EVALUATION OF DIOXIN-LIKE POLLUTANTS IN AMBIENT AIR VIA LONG RANGE TRANSPORT

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Abstract
In this study, the contents of persistent organic pollutants (POPs) existing in suspended particles via long range transport have been investigated. During three Asian dust storm (ADS) episodes and one Eastern Asia biomass burning event, the concentrations of total suspended particles (TSP) and vapor/solid-phase dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are monitored at three sampling sites, one along the Northern coast of Taiwan (Site A),one in Taipei city (Site B) and the other at Lulin atmospheric background station in central Taiwan (Site C). During the ADS episode I (2006/3/15-3/17), atmospheric PCDD/F concentration measured in Taipei city increased from 52.5 to 108 fg-I-TEQ/m^3, while PCB concentration increased from 4.49 to 8.36 fg-TEQ_{WHO}/m^3. During the ADS episode II (2007/1/27-2/4), atmospheric PCDD/F concentration measured in Northern coast increased from 35.3 to 72.4 fg-I-TEQ/m^3, while PCB concentration increased slightly from 1.23 to 1.73 fg-TEQ_{WHO}/m^3. However, during the ADS episode III (2007/4/16-4/17), no significant increases of atmospheric PCDD/Fs are observed at Sites A and B. That is attributed to the fact that the moving trajectory of air mass during ADS episode III is quite different with other two ADS episodes. In addition, PCDD/F concentrations measured at Site C during the Asian biomass burning event ranged from 1.29 to1.55 fg-TEQ/m^3. Compared to the normal period (1.10 to 1.15 fg-TEQ/m^3), only the slight increase (10 to 25%) of PCDD/Fs is observed during biomass burning event. The results obtained from simulation results of the backward trajectory simulation indicated that as the air mass pass through the coastal area of China during the ADS episode, the atmospheric PCDD/F contents in suspended particles measured in northern Taiwan increase by 35%. In the past, ADS episodes were mainly a concern because of the associated increase in TSP and metallic element concentrations in the atmosphere. It is worth noting that the significant increases of dioxin-like compounds measured in the ambient air of northern Taiwan during the ADS episode can also have negative health effects.

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. In addition, Eastern Asia biomass burning has also caused global concerns during the past decade due to its adverse effects on visibility, human health and global climate by emitting particulate matter and other gaseous pollutants such as CO、SO_x、NO_x and VOCs. Relevant epidemiological study[3] reveals that suspended particle considerably influences respiratory health. Previous study[4] indicated that around 70 to 80% PCDD/F concentrations in the atmosphere were essentially bounded to particles. 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. To our knowledge, few studies have been conducted toward examining the relationship between the high levels of dust particles and the concentrations of atmospheric polychlorinated PCDD/F and PCB concentrations during ADS episodes. Measurements of atmospheric PCDD/Fs in Korea[5] show that the concentrations of particle-bound PCDD/Fs collected under ADS (28~80 fg-I-TEQ/m^3) and non-ADS (38~120 fg-I-TEQ/m^3) conditions do not differ widely. However, recent study[6] further indicates that around 972~51,200 fg-I-TEQ/m^3 are measured in the vicinity of electronic wastes plants in the Guangdong provinces. These values are dramatically higher than others measured around the world. Therefore, we consider that significant amounts of PCDD/Fs are possibly transported with dust across the Taiwan Strait and reach northern Taiwan during ADS episode. In this study, the concentrations of particulate matter and seventeen 2, 3, 7, 8-substituted PCDD/F and twelve toxic PCB

congeners were monitored in Taiwan using ambient air samplers at three sampling sites. The objective of this study is to evaluate the effects of dust storm and biomass burning 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 during the periods of long range transport events, three sampling sites (A, B and C) were set up based on the meteorological information and relative locations to the ADS and biomass burning (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. Sampling site C is located at Lulin atmospheric background station (altitude: 2,862 m) in Lulin mountain. All PCDD/F samples were taken during normal periods and long range transport events in this study. Ambient air samples for both vapor phase and solid phase of dioxin-liked compounds 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 and PCB 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 and PCBs analysis, the dioxin-liked 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

When the ADS event encountered in Taiwan, the dioxin-liked compound and total suspended particle (TSP) concentrations increased dramatically. Table 1 indicates that the atmospheric PCDD/F concentration measured in northern coast (site A) ranges from 72.4 to 81.8 fg-I-TEQ/m^3 during the ADS episode I (2006/3/15-3/17) while that measured in Taipei city (site B) ranges from 79.8 to 108 fg-I-TEQ/m^3. Table 3 shows the atmospheric PCDD/F and PCB concentration in northern Tawain during the ADS episode II (2007/1/27-2/4). The significant increases of dioxin-like compounds are also observed at two sampling sites. Interestingly, Tables 1 and 2 both indicate the atmospheric PCDD/F, PCB and TSP concentrations measured at the two sampling sites decreased dramatically one day after the ADS episode. Based on the simulation results of the backward trajectory simulation (Figure 2), the atmospheric mass flows pass through the coastal area of southern China and into Taiwan during the ADS episodes I and II. However, the moving trajectory of air mass during ADS episode III did not pass through the coastal area of China (Zhejiang and Fukien provinces). Therefore, no significant increases of atmospheric PCDD/Fs are observed in sites A and B (Table 3) during the ADS episode III (2007/4/16-4/17). In addition, Table 4 indicates that the atmospheric PCDD/F concentrations measured at Lulin atmospheric background station (Site C) during the Asian biomass burning event ranged from 1.29 to1.55 fg-TEQ/m^3. Compared to the normal period (1.10 to 1.15 fg-TEQ/m^3), only slight increase (10 to 25%) of PCDD/Fs is observed during biomass burning event. Figure 3 shows the particle-bound PCDD/Fs and PCBs relative to the TSP at both sampling sites during ADS episodes and normal periods. During normal periods, the quantities of PCDD/Fs and PCBs adsorbed onto suspended particles are quite similar at both sites. As the ADS reaches Taiwan, the mass of PCDD/Fs adsorbed onto suspended particles increases by nearly 25% at Site A, though an even more significant increase, from 259 to 512 pg-TEQ/g, is observed at Site B. As Site B is surrounded by six large-scale municipal wastes incinerators in the Taipei basin, the vapor-phase PCDD/Fs emitted from local facilities in Taipei city are thought to be transferred to solid-phase in the ambient air during ADS episodes in Taipei basin. However, the particle-bound PCBs, however, do not change significantly at the two sampling sites. In general, PCB congeners with higher vapor pressures are mostly distributed in the vapor phase within the ambient air, and the partitioning of solid-phase PCBs are not significantly affected by the ADS.

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Table 1 PCDD/F concentrations measured at sampling sites A and B during ADS episode I (2006/3/15-3/17).

Sampling Period		2006/2/21~2/23 (1 month prior to ADS episode I)	2006/3/15~3/16 (ADS episode I-1)	2006/3/17~3/18 (ADS episode I-2)	2006/3/20~3/21 (1 day after ADS episode I)
Northern coast (Site A)	Temperature (°C)*	13.9	17.6	21.8	17.8
	Rainfall (mm)	0.0	0.46	0.0	18.0
	TSP (μg/m^3)	61.6	119	127	62.4
	PCDD/Fs (fg-I-TEQ/m^3)	32.2	72.8	81.8	27.1
	PCBs (fg-TEQ$_{WHO}$/m^3)	2.23	4.92	7.05	2.40
Taipei city (Site B)	Temperature (°C)*	14.7	18.6	22.6	18.4
	Rainfall (mm)	0.0	0.0	0.0	2.7
	TSP (μg/m^3)	75.8	147	167	72.3
	PCDD/Fs (fg-I-TEQ/m^3)	52.5	103	108	59.4
	PCBs (fg-TEQ$_{WHO}$/m^3)	4.49	7.30	8.36	4.96

Table 2 PCDD/F concentrations measured at sampling sites A and B during ADS episode II (2007/1/27~2/2).

Sampling Period		2007/1/27~1/30 (ADS episode II-1)	2007/1/30~1/31 (ADS episode II-2)	2007/1/31~2/2 (ADS episode II-3)	2007/2/2~2/4 (1 day after ADS episode II)
Northern coast (Site A)	Temperature (°C)*	12.5	14.2	11.5	16.0
	Rainfall (mm)	0.0	0.0	0.0	0.0
	TSP (μg/m^3)	144	102	137	77.2
	PCDD/Fs (fg-I-TEQ/m^3)	35.3	39.0	72.4	37.2
	PCBs (fg-TEQ$_{WHO}$/m^3)	1.23	1.41	1.73	0.99
Taipei city (Site B)	Temperature (°C)*	13.3	15.0	13.0	17.0
	Rainfall (mm)	0.0	0.0	0.0	0.0
	TSP (μg/m^3)	113	77.3	105	50.3
	PCDD/Fs (fg-I-TEQ/m^3)	41.7	28.2	79.8	34.3
	PCBs (fg-TEQ$_{WHO}$/m^3)	1.49	1.09	1.68	1.02

Table 3 PCDD/F concentrations measured at sampling sites A and B during ADS episode III (2007/4/16~4/17).

Sampling Period		2007/4/16~4/17 (ADS episode III)	2007/4/17~4/20 (1 day after ADS episode III)	2007/5/1~5/4 (2 weeks after ADS episode)
Northern coast (Site A)	Temperature (°C)*	23.0	18.3	23.2
	Rainfall (mm)	0.6	6.4	5.0
	TSP (μg/m^3)	156	54.0	68.3
	PCDD/Fs (fg-I-TEQ/m^3)	33.8	14.6	31.1
Taipei city (Site B)	Temperature (°C)*	23.5	19.7	23.8
	Rainfall (mm)	0.2	32.2	0.0
	TSP (μg/m^3)	193	78.3	74.4
	PCDD/Fs (fg-I-TEQ/m^3)	33.0	35.4	30.0

Table 4 PCDD/F concentrations measured in Lulin mountain (Site C) during Asian biomass burning event (2007/3/10~3/17).

Sampling Period		2007/3/6~3/8 (Normal period)	2007/3/8~3/10 (Normal period)	2007/3/10~3/13 (Episode 1)	2007/3/13~3/15 (Episode 2)	2007/3/15~3/17 (Episode 3)
Lulin atmospheric background station (Site C)	Temperature (°C)	5.0-5.6	5.7-7.1	7.5-9.1	9.7-8.7	8.8-9.9
	Rainfall (mm)	23	3.8	0.0	0.2	0.0
	TSP (μg/m^3)	13.4	35.7	52.7	54.9	74.3
	PCDD/Fs (fg-I-TEQ/m^3)	1.15	1.10	1.29	1.46	1.55

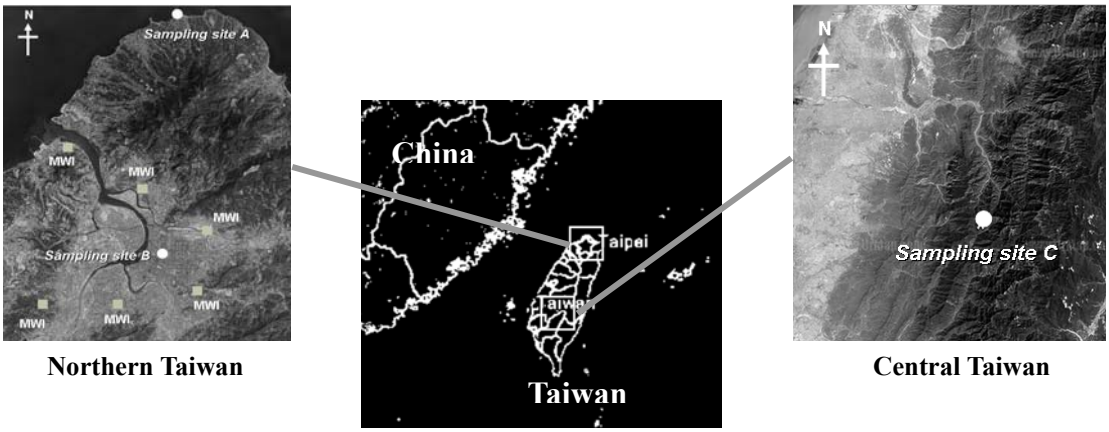

Figure 1 Relative locations of sampling sites A, B and C.

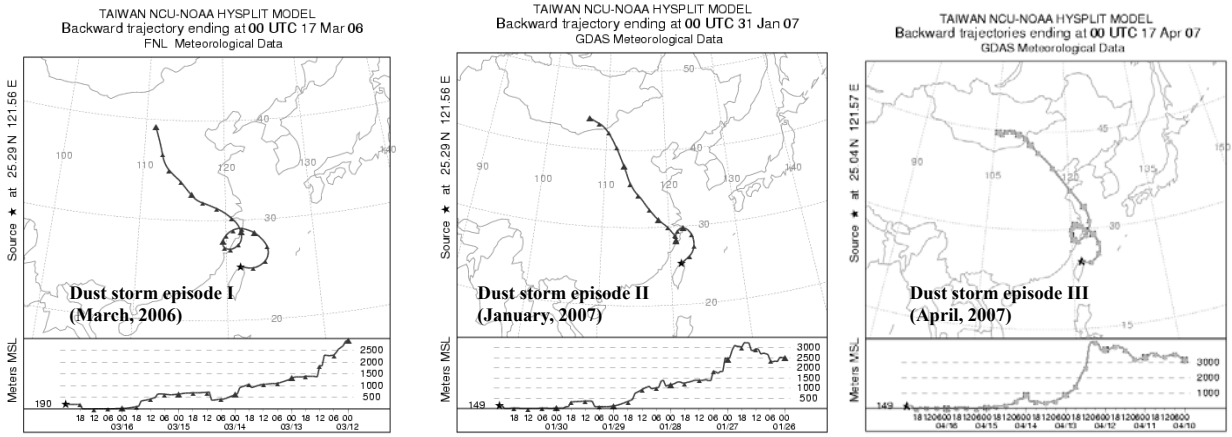

Figure 2 Five-day backward trajectories of sampling Sites A and B during different ADS episodes.

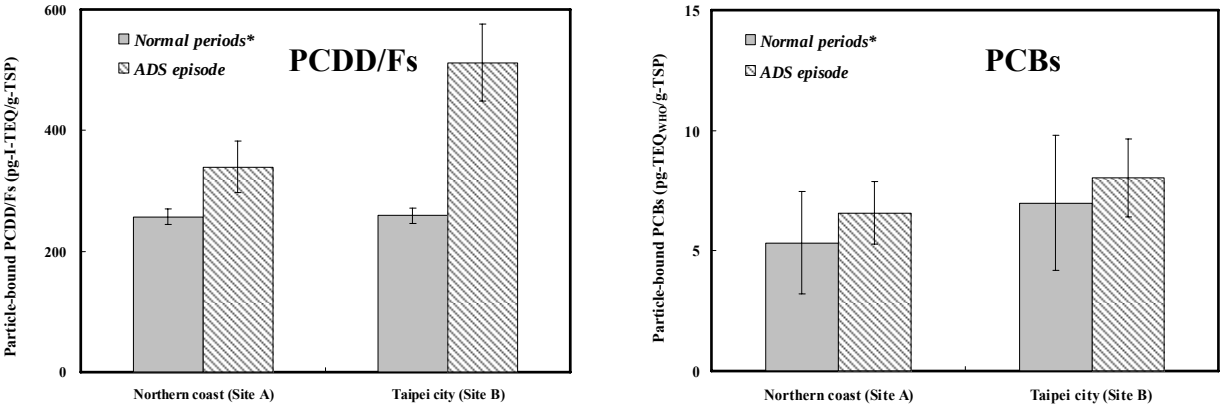

Figure 3 Comparison of particle-bound PCDD/Fs and PCBs in total suspended particle (TSP) at two sampling sites during the ADS episodes and normal periods.