

## EVALUATION OF AUTO SAMPLER FOR DIOXIN DEPOSITION IN NORTHERN TAIWAN

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### Abstract

Most of polychlorinated dibenzo-*p*-dioxin and furan (PCDD/F) concentrations in the atmosphere 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 (wet/dry) is one of the most important flux to trace the environmental fate and/or 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 sampling results indicate that the PCDD/F deposition flux are 23.7 and 15.2 pg-I-TEQ/m<sup>2</sup>-day on February 2007 and March 2007, respectively. Compare with relevant studies, the PCDD/F deposition flux measured in northern Taiwan is significantly higher than that measured in other nations. In addition, the dry deposition velocities of PCDD/Fs observed in this study were 0.10 and 0.15 cm/s in February and March 2007, respectively.

### Introduction

PCDD/Fs are released directly into the atmosphere from a variety of combustion sources and manufacturing processes. They are mainly transported over deposited 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<sup>1</sup>. However, due to re-scattering 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<sup>2</sup>. 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 is able to indicate 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 such as OH radical reaction<sup>3</sup>. 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<sup>4-5</sup>. Until now, domestic studies have focused on the flux of deposited particles, the chemical composition of inorganic compounds, the characteristics of acid rain, and the origin of aerosol<sup>6-7</sup>. However, only appropriate measurement the ambient air PCDD/F deposition flux, the deposition velocity calculated will be accurate and objective. In this study, to focus on the understanding of the dry/wet deposition of dioxin-like compounds in different sampling area (urban, sub-urban and rural area) via auto samplers for PCDD/F deposition in atmospheric environment. An air precipitation trap sampler was developed in order to obtain more accurate data regarding "Flux" of dioxins from air to land.

### Materials and Methods

To measure the PCDD/F deposition and obtain liquid/solid partitioning 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. Figure 1 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 a 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<sup>2</sup> made in Japan. In the meantime, 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 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<sup>3</sup> for a typical sampling duration of 5-6 days. The deposition and ambient air PCDD/F samples were taken from February 2007 to March 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 0.25 $\mu$ m, J&W).

### Results and Discussion

To investigate the influence of sampling periods, the matrix spike solutions (80~800 pg PCDD/Fs) were added into the PUF (blank sample) for the purpose of quality control. After 5-day and 20-day operation, the PCDD/F recovery efficiencies range from 83.2 to 111% and 83.8 to 107%, respectively (shown in Table 1). The results of this experimentation verify that the deposition of PCDD/Fs can be effectively collected by PUF achieved with automated PCDD/F ambient air precipitation sampler used in this study. Table 2 indicates that the PCDD/F deposition are 23.7 and 15.2 pg-I-TEQ/m<sup>2</sup>-day on February 2007 and March 2007, respectively. Additionally, the dry deposition flux of PCDD/Fs measured in this study is higher than then wet deposition flux. In meantime, the average atmospheric PCDD/F concentrations measured in the northern Taiwan ranges from 0.063 to 0.152 pg-I-TEQ/m<sup>3</sup> from February 2007 through March 2007. The PCDD/F concentrations measured in this study are considerably lower than the concentrations measured in Korea and Japan and the ambient air quality standards proposed in Japan (600 fg-TEQ/m<sup>3</sup>). However, the PCDD/F deposition flux measured in this study is significantly higher than that measured in other nations<sup>8</sup>. Figure. 2 shows PCDD/F congener distributions in deposition and ambient air samples. For deposition samples, PCDDs account for 60 to 70% 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 OCDDs are higher than 45%. In addition, the results of ambient samples indicate that OCDD accounts for 20 to 30% of total concentrations. Major contributors include 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, OCDD and OCDF. The dry deposition velocities of PCDD/Fs can be calculated as follows:  $V = K \cdot F / C$ , where  $V$  = dry deposition velocity of PCDD/Fs (cm/s);  $K$  = unit conversion factor = (pg/m<sup>2</sup>-day)(m<sup>3</sup>/pg)(100 cm/m) (1 day/86400s);  $F$  = dry deposition flux (pg/m<sup>2</sup>-day);  $C$  = ambient air concentration of PCDD/Fs (pg/m<sup>3</sup>). The dry deposition velocities of total PCDD/Fs were 0.10 and 0.15 cm/s in February and March 2007, respectively. Those values were lower than the deposition measurements by Koester and Hites<sup>9</sup> of 0.2 to 0.3 cm/s.

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Table 1 PCDD/F recovery efficiencies of matrix spike solutions added into the blank sample after 5-day and 20 day testing.

Congener	Matrix spike (pg)	5-day testing		20-day testing	
		pg	Recovery (%)	pg	Recovery (%)
2,3,7,8-TeCDD	80	74	92	70	87
1,2,3,7,8-PeCDD	400	412	103	377	94
1,2,3,4,7,8-HxCDD	400	434	109	335	84
1,2,3,6,7,8-HxCDD	400	413	103	392	98
1,2,3,7,8,9-HxCDD	400	416	104	377	94
1,2,3,4,6,7,8-HpCDD	400	418	105	399	100
OCDD	800	888	111	783	98
2,3,7,8-TeCDF	80	84	105	68	86
1,2,3,7,8-PeCDF	400	421	105	389	97
2,3,4,7,8-PeCDF	400	407	102	416	104
1,2,3,4,7,8-HxCDF	400	388	97	385	96
1,2,3,6,7,8-HxCDF	400	429	107	430	107
2,3,4,6,7,8-HxCDF	400	361	90	380	95
1,2,3,7,8,9-HxCDF	400	376	94	389	97
1,2,3,4,6,7,8-HpCDF	400	407	102	392	98
1,2,3,4,7,8,9-HpCDF	400	333	83	377	94
OCDF	800	698	87	746	93

Table 2. Deposition flux and ambient air PCDD/F concentrations measured in northern Taiwan.

	February 2007	March 2007
Sampling periods (days)	18	28
Total rain fall (mm)	162	228
PCDD/F dry deposition flux (pg-ITEQ/m <sup>2</sup> -day)	14.3	9.59
PCDD/F wet deposition flux (pg-ITEQ/m <sup>2</sup> -day)	9.44	5.65
Total PCDD/F deposition flux (pg-ITEQ/m <sup>2</sup> -day)	23.7	15.2
Atmospheric PCDD/F concentration (pg-ITEQ/m <sup>3</sup> )	0.152	0.063
Total suspended particle ( $\mu$ g/m <sup>3</sup> )	59.6	36.7

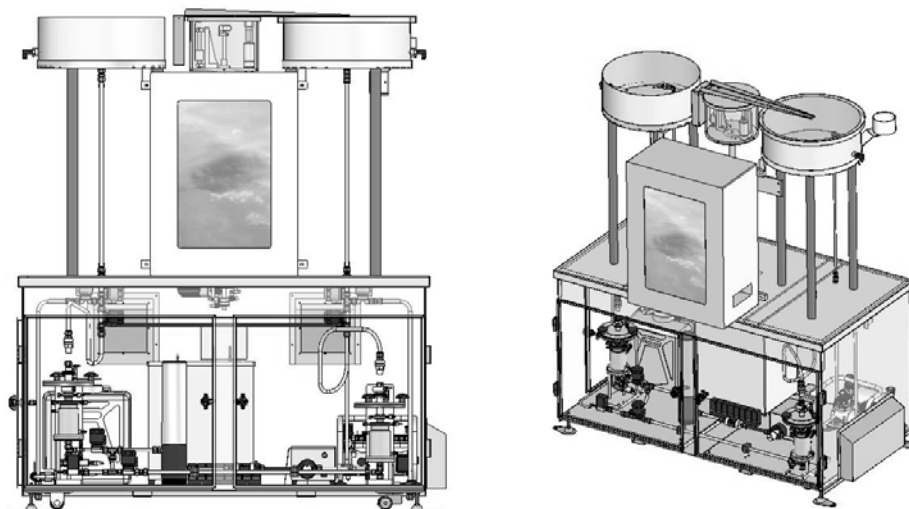


Figure 1 Schematic diagram of automated PCDD/F ambient air precipitation sampler.

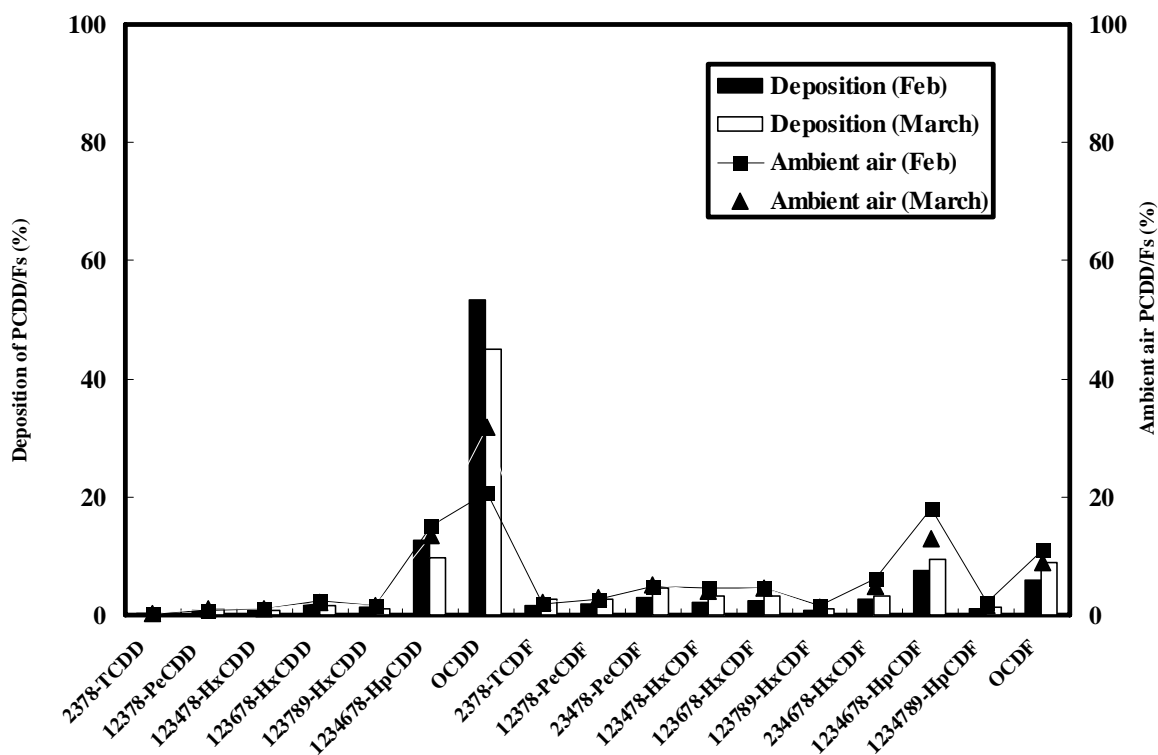


Figure 2 PCDD/F congener distribution in deposition and ambient air samples.