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Agricultural soil monitoring of PCDD/Fs in the vicinity of a municipal solid waste incinerator in Eastern China: Temporal variations and possible sources

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ABSTRACT

The temporal variations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in 33 agricultural soil samples in the vicinity of a municipal solid waste incinerator (MSWI) in Eastern China were determined one year after the initial investigation in 2006. The soil PCDD/F concentrations in 2007 ranged from 73.6 to 377 ng kg^{-1} (0.60–6.38 ng I-TEQ kg^{-1}). During 2006–2007, the overall soil PCDD/F levels increased significantly, i.e., 33% and 39% for total concentration and I-TEQ (median value), respectively. Moreover, soils in the study area are proved to be almost free from previously suspected PCDD/F sources, i.e., pentachlorophenol/sodium penta-chlorophenate (PCP/PCP-Na) and 1,3,5-trichloro-2-(4-nitrophenoxy) benzene (CNP) contaminations. Furthermore, the results from a congener-specific factor analysis between soils (collected in two investigations) and dioxin emission sources suggest that diffuse sources including open burning of wastes, traffic and hot water boilers are major contributors that are responsible for the accumulation of PCDD/Fs in soils. By contrast, the impact of the presumably major PCDD/F source identified in our previous study, i.e., the MSWI, seems to be limited.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are two groups of semi-volatile, hydrophobic and extremely hazardous chemicals that can be easily accumulated in organic carbon-rich media such as soil and sediment [1]. Since the first detection of PCDD/Fs in the flue gas of municipal solid waste incinerator (MSWI), the emission of these compounds has stirred public concerns worldwide due to their environmental toxics and associated adverse health effects [2]. In addition to MSWIs, PCDD/Fs can also be released unintentionally through various incineration, combustion, industrial and reservoir sources [3].

Identifying the major sources of PCDD/Fs in the environment is considered the preliminary step toward efficiently controlling and reducing PCDD/F pollution [4]. Recent studies on the inventories of potential PCDD/F emission sources in a number of European countries indicate that although the emission levels have been significantly reduced in the past two decades, MSWIs are still an important PCDD/F contributor [5]. Consequently, during the last three decades, comprehensive research has been conducted to investigate the occurrence of PCDD/Fs in soils around the MSWIs in Italy [6,7], Spain [1,8–16], the USA [17], Portugal [18], Japan [19], Taiwan [20], Korea [21,22], UK [23], France [24] and Norway [25].

As for mainland China, the construction of MSWIs has only been booming since 2000 due to the lack of landfill sites and unsuccessful management of composting. As a result, 67 MSWIs were running by 2005, with a total daily treatment capacity of 33 000 t. It is estimated that by the year of 2015, 200 MSWIs with a total daily treatment capacity of 100 000 t will be operating in the country [26]. Therefore, the MSWIs may become a significant PCDD/F source in the future due to the rapid increase in incineration capacity anticipated. However, to date, in mainland China only a few studies have examined the PCDD/Fs in the environmental sinks (e.g. soil and sediment), and are mainly focused on the schistosomiasis and E-waste recycling areas [27]. Therefore, it is urgent to fill a large data gap in order to better understand the environmental impact of the MSWI.

In 2006, our research group initiated an investigation of PCDD/F concentrations in agricultural soils in the vicinity of an MSWI in Hangzhou, China [28]. The comparisons of homologue and congener patterns as well as multivariate analysis indicated that most soils in the local area were presumably influenced by the MSWI. However, it is important to note that due to the rapid urbanization, farmland in China was decreased by 7.6 million ha from 1998 to 2005 [29]. The mixed urban-agricultural setting around the MSWI

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in Hangzhou is a typical example of an area undergoing such substantial development. As a result, the local environment has been deteriorating by intense anthropogenic activities including traffic, open burning of wastes (OB) and the operation of the hot water boilers (HWBs). Therefore, significant temporal variations of PCDD/Fs in soils are expected to occur in such a complex setting.

Accordingly, a second investigation was conducted one year later in 2007 at the same sites to gain a clearer picture of the occurrence of PCDD/Fs in agricultural soils around the MSWI. The main objectives of this study are to: (1) compare the current concentrations, temporal variations and profiles of PCDD/Fs in soils with regulations and results reported by other investigators; (2) re-identify the major contributors that are responsible for the accumulation of PCDD/Fs in soils by taking into account the diffuse dioxin sources, i.e., HWBs, traffic and OB.

2. Materials and methods

2.1. The study area

The detailed descriptions of the study area as well as the MSWI were previously reported [28]. Briefly, it is a satellite town (up to 41 600 inhabitants) in Hangzhou, with agriculture as the dominant land use (57%). The MSWI is situated just in the center of the town, adjacent to two motorways with heavy traffic. It is equipped with three fluidized bed incinerators (FBIs) and has been in full operation since 2003, with a daily treatment capacity of 800 t. The average PCDD/F emission levels of FBI-2 and FBI-3 measured in 2007 were 0.074 and 0.94 ng I-TEQ N m^{-3}, respectively. The location of the MSWI and the distribution of soil samples within a radius of 1.5 km from the stack are depicted in Fig. 1. Also illustrated is the wind frequency distribution during 2006–2007 obtained from the Meteorological Bureau of Hangzhou. It should be noted that wood-fueled HWBs are prevalent in town as an important hot water supplier to local habitants. Moreover, hundreds of small garment factories have been established in the local area in the past few years, causing an influx of migrant workers. Consequently, large amounts of household garbage and cloth residues are discarded everyday, and some is directly burnt in the open dumping sites.

2.2. Agricultural soil samples

A second round of soil sampling was performed one year later in September 2007. Samples were collected at the same places as in the initial investigation with the aid of a handheld GPS device (~10 m of accuracy) over a period of two days. Thirty samples were collected within a radius of 3 km from the MSWI mainly in the historical prevailing downwind directions, designated as near-site soils. The remaining three samples collected 6–7 km to the east of the stack, the direction least frequently downwind, were served as background controls, i.e., E-2, E-3 and E-4. The details of the soil sampling techniques and preparations were previously reported [28].

2.3. PCDD/F source samples

The PCDD/F emissions from the HWBs, traffic and open burning of wastes were investigated during May 2008 to trace the origins of PCDD/Fs in soils. One flue gas sample was collected from a wood-fueled HWB (~2 N m^3, hereafter designated as HWB-W) following the US EPA Method 23 [30]. Moreover, three ambient air samples were collected using a high volume air sampler (Model HV-1000F, SIBATA) following the US EPA Method TO-9A [31]: one sample (~250 m^3, hereafter designated as Traff) was taken in the downwind direction next to a motorway; another one (~100 m^3, hereafter designated as OB-H) was collected near an open dumping site several minutes after a pile of household garbage was completely burnt and extinguished; the third one (~30 m^3, hereafter

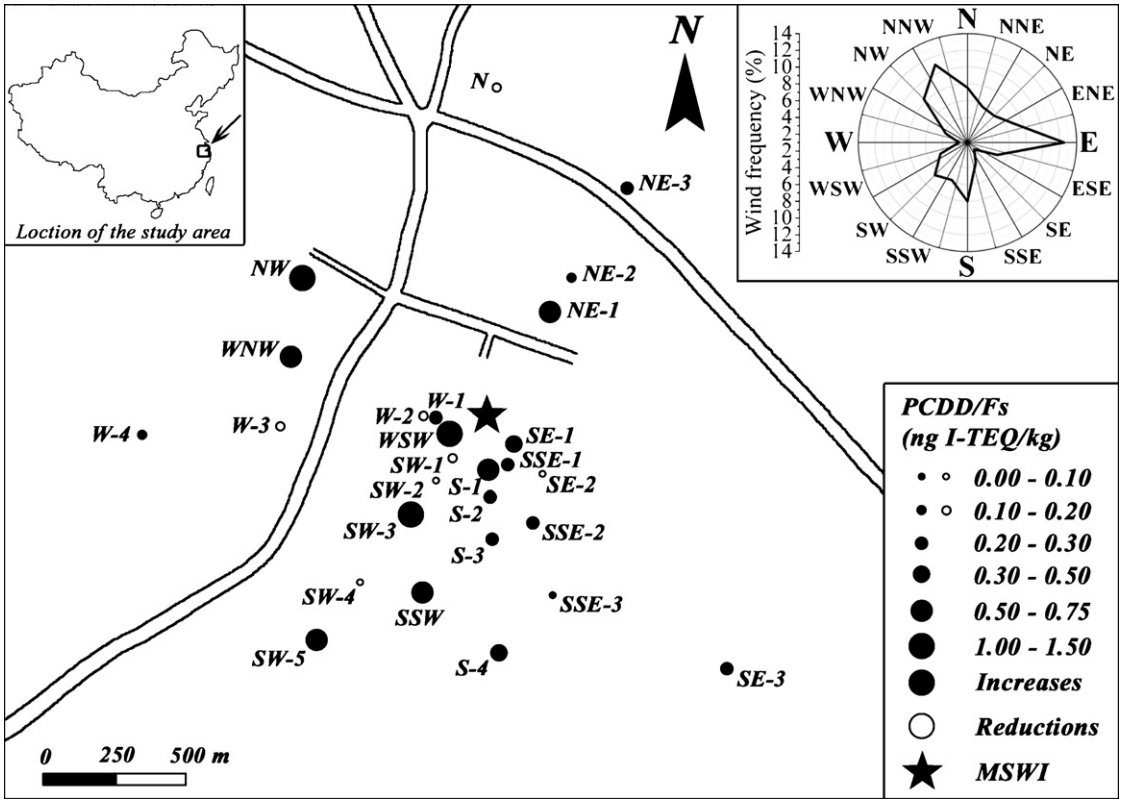

Fig. 1. Location of the study area and the distribution of agricultural soil samples in the vicinity of the MSWI, with the sizes of circles show direct proportionality with the variations of soil PCDD/F concentrations observed in respective sampling sites.

designated as OB-C) was located in the same place as OB-H but witnessed smoke plumes from open burning of cloth residues.

2.4. PCDD/F analysis

The extraction and clean-up procedures for soils as well as the analytical determinations of PCDD/Fs were previously reported [28]. Seventeen toxic congeners and tetra- to octa-chlorinated homologues were identified and quantified by HRGC/HRMS (JEOL, JMS-800D). Method blanks and duplicated samples were analyzed for each batch of six samples, and all quality criteria specified by the method were met. The recoveries of internal standards generally varied between 60 and 100% and all satisfied the requirements of US EPA Method 1613 [32]. Additionally, the average limits of detection (LOD) for soil samples varied between 0.030 and 0.366 ng kg^{-1} from tetra- to octa-PCDD/Fs, respectively. All the experimental results were on a dry weight basis and the toxic equivalents were expressed in I-TEQ. In the case of values below the LOD, I-TEQ calculations were carried out by using half of the LOD. Statistical significance ($p < 0.05$) between groups was computed by an analysis of variance (ANOVA) or the non-parametric Mann–Whitney test, depending on whether the data followed a normal distribution with equal variance. All the statistical analyses were performed using the SPSS 13.0 software package.

3. Results and discussion

3.1. Current concentrations and temporal variations of PCDD/Fs

The PCDD/F concentrations of soil in 2007 ranged from 73.6 to 377 ng kg^{-1} (0.60–6.38 ng I-TEQ kg^{-1}) with a median and an average value of 1.17 and 1.50 ng I-TEQ kg^{-1} (114 and 135 ng kg^{-1}), respectively (Table 1). According to the international guidelines and regulations for agricultural soils summarized by Leung et al. [33], PCDD/F contaminations in the current study are comparatively light, with only two soil samples (i.e., WSW and NW) exceeding the stringent Canadian standard (4 ng I-TEQ kg^{-1}). However, in comparison to the initial investigation in 2006 [28], the soil PCDD/F concentrations in 2007 as a whole increased significantly ($p < 0.01$), i.e., 33% and 39% for total concentration and I-TEQ (median value), respectively (Table 1).

The soil temporal variations of PCDD/Fs within a radius of 1.5 km from the MSWI are illustrated in Fig. 1. During 2006–2007, the I-TEQ decreased in 7 of the 27 soil samples, while they increased in the remaining 20 samples. Among them, three sampling sites exhibited relatively large increases in I-TEQs (>1.0 ng kg^{-1}), i.e., SW-3, WSW and NW, with SW-3 being the greatest change (1.41 ng I-TEQ kg^{-1}). Soil samples SSW, WNW, SW-5, NE-1 and S-1 also showed increases in I-TEQs, but to a lesser extent (>0.5 ng kg^{-1}). Given the long half-lives of PCDD/Fs in soil (>10 years), the decrease of I-TEQ values (with a maximum decrease of 0.17 ng kg^{-1}) observed in 7 soil samples might be due to the overall sampling and analytical uncertainties [12].

To gain perspective on the relative levels and temporal variations of PCDD/Fs in soils around the MSWI, the I-TEQ values were compared with those observed in a number of investigations in Spain (Table 2). Generally, the soil PCDD/F levels observed in this study were comparable with that of Tarragona [9], lower than those in Barcelona [11] and Montcada [13], and higher than those in Sites B and C [14]. As indicated by Table 2, the soil PCDD/F levels correlated well with the emission levels of the MSWI. Decreases in I-TEQ values of soils were observed primarily near the MSWI emitting low levels and/or experiencing significant reductions of PCDD/F emissions. Moreover, the highest I-TEQ increases in soils,

Table 1
Concentrations and temporal variations of PCDD/Fs in agricultural soils in the vicinity of the MSWI.

Samples and distances from the MSWI (m)			ΣPCDD/Fs		%[a]	I-TEQ		%[a]	PCDD/PCDF ratio		%[a]
			2006	2007		2006	2007		2006	2007	
01	W-1	185	92.3	115	***25***	1.01	1.25	***24***	1.60	1.58	***−1***
02	W-2	225	111	111	***0***	1.55	1.42	***−8***	1.15	1.77	***54***
03	W-3	750	76.5	73.6	***−4***	1.03	0.88	***−14***	1.43	1.80	***26***
04	W-4	1250	87.8	98.2	***12***	1.07	1.21	***14***	1.56	1.61	***4***
05	W-5	2250	82.0	135	***65***	0.89	1.26	***43***	2.23	2.05	***−8***
06	WNW	750	112	159	***42***	1.45	2.11	***46***	1.58	1.64	***4***
07	NW	850	269	320	***19***	4.03	5.19	***29***	1.76	1.62	***−8***
08	N	1250	244	237	***−3***	3.56	3.39	***−5***	1.79	1.76	***−2***
09	NE-1	450	86.1	117	***36***	0.88	1.42	***61***	2.58	1.74	***−32***
10	NE-2	600	77.9	95.1	***22***	0.58	0.79	***36***	3.77	2.94	***−22***
11	NE-3	1000	118	159	***35***	0.78	1.08	***39***	3.66	3.39	***−7***
12	E-1	2000	152	204	***34***	0.73	1.08	***48***	1.20	1.09	***−9***
13	E-2	6250	107	104	***−3***	0.65	0.60	***−7***	2.77	2.89	***4***
14	E-3	6660	116	118	***2***	0.55	0.62	***12***	5.08	3.51	***−31***
15	E-4	6660	91.9	119	***29***	0.49	0.64	***29***	4.81	2.81	***−42***
16	SE-1	150	111	143	***30***	1.09	1.43	***31***	2.01	1.74	***−13***
17	SE-2	300	82.8	105	***27***	0.84	0.82	***−2***	2.27	2.05	***−10***
18	SE-3	1250	56.1	80.1	***43***	0.39	0.65	***65***	3.32	2.24	***−33***
19	SSE-1	200	81.5	113	***38***	0.82	1.11	***35***	1.89	1.60	***−16***
20	SSE-2	425	120	148	***24***	1.43	1.65	***16***	2.37	1.91	***−20***
21	SSE-3	675	92.7	93.6	***1***	1.09	1.17	***8***	1.97	2.00	***2***
22	S-1	200	66.4	114	***72***	0.62	1.13	***81***	2.02	1.41	***−30***
23	S-2	300	88.8	102	***15***	0.83	1.12	***34***	2.14	1.87	***−13***
24	S-3	450	70.6	113	***60***	0.76	1.06	***39***	1.97	2.44	***24***
25	S-4	850	77.7	107	***37***	0.77	1.16	***50***	1.78	1.75	***−1***
26	S-5	3000	68.8	120	***74***	0.80	1.21	***51***	2.06	1.79	***−13***
27	SSW	675	64.7	119	***84***	0.70	1.41	***101***	2.03	1.52	***−25***
28	SW-1	200	103	108	***5***	1.35	1.23	***−9***	1.50	1.58	***5***
29	SW-2	300	78.4	104	***33***	0.98	0.94	***−4***	1.88	1.70	***−10***
30	SW-3	450	54.1	149	***175***	0.67	2.07	***210***	1.31	1.36	***4***
31	SW-4	750	69.9	76.7	***10***	0.84	0.76	***−10***	2.44	2.07	***−15***
32	SW-5	1000	81.9	107	***31***	0.75	1.33	***76***	1.94	1.54	***−21***
33	WSW	150	285	377	***32***	5.04	6.38	***27***	0.99	1.03	***4***

[a] The variation between 2006 and 2007.

Table 2
Recent reports on concentrations and temporal variations of PCDD/Fs in soils in the vicinity of the MSWIs.

Country	Location	Year	No.[a]	Emission levels[b]	Capacity ($t\,yr^{-1}$)	Concentration[c]	Variations[d]	Reference
Spain	Tarragona	1996	24	2	140,000	0.22–5.80	–	Schumacher et al. [9]
		1997	24	2	140,000	0.11–3.88	(0.08, 0.09)	Schumacher et al. [9]
		1999	24	0.003	140,000	0.15–4.89	(0.12, 0.03)	Domingo et al. [10]
	Barcelona	1998	24	1.4	300,000	1.22–34.28	–	Domingo et al. [11]
		1999	24	1.4	300,000	1.33–54.23	(2.79, 2.17)	Domingo et al. [11]
		2000	24	0.06	300,000	0.41–121.46	(−4.76, 0.54)	Domingo et al. [12]
	Montcada	1996	24	–	~40,000	0.30–44.3	–	Schumacher and Domingo [13]
		1997	24	–	~40000	0.20–29.3	(−0.95, −2.42)	Schumacher and Domingo [13]
		1998	24	44–111	~40,000	0.10–127	(2.25, 5.47)	Schumacher and Domingo [13]
		2000	24	0.086–15.72	~40,000	0.20–49.4	(−2.65, −4.47)	Schumacher and Domingo [13]
		2002	16	0.037–0.1	~40,000	0.40–16.9	(−0.25, 1.01)	Schumacher and Domingo [13]
	Site B	1995	8	–	–	0.18–1.87	–	Eljarrat et al. [14]
		1996	5	<0.1	–	0.18–1.15	(−0.16, −0.16)	Eljarrat et al. [14]
		1998	5	<0.1	–	0.34–0.78	(0.26, 0.06)	Eljarrat et al. [14]
	Site C	1996	10	<0.1	–	0.37–1.75	–	Eljarrat et al. [14]
		1998	25	<0.1	–	0.16–3.98	(−0.20, 0.06)	Eljarrat et al. [14]
China	Hangzhou	2006	33	–	300,000	0.39–5.04	–	Yan et al. [28]
		2007	33	0.083–0.795	300,000	0.62–6.38	(0.33, 0.28)	This study

[a] No.: Number of samples.
[b] Emission levels: in ng I-TEQ N m^{-3}.
[c] Concentrations: in ng I-TEQ kg^{-1}.
[d] Variations: between this survey and the preceding one, values in the parentheses are median and mean variations, and are given in ng I-TEQ kg^{-1}.

i.e., 5.47 ng kg^{-1} (mean value) was found in Montcada (1997–1998) with emission levels as high as 44–111 ng I-TEQ N m^{-3}. Given the similar treatment capacity and comparable or even an order of magnitude lower of emission levels, the I-TEQ increases in soils found in this study, i.e., 0.28 ng kg^{-1} (mean value) was roughly 3 times higher than the counterparts in Tarragona (1996–1997), indicating the MSWI might not be the dominant dioxin source in the local area.

3.2. Homologue and congener profiles of PCDD/Fs

The homologue and congener profiles in agricultural soils in the vicinity of the MSWI and flue gases of the FBIs are depicted in Fig. 2, with data normalized to the total concentration and I-TEQ, respectively.

Generally, the homologue and congener profiles of soils observed in this study resembled the fingerprints in the world averaged ambient air [34]. OCDD and 2,3,4,7,8-PeCDF was the single most important contributor in terms of total concentration and I-TEQ, respectively, regardless of sampling location and year (Fig. 2a). This was in accordance with recent studies reported by other investigators [24,25,35,36]. It has been reported that OCDD and 2,3,4,7,8-PeCDF dominate in the total concentration and I-TEQ of most primary and secondary dioxin emission sources, respectively [37]. Therefore, the dominance of these two congeners could also be found in soils through the dispersion and wet/dry depositions. It is well-acknowledged that the homologue profiles are similar among various thermal processes with total PCDF concentrations higher than the PCDDs [21,38,39]. Being a conservative matrix, soil can act as a natural sink for the long-term accumulation of PCDD/Fs. Therefore, the PCDD/PCDF (D/F) ratio in soil can serve as an indicator of contamination from combustion sources. As shown in Table 1, the D/F ratios of soils in 2007 were generally lower than those of 2006. Moreover, the D/F ratios of background soils were greater than the near-site ones in each year, i.e., 4.8 and 2.0 in 2006 and 2.9 and 1.7 in 2007 (median value), respectively. This implied that during 2006–2007, the soils around the MSWI were deteriorated by the combustion sources, with the situation more severe for the near-site soils than the background controls.

By contrast, distinct PCDD/F profiles were observed for flue gases in the three FBIs, especially for the homologue patterns (Fig. 2b). In general, a TCDF-dominant homologue profile characterized by decreasing concentrations of PCDF homologues with increasing levels of chlorination was noticed. However, during 2003–2007, large variations of TCDF and higher chlorinated PCDD homologues were found in the flue gases of FBI-3. Nevertheless, the proportions of the counterparts in soils remained almost constant. Since the PCDD/F emission level of FBI-3 in 2007 was more than an order of magnitude higher than that of FBI-2, the impact of the MSWI on soils was primarily caused by the FBI-3. Therefore, the large discrepancies of PCDD/F patterns observed between the flue gases of FBI-3 and soils strongly imply that the MSWI may not be the most influential PCDD/F source in the study area.

3.3. Source identification of PCDD/Fs

Our previous study based on the isomer-specific factor analysis indicated that agricultural soils within the study area were presumably contaminated by two agrochemicals, i.e., pentachlorophenol/sodium pentachlorophenate (PCP/PCP-Na) (factor 2) and 1,3,5-trichloro-2-(4-nitrophenoxy) benzene (CNP) (factor 3) [40]. However, it seems inappropriate to interpret factor 2 as PCP/PCP-Na without the indicator isomer OCDD, which dominated in the PCP-contaminated soils. According to the local investigation conducted in 2007, the PCP/PCP-Na had historically been applied only in some lakes to control the spreading of snailborne schistosomiasis, and the application of CNP in the agricultural fields was not recorded. Actually, the OCDD levels (<100 pg kg^{-1}) of soil samples observed in 2006 and 2007 were three orders of magnitude lower than the sediment samples from Chinese schistosomiasis areas [41]. Moreover, only soil sample E-1 in both surveys showed high concentrations (45.1 and 60.6 ng kg^{-1}, respectively) of the indicator isomer, i.e., 2,4,6,8-TCDF, in the impurities of CNP [42]. However, in all commercial CNP products, the quantities of 1,3,6,8-/1,3,7,9-TCDD were an order of magnitude higher than that of 2,4,6,8-TCDF [43], which was not the case observed in sample E-1. Therefore, it proved that agricultural soils in the study area were almost free from PCP/PCP-Na and CNP contamination. Consequently, these two agrochemicals were excluded from source identification of PCDD/Fs in soils.

Congener-specific factor analysis was applied to gain insight into the similarities and differences in congener profiles (data

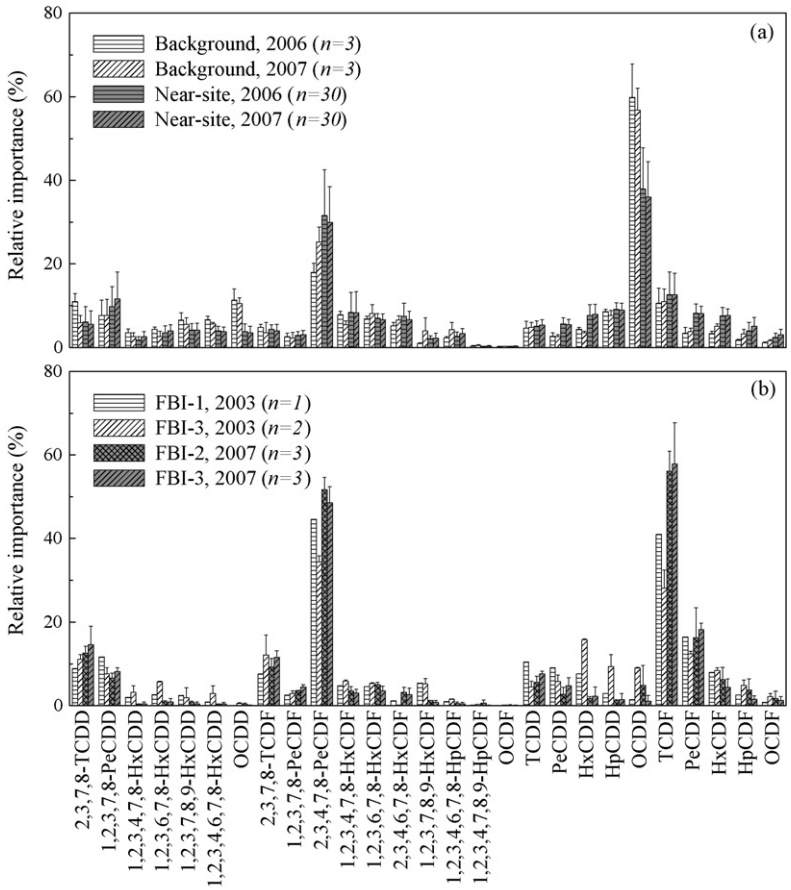

Fig. 2. Homologue and congener profiles in the background and near-site soils in the vicinity of the MSWI (a) and flue gases of the FBIs (b), with data normalizing to the total concentration and I-TEQ, respectively.

normalized to total congener concentration) between agricultural soils and reported PCDD/F emission sources. Since a large number of data that lower than the LOD (defined as censored values) in the variables may produce a large bias in the results, variables with more than 20% of their observations censored were excluded from the analysis [40,44]. Consequently, 14 congeners, 62 soil samples collected in two investigations, i.e., 60 near-site ones and 2 averaged background controls (hereafter designated as Back) and 5 PCDD/F emission sources, i.e., MSWI (average of FBI-2/-3 in 2007), HWB-W, Traff and OB-H/-C were regarded as variables and cases, respectively, and factor analysis was performed.

Three major factors were extracted after varimax rotation with an eigenvalues greater than 1, together accounting for 84.5% of the total variance (Fig. 3). All soil samples are clustered into one large circle with four PCDD/F emission sources, i.e., OB-C/H, Traff and HWB-W (Fig. 3a and b), indicating that soils within the study area were primarily influenced by emissions from OB, traffic and HWBs. Moreover, soil samples could be further divided into two groups. Group I contains the majority, i.e., 58 out of 62, being characterized by low dioxin level (<2.0 ng I-TEQ kg^{-1}) (except for SW-3). By contrast, soil samples in Group II are most dioxin-contaminated (Fig. 3c and d), i.e., WSW, NW, N and WNW, with the first two exhibiting high PCDD/F variations (>1.0 ng I-TEQ kg^{-1}).

As shown in Fig. 3a and b, soil samples in Group I have close relationships with OB-H/-C and Traff. A perfect example is for SW-3. Since soil samples in the same direction, i.e., SW-1, SW-2 and SW-4, experienced even reductions of I-TEQ during 2006–2007 (Fig. 1), the highest I-TEQ increment observed in SW-3 could not be primarily attributed to the depositions of PCDD/Fs from the MSWI. In fact, an open dumping site was discovered nearby emitting thick smoke plumes during the second soil investigation in 2007. Moreover, high atmospheric PCDD/F levels were detected adjacent to the dumping site, i.e., 2.71 and 6.14 pg I-TEQ m^{-3} for OB-H and OB-C, respectively, which were roughly an order of magnitude higher than the Japanese ambient air quality standard of 0.6 pg I-TEQ m^{-3} for dioxins [45]. It is, therefore, strong indications that soil sample SW-3 was significantly influenced by the OB. Furthermore, the road near sampling site SW-3 was broadened several months after the initial investigation in 2006. Therefore, during 2006–2007, more impact from the emissions of traffic was expected for this site than ever before.

On the other hand, soil samples in Group II exhibited close relationship with OB-H and Traff, indicating the relatively high PCDD/F levels observed in these soil samples were primarily attributed to the open burning of household garbage and traffic. This was reasonable since most of the soil sampling sites in this group are adjacent to motorways with heavy traffic (Fig. 1) and open dumping sites. Actually, ambient air adjacent to motorway exhibit high dioxin level, i.e., 0.439 pg I-TEQ m^{-3}, approximately 7–8 times greater than that in tunnel air in Taiwan [46], indicating traffic also played an important role on the variation of PCDD/Fs in soils. As indicated by Fig. 3b, HWBs might also be an important contributor to the accumulation of dioxins in soils. Since the wood used in the HWBs is often treated and/or painted, the emission level measured was pretty high, i.e., 1.95 ng I-TEQ N m^{-3}, generally 2 orders of magnitude higher than various types of wood combustions [47].

By contrast, the MSWI seems to be an outlier from soil samples, especially for the most contaminated ones (Fig. 3a and b), which reinforced the earlier implications in this study that the MSWI was not major contributor to the soil PCDD/F variations. This is quite contradictory to the results from our previous study based

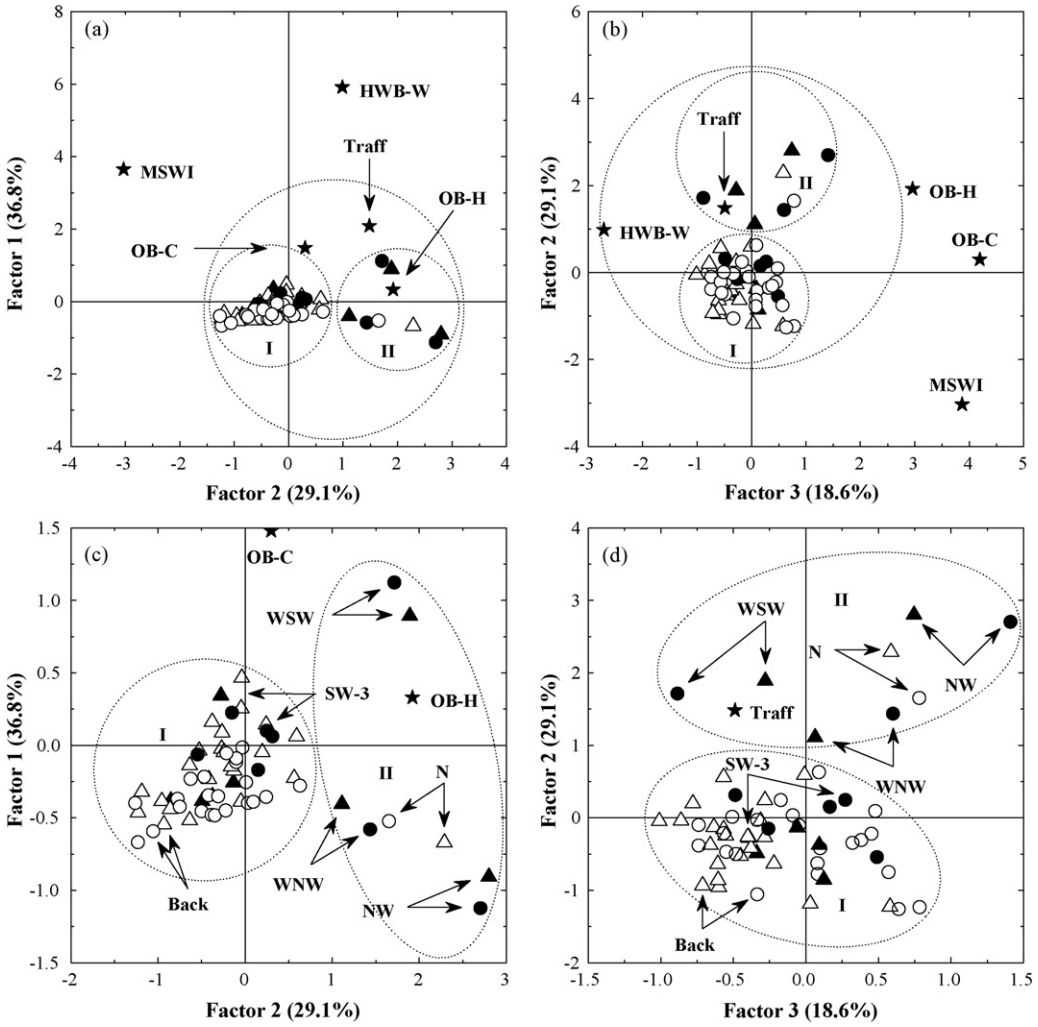

Fig. 3. Congener-specific factor analysis of soils and PCDD/F emission sources: (a) and (c), vector 1 vs vector 2; (b) and (d), vector 2 vs vector 3. The soil samples were marked with triangles (2006) and circles (2007), and those with variations lower/greater than 0.5 ng I-TEQ kg^{-1} were shown in white and dark colors, respectively; PCDD/F emission sources were marked with dark asterisks.

on homologue-specific factor analysis between soils and the MSWI [28]. Several reasons may account for the distinct results obtained: (1) different categories of fingerprints, i.e., homologue and congener, were adopted in two studies, and as suggested by Fiedler et al. [48], the latter one is more stable in the environment than the former one and was therefore used in this study; (2) the fingerprints of flue gases from the MSWI changed quite a bit during 2003–2007, e.g., congener profiles of the MSWI used in this study were quite different from the data adopted in our previous study (Fig. 2); (3) additional diffuse dioxin sources, i.e., HWB-W, traffic and OB-H/-C were included in the multivariate analysis in this study while only the MSWI was considered in the former one; (4) diffuse PCDD/F sources played a more important role on soils than the MSWI during 2006–2007. In fact, a modification of PCDD/F sources for soils occurred between the two sampling events. A shift toward OB-H/-C and/or Traff could be observed for soils with PCDD/F variations greater than 0.5 ng I-TEQ kg^{-1} (in dark triangles and circles), indicating that during 2006–2007, OB and traffic dominated the occurrence of PCDD/Fs in these sampling sites. This is even true for background controls (Back), but to a lesser extent.

4. Conclusions

Significant temporal variations of PCDD/F during 2006–2007 were observed in soils in a mixed agricultural-urban setting around an MSWI in Eastern China. Moreover, soils within the study area are proved to be almost free from previously suspected PCDD/F sources, i.e., PCP/PCP-Na and CNP. Furthermore, the sources of dioxins in soils collected in two investigations are re-identified based on the congener-specific factor analysis by taking into account the additional diffuse PCDD/F sources. The results indicate that OB, traffic and HWBs were major contributors that were responsible for the accumulation of PCDD/Fs in soils. By contrast, the impact of the presumably major PCDD/F source identified in our previous study, i.e., the MSWI, seems to be limited. Therefore, it suggests that public concern over the dioxin emissions from modern MSWI may be exaggerated. Consequently, effective management policies, especially for diffuse PCDD/F sources, should be urgently undertaken to prevent the deterioration of environmental quality in the local area.

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