CHARACTERIZATION OF PCDD/F DISTRIBUTION BETWEEN VAPOR AND SOLID PHASES DURING ASIAN DUST STORM EVENT IN NORTHERN TAIWAN

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Abstract
In spring, Asian dust storm (ADS) originating in the deserts of Mongolia and China make their way to populated area of East Asia, including Taiwan. In this study, the concentrations of total suspended particle (TSP) and vapor/solid-phase PCDD/Fs are monitored at two sampling sites, one along the Northern coast of northern Taiwan (Site A), and the other in Taipei city (Site B). This study indicates that during ADS event (2006/3/15 to 3/18 and 2007/1/31 to 2007/2/1), the ambient air PCDD/F and concentration increases 4.91 times measured in northern coast (site A); 3.43 times measured in Taipei city (site B), respectively. Because no specific dioxin emission sources existed nearly 20 km of the vicinity area of site A, the increases of PCDD/F concentrations observed in site A is likely to be provided by ADS via the long range transport from mainland China. In the meantime, the PCDD/Fs bound to suspended particles increased from 244~261 to 370~491 pg-I-TEQ/g during ADS event. The results obtained from this study provide essential information for conducting health and environmental impact assessments.

Introduction
In spring, windblown dust storms originating in the deserts of Mongolia and northern China make their way to populated area of East Asia, including Taipei, Taiwan[1]. These occurrences are known as Asian dust storm (ADS) events. The ADS leads to enhanced PM_{10} and $PM_{2.5}$ levels beyond those due to usual local sources[2]. Strong dust storms usually contain diversified organic matter and nutrients that may cause adverse effects on human health and substantial economic damage. Relevant epidemiological study[3] reveals that suspended particle considerably influences respiratory health. Particularly, relationships between suspended particulate matter and lung function parameters, respiratory symptoms and mortality have been studied[2]. Previous study[4] indicated that around 70 to 80% PCDD/F concentrations in the atmosphere were essentially bounded to particles. Generally, PCDD/Fs are emitted into the atmosphere in both vapor and solid phases, and may reach a partitioning equilibrium according to temperature dependences and the vapor pressure. The solid-phase PCDD/Fs are brought into the atmosphere through wind blowing, and eventually settle to water bodies or other receptors in the environment via either dry or wet deposition mechanism. Some of those PCDD/Fs may eventually enter human bodies via food chain. So far, no studies have been conducted to examine the variation of ambient PCDD/F concentration during the ADS events. In this study, the concentrations of particulate matter and seventeen 2, 3, 7, 8-substituted PCDD/F were monitored in northern Taiwan using ambient air samplers at three sampling sites. During theses periods, ADS moved across northern Taiwan from 2006/3/15 to 3/18 and 2007/1/31 to 2007/2/1. The objective of this study is to evaluate the effects of ADS on the partitioning of dioxin compounds between vapor and solid phases.

Materials and Methods
To measure dioxin-like concentrations and obtain vapor/solid partitioning of PCDD/Fs in ambient air of northern Taiwan during the periods of ADS, two sampling sites (A and B) were set up based on the meteorological information and relative locations to the ADS (Fig. 1). Sampling site A is located at radar station in Taipei county and near the coast of East China sea. Sampling site B is located at Central Weather Bureau in Taipei city. Taipei City is situated in a basin in the northern Taiwan and has a population of 2.6 million. All PCDD/F samples were taken during normal periods and ADS events in this study. Ambient air samples for both vapor phase and solid phase of PCDD/Fs were collected using semi-volatile sampling trains (General Metal Works PS-1). The PS-1 samplers are equipped with Whatman fiber glass filters for collecting particle-bound compounds while polyurethane foam (PUF) plugs are used for retaining PCDD/F compounds in the vapor phase. The total volume of the air sampled was more than 300 m^3 for a typical sampling duration of 1-2 days. For PCDD/Fs analysis, the extract was concentrated to about 1 ml by rotary evaporation and was replaced by 5 mL

hexane for pretreatment process. Having been treated with concentrated sulfuric acid, the sample was then subjected to a series of clean-up columns including sulfuric acid silica gel column, acidic aluminum oxide column and celite/carbon column. After those procedures, the cleaned up solution was spiked with known amounts of Method 23 recovery standard solution, respectively. Finally, seventeen 2,3,7,8-substituted PCDD/F congeners are analyzed with high resolution gas chromatography (HRGC) (Hewlett Packard 6890 plus)/high resolution mass spectrometer (HRMS) (JEOL JMS-700) equipped with a fused silica capillary column DB-5 MS (60m x 0.25 mm x 0.25μm, J&W).

Results and Discussion

During the normal periods, Table 1 indicates that the average atmospheric PCDD/F concentrations measured in the northern coast (site A) are 25.0, 16.3, 7.46 and 34.3 fg-I-TEQ/m^3, respectively, from March 2006 through January 2007. In meantime, the PCDD/F concentrations measured in Taipei city (site B) are 28.2, 21.3, 22.1 and 37.2 fg-I-TEQ/m^3, respectively. The PCDD/F concentrations measured at two sampling sites are considerably lower than the concentrations measured in other nations[4] and the ambient air quality standards proposed in Japan (600 fg-TEQ/m^3). Besides, the PCDD/F concentrations measured in winter are significantly higher than those measured in other seasons. The PCDD/F concentrations in ambient air are closely correlated with the meteorological conditions as well as the emission strength[5]. Local rainfall is mainly from plum rains in spring in northern Taiwan. As a result, the rainfall during the spring is significantly higher than that in wintertime in Taiwan. Previous study[6] indicated that the ambient air PCDD/F concentrations measured in the vicinity area of municipal wastes incinerator (MWI) in Taiwan ranged from 59.0 to 348 fg-I-TEQ/m^3. Therefore, the PCDD/F concentrations measured in site A during normal periods are lower compare to those measurements. That is attributed to the fact that there are no specific dioxin emission sources and industrial sources of air pollution in nearly 20 km of the vicinity area of site A.

However, when the ADS event encountered in Taiwan, the PCDD/F and total suspended particle (TSP) concentrations increased dramatically. During ADS event, the PCDD/F concentration measured in northern coast (site A) ranges from 72.4 to 81.8 fg-I-TEQ/m^3 while that measured in Taipei city (site A) ranges from 79.8 to 108 fg-I-TEQ/m^3. However, the ambient air PCDD/F concentrations measured at site A are still lower than that measured in site B during ADS event. Fig. 2 shows PCDD/F congener distributions in ambient air measured during normal periods and ADS events. PCDDs account for 21~25% of total PCDD/Fs during normal periods (winter season) whereas PCDDs measured during ADS events are higher (35~39%). Especially for the highly chlorinated PCDD/F congeners such as OCDD and OCDF with lowest vapor pressure in dioxin groups, the distribution of OCDD/Fs increase observed during ADS events. Fig. 3 also demonstrates that obvious PCDD/F mass adsorbed on suspended particles measured in ambient air during the ADS event. The PCDD/Fs bound to suspended particles increased from 244~261 to 370~491 pg-I-TEQ/g. Wallenhorst et al.[7] indicated that the concentrations of PCDD/Fs in suspended particle observed in rural area was 320 pg-I-TEQ/g. That is lower than that measured in this study during ADS event. We speculate that the particulate matter provided by ADS greatly facilitates the transferring of vapor-phase PCDD/Fs to solid phase. Therefore, the PCDD/F content in suspended particle measured during ADS events is significantly higher than that measured during normal periods.

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Table 1 PCDD/F concentrations measured in ambient air at sampling sites A and B during different seasons.

	Period	***2006/4/23~4/26*** **(Spring)**	**2006/8/3~8/6 (Summer)**	**2006/10/31~11/5 (Fall)**	**2007/1/27~1/30 (Winter)**
Northern coast *(Site A)*	**Temperature (^oC)**	**22.1 (±2.0)**	**28.0 (±2.0)**	**22.5 (±1.4)**	**13.9 (±1.8)**
	Rainfall (mm)	**71.8**	**0.2**	**14.2**	**0.0**
	TSP concentration (μg/m^3)	**43.3**	**18.1**	**49.3**	**50.3**
	PCDD/F concentration (fg-I-TEQ/m^3)	**25.0**	**16.3**	**7.46**	**34.3**
Taipei city *(Site B)*	**Temperature (^oC)**	**23.7 (±1.6)**	**31.2 (±2.4)**	**23.8 (±1.8)**	**14.7 (±2.4)**
	Rainfall (mm)	**51.4**	**0.8**	**15.4**	**0.0**
	TSP concentration (μg/m^3)	**50.5**	**26.0**	**68.8**	**77.2**
	PCDD/F concentration (fg-I-TEQ/m^3)	**28.2**	**21.3**	**22.1**	**37.2**

Table 2 PCDD/F concentrations measured at sampling sites A and B during different dust storm events.

	Period	***2006/3/15~3/16 (ADS 1)***	***2006/3/17~3/18 (ADS 2)***	***2007/1/31~2/1 (ADS 3)***
Northern coast *(Site A)*	**Temperature (^oC)**	**17.8 (±1.2)**	**22.9 (±3.8)**	**14.8 (±2.2)**
	Rainfall (mm)	**0.2**	**0.0**	**0.2**
	TSP concentration (μg/m^3)	**72.9**	**118**	**105**
	PCDD/F concentration (fg-I-TEQ/m^3)	**72.8**	**81.8**	**72.4**
Taipei city *(Site B)*	**Temperature (^oC)**	**19.2 (±1.2)**	**25.2 (±3.4)**	**16.2 (±2.9)**
	Rainfall (mm)	**0.0**	**0.0**	**0.0**
	TSP concentration (μg/m^3)	**120**	**121**	**137**
	PCDD/F concentration (fg-I-TEQ/m^3)	**103**	**108**	**79.8**

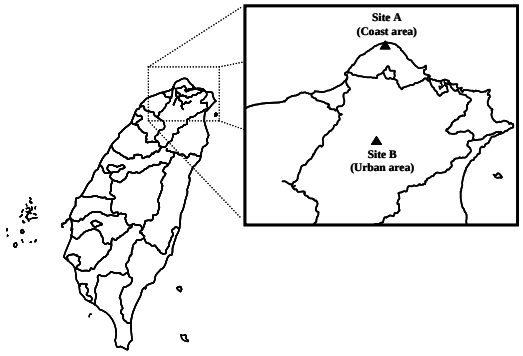

Figure 1 Relative locations of sampling sites A and B.

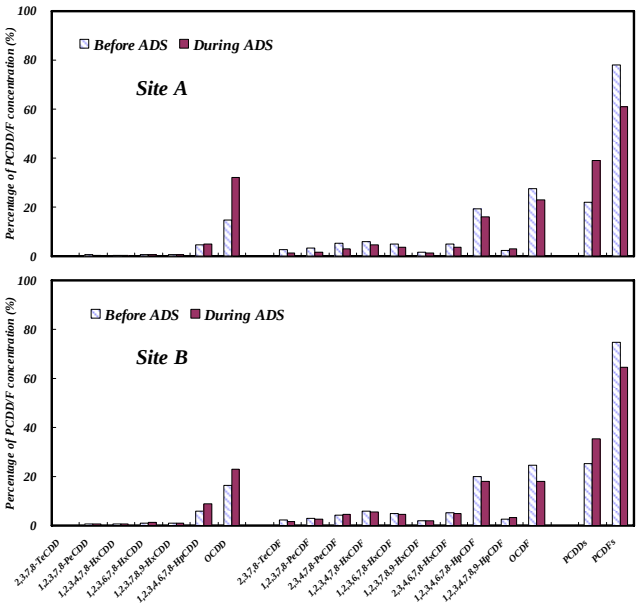

Figure 2 PCDD/F congener distribution in two sampling sites during before and during ADS event.

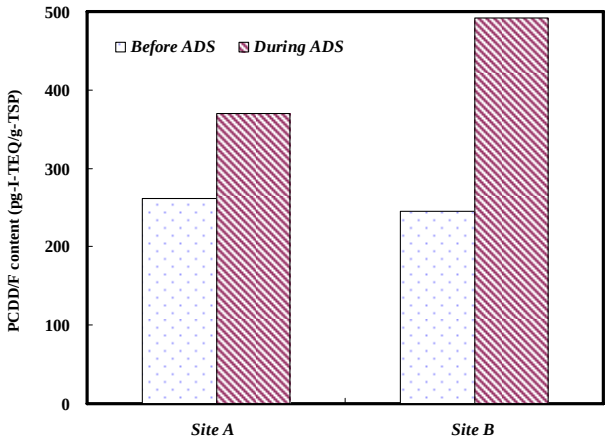

Figure 3 Comparison of particle-bound PCDD/Fs in total suspended particle (TSP) measured in ambient air before and during ADS event.