

## DIOXIN CONTAMINATION IN THE SOIL - SOUTH OF VIETNAM

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### Introduction

Dioxin is a common name given to a group of persistent and very toxic chemicals, also known as dioxins and furans. These chemicals include 75 chlorinated dibenzo-p-dioxins and 135 chlorinated dibenzo furans. The most toxic of these compounds is 2,3,7,8-tetrachlorodibenzo-p-dioxin and the isomers with chlorines substituted in the 2,3,7,8 positions<sup>1,8</sup>. Dioxin in the environment is measured and reported in terms of 2,3,7,8-TCDD equivalents, which are the actual concentrations of each dioxin or furan congener multiplied by its relative toxicity. The amount of dioxin in a sample is the sum of the concentration of 2,3,7,8-TCDD and 2,3,7,8-TCDD-equivalents.

The problem of dioxin contamination in South of Vietnam has been reported in many documents as a typical case because there are many areas affected by the toxic chemicals from US-Vietnam War<sup>9,11,12,13</sup>. Although the War ended in 1975, to date no large-scale epidemiological study has been performed to assess the effects of the herbicides used on the Vietnamese people and ecosystem. Nowadays, the study on this problem is relatively difficult because many times passed (over 28 years) and every thing has been changed (not in origin form): a grand part of dioxin had been degraded or transferred into biological food web. In addition, the document collection and sampling planning are not easy work due to the complete formalities or military secrets.

In this paper we present our primary result on dioxin contamination of three selected areas, including: Ma Da Forest, Cam Lo District – Quang Tri Province and Da Nang Airport. These are also the common names that reported in the documents related to the dioxin contamination problem.

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soil is an important sampling medium for the investigation of the D/Fs mobility into soil is controlled by the equilibrium among several environmental compartments (air, water, mineral and organic carbon) and adsorbs strongly to soils with typical organic carbon concentrations. D/Fs are found in the top layers of soil in the first few centimeters. Hence we conducted this study.

The study was conducted in April and May 2003. The sampling sites belong to three areas

near Ho Chi Minh City, belong to the Dong Nai and Binh Phuoc provinces. The sampling sites are located in an Old Military Helicopter Airport – Rang Rang Airport. The vegetation development is still poor. The samples were taken from a left (RRT) and right (RRP), along road 322.

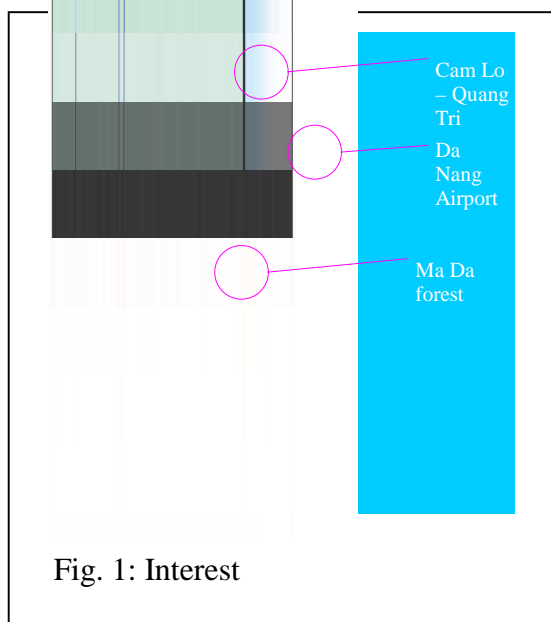


Fig. 1: Interest

Quang Tri lies just 30 kilometres north of the McNamara Line and 60 kilometres to the west of the Ho Chi Minh Trail, the most heavily bombed area in the war. The McNamara Line, named after the former US defence minister, refers to a borderline that the American armed forces set up at the 17th Parallel separating North and South Vietnam. Cam Lo is a district in central Quang Tri province – The most herbicide sprayed area in the Middle of Vietnam. The sampling was done in three sub-districts: Cam Chinh, Cam Nghia and Minh Huong. Samples were taken from the sites contaminated by defoliant follow a local veteran: in the garden of the families having deformity born children, in the old military air port and near old military base.

Da Nang Airport was used as a military base during the war. There are many people living nearby whose water supply is compromised

by hazardous contamination. Vietnamese scientists would suggest collaboration on projects to assess and remediate an area near Da Nang airport as a model for how such technologies could work. The samples were taken near the plane runway, where are the vegetable fields now.

### Sampling Technique

As we know that an acre (0.4 ha) of soil to a 6-inch depth weighs about 1,000 ton, yet only few grams of soil is used for the test in the laboratory. Therefore, it is very important that the soil samples are characteristic of the entire site. Normally, sampling locations should be clearly accessible to the fall-out to be studied and should be open and not excessively covered by vegetation. The area of interest should have been left undisturbed during at least the time period of interest.

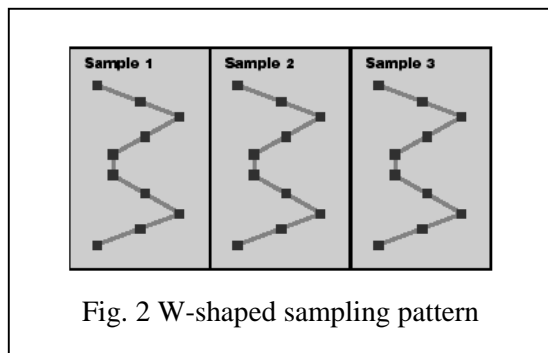


Fig. 2 W-shaped sampling pattern

We have used grid sampling - a systematic approach that divides the interest field into squares of 30x30 m (usually referred to as "grid cells"). Soil samples are collected from within each of these "cells." The location of each "grid cell" is usually geo-referenced using global positioning system technology. The topsoil samples were taken by using soil hand-borer. The samples for analysis are the composite samples consisting of at least 10 cores collected from the same cell as described in the Fig. 2.

The composite sample was mixed thoroughly in a tray by a spoon (both stainless steel made), then put in to alum box during transport to laboratory.

### Sample preparation and analysis

Samples were crushed by mean a ceramic mortar than sifted through a 1x1mm stainless steel sieve. Samples were stored in a brown glass flask at 4 °C until their analysis.

The water and organic contents were determined before analysis. The analytical procedure is similar to the one proposed by EMPA<sup>6,7,10,14</sup>: The PCDD/Fs analysis was performed using isotope dilution technique<sup>15,16</sup>. 25-40 g of soil (exactly weighted) is spiked with <sup>13</sup>C<sub>12</sub>-2,3,7,8-PCDD internal standard (CIL standard EDF-4053). Extraction was carried out in a Soxhlet apparatus using 200 mL toluene for 24 h. Sample clean-up achieved by several steps are described as follow:

(1) Liquid-liquid partition with:

- 3 times x 20mL 0.5M H<sub>2</sub>SO<sub>4</sub>
- 2 times x 20mL 5% NaCl
- 2 times x 20mL 20% KOH
- 2 times x 20mL 5% NaCl

The organic phase recovered was filtered through Na<sub>2</sub>SO<sub>4</sub> and concentrated about 1 mL

(2) Silica mix column (from bottom to top): 1g of activated silica, 2g of basic silica (CsOH), 1g of activated silica, 4g of acidic silica, 1g of activated silica) covered with 2g of Na<sub>2</sub>SO<sub>4</sub> (anhydrous), wet filled with n-hexane and prewashed with 50mL n-hexane. The sample was eluted with 60mL n-hexane

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(3) Basic alumina column (3g of basic alumina Super I) covered with 2g of  $\text{Na}_2\text{SO}_4$  (anhydrous), wet filled with n-hexane and prewashed with 50mL n-hexane. The sample eluted with:

- i) 20mL n-hexane
- ii) 20mL n-hexane/DCM (98:2)
- iii) 20mL n-hexane/DCM (1:1)
- iv) 20mL DCM

The fraction (iii) and (iv) were concentrated with nitrogen flux to 200  $\mu\text{L}$ , transferred into glass insert and evaporated just to dryness under a stream of nitrogen at ambient temperature. The residue was immediately redissolved in 40  $\mu\text{L}$  iso-octane containing internal recovery standard (CIL standard ED-2521).

PCDD/Fs identification and quantification were accomplished with a HRGC/LRMS system (Shimadzu GCMS-QP2010 and Varian GC-3800/MS-1200). The column used was DB-5 and DB-Dioxin (60m x 0.25mm x 0.25  $\mu\text{m}$ ). The temperature program was as follows: 80°C(1.0 min) to 200°C(2min)(40°C/min), then to 310°C (26.5 min). The injector temperature was 250°C. The interface was heated to 250°C. The column flow was constant at 1.0mL/min. The PCDD/Fs were identified by mass spectrometry in the EI-SIM mode by tracing  $\text{M}^+$ ,  $(\text{M}+2)^+$  and  $(\text{M}+4)^+$  ions - the most intensive ions of the isotope cluster. Detail including the validation and quality assurance of the method is described elsewhere<sup>10,14</sup>. The recovery calculated for the  $^{13}\text{C}_{12}$ -PCDD/Fs internal standard varied from 48.5-119.6%. Quality control Quality control has been achieved by analysing the certified soil - SRM EDF-2513 (CIL).

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## Results and Discussion

The 2,3,7,8-PCDD/Fs congener concentrations are presented in the Table 1 below:

**Table 1: 2,3,7,8-PCDD/Fs concentration (ng/g dry weight)**

Site	TCDF	TCDD	PnCDF	PnCDD	HxCDF	HxCDD	HpCDF	HpCDD	OCDD	OCDF
CL1	nd	nd	0.13	nd	0.11	0.14	0.87	0.98	0.20	nd
CL2	nd	nd	nd	nd	nd	Nd	0.69	3.10	21.11	0.77
CL3	nd	nd	nd	nd	nd	Nd	0.03	nd	0.49	nd
CL4	nd	nd	nd	nd	nd	Nd	nd	0.05	0.37	nd
CL5	nd	nd	nd	nd	nd	Nd	nd	0.18	1.35	nd
CL6	nd	nd	nd	nd	nd	0.08	0.26	0.24	0.12	nd
CL7	nd	nd	0.08	nd	nd	0.07	0.19	0.10	nd	nd
CL8	nd	nd	nd	nd	0.08	0.09	nd	nd	0.41	nd
CL9	nd	nd	0.08	nd	0.08	0.14	nd	nd	0.34	nd
CL10	nd	nd	nd	nd	nd	Nd	nd	nd	4.88	nd
DN1	nd	nd	0.08	nd	nd	0.08	0.20	0.17	0.13	nd
DN2	nd	nd	0.08	nd	0.05	0.10	0.20	0.27	30.94	0.06
RRT1	nd	nd	0.07	nd	nd	0.03	0.13	0.13	0.28	nd
RRT2	nd	nd	0.10	nd	0.06	0.14	0.33	0.91	14.04	nd
RRT3	0.18	nd	nd	nd	nd	Nd	nd	0.15	nd	nd
RRP1	0.20	nd	nd	nd	nd	Nd	nd	nd	nd	nd
RRP2	2.60	nd	nd	nd	nd	Nd	0.49	nd	nd	nd
RRP3	nd	nd	nd	nd	nd	Nd	nd	0.33	nd	nd
RTN1	nd	nd	nd	nd	nd	Nd	nd	nd	nd	nd
RTN2	0.20	nd	nd	nd	nd	Nd	nd	0.20	nd	nd

Note:

- Values presented in the Table above are the sum of 2,3,7,8-isomers
- nd-non detectable
- CL: Cam Lo District
- DN: Da Nang Airport
- RR: RangRang Airport – Ma Da Forest
- RTN : Natural Forest – Ma Da Forest

### Cam Lo:

- The result shows that however very long time has been passed, but there is still the residue of PCDD/Fs.

- The presence of light PCDD/Fs (tetra to penta) was very rarely (especially we did not detect the TCDD/Fs and PnCDD in all samples). 1,2,3,7,8-PeCDF has been found at 3/10 sites (garden soil) with concentration 0.08-0.13 ng/g.

- The heavy PCDD/Fs (hexa to octa) were presented in almost samples, especially OCDD presented at 9/10 sites with concentration at least of 21.11 ng/g. The origin of OCDD is still not clear because base on the documents it not come from defoliants. 1,2,3,7,8,9-HxCDD presented at 5/10 sites with concentration 0.07-0.14 ng/g. 2,3,4,6,7,8-HxCDF presented at 3/10 sites with concentration 0.08-0.11 ng/g. 1,2,3,4,6,7,8-HpCDF presented at 5/10 sites with concentration 0.03-

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0.87 ng/g. 1,2,3,4,7,8,9-HpCDF presented at 2/10 sites with concentration 0.04-0.51 ng/g. 1,2,3,4,6,7,8-HpCDD presented at 6/10 sites with concentration 0.05-3.10 ng/g. OCDF presented at 1/10 sites with concentration 0.77 ng/g.

### Da Nang and Rang Rang Airport

- Similar to the Cam Lo sample, we did not find the TCDD/Fs in the Da Nang soil samples. But we have detected other 2,3,7,8 PCDD/Fs congeners with concentration varied from 0.06 (OCDF) to 30.94 (OCDD).

- In the Rang Rang soil we have found the 2,3,7,8-TCDF in almost analyzed samples with concentration 0.18-2.6 ng/g. On the contrary, OCDD presented only at two analyzed samples.

Base on the Toxic Equivalency Factors (TEFs) for 2,3,7,8-PCDD/Fs<sup>8</sup>, we calculated the I-TEQ for each site. The calculated result shown in the Table 2:

**Table 2: TEQ value in comparison with the Canadian Guideline**

Site	I-TEQ (ng/g)	TEQ/TEQ –limit	Site	TEQ (ng/g)	TEQ/TEQ –limit
CL1	0.049	12.3	DN1	0.015	3.8
CL2	0.060	14.9	DN2	0.055	13.7
CL3	0.001	0.2	RRT1	0.010	2.5
CL4	0.001	0.2	RRT2	0.052	13.0
CL5	0.003	0.8	RRT3	0.033	8.25
CL6	0.013	3.4	RRP1	0.02	5
CL7	0.013	3.4	RRP2	0.2649	66.225
CL8	0.018	4.4	RRP3	0.0033	0.825
CL9	0.026	6.6	RTN1	0	0
CL10	0.005	1.2	RTN2	0.022	5.5

*TEQ-limit : the values of the Canadian Soil Quality Guideline for the Protection of Environmental and Human Health*<sup>17</sup>: *TEQ-limit = 0.004 ng/g*

Base on the data on the Table 2, we can see that 15/20 sites having the TEQ bigger than TEQ-limit in the Canadian Guidelines (**at least more than 60 times**). That means these sites are really contaminated by Dioxin and need the more monitoring activities. The result again confirmed that there is really a big problem of Dioxin Contamination in South – Vietnam and needed an integrated solution as well as collaboration in research for it.

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