# SAMPLING AND ANALYSIS OF ATMOSPHERIC PCDD/FS IN SOUTH CHINA SEA AND CENTRAL VIETNAM

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## Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are persistent organic pollutants (POPs), which are formed and released unintentionally from anthropogenic sources. These compounds have accumulated for many years in environmental sinks such as soils and sediments due to their lipophilicity and persistence in environmental matrices. They are unwanted by-products of various combustion processes that can be emitted directly into the atmosphere if not properly treated. In addition, pentachlorophenol (PCP) and other defoliant s are widely used as biocides in the preservation of timber and textiles throughout the world [1]. Moreover, it has been shown that PCDD/Fs are impurities found in commercial defoliant products especially of Agent Orange [2]. Therefore, these impure compounds found in soils and sediments have been shown to be another source of PCDD/F contamination in addition to those from combustion and industrial processes. During the American War in Vietnam, United States (US) forces sprayed a greater volume of defoliant (Agent Orange) with higher dioxin content than originally estimated [2]. The Vietnamese have been exposed to these levels during spraying, and it is suspected on a regular basis for the past 30 years, primarily through contact with former US military infrastructure. Stellman et al. [2] raise the profile of the ''Hatfield hot spot theory'', which was proven through field validation studies in the Aluoi Valley, central Vietnam [3]. Hot spots labeled by Hatfield exist today, that is, soils that have very high TCDD levels due to higher levels of TCDD loading during the conflict. A significant point is that Hatfield hot spots are not the expansive forested areas targeted by routine flights of Operation Ranch Hand, the US military code name for the spray program [4]. Ranch Hand bases at Bien Hoa and Da Nang are examples of major hot spots. A TCDD concentration in soil from Bien Hoa was reported up to 1.2 million parts per trillion (ppt) [5]. Anecdotal information from Vietnamese scientists suggests soil PCDD/F levels from Da Nang are in the several hundred thousand ppt ranges. In this study, no significant PCDD/F stationary emission sources were existed in the vicinity two sampling stations in South China Sea and central Vietnam. To date, no comprehensive measurements of the PCDD/F concentrations in ambient air have been documented from the area. This study was initiated to address this important issue.

## Materials and methods

In this study, two sampling sites (Site A and B) were chosen based on meteorological conditions and locations relative to the winter monsoon circulation (Fig. 1). For the remote island station in South China Sea, Site A was located at a weather station on Dongsha Island (116°43'42"E, 20°42'6"N; 5 m above mean sea level), in the northern South China Sea about 440 km from Taiwan and 1,050 km from Vietnam. In this study, all PCDD/F and TSP samples were taken at 24 hr intervals at the two stations during spring season (March and April) in 2010 for the analysis of PCDD/Fs. Of the station in central Vietnam, Site B was located at the National Hydro-Meteorological Service of Vietnam Middle of Central Regional Hydro-Meteorological Observatory (108°12'24"E 16°02'35"N; 60 m above mean sea level) in Da Nang near the South China Sea. Ambient air samples for both the vapor and solid phases of PCDD/F compounds were collected using high-volume sampling trains (Shibata HV-1000F). The HV-1000F samplers were equipped with Whatman quartz fiber filters (8 × 10 inch) for collecting particle-bound compounds and polyurethane foam (PUF) plugs were used to retain PCDD/F compounds in the vapor phase. For PCDD/F analysis, the ambient air samples were spiked with known amounts of internal quantification standards according to USEPA method 23. Finally, the dioxin congeners were analyzed using high resolution gas chromatography (HRGC) (Thermo Trace GC) and high resolution mass spectrometry (HRMS) (Thermo DFS) using a fused silica capillary column DB-5 MS (60 m x 0.25 mm x 0.25 μm, J&W).

**Results and discussion:**

Measurements (Table 1) indicated that the average atmospheric PCDD/F and TSP concentrations at Site A were 4.02±1.3~5.49±3.4 fg I-TEQ/$m^3$ and 28.2±13~55.0±31 μg/$m^3$, respectively, in South China Sea during the spring season. Equivalent studies at a background station [6,7] found atmospheric PCDD/F concentrations of 6.15-24.0 fg I-TEQ/$m^3$ in a primary forest in Denmark and 1.48-6.57 fg I-TEQ/$m^3$ in a regional park of the Simbruini Mountains in Italy. Atmospheric PCDD/F concentrations measured on the remote island in South China Sea were significantly lower than those measured at other background stations. The significantly lower PCDD/F concentrations (1.66~10.8 fg I-TEQ/$m^3$) and contents in suspended particles (23.7~33.9 pg I-TEQ/g-TSP) measured at Dongsha Island (Site A) in the South China Sea can be attributed to the lack of any combustion sources within almost 300 km of this island. In central Vietnam, Table 1 shows that the atmospheric PCDD/F and TSP concentrations measured at Site B were in the ranges 62.8±26~67.6±42 fg I-TEQ/$m^3$ and 87.7±23~98.1±39 μg/$m^3$, during the spring season. In other Asian countries (such as Korea and Japan) [8,9], the atmospheric PCDD/F concentrations in urban areas have been shown to range from 28 to 120 fg I-TEQ/$m^3$, similar to another of our previous study [10] that measured atmospheric PCDD/F concentrations in the urban area of Taiwan to be in the range 20 to 110 fg I-TEQ/$m^3$. However, the significantly higher PCDD/F concentrations (23.4~116 fg I-TEQ/$m^3$) and contents in suspended particles (270~300 pg I-TEQ/g-TSP) were measured at Da Nang in the central Vietnam. Figure 2 also shows that the partitioning of PCDD/Fs between vapor and solid phases measured at Sites A and B were quite different. The significantly higher partition (89%±4.7%) of solid-phase PCDD/Fs was observed at Da Nang station. However, the solid-phase portion of atmospheric PCDD/Fs observed in South China Sea was lower than 65%. Figure 3 also shows that the distribution of PCDD/F congeners measured at Da Nang station was also quite different from those measured at other station with high PCDD distribution (>85%) especially in OCDD (>70%). Previous studies[11, 12] have indicated that the distributions of PCDF congeners observed in the emission gases from waste burning and industrial process are generally higher than 70%. Because of photodegradation, volatilization, microbial degradation, American War in Vietnam was ended 40 years ago, dioxin levels are significantly decreased and only some "hot spots" are still at elevated levels at Bien Hoa airbase, Da Nang airbase and some places at Hue which are much higher than the background concentration in many industrialized countries [13]. Most of the recent researches focus on dioxin problem caused by Agent Orange. In general, dioxin contamination by Agent Orange can be characterized by the predominant of 2,3,7,8-TCDD, the contaminant of the herbicide 2,4,5-T. In this study, our atmospheric sampling station (Site B) in Da Nang is around 10 km from the Da Nang airbase (hot spots). We consider that the high fraction of PCDDs observed at Site B probably originated as anthropogenic emission from the specific source in Vietnam.

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Table 1 PCDD/F concentrations and particle-bound PCDD/Fs in total suspended particles (TSP) measured in Taiwan and on remote islands surrounding Taiwan.

| *Location* | *Sampling period* | *TSPs (μg/m³)* | *PCDD/F concentration (fg I-TEQ/m³)* | *PCDD/F content in TSP (pg I-TEQ/g-TSP)* |
|---|---|---|---|---|
| ***Site A (Dongsha Island)*** | 2010/3/14~3/20 (n=6) | 55.0 (±31) | **1.66~10.8 (5.49 ±3.4)** | **33.9 (±5.5)** |
| | 2010/4/10~4/17 (n=7) | 28.2 (±13) | **2.79~6.49 (4.02 ±1.3)** | **23.7 (±18)** |
| ***Site B (Da Nang)*** | 2010/3/14~3/22 (n=8) | 98.1 (±39) | **23.4~146 (67.6 ±42)** | **300 (±190)** |
| | 2010/4/11~4/19 (n=8) | 87.7 (±23) | **34.6~118 (62.8 ±26)** | **270 (±86)** |

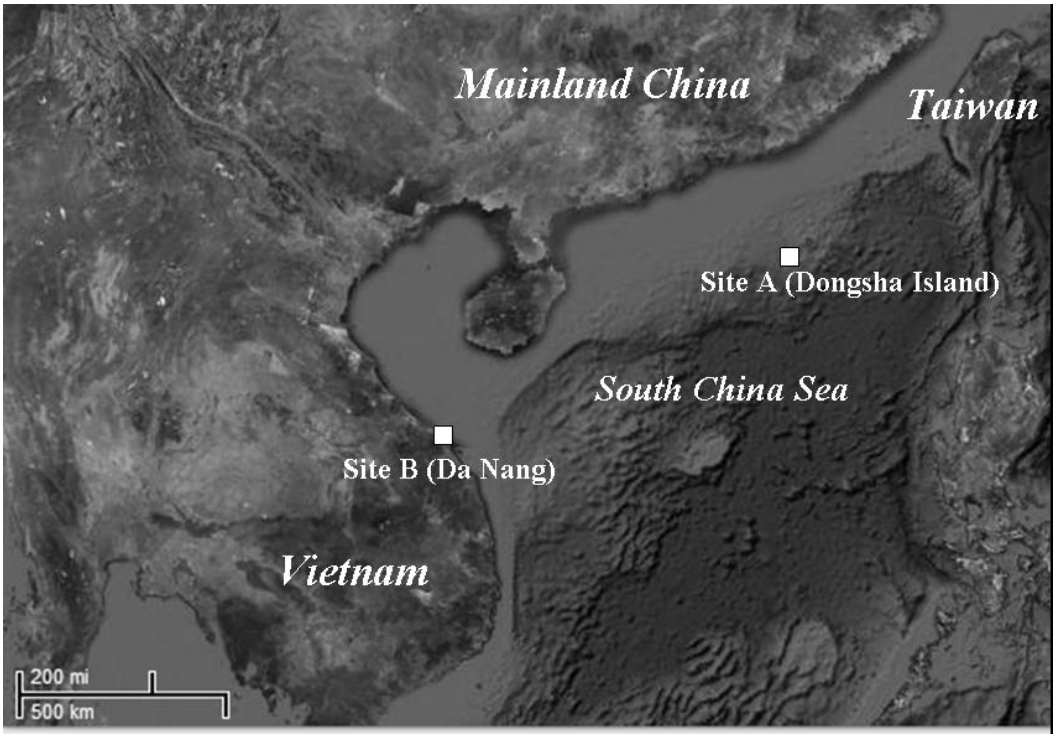


Fig. 1 Relative locations of costal and remote island sampling sites.

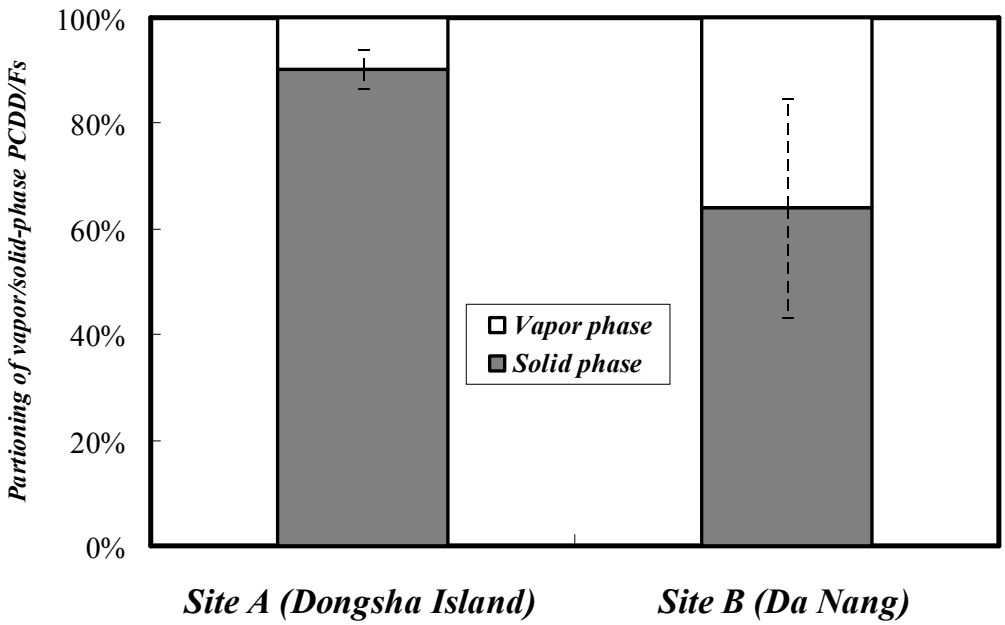


Fig. 2 Partitioning of atmospheric PCDD/Fs between vapor and solid phases in South China Sea and central Vietnam.

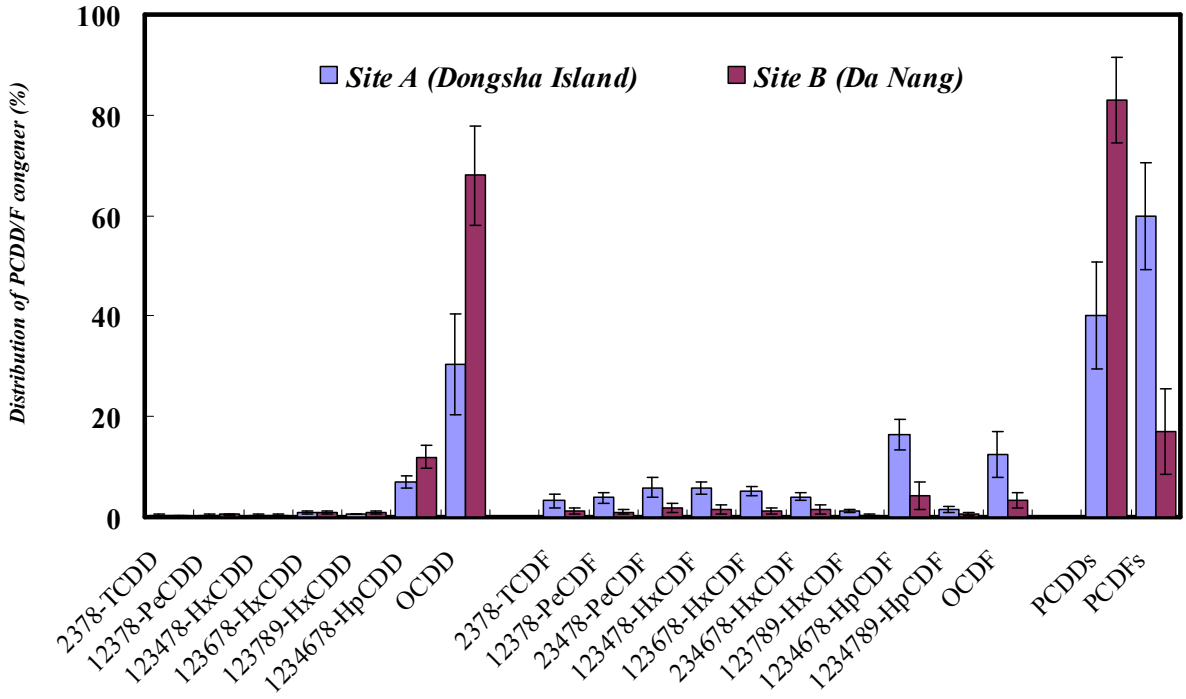


Fig. 3 PCDD/F congener distribution in ambient air in South China Sea and central Vietnam.