NATIONAL AND CONTINUOUS DIOXIN AIR MONITORING NETWORK IN TAIWAN (2006-2016): 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 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. Recently, the monitoring of atmospheric dioxin is just in the representative areas, including the industrial areas and adjacent areas. 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[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 possible sources. Applications of PMF receptor modeling have been widely employed in air pollution and sediment pollution studies [5,6]. 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 2016, and there are 86 air monitoring stations at different regions in Taiwan (Fig.1), 26 stations in northern, 8 stations in northwestern, 14 stations in central, 12 stations in southwestern, 19 stations in southern, 3 stations in northeastern, 3 stations in eastern and one background station in Mt. Lulin (2,862 m above mean sea level). 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. 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 PMF 5.0[7] was used in this study which is provided by US EPA, to establish and analysis of the data set.

Results and discussion

Annual variations (2006-2016) 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 48.1±44 and 31.7±31 fg I-TEQ/m^3 in 2007 and 2016, respectively, decreasing of 35% in ten years. From 2006 to 2016, the annual mean concentrations of PCDD/Fs for all regions was shown in Fig.3. At different regions, there was the highest and lowest concentrations in central Taiwan and background station at Mt. Lulin, respectively. The median concentrations of dioxin for other regions were 16.0 (n=195), 24.0 (n=116), 38.0 (n=165), 41.0 (n=190), 40.0 (n=147), 13.5 (n=38), 11.0 (n=69) and 1.47 (n=185) fg I-TEQ/m^3 in northern, northwestern, entral, southwestern, southern, northeastern, eastern and background station, respectively. The average concentrations of PCDD/Fs at all regions in Taiwan were lower than the Japanese annual standard (600 fg WHO-TEQ/m^3)[8] and the national Germany target value (150 fg I-TEQ/m^3)[9]. The seasonality of PCDD/Fs in atmospheric in Taiwan, where the levels in autumn and winter were higher than which in spring and summer (Fig.3). The mean concentrations were 31.5±28.5, 26.5±23.0, 37.3±33.2, and 61.5±48.3 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. 4 demonstrated that the distribution of OCDD, OCDF, 1,2,3,4,6,7,8-HpCDF at all regions in Taiwan, which accounted for 50-60%. The factor numbers of PMF model in Taiwan and in the different regions are presented in Table 1, 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. In Taiwan, the dioxin emissions from different stationary sources had been monitored by Taiwan EPA since 1999. 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[10]. The PCDD/Fs in stack gases from cement kilns (CK) wearcharacterized 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[12] 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.[12] 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. 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. In addition, the candidate sources contributed to atmospheric PCDD/Fs at different regions in Taiwan were listed in Table 1. 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, eastern and background station 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.

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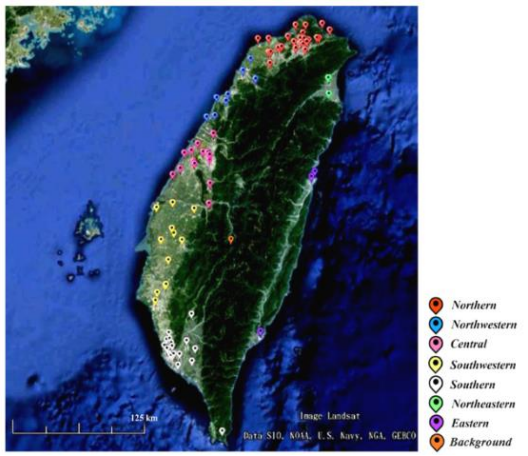

Figure 1. Ambient air monitoring network stations in Taiwan.

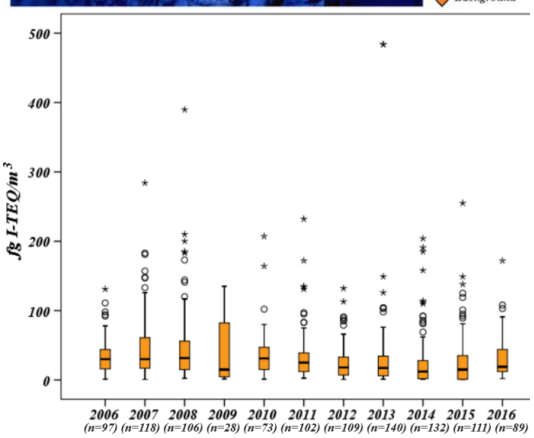

Figure 2. Annual variation of atmospheric PCDD/Fs in Taiwan during 2006 to 2016. (Any data not included between the whiskers would be plotted as an outlier with ○ and ★.)

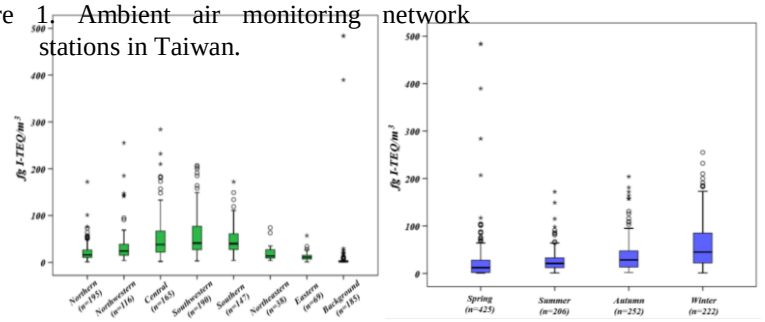

Figure 3. Variation of Atmospheric PCDD/Fs at different regions and season in Taiwan.

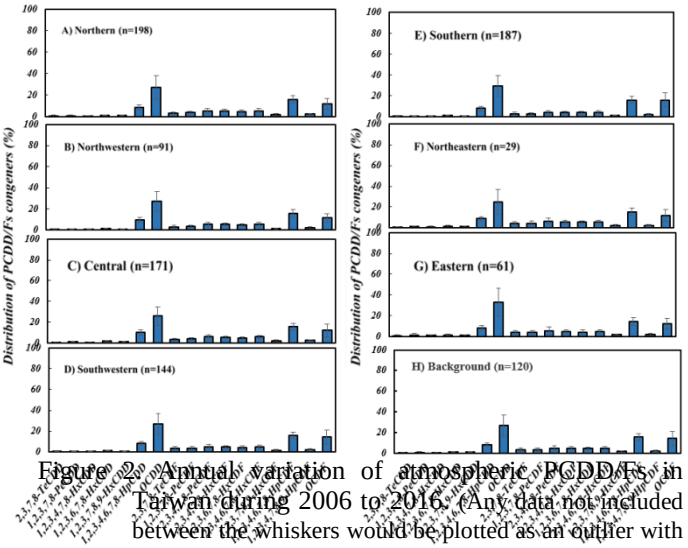

Figure 4. Congener profiles for PCDD/Fs in atmospheric of different regions in Taiwan.

(Any data not included between the whiskers would be plotted as an outlier with ○ and ★.)

Table 1. The possible sources contributed to atmospheric PCDD/Fs at 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	Background	A	BB	52.4
	B	SZS	21.3		B	Open-B	25.4
	C	EAF	55.7		C	Unknown	22.2
	D	Sinter plant	1.2				