Continuous Nationwide PCDD/F Air Monitoring Network In Taiwan (2006-2017): Concentration Variation, Emission Source Apportionment And Exposure Risk Assessment

Yang YH[1], Ngo TH[1], Pan SY[1], Wu CP[2], Tsai HT[3], Chi KH [1*]

[1]Institute of Environmental and Occupational Health Sciences, National Yang Ming University, Taipei, Taiwan, 112, baby830412@gmail.com; [2]Environmental Analysis Laboratory, Taiwan EPA, Chungli, Taiwan 320, [3] Department of Air Quality Protection and Noise Control, Taiwan EPA, Taipei, Taiwan 100

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]. Therefore, 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]. Principal component analysis (PCA) is a very powerful technique widely used in this field[4] for investigating large sets of data using the smallest number of variables preserving the greatest amount of information. 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. For humans, exposure routes of PCDD/Fs and DL-PCBs from contaminated matters include ingestion, inhalation, and dermal contact. Dietary intake is regarded as the main pathway of exposure to dioxins. In general, food ingestion is known to account for >90% of total human exposure. Thus, in many countries and regions, the contamination levels of PCDD/Fs and DL-PCBs in foodstuffs have been extensively investigated[8].

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 2017 (n=1024), 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, Principal Component Analysis (PCA) was performed using SPSS v22 to identify the spatial and temporal characteristics. Data for these samples were organized into a matrix having n objects(samples) and p

variables(PCDD/F congeners). PCDD/F data were normalized to the total concentration of PCDD/F by expressing each homologue as a percentage of the sum of the total PCDD/F. The PMF 5.0[9] was used in this study which is provided by US EPA, to establish and analysis of the data set.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. To evaluate the potential risk from food intake, the daily intakes of PCDD/Fs were determined by deterministic assessment using the atmospheric PCDD/F concentration measured during 2006-2016 and consumption data to calculate the exposure level for local residents at each region in Taiwan.

Results and discussion

Annual variations (2006-2017) in atmospheric PCDD/Fs I-TEQ concentrations measured at all stations in Taiwan were shown in Fig.2. From 2006 to 2017, the annual mean concentrations of PCDD/Fs for all regions was shown in Fig.3.The Geometric mean concentrations decreased gradually during 2006-2016(β=-1.86, P-value<0.001). The annual mean concentrations were 38.4 and 19.5 fg I-TEQ/m^3 in 2010 and 2016, respectively, decreasing of 49% in ten years. At different regions, there was the highest and lowest concentrations in Southern Taiwan and background station at Mt. Lulin, respectively(Table.1). The geometric mean concentrations of dioxin for other regions were 15.7 (n=166), 23.8 (n=120), 38.0 (n=168), 43.4 (n=199), 42.7 (n=127), 14.6 (n=42), 10.5 (n=77) and 1.14 (n=125) 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)[10] and the national Germany target value (150 fg I-TEQ/m^3)[11]. The seasonality of PCDD/Fs in atmospheric in Taiwan except for northern, northeastern Taiwan and background station, where the levels in winter were higher than which in summer (Table.1). The geometric mean concentrations were 23.5, 18.9, 28.7 and 42.2 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. 4 demonstrated that the distribution of 2,3,4,7,8-PeCDF and 2,3,4,6,7,8-HxCDF at all regions in Taiwan, which accounted for 50-60%. Fig.5 demonstrated the results of atmospheric PCDD/F homologue groups analyze by PCA The results showed that the distribution of PCDD/F congener was diverse in four seasons especially for summer and winter season separated by Factor 1 The spatial of PCDD/Fs in atmospheric in Taiwan was significantly different in each region. The factor numbers of PMF model in Taiwan and in the different regions are presented in Fig.6, 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[12] 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[13] investigated the characteristics of PCDD/Fs in stack gases from coal-fired power plants in Taiwan, indicated 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] 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 addition, the candidate sources contributed to atmospheric PCDD/Fs at different regions in Taiwan were listed in Fig.6. For different regions, the major contributors were MSWI (44.1%), EAF(41.5%), EAF (39.0%), Open burning (54.8%), sinter plants (46.7%), LRT (46.1%), SMS (35.0%) and BB (52.4%) in northern, northwestern, central, southwestern, southern, northeastern, eastern and background station in Taiwan, respectively. The PCDD/F concentrations tended to decrease, but the higher concentration was still observed particularly in southern Taiwan. It is important to continuous monitoring at the regular and futher control in industrial areas. Summarize the 95th percentile of atmospheric PCDD/F concentration in each regions in Taiwan between 2006 to 2016 and use the Multimedia Environmental Pollutant Assessment System (MEPAS) to calculate the lifetime risk of dioxin in all areas. The results showed that the lifetime average daily dose (LADD) of Dioxin in Taiwan ranged from 2.10×10^{-4} to 4.43×10^{-2} pg I-TEQ/kg/d (WHO regulation: 1-4 pg TEQ/kg/day). Among, the total carcinogenic risk in central Taiwan was the highest (4.43×10^{-6}), followed by southwestern (4.12×10^{-6}) and southern Taiwan (3.04×10^{-6}),the lowest risk was observed in eastern Taiwan (4.93×10^{-7}).

Acknowledgements

The authors gratefully acknowledge the financial support provided by the Environmental Protection Administration (102-EPA-F-006-001) and Ministry of Science and Technology (MOST 104-2628-M-010-001-MY3 and MOST 106-EPA-F-001-002) of Taiwan.

References:

1. Kouimtzis T, Samara C, Voutsa D, Balafoutis Ch, Müller L. (2002); *Chemosphere*. 47: 193-205.
2. Chi KH, Hsu SC, Wang SH, Chang MB. (2008) *Science of the Total Environment.* 401: 100-108.
3. Chi KH, Lin CY, Ou Yang CH, Hsu SC, Chen YF, Luo S, Kao SJ.(2013) *Journal of Asian Earth Sciences* 83: 745-752.
4. Colombo, A., Benfenati, E., Mariani, G., Lodi, M., Marras, R., Rotella, G., Senese, V., Fattore, E., Fanelli, R. (2009); *Chemosphere* 77: 1224-1229.
5. Paatero P, Tapper U. (1994); *Environmetrics*. 5: 111-126.
6. Sundqvist K, Tysklind M, Geladi P, Hopke P, Wiberg K. (2010); *Environmental Science & Technology*. 44: 1690-1697.
7. Uchimiya M, Arai M, Masunaga S. (2007); *Environmental Science & Technology*. 41: 3864-3870.
8. Wu WL, Deng XL, Zhou SJ, Liang H, Yang XF, Wen J, Li XM, Zhang CZ, Zhang YH, Zou F. (2017); *Science of the Total Environment.* 615: 412-421.
9. Paatero P. (1997); *Chemometrics and Intelligent Laboratory Systems*. 37: 23–35.
10. Government of Japan. (2012)
11. Bruckmann P, Hiester E, Klees M, Zetzsch C. (2013); *Chemosphere*. 93(8): 1471-1478.
12. Taiwan Kaohsiung EPA. (2010) *(in Chinese)*
13. Kao JH, Chen KS, Chang-Chine GP, Chou IH. (2006); *Aerosol Quality Research.* 6(2): 170-179.

14. Blacka RR, Meyer CP, Yates A, Zweitend VL, Chittime GB, Mueller JF. (2012); *Atmospheric Environment*. 59: 125-130.

Table 1. Variation of Atmospheric PCDD/Fs at different regions and season in Taiwan.

(fg I-TEQ/m^3)	*Spring*	*Summer*	*Autumn*	*Winter*	*Average*
Northern	14.8(10.1, 26.2)	17.1(10.3, 26.4)	14.3(10.0, 25.9)	17.0(10.0, 32.0)	16.2(10.0, 27.2)
Northwestern	18.9(12.9, 29.0)	19.0(13.5, 28.9)	22.3(13.2, 38.8)	41.1(19.6, 65.5)	24.7(14.5, 40.0)
Central	30.4(20.1, 41.6)	20.5(12.0, 35.0	39.4(25.9, 49.0)	79.9(53.0, 117)	37.5(21.8, 69.6)
Southwestern	34.5(23.1, 57.4)	21.0(14.3, 33.0)	57.1(37.3, 81.9)	81.2(56.2, 109)	42.6(27.8, 80.5)
Southern	36.4(29.0, 46.2)	31.1(22.1, 40.0)	47.0(35.2, 68.8)	62.4(46.0, 88.9)	42.9(29.6, 62.0)
Northeastern	17.5(8.56, 40.3)	14.6(10.2, 23.5)	13.0(7.00, 29.3)	13.9(8.97, 22.0)	15.0(9.03, 27.1)
Eastern	10.1(6.05, 16.9)	7.28(6.66, 11.9)	11.3(6.93, 17.5)	14.7(10.1, 18.2)	10.5(7.40, 15.6)
Background	2.46(1.16, 4.14)	0.67(0.53, 1.03)	0.78(0.56, 1.11)	0.65(0.42, 0.99)	1.14(1.09, 3.66)
Taiwan**	23.3(13.3, 39.0)	18.9(11.9, 31.2)	28.7(16.3, 50.3)	42.2(21.6, 89.1)	27.4(14.4, 49.9)

(* Geometric mean (P25, P75) ** Background not included in Taiwan concentrations)

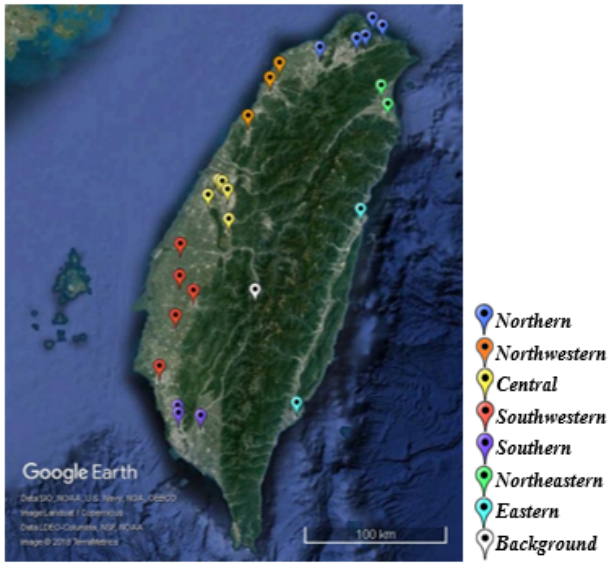

Figure 1. Ambient air monitoring network stations in Taiwan.

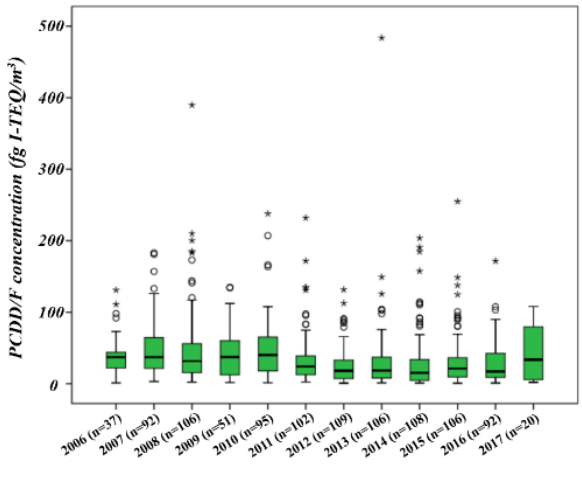

Figure 2. Annual variation of atmospheric PCDD/Fs in Taiwan during 2006 to 2016. (Any data not included between the whiskers would be plotted as an outlier with ○ and □.)

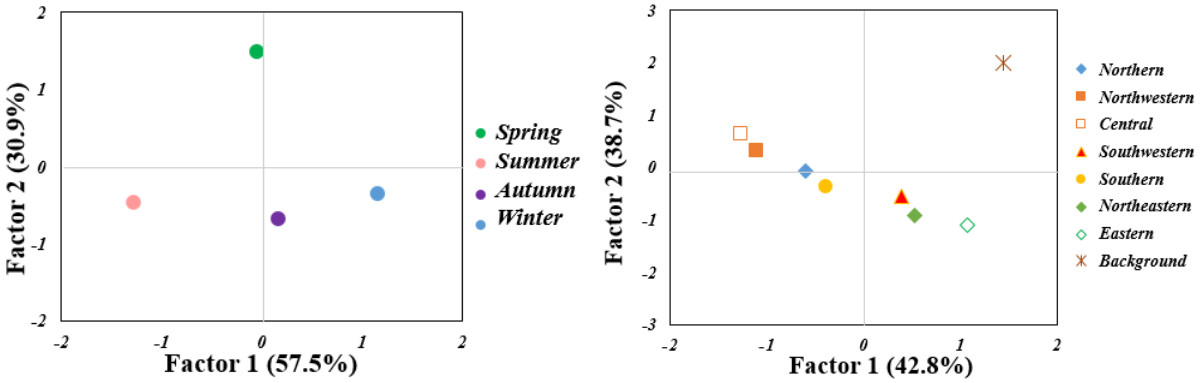

Figure 5. Principal component analysis (PCA) score plot on the PCDD/F congener groups of air samples

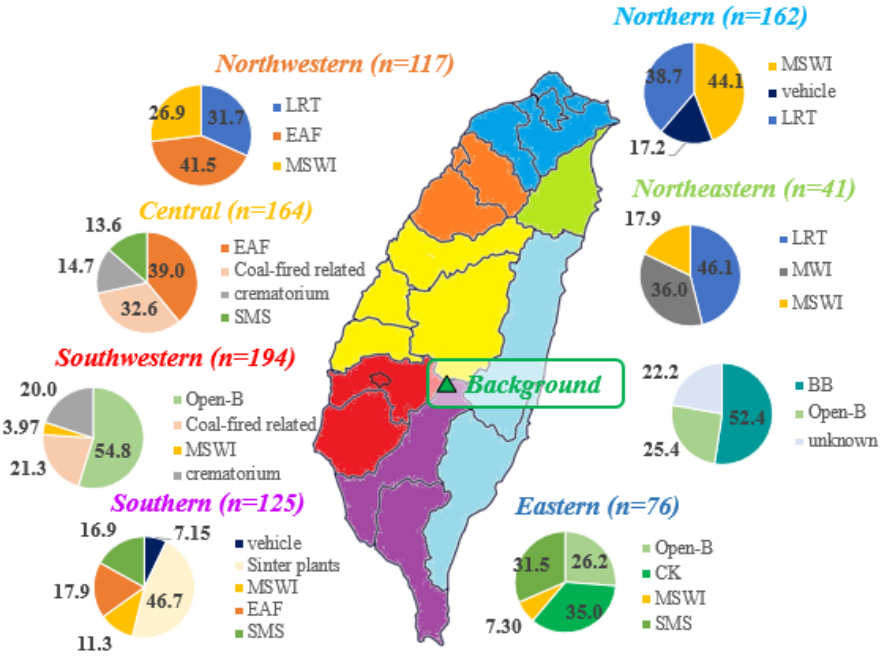

Figure 6. The possible sources contributed to atmospheric PCDD/Fs at different regions in Taiwan.