EVALUATION OF ATMOSPHERIC PCDD/F DEPOSITIONS VIA AUTOMATED AND TRADITIONAL WATER SURFACE SAMPLERS IN TAIWAN

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Introduction

Once emitted into the atmosphere, PCDD/Fs partition between the solid and vapor phases, undergo photochemical reactions [1,2] and enter other environmental compartments via wet and dry deposition[3,4]. Generally, direct particle phase flux measurements were carried out using an aerodynamically designed water surface sampler, which is assumed to capture deposited particles with 100% efficiency[5]. Furthermore, a water surface sampler was successfully used for particle phase flux collections of semi-volatile organic compounds including polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs)[6,7]. In addition, dechlorination rates differ for each dioxin congener[8]; hence, the congener and isomer distributions observed might differ from actual distribution patterns at the time of collection. Investigation of deposition samples provides information on the status of PCDD/F pollution loading. During their transport and deposition in the atmosphere, PCDD/Fs can be removed by chemical degradation mechanisms, including the reaction with OH radicals[9]. Potential sampling artifacts of main concern in sampling bulk deposition of PCDD/Fs include volatilization and photolysis. This study was motivated by the need to obtain more accurate data regarding the deposition flux of PCDD/Fs from the atmosphere by using an automated sampler and traditional cylindrical vessels, respectively. Evaluation of the resulting data may help to determine the possible underestimation of deposition flux recorded by the traditional cylindrical vessels.

Materials and methods

To measure PCDD/F deposits in Taiwan, four sampling sites of the campus of National Yang Ming University, Feitsui Reservoir, Sun Moon Lake, and Tsengwen River were selected in northern, central and southern Taiwan, respectively. Ambient air samples were collected using high-volume sampling trains (Shibata HV-700F). Both solid and vapor phases were collect by using fiber filters (Whatman quartz fiber filters, 8X10 inch) and polyurethane foam (PUF) plugs. The total volume of the air sampled was greater than 1,000 m^3 for a typical sampling duration of 7 days (gas flow rate: 100 L min^{-1}). In the same location, PCDD/F deposits were also collected with stainless steel cylindrical vessels to enable a comparison with the automated sampler. The deposition sampler used in this study was modified from an automated air precipitation trap sampler originally made in Japan[10]. For better comparison, the surface edges of the automated and traditional vessel samplers used in this study were manufactured with the same design. The ambient air and deposited PCDD/F samples were measured from 2008 to 2011. Sampling information and meteorological parameters are summarized in Table 1. In this study, only the seventeen 2,3,7,8-substituted PCDD/F congeners were analyzed with high-resolution gas chromatography /high-resolution mass spectrometry (Thermo DFS).

Results and discussion

The atmospheric PCDD/F concentrations were 4.90~39.0 (n=10), 6.11~24.3 (n=7) and 3.93~18.3 (n=6) fg I-TEQ/m^3 by the ambient air sampler, respectively, measured in northern, central and southern Taiwan. In some Asian countries, like Korea and Japan, the atmospheric PCDD/F concentrations in the urban area ranged from 28 to 120 fg I-TEQ/m^3 [11,12]. Our previous study[13] also indicated that the atmospheric PCDD/F concentrations measured in the urban area in Taiwan ranged from 20 to 110 fg I-TEQ/m^3. Compared to ambient air sampling, the depositional samples with long sampling duration have the characteristics of higher representation and stability. Table 1 indicates that the PCDD/F deposition flux collected. Results are shown the PCDD/F deposition flux collected by the automated PCDD/F deposition sampler was significantly higher than the traditional cylindrical (p value=0.037). Hence, we consider that the difference of PCDD/F deposition flux between those two samplers collection is significant. Compared to the atmospheric deposition fluxes of PCDD/Fs measured in other Asian countries, the PCDD/F deposition flux measured in Taiwan was not high. However, the PCDD/F

deposition flux in winter was significantly higher than that in summer. Table 1 also shows that the ratios of total PCDD/PCDF to TEQ flux obtained from the automated and traditional samplers were quite different. The ratio of mass to TEQ flux obtained with the automated sampler (33±14, n=27) was substantially lower than that obtained with the traditional sampler (42±30, n=27). This may be attributed to the fact that low-chlorinated PCDD/Fs with high toxicity vary significantly between the two types of samplers, leading to the different ratios of mass to TEQ flux as measured by the two samplers. Figure 1 demonstrates the congener pattern of PCDD/Fs in ambient air and atmospheric deposition (collected by automated and traditional sampler). The results reveal that the highest distribution of PCDFs (75%) was observed in the vapor-phase ambient air sample. Increased distributions of PCDDs were observed in the samples of aerosols and atmospheric deposition. Generally, PCDDs are primarily distributed in the solid phase in ambient air; therefore, deposited particles collected in the atmosphere enhance the PCDD distribution. The results also indicate that the high-chlorinated PCDD/Fs dominate the congener distribution of the PCDD/Fs deposition flux in both samplers while OCDD is the major congener in deposition. However, the deposition fluxes of the 17 congeners collected by the automated sampler are all significantly higher than those gathered by the traditional sampler. The most significant difference between the automated sampler and the traditional one is that the automated sampler features a mechanism which can immediately take particles into the sampling system through eddy action. The traditional sampler needs to be placed outdoors for one entire month before a sample collection is complete. The difference between these two sampling methods can be ascribed to sunshine causing photolysis and re-volatilization of PCDD/Fs in the collected samples. The PCDD/F deposition fluxes collected with the automated sampler and the traditional one are compared and expressed as the relative difference of the deposition flux. During the summer season (June to August), the average PCDD/F deposition flux (3.72±2.6 pg I-TEQ/m^2/day, n=7) collected with an automated PCDD/F sampler is 1.8 times higher than that sampled with cylindrical vessels (2.11±1.5 pg I-TEQ/m^2/day, n=7). However, the relative difference of the PCDD/F deposition flux between automated (11.8 pg I-TEQ/m^2/day, n=4) and cylindrical vessels (8.08 pg I-TEQ/m^2/day, n=4) measurement is less than 18% during the winter season (November to January). Figure 2 demonstrates the relative difference of PCDD/F deposition fluxes between the measurements of automated and traditional samplers in northern, central and southern Taiwan. The relative difference (58±48%) of deposition flux measured in southern Taiwan was significantly higher than that observed in northern (50±24%) and central (52±19%) Taiwan. Table 1 indicates that the average ambient air temperature was 20.6±4 ^{o}C, 22.8±3 ^{o}C, 20.4±2 ^{o}C and 25.0±4 ^{o}C during the sampling periods measured in northern, central and southern Taiwan, respectively. In general, the temperature in ambient air significantly affects the evaporation of organic compounds. The vapor pressure of PCDD/F congeners increases as the temperature increases. It also results in higher fractions of PCDD/F congeners being vaporized from the traditional sampler, therefore, the photolysis and evaporation may influence the PCDD/F deposition fluxes collected by the two types of different samplers. Figure 3 demonstrates that the relative difference in low-chlorinated PCDD/Fs was higher than that of high-chlorinated PCDD/Fs, and the relative difference in the 17 congeners was largest in southern Taiwan. The changes in 2,3,7,8-TeCDD and TeCDF were significantly higher, ranging from 122% to 134% measured in southern Taiwan. The causes leading to a higher relative difference in the low-chlorinated PCDD/Fs were related to the difference in the half-lives of PCDD/Fs with different chlorination levels[14]. As the half-life of low-chlorinated PCDD/Fs is shorter than that of high-chlorinated PCDD/Fs, low-chlorinated PCDD/Fs are more likely to be influenced by photolysis[15].

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References:

1. Tysklind M, Lundgren K, Rappe C. (1993) *Chemosphere*. 27(4): 535-546
2. Brubaker WW, Hites RA. (1998) *J Phys Chem A*. 102 (6): 915–921
3. Koester CJ, Hites RA. (1992) *Environ Sci Technol*. 26 (7): 1375–1382
4. Ogura I, Masunaga S, Nakanishi J. (2001) *Chemosphere*. 44(6): 1473–1487
5. Odabasi M, Tasdemir Y, Vardar N, Sofuoglu A, Holsen TM. (1999) *Environ Sci Technol*. 33 (3): 426–434
6. Odabasi M, Sofuoglu A, Holsen TM. (2001) *Atmos Environ*. 35(9): 1655-1662
7. Tasdemir Y, Odabasi M, Holsen TM. (2007) *Chemosphere*. 66(8): 1554–1560

8. Kim M, O'Keefe PW. (2000) *Chemosphere*. 41(6): 793-800
9. Dobbs AJ, Grant C. (1979) *Nature*. 278: 163-165
10. Matsumura T, Shamoto H, Ohtsuka T Morita M. (1999) *Organohalogen Compd*. 40: 211-214
11. Lee SJ, Park H, Choi SD, Lee JM, Chang YS. (2007) *Atmos Environ*. 41(28): 5876–5886
12. Makiya K. (1999) *Organohalogen Compd.* 43: 217-220
13. Chi KH, Lin TY, Ou Yang CH, Wang JL, Lin NH, Sheu GR, Lee CT. (2010) *Environ Sci Technol*. 44 (8): 2954–2960
14. Sinkkonen S, Paasivirta J. (2000) *Chemosphere*. 40(9-11): 943-949
15. Halsall CJ, Coleman PJ, Jones KC. (1997) *Chemosphere*. 35(9): 1919-1931

Table 1 Sampling information and deposition flux of PCDD/Fs in Taiwan.

Sampling location		*Sampling periods*	*Cylindrical vessel*	*Automated sampler Duration (days)*		*PCDD/F deposition flux collected by cylindrical vessels*	*PCDD/F deposition flux collected by automated sampler*	*Average air temperature*	*Rainfall*
			Duration (days)	*Sunny day*	Rainy day	pg/m^2/day (pg I-TEQ/m^2/day)		^{o}C	mm
Northern Taiwan	*Rural area*	*Mar. 2008*	*23*	*19.3*	3.8	135 (3.61)	252 (11.8)	16.5	189
		Apr. 2008	*25*	*22.1*	2.7	118 (3.33)	215 (8.40)	20.0	260
		May. 2008	*30*	*25.8*	4.1	171 (7.08)	183 (10.1)	22.2	474
		Jun. 2008	*29*	*26.2*	2.8	327 (4.91)	430 (8.09)	24.9	396
		Jul. 2008	*31*	*28.3*	2.7	36.0 (1.37)	369 (6.65)	26.8	245
		Aug. 2008	*30*	*28.8*	1.5	84.6 (2.67)	131 (3.11)	26.8	139
		Sep. 2008	*24*	*16.8*	7.6	69.2 (2.10)	132 (4.52)	25.3	1,220
		Oct. 2008	*29*	*26.7*	2.1	156 (4.48)	163 (5.02)	26.0	47
		Nov. 2008	*27*	*23.4*	3.4	312 (7.57)	364 (8.15)	21.5	117
		Dec. 2008	*17*	*16.5*	0.5	471 (19.3)	495 (21.0)	18.4	9.60
	Urban area	*Sep. 2011*	*32.8*	*25.2*	1.7	24.7 (1.59)	74.5 (4.45)	27.2	24.9
		Oct. 2011	*29*	*26.6*	2.3	194 (3.25)	61.6 (3.10)	21.3	118
		Nov. 2011	30.1	16.1	1.9	70.3 (3.79)	152 (9.70)	20.7	174
		Dec. 2011	31.8	22.7	1	46.1 (1.65)	130 (8.27)	15.3	86.2
Central Taiwan		*Feb. 2009*	19	18.7	0.1	41.5 (1.15)	146 (3.32)	18.3	3.0
		Mar. 2009	29	27.6	1.5	37.9 (1.17)	30.6 (1.32)	17.4	154
		Apr. 2009	30	27.8	2.0	86.6 (1.88)	151 (3.43)	18.1	191
		May. 2009	31	30.3	0.5	40.3 (1.29)	39.5 (1.56)	20.5	70.2
		Jun. 2009	29	27.6	1.3	37.5 (0.98)	69.0 (2.63)	22.0	283
		Jul. 2009	23	23.1	0.1	151 (2.95)	71.2 (1.19)	22.9	24.4
		Aug. 2009	19	18.5	0.5	30.0 (1.19)	99.1 (2.70)	23.3	88.7
Southern Taiwan		*Feb. 2010*	19	18.0	1.2	27.2 (0.62)	25.0 (0.98)	19.6	60.6
		Mar. 2010	30	29.4	0.3	23.0 (0.77)	32.3 (1.61)	22.7	9.2
		Apr. 2010	31	29.9	1.3	37.5 (0.78)	34.8 (1.12)	23.2	59.6
		May. 2010	27	25.3	1.7	70.3 (1.32)	94.7 (2.19)	27.4	104
		Jun. 2010	30	27.3	2.6	34.2 (0.73)	54.6 (1.69)	28.0	254
		Sep. 2010	30	27.4	2.8	429 (2.42)	230 (3.46)	28.3	231

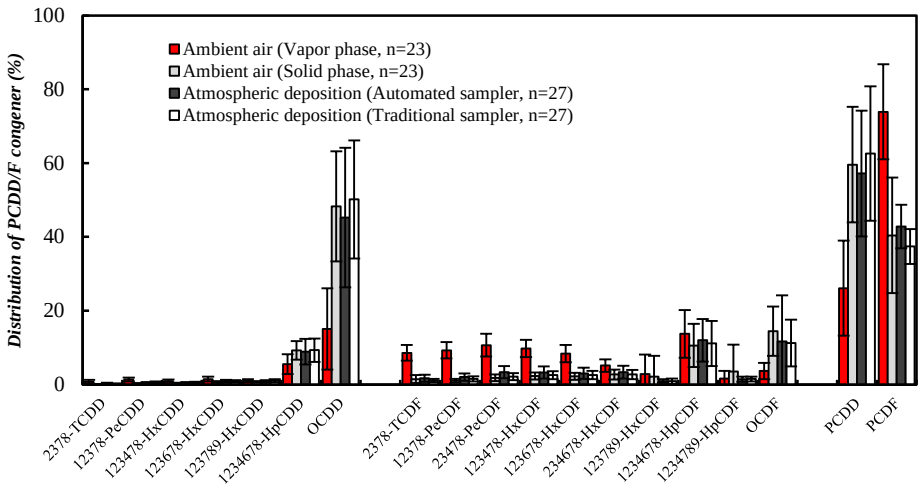

Fig. 1. Congener distribution of PCDD/Fs in ambient air and deposition flux measured by automated sampler and traditional cylindrical vessels.

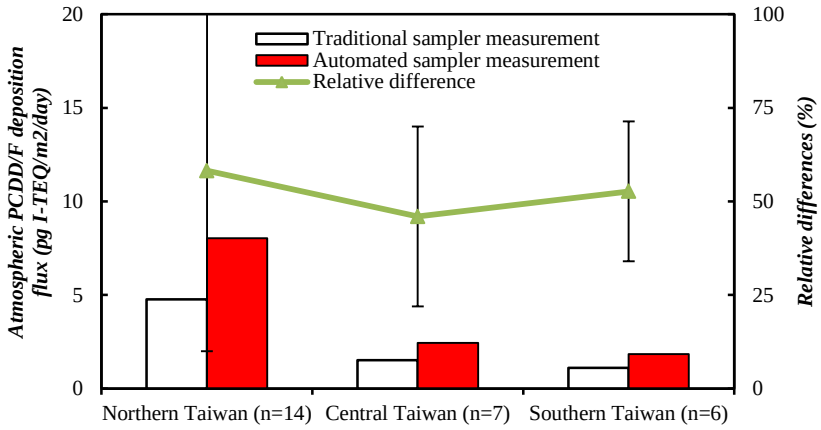

Fig. 2. The relative difference in PCDD/F deposition fluxes between the measurements obtained using the automated sampler and the traditional cylindrical vessels in northern, central and southern Taiwan.

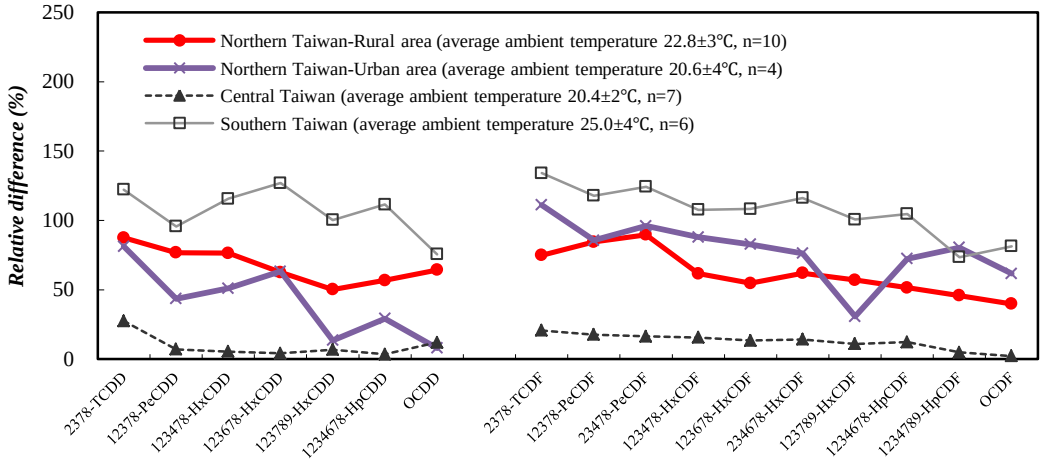

Fig. 3. The relative difference of the seventeen 2,3,7,8- chlorinated PCDD/Fs deposition fluxes between the measurements conducted by automated sampler and traditional cylindrical vessels in northern, central and southern Taiwan.