DIOXIN MONITORING IN SOUTHERN VIETNAM: SITUATION AND CHALLENGES

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1. Introduction

During Vietnam War (Ranch Hand Operation from 1961 to 1971): 11 million gallons (72 million litters) of defoliants (estimated quantity of 2,3,7,8-TCDD about 170 kilograms) have been sprayed[1]. Its consequences on our environment and human health is still present and not yet completely solved until today. Five chemicals used in Ranch Hand Operation are A.O, A.W, A.B, CS, and Malathion. Beside that, there are the additional sources of PCDD/Fs from socio-economic innovating process: many new export processing zones, industrial zones and factories are emitting a big unexpected amount of toxic wastes possibly containing dioxin (chemical, pulp-and-paper, metallurgical and others; burning of industrial and municipal waste, leaded gasoline, diesel fuel, etc). Futhermore, the agricultural boom has been accompanied by a huge increase in the use of pesticides leading to the contaminants remain in the soil.

The studies on dioxin residue in Southern Vietnam have many difficulties: the lack of related documents ("fog of war" effect) ; difficulties for linking of local present contamination status with human health long-term effects; the precise location and the uncertainties in the duration of exposures; the lack of an overall regulatory framework of a national plan to deal with dioxin Contamination as well as national standards for PCDD/Fs residue assessment; the lack of good quality data on monitoring sites, etc.

2. Materials and methods

There are two places are selected for dioxin source from the war: one is a "hot spot" of dioxin contamination – Bien Hoa Airbase and one is a highland province – Dak Nong that was sprayed a lot of defoliants based on the dioxin spraying map of Office 33.

Bien Hoa Airbase was the primary operational center for the Ranch Hand activities (98,000 barrels of Agent Orange, 45,000 barrels of Agent White, and 16,000 barrels of Agent Blue were used). During the Pacer Ivy campaign (1970): 11,000 barrels of Agent Orange was transited on the airport[2]. For this place we have taken 50 samples, including 28 samples soil, 10 samples sediment, 8 samples water, 4 samples biological matrix.

Based on the dioxin spraying map of Office 33 of Daknong Province we have selected 21 monitoring sites belonging to 6 districts: Krong No, Dak Song, Dak Mil, Tuy Duc, Dak G'long and Dak R'Lap. The monitoring matrices are soil (105 samples topsoil and 50-80 cm depth layer), surface sediment (12 samples) , and water (27 samples).

For dioxin source from industries we have chosen the hazadous waste incinerators (HWIs) from Nha Be, Hoc Mon (Hochiminh City), Ba Ria-Vung Tau, and Can Tho.

Sampling technique:

For soil samples: used a grid sampling - a systematic approach that divides the sampling site into squares of 30x30 m (usually referred to as "grid cells"). Soil is collected from within each of these "cells." The location of each "grid cell" was geo-referenced using global positioning system technology (GPS). The topsoil was taken by using soil hand-borer. The composite samples for analysis consisted of at least 10 cores collected from the same cell. The composite soil was mixed thoroughly in a tray with a spoon (both stainless steel made).

For sediment samples: were sampled with an Eckman Grab. Water samples were taken and stored in brown glass flask with volume 2.5 L.

For Biological samples: were taken by help of local people.

* All soil, sediment and biological samples were stored in aluminum box at 4°C during transport to laboratory.

For stack gas: According to US EPA Method 23 Determination of Polychlorinated dibenzo-p-Dioxins and Polychlorinated dibenzofurans from stationary sources, stack gas samples were collected with Keika Ventures sampler. The sampling box consisted of glass fiber filter, resin XAD-2, Supelco and impingers. The $^{13}C_{12}$ – labelled with concentrating 50 pg/µl in nonane as sampling standard was spiked to XAD-2 before sampling of stack gas.

Analytical method:

The analytical procedure is the certified methods proposed by US EPA [3, 4] modified to adapted with available conditions in the laboratory: The PCDD/Fs analysis was performed using an isotope dilution technique.

Samples were spiked with a mixture of $^{13}C_{12}$ –labelled PCDD/F_s internal standards, then extracted with toluene for 24h. The clean- up procedure for PCDD/F_s analysis was performed with two columns, namely multi-layer silicagel column and basic alumina column.

All standard solutions (C1 – C5) and labelled internal standard including 17 isotope 2,3,7,8-PCDD/Fs were purchased from Wellington (Canada). The solvents and absorbents were purchased from Merck (Germany).

The purified extract was analyzed using a high resolution mass spectrometer (Micromass, UK). The capillary GC column BPX-5 60m×0.25mm×0,25µm was used with the temperature program: 140 °C (4') → 220°C (8^0C/1') → 260°C (1.4^0C/1') → 310 °C (3^0C/1', 5'). The ion source was operated at 250^{0}C, the electron energy was 35eV, trap current was 650µA and interface temperature was 260°C. All data were obtained in the selected ion monitoring (SIM) mode. Toxic equivalents values for PCDD/F_s were caculated by using international-toxicity equivalency factor (I-TEF).

3. Results and discussions

3.1 Bien Hoa Airport

* *For sediment samples*

We detected TCDD in almost of sediment samples (7/10 samples). Almost of monitoring sites hasTEQ varied from 0.18 to 0.28 ng/g dry weight (8 – 12 times higher than PEL value - 0.0215 ng/g dry weight[5]). One site - a stream connecting with wastewater/runoff from the airport has very high TEQ (up more 50 times than PEL value). This value is except the limit that needed an urgent decontamination solution.

* *For soil samples*: We detected TCDD in a half of total of soil samples (16/28 samples). Max detected TCDD concentration was 1.285 ng/g (321 times higher than PEL value - 0.004 ng/g dry weight[5]). This value could make a very high risk of exposure for whom in contact with it. TEQ of topsoil varied from 0.002 to 1.33 ng/g dry weight. TEQ of deeper layer (50 – 80 cm) was much lower, varied from 0.0001 to 0.267 ng/g dry weight.

* *For water samples*: TEQ of ground water samples was very low (below US EPA TEQ-Limit : 0.03 ng/L[6]). We have detected TCDD in three samples (the streams connecting with wastewater/runoff from the airport and in the lake of entrance N^{0}2) with concentration varied from 0.0359 ng/L to 0.1348 ng/L. The TEQ of these samples was higher US EPA TEQ-Limit from 2.71 to 8.04 times.

3.2. Dak Nong Province

We have detected TCDD in almost of sediment samples (8/10 samples) with low concentration, varied from 0.004 to 0.011 ng/g dry weight. The presence of TCDD means that these sites were contaminated by toxic chemicals such Argent Orange, but due to the digestion by effects of time, weather, runoff, etc. it's residue is now at safe level for ecosystem and human health. Octa- groups of PCDD/Fs was always presented with relative high concentration, varied from 0.48 to 9.75 ng/g dry weight. The result showed that the main PCDD/Fs source now is coming from burning activities and used pesticides.

There are two sites should to pay attention: bridge 20 – Dak Song and District Tuy Duc that having TEQ always higher than PEL value. These areas are also noted as red lines (heavy sprayed) in spraying map of Office 33. These areas need a comprehensive study to assess the possible risks for ecosystem and local human health.

TEQ of deeper layer of soil (50 – 80cm) was lower than PEL value in almost of samples. For topsoil we have detected TCDD, but concentration was not very high. TEQ of topsoil was higher than PEL value, but mainly contaminated by higher chlorinated PCDD/Fs with lower toxicity. We not detected TCDD in all water samples, but instead that we detected PCDF in grand past of samples (8/10 samples). The TEQ varied from 0.01 – 0.30 ng/L (3 to 10 times higher than US EPA TEQ-Limit). Presence of PCDFs means that main contamination source is coming from burning activities.

3.3. TEQ contribution of PCDD/Fs in stack gas

Gas emission from HWIs in Southern Vietnam are investigated between 2011 and 2012 and the analyzed data are presented in below table:

Table 1: The PCDD/Fs concentration in exhaust of investigated HWIs

Name	Locations	Type of oven (level)	Type of waste	Capacity (tons/day)	Collecting time	PCDD/Fs (pgTEQ/m^3)	Note
S01	Nha Be	1	Greasy Clout, oil waste	0.18	2/2011	269.259	HWI
S02	Hoc Mon	2	Medical waste	20	4/2011	0.7193	-//-
S03	-//-	2	Medical waste	20	8/2011	0.5190	-//-
S04	-//-	2	Medical waste	20	9/2011	0.1139	-//-
S05	-//-	2	Medical waste	20	-//-	19.7812	-//-
S06	-//-	2	Medical waste	20	-//-	16.3039	-//-
S07	-//-	2	Medical waste	20	10/2011	5.2764	-//-
S08	BR-VT	2	Glove, Clout, Pesticides, oil waste, industrial waste	5	2/2012	4269.3000	-//-
S09	Hoc Mon	2	Medical waste	20	5/2012	24.6172	-//-
S10	Can Tho	2	Medical waste	0.5	6/2012	8.0705	MWI

The obtained result showed that PCDD/Fs concentration was largely varied from 0.114 to 4269.2979 pgTEQ/Nm^3. Compared with Vietnamese regulation (QCVN30:2010/BTNMT[7]: 600 pgTEQ/Nm^3), almost of them (9 HWIs) have PCDD/Fs concentration below the standard value, and 8 HWIs have PCDD/Fs concentration below the standard value set up by European Union Directive[8] (100 pgTEQ/Nm^3). There was only one HWI has the PCDD/Fs concentration 7 times higher than Vietnamese standard and 42 times higher than European Union standard, while other is double higher than European Union standard.

2,3,4,7,8-PeCDF was the highest in the pattern of PCDFs, while 2,3,7,8-TCDD was the highest in the pattern of PCDDs for S01 and S08 incinerators. The ratios of PCDFs to PCDDs for all gas samples were more than 1, implied the de novo synthesis is always dominant[9].

Table 2: Comparison between our result with other studies

Country	**Type of samples**	**i-TEQ**
China	Stack gas from hospital waste incinerators	0.08-31.6 (ngTEQ/Nm^3)[10]
Taiwan	Stack gas fromMuticipal waste incinerators	0.063- 0.127 (pgTEQ/Nm^3)[11]
Our result		
	Stack gas from Hazardous waste incinerators	0.114 to 4269.2979 (pgTEQ/Nm^3)
	Stack gas of of an incinerator for medical waste	8.0705 (pgTEQ/Nm^3)

The results from this table show that gas emission from HWI_ Việt Nam belongs to our researches is higher than the results of Taiwan, but is lower than that of China. That means this type of waste is a considerable source of PCDD/Fs and needed a strict regulation to manage it.

4. References

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