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SIZE DISTRIBUTION OF PARTICLE-BOUND POLYCHLORINATED DIBENZO-*P*-DIOXINS AND DIBENZOFURANS IN AMBIENT AIR AROUND MUNICIPAL WASTE INCINERATOR IN TAINAN, TAIWAN

Po-Chin Huang and Ching-Chang Lee

Department of Environmental and Occupational Health, Medical College, National Cheng Kung University, 138 Sheng-Li Rd. Tainan 70428 Taiwan ROC

Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are well known persistence organic pollutants (POPs). They are characterized as persistent, semi-volatile and toxicologically significant trace organic contaminants. Municipal waste incinerator (MWI) is one of the important sources of PCDD/Fs as we known. Fine particle-bound PCDD/Fs emitted from incinerators can be transported over long distances and are distributed into various environmental components[1, 2]. Hence, atmospheric deposition is the main pathway of PCDD/Fs delivered into ecosystem and then via food chain bio-accumulated to human. Particle size plays an important role on the transport and deposition processes of particle-bound contaminants. Many studies have reported that particle-bound polycyclic aromatic hydrocarbons (PAHs) were predominantly associated with small particles, especially on fine particles (d_{ae}<2μm)[3, 4, 5]. Few information of distribution of PCDD/Fs with the respect to particle size was reported on this subject. Due to the influence of transport and removal mechanism of PCDD/Fs and contribution of human exposure to PCDD/Fs through inhalation, size distribution of particle-bound PCDD/Fs in the atmosphere is the main issue to explore. The aim of this study was to investigate the size distribution of particle-bound PCDD/Fs in the atmosphere near the MWI using a five stage multijet cascade impactor back up by quartz fiber filter (QFF).

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 Tu-Cheng, An-Dian, Xian-Gong and Jian- Gong elementary school near Cheng-Xi MWI 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 Airborne particles were collected using a five-stage cascade impactor and high-volume air sampler backed up by quartz fiber filter at four sites during October to December 2001. Volumetric sampling flow rate was set on 1.13 m^3/min 40 cfm and samplers were calibrated by orifice calibrator in the beginning and the end of each sampling period. Sampling time was 144-216 hours and quartz fiber filters were replaced every 72 hours. The particles were separated into the following size ranges: <0.49, 0.49–0.95, 0.95–1.5, 1.5–3.0, 3.0–7.2, and >7.2 μm in aerodynamic diameter (d_{ae}). Before sampling, quartz fiber filters were baked at 400 for 5h and equilibrated for 48 h in a desiccator.

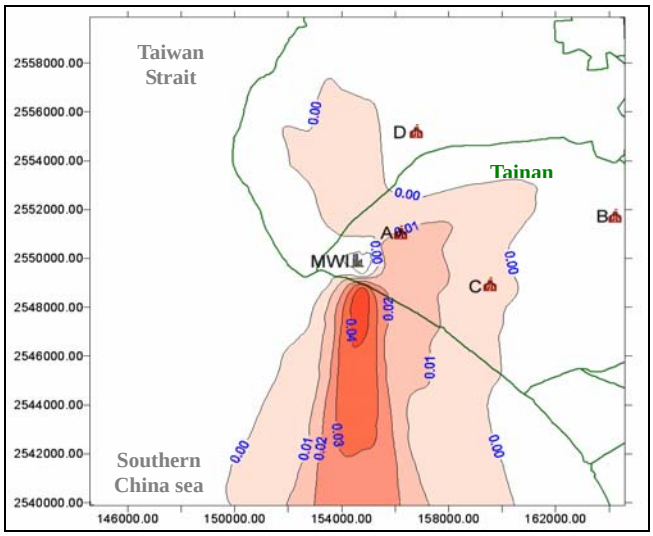

Figure 1 Equal concentration lines of PCDD/Fs and sampling sites near Cheng-xi MWI concentration unit: 10^{-3}pg I-TEQ/Nm^3, A: Tu-Cheng , B: An-Dian, C: Xian-Gong and D: Jian-Gong

Pretreatment and Analysis Sample preparation was done according to the method TO-9A developed by USEPA. Each sample was 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 high-resolution gas chromatography/high-resolution mass spectrometry (Hewlett-Packard Model 6890 plus/Micromass VG M271) 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 40-130%. The levels were expressed in 2, 3, 7, 8-TCDD Toxic Equivalent Factors (I-TEFs) for PCDD/Fs.

Results and discussions

Table 1 shows the particle concentration with respect to particle size in each sample. The total suspended particulate (TSP) concentrations ranged from 33.1 to 54.7μg/m^3, which is within a lower level. So, even the particle rebounding are unavoidable, the influence of particle size redistribution is minor. The particle size distribution was bimodal distribution and very similar for four sites (Figure 2). The largest concentration of particle was collected in the back filter (d_{ae}< 0.49μm), and over 55% of particles were with particle size < 1.5 μm. In general, atmospheric particle in urban air have two major peak in their distribution, one peak consist of large particles that can be mostly attributed to natural sources such as soil particle, and the other peak corresponds to small particles(d_{ae}< 1μm), which are mainly produced by combustion sources such as municipal waste incinerators[6]. The measured size distribution data from all of the sampling sites showed the characteristic pattern of urban particles in this study.

Table 1 Particle concentrations with respect to particle size (μg/Nm^3)

Stage	Range(μm)	A1	B1	C1	D1	A2	B2	C2	D2	A3	B3	C3	D3
1	> 7.2	6.5	6.7	3.1	5.4	4.7	6.2	4.4	3.6	5.2	7.8	6.2	6.1
2	7.2~3	12.3	12.3	7.8	11.2	8.6	11.4	8.8	7.5	8.0	12.1	10.2	9.9
3	3~1.5	5.4	5.7	4.5	4.6	3.7	4.4	3.5	3.6	3.9	4.1	4.4	3.8
4	1.5~0.95	4.4	4.6	3.3	4.0	4.3	5.5	3.7	3.8	2.7	3.5	3.1	3.1
5	0.95~0.49	3.9	4.2	3.0	4.0	5.3	7.8	5.4	5.4	3.2	4.9	2.8	3.6
BF	< 0.49	21.9	21.1	17.6	16.9	15.8	15.6	11.5	10.8	10.1	16.2	16.5	13.1
Total	-	54.5	54.7	39.1	45.9	42.4	51.0	37.4	34.8	33.1	48.7	43.2	39.6

Table 2 PCDD/Fs concentration with respect to particle size (pg/Nm^3)

Stage	Range (μm)	A1	B1	C1	D1	A2	B2	C2	D2	A3	B3	C3	D3
1	>7.2 μm	0.034	0.012	0.012	0.012	0.010	0.029	0.023	0.010	0.011	0.010	0.028	0.006
2	7.2~3	0.007	0.026	0.036	0.093	0.018	0.033	0.034	0.014	0.010	0.021	0.046	0.018
3	3~1.5	0.021	0.019	0.025	0.020	0.029	0.025	0.016	0.014	0.006	0.014	0.022	0.011
4	1.5~0.95	0.039	0.041	0.023	0.041	0.059	0.051	0.026	0.023	0.038	0.028	0.029	0.020
5	0.95~0.49	0.080	0.086	0.048	0.090	0.068	0.119	0.053	0.049	0.074	0.089	0.063	0.050
BF	<0.49	0.500	0.488	0.441	0.496	0.467	0.649	0.381	0.308	0.251	0.451	0.428	0.304
Total conc (pg/Nm^3)		0.681	0.673	0.585	0.752	0.652	0.906	0.533	0.418	0.389	0.614	0.616	0.410
Total TEQ (pg I-TEQ/Nm^3)		0.013	0.012	0.011	0.013	0.023	0.024	0.012	0.010	0.011	0.018	0.016	0.012
PCDFs/PCDDs		1.8	3.0	3.3	2.7	1.9	3.8	0.7	3.3	2.7	5.0	4.5	4.3
<1.5 μm / Total TEQ		85%	80%	80%	78%	91%	89%	88%	88%	88%	89%	88%	88%

Table 2 shows the concentration of PCDD/Fs with respect to particle size in each sample. PCDD/Fs concentration ranged from 0.389 to 0.906 pg/ Nm^3 (0.011 to 0.018 pg I-TEQ/Nm^3). The size distribution of particle-bound PCDD/Fs is uni-modal distribution, which is different from particle distribution. The largest amount of particle-bound PCDD/Fs was collected in the back filter (d_{ae}<0.49μm), and over 83% of particle-bound PCDD/Fs were with particle size <1.5 μm in the all sampling sites. The fraction of PCDD/Fs concentration was higher than that of particle concentration for d_{ae}< 0.95μm, on the contrary, the reverse point was observed for d_{ae}>0.95μm (Figure 3). The distribution of particle-bound PCDD/Fs was toward fine particles in comparison with the particle distribution. It is possible that there are more PCDD/Fs on fine particles deriving from incinerator, which is consistent with previous studies[3].

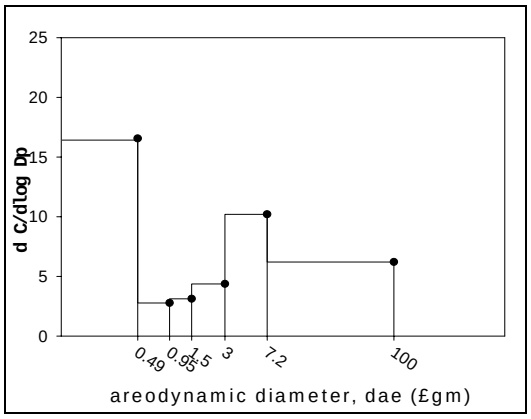

Figure 2 Distribution of TSP with respect to particle size (site A).

Table-2 also shows the TEQs with respect to particle size. PCDD/Fs on particles of d_{ae}< 1.5 μm mostly contributed to the toxicity, contributing 78-91% of the total TEQ. The ratio of PCDFs/PCDDs in the total TEQs were illustrated 1.8-5.0, which indicated the PCDFs concentration were two times higher than PCDDs, in the all sampling sites beside C2. The result is similar to the previous investigation in the suburban residential area near an incinerator within 3 km [6].

Interestingly, there is a trend between distributions of particle-bound PCDD/Fs and atmospheric temperature. Figure 4 shows that the proportion of PCDD/Fs on particles of d_{ae}< 0.49μm decreased with decreasing atmospheric temperature. Otherwise, the PCDD/Fs levels of 0.49-0.95 and 0.95-1.5μm were increased with temperature. This phenomena that particles of d_{ae} <0.49μm grow up to 0.49-0.95μm and 0.95-1.5μm with temperature decreasing could be explained as the condensation of water vapor and gas phase pollutant[7, 8]. So, the particles with d_{ae}< 0.49μm could be grown up to particles with d_{ae} in the range of 0.49-0.95 and 0.95-1.5μm. Therefore, the difference of the proportion of PCDD/Fs in different size ranges with decreasing ambient temperatures is due to grow up of fine particle.

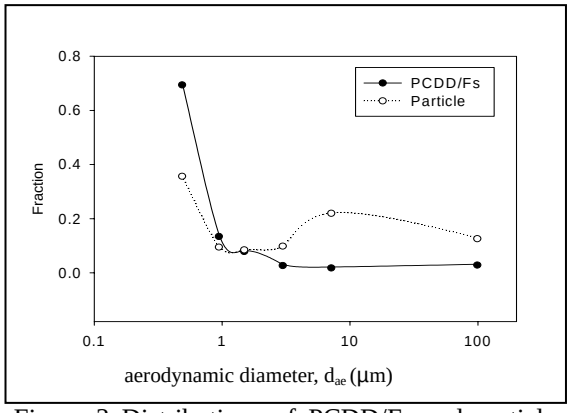

Figure 3 Distributions of PCDD/Fs and particles with respect to particle size (site A).

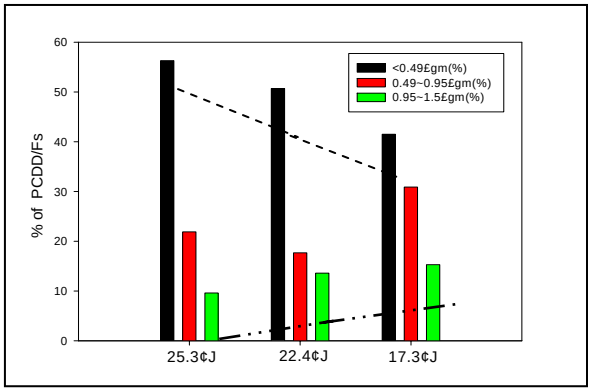

Figure 4 Relationship between the proportions of PCDD/Fs in different size particles with ambient temperature

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