NATIONAL AND CONTINUOUS DIOXIN AIR MONITORING NETWORK IN TAIWAN (2006-2013): SPATIAL, TEMPORAL VARIATION AND EMISSION SOURCES APPORTIONMENT VIA POSITIVE MATRIX FACTORIZATION

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are persistent organic pollutants (POPs), of the 75 PCDDs and 135 PCDFs compounds, only seventeen PCDD/F congeners, which have chlorines in 2,3,7,8 positions are most toxic to humans. PCDD/Fs are formed and released unintentionally from anthropogenic sources, and may be transported long distances to other environmental compartments, so the atmosphere is a major pathway for the transport and deposition[1]. Due to the reasons, it is important to monitor the atmospheric PCDD/Fs concentrations and evaluate the potential sources. The Environmental Protection Administration of Taiwan established the ambient dioxin air monitoring network in 2006. The objective was to determine the concentrations of PCDD/Fs of different regions in Taiwan. During 2006~2013, there was a extensive monitoring of atmospheric dioxin in Taiwan, the range of the average concentrations were 29 to 56 fg I-TEQ /m^3 [2]. Recently, the monitoring of atmospheric dioxin is just in the representative areas, including the industrial areas and adjacent areas. The major dioxin emission sources are located in industrial parks in central 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[3,4]. 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[5]. The PMF statistical results can be interpreted quantitatively and estimate the relative contribution of the various possible sources. Applications of PMF receptor modeling have been widely employed in air pollution and sediment pollution studies [6,7]. The objective of this study is to determine the concentrations and congener profiles of atmospheric PCDD/Fs and to identify the spatial and temporal characteristics, moreover, estimate the relative contribution of various emission sources by applying the PMF receptor modeling to apportion of PCDD/Fs in atmospheric in Taiwan.

Materials and methods

The Environmental Protection Administration of Taiwan established the ambient dioxin air monitoring network in 2006. Ambient air sampling was conducted from 2006 to 2013, and there are 85 air monitoring stations at different regions in Taiwan, 26 stations in northern, 8 stations in northwestern, 14 stations in central, 12 stations in southwestern, 19 stations in southern, 3 stations in northeastern, and 3 stations in eastern (Fig.1). Based on the Taiwan EPA standard method (NIEA A809.11B), ambient air samples for both PCDD/F compounds and total suspended particles were collected using high-volume sampling trains equipped with quartz fiber filters for collecting solid-phase PCDD/Fs. Polyurethane foam (PUF) plugs were used to retain PCDD/F compounds in the vapor phase. For PCDD/F analysis, the vapor and solid-phase samples were spiked with known amounts of internal quantification standards according to USEPA method 23. The dioxin congeners were analyzed using high resolution gas chromatography (HRGC) and high resolution mass spectrometry (HRMS) using a fused silica capillary column. The mass spectrometer was operated with a resolution greater than 10,000 under positive EI conditions, and datasets for the seventeen 2,3,7,8-substituted PCDD/F congeners were analyzed in the selected ion monitoring (SIM) mode. 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[8] was used in this study and 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

Annual variations (2006-2013) in atmospheric PCDD/Fs I-TEQ concentrations measured at all stations in Taiwan were shown in Fig.2. The mean concentrations decreased gradually, particularly during 2010-2013. The annual mean concentrations were 43.5 $\pm$ 24.3 and 26.1 $\pm$ 14.5 fg I-TEQ / m^3 in 2007 and 2013, respectively, decreasing of 40% during 2007 to 2013. Regarding the distribution of PCDD/F congener in ambient air in Taiwan, the measurements indicated that the dominate congeners were OCDD, OCDF, and 1,2,3,4,6,7,8-HpCDF in Taiwan, which accounted for 96.5% for the total concentrations. From 2006 to 2013, the annual mean concentrations of PCDD/Fs for all regions was shown in Fig.3. At different regions, there was the highest and lowes concentrations in central and eastern Taiwan, respectively. The mean concentrations for other regions were 42.8±16.1, 42.4±14.7, 35.1±25.7, 20.0±9.75, and 17.6±6.36 fg I-TEQ/m^3 in southern, southwestern, northwestern, northern, and northeastern, respectively. The concentrations of PCDD/Fs at all regions in Taiwan were lower than the Japanese annual standard (600 fg WHO-TEQ/m^3)[9] and the national Germany target value (150 fg I-TEQ/m^3)[10]. The seasonality of PCDD/Fs in atmospheric in Taiwan, where the levels in spring and winter were higher than which in summer and autumn (Fig.4). The mean concentrations were 54.9±40.0, 32.8±31.0, 29.1±23.1, and 47.8±43.2 fg I-TEQ/m^3 in spring, summer, autumn, and winter, respectively. Due to the increase of industrial activities and the seasonal variations were the likely causes. Fig. 5 demonstrated that the prevalence of OCDD, OCDF, 1,2,3,4,6,7,8-HpCDF at all regions in Taiwan, which accounted for 96-97%. 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 in Taiwan and in the different regions, years, and seasons are presented in Table 1, Table 2, Table 3, and Table 4, respectively. The factor numbers selected could adequately reproduce the data set. The PCDD/F fingerprint patterns of the plausible sources (factors) in Taiwan was generated by PMF model. The results indicated that the first factor A of PCDD/F profile dominated by OCDD and OCDF. The second factor was dominated by OCDD and 1,2,3,4,6,7,8-HpCDF. The third factor was dominated by 1,2,3,4,6,7,8-HpCDF, 1,2,3,7,8-PeCDF, 1,2,3,4,6,7,8-HpCDD, and 2,3,7,8-TeCDF. The fourth factor was dominated by OCDF and 1,2,3,4,6,7,8-HpCDF, additionally, the low contribution from PCDD congeners were observed. The final factor profile was dominated by OCDD and 1,2,3,4,6,7,8-HpCDD, additionally, the low contribution from PCDF congeners were observed. In Taiwan, the dioxin emissions from different stationary sources had been monitored by Taiwan EPA since 1999[2]. The results indicated that the high abundances of PCDFs in the stack gas were observed in sinter plant and electric arc furnace (EAF), moreover, the difference between them were the amounts of PCDDs which were significantly higher in EAF 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. On the other hand, the secondary aluminum smelt plant (SAS) was characterized by higher amounts of OCDD, OCDF and 1,2,3,4,6,7,8-HpCDD, and the amount of PCDFs were higher than PCDDs. In contrast to SAS, the secondary zinc smelting plant (SZS) was characterized by higher amounts of OCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, and the amount of PCDDs were higher than PCDFs[11]. Kao et al.[12] investigated the characteristics of PCDD/Fs in stack-flue gases from cement kilns (CK), indecated that characterized by higher amounts of 1,2,3,4,6,7,8-HpCDF, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, and 2,3,4,7,8-PeCDF, and the amount of PCDFs were higher than PCDDs. Kuo[13] investigated the characteristics of PCDD/Fs in stack-flue gases from coal-fired power plants in Taiwan, indecated that characterized by higher amounts of OCDF, OCDD, 1,2,3,4,6,7,8-HpCDF, and 1,2,3,4,6,7,8-HpCDD, and the amount of PCDFs were also higher than PCDDs. Based on the previous atmospheric measurements during the long-range transport (LRT) events such as winter monsoon and dust storm event[2,3], the similar features of the atmospheric PCDD/F profiles can be observed. The results indicated mainly dominated by the high-chlorinated PCDD/F congeners of OCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, and OCDF, moreover, the fraction of total PCDFs were higher than the total PCDDs. Black et al.[14,15] indicated the characteristics of PCDD/Fs from open burning and biomass burning (BB), indecated that characterized by higher amounts of PCDFs and PCDDs, respectively. Considering these observations, in this present study, those factors were hypothesized to describe the individual contributions in Table 1. The result indicated that the major contributors were EAF (50.8%), LRT (25.0%), MSWI/IWI (14.2%), BB (9.2%), and sinter plant (0.81%) in Taiwan. From 2006 to 2013, the major contributors were EAF (33.3% ~ 67.5%), MSWI/IWI (9.1% ~ 44.1%), LRT (1.7% ~ 36.7%) in Taiwan (Table 2). Table 3 indicated that the candidate sources contributed to atmospheric PCDD/F during different seasons in Taiwan. In spring and winter, the major contributors were EAF (43.9% for spring, 60.4% for winter) and LRT (4.3% for

spring, 12.1% for winter). In addition, the candidate sources contributed to atmospheric PCDD/Fs at different regions in Taiwan were listed in Table 4. For different regions, the major contributors were MSWI (62.9%), EAF (60.1%), EAF(69.5%), IWI (62.6%), EAF (55.7%), LRT (51.9%), and co-combustion (86.1%) in northern, northwestern, central, southwestern, southern, northeastern, and eastern in Taiwan, respectively. The PCDD/F concentrations tended to decrease, but there were high concentration observed particularly in central Taiwan. It is important to continuous monitoring at the regular and futher control in industrial areas.

Acknowledgements
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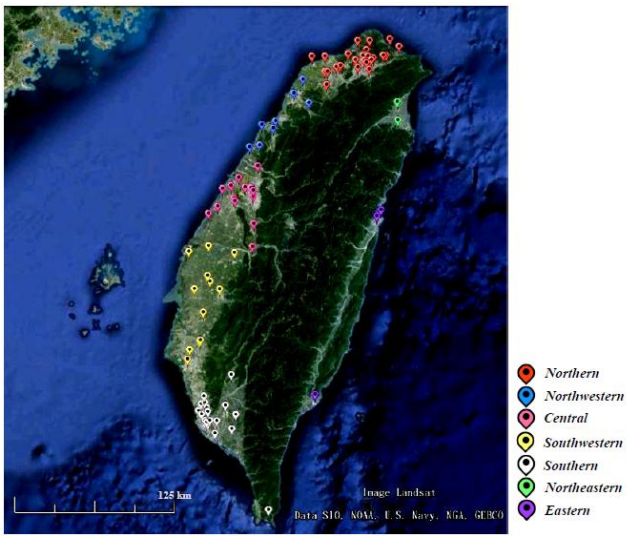

Figure 1. Ambient air monitoring network stations in Taiwan.

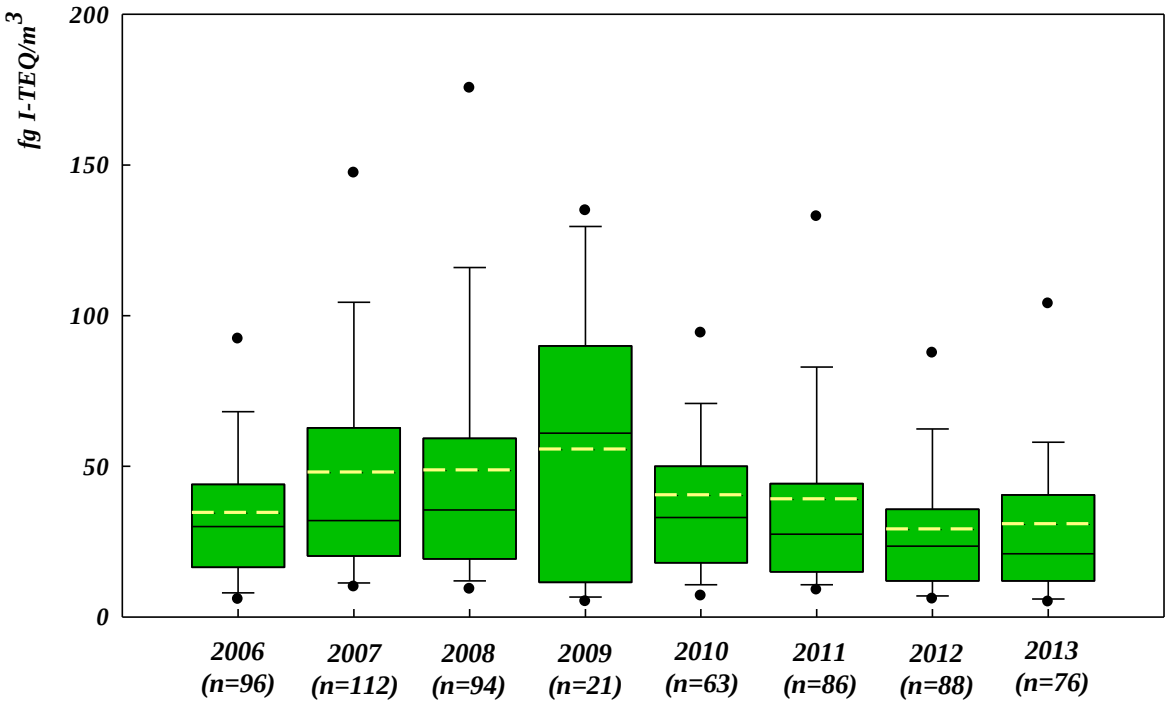

Figure 2. Annual variation in atmospheric PCDD/F concentrations in Taiwan during 2006 to 2013.

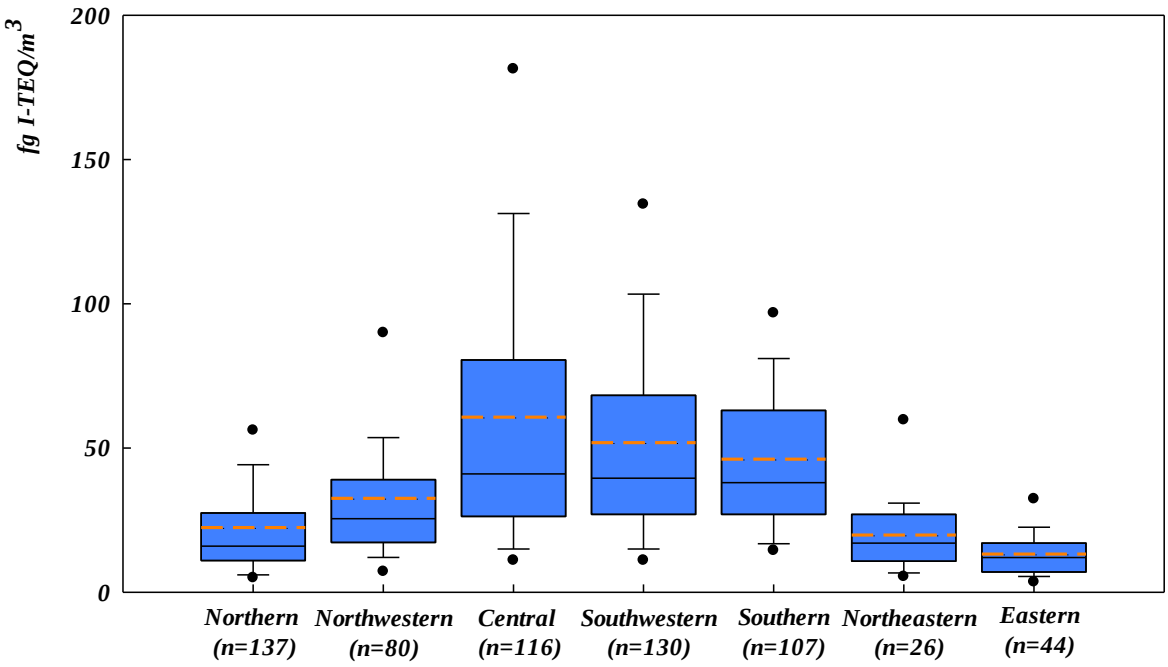

Figure 3. Atmospheric PCDD/F concentrations of different regions in Taiwan.

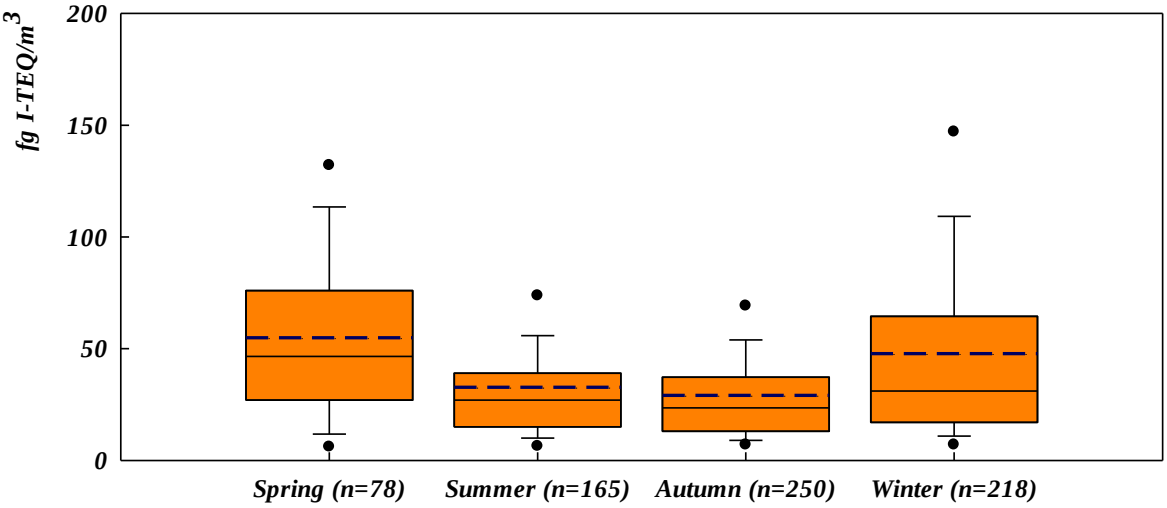

Figure 4. Seasonal variation in atmospheric PCDD/F concentrations in Taiwan.

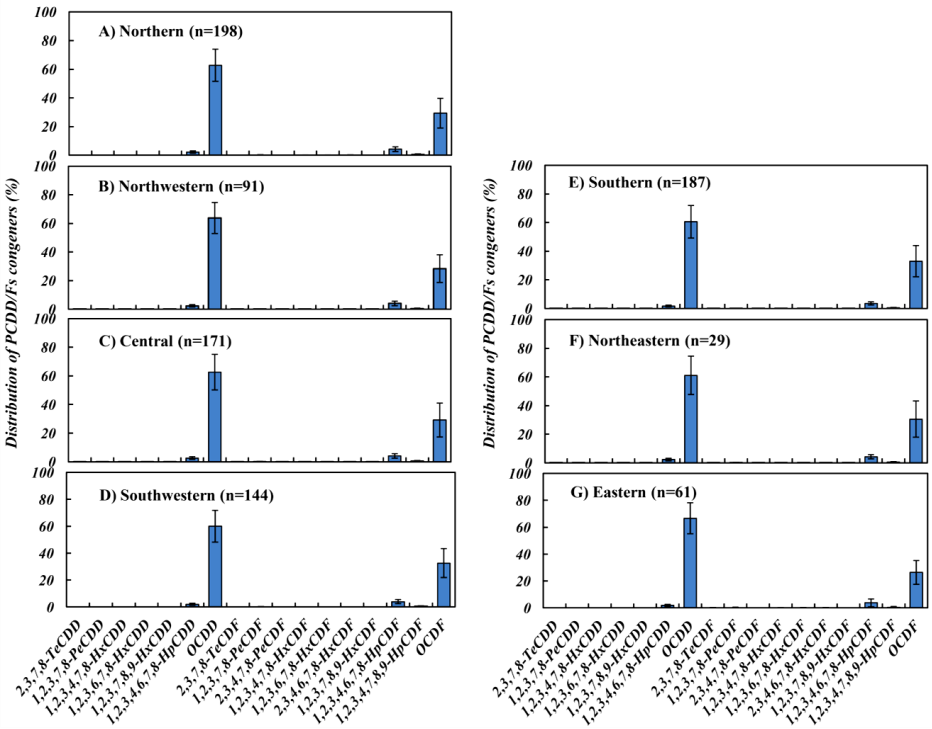

Figure 5. Congener profiles for PCDD/Fs in atmospheric of different regions in Taiwan.

Table 1. The candidate sources contributed to total PCDD/F concentrations of Taiwan.

Factor	Candidate source	Contribution (%)
A	EAF	50.8
B	MSWI/IWI	14.2
C	Sinter plant	<1.0
D	LRT	25.0
E	BB	9.2

Table 2. The candidate sources contributed to total PCDD/F concentrations of different years.

Year	Factor	Candidate source	Contribution (%)	Year	Factor	Candidate source	Contribution (%)
2006	A	LRT	21.8	2010	A	MSWI/IWI	14.2
	B	EAF	33.3		B	EAF	67.5
	C	Sinter plant	0.8		C	LRT	18.3
	D	MSWI/IWI	44.1				
2007	A	LRT	5.24	2011	A	EAF	49.7
	B	Power plant	6.58		B	LRT	7
	C	EAF	45.1		C	BB	14.1
	D	MSWI/IWI	43.1		D	MSWI/IWI	29.1
2008	A	MSWI/IWI	42.8	2012	A	LRT	4
	B	LRT	1.7		B	Power plant	44.9
	C	EAF	55.5		C	EAF	43.4
					D	Vehicle Emission	7.7
2009	A	LRT	10.3	2013	A	LRT	36.7
	B	MSWI/IWI	33.3		B	EAF	50.3
	C	EAF	56.4		C	MSWI/IWI	9.1
					D	Open burning	3.8

Table 3. The candidate sources contributed to total PCDD/F concentrations of different seasons.

Seasons	Factor	Candidate source	Contribution (%)	Seasons	Factor	Candidate source	Contribution (%)
Spring	A	LRT	4.3	Autumn	A	MSWI/IWI	71.6
	B	EAF	43.9		B	BB	11.1
	C	MSWI/IWI	51.8		C	LRT	17.3
Summer	A	Vehicle Emission	9.0	Winter	A	MSWI/IWI	27.5
	B	BB	14.2		B	EAF	60.4
	C	MSWI/IWI	76.8		C	LRT	12.1

Table 4. The candidate sources contributed to total PCDD/F concentrations of different regions in Taiwan.

Regions	Factor	Candidate source	Contribution (%)	Regions	Factor	Candidate source	Contribution (%)
Northern	A	MSWI	62.9	Southwestern	A	BB	23.2
	B	EAF	19.6		B	Power plant	14.1
	C	LRT	17.5		C	IWI	62.6
Northwestern	A	EAF	60.1	Northeastern	A	LRT	51.9
	B	MSWI	17.5		B	EAF	4.2
	C	LRT	22.4		C	MSWI	33.7
Central	A	Power plant	15.3	Eastern	A	Co-combustion	86.1
	B	EAF	69.5		B	CK	8.4
	C	MSWI	15.1		C	BB	5.5
Southern	A	SAS	21.9				
	B	SZS	21.3				
	C	EAF	55.7				
	D	Sinter plant	1.2				