

MINISTRY OF NATURAL RESOURCES AND ENVIRONMENT
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OF THE CONSEQUENCES OF TOXIC CHEMICALS USED BY USA
IN THE WAR IN VIETNAM (OFFICE 33)

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TABLE OF CONTENT

1. OVERCOMING CONSEQUENCES OF CHEMICAL WAR - A DIFFICULT AND LONG-TERM TASK.....	2
2. STUDY ON DISEASES RELATED TO CHEMICAL TOXIC/DIOXIN ON VIETNAMESE VETERANS	6
3. STUDY ON VARIATION OF SOME BIOLOGICAL FACTORS SUCH AS GENETICS, IMMUNOLOGY, BIOCHEMISTRY, HEMATOLOGY IN PATIENTS WITH HIGH RISK OF EXPOSURE TO DIOXIN	9
4. THE AGENT ORANGE DIOXIN ISSUE IN VIET NAM: A MANAGEABLE PROBLEM.....	11
5. THE ADSORPTION EFFICIENCY OF PCDDS/PCDFS FROM AQUEOUS SOLUTION ON ACTIVATED CARBONS	16
6. DETOXIFICATION OF DIOXIN IN SOIL BY ACTIVE LANFILL BIOREACTOR.....	19

OVERCOMING CONSEQUENCES OF CHEMICAL WAR- A DIFFICULT AND LONG-TERM TASK

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1. The chemical war conducted by American Army in the South of Vietnam was the biggest chemical war in history of mankind

In 1959, the War Research Branch of American based in Fort District, Maryland had been successful in maneuver of spraying a mixture of chemicals such as butyl ester, 2,4-D, 2,4,5-T for destroying crops. This achievement had been rapidly recorded by Ministry of Defense and a program for spraying these herbicides and defoliants in battle fields in the South of Vietnam was initiated.

After being inaugurated, President E. Kennedy had held a meeting with National Security Council in January 15th 1961 and declared "...in order to prevent communists from invasion of South Vietnam, I declare to use herbicides and other innovative technologies for control land and sea roads along border lines of Vietnam". Immediately, equipments and a huge amount of toxic substances were transported into the South of Vietnam. On August 10th, 1961 the first air mission was carried out for chemicals spraying along national road 14, in the north of Kontum town. Therefore, the day August 10th is chosen to be "The day of Agent Orange's Victims".

Approximately 10 years passed with three generations of American presidents, US Army had sprayed about 80 million liters of toxic chemicals over the South of Vietnam including 20 different toxic substances in which Agent Orange, a mixture of 2,4-D and 2,4,5-T, was a significant composition.

Herbicide 2,4,5-T is an organic compound contained chlorine. This substance does not only exist in Agent Orange but also appearing in other toxic chemicals (such as purple, blue agent...). Due to the manufacture technology of 2,4,5-T, a by-product called dioxin (2,3,7,8- Tetra Chloro Dibenzo Dioxin-TCDD) is created. With an extremely tiny amount about part per billion, dioxin could cause cancer and reproductive failures in test animals. American scholars have presented different data of estimated dioxin quantity sprayed over the South of Vietnam. (170 kg as A.H. Westing, 366 kg as J. Stellman). Scientists from Vietnam- Russia Tropical Center reported much higher estimation (about 1000 kg).

However, the term toxic chemicals or chemical war have been ignored in front of public and Courts. They only accept that they used herbicides and defoliants as they used to do in other places. The term "toxic chemicals" and "chemical war" are considered to be "sensitive" because chemical companies who produced these substances involve in. This is explained by two reasons:

- First, a huge amount of herbicides and defoliants were used with exceeded concentration permitted for weed clearance and defoliation purposes (20 to 30 folds over permitted concentration) and then these herbicides and defoliants has seriously destroyed ecosystem and affected human health. A basic principle of toxicology is reminded: any chemical can be toxic and any chemical can be non-toxic, the matter of fact is dose. Being over permitted dose, the non-toxic could be toxic substance even very toxic.

- Second, herbicides and defoliant do contain dioxin, the most toxic substance in toxic substances ever found by human. Chemical companies who produced herbicides and defoliant containing dioxin must be responsible for this toxic product. Scientists around the world, including American scientists have affirmed that dioxin causes very various diseases especially cancer, reproductive failure and congenial malformation. Until now, the typical signs that differentiate between effect of dioxin and effect of other factors available in environment have not been found yet. Taking the point, some people are trying to disparage scientific evidences about bad effects of toxic chemicals containing dioxin in Vietnam. This way of access is non-scientific and unscrupulous.

Factually, the USA has been in contradiction itself with opponents of America chemical company's attorneys and Brooklyn district court in last March 2005. The event that American chemical companies under US Court's negotiation had to pay \$180 millions compensation to get claim waiver from US veterans poisoned with toxic chemicals, had indirectly recognized the bad effect of toxic chemicals on these veterans. Previously, in February, 1967, being aware of harms of toxic chemicals containing dioxin, about 5000 American scientists including 17 Nobel receivers and 129 academicians of US National Academy of Science had required President Lyndon Johnson to immediately cease this deleterious chemical war.

2. Consequences of chemical war still prolonged through decades

According to insufficient statistic, 25,585 villages and hamlets in South Vietnam had been sprayed with toxic chemicals. During chemical war, there are 14 millions inhabitants, about 2 millions officers and soldiers from the North lived and served in the in the South of Vietnam. Scientists from Columbia University (USA) had estimated minimum 2.1 millions and maximum 4.8 millions Vietnamese people have been suffered from toxic chemicals.

Total 3,104,000 ha (17% area natural forest) of forest area including 2,954,000 ha of domestic forest (95% and rest 5% is marsh forest) was sprayed with toxic chemicals. Amount of wood destroyed due to toxic chemicals was about 82,830,000 m³ (approximately \$billion).

In sprayed areas, though dioxin concentration has been significantly decreased but the consequences are very obvious. Soil and land are degraded, ecosystems destroyed, and many kinds of animals and plants deteriorated. More seriously are the weak recovery ability of ecosystem and possibility of disappearance of watershed protective forest.

In some areas used to be army depots and US army's air fields, concentration of dioxin is reported high and very high (even up to hundred thousands ppt while permitted dioxin concentration in agricultural soil is 1000 ppt in USA). The expense is estimated over hundreds billions VND for detoxification conducted in some air fields which currently regarded as "hot spots", by mechanic land fill combined with biochemical method.

Due to the sophistication of disease mechanism and under monitoring and diagnostic condition in Vietnam, we have been unable to determine sufficient quantity of toxic chemical's victims. Many patients died due to unclearly diagnosed diseases. Many people are in incubation period, which means just some alternation of metabolic conversion and gene without any expression.

The most concerning currently are congenial malfunction children due to toxic chemicals. There are 169,193 of first generation (F1) and 5,505 people of second generation (F2) in an investigation on 174,198 toxic chemical's victims. Is there possible to find any congenial deformity in third generation (F3) in next 20 years? It is probable to occur because some scientists have recently found gene mutation in victims of toxic chemicals. There maybe no disease expressed but it could be appeared in their second or third generation. Congenial deformity due to toxic chemicals is various and multi form

in a certain body. Therefore, these victims are usually in serious diseases which are physical, mental burdensome themselves and society.

Loss due to chemical war is extremely huge in many aspects. We have not had any sufficient research work to thoroughly and precisely determine economic, social, environment and human damage caused by this unique war in mankind history.

3. Overcoming consequences of chemical war- A difficult, long-term and sophisticated task

Early in 70's decade, Professor Ton That Tung and some Vietnamese scientists has considered to the damage of chemical war, especially the effects on liver cancer, reproductive failure and congenial deformity. Initial researches on the dioxin residue in human body and environment of Vietnam were conducted and published by American researchers, Baughmann and Messelson in 1973.

In October, 1980, Vietnamese Government established the National Committee for Investigation on Consequences of toxic chemicals used in Vietnam War (The Committee 10-80). The Committee has collected domestic and international information, conducted many research projects, and determined the scale and consequences of chemical war in Vietnam.

In order to basically shift from investigation to overcoming consequences of toxic chemicals, Vietnam Prime Minister had dissolved the Committee 10-80 in March 1st, 1999 and promulgated Decision no. 33/1/1999 to found The National Steering Committee for the Overcoming Consequences of Toxic Chemicals used in Vietnam War (National Steering Committee 33). Head of National Steering Committee 33 was Minister of Ministry of Science, Technology and Environment. Being participated in the Committee 33 were leaders of national ministries such as Defense, Foreign Affair, Health, Justice, Labor- Invalids and Social Affairs, Government Office... After the Ministry of Natural Resources and Environment (the MONRE) established, Prime Minister has issued the Decision no. 173/2002 in December 12th, 2003 to assign Minister of the MONRE as the Head of National Steering Committee 33. Assisting to National Steering Committee 33 is the Office of National Steering Committee 33 headquartered in the MONRE.

National Steering Committee 33 is in charge of steering; instructing and coordinating with related ministries and departments for conducting organization of tasks on overcoming the consequences of chemical war. Series of activities had and have been deployed on fields such as research on detoxification, environment recovery, disease identification, proposal on policy to victims of toxic chemicals...

Up to now, over 209,000 toxic chemical's victims have been benefited from subsidy regulation according to Decision no. 120/2004/Prime Minister Decision for people served in resistance as well as their ill- offspring due to toxic chemicals; 3,400 families with two or more than two victims will be benefited from Decision no. 16/2004/ Prime Minister Decision. In parallel to governmental supports, other politic- social, charity-humanity organizations have many useful activities in victim relief especially the Agent Orange Fund, Vietnam Association for Victims of Agent Orange-Dioxin. Physical and mental life of hundred thousands of victims have been supported and ameliorated as well as being health care serviced.

However, the burden of consequences of chemical war is still ahead. Heavily contaminated areas due to toxic chemicals must be isolated, localized and detoxified. Solutions for ecosystem and environment recovery need to be synchronized with warranty of health and life of residents in sprayed areas. Being concentrated on instruction and organization of function rehabilitation for victims in community and community-based, especially for about 200 thousand congenial deformity children; on one hand, being well organized and operated remediation centers and basis for toxic chemical's victims are necessary and exigent. Furthermore, gradual establishment of consulting stations for reproductive health in order

to restrict congenial deformity children being born. These works require mobilizing huge efforts from people as well as materials in a long period. The expense for the overcoming consequences of toxic chemicals used by USA during Vietnam War is estimated to reach up to ten thousands of billions VND.

STUDY ON DISEASES RELATED TO TOXIC CHEMICAL /DIOXIN ON VIETNAMESE VETERANS

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Introduction

During the war in Vietnam, the use of herbicides/dioxin by American army had caused negative effects to human health and environment. Many literatures have showed that dioxin might cause congenital deformities, cancer, blood diseases and so on. The American Science Institute has certified certain diseases related to dioxin, 4 out of which are surely evidence certified concern to dioxin (sarcoma, non-hodgkin lymphoma, hodgkin lymphoma and chloracne) and 7 of which are considered to have evidence concern to dioxin (lung cancer, larynx cancer, cancer of postate gland, myeloma, spina bifida, porphyris cutanea tarda, peripheral nervous disorder and diabetes). Apart from this, recent researches have indicated that herbicides/dioxin also has relations to some diseases of respiratory system, immune system, cutaneous, genetic,...Therefore, the list of diseases relate to toxic chemical/dioxin should be further added.

The aim of the study is as following:

- Identify ratio and mechanism of diseases related to toxic chemical/dioxin (American Science Institute) on Vietnamese exposed veterans.
- Propose list of diseases related to toxic chemical/dioxin.

Materials and Methods

1. Subjects: 47,893 veterans aged from 47 to 65, living at 8 provinces/cities in Vietnam (Hoabinh, Thainguyen, Quangtri, Binhdinh, Daclac, Binhduong and Cantho), participated in war in the South of Vietnam from 1962 to 1975 have been as volunteers in our study. The study was conducted from 1994 to 2004.
2. Methods:
 - Cross sectional study
 - Individual interviews with a set of questionnaire
 - Clinical and preclinical examinations
 - Data processing with EPI-INFOR 6.04 and SPSS 12.0

Results and Discussion

Investigation of 47,893 veterans in eight provinces has detected 9 out of 11 diseases that have been identified by American Science to be related to toxic chemical/dioxin exposures. This diseases includes diabetes (7,64%), lung cancer (1,3%), Hodgkin Lymphoma (0,20%), non Hodgkin Lymphoma (0,49%), Sarcoma (0,19%), peripheral nervous disorder (0,09%) and cancer of postate gland (0,57%).

Additionally, rare incidents of diseases such chloracne, 3 cases of malignant multiple myeloma have been found.

The prevalence of diseases in exposed group is significantly higher than non-exposed group ($p < 0,01$). No differences were found between directly exposed group and indirectly exposed group.

The two diseases which are proposed to the list of diseases related to chemical/dioxin are liver cancer and mental disorder.

Table 1. Ratio of diseases related to toxic chemical/dioxin in exposed and non-exposed veterans

<i>List of related diseases</i>	<i>Case of exposed (n=28.817)</i>		<i>Non exposed (n=19.076)</i>		<i>p</i>
	<i>Quantity</i>	<i>Ratio (%)</i>	<i>Quantity</i>	<i>Ratio (%)</i>	
<i>Sarcoma</i>	54	0,19	5	0,03	< 0,01
<i>Hodgkin Lymphoma</i>	58	0,20	3	0,02	< 0,01
<i>Non - Hodgkin Lymphoma</i>	142	0,49	29	0,15	< 0,01
<i>Chloracne</i>	2	0,01	-	-	-
<i>Multiple Myeloma</i>	3	0,01	1	0,005	> 0,05
<i>Porphyria Cutanea Tarda</i>	-	-	-	-	-
<i>Spina Bifida</i>	-	-	-	-	-
<i>Peripheral nervous disorder</i>	25	0,09	4	0,02	< 0,01
<i>Respiratory cancer</i>	201	0,70	67	0,35	< 0,01
<i>Lung cancer</i>	376	1,30	44	0,23	< 0,01
<i>Postate gland cancer</i>	164	0,57	37	0,19	< 0,01
<i>Diabetes</i>	2201	7,64	799	4,20	< 0,01
<i>Liver cancer</i>	267	0,93	35	0,18	< 0,01
<i>Mental disorder</i>	242	0,84	57	0,30	< 0,01

Table 2. Ratio of diseases related to toxic chemical/dioxin in exposed veterans

<i>List of related diseases</i>	<i>Direct</i> (n=7,434)		<i>Indirect</i> (n= 21,383)		<i>p</i>
	<i>Quantity</i>	<i>Ratio(%)</i>	<i>Quantity</i>	<i>Ratio (%)</i>	
<i>Sarcoma</i>	14	0,19	40	0,18	p > 0,05
<i>Hodgkin Lyphoma</i>	13	0,18	45	0,21	p > 0,05
<i>Non -Hodgkin Lymphoma</i>	33	0,44	109	0,51	p > 0,05
<i>Chloracne</i>	1	0,01	1	0,004	-
<i>Multiple Myeloma</i>	1	0,01	2	0,009	-
<i>Peripheral nervous disorder</i>	8	0,11	17	0,08	p > 0,05
<i>Respiratory cancer</i>	64	0,86	137	0,64	p < 0,05
<i>Lung cancer</i>	108	1,45	268	1,25	p > 0,05
<i>Postate gland cancer</i>	45	0,61	119	0,56	p > 0,05
<i>Diabetes</i>	579	7,79	1622	7,58	p > 0,05
<i>Liver cancer</i>	69	0,93	198	0,92	p > 0,05
<i>Mental disorder</i>	89	1,19	153	0,71	p < 0,01

References

1. Ta Van Binh, Hoang Kim Uoc, Nguyen Minh Hung (2002) *Typical researches of National projects implemented at endocrine hospital 1969 – 2003*. Medical Press. 339 –352
2. Bui Dai, Le Cao Dai (1993) *Longterm effects of herbicide to human and nature*. Proceeding of 2nd International Conference in Hanoi. 188-205 pp.
3. Nguyen Van Nguyen, Le Bach Quang (1998), *Biomedical researches of Z1 project*. Military Academy of Medicine, Ministry of Defense.
4. Yamamotos, MiuraH (1993), *Longterm effects of herbicide to human and nature*. Proceeding of 2nd International Conference in Hanoi, 206-233 pp.
5. Anna Sweeney (1994) *Reproductive Epidemiology of Dioxin, Dioxin and Health*, New York, pp 549 – 586
6. Allan Smith (2002) *Finding from epidemiological studies of populations exposed to dioxin*. University of California – Berkerley, U.S.

STUDY ON VARIATION OF SOME BIOLOGICAL FACTORS SUCH AS GENETICS, IMMUNOLOGY, BIOCHEMISTRY, HEMATOLOGY IN PATIENTS WITH HIGH RISK OF EXPOSURE TO DIOXIN

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Introduction

During the war in Vietnam, over 80 million liters of Agent Orange containing 600 kg of 2,3,7,8 TCDD was sprayed over the South of Vietnam. Many literatures have been shown exposure to dioxin, especially 2,3,7,8 TCDD, to cause numerous adverse effects in human and environment. Dioxin is the super-toxic one, the mechanism of dioxin action on human health is very complicate because it depends on respond by each individual. Study on dioxin seems to be very complicated and many problems still have not been made clearly.

Target: Analysis of some basic changes on immunological genetics, biochemistry, hematology in patients with high risk of dioxin exposure.

Objectives: Screening and selecting patients through epidemiological researches, classification based on medical records and researches conducted in Bienhoa (Dongnai), Namdong (Thua Thien Hue), Thanhkhe (Danang), Ngoquyen and Anhai (Haiphong). There were totally 1,584 objectives included 31 children in Danang and 27 children in Haiphong aging from 8-15 years, the remains were or 16 years and above.

Materials and Methods

Determine criteria on genetics, genes, immunology, biochemistry, and hematology according to standardized procedures with high accuracy and confidence.

Results and Discussions

Obtained data could be summarized as followings:

1. Analyzed gene of 5 generations which are prehistoric expose to dioxin and whose dioxin in blood have been found in exposed subjects during war, changes in Gene P53, gene Cyp aA1 and gen AhR, particularly changes in amino acids related to specific cancers have been seen.
2. Ability of respond to making good antibody in group with high risk of exposure to dioxin (HRE) is significantly lower than the control group and group with lower risk of expose to dioxin.

3. There is difference in Enzyme activity for preventing oxidation between groups.
4. Frequency of disorder in lymphocytes form is found in HRE
5. For the investigation in the relationship between exposure to dioxin and changes in immune system, bio-chemical, hematology in HRE, we found no corresponding changes between dioxin concentration in mixed blood samples and individual blood samples with changes in genetic, immune system, bio-chemical and hematology on these individuals.

THE AGENT ORANGE DIOXIN ISSUE IN VIET NAM:

A MANAGEABLE PROBLEM

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Introduction

Since the early 1990's, Hatfield Consultants Ltd. (Hatfield) and the 10-80 Division, Ministry of Health (10-80) investigated the impacts of Agent Orange dioxin on the environment and human populations in several provinces of Viet Nam.^{1,2} As early as 1970, a number of Vietnamese and international researchers have contributed to our understanding of Agent Orange impacts in Viet Nam.³⁻⁹

In 1962, the US military initiated use of herbicides in Viet Nam for general defoliation and crop destruction through a program codenamed Operation Ranch Hand.¹⁰ Application of herbicides was primarily through cargo aircraft, and ground mechanisms; helicopters were also used in certain areas of the country. More than 80 million litres of herbicide were applied over approximately 10-12% of southern Viet Nam.^{11,12} This figure was recently revised to over 80 million litres.¹³ Herbicide applications ceased in 1971.

Military installations throughout southern Viet Nam (e.g., Bien Hoa, Da Nang, Nha Trang, and Phu Cat) served as bulk storage and supply facilities for Agent Orange.¹⁴⁻¹⁶ Herbicides are known to have been spilled at these sites. In 1970, for example, a 7,500 US gallon spill of Agent Orange occurred on the Bien Hoa base; between January and March 1970, three other spills of lesser volume occurred at Bien Hoa.¹⁶

As a consequence of aerial applications and handling of Agent Orange at US military installations, two primary sources of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) contamination in Viet Nam have been identified: spray missions by C-123 aircraft, and contamination at former US military installations where herbicides were stored and deployed.

10-80 Division and Hatfield theorize that the pattern of TCDD contamination recorded in Aluoi District (Thua Thien Hue Province) serves as a model for contamination throughout southern Viet Nam.¹ Direct human exposure during the war, and subsequent ongoing contamination through food chain transfer of TCDD, are expected to be highest in areas adjacent to former US military installations where elevated concentrations of TCDD may still be residing in soils, particularly as a result of herbicide spills, washing out herbicide tanks, and high volume ground applications.

Soils in regions aerially sprayed did not have the same loading of Agent Orange, and therefore TCDD, as military bases.

The principal concern today, regarding dioxin in the environment of Viet Nam, is that people living near some former US military installations continue to be exposed to dioxin. People born after the war

are also at risk of contamination. Through the use of dioxin-laden herbicides, the Viet Nam War has left a legacy of environmental contamination that continues to this day; however, with simple mitigation measures this problem can be addressed and the probability of exposure significantly reduced.

Materials and Methods

Between 1996 and 2004, over 250 samples of soil, aquatic sediment, foods, whole human blood and human breast milk were collected and analyzed from a number of locations in Viet Nam, including areas aerially sprayed with herbicides during the American-Viet Nam War. Sampling sites included remote districts in Viet Nam (e.g., Aluoi District), and downstream of former US military installations (e.g., Bien Hoa, Da Nang, Phu Cat and others).^{1,2}

Field supplies for sample collection, storage and shipment originated in Canada. A stainless steel soil corer was used to collect soil samples. A landmine detector was used to ascertain that sampling locations were free of unexploded ordnance. Each tested soil sample was a composite of 10 subsamples. Subsamples were collected within a 30 m radius of the primary site. All samples were placed in pre-cleaned glass jars with Teflon lids and frozen. Following collection of each core, equipment was rinsed with acetone and hexane to prevent cross contamination. A grab sample constituted a sediment sample in aquatic systems.

All samples from Viet Nam were forwarded in a frozen state to AXYS Analytical Services, British Columbia, Canada. For the earlier studies, total toxic equivalents for each sample analyzed were calculated in the laboratory using the “international” dioxin toxic equivalents.¹⁷ More recent studies applied the revised WHO TEF units.¹⁸

High resolution GC/MS was performed on samples for detection of dioxins and furans. For non-detectable (ND) and NDR (chromatographic peak was detected, but did not meet quantification criteria) designations, ½ the detection limit of the sample was used in the Total-TEQ calculation.

Results and Discussions

After over a decade of research, the 10-80 Division (Viet Nam) and Hatfield Consultants Ltd. (Canada) have concluded that residual levels of wartime Agent Orange dioxin (TCDD) in soils of southern Viet Nam are generally at or below background levels found in industrialized nations of North America. However, 10-80/Hatfield research has shown that significant hot spots of TCDD remain in select areas of southern Viet Nam.

Studies in the vicinity of the former Aso US military base in Aluoi District demonstrate that TCDD contamination has spread from soils to humans via the food chain.² Soils from heavily contaminated areas remain a reservoir/source of TCDD, and warrant the term ‘primary hot spot’. The fact that food, human blood and breast milk in the Aso Commune were found to have elevated dioxin concentrations, relative to aerially sprayed regions of the valley, creates concern related to nutritional and public health issues. Results from the Aluoi District study emphasize that

former US military bases should be the primary sites on which to concentrate further studies and direct remediation measures, thereby helping reduce potential TCDD exposure for local Vietnamese.

Schechter et al. sampled near the former US Bien Hoa base, and measured high levels of TCDD in soils (e.g., 1,164,699 pg/g dry weight) and in human blood (e.g., 271.1 pg/g lipid).⁸ These levels may be related to Agent Orange spill(s) at Bien Hoa in 1970.¹⁵ Additional studies near Bien Hoa found elevated levels of TCDD in human blood.⁹ Schechter et al. reported 2 pg/g TCDD in pooled blood from

a Ha Noi control group.⁸ These data support the theory that contamination hot spots are located near former US military installations.

The former US airbases at Da Nang, Phu Cat and Bien Hoa may be categorized as significant dioxin 'hot spots' on the basis of the TCDD concentrations recorded in areas 'downstream' of suspected Ranch Hand sites. Suspected 'primary sites' were not sampled directly in this study due to restricted access by Vietnamese authorities. However, the elevated TCDD values (Table 1), suggest significant involvement of Agent Orange herbicide in the overall toxicity of these soil/sediment samples, given that TCDD was the characteristic dioxin congener in Agent Orange.

Table 1. Range of Total TEQ values (pg/g dry weight) and maximum TCDD levels (pg/g dry weight) of soils and sediments near former US military installations in southern Viet Nam (N=number of samples analyzed), collected in March 2005.

	N	TOTAL	MAXIMUM
		TEQ (pg/g)	TCDD (pg/g)
<i>Da Nang</i>	21	<1 – 269	227 (soil)
<i>Pleiku</i>	13	<1 – 64.2	53.4 (soil)
<i>Phu Cat</i>	18	<1 – 201	194 (sediment)
<i>Nha Trang</i>	5	13.5 – 133	48.7 (soil)
<i>Bien Hoa</i>	24	1.19 – 833	797 (sediment)
<i>Can Tho</i>	5	2.04 – 70.4	68.7 (soil)
<i>Tan Son Nhut</i>	5	2.06 – 341	157 (sediment)

A review of international guidelines for soils and sediments suggests that if the concentrations of TCDD recorded at, for example, Da Nang, Phu Cat, and Bien Hoa were found in Europe and North America, remedial action and further investigations would be prescribed. However, in Viet Nam, given economic conditions, there is currently minimal capacity and funding for remediation dioxin contamination. The issue of remediating dioxincontaminated lands/waterbodies has not been addressed in Viet Nam to any large degree. Remediation always raises complex questions, and all commonly accepted remediation methods are expensive. Therefore, international cooperation and international financial assistance are required.

Military bases listed as dioxin hot spots during our investigations were categorized on the basis of dioxin levels recorded at sampling sites distributed near each installation. As noted above, 'primary' sites of contamination were not identified/sampled; therefore, even if a base was categorized as not significantly contaminated, the base may still be 'hot' if the exact location of Ranch Hand activities were identified and sampled. Exclusion from the 'hot' category does not necessarily mean a former US military base in Viet Nam is not contaminated, but is indicative that based on limited sampling; no significant contamination was identified (i.e., significant, in this study, is defined as ≥ 190 pg/g TCDD.).

For bases identified as hot spots (Bien Hoa, Da Nang, and Phu Cat), simple methods could be applied within each area to better understand the level and extent of dioxin contamination and protect local populations. Mitigation measures are required to eliminate potential exposure of populations living

immediately near or downstream of contaminated bases. Protection of human populations living near hot spots should be the first priority. Given that sites are so specific and presumed limited to sluices or streams running from the 'primary hot spot,' communitybased programs should be implemented in those specific areas. This can begin immediately with familyfamily awareness raising by local health officials in hot spot areas to help people reduce their exposure to dioxins.

Following more than twelve years of research, the authors conclude that there does remain a dioxin problem in Viet Nam in key 'hot spots.' However, we suspect levels of dioxin found in soils of most areas of Viet Nam are below international guidelines and that the majority of land in Viet Nam is not contaminated by dioxin. The authors feel that the dioxin problem in Viet Nam is manageable. Current levels of dioxin contamination in soils in most of southern Viet Nam do not generally pose a human health concern. This is good news for residents in areas sprayed during the war and for the economic development of Viet Nam. However, some former US bases and specific runoff areas in their vicinity do remain a serious problem requiring international cooperation and international financial assistance.

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References

1. Dwernychuk LW, Cau HD, Hatfield CT, Boivin TG, Hung TM, Dung PT, Thai ND. *Chemosphere* 2002; 47:117.
2. Dwernychuk LW. *Chemosphere* 2005; 60:998.
3. Cau HD, Dai LC, Hanh LH, Thuy LB, Quynh HY, Hein NM, Thom LH, Schecter A, Constable J. *Herbicides in War - The Long-term Effects on Man and Nature. 2nd International Symposium* 1994:25.
4. Dai LC, Minh DQ, Quynh HT, Thom LH, Thuy LB. *Herbicides in War – The Long-term Effects on Man and Nature. 2nd International Symposium* 1994:5.
5. Dai LC, Hanh LH, Giay T, Hue ND, Thuy LB. *Herbicides in War – The Long-term Effects on Man and Nature. 2nd International Symposium* 1994:40.
6. Dai LC, Thuy LB, Minh DQ, Quynh HT, Thom LH. *Organohalogen Compounds* 1995; 26:161.
7. Schecter A(Ed). *Dioxins and health* 1994:710.
8. Schecter A, Dai LC, Papke O, Prange J, Constable JD, Matsuda M, Thao VD, Piskac AL. *J Occup Environ Med* 2001; 43: 435.
9. Schecter A, Pavuk M, Constable J, Dai LC, Papke O. *J Occup Environ Med* 2002;44:218.
10. IOM (Institute of Medicine). *Veterans and Agent Orange - Update 2000* 2001:604.
11. Westing AH. *Herbicides In War, The Long-term Ecological and Human Consequence.* 1984:3.

12. IOM (Institute of Medicine). *Veterans and Agent Orange - Health effects of herbicides used in Viet Nam*. National Academy Press, Washington, D.C. 1994:812.
13. Stellman JM, Stellman SD, Christian R, Weber T, Tomassallo C. *Nature* 2003; 422:681.
14. US Army documents (declassified). *The US Army Center of Military History, Fort Lesley J. McNair DC, 20319-5048, USA 1969*.
15. US Army documents (declassified). *The US Army Center of Military History, Fort Lesley J. McNair DC, 20319-5048, USA 1970*.
16. Cecil PF. *Herbicide Warfare: the RANCH HAND Project in Viet Nam* 1986:290.
17. NATO (North Atlantic Treaty Organization). *Committee on the Challenges of Modern Society* 1988; 176:26.
18. Van den Berg M, Birnbaum L, Bosveld BTC, Brunström B, Cook P, Feeley M, Giesy JP, Hanberg A, Hasegawa R, Kennedy SW, Kubiak T, Larsen JC, van Leeuwen FXR, Liem AKD, Nolt C, Peterson RE, Poellinger L, Safe S, Schrenk D, Tillitt D, Tysklind M, Younes M, Waern F, Zacharewski T. *Environmental Health Perspective* 1998; 106(12):775.

THE ADSORPTION EFFICIENCY OF PCDDs/PCDFs FROM AQUEOUS SOLUTION ON ACTIVATED CARBONS

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1. Introduction

Activated carbon was widely used in processes of odour filter, colour wiping, removal of inorganic and organic contaminants from drinking water, air, applied in wastewater and waste gases treatment, in chemical, pharmaceutical, beverage and food industries. There were many reports on adsorption of organic compounds having benzene rings, aromatics, phenolic compounds, polychlorophenol [1-6], dyes [7,8], tannic [9], anthrazine, methylene blue [10], trinitrotoluene [11] from aqueous solutions on various activated carbons. Nevertheless researches are still rarely conducted on adsorption capacity of PCDDs/PCDFs from aqueous solution on activated carbons with the aim of applying to water treatment in dioxin contaminated site, for example, in "hot-spot". In Vietnam, there were reports on researches on adsorption efficiency of PCDDs/PCDFs on activated carbons produced from certain domestic raw materials as wood-based carbon, rice husk carbon, coconut shell carbon [12]. This report presents research results on possibility of applying certain domestically produced activated carbons with the aim of water treatment in heavy PCDDs/PCDFs contaminated sites.

2. Materials and methods

2.1. Preparation of activated carbons

Selected domestically produced activated carbons are coconut shell activated carbon T2, wood-based activated carbon T3, coconut shell activated carbon-anthracite T4, bituminous coal-based activated carbons T5, T6 and oxidized coconut shell activated carbons T7, T8. Russian activated carbon BAU-A is used in comparison research. Activated carbons are ground into small granules, those of size < 0,25mm, are chosen, dried at 110°C during 3 hours before the experiment.

2.2. Preparation of solution PCDDs/PCDFs

In order to limit the pollution caused by the spreading of PCDDs/PCDFs following water flows from sites where the soil is heavily contaminated by PCDDs/PCDFs, we used mixed PCDDs/PCDFs contaminated soil samples at high concentration that is previously known. Mixed soil sample was not added any labeled standard, soxhlet extracted with toluene and cleaned up following US. EPA method 8280A [13]. The final extract was concentrated and dissolved in 36ml of acetone. PCDDs/PCDFs concentration in this solution was determined by HRGC/LRMS Hewlett Packard HP6890/5972A.

2.3. Experimental method

Weighting exactly 50mg of each activated carbon and putting it into each of nine vessels containing 50ml of study solution (2ml of PCDDs/PCDFs solution in acetone and 48ml bidistilled water). The control sample is denoted by DC1. The duration of experiment is 3 days (72h), for each day the study solution is shaken during 8h at the speed of 200 rounds/minute.

2.4. Sample preparation and analysis

Filter to eliminate carbon and obtaining the solution, add labeled standards ^{13}C -PCDDs/PCDFs, extraction by shaking 3 times, each time with 15ml dichloromethane, in 20 minutes, 300 rounds/minute. The extract is cleaned up following [13], PCDDs/PCDFs containing fraction is concentrated to analyze by HRGC/LRMS HP6890/5972A.

3. Results and discussion

Concentration of each 2,3,7,8-substituted isomers, I-TEQ of PCDDs/PCDFs were found in study solutions of eight activated carbons and control sample DC1, the adsorption efficiency of each activated carbon in comparison with control sample were presented in the Table 2 and illustrated in the Figure 1.

Table 2. Concentration of 2,3,7,8-substituted isomers, I-TEQ and adsorption efficiency of investigated samples.

Symbol	DC1	T1	T2	T3	T4	T5	T6	T7	T8
2,3,7,8-substituted	control sample	BAU-A	Type D	Type H2	$\phi 4$	1NBC	2NBC	1H	3H
TCDD	412,69	30,74	269,82	2,67	2,60	9,31	11,73	175,50	245,71
OCDD	109,56	19,02	55,34	1,48	1,82	5,61	5,32	45,66	58,21
I-TEQ	414,18	30,82	270,49	2,68	2,60	9,34	11,75	176,01	246,46
Adsorption efficiency	-	92,6%	34,7%	99,4%	99,4%	97,7%	97,2%	57,5%	40,5%

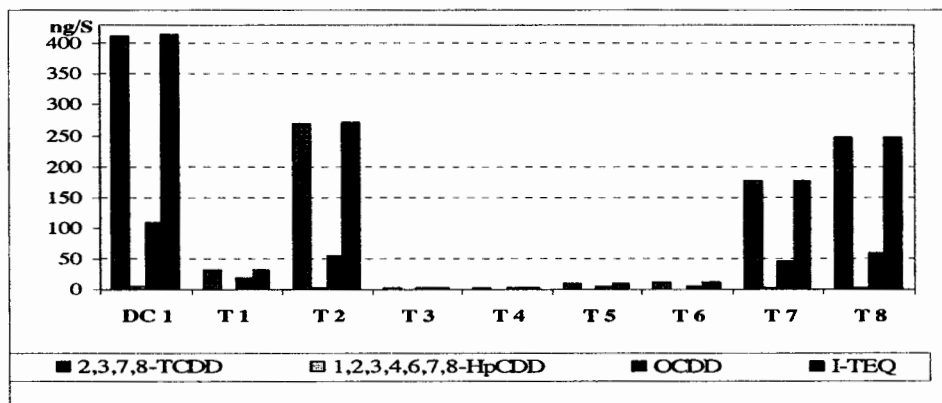


Fig. 1. Concentration 2,3,7,8-TCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, I-TEQ found in investigated samples.

4. Conclusion

Wood-based activated carbon Type H2, coconut shell carbon-anthracite (30-70%) $\phi 4$, bituminous coal-based activated carbon 1NBC, 2NBC of Vietnam are activated carbons that may be very well used as water treatment material in heavy PCDDs/PCDFs polluted sites. The adsorption efficiency on these four activated carbons is between 97.2 and 99.4% in comparison with control sample without activated

carbon and is higher than that of Russian activated carbon BAU-A. Research results shown the possibility of using available, cheap, domestically produced activated carbons as PCDDs/PCDFs polluted water treatment material.

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5. References

- [1]. Anna Derylo-Marczewska, Jacek Goworek, Andrzej Swiatkowski. Carbon 42 (2004) 301-306.
- [2]. F. Haghseresht, S. Nouri, G.Q. Max Lu. Carbon 41 (2003) 881-892.
- [3]. X. Liu, N.G. Pinto. Carbon 35 (1997) 1387-1397.
- [4]. K. Laszlo, A. Bota, L.G. Nagy. Carbon 35 (1997) 593-598.
- [5]. Krisztina Laszlo, Andras Szucs. Carbon 39 (2001) 1945-1953.
- [6]. Carlos Moreno-Castilla. Carbon 42 (2004) 83-94.
- [7]. Ru-Ling Tseng, Feng-Chin Wu, Ruey-Shin Juang. Carbon 41 (2003) 487-495.
- [8]. Manuel Fernando R. P., Samanta F. S., Jose J.M. Orfao, Jose L. Figueiredo. Carbon 41 (2003) 811-821.
- [9]. Chien-To Hsieh, Hsinheng Teng. Carbon 38 (2000) 863-869.
- [10]. Costas Pelekani, Vernon L. Snoeyink. Carbon 38 (2000) 1423-1436.
- [11]. Nguyen Hung Phong, et al. The 1st scientific symposium, Military STTC Center (2004), 396-400.
- [12]. Trinh Khac Sau, et al. The 4th National Chemistry Conference (2003), Vol. I, 131-134.
- [13]. Method 8280A. US. Environmental Protection Agency (1996).

DETOXIFICATION OF DIOXIN IN SOIL BY ACTIVE LANDFILL BIOREACTOR

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Introduction

During the invasion war in Vietnam, US army had sprayed about 80 million liters of herbicides including 45 million liters of Agent Orange over provinces in South of Vietnam. As scientific estimation about 170-600kg dioxin, the most toxic ever known, contained in 45 million liters of Agent Orange [1,2,3].

War had gone over 30 years but its consequences are still serious. Herbicides, especially Agent Orange/dioxin is existing in some areas with dangerous levels, so-called "hot spots". These hot spots used to be US air fields, army installations. There some common features of these areas: including herbicide storages, loading bases for mission air crafts, craft washing bases after missions and lands storage used herbicides casks. There exist lands contaminated with Agent Orange/dioxin from 1 to 5 ha; dioxin contents in soil from some thousands to some hundred thousands ppt. Particularly, once dioxin has permeated 1.5 m deep in soil with approximately concentration of 1.000 ppt.

Therefore, the decontamination and treatment of these contaminated areas have been raised imperatively. Vietnam scientists have conducted some solutions such as photochemical, chemical, dumping, biological methods... [4,5,6,7,8,9,10]. This paper is to present some initial results of research on active landfill bioreactor for dioxin decontamination in soil in hot spots in Vietnam.

Methods and Materials

- Isolation method: employing HDPE material with 1.5-2 m thick to isolate toxic compounds in contaminated soil away from environment and filtered material such as environmat for adsorption toxic compounds. Bentonite in Vietnam is the main component in manufacturing filtration material environmat with following parameters:

+ *Mineral content of montnonrilonit 35- 40% in form of sodium*

* *Outer surface area: 14.3 m²/g*

* *Inner surface area: 28.0 m²/g*

* *Specific surface area: 42.3 m²/g*

* *Average diameter of hole: 51.5 A⁰*

+ *Ion exchange capacity: 60- 80 mEg/100g*

+ Swelling capacity: 600- 800%

+ Dioxin adsorption capacity: >99.75%

- Methods for biological decomposition of dioxin: base on the supply of products containing nutrients, substrates, minerals, stuffs, additives in order to promote the composition process of endemic microorganisms. The application of slow adsorption product (18-24 months) is to maintain supplying nutrients in a long time.

- Experimental scope: conduct active dumping compartments with scale of 10m² and 100 m³ of dioxin contaminated soil in hot spots. Monitoring, evaluating the biological variation and sampling, analyzing dioxin concentration in soil in dumping compartment with time.

- Analysis method: dioxin is determined by CALUX and low resolution GC/MS (GC 6890/MSD 5972A Hewlett Packard) following EPA methods 1613, 8280 and 8290. Determination of 2,4-D and 2,4,5-T was carried out on HPLC 1090 and EPA method 8321A.

Results and Discussions

Table 1. Parameters of Enviromat material

Parameter	Unit	Measure method	Measure equipment	Enviromat Vietnam	Reference material
Tensile strength	kN/m	DIN 53857/2	AIM 2661 India	7.6/5,5	8.1/6
Tensile elongating	%	DIN 53857/2	AIM 2661 India	9/8.5	8/8
Peel strength	N/10 cm	ATMD 413	AIM 2611/5 India	18.6	19.8
Permeability coefficient	x 10 ⁻¹¹ m/s	DIN 18130	AIM 2676 India	5	4.5

- Similar characteristics have been seen in comparison between environmat from Vietnam and reference material (environmat from Italia). Most important parameters are permeability coefficient and peel strength.

- No agent orange and dioxin permeation out of isolation compartment had been observed after 2 years of monitoring. This proved that HPDE with 1.5-2 m thick and environmat material could completely restrain toxic compounds to surroundings which filtration materials showed excellent adsorption of organochlorine and dioxin compounds. Due to large swelling capacity (600-800%), bentonite had blocked pores on the dumping walls. Beside the high adsorption capacity (>99.75%); bentonite in filtration material could be employed to be carrier for microorganism development which facilitate dioxin decomposition and other harmful substances.

- Results on variation of microorganisms: number of heterotrophic microorganisms increases from 10⁴ MPN/g to 10⁵, 10⁶ and 10⁷ MPN/g in the control landfill bioreactor without application of bioremediation. In the active landfill bioreactor, the number of heterotrophic microorganisms increased to 10⁹ MPN/g in dry soil.

- Results on dioxin decomposition in active landfill bioreactor: the total toxic equivalence in soil decreased 50-70%. Beside dioxin decomposition, other toxic chemicals such as 2,4-D, 2,4,5-T, chlorophenols were decomposed strongly by microorganisms; undetectable in soil after 2 years.

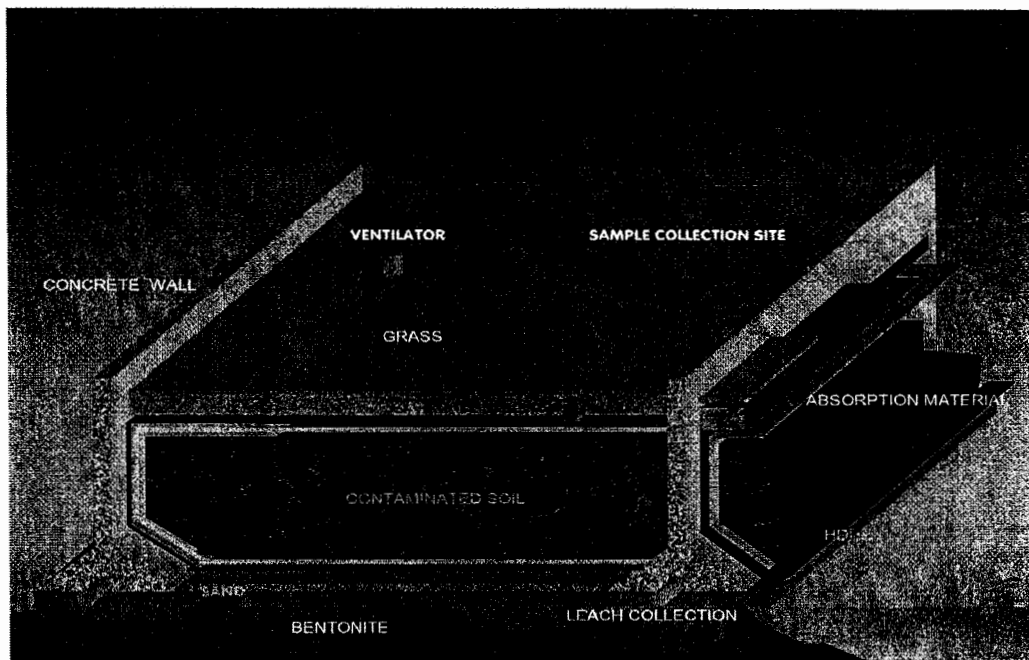


Figure 1. The model of active landfill bioreactor

Dumping compartment composed by isolating materials and filtration materials has created a bioreactor which facilitated the biological decomposition of dioxin. Some parameters could be controlled actively for dioxin decomposition process such as humidity, temperature, pH, nutrients, substrates...

The results of experiment and trial had shown that active landfill bioreactor (isolation combined with adsorption and dioxin composition by microorganism) is a feasible method for dioxin decontamination in hot spots in Vietnam due to its reasonable cost and simple implementation.

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References

- 1- Westing A.H. (1984) *Herbicides in war: The long-term ecological and human consequences*, Sipri, 1984
- 2- Stellman, J.M.; Stellman, S.D.; Christian, R.; Weber, T. & Tomasallo, C. (2003) *Nature* **422**, 681-7.

- 3- Dwernychuk, L.W. (2005) Dioxin hot spots in Vietnam, *Chemosphere* 60 (2005), 998 - 999
- 4- Nguyen Van Minh (2002), Vietnam - United States scientific conference on human health and environmental effects of dioxin, March 3-6, 2002, Hanoi, Vietnam
- 5- Nguyen Van Minh (2003), U.S. - Vietnam scientific workshop on dioxin screening, remediation methodologies and site characterization, Nov. 3-5, 2003, Hanoi, Vietnam
- 6- Dang Thi Cam Ha (2002), Vietnam - United States scientific conference on human health and environmental effects of dioxin, March 3-6, 2002, Hanoi, Vietnam
- 7- Dang T.C.H., Nguyen B.H., Nguyen T.D., Tran N.H., Nguyen V.M., Do Q.H., Pham H.L., Dang V.M. (2001) in: *Dioxin 2001*, vol.54, 259 - 261
- 8- Dang Thi Cam Ha, Nguyen Ba Huu, Pham Thi Quynh Van, Nguyen Thi De, Nguyen Quoc Viet, Nguyen Duong Nha, La Thanh Phuong, Tran Nhu Hoa, Mai Anh Tuan, Pham Huu Ly, Nguyen Van Minh, Le Van Hong, Do Quang Huy, Dang Vu Minh (2002) in *Dioxin 2002*, vol.56, 433-436
- 9- Dang Thi Cam Ha, Mai Anh Tuan, Nguyen Quoc Viet, Trinh Khac Sau, Olaf Papke, Nguyen Thi Sanh (2004), *Organohalogen Compound* vol.66, 3695- 3701
- 10- Ha Thi Cam Dang, Huu Ba Nguyen, Tuan Anh Mai, Truong Xuan Nghiem, Minh Ngoc Nguyen, Minh Vu Dang (2005), *Organohalogen Compound* vol.67, 1961-1966