IDENTIFICATION OF PCDD/F ATMOSPHERIC DEPOSITION AND EMISSION SOURCES VIA POSITIVE MATRIX FACTORIZATION

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Introduction

PCDD (polychlorinated dibenzo-p-dioxins) and PCDF (polychlorinated dibenzofurans) are commonly known as dioxin which has been listed as persistent organic pollutants (POPs). The seventeen PCDD/F congeners with chlorine substitution in 2,3,7,8 positions are most toxic to humans. In Taiwan, the inventory of PCDD/F emission from 1999 to 2010 demonstrated thatthe significant reduction of PCDD/F emission into the atmosphere was observed. However, around 57.8 gI-TEQ/year of PCDD/Fs were still emitted into the atmosphere in 2010 in Taiwan[1]. The major dioxin emission source was locatedin industrial parksin western Taiwan, and there are various industrial facilities such as power plants, waste incinerators, as well as sinter plant.Furthermore, the winter monsoon and dust storm event not only brings cold air but also transports air pollutants and dust over long distances from mainland China to Taiwan measured by our previous studies[2,3].Receptor models are statistical methods to analyze the relationship between receptor sites and emission sources. Positive Matrix Factorization (PMF) is a multivariate receptor method and it was developed by Paatero and Tapper in 1994[4].The PMF statistical results can be interpreted quantitatively and estimate the relative contribution of the various plausible sources.Applications of PMF receptor modeling have been widely employed in air pollution and sediment pollution studies[5,6]. However, few studies have applied PMF to apportionment of PCDD/F in atmosphericdust particles.The objective of this study is to quantitatively determine the factors causing the PCDD/F contamination in industrial parks of northern, central and southernTaiwan, moreover, estimate the relative contribution of various sources.

Materials and method

To measure atmospheric PCDD/F depositions in Taiwan, the sampling regionsincluded the campus of National Yang Ming University in urban area andthree industrial parks selected in northern, central and southern Taiwan, in the vicinity of densely populated.The atmospheric PCDD/F depositionswere collected at eleven locations from July 2011 to Oct 2012.Atmospheric deposition samples were collected with the stainless steel cylindrical vessel, which was constructed of mirror-polished stainless steel (D: 500 mm, H: 600 mm). Before sampling, about 10 L of deionized water was added to the vessel to cover the bottom surface. When sampling was complete, the water and dust remaining in the cylindrical vessel were collected by the portable sampling system using the glass fiber filter, PUF and gear pump. 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).In this study, the analysis tool was used to reconstruct plausible contamination source of PCDD/F fingerprint patterns and calculate fraction contribution of plausible sources with PMF that is a receptor model and a multivariate method. The PMF2[7] was used in this studyand refer “EPA PMF 3.0 Fundamentals and User Guide”, which is provided by US EPA, to establish and analysis of the data set.

Results and discussion

Table 1 indicates that the PCDD/F deposition flux measured at different locations in Taiwan. In urban area, the atmospheric PCDD/F deposition fluxes were 0.74~6.85 pg I-TEQ/m^2/day (n=13); furthermore, the deposition fluxes of PCDD/F were 3.18~20.2 (n=12), 9.30~38.9 (n=12) and 4.26~21.0 (n=24) pg I-TEQ/m^2/day, respectively, measured in industrial parkin northern, central and southern Taiwan. The deposition flux (2.64±1.57 pg I-TEQ/m^2/day) of PCDD/F measured in urban area was significantly lower than that observed in industrial park of northern (11.0±4.89pg I-TEQ/m^2/day), central (18.1±8.65pg I-TEQ/m^2/day) and southern (11.5±5.94pg I-TEQ/m^2/day) Taiwan. Moreover, the deposition flux of PCDD/Fin industrial park of central

Taiwan was the highest. In this study, Coefficient of Determination (COD) is used to be the diagnostic tool to determine the factor numbers in the model.The factor numbers of PMF model were 3 (n=13), 3 (n=12), 4 (n=12), 5 (n=24), respectively, be used in urban area, northern, central and southern industrial park in Taiwan.The factor numbers selected could adequately reproduce the data set.Figure 1 shows that the PCDD/F fingerprint patterns of the plausible sources (factors) in various regions were generated by PMF model.

In urban area (Figure 1, Ⅰ), the results indicated that the first factor Aof PCDD/F profile dominated by the 1,2,3,4,6,7,8-H7CDF, O8CDD, O8CDF and 1,2,3,4,6,7,8-H7CDD with minor contributions from 1-6 substituted PCDF congeners.The second factor was characterized by O8CDD, 1,2,3,4,6,7,8-H7CDD, 1,2,3,4,6,7,8-H7CDF, and O8CDF(figure 1, I-B), while the I-B factor was different from the third factor increasing ratio for the other PCDF congeners (figure 1, I-C).In northern industrial park (figure 1, Ⅱ), the first source pattern was dominated by O8CDD, 1,2,3,4,6,7,8-H7CDD and 1,2,3,4,6,7,8-H7CDF (figure 1, Ⅱ-A).The second factor was dominated by O8CDD, 1,2,3,4,6,7,8-H7CDD with contributions from PCDFs which had increased (Figure 1, Ⅱ-B). the final source pattern was clearly dominated by the O8CDD, O8CDF, 1,2,3,4,6,7,8-H7CDF and 1,2,3,4,6,7,8-H7CDD (Figure 1, Ⅱ-C).In central industrial park (Figure 1, Ⅲ), The first factor was dominated by the O8CDD, 1,2,3,4,6,7,8-H7CDD, 1,2,3,4,6,7,8-H7CDF and O8CDF (Ⅲ-A) while the final factor was dominated by O8CDD, 1,2,3,4,6,7,8-H7CDD and 1,2,3,4,6,7,8-H7CDF and O8CDF (Ⅲ-B). The third factor of PCDD/F profile consisted of multitude of PCDFs (Ⅲ-C).The final factor was dominated by1,2,3,4,6,7,8-H7CDD, 1,2,3,4,6,7,8-H7CDF with other PCDF which had clearly increased, additionally, thelow contribution from PCDD congeners were observed (Ⅲ-D).In southern industrial park (Figure 1, Ⅳ), the first factor fingerprint pattern dominated by the O8CDD and 1,2,3,4,6,7,8-H7CDD, 1,2,3,4,6,7,8-H7CDF, and O8CDF (Ⅳ-A). According to the characteristics of the second factor profile, it was difficult to recognize it as a possible source of contamination, nevertheless, it was plausible to IWI and a local secondary aluminum smelter profiles (Ⅳ-B). The third factor profile dominated by the PCDFs (Ⅳ-C). The final factor was characterized by 1,2,3,4,6,7,8-H7CDD, 1,2,3,4,6,7,8-H7CDF and O8CDF with other PCDF congeners had clearly increased (Ⅳ-D).

Based on the previousatmospheric measurements during the long-range transport (LRT) events such as winter monsoon and dust storm event[2,3], the similar features of the atmosphericPCDD/F profiles can be observed. The results indicated mainly dominated by the high-chlorinated PCDD/F congeners of O8CDD, 1,2,3,4,6,7,8-H7CDD, 1,2,3,4,6,7,8-H7CDF, and O8CDF, moreover, thefraction of total PCDFs were higher than the total PCDDs. In Taiwan, the PCDD/Fs emissionsfrom stationary sources were monitored by Taiwan EPA in 2010[1]. The resultsindicatedthat the high abundances of PCDFs in the stack gas were observed in sinter plant and electric arc furnace, that were similar to previous study[8,9], moreover, the difference between them were the amounts of PCDDs which were significantly higher in electric arc furnace compared to sinter plant emission.The difference between the municipal solid waste incinerator (MSWI)and the industrial waste incinerator (IWI) were the proportion of PCDFs. Generally, the abundances of PCDFs in IWIs were higher than in MSWIs in Taiwan. Lin et al.[10] suggested the fraction of low chlorinated substituted PCDD/Fsof the IWIs was higher than that of the MSWIs.On the other hand, the secondary aluminum smelt plant was characterized by higher amounts of OCDD, OCDF and 1,2,3,4,6,7,8-H7CDD, and the amount of PCDFs were higher than PCDDs.Considering these observations, in this present study, those factors were hypothesized to describe the individual contributions in Figure 1.The fraction of these factors contributed to total PCDD/F concentrations in Table 2. The result indicated that the major contributorswere long range transport (50.2%), MSWI (54.9%), sinter plant (37.9%)and electric arc furnace (39.0%) in urban area and industrial park of the northern, central, and southern Taiwan, respectively. This study suggests that the importance of the mostly sources of PCDD/F contaminated in research regions.

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

Sampling period	*Urban area*		*Average air temperature*	*Rainfall*
	A			
	PCDD/F deposition flux [1]	*Duration (days)*	°C	mm
Jul. 2011	21.1 (0.74)	33.2	26.7	73.8
Aug. 2011	86.2 (3.73)	27.9	26.7	150
Sep. 2011	24.7 (1.59)	32.8	24.9	27.2
Oct. 2011	194 (3.25)	29.0	21.3	118
Nov. 2011	70.3 (3.79)	30.1	20.7	174
Dec. 2011	46.1 (1.65)	31.8	15.3	86.2
Jan. 2012	76.7 (2.45)	31.1	14.3	93.2
Feb. 2012	96.6 (2.58)	27.8	14.6	182
Mar. 2012	129 (1.77)	33.2	16.3	66.0
Apr. 2012	227 (6.85)	30.8	20.2	319
May. 2012	64.3 (1.41)	26.2	22.9	277
Jun. 2012	86.5 (2.82)	22.3	24.9	442
Jul. 2012	35.7 (1.70)	38.9	27.8	114

Sampling periods	Industrial Parks in Northern Taiwan						*Average air temperature*	*Rainfall*
	B		*C*		*D*			
	PCDD/F deposition flux [1]	*Duration (days)*	*PCDD/F deposition flux*	*Duration (days)*	*PCDD/F deposition flux*	*Duration (days)*	°C	mm
Jul. 2012	167 (6.71)	25	303 (9.96)	21	417 (16.0)	21	30.2	85.4
Aug. 2012	79.7 (3.18)	21	268 (9.54)	25	275 (7.80)	25	29.2	341
Sep. 2012	279 (8.12)	24	1025 (20.2)	24	1210 (12.8)	24	27.4	5.60
Oct. 2012	226 (7.38)	21	344 (14.6)	21	291 (15.8)	21	24.3	77.8

Sampling periods	Industrial Parks in Central Taiwan						*Average air temperature*	*Rainfall*
	E		*F*		*G*		°C	mm
Jul. 2012	288 (8.83)	21	512 (26.8)	21	336 (15.1)	21	29.3	129
Aug. 2012	206 (13.2)	25	272 (17.9)	25	222 (13.6)	25	28.3	380
Sep. 2012	468 (23.3)	24	706 (38.9)	24	432 (14.5)	24	27.3	0.60
Oct. 2012	194 (12.8)	21	383 (23.4)	21	145 (9.30)	21	23.8	0.40

Sampling periods	Industrial Parks inSouthern Taiwan								*Average air temperature*	*Rainfall*
	H		*I*		*J*		*K*		°C	mm
Jan. 2012	442(18.7)	28	238(11.2)	28	134(5.39)	27	164(6.64)	27	19.6	0.20
Feb. 2012	463(18.5)	29	209(9.06)	29	158(5.14)	29	158(5.62)	29	20.3	29.0
Mar. 2012	471(17.1)	28	317(13.0)	28	143(4.26)	28	158(5.22)	28	23.8	7.60
Apr. 2012	316(14.3)	27	363(18.7)	27	121(4.78)	27	232(6.73)	27	26.9	111
May. 2012	441(14.0)	29	433(20.7)	29	139(5.44)	29	330(10.7)	29	28.4	264

Jun. 2012	334(12.3)	28	403(21.0)	28	179(6.59)	28	555(19.9)	28	29.0	835

[1]pg/m^2/day (pg I-TEQ/m^2/day)

Table 2.The candidate sources contributed to total PCDD/F concentrations of difference regions.

area	factor	candidatesource	Contribution (%)
(Ⅰ) Urban area	A	LRT	50.2
	B	MSWI	20.2
	C	IWI	29.6
(Ⅱ) Industrial Parks of Northern Taiwan	A	MSWI	54.9
	B	EAF	21.8
	C	SAS	23.3
(Ⅲ) Industrial Parks of Central Taiwan	A	MSWI	10.7
	B	IWI	20.5
	C	Sinter plant	37.9
	D	EAF	30.9
(Ⅳ) Industrial Parks of Southern Taiwan	A	MSWI	12.3
	B	IWI	19.3
	C	Sinter plant	29.5
	D	EAF	39.0

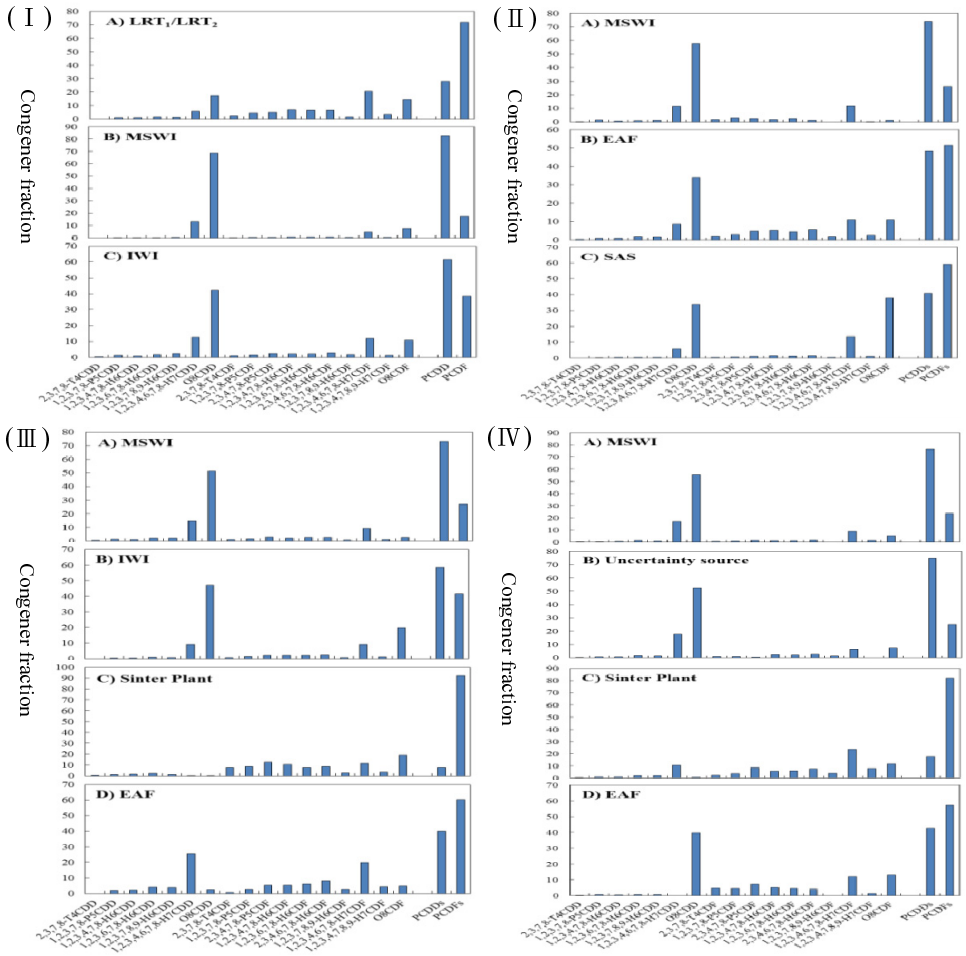

Figure1. Normalized congener patterns of the difference regions resolved source profiles (factors). (Ⅰ) urban area (Ⅱ) northern industrial park (Ⅲ) central industrial park (Ⅳ) southern industrial park.