CHEMOMETRIC STUDY OF SOURCE AND AMBIENT PCDD/FS AROUND A MODERN MUNICIPAL SOLID WASTE INCINERATOR

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Introduction

Since Olie first detected the PCDD/Fs emission from MSWI in 1977[1]. The emission of PCDD/Fs from municipal solid waste incinerators (MSWIs) became a serious environmental concern worldwide. The determination of the relation between the source and ambient PCDD/Fs around the MSWI evolve into a controversial and challenging issue. The Hsinchu MSWI locating on the seashore still faces the same arguments. Even though it is equipped with modern air pollution control device consists of lime plus activated carbon injection, a semi-dry scrubber, and a bag-house filter. In this work we present the PCDD/Fs measured in ambient air and soil as well as in the source, i.e., stack gas, of the fully operational Hsinchu MSWI in 2001, and compare the results to those measured during the trial burns in 2000[2]. Chemometric methods, including principal component analysis (PCA) and hierarchical cluster analysis (HCA), are used to compare the PCDD/Fs distribution with an aim to decipher the relationship between the source and ambient PCDD/Fs.

Methods and Materials

During the trial burn of Hsinchu MSWI, a total of 10 ambient air samples were collected in March 2000 in a period of two weeks from various sampling sites distributed through the city (site A, B, E, F, G, H, I, J, K and L). Figure 1 shows the sampling sites distribution around the Hsinchu city in Taiwan. They are represented using dark circles with the alphabet. The two concentric circles around the MSWI marked with star represents a radius of 2.5 and 5 Km, respectively. In March 2001(winter), 4 ambient air samples and 4 soil samples were collected at the sampling sites A, B, C and D, respectively. At the same time 2 stack gas samples were also collected. The Hsinchu MSWI was in fully operation. In June 2001 (summer), 2 indoor air samples (site M and N, in the office of the MSWI) and 1 outdoor air sample (site O, in the filed of the MSWI) were collected. In August 2001(summer), 1 ambient air sample and 1 soil sample were collected at each sampling site A, B, C and D, respectively. No stack samples were collected then.

US EPA Compendium Method TO-9A was followed for ambient air sampling and analysis. The sample was collected in a glass fiber filter followed by a polyurethane foam plug using a Graseby-Anderson PS-1. The representative soil sample was obtained by collecting and mixing five different aliquot samples from a 10 m^2 area around the sampling site. Sufficient amount of soil sample were collected to assure that *ca.* 500 g of homogeneous soil was obtained after sieve through a 60-mesh screen. US EPA Method 1613B was followed for soil analysis. The samples were Soxhlet extracted in 300 ml toluene for 18 to 24 hours followed by rotary evaporation. The concentrates were then treated with sulfuric acid, acid silicon gel, acid alumina and carbon column for clean up. A VG AutoSpec Ultima HRGC-HRMS with a dynamic mass resolution of 10,000 coupled to a HP 5890 GC system using a 60-m DB5-MS column were used for instrumental analyses. PCA and HCA were executed using the Statistica 6.0 statistical software.

Results and Discussion

The PCDD/Fs levels in ambient air and soil samples expressed using international toxic equivalent factors (I-TEF) are listed in Table 1. The dioxin levels in ambient air samples collected in year 2000 range from 0.058 pg-TEQ/m^3 to 0.127 pg-TEQ/m^3 with an average value of 0.085 pg-TEQ/m^3. The size of the circle in Fig. 1 is proportional to the ambient air dioxin level collected at that site. The circle distribution pattern in Fig. 1 indicates that the ambient air dioxin level reduced from the northeast to southwest direction, which accords well with the wind direction [2]. The dioxin levels in ambient air samples collected in March 2001 range from 0.088 to 0.113 pg-TEQ/m^3 with an average value of 0.103 pg-TEQ/m^3. Those collected in August 2001 have dioxin levels ranging from 0.071 to 0.101 pg-TEQ/m^3 with an average value of 0.080 pg-TEQ/m^3. The ambient air dioxin levels in Hsinchu from this study are at the same level as Germany (0.052 pg-TEQ/m^3)[3] and Spanish urban area (0.11-0.13 pg-TEQ/m^3)[4], but are lower than USA (0.17-0.35 pg-TEQ/m^3)[5] and Japan (0.25 pg-TEQ/m^3)[6].

The dioxin levels in soil samples collected in winter 2001 range from 1.29 pg-TEQ/g d.m. to 5.02 pg-TEQ/g d.m. with an average value of 3.03 pg-TEQ/g d.m.. Those collected in summer 2001 have dioxin levels ranging from 0.52 pg-TEQ/g d.m. to 1.97 pg-TEQ/g d.m. with an average value of 1.19 pg-TEQ/g d.m.. No significant difference in the PCDD/Fs levels in soil samples was observed, irrespective of the season and site variation. The soil dioxin levels in Hsinchu from this study are at the same level as USA (4 pg-TEQ/g d.m.)[5], Spain (1.08 pg-TEQ/g d.m.)[7] and Japan (7.1 pg-TEQ/g d.m.)[6], and tallied with the most severest regulations of Germany and Sweden[8], which are 5 and 10 pg-TEQ/g d.m., respectively.

The TEQ profiles of ambient air and soil samples collected in 2001 were investigated. For ambient air sample, similar TEQ profiles were obtained at all sampling sites, except that site D in summer had two times higher 2,3,7,8-TeCDD. For soil samples, dissimilar TEQ profiles were obtained. We have observed that concentration profiles varied with season. For winter air samples, the contributor in decreasing order is: OCDF, OCDD, 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,6,7,8-HpCDD. The order has drastically changed for summer air samples. The contributor in decreasing order is: 1,2,3,4,6,7,8-HpCDF, OCDD, 1,2,3,4,6,7,8-HpCDD and OCDF. For soil samples, OCDD was the sole major congener with more than 75 % concentration contribution. However, all TEQ and concentration profiles are dissimilar to those from the MSWI stack gas.

We have adopted two chemometirc methods to combine a large amount of variables into several underlying components, which summarize the systematic information and provide the major trends of the data. We used PCA to estimate possible similarities and/or discrepancies in concentration profiles of all data including 21 air, 8 soil and 2 stack gas samples collected during 2000 and 2001. Scatter plot of the factor loading with three principal components is shown in Fig. 2. The first, second and third principal component respectively explains 84.8 %, 11.4 % and 3.1 % of the total variance in Fig. 2. The total variance from the three principal components accounts for 99.3 %. The data points cluster into 6 groups as marked on the PCA plot. Group 1 comprises city air samples collected in 2000 excluding A, E and G. Group 2 comprises ambient air samples collected in winter 2001. Group 3 comprises ambient air sampled collected in summer 2001. All 8 soil samples assemble into group 4. The data points in group 5 and group 6 represents the indoor air samples and stack gas samples, respectively, from Hsinchu MSWI. HCA reveals the same conclusions. Both results from PCA and HCA show that concentration profiles of soil, ambient air and stack gas were classified into distinct categories. The stack gas profile was different to the profiles from soil and ambient air. The HCA results in data clusters of soil, ambient air and stack gas samples ling apart from each other, according well with the PCA results. We therefore conclude that the PCDD/Fs in the air and soil of Hsinchu City could not be dominantly attributed to the PCDD/Fs emission from the Hsinchu MSWI.

Table 1. The PCDD/F levels in ambient air and soil samples at each sampling site.

		Sampling site & TEQ									
Ambient Air (pg-TEQ / Nm^3)		A	B	E	F	G	H	I	J	K	L
	March 2000	0,127	0,063	0,107	0,070	0,090	0,081	0,058	0,095	0,084	0,100
		A	B	C	D						
	March 2001	0,113	0,104	0,106	0,088						
	August 2001	0,079	0,071	0,071	0,101						
		M	N	O							
	June 2001	0,103	0,085	0,106							
Soil (pg-TEQ / g d.m.)		A	B	C	D						
	March 2001	1,841	5,022	3,952	1,286						
	August 2001	0,524	0,648	1,971	1,631						

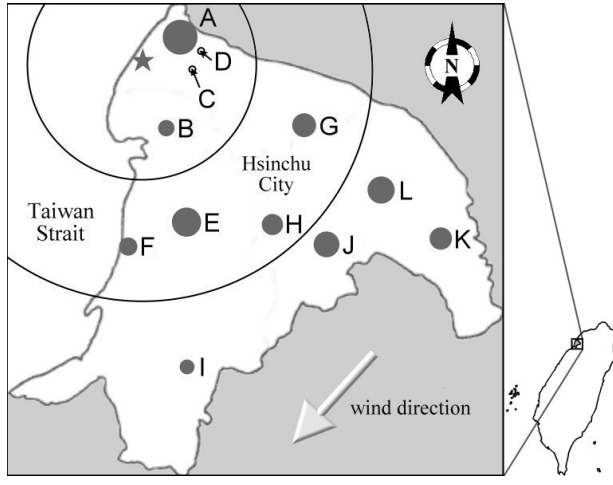

Figure 1. The sampling sites around Hsinchu city in Taiwan marked with dark circles. The size of the circles shows direct proportionality with the concentration of PCDD/Fs levels observed in respective sampling sites.

Acknowledgements

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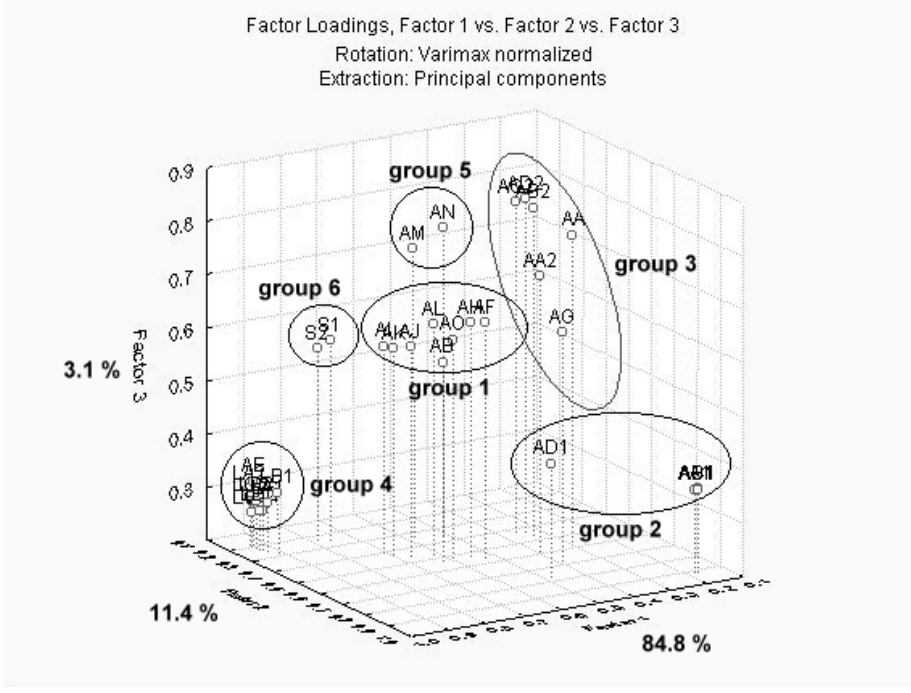

Figure 2. Principal component analysis plot of ambient air, soil and stack gas samples collected in Hsinchu. (The first letter represents the categories, A: air, L: soil, S: stack and the second letter represents the sampling sites. The number 1 indicates winter and 2 indicates summer.)

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