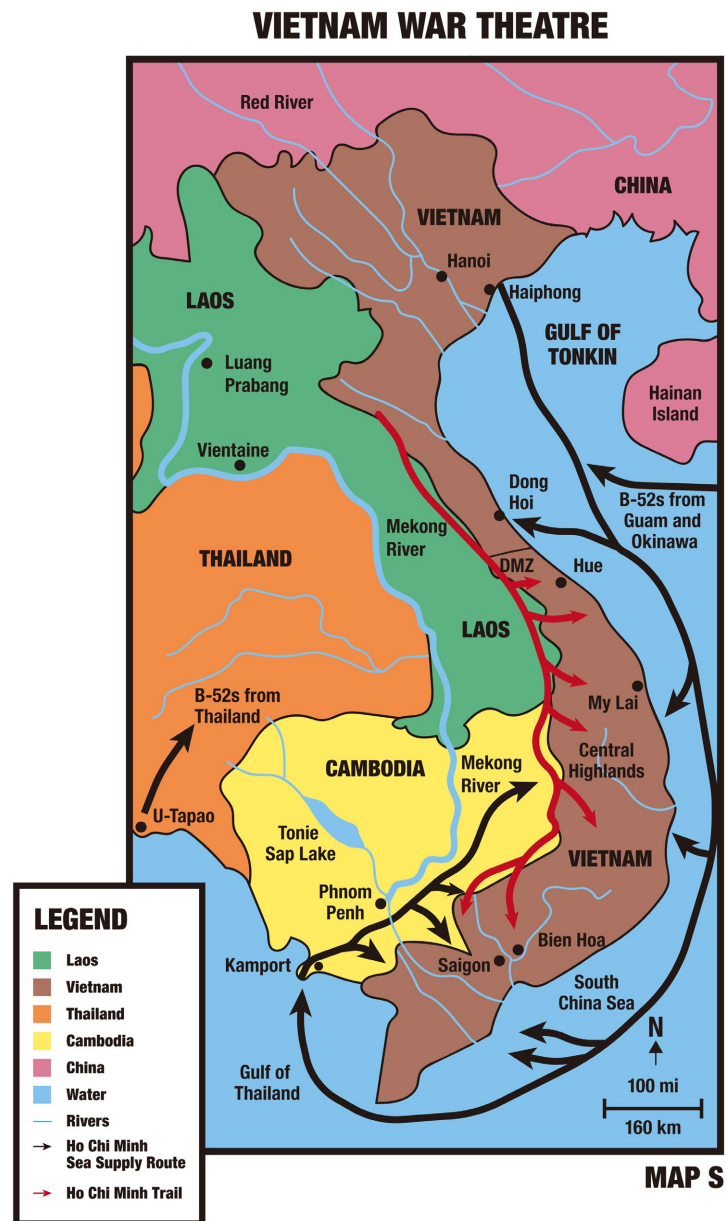


Figure 25. The Ho Chi Minh Trail through the mountains and jungles of Vietnam, Laos and Cambodia was a system of trails and paths controlled by the Democratic Republic of Vietnam (1959-1975) used for transporting food, military equipment and North Vietnamese Army soldiers into southern Vietnam during the Vietnam War. Map by Cruz Dragosavac. Reprinted with permission from Editor of Open Journal of Soil Science.

5. Discussion—Environmental and Human Impact of Agent Blue, Cacodylic Acid, and Arsenic on Drinking Water, Food Supply and Air Resources

5.1 Quantification of the Amount of Arsenic Applied by South Vietnam and US Militaries

The Institute of Medicine estimated a total of 7.8 million liters of Agent Blue was applied to southern Vietnam landscape from 1962 to 1971 [5]. This total includes both the 1962 to 1965 RV Khai Huang program with the assistance of the CIA, US Army and US Navy, and the total Agent Blue applied by US Air Force Operation Ranch Hand from 1962 to 1971. A portion of the 4.6 million liters of Agent Blue was sprayed between 1962 and 1965 by the US Air Force as part of Operation Ranch Hand and prior to the official start of the American-Vietnam War in August 1964. Operation Ranch Hand began in 1962 and ended in 1971. However, the Operation Ranch Hand spray total does not include the approximately 3.2 million liters of Agent Blue that was sprayed by the RV military with the assistance and support of the Central Intelligence (CIA), US Army and US Navy, during the 1962-1965 Khai Huang (Hamlet) Program. Since DoD did not keep records of the amount of Agent Blue or arsenic applied by RV military during the Khai Huang program, DoD records can only be used to validate part of the Institute of Medicine spray total and are much lower. However, Olson and Chau [12] were able to validate the RV military Khai Huang program total spraying of Agent Blue.

Olson and Cihacek [5] found the Agent Blue consists of 59.5% water, 26.4% sodium cacodylate (sodium dimethylarsenic acid), 5.5% sodium chloride, 4.7% cacodylic acid (hydroxydimethylarsine oxide), 3.4% surfactant, 0.5% antifoam agent. Arsenicals compose 31.1% of Agent Blue, 15.4% is elemental arsenic, in the form of +5 oxidation state arsenical. The multiplied the total 7.8 million liters of Agent Blue applied by the percent elemental arsenic (15.8%) to calculate the total arsenic applied during the war. To date, the author is not aware of any other source validating the 1,132,400 total anthropic arsenic applied during the Vietnam War. The DoD spray records did not include the RV Khai Huang program total, so they underestimated the total arsenic applied during the Vietnam War (1,132,400 kg As) and only included the Operation Ranch Hand (664,392 kg of As) total and excluded the RV Khai Huang (468,008 kg As) program total. 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 and validated [12] 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.

5.2. Origins of Agent Blue, an Arsenic Based Chemical Weapon

Numerous arsenic based chemical agents were invented and used in past warfare

[14]. The Chinese invented the poisonous smoke ball, around 1000 BC, which contained arsenic oxide (As_2O_3) [15]. It was the precursor to modern-day grenades. The first known arsenic based chemical weapon use was in 431-404 BC by the Spartans. Arsenic was used as a noxious smoke against Athenian-allied cities during the Peloponnesian War. During WWI, the first modern arsenic based chemical weapon appeared and contained arsenic and organic compounds. Lewisite, one of the deadliest poisonous gases, was developed after WWI [16]. Large-scale production of Lewisite began during WWII in the United States, Germany, Great Britain, Japan and the former Soviet Union. Later, North Korea, Iraq and Libya manufactured and used Lewisite. The era of Rainbow herbicides (specific herbicides were coded by color) started during the Vietnam War. From 1961 to 1971, Agent Blue was used by the South Vietnamese and American military to kill rice, bamboo and banana vegetation in South Vietnam [17]. Arsenic undergoes a cycle in an agricultural ecosystem involving arsenic herbicides and fertilizers, up-takes by the plants and consumption by the animals, release by plants and animals, binding with soil and transferred between soil and water. Arsenate is the most stable and generally tends to accumulate in oxidizing (oxygen rich) environments. The arsenite occurs near the root under reducing anaerobic soil conditions. Most bacteria are unable to use arsenic compounds as respiratory metabolites. Arsenic poisoning of organisms occurs when exposed to quantities much larger than needed. Arsenic contamination of groundwater is a problem that affects millions of people living on Southeast Asia deltas including the Mekong Delta. The United States Environmental Protection Agency (EPA) considers all forms of arsenic a significant risk to human health [18]. Arsenic is classified as a Group-A carcinogen. The US Agency for Toxic Substances and Disease Registry (ATSDR) ranks arsenic No. 1 on its Hazardous Substances at Superfund sites [19]. Synthetic arsenates include calcium arsenate, cupric hydrogen arsenate, and lead hydrogen arsenate. These 3 synthetic compounds, used prior to and during the Vietnam War, have also been used in agricultural herbicides, insecticides, and poisons. The list is based on overall toxicity and potential for human exposure and frequency of occurrence at National Priority List Superfund sites. This list ranks chemicals using an algorithm or formula that translates potential public health hazards on a points-scaled system [19]. No human body system is immune to harm caused by arsenic.

5.3. Cacodylic Acid

Olson and Cihacek [14] suggested “*Cacodylic Acid Cacodylic acid, $\text{C}_2\text{H}_7\text{AsO}_2$, is created by reducing disodium methylarsenate sulfur dioxide and converting the sodium salt to the resultant arsenomethane. The solubility in water of both sodium salt and acid are extremely high (over 83 kg/liter). The active component of Agent Blue, cacodylic acid, is water soluble and non-volatile but, being an organic (C or carbon-containing) compound, it decomposes rapidly to non-soluble, relatively non-toxic, inorganic arsenical compounds in water and soil. The chemical is stable in sunlight. Chemical and physical properties of cacodylic acid effect the*

fate in the soil and plants. Cacodylic acid is a contact herbicide and only kills tissues with chemical symptoms appearing within two days since it lacks mobility. It is not effective if rain falls within a few hours of the treatment. Sub-lethal doses induce malformed inflorescence, defoliation and fewer seeds. Cacodylic acid appears to undergo limited breakdown in plant tissues. Since it contains C in its chemical structure, microflora in the soil degrades cacodylic acid. Under aerobic conditions the breakdown is slow but is much more rapid under flooded and anaerobic conditions. The ultimate environmental fate is a change from organic to inorganic arsenate which occurs primarily in soil. Soils naturally contain 5 ppm of arsenic in the inorganic form [20]. In Southeast, Asia rubber plantations sodium arsenite has been applied for over 20 years at high rates without causing any crop damage due to As fixation by soil minerals and compounds under aerobic conditions. Plants absorb cacodylic acid from the soil more readily than inorganic arsenic. Evidence suggests that crops do not suffer injury on the land which was previously treated. However, excessive rates on soil unusually rich in phosphates can cause injury to sensitive plants such as peanuts and rice. In humans' toxicity rating of cacodylic acid is 3, or medium toxicity. Toxicological data for Ansar 160 (16.8% arsenic) and Ansar 560 (15% arsenic) are like Agent Blue”.

5.4. Arsenic

Olson and Cihacek [14] found “Arsenic, a natural element with an atomic number of 33, is present in the biosphere, hydrosphere, pedosphere and atmosphere. Arsenic is the 12th most common element in the earth's crust, 12th most abundant element in the human body, and 14th most abundant in seawater [21]. There are four oxidation states of arsenic: -3 , 0 , $+3$ and $+5$. Gaseous arsine, in the form of AsH_3 , is characteristic of the -3 oxidation state and elemental arsenic is characteristic of the 0 -oxidation state. The most common As species are arsenite [$As(III)$] which is characteristic of the $+3$ oxidation state; and arsenate [$As(V)$] which is characteristic of the $+5$ oxidation state [22]. The most readily available oxidation states for bioaccumulation are the $+3$ and $+5$ oxidation states but can be ingested in the As (-3) form by inhalation. Arsenic, as the crystalline oxides As_2O_3 and As_2O_5 , is hygroscopic and readily soluble in water to form acidic solutions. Arsenic salts are called arsenates which are weak acids and the most abundant arsenic contaminants in groundwater and contaminate the drinking water of the millions of Vietnamese living on the Mekong Delta [23]. These arsenic oxides can also be decomposed when As-containing biomass is burned forming As-containing aerosols at burning temperatures below $400^\circ C$. This decomposition and formation of aerosol compounds are aided by the presence of carbon (charcoal) even at temperatures below $200^\circ C$. Particulate As-containing aerosols (airborne ash) can also contain inhalable As during smoke exposure [23]. Arsenic is a natural constituent of water, soil, animals and plants.”

“The average arsenic content in soil is 5 ppm but can vary from 1 to 40 ppm while fresh and sea water contain between 0.003 to 0.05 ppm. Crystalline rock has

an average 2.0 ppm, table salt 2.71 ppm, and most edible parts of plants are between 0.1 and 1.0 ppm but sometimes as high as 3 ppm and higher on a dry weight basis [24]. Arsenic is water soluble but rarely found in its elemental form, rather, it forms compounds called arsenicals. Arsenicals are detected in more than 200 different minerals [25]. Arsenicals are often associated with complex sulfurous minerals made up of sulfur, gold, iron, copper, silver, nickel, antimony and cobalt due to the anionic ion structure being similar to sulfate (2SO_4^-). Arsenic is a chemical element which occurs in many minerals. Arsenic and its compounds including the trioxide are used in insecticides and pesticides. Arsenical herbicide use is declining due to the toxicity of arsenic and its compounds. Arsenic the 53rd most common element in nature comprises about 0.00015% of the Earth's crust. Typical background concentrations of arsenic are about 100 mg/kg in the soils, usually less than 10 ug/L in freshwater and 3 ng/m³ in the atmosphere.”

“There are two geological layers in Mekong Delta geological strata that produce the abundance of arsenic, and they are the natural sources of arsenicals in both groundwater and soil [25]. The upper layer was deposited during the Holocene period and above alluvial sediment from the late Pleistocene period. These two geologic layers with arsenic were derived from the Tibet Highlands (Himalayas) sediment transported to the Mekong Delta by rainfall and runoff). The Holocene sediment layer usually occurs at a 20 and 120 m depth but can be as deep as 250 m. It is an arsenic rich top layer that is more susceptible to weathering and groundwater flow [21]. The underlying Pleistocene sediment layer has low pH, is rich in organic matter, contains pyrite and sulfate and creating reducing condition that contributes to the release of arsenic from the overlying Holocene sediment.” [14]

5.5. Arsine

Arsine (IUPAC name: arsane) is an inorganic compound with the formula AsH_3 [26]. This flammable, pyrophoric, and highly toxic pnictogen hydride gas is one of the simplest compounds of arsenic [27]. Despite its lethality, it finds some applications in the semiconductor industry and for the synthesis of Organo arsenic. The term *arsine* is commonly used to describe a class of Organo arsenic compounds of the formula $\text{AsH}_{3-x}\text{R}_x$, where R = aryl or alkyl. For example, $\text{As}(\text{C}_6\text{H}_5)_3$, called triphenylarsine, is referred to as “an arsine”.

In its standard state arsine is a colorless, denser-than-air gas that is slightly soluble in water (2% at 20°C) [28] and in many organic solvents as well. Arsine itself is odorless [29], but it oxidizes in air and this creates a slight garlic or fish-like scent when the compound is present above 0.5 ppm [30]. This compound is kinetically stable: at room temperature, it decomposes only slowly. At temperatures of ca. 230°C, decomposition to arsenic and hydrogen is sufficiently rapid to be the basis of the Marsh test for arsenic presence. Similar to stibine, the decomposition of arsine is autocatalytic, as the arsenic freed during the reaction acts as a catalyst for the same reaction [31]. Several other factors, such as humidity, presence of light

and certain catalysts (namely alumina) facilitate the rate of decomposition [32].

Since before WWII, AsH_3 was proposed as a possible chemical warfare weapon. The gas is colorless, almost odorless, and 2.5 times denser than air, as required for a blanketing effect sought in chemical warfare. It is also lethal in concentrations far lower than those required to smell its garlic-like scent. In spite of these characteristics, arsine was never officially used as a weapon, because of its high flammability and its lower efficacy when compared to the non-flammable alternative phosgene. On the other hand, several organic compounds based on arsine, such as lewisite (β -chlorovinylchloroarsine), adamsite (diphenylaminechloroarsine), Clark 1 (diphenylchloroarsine) and Clark 2 (diphenylcyanoarsine) have been effectively developed for use in chemical warfare [33].

5.6. Forensic Science and the Marsh test

AsH_3 is well known in forensic science because it is a chemical intermediate in the detection of arsenic poisoning. The old (but extremely sensitive) Marsh test generates AsH_3 in the presence of arsenic [27]. This procedure, published in 1836 by James Marsh, is based upon treating an As-containing sample of a victim's body (typically the stomach contents) with As-free zinc and dilute sulfuric acid: if the sample contains arsenic, gaseous arsine will form. The gas is swept into a glass tube and decomposed by means of heating around 250°C - 300°C . The presence of As is indicated by formation of a deposit in the heated part of the equipment. On the other hand, the appearance of a black mirror deposit in the *cool* part of the equipment indicates the presence of antimony (the highly unstable SbH_3 decomposes even at low temperatures).

The Marsh test was widely used by the end of the 19th century and the start of the 20th; nowadays more sophisticated techniques such as atomic spectroscopy, inductively coupled plasma, and X-ray fluorescence analysis are employed in the forensic field. Though neutron activation analysis was used to detect trace levels of arsenic in the mid-20th century, it has since fallen out of use in modern forensics.

5.7. Toxicology of Arsine

The toxicity of arsine is distinct from that of other arsenic compounds. The main route of exposure is by inhalation, although poisoning after skin contact has also been described. Arsine attacks hemoglobin in the red blood cells, causing them to be destroyed by the body [34] [35]. The first signs of exposure, which can take several hours to become apparent, are headaches, vertigo, and nausea, followed by the symptoms of haemolytic anaemia (high levels of unconjugated bilirubin), haemoglobinuria and nephropathy. In severe cases, the damage to the kidneys can be long-lasting [28].

Exposure to arsine concentrations of 250 ppm is rapidly fatal: concentrations of 25 - 30 ppm are fatal for 30 min exposure, and concentrations of 10 ppm can be fatal at longer exposure times [36]. Symptoms of poisoning appear after expo-

sure to concentrations of 0.5 ppm. There is little information on the chronic toxicity of arsine, although it is reasonable to assume that, in common with other arsenic compounds, long-term exposure could lead to arsenicosis.

Winternitz [37] determined that “*Arsine can cause pneumonia in two different ways either the extensive edema of the acute stage may become diffusely infiltrated with polymorphonuclear leucocytes, and the edema may change to ringed with leucocytes, their epithelium degenerated, their walls infiltrated, and each bronchiole the center of a small focus or nodule of pneumonic consolidation*”, and in the second Case “*the areas involved are practically always the anterior tips of the middle and upper lobes, while the posterior portions of these lobes and the whole of the lower lobes present an air-containing and emphysematous condition, sometimes with slight congestion, sometimes with none*”, which can result in death.

5.8. Arsenic Accumulation in Rice

Rokonuzzaman *et al.* [38] noted, “*The human body loading with arsenic (As) through rice consumption is a global health concern. There is a crucial need to limit As build-up in rice, either by remediating As accumulation in soils or reducing As levels in irrigation water. Several conventional approaches have been utilized to alleviate the As accumulation in rice. However, except for some irrigation practices, those approaches success, and the adoption rate are not remarkable. This review presents human health risks posed due to consumption of As contaminated rice, evaluates different biomarkers for tracing As loading in the human body, and discusses the latest advancement in As reducing technologies emphasizing the application of seed priming, nanotechnology, and biochar application for limiting As loading in rice grains. They also evaluate different irrigation techniques to reduce As accumulation in rice. Altering water management regimes significantly reduces grain As accumulation. Bio- and nano-priming of rice seeds improve germination and minimize As translocation in rice tissues by protecting cell membrane, building pool around seed coat, methylation and volatilization, or quenching harmful effects of reactive oxygen species. Nanoparticle application in the form of nano-adsorbents or nano-fertilizers facilitates nano-remediation of As through the formation of Fe plaque or sorption or oxidation process. Incorporating biochar in the rice fields significantly reduces As through immobilization, physical adsorption, or surface complexation. In conclusion, As content in cooked rice depends on irrigation source and raw rice As level*”.

Flooded soils are important environments for the biomethylation and subsequent volatilization of arsenic (As), a contaminant of global concern [39]. Conversion of inorganic to methylated oxyarsenic species is thought to be the rate-limiting step in the production and emission of volatile (methyl) arsines. While methanogens and sulfate-reducing bacteria (SRB) have been identified as important regulators of methylated oxyarsenic concentrations in anaerobic soils, the effects of these microbial groups on bio volatilization remain unclear. Here, microcosm and batch incubation experiments with an Arkansas, USA, rice paddy

soil were performed in conjunction with metabolic inhibition to test the effects of methanogenic activity on As speciation and bio volatilization. Inhibition of methanogenesis with 2-bromoethanesulfonate (BES) led to the accumulation of methylated oxyarsenic species, primarily dimethylarsinic acid (DMAs(V)), and a four-fold increase in As bio volatilization compared to a control soil. Our results support a conceptual model that methanogenic activity suppresses bio volatilization by enhancing As demethylation rates. This work refines understanding of biogeochemical processes regulating As bio volatilization in anaerobic soil environments, and extends recent insights into links between methanogenesis and As metabolism to soils from the mid-South United States rice production region.

5.9. Arsenic in the Air

Microbes in the soil of rice paddies or forest floors convert inorganic arsenic into a group of toxic organoarsenic gases called arsines (**Figure 26**). Scientists have long known about this process in arsenic's life cycle but knew very little about its details or significance. Now researchers report the first field measurements of arsine, which could help scientists understand how arsenic accumulates in contaminated soil [40].



Figure 26. Arsine gas rising from a wetland area. First field measurements. Photo Credit: Charles Schmidt.

Schmidt [40] found “*In countries such as Bangladesh, people grow rice in paddies contaminated by arsenic in the groundwater. Scientists model how much arsenic can accumulate in the soil by studying how it moves from geological settings to biological ones and back. Two ways that arsenic leaves the paddies are by washing away in flood waters or by wafting into the atmosphere as arsines, a process called bio volatilization.*”

“*Researchers knew little about the extent of bio volatilization because arsines*

are difficult to measure. Previously, researchers collected arsine from air samples using “cryotrap” that condense gases onto a frigid surface. Cryotrap must stay cold, however, which makes them impractical for field research. Andrew Meharg, a professor at the University of Aberdeen, in the U.K., and his colleagues developed a trap that captures different species of arsine when the gases adsorb onto silica gel impregnated with silver nitrate. Imbedded in the gel, arsine gas samples can be stored for months at ambient temperature.”

“For their current study, Meharg and his colleagues sampled arsine emanating from a range of soil types across the globe, including rice paddy soils fed by arsenic-contaminated groundwater, soils contaminated by arsenic-containing mine tailings, and soils from an uncontaminated mangrove forest. They used mass spectroscopy to quantify the arsine caught by their traps.

The researchers found that arsine levels depend more on a soil’s organic content than on its arsenic concentrations. The highest arsine emission levels—up to 240 mg per hectare per year—occurred in organic-rich rice paddy soils contaminated with 11.3 ppm arsenic, while the lowest arsine levels—below the method’s limit of detection—were detected in less-organic mine tailings, containing about 1,300 ppm arsenic.”

“Meharg is not sure why organic matter is so important. He thinks that anaerobic microbes use organic matter as a substrate to reduce arsenic. The bacteria then can methylate the reduced arsenic to produce arsine gas, he says.”

“David Polya, a professor of geochemistry at the University of Manchester, in the U.K., calls the work ‘a major contribution’ because it suggests that previous estimates of the amount of bio volatilization were off by an order of magnitude. Scientists thought that the process accounted for 58% of natural arsenic emissions to the air, he says. But, extrapolating the study’s measurements globally suggests a far lower range of 2 to 6%, Polya says. Meharg points out that lower levels of bio volatilization mean other mechanisms of arsenic removal, such as by flood waters, play a greater role in contaminated soils than previously thought” [40].

5.10. Arsenic Removal Processes in Wetlands

Arsenic pollution in aquatic environments is a worldwide concern due to its toxicity and chronic effects on human health [41]. This concern has generated increasing interest in the use of different treatment technologies to remove arsenic from contaminated water. Constructed wetlands are a cost-effective natural system successfully used for removing various pollutants, and they have shown capability for removing arsenic. This paper reviews current understanding of the removal processes for arsenic, discusses implications for treatment wetlands, and identifies critical knowledge gaps and areas worthy of future research. The reactivity of arsenic means that different arsenic species may be found in wetlands, influenced by vegetation, supporting medium and microorganisms. Despite the fact that sorption, precipitation and coprecipitation are the principal processes responsible for the removal of arsenic, bacteria can mediate these processes and can play a significant role under favorable environmental conditions. The most

important factors affecting the speciation of arsenic are pH, alkalinity, temperature, dissolved oxygen, the presence of other chemical species—iron, sulfur, phosphate—a source of carbon, and the wetland substrate [41]. Studies of the microbial communities and the speciation of arsenic in the solid phase using advanced techniques could provide further insights into the removal of arsenic. Limited data and understanding of the interaction of the different processes involved in the removal of arsenic explain the rudimentary guidelines available for the design of wetland systems.

5.11. Toxicity of Arsenic and Effects on Human Health

Olson and Cihacek [14] noted, “*The organic and inorganic forms of arsenic can be found in soil, water and food around the world. Inorganic arsenic is not usually in water and food that we ingest but is found in the soil. Organic arsenic is not thought to be harmful except in high doses. However, inorganic arsenic is highly poisonous and is a known carcinogen. Approximately 29% of As exposure by humans comes from water and 70% from ingested food [42]. Once ingested arsenic can be bioaccumulated in the body. Arsenic in groundwater [43] is a significant source of arsenic in humans and the two arsenicals most abundant in water are arsenite (+3) and arsenate (+5). In order of toxicity from the most toxic to least toxic are arsines, arsenites, arsenoxides, pentavalent arsenicals, arsenium compounds, arsenates, and metallic arsenic [34]. It accumulates in the body when ingested in small doses due to low excretion rates. It often takes decades before physical symptoms of arsenic poisoning show. While arsenic is highly toxic in excess amounts, it is a common element in the human body because it commonly exists in the environments that humans inhabit. The lethal dose for rats is 48 ug/L which translates to 125 mg for a middle-aged male [43]. The maximum safe limit for arsenic ingestion of an average middle-aged male is 220 ug per day. This lethal dosage puts arsenic in a high toxic category within food toxicology. Environmental toxicity of As is affected by organic matter content, redox potential (Eh), hydrogen potential (pH), adsorption to solid mineral particles, and the presence of iron and magnesium and other substances in soil. Arsenic cannot be produced by the human body. Immune system effects of arsenic exposure include cytokine production in lymphocytes and immune-related gene expression inflammation [19]. Arsenic is associated with increases in infant morbidity from infectious disease and related to reduced T-cell numbers alongside altered cytokine profiles in core blood and increased*”.

5.12. Effect of Spraying of Rainbow Herbicides on South Vietnam Environment and Food Supply

Agent Blue herbicide damage effects include: 1) loss of potential production at a plant stage before the growth becomes economically valuable, and 2) loss of commercial products such as grain, timber and fruit and lack of young plants including seedlings and seeds required to maintain food production [14]. The effects of

crop damage were obtained mainly by studies of rural settlements and from interviews with villagers. The results were reported under the “Effects of Herbicides and Humans”. Human reactions to US and South Vietnam military spraying of Agent Blue herbicide was included in studies on mangrove forests and Vietnamese and Montagnard rice paddies, coconut plantations, gardening and upland crop areas) [44]. After spraying, individuals in every community interviewed reported on domestic animals and humans who became ill or died after Agent Blue herbicide was sprayed or the eating of herbicide-treated plants or drinking contaminated water. Thus, Agent Blue, the arsenic-based herbicide, was destructive to livelihoods of the people whose land was sprayed.

5.13. National Academy of Sciences 1974 Report and Agent Blue

The National Academy of Sciences (NAS) and their fieldwork and research in southern Vietnam, its scope was limited to the on-going American-Vietnam War and its findings are now dated. This NAS study (1971-1972) (Figure 27) was conducted, after DoD ordered the stopping of Agent Orange spraying in 1970 and all tactical herbicide spraying in 1971. President Nixon signed the Paris Peace Accords on January 27, 1973, ending the direct US involvement in the Vietnam War. Furthermore, the scientific study was conducted from aerial observations due to the unstable political environment on the ground. This gave little chance for boots-on-the-ground scientists to gather first-hand soil, water and vegetation samples and observe herbicide use effects on the landscape or the Vietnamese people close-up. Subsequent research and re-assessments of the fate of Agent Blue, cacodylic acid, and arsenic including both water soluble and inorganic arsenate and arsenite make it clear that NAS conclusions were inadequate. It is now time for new assessments and a fresh look at past data and current conditions [4] [45].

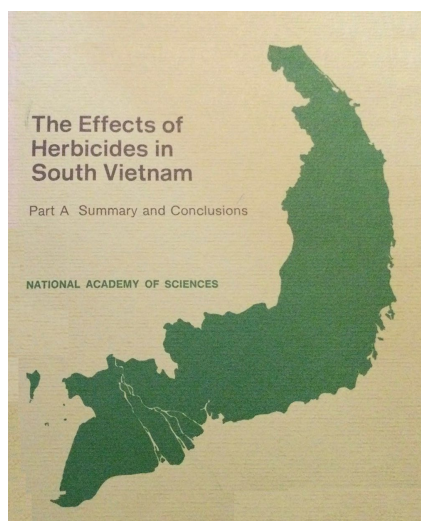


Figure 27. Picture of the 1974 National Academy of Sciences report. The NAS study was conducted during the Vietnam War years of 1971 and 1972. Photo credit: Cover picture taken by Pam Olson. Re-published with copyright permission from Managing Editor of Open Journal of Soil Science.

Olson and Cihacek [4] found “*For the last 46 years the NAS [44] Part A: Summary and Conclusion report appears to have been the ‘final word’ on the fate of Agent Blue and its active component cacodylic acid. Cacodylic acid breaks down in the soil and thought to bind tightly as arsenate (+5) to soil compounds. In the paper, they explain that the arsenic exists in four forms including two water soluble forms arsenite (+3) and arsenate (+5), which is a water-soluble arsenic salt, and much of the water-soluble arsenic was not tightly bound and leached from the rice paddy and root zone into the Mekong Delta or Central Highland groundwater potentially contaminating the groundwater. The arsenic rich groundwater (from natural and anthropic sources) was then pumped back (after 1975) to the surface by hundreds of thousands of tube wells and the water was then used for rice paddies, shrimp ponds and to meet the drinking water and household water needs of 15 million Vietnamese living on the Mekong Delta and in the Central Highlands.*”

“*The National Academy of Sciences Part A: Summary and Conclusions report [44] states: ‘Cacodylic acid, the active component in Agent Blue, is a non-selective herbicide killing a wide variety of herbaceous plants. It is a non-volatile, highly soluble organic compound which is broken down in soil, mostly to inorganic arsenate bound as insoluble compounds which also exist naturally in the soil. Acute and chronic toxicity studies in a variety of animals indicates a low to medium toxicity rating. No teratological studies, nor toxicity studies in man seem to have been reported’. While the author and our committee have great respect for the National Academy of Sciences (NAS) and their field work and research in South Vietnam its scope was limited. The NAS study (1971-1972) was conducted after President Nixon ordered the stop of herbicide spraying and completed just before he ordered in January 1973 the withdraw of soldiers from the American Vietnam War [46]. Furthermore, the study was conducted mostly from the air due to the un-stable political environment on the ground. This gave little chance for scientist boots on the ground. It is now time for a fresh look. Their findings and a re-assessment of the fate of Agent Blue, cacodylic acid, and arsenic including both water soluble and inorganic arsenate and arsenite makes this clear. In addition, there has been recent research [47] studying the effects of feeding chickens’ organic arsenic (non-toxic) supplements and their ability to convert it into inorganic arsenic (toxic Group-A carcinogen). As a result of these findings the use of organic rich chicken feed was banned in the United States. The feed had been used to make chickens more marketable (more plump, redder and prevent certain chicken diseases). Arsenic is a heavy metal and thought to be a carcinogen and dangerous.*”

“*It is not clear to this day if the VA medical doctors treating the Vietnam veterans for the last 50 years knew much about Agent Blue, the arsenic-based herbicide. Evidence suggests they probably did not, and they apparently made no attempt (prior to 2022) to measure the arsenic levels in the Vietnam veterans since dioxin TCDD was their focus. Rather than determining whether any of the health issues were linked to Agent Blue and arsenic, the medical doctors apparently*

lumped Agent Blue exposed veterans in with the other veterans exposed to Agent Orange, Agent Pink, Agent Purple and Agent White which contained dioxin TCDD but not arsenic. Agent Orange plus Agent Purple, Agent Green, Agent Pink and Agent White were applied more widely and frequently than Agent Blue by a factor of 10 or 20 based on all Rainbow herbicide shipment records. Therefore, Agent Blue, the arsenic-based herbicide, was less of a medical concern and not everyone was aware that Agent Blue did not contain dioxin TCDD. If the Agent Blue military handlers, spraying Agent Blue on rice paddies, Mangrove forests and military base perimeter fences, were exposed to arsenic they might have been grouped with the Agent Orange dioxin TCDD exposed US military veterans working in Operation Ranch Hand' [4].

5.14. Palmoplantar Keratoderma and Bowen's Disease in a Vietnam Veteran: Could Agent Blue Be Implicated?

Agent Blue was an arsenical herbicide used extensively in the Vietnam War. Arsenic is one of the known causes of acquired palmoplantar keratoderma (PPK). The most common manifestation of arsenic exposure in susceptible individuals is bilateral palmoplantar hyperkeratosis. Cognetta *et al.* [48] reported "A 67-year-old man with no known prior exposure to arsenic in the USA or family history of PPK who developed multiple squamous cell carcinoma in situ (SCCIS) and palmoplantar hyperkeratotic lesions beginning 25 years after service in Vietnam. The SCCIS were located on the trunk and extremities in both sun-exposed and not-sun exposed sites and his palmoplantar lesions were diagnosed concurrently with his SCCIS. He has continued to develop SCCIS since his first visit to their clinic 25 years ago". In summary, Cognetta *et al.* reported "A unique case of palmoplantar hyperkeratotic lesions and numerous SCCIS developing in a Vietnam veteran. 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".

5.15. Agent Blue and Agent Orange Exposures

Known as the "6 rainbow herbicides", based on their identifying color on storage containers, the United States widely deployed the herbicides agent's orange, green, pink, purple, white, and blue during the Vietnam War to deny the enemy cover and destroy crops [8]. Unfortunately, McMurray and Singardiu [49] found "All these herbicides were found to have contained some form of carcinogen. Agent Blue's active ingredient consisted of sodium cacodylate trihydrate ($C_2H_6AsNaO_2$), a compound that is metabolized into the organic form of carcinogen arsenic before eventually converting into its more toxic inorganic form [5]. Agent Orange's defoliating agent is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). All rainbow herbicides except Agent Blue were unintentionally contaminated with carcinogenic di-

oxins. Agent Blue contained the carcinogen cacodylic acid, an organo-arsenic acid. Today, herbicides no longer contain polychlorinated dibenzo-p-dioxins such as TCDD or arsenic due to strict manufacturing restrictions [5] [50]. In the treatment of veteran populations, knowledge of the 6 rainbow herbicides' carcinogenic potential is important."

"Between 1962 and 1971, the United States sprayed more than 45 million liters of Agent Orange on Vietnam and at least 366 kg of TCDD on South Vietnam [8] [51]. However, because Agent Orange was not a known carcinogen during the Vietnam War, records of exposure are poor. Additionally, individuals in Vietnam during this period were not the only ones exposed to this carcinogen as Agent Orange also was sprayed in Thailand and Korea [52]. Even today there are still locations in Vietnam where Agent Orange concentrations exceed internationally acceptable levels. The Da Nang, Bien Hoa, and Phu Cat airports in Vietnam have been found to have dioxin levels exceeding 1000 ppt (parts of dioxin per trillion parts of lipid) toxicity equivalence in the soil."

"Although the Vietnam government is working toward decontaminating these and many other dioxin hotspots, residents in these locations are exposed to higher than internationally acceptable levels of dioxin [53]. Despite receiving less media attention, Vietnam War veterans and Vietnamese soldiers and civilians were exposed to significant amounts of arsenic-based Agent Blue. Arsenic is a compound which has no environmental half-life and is carcinogenic humans if inhaled or ingested. Between 1962 and 1971, the United States distributed 7.8 million liters of Agent Blue containing 1,232,400 kg of arsenic across 300,000 hectares of rice paddies, 100,000 hectares of forest, and perimeters of all military bases during the Vietnam War [5] [54]. According to a review by Saha and colleagues, lower levels of arsenic exposure are associated with acute and chronic diseases, including cancers, of all organ systems [54]. The following case presentation involves a Vietnam War veteran aged 70 years who was exposed to Agent Orange and developed 3 primary cancers, including cutaneous large B-cell non-Hodgkin lymphoma (NHL), high-grade urothelial carcinoma, and anal carcinoma *in situ*."

"Epidemiologically, this is an uncommon occurrence as only 8% of cancer survivors in the United States have been diagnosed with > 1 cancer [54]. With no family history of cancer, the development of multiple malignancies raises concern for a history of toxin exposure. This report of a Vietnam War veteran with multiple conditions found to be associated with Agent Orange exposure provides an opportunity to discuss the role this exposure may have on the development of a comprehensive list of medical conditions as described by the literature. Additionally, the potential contributions of other confounding toxin exposures such as cigarette smoking, excessive alcohol use, and potential Agent Blue exposure on our patients' health will be discussed."

"This case describes a Vietnam War veteran with significant exposure to rainbow herbicides and considerable polysubstance who developed 3 primary cancers and several chronic medical conditions. His exposure to Agents Orange and Blue

likely contributed to his medical problems, but these associations are confounded by his substance use, particularly cigarette smoking. Of all his comorbidities, our patient's NHL is the condition most likely to be associated with his history of Agent Orange exposure. His Agent Blue exposure also increased his risk for developing bladder cancer, cardiovascular disease, and PAD. This case also highlights the importance of evaluating Vietnam War veterans for rainbow herbicide exposure and the complexity associated with attributing diseases to these exposures. All veterans who served in the inland waterways of Vietnam between 1962 and 1975; in the Korean Demilitarized Zone between April 1, 1968 and August 31, 1971; or in Thailand between February 28, 1961 and May 7, 1975 were at risk of rainbow herbicide exposure. These veterans may not only be eligible for disability compensation but also should be screened for associated comorbidities as outlined by current research. We hope that this report will serve as an aid in achieving this mission" [18].

The legacy of the human misery caused by the application of the herbicides including Agent Blue, the arsenic-based herbicide, and Agent Purple and Agent Orange contaminated with unknown amounts of dioxin TCDD sprayed over the jungles, rice fields, military base perimeter fences and hamlets of Vietnam is still haunting us. Why did this happen? Could it have been prevented? Was it necessary United States military strategy? Was it an intentional decision to inflict this blight on the enemy soldiers and the Vietnamese, Cambodian, and Laotian civilians, to poison their land and cause generations of harm? Alternatively, was it an unpreventable accident in the march of military history? What patterns in the US government's thought process could be identified as the cause, which led to the decision to use these herbicides as tactical chemical weapons? If the introduction of herbicide (chemical) weapons had not been made, would the outcome of the Vietnam War and the Secret Wars in Laos and Cambodia have been any different? The objective of this treatise was to outline the role of world events and backgrounds and the role of the leaders, US military, CIA, USDA, US State Department, the US President appointed Ambassadors to Vietnam and Laos, chemical companies, and President Diệm's Republic of Vietnam (RVN) government and military. Their collective advice led to the decision to use herbicides as military and environmental chemical weapons in the Second Indochina War. Were the National interests achieved by US military strategy in the RVN using herbicide weapons worth the long-term environmental and human health consequences in Vietnam, Cambodia, and Laos? Did it impact the outcome of the Second Indochina War?

6. Conclusions—Evaluation of the Impacts and Consequences of Using Agricultural Herbicides as Military Chemical Weapons in Second Indochina War

Today arsenic contaminated rice and groundwater are growing concerns as neither naturally occurring arsenic nor anthropic arsenic have a half-life and cannot

be destroyed. Anthropogenic arsenic has remained in the Mekong Delta environment for the last 60 years and added to persistent As contamination in water supplies, sediments and soils. Water soluble arsenic primarily leaches into the soil root zone and the groundwater or is carried by floodwater into adjacent waterways or volatilized under anaerobic rice paddy conditions as gaseous arsine. Increases in CO₂ and temperature resulted in a synergistic increase of inorganic arsenic in rice grain. The observed increase is likely to be related to changes in soil biogeochemistry that favored reduced arsenic species. The health of 15 million Vietnamese people living in the Mekong Delta is at risk from the combination of manufactured and natural As in drinking water and food supply. The As in the contaminated rice paddy soil, sediment and water are taken up by fish, shrimp or crop vegetation and trace amounts can end up in the food supply (rice grain) or be bioaccumulated by the fish, shrimp and birds which when eaten were bioaccumulated in the Vietnamese people. This research reinforces the urgent need for mitigation of arsenic exposure from drinking water and food grown in flooded rice production systems.

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Conflicts of Interest

The author declares that there is no conflict of interest.

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