EVALUATION OF ATMOSPHERIC DIOXIN DEPOSITION IN NORTHERN TAIWAN VIA AUTOMATED AND TRADITIONAL SAMPLERS

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Abstract
Most of polychlorinated dibenzo-*p*-dioxin and furan (PCDD/F) in ambient air are bounded to particles which are brought into the atmosphere through wind blowing, and eventually settle to water bodies or other receptors in the environment either via dry or wet deposition mechanism, then through food chain to enter human body. Deposition from air (dry/wet) is one of the most important flux to trace the environmental fate and behavior of dioxin-like compounds. Several studies demonstrate that one of the key parameters in accurate modeling of these pollutants in environment is the deposition flux in atmosphere. Hence, understanding PCDD/F deposition is important in conducting dispersion modeling and risk assessment. The automated PCDD/F ambient air precipitation sampler used in this study can inhibit the decomposition and dechlorination of PCDD/F collected and also effectively collect the PCDD/F samples in dry and wet depositions simultaneously. PCDD/F deposition was sampled via automated PCDD/F ambient air precipitation sampler and traditional cylindrical vessels from March 2007 to July 2007. The ambient air sampling results indicate that the atmospheric PCDD/F concentrations collected by PS-1 sampler ranged from 0.073 to 0.309 pg-I-TEQ/m^3 in northern Taiwan. In the mean time, the sampling results indicate that the PCDD/F deposition flux measured with automated PCDD/F precipitation sampler (15.0 to 20.4 pg-I-TEQ/m^2-day) are significantly higher than that sampled with cylindrical vessels (5.38 to 6.89 pg-I-TEQ/m^2-day). That is attributed to the fact that part of PCDD/F depositions collected by traditional cylindrical vessels are photodegraded. In addition, the dry deposition flux of PCDD/Fs (274to 515 pg-I-TEQ/m^2-month) observed in this study is significantly higher than wet deposition flux (45.3 to 278 pg-I-TEQ/m^2-month).

Introduction
PCDD/Fs are released into the atmosphere from a variety of combustion sources and manufacturing processes. They are transported to the terrestrial and aquatic ecosystems through dry or wet deposition. Therefore, atmospheric transport and deposition is the primary distribution pathway moving PCDD/Fs from numerous emission sources to the environmental compartments[1]. However, due to resuspension of collected particles and decomposition (dechlorination for organohalogen compounds) of compounds by sunlight or volatilization of collected compounds, these sampling methods are not suitable to estimate the "flux" of organic compounds[2]. These phenomena result in an under-estimation of compounds' "flux". In addition, because dechlorination rates of each dioxin congener is different, congener and isomer distributions observed might differ from actual distributions patterns at the time of collection. Investigation of deposition samples provides information on the status of environmental pollution of PCDD/Fs. During their transport and deposition in the atmosphere, PCDD/Fs can be removed by chemical degradation mechanism including the reaction with OH radicals[3]. In addition, certain meteorological parameters (such as temperature, rainfall, wind speed, solar intensity and humidity) may be reflected in fluctuation of atmospheric deposition fluxes for PCDD/Fs[4-5]. However, only appropriate measurement the ambient air PCDD/F deposition flux, the deposition velocity calculated will be accurate and objective. In this study, we focus on the understanding of the dry/wet deposition of PCDD/Fs in northern Taiwan via automated samplers and traditional cylindrical vessels for PCDD/F deposition in atmospheric environment. An automated air precipitation trap sampler is developed in order to obtain more accurate data regarding deposition flux of PCDD/Fs from atmosphere to land.

Materials and Methods
To measure the PCDD/F deposition and obtain dry/wet deposition of PCDD/Fs in ambient air of northern Taiwan, the sampling site was set up at the campus of National Central University in Taoyuan county. In the meantime, the PCDD/F deposition is also collected with stainless cylindrical vessels to make comparison with automated

sampler. Figure 1(a) shows a schematic diagram of the automated PCDD/F ambient air precipitation sampler. The main apparatus is constructed of mirror polished stainless steel (D: 460 mm). The system includes two glass fiber filter (D:146 mm) holder, polyurethane form polyurethane foam (PUF) holder, gear pump, diaphragm valves, compressor, pressure, temperature and flow rate sensors, cooling circulator and PID controller. The deposition sampler used in this study is modified from the automated air precipitation trap sampler[2] made in Japan. Figure 1(b) shows a schematic diagram of the stainless cylindrical vessels. The main apparatus is constructed of mirror polished stainless steel (D: 500 mm, H: 600 mm). Ambient air samples for both vapor 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 PUF plugs are used for retaining PCDD/F compounds in the vapor phase. The total volume of the air sampled was more than 2,000 m^3 for a typical sampling duration of 5-6 days. The deposition and ambient air PCDD/F samples were taken from March to July, 2007. 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

Table 1 indicates that the total deposition flux of PCDD/Fs collected by automated sampler ranged from 15.0 to 20.4 pg-I-TEQ/m^2-day during March ~ July, 2007. However, the deposition flux of PCDD/Fs collected by traditional cylindrical vessels was much lower ranging from 2.07 to 6.89 pg-I-TEQ/m^2-day. In addition, the PCDD/F deposition flux collected by cylindrical vessels decreased with increasing ambient air temperature. The average atmospheric PCDD/F concentrations measured in the northern Taiwan ranged from 0.073 to 0.309 pg-ITEQ/m^3 from March through July, 2007. The atmospheric PCDD/F concentrations measured in this study are considerably lower than that measured in Korea and Japan and the ambient air quality standards proposed in Japan (600 fg-TEQ/m^3). However, the PCDD/F deposition flux measured in this study is higher than that measured in other **countries** [5-8]. Figure 2 shows the congener distribution of PCDD/F deposition flux measured by automated sampler and traditional cylindrical vessel in cold and hot seasons. The sampling results indicate that the relative difference of PCDD/F deposition flux between the measurement of automated sampler and cylindrical vessel are all higher than 30% during cold season. However, the relative difference increased to over 70% especially for PCDF congeners in hot season. The relative difference also decreased with increasing chlorinated level of PCDD/F congener at both sampling seasons. As a result, strong sunlight during summer time enhances the photolysis of PCDD/F. Therefore, PCDD/F deposition flux collected by traditional sampler in summer would be generally lower than that measured in other seasons. Additionally, Table 2 indicates that the dry deposition flux of PCDD/Fs (274 to 515 pg-I-TEQ/m^2-month) observed in this study is significantly higher than that of wet deposition (45.3 to 278 pg-I-TEQ/m^2-month). That is attributed to the duration of rainy and sunny days in different month. Figure 3 shows the average PCDD/F congener distributions in deposition (dry/wet) and ambient air samples (vapor/solid phase). For deposition samples, PCDDs account for 50 to 55% of total PCDD/Fs. Especially for the highly chlorinated PCDD/F congeners such as OCDD and OCDF with lowest vapor pressure in dioxin groups, the distribution of OCDD is even higher than 40%. In addition, the results of ambient sample indicate that the conger distribution of solid-phase PCDD/Fs is similar to that of PCDD/F depositions.

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Table 1 Deposition flux and ambient air concentration of PCDD/Fs in northern Taiwan.

Sampling period	PCDD/F deposition flux collected by automated sampler (pg-I-TEQ/m^2-day)	PCDD/F deposition flux collected by cylindrical vessel (pg-I-TEQ/m^2-day)	Atmospheric PCDD/F concentrations (pg-I-TEQ/m^3)	Average ambient air temperature (^oC)
March 2007	15.0	5.38	0.152	18.2
April 2007	18.6	6.89	0.111	19.9
May 2007	20.4	6.05	0.309	24.9
June 2007	19.9	3.17	0.092	26.3
July 2007	18.0	2.07	0.073	29.5

Table 2. Dry and wet deposition flux of PCDD/Fs measured in northern Taiwan.

Sampling period	**Duration (days)**			**Dry PCDD/F deposition flux (pg-I-TEQ/m^2-month)**	**Wet PCDD/F deposition flux (pg-I-TEQ/m^2-month)**
	Sunny day	**Rainy day**	**Rainwater (mm)**		
March 2007	25	4	180	274	161
April 2007	22	7	221	274	278
May 2007	26	2	96.2	355	213
June 2007	27	4	611	358	251
July 2007	30	1	4.6	515	45.3

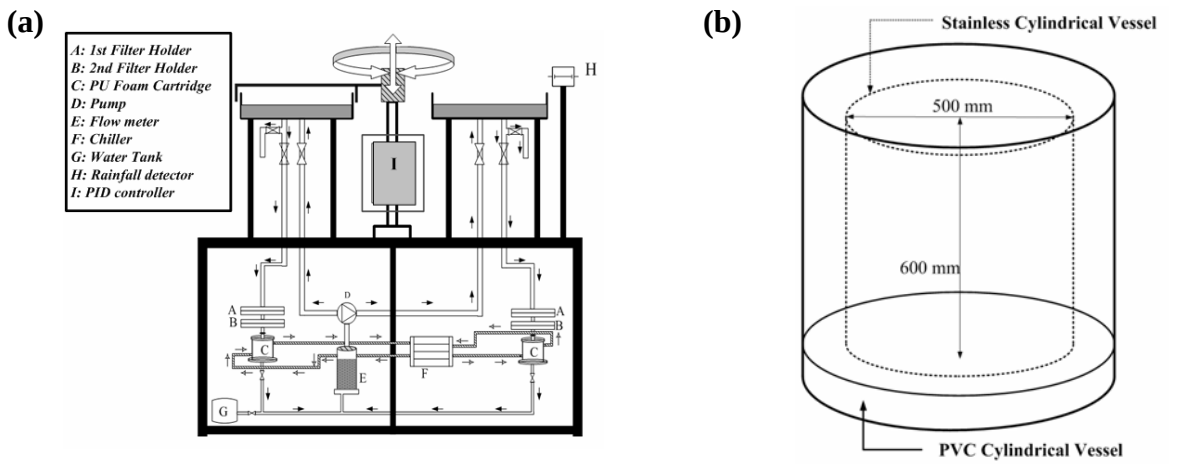

Figure 1 Schematic diagrams of (a) automated PCDD/F ambient air precipitation sampler and (b) traditional cylindrical vessels.

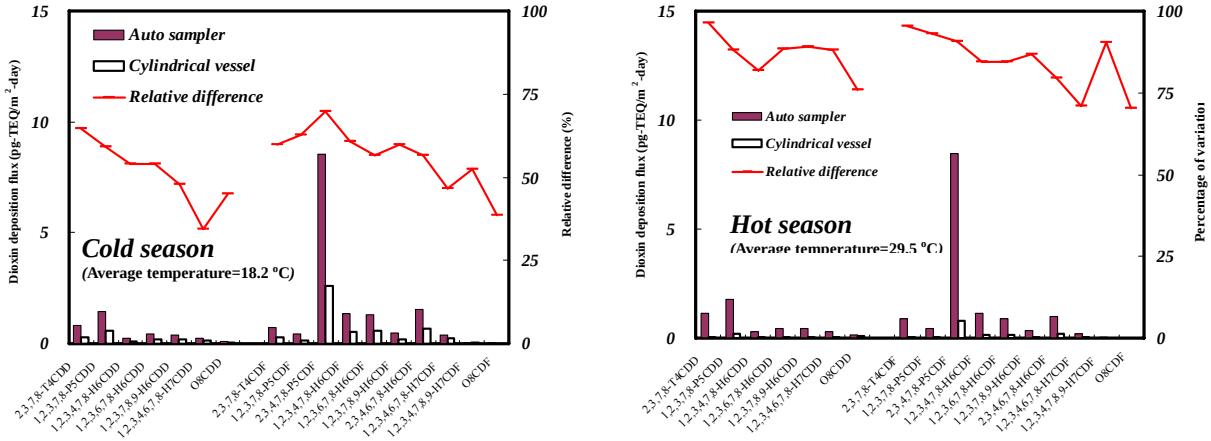

Figure 2 Congener distribution of PCDD/F deposition flux measured by automated sampler and traditional cylindrical vessel in different seasons.

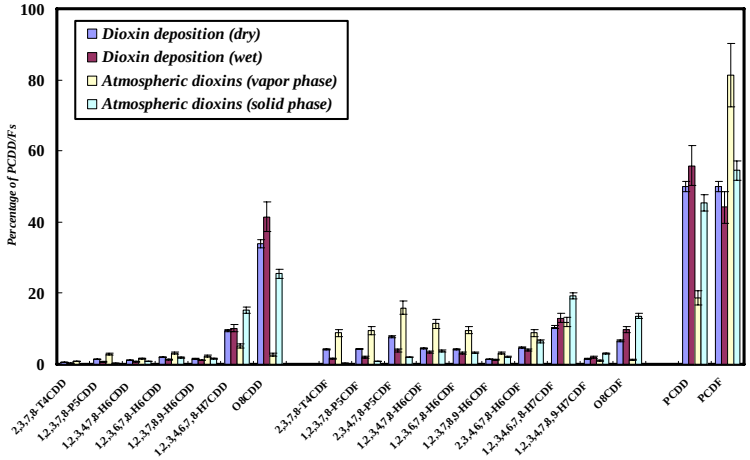

Figure 3 Distribution of PCDD/F congener in deposition (dry/wet) and atmospheric (vapor/solid phases) samples.