INVESTIGATION OF SOIL PCDD/F CONTAMINATION AND POSSIBLE SOURCE IDENTIFICATION IN TAIWAN USING POSITIVE MATRIX FACTORIZATION

Chen HW[1], Tsou HH[1], Tsai HT[2], Ho JR[2], Liang BWP[3], Chao HR[4], Chi KH [1]*

[1] Institute of Environmental and Occupational Health Sciences, National Yang Ming University, Taipei 112, Taiwan.
[2] Soil and Groundwater Pollution Remediation Fund Management Board, Environmental Protection Administration, Executive Yuan, R.O.C., Taipei 110, Taiwan.
[3] Environmental Engineering Department Ⅱ, Sinotech Engineering Consultants, Ltd., Taipei 114, Taiwan.
[4] Emerging Compounds Research Center, Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, Pingtung 912, Taiwan.

Introduction

PCDD (polychlorinated dibenzo-p-dioxins) and PCDF (polychlorinated dibenzofurans) are commonly known as dioxin which has been listed as persistent organic pollutants (POPs) and released unintentionally from anthropogenic sources. PCDD/Fs can be formed during combustion processes and chlorine bleaching in the pulp and paper industry[1]. In addition, pentachlorophenol (PCP) and its salts are used throughout the world as biocides in the preservation of timber and textiles. Moreover, it has been shown that PCDD/Fs are impurities found in commercial PCP products[2]. Therefore, the impurities found in soils are another source of PCDD/F contamination in addition to those resulting from combustion and industrial processes. Soil can be significantly contaminated with PCDD/Fs through airborne transport, and it is a potential route for human or animal exposure to PCDD/Fs[3]. Recently, several environmental studies have examined soils near stationary points with high dioxin emissions[4,5]. In this study, a national monitoring of dioxin-contaminated soil was carried out in Taiwan. 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[6]. 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[7, 8]. However, few studies have applied PMF to apportionment of PCDD/F contamination in soils at urban, industrial, farmland and background area in Taiwan. The objective of this study is to quantitatively determine the factors causing the PCDD/F contamination at different area in northern, central and southern Taiwan, moreover, estimate the relative contribution of various sources.

Materials and method

The comprehensive soil sample of PCDD/F analysis in this study is part of the first national survey of dioxin contamination in Taiwan from September 2011 to March 2013. Purposive sampling was used, and Taiwan was divided into four regions (northern, central, southern, and eastern areas) (Figure 1). Owing to the lack of existing data on dioxin contamination in Taiwanese soil, the inventory of dioxin emissions from stationary sources in Taiwan was initially used for the selection of potentially dioxin-contaminated areas and reference sites. Soil samples were obtained by grid sampling (one sample per five hectares) from the potentially dioxin-contaminated areas and reference sites in each region. Eighty-four samples were obtained following this sampling strategy. After sample collection, soil samples were freeze-dried and then ground to 100-200 mesh-sized powder using an agate mortar and pestle. For PCDD/F analysis, the samples were then spiked using known amounts of internal quantification standards according to USEPA methods 1613. Detailed information regarding the extracted and clean-up procedure of the PCDD/F samples is provided elsewhere[9, 10]. Finally, the PCDD/F samples were analyzed using high-resolution gas chromatography (HRGC)/high-resolution mass spectrometer (HRMS) equipped with a fused silica capillary column (60 m x 0.25 mm x 0.25μm, J&W). In addition, 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[11] 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

Table 1 indicated that the PCDD/F concentrations measured in soil samples collected at difference regions in Taiwan. The PCDD/F concentrations (1.52-134 pg WHO-TEQ/g, n=84) in soils measured at difference area in Taiwan higher than other measurements in South Africa (0.34-20 pg WHO-TEQ/g)[12], Italy (0.5-28.9 pg WHO-TEQ/g)[13], but lower than other measurement in Japan (3.0-380 pg I-TEQ/g)[14], Korea (0.2-3720 pg I-TEQ/g)[15], southern Vietnam (4.6-184 pg I-TEQ/g)[16]; furthermore, the soil PCDD/F concentration were 1.99-134 (n=28), 4.75-24.8 (n=7), 1.52-114 (n=46) pg WHO-TEQ/g measured in northern, central, southern Taiwan, respectively. Moreover, the soil PCDD/F concentration measured in southern Taiwan was significantly higher than northern and central Taiwan. Figure 2 shows the PCDD/F congener distribution at different area in Taiwan. The distribution of PCDD/F congener in soil samples at different area were quite similar, however, the OCDD (54%-65%) and OCDF (13%-14%) were the dominate congeners at all region in Taiwan.

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 4 estimated in northern, central, southern Taiwan. The factor numbers selected could adequately reproduce the data set. Figure 3 shows the distribution of PCDD/F congener for the plausible sources (factors) in various regions generated by PMF model. In northern Taiwan (Figure 3, A), the results indicated that the first factor was fly ash disposal (4%). The second factor was bottom ash disposal (33%). The third factor was atmospheric deposition from urban area (16%). The fourth factor was atmospheric deposition from background area (47%). Therefore, the result indicated that the major contributor of soil PCDD/F contamination was atmospheric deposition (63%) in northern Taiwan. In central Taiwan (Figure 3, B), the first factor was fly ash disposal (2%). The second factor was industrial area of atmospheric deposition (73%), and the factor higher than the third factor was background of atmospheric deposition (23%). The final factor was bottom ash disposal (2%). Therefore, the result indicated that the major contributor was atmospheric deposition (96%) in central Taiwanese soil. And the other hand, due to industrial area of atmospheric deposition contribution percentage was higher, then it was influence background of atmospheric deposition contribution percentage in central Taiwan. In southern Taiwan (Figure 3, C), the results indicated that the first factor was bottom ash bottom ash disposal (20%). The second factor was industrial area of atmospheric deposition (20%), and the contribution of the second factor lower than the third factor was background of atmospheric deposition (57%). The final factor was fly ash disposal (3%). Therefore, the result indicated that the major contributor was atmospheric deposition (77%) in southern Taiwanese soil. Figure 4 shows the source contribution to the soil samples in Taiwan for PCDD/F contamination via PMF analysis.

Our results indicated that the major contributors of soil PCDD/F contamination in Taiwan were atmospheric deposition from industrial area (44%), atmospheric deposition from background (39%) and fly ash disposal (17%), respectively. In this study, we speculate the relative contribution of various emission sources in soil PCDD/F contamination at different area in Taiwan by applying PMF model. The results via PMF analysis also indicated that the local air emissions from industrial park are more important in central Taiwan compared to those in other areas. Therefore, our results can provide the important information to government to propose the PCDD/F contamination reduction in the future.

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A: Hualien city
B: Dashu district
C: Xincheng township
D: Pitou township
E: Shengang township
F: Kuanhsi township
G: Houli district
H: Xiaogang district
I: Guanyin township
J: Bade City

Figure 1. The sampling location of soil samples collected from northern, central, southern, and eastern Taiwan.

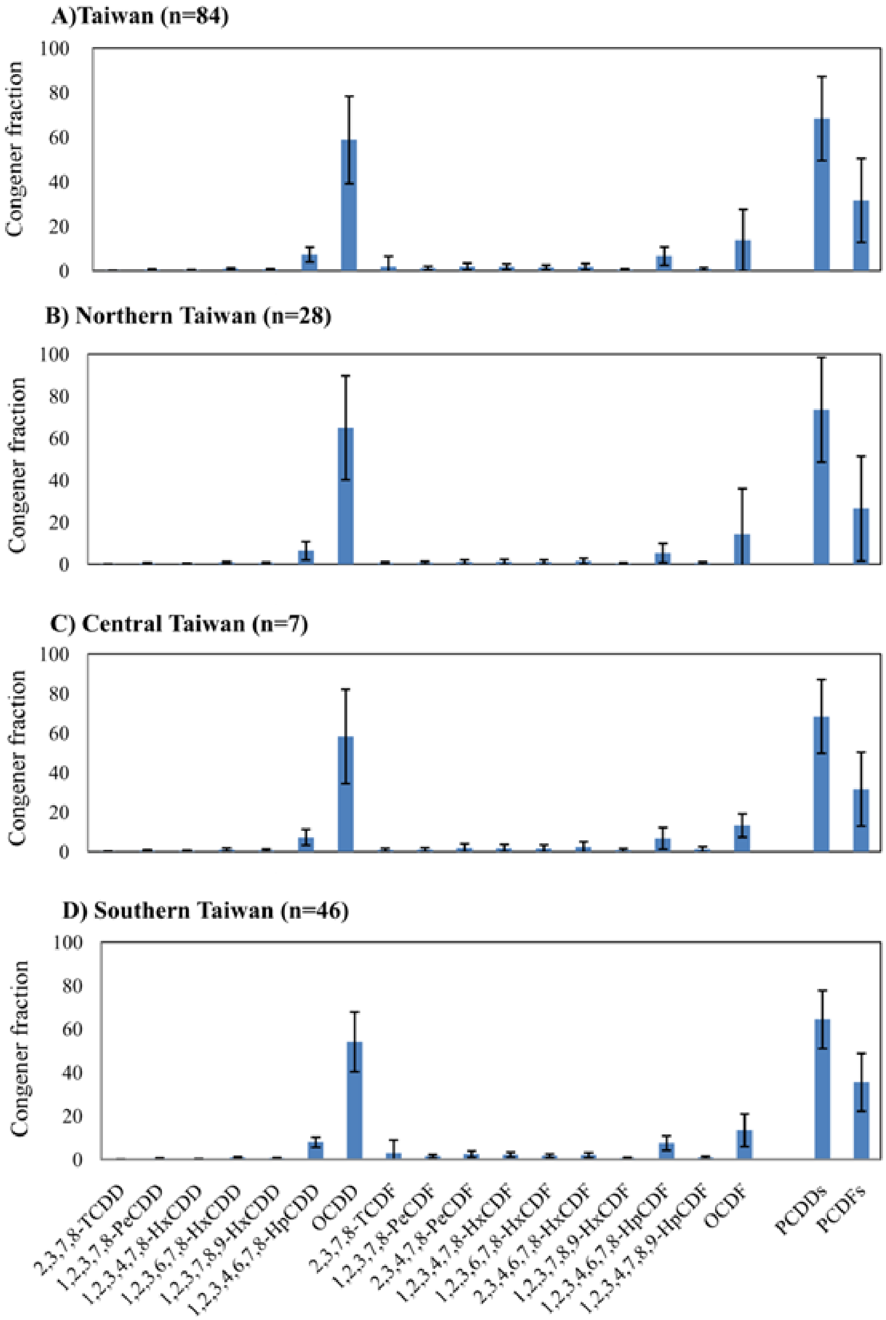

Figure 2. The distribution of PCDD/F congeners in soil samples at different area in Taiwan.

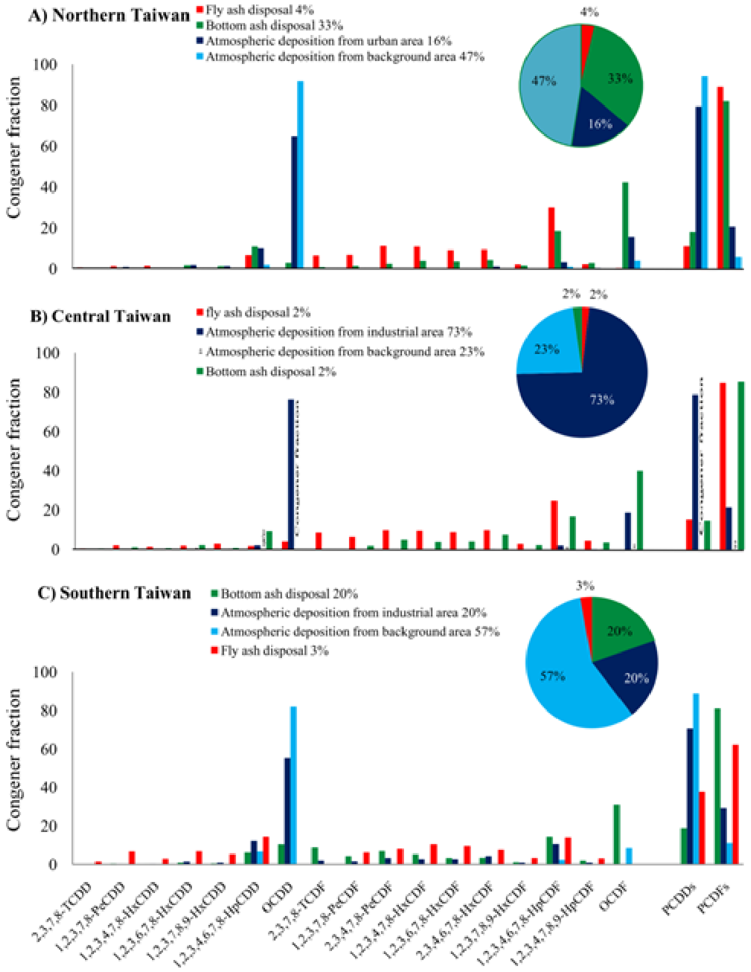

Figure 3.Normalized congener patterns of the different area resolved source profiles (factors). (A) Northern Taiwan (B) Central Taiwan (C) Southern Taiwan.

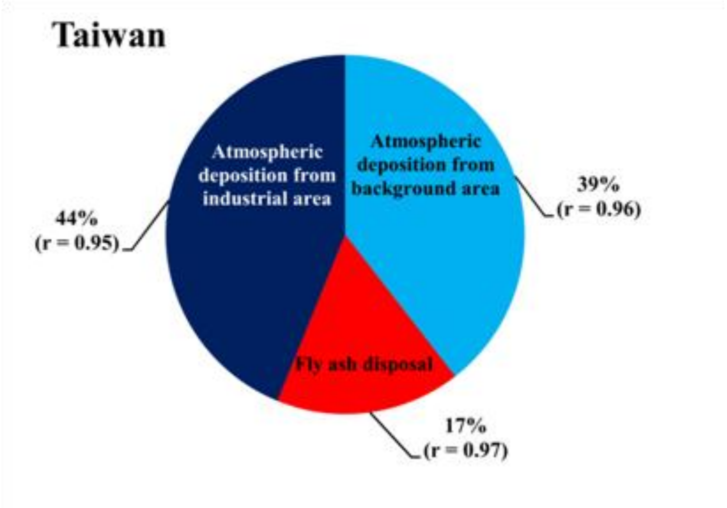

Figure 4. Source contribution to the soil samples in Taiwan for PCDD/F contamination via Positive Matrix Factorization.

Table 1. PCDD/F concentration measured in soil samples at difference region in Taiwan.

PCDD/Fs	Taiwan (n=84)		Northern Taiwan (n=28)		Central Taiwan (n=7)		Southern Taiwan (n=46)	
	Conc. ± SD[1]	mean [2]	Conc. ± SD	mean	Conc. ± SD	mean	Conc. ± SD	mean
2,3,7,8-TCDD	0.556 ± 0.621	0.556	0.692 ± 0.735	0.692	0.723 ± 0.391	0.723	0.471 ± 0.578	0.471
1,2,3,7,8-PeCDD	2.88 ± 2.84	2.88	3.67 ± 3.74	3.67	2.89 ± 1.56	2.89	2.52 ± 2.31	2.52
1,2,3,4,7,8-HxCDD	1.86 ± 2.45	0.186	2.17 ± 3.61	0.217	2.77 ± 1.66	0.277	1.60 ± 1.61	0.160
1,2,3,6,7,8-HxCDD	7.66 ± 12.5	0.766	9.33 ± 14.9	0.933	10.1 ± 9.10	1.01	6.54 ± 11.8	0.654
1,2,3,7,8,9-HxCDD	4.7 ± 7.63	0.474	6.46 ± 11.3	0.646	6.33 ± 4.60	0.633	3.62 ± 4.86	0.362
1,2,3,4,6,7,8-HpCDD	76.7 ± 120	0.767	84.8 ± 142	0.848	131 ± 141	1.31	64.3 ± 104	0.643
OCDD	807 ± 1,604	0.242	787 ± 808	0.236	2,567 ± 3,665	0.770	509 ± 1,322	0.153
2,3,7,8-TCDF	12.9 ± 30.8	1.29	5.69 ± 8.86	0.569	5.51 ± 5.31	0.551	19.2 ± 40.2	1.92
1,2,3,7,8-PeCDF	7.79 ± 11.5	0.234	6.61 ± 12.0	0.198	4.87 ± 3.80	0.146	9.33 ± 12.2	0.280
2,3,4,7,8-PeCDF	13.3 ± 21.3	4.00	10.6 ± 19.7	3.19	8.66 ± 6.90	2.60	16.4 ± 24.0	4.91
1,2,3,4,7,8-HxCDF	13.0 ± 20.8	1.30	12.2 ± 24.6	1.22	8.62 ± 5.96	0.862	14.7 ± 20.5	1.47
1,2,3,6,7,8-HxCDF	10.6 ± 17.0	1.06	11.5 ± 24.1	1.15	8.37 ± 5.83	0.837	10.8 ± 13.2	1.08
2,3,4,6,7,8-HxCDF	13.5 ± 22.7	1.35	16.1 ± 32.9	1.61	12.0 ± 8.57	1.20	12.8 ± 16.7	1.28
1,2,3,7,8,9-HxCDF	3.98 ± 7.57	0.398	4.29 ± 11.1	0.429	3.51 ± 3.15	0.351	4.04 ± 5.44	0.404
1,2,3,4,6,7,8-HpCDF	71.1 ± 147	0.711	95.4 ± 227	0.954	80.5 ± 67.1	0.805	58.3 ± 85.5	0.583
1,2,3,4,7,8,9-HpCDF	6.97 ± 11.4	0.070	7.75 ± 16.3	0.078	8.35 ± 5.45	0.083	6.60 ± 8.69	0.066
OCDF	584 ± 3,000	0.175	1,317 ± 5,079	0.395	466 ± 572	0.140	188 ± 756	0.056
Total PCDDs	901 ± 1,750	5.87	894 ± 985	7.24	2,720 ± 3,823	7.62	588 ± 1,447	4.96
Total PCDFs	737 ± 3,290	10.6	1,487 ± 5,455	9.80	606 ± 684	7.58	340 ± 982	12.0
Total PCDD/Fs	1,638 ± 5,040	16.0	2,381 ± 6,440	17.0	3,327 ± 4,507	15.2	928 ± 2,429	17.0

[1] pg/g [2] pg WHO-TEQ/g