

CHARACTERIZATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS IN SOIL AND BIOTA AT THE BIEN HOA AGENT ORANGE HOTSPOT IN VIETNAM

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Introduction

Bien Hoa is a city of the Dong Nai province and located about 35 km east of Ho Chi Minh City. The area of Bien Hoa city is about 155 kilometer square with a population of approximately 1 million people in 2012. During the Vietnam War, Bien Hoa airbase was one of the most important military facilities of the United States (US) army in Vietnam. From 1961 to 1972, under the Operation Ranch Hand carried out by the US army, about 74 millions litres of defoliants were sprayed to destroy forest canopies and crops belonging to the north liberty army¹. The defoliants contained the chlorinated phenoxyherbicides 2,4,5-T- and 2,4-D as active ingredients in different concentrations in the formulations labeled as Agent Orange, Agent Purple, Agent White, Agent Blue with Agent Orange nearly contributing half of total defoliant volume². More importantly, most of the defoliants contained the extremely toxic byproducts dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs), especially the most toxic isomer 2,3,7,8-Tetrachlorinated dibenzo-p-dioxins (2,3,7,8-TCDD).

The objective of this study is to carry out a comprehensive assessment of the area including possibly affected fish to understand the present distribution and transport of the AO/Dioxins contamination in Bien Hoa airbase and its vicinities. The results will help to identify the extension and scale of the contamination and thus provide useful information for subsequent environmental remediation steps.

Materials and methods

In this study, 106 samples (surface and sub-surface soil down to a depth of 2.4 m) were collected in the Pacer Ivy contaminated area and vicinities based on topographic surveys. The whole area was divided into many lots (50 x 50 m) and each surface soil samples consisted of five sub-samples composites. Beside, sediment cores samples were collected by core sampler and divided into several segments of 5 cm which were then considered sub-samples. Tilapias (*Oreochromis niloticus*) were collected in ponds and lakes and also muscles were taken for analysis of PCDD/Fs. A duck sample (muscle tissue) was also collected in the pond near Pacer Ivy site. The samples were transferred into pre-cleaned glass jars and transported to the laboratory.

All samples were analyzed for seventeen 2,3,7,8-substitute PCDD/Fs and TEF values given by WHO, 2005 was used for calculate TEQ concentration. Soil and sediment samples were expressed on dry weight basis while biological samples were fresh weight basis. The analytical procedure followed the US EPA Method 1613 for determination of PCDD/Fs by isotopic dilution with gas chromatography and high resolution mass spectrometer HRGC/HRMS³ (Micromass Autospec Ultima system (Waters, UK) with Agilent 7890A gas chromatograph (Agilent, USA)). The method was according to US EPA Method 1613 with minor modifications considering available recent advanced techniques. All modifications were adequately validated prior to regular usage.

Results and discussion:

PCDD/Fs contamination in the Pacer Ivy site

Analytical results from 59 surface soil samples showed very high TEQ concentrations of PCDD/Fs at the Pacer Ivy site. The TEQ levels range from 7.6 – 962,000 pg TEQ/g with the mean concentration of 18,260 pg TEQ/g dry wt. Furthermore, the 2,3,7,8-TCDD TEQ contribution for these samples were extremely high with 98% on average (data not showed). The most elevated concentrations were found at the southwest corner of the site which is close to a taxiway of airplanes. The mean and the highest TEQ concentrations in this site are hundred

folds higher compared to those found in the A Luoi former airbase in the North Central Coast region of Vietnam and somewhat comparable to the concentrations in Da Nang AO/Dioxin hot spots⁴.

PCDD/Fshomologue profiles

The PCDD/F homologue profiles on mass basis are given in the Fig. 1 for sediment samples collected from six different sites in and around the airbase. Even though, TCDD is the most abundant congener contributing to TEQ in sediment, the profile on mass basis showed higher levels of OCDD compare to TCDD. It is also known that from tetrachlorinated to octachlorinated CDDs, the water solubility decreases by about 4 orders of magnitude and thus favouring accumulation of OCDD in the sediment⁵⁻⁷. Czuczwa and Hites (1986)⁸ studied PCDD/Fs profiles in the atmosphere and in lake sediment and reported the significant enhancement of OCDD in sediment compared to all other congeners.

In the present study, we found that sediment samples collected in ponds/lakes close to the original contaminated sites (e.g Pacer Ivy and Z1 sites) contained much higher proportion of TCDD (Fig. 1A-C) than those in ponds/lakes located far away from the contaminated sites (Fig. 1D-F). On the other hand, the proportion of OCDD showed a reverse trend (Fig. 1). These phenomena could be due to the fact that erosions in the contaminated sites by weathering processes (rains, floods, winds, etc) had brought the contaminated soil/sediment to the farther ponds/lakes where the contaminated soil/sediment mixed with the existing sediment and therefore decreased both the concentration and the proportion of TCDD. This observation might be relevant for the assessment of monitoring data in the search of unknown AO/Dioxin contamination sites.

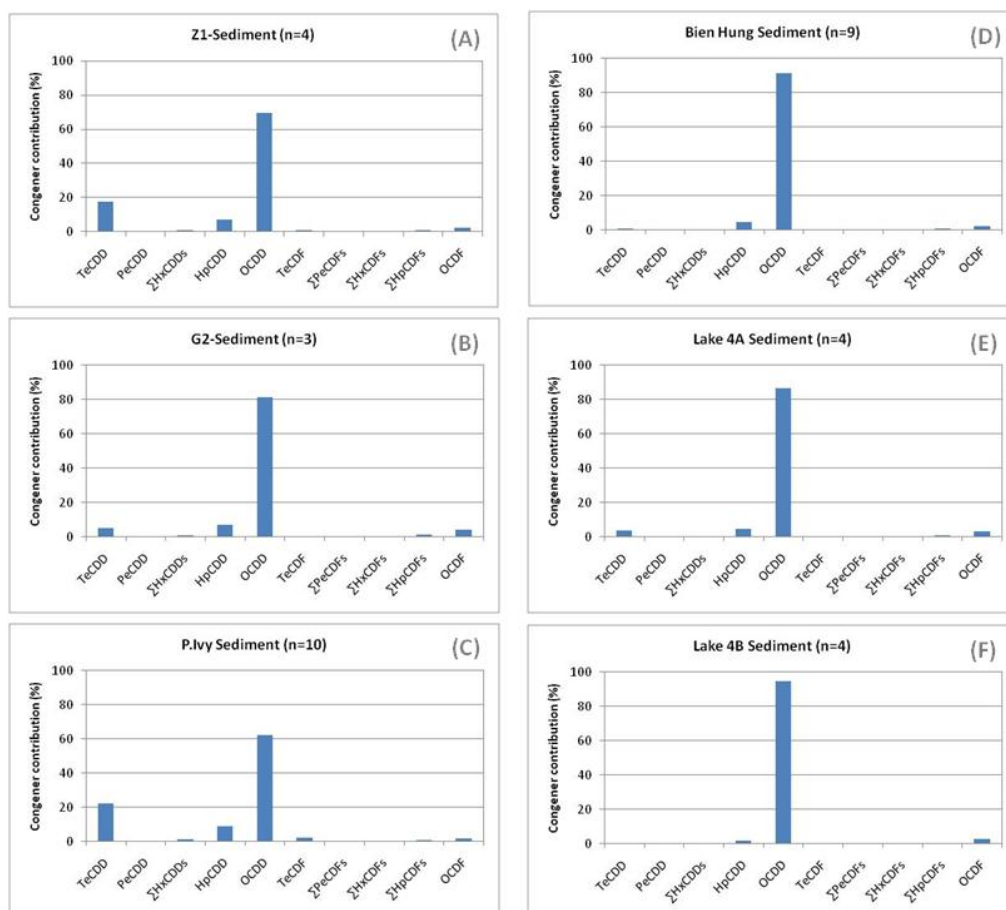


Fig. 1: PCDD/F Congeners profiles (on mass basis) in sediment from areas in and around Bien Hoa Airbase

In the Figure 2, the PCDD/F profiles in soil, sediment, fish and duck samples which were collected from the same area were presented. It is interesting to observe large variation of the profiles among these samples. The TCDD contribution is higher in the profile of biota samples (fish and duck) compared to those in abiotic matrices (soil and sediment). Vice versa the HpCDD and OCDD show a higher contribution in abiotic matrices.

It is suggested that in aquatic environment, hydrophobic compounds such as OCDD with extremely high log KOW values are less effectively bioaccumulated than those compounds with lower log KOW values, with a tendency to strongly adsorb to sediments, making them less bioavailable to organisms⁹. On the other hand this shows the high bioaccumulation potential of 2,3,7,8-TCDD compared to the higher chlorinated congeners.

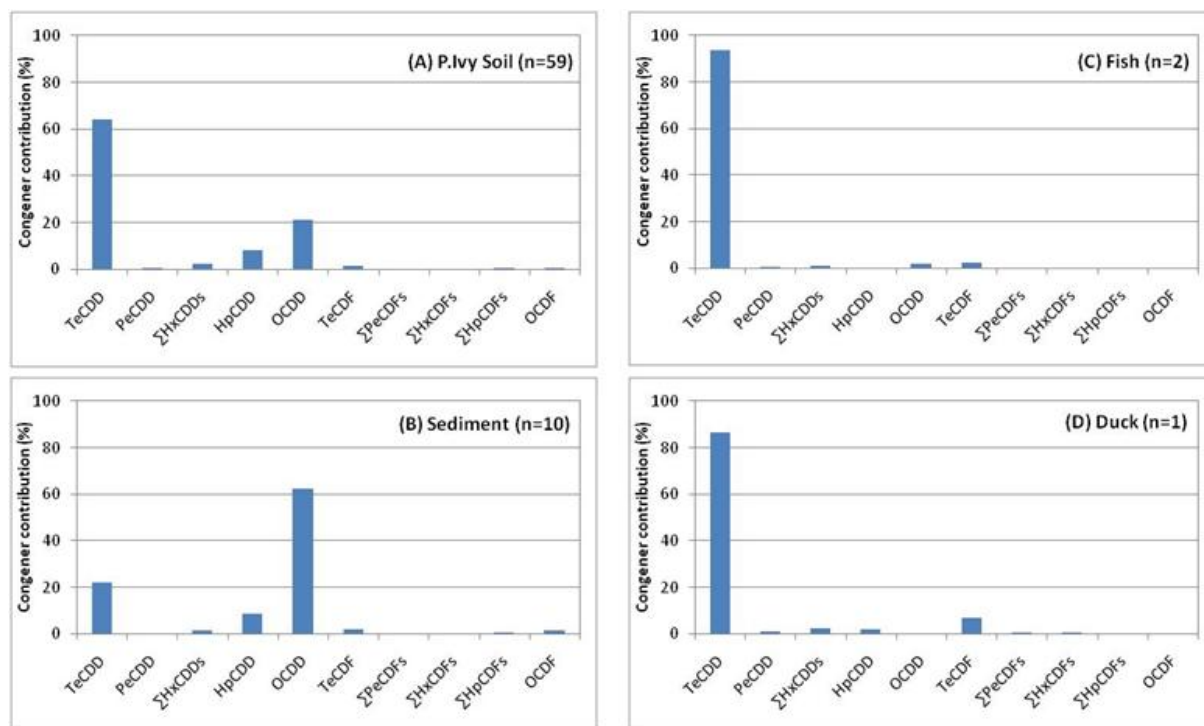


Fig. 2: Congener profiles (on mass basis) in soil, sediment, fish and duck at the contaminated sites

This study demonstrates elevated contamination of PCDD/Fs in the Bien Hoa airbase as well as their widespread contamination in the surrounding area. The due to weathering processes. The congener fingerprint with 2,3,7,8-TCDD as marker congener show that the contamination of PCDD/Fs is derived from uses and handlings of Agent Orange by the US Army during the wartime in Vietnam. As a consequence, several lakes and ponds located in and near the Bien Hoa airbase have become sinks for dioxin's residues over the time. These Dioxin reservoirs in sediments and soils serve as source for PCDD/Fs contamination in aquatic biota such as fish by bioaccumulation and thus also as exposure risk to human consumers. Despite the ban of catching fish by local authorities it is suspected that a portion of the local population may consume fish and other local foods and be exposed to dioxins through other environmental exposure pathways with associated health risk.

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