GAS/PARTICLE PARTITIONING OF POLYCHLORINATED DIBENZO-*P*-DIOXINS AND DIBENZOFURANS IN AMBIENT AIR AROUND MUNICIPAL WASTE INCINERATOR IN TAINAN, TAIWAN

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are derived from a variety of combustion process which likes municipal and industrial waste incinerator, automobiles, and steel mill. The atmosphere is the dominant transport pathway for PCDD/Fs to enter the environment. The fate of PCDD/Fs in the atmosphere is primarily governed by their gas-particle partition. It usually has an important effect on deposition process, photolysis and reaction with OH radicals[1]. Since the atmospheric input is of importance for the different phase of PCDD/Fs to the terrestrial and aquatic food chains and compartments, it is necessary to study how the levels and the gas/particle partitioning of PCDD/Fs during their transport . The gas/particle partitioning of PCDD/Fs depends upon the available particle properties, the ambient temperature, the relative humidity and the compound's subcooled liquid vapor pressure[2]. Therefore, the aims of this study were to measure the gas and particle-bound concentrations of PCDD/Fs in the atmosphere near the MWI using a PUF PS-1 sampler, and to predict their partitioning behaviour using the Junge-Pankow and Yamasaki adsorption model[3-5].

Methods and Materials

Selection of sampling sites Industrial Sources Complex short-term model (ISCST3) is applied to estimate the annual averaged ambient PCDD/Fs concentrations by measured PCDD/Fs data emitted from Cheng-Xi municipal waste incinerator in Tainan and local meteorological data from 1996-1999. Surfer6.02 and geographic information system were used to draw the equal concentration lines of PCDD/Fs around MWI. According to the distribution of annual averaged ambient PCDD/Fs concentrations, four elementary schools within the modeled impact and un-impact zone were selected as sampling sites (Figure 1). Cheng-Xi MWI has operated since 1999 with a treatment capacity of 900 tons/d.

Sampling 24 seasonal gas and particle-bound PCDD/Fs were collected at a flow rate of 0.225±10% m^3/min with PS-1 samplers consisting of a quartz fiber filter (QFF) backup by a polyurethane foam (PUF) cartridge at four sites concurrently from December 2000 to September 2002. The PS-1 samplers were calibrated by orifice calibrator in the beginning and the end of each sampling period and showed no variation in the air flow over the sampling period. According to the preliminary test (sampling time set at 24, 48, 72 hours), the 17 PCDD/Fs patterns of particle phase and gas phase were not changed and the gas/particle partitioning of PCDD/Fs of 72 hours samples were the same as 24 hours samples. The sampling time was set as 72 hours .

Pretreatment and Analysis Sample preparation was done according to the method TO-9A developed by USEPA. QFF and PUF sample were separately spiked with a cocktail of $^{13}C_{12}$-labeled PCDD/Fs and extracted for 24 h with toluene by Soxhlet extractor. The extracted sample was washed with H_2SO_4 and then extracted with hexane. Sample cleanup was accomplished with acidic silica-gel column, alumina

column and activated carbon column, and concentrated with N_2 gas. $^{13}C_{12}$-labeled PCDD/Fs recovery standards were spiked before mass analysis. The quantification of PCDD/Fs was performed with HRGC/HRMS with a Rtx-5MS column (60 m, 0.25mm i.d. 0.25 μm film thickness). Seventeen toxic 2,3,7,8-substituted congeners were quantified. The peaks were quantified when the criteria were met: (1) isotope ratio within ±15% of theoretical values and (2) signal/noise ratio ≥2.5. Recoveries of $^{13}C_{12}$-labeled PCDD/Fs internal standards in samples ranged from 40 to 130%.

Results and discussions

Table 1 showed the yearly averaged concentration in this study was 2.79 pg/Nm^3(0.169 pg I-TEQ/m^3) and ranged from 0.4 to 7.81 pg/Nm^3(0.026 0.37 pg I-TEQ/m^3). In seasonal variation, the highest concentration of PCDD/Fs was measured in spring (0.269 pg I-TEQ/m^3), and the lowest concentration was in summer (0.068 pg I-TEQ/m^3), and showed consistent at four sampling sites. Besides, the average particle fraction of PCDD/Fs was 0.604 and ranged from 0.442 to 0.767, which contains a significant portion of atmosphere burden. Table 2 showed the higher chlorinated homologues and lower temperatures give a higher particle bound fraction whether PCDDs or PCDFs. The percentage of particle bound fraction of homologues of PCDD/Fs for different countries and temperatures was showed the same phenomenon[6] (Table 3). The average temperatures during sampling periods of different seasons were 30.2 in summer and 21.9 in winter. Gas/particle partitioning of PCDD/Fs seemed to depend on the temperature and vapor pressure of the compounds[7].

An equation developed by Junge-Pankow and Yamasaki[3-5] has been successfully used to describe gas-particle partitioning as follows:

$$K_p = \frac{F/TSP}{A}$$

where K_p (m^3/μg) is temperature dependent partitioning constant, TSP (μg/m^3) is the concentration of total particulate matter, and F (ng/m^3) and A (ng/m^3) are particulate associated and gaseous concentrations of PCDD/Fs, respectively. The K_p value is widely used to investigate gas-particle partitioning. The relationship between logarithm subcooled liquid vapor pressure (log P_L^o) and log K_p is shown in Figure 2. Beside summer 2001, the slopes of the plot were ranged from -0.595 to -0.8775 and the values were similar to other studies[8-9]. In summer 2001, the log K_p –log P_L^o regression coefficient (R^2=0.6827) was lower than other seasons and the slopes were different from the other samples, because there was raining happened during sampling. And particle-phase of PCDD/Fs was washed out by the rain. From above results, we could conclude that the P_L^o indeed has a great influence on the gas-particle distribution. This was in aggrement with theoretical expectation and other reports from the literature. And it also explained why lower chlorinated PCDD/Fs with higher P_L^o would easily exist in gas-phase and the higher chlorinated PCDD/Fs with lower P_L^o would easily adhered to particle-phase.

Acknowledgement

Reference

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Table 1 The average and range of PCDD/Fs levels in ambient air at different seasons.

	All the year	spring	summer	autumn	winter
PCDD/Fs levels (pg/Nm^3)	2.80 (0.4-7.81)	5.26 (3.02-7.81)	0.96 (0.4-1.41)	3.82 3.33-4.26	2.89 (1.87-4.09)
PCDD/Fs levels (pg I-TEQ/Nm^3)	0.169 (0.026-0.370)	0.269 (0.164-0.370)	0.068 (0.026-0.105)	0.232 (0.205- 0.258)	0.188 (0.104-0.260)
Particle fraction of PCDD/Fs according to compound abundance	0.604 (0.442-0.767)	0.571 (0.5-0.684)	0.551 (0.442- 0.684)	0.603 (0.561-0.637)	0.674 (0.596-0.767)

Table 2 The averaged particle fraction of homologue of PCDD/Fs in ambient air at different seasons.

	All the year	spring	summer	autumn	winter
F4	7.0%	3.7%	9.5%	4.4%	10.5%
F5	14.7%	8.0%	10.0%	13.6%	27.4%
F6	39.1%	31.3%	31.5%	39.0%	54.4%
F7	68.0%	68.7%	53.8%	68.7%	80.7%
F8	90.7%	94.0%	82.0%	91.5%	95.3%
D4	17.9%	7.6%	32.8%	12.7%	18.5%
D5	16.0%	4.4%	15.7%	16.1%	27.9%
D6	41.8%	31.6%	32.4%	45.4%	57.9%
D7	77.9%	82.5%	63.7%	78.0%	87.5%
D8	89.9%	96.2%	78.2%	94.6%	90.5%
Temperature( )	-	25.0	30.2	25.3	21.9

Table 3 The proportion of particle bound PCDD/Fs in ambient air of different countries and temperatures.

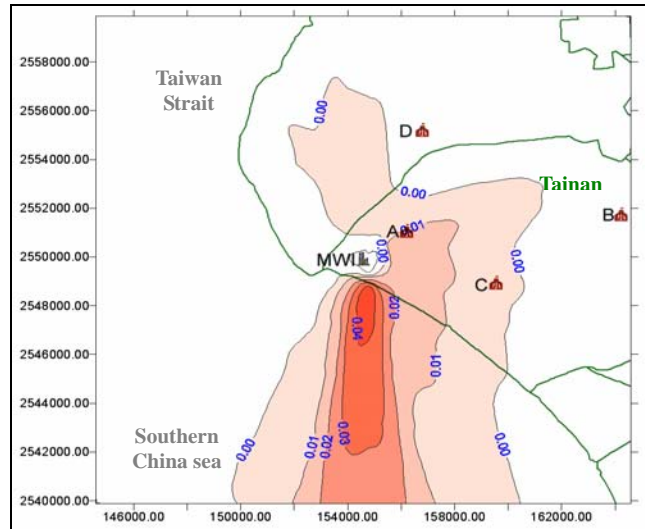| Homologue	% particle bound [p/(g+p)]					
	Bloomington	Stockholm	Augsburg	Augsburg	Tainan	Tainan
F4	9	29	59	14	8	6
F5	37	63	94	29	21	12
F6	74	89	99	52	47	37
F7	92	98	>99	80	77	64
F8	95	100	>99	>86	95	88
D4	13	61	76	20	15	19
D5	33	70	93	37	20	16
D6	78	91	99	59	49	41
D7	97	98	>99	>90	86	73
D8	99	100	>99	>98	92	89
Temp	-	-	0	20	< 25	> 25

Figure 1 Equal concentration lines of PCDD/Fs and sampling sites near Cheng-xi MWI   concentration unit: 10^{-3}pg I-TEQ/Nm^3, A: Tu-Cheng , B: An-Dian, C: Xian-Gong and D: Jian-Gong
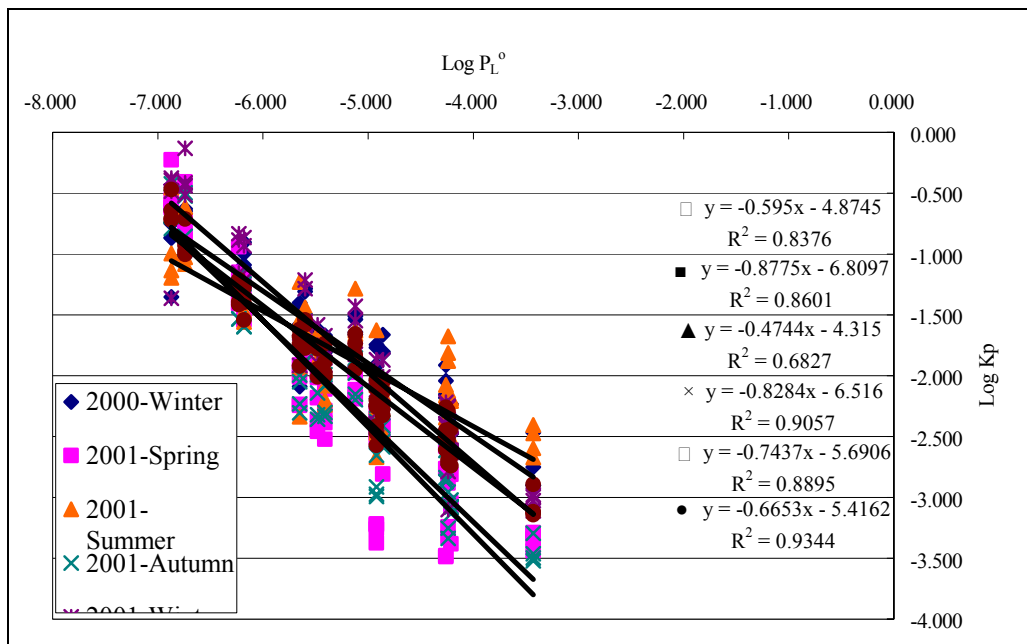

Figure 2 Log Kp - log P_L^o plot for 2, 3, 7, 8-substitued PCDD/Fs.