

## Levels of PCDD/Fs in Agricultural Soils near Two Municipal Waste Incinerators in Shanghai, China

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**Abstract** A study was conducted on polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) in agricultural soils at 41 sites within a radius of 3 km from two municipal solid waste incinerators in Shanghai. The PCDD/F concentrations ranged from 71.32 to 3,881.44 pg g<sup>-1</sup> (0.64–61.15 pg I-TEQ g<sup>-1</sup>). The highest PCDD/F concentrations were found approximately 1,000 m from the municipal solid waste incinerators. The PCDD/F homologue profiles of all soil samples were compared with the profiles from suspected PCDD/F sources by multivariate statistical analysis. The results showed that, the PCDD/F pollutions in some soil samples can be attributed to emissions from the municipal solid waste incinerators.

**Keywords** MSWI · Soil · PCDD/Fs · Distribution

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) are two groups of semi-volatile organic contaminant that are extremely toxic and can accumulate in organic carbon-rich media such as soil and sediment, due to their hydrophobic properties. Many studies have evaluated the PCDD/F levels near emission sources and their impact on the environment (Oh et al. 2006; Domingo et al. 2000, 2001; Park et al. 2004). In China, it was found that important sources for PCDD/Fs include the production and use of ferrous/non-ferrous metal

products, and sodium pentachlorophenate (PCP-Na). In addition, the incineration of municipal, industrial and medical waste is considered to be another significant source owing to the rapid increase in the use of incineration for waste disposal in China (Zhu et al. 2008a, b). Shanghai is the center of economy, culture, science and technology in eastern China. There are only two MSWIs in Shanghai currently. MSWI A is located in the Puxi area, has three incineration processing lines and a daily capacity of 500 tons for each line. This incinerator adopted the flue gas purification technology which was widely used all over the world in the late 1990's. MSWI A formally entered production test runs in 2003. MSWI B is located in the Pudong area with a daily capacity of 1,000 tons. It was the first kiloton sized modern garbage incineration plant in China, and officially began operation in July 2003.

Soils have a high capacity to act as reservoirs for organic pollutants such as PCDD/Fs. Therefore soil represents a suitable environmental monitor to assess long-term exposure to PCDD/Fs. In recent decades, some developed countries or regions have investigated the levels and sources of PCDD/Fs in environmental sinks (e.g., soil and sediment) (Andersson and Ottesen 2008; Jou et al. 2007; Gaus et al. 2001). However, in China, due to the high cost of dioxin monitoring and the huge land area, only a few studies have examined environmental sinks for PCDD/Fs, and these studies mainly focused on the schistosomiasis and E-waste recycling areas (Cai et al. 2008). To generate overall information on the environmental impact of MSWIs, this study investigated the levels of PCDD/Fs in agricultural soils near two MSWIs in Shanghai, China and used a homologue pattern comparison and multivariate statistical analysis to determine the relationship between PCDD/F emissions from MSWIs and their concentrations in soil.

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## Materials and Methods

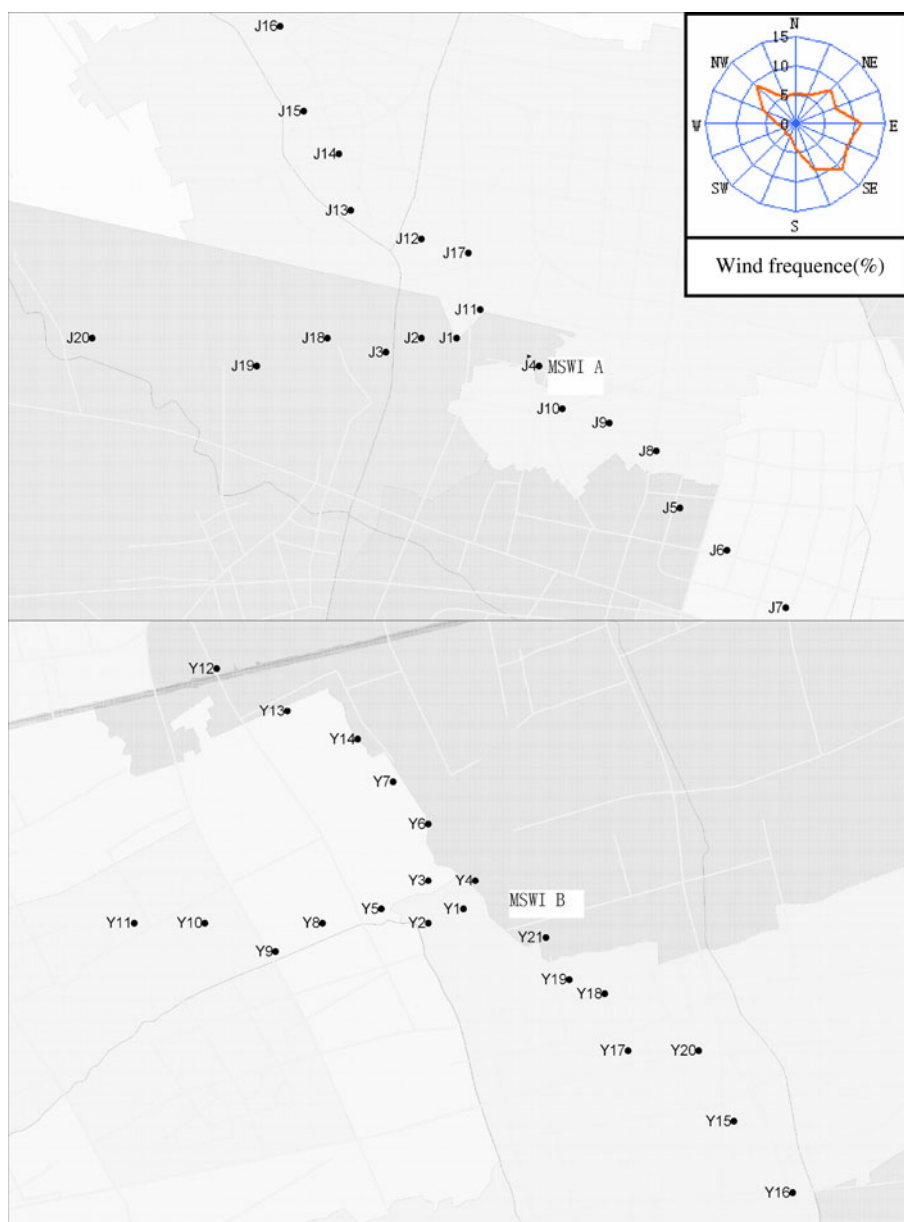
The soil samples were collected during spring (from April to May) in 2007, with a total of 41 soil samples (MSWI A: 20 samples; MSWI B: 21 samples) collected within a 3 km radius of the two MSWIs, mainly in the prevailing year-round downwind directions (E, NW, SE) (Fig. 1). In each direction, one sampling site was set every 300 m in the first 1,000 m from the incinerator, every 500 m from 1,000 to 3,000 m, with one sampling site located outside the 3,000 m radius. Every site was located using the global positioning system (GPS). The sampling locations were on open fields, not excessively covered by crops. Three samples of top soil were taken within a 5–10 m radius of each

sampling site at a depth of 0–20 cm using a pre-cleaned steel spoon. The three samples were then mixed in a glass bottle and transported to the laboratory.

The samples were dried at room temperature for 10–14 days. Dried soils were crushed by a ceramic cutting mill and then passed through a stainless steel sieve with a mesh size of  $1 \times 1$  mm. The moisture level of these soil samples was less than 3%. The samples were then labeled and stored in glass flasks at a temperature of  $-20^{\circ}\text{C}$  until analysis.

The PCDD/Fs were extracted from the soil samples using a selective pressured liquid extraction (SPLE) method with a fully automated ASE 200 system (Dionex, Sunnyvale, CA, USA). Briefly, 10 g soil samples (dry

**Fig. 1** Map of sampling sites



weight) were filled into 22 mL extraction cells and spiked with a mixture of  $^{13}\text{C}_{12}$ -labeled compound stock solution (10  $\mu\text{L}$ ) before extraction. The samples were extracted using 1:1 mixture of hexane and dichloromethane (Temperature: 150°C; Pressure: 1,500 psi; Flush: 60%; Purge time: 90 s; Cycles: 3). The extracts from the ASE were then concentrated under  $\text{N}_2$  and cleaned-up using an acid silica bed, multilayer silica gel column and florisil column in accordance with USEPA Method 1613. The final extracts were blown-down to 20  $\mu\text{L}$  under a gentle  $\text{N}_2$  stream and 10  $\mu\text{L}$  of  $^{13}\text{C}_{12}$ -internal standard spiking solution was added before the samples were analyzed by high-resolution gas chromatography coupled with a high-resolution mass spectrometry (HRGC/HRMS) (Autospec Premier, Waters) using a DB-5MS column (60 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ). A blank sample was analyzed for every batch of ten samples, and a duplicate sample was analyzed for every two batches. The blank samples did not contain any PCDD/F concentrations above the method detection limit, which varied between 0.063 and 0.249  $\text{pg g}^{-1}$  from tetra- to octa-PCDD/Fs. The recoveries generally varied between 55% and 89%, which satisfied the requirements of USEPA Method 1613.

Principal component analysis (PCA) was performed using the Multi-Variate statistical package (MVSP) version 3.13n. Prior to the PCA, the PCDD/Fs homologue data set was normalized towards its own total values. Concentrations

that were below the detection limit were assigned a value zero in the normalization processing.

## Results and Discussion

Table 1 summaries the 2,3,7,8-substituted PCDD/Fs concentrations of the 41 soil samples collected around MSWI A and B in three wind directions (Table 1). The total PCDD/F concentrations of agricultural soils ranged from 71.32 to 3881.44  $\text{pg g}^{-1}$  (0.64–61.15  $\text{pg I-TEQ g}^{-1}$ ), with an average value of 349.47  $\text{pg g}^{-1}$  (4.73  $\text{pg I-TEQ g}^{-1}$ ). Comparing the average PCDD/F levels in soil samples in Shanghai from our study with different sites from Spain (1.22–34.28  $\text{pg I-TEQ g}^{-1}$ ) (Domingo et al. 2000), Finland (13–252  $\text{pg I-TEQ g}^{-1}$ ), England (2–272  $\text{pg I-TEQ g}^{-1}$ ) (Li et al. 2004), Korea (1.25–74.98  $\text{pg I-TEQ g}^{-1}$ ) (Oh et al. 2006), Japan (average 7.10  $\text{pg I-TEQ g}^{-1}$ ) (Takei et al. 2000) and the US (average 4.0  $\text{pg I-TEQ g}^{-1}$ ), which were also near MSWIs, the PCDD/F concentrations in soil samples from Shanghai, Spain, Korea, Japan and the United States are of the same order of magnitude and are comparable with the soil guidelines in Germany and Sweden, which are 5 and 10  $\text{pg I-TEQ g}^{-1}$ , respectively. The I-TEQ values observed in the present study were much lower than those from Finland and England. Although no great variation in the PCDD/F concentrations was observed

**Table 1** The PCDD/F concentrations of the agricultural soils in vicinity of the two MSW incinerators ( $\text{pg g}^{-1}$ )

		Distance (m)	$\Sigma$ PCDD/Fs	I-TEQ			Distance (m)	$\Sigma$ PCDD/Fs	I-TEQ
MSWI	J1	400	241.97	2.58	MSWI	Y1	400	132.1	2.78
A-W	J2	700	681.22	10.22	B-W	Y2	700	114.95	1.63
	J3	1,000	2149.01	61.16		Y5	1,000	147.87	3.07
	J18	1,500	813.35	2.21		Y8	1,500	144.36	0.86
	J19	2,070	432.71	2.65		Y9	2,000	171.62	1.27
	J20	3,400	162.71	2.62		Y10	2,500	121.77	2.28
MSWI	J11	300	233.39	3.13		Y11	3,090	162.95	1.62
A-NW	J17	700	176.34	2.33	MSWI	Y4	400	162.89	1.65
	J12	1,000	3881.44	29.91	B-NW	Y3	724	212.68	1.81
	J13	1,500	305.34	2.04		Y6	1,000	111.54	0.95
	J14	2,000	227.86	5.58		Y7	1,500	105.91	0.64
	J15	2,500	114.7	1.12		Y14	1,900	71.31	0.88
	J16	3,000	133.05	0.77		Y13	2,500	216.1	6.3
MSWI	J4	300	183.89	3.59		Y12	3,100	84.26	1.01
A-SE	J10	685	262.54	1.97	MSWI	Y21	300	178.66	1.29
	J9	1,000	170.02	1.17	B-SE	Y19	700	120.87	1.1
	J8	1,500	119.09	1.53		Y18	1,000	181.48	1.92
	J5	2,000	124.82	1.4		Y17	1,500	98.36	0.73
	J6	2,500	114.38	2.29		Y20	1,500	118.73	1.87
	J7	3,000	174.64	2.46		Y15	2,400	120.85	1.05
						Y16	3,000	846.73	3.72

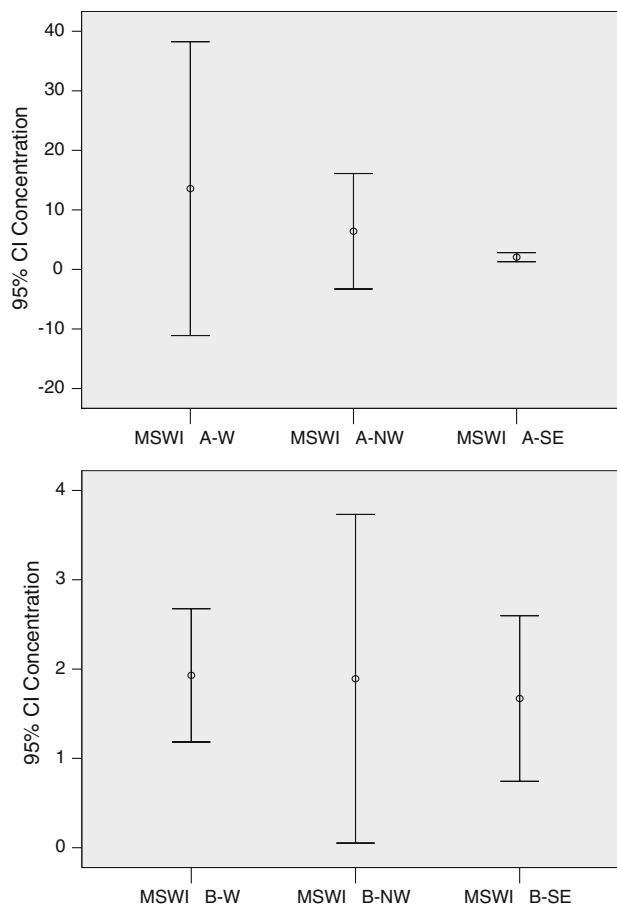
for most of the soil samples, unusually high values for both TEQ and  $\sum_{PCDD/Fs}$  were found in five soil samples (J3, J12, J2, Y13, J14), with concentrations of 61.15 pg I-TEQ g<sup>-1</sup>, 29.91 pg I-TEQ g<sup>-1</sup>, 10.22 pg I-TEQ g<sup>-1</sup>, 6.30 pg I-TEQ g<sup>-1</sup> and 5.58 pg I-TEQ g<sup>-1</sup>, respectively. These observed PCDD/F concentrations all exceed the 5 pg I-TEQ/g<sup>-1</sup> limit which restricts the cultivation of certain vegetables, with one sample (J3) exceeded 40 pg I-TEQ g<sup>-1</sup>. According to the soil dioxin guideline concentrations of Germany, this soil should be limited to cultivation of plants with minimum dioxin transfer, e.g., corn and soybeans.

Among all soil samples, OCDD was the predominant congener, accounting for around 69.65% of the total concentration of 17 congeners, followed by the highly-chlorinated congeners including 1,2,3,4,6,7,8-HpCDD and OCDF, which account for 11.80% and 9.82% respectively. This distribution profile is similar to those found in soils around numerous MSWIs (Domingo et al. 2000, 2001; Park et al. 2004). With respect to the TEQ concentrations, the main contributor to the TEQ was 2,3,4,7,8-PeCDF (accounting for 28.14% of the total TEQ), which is also consistent with previous research (Domingo et al. 2000, 2001; Park et al. 2004).

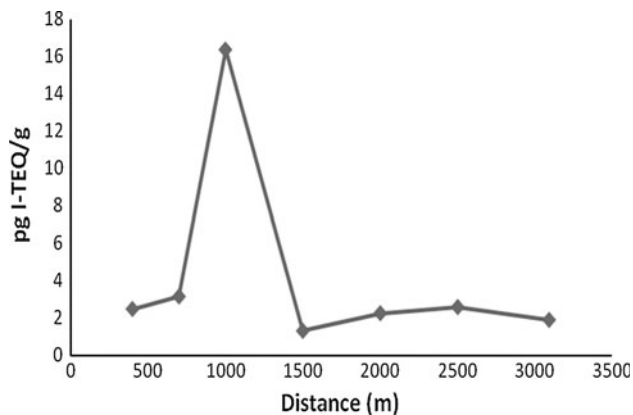
At the mean time, 60 soil samples were collected simultaneously and analyzed primarily to reflect the PCDD/F level of the background agricultural field from nine districts around Centertown in Shanghai. The specific content can be found in Li et al. (2009) and Rong et al. (2010). The concentrations of the soil samples from background area were ranged from 114.24 to 687.93 pg g<sup>-1</sup> (0.71 to 7.84 pg I-TEQ g<sup>-1</sup>), with an average value of 211.89 pg g<sup>-1</sup> (2.20 pg I-TEQ g<sup>-1</sup>).

Compared with our previous report on the background soil concentrations in Shanghai, the average concentrations in soil near the two MSWIs (349.47 pg g<sup>-1</sup>, 4.73 pg I-TEQ g<sup>-1</sup>) were relatively higher than those from the background area. Further, the congener distribution of the soil near the two MSWIs was different from the soil samples from the background area. Although both sets of samples had the same predominant congener compound, the OCDD in the background area accounted for 86.29% of the 17 congeners, which is somewhat higher than the contribution of OCDD to soil near the two MSWIs (69.65%). The profile of averaged soil samples analyzed in this study had higher fractions of PCDFs than those of background soil samples, even though OCDD was the most abundant.

Figure 2 represents the I-TEQ concentrations in different directions for each incinerator plant. It shows that both the concentrations and the discrete degree in samples from the W and NW directions were slightly higher than those from the SE direction. For the plot of the distance against average concentration (Fig. 3), the 41 soil samples were roughly



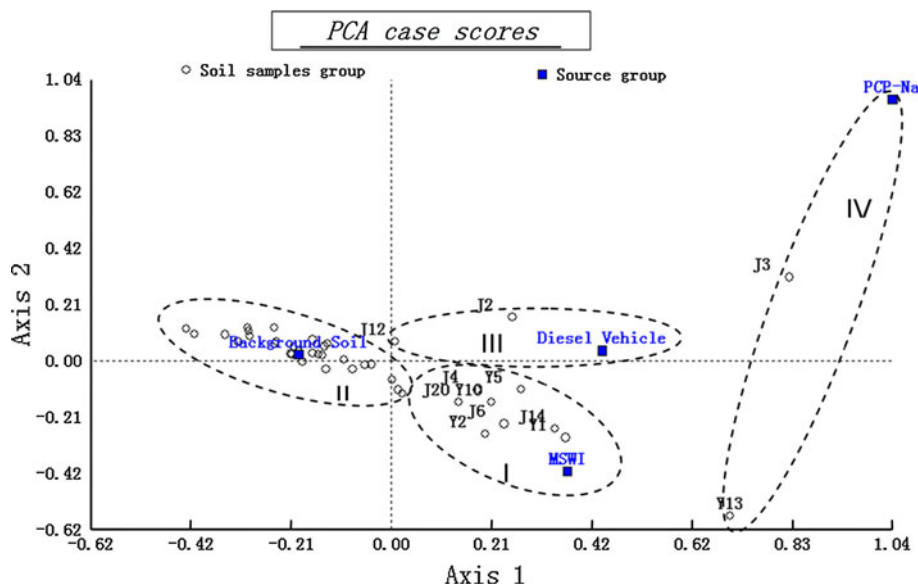
**Fig. 2** Error bar charts of the I-TEQ concentrations in different wind directions



**Fig. 3** Trend of PCDD/Fs levels in the soil with increasing distances

divided into seven groups based on distance from the MSWIs (500, 700, 1,000, 1,500, 2,000, 2,500 and 3,000 m). Initially, the mean concentrations of PCDD/Fs in the soil samples increased with the distance from the incinerators until peak levels occurred, and then the concentrations decreased with further distance. The maximum PCDD/F levels were observed approximately 1,000 m from the

**Fig. 4** Principal component plot of the 41 agricultural soil samples and some emission sources



MSWIs as the Fig. 3 showed. Incinerator fly ash will be released into the environment during the transport, processing and storage. The effect of atmospheric diffusion and dry/wet deposition will result in the presence of the peak concentrations at a certain distance (not the closest) from MSWIs, which is in accordance with the skewed or normal Gaussian model relating to the diffusion of gaseous pollutants. Based on meteorological data for Shanghai, the prevailing wind direction in Shanghai is southeast throughout the year. The soil samples collected from southeast of the incinerators are located at the windward direction of this prevailing wind direction, which may explain why the soil samples in the SE direction had lower concentrations than those from the W and NW directions and showed no obvious patterns between concentration and distance.

As dioxin emissions from MSWI, PCP-Na, which has been widely produced and used principally to control snailborne schistosomiasis along Yangtze River including Shanghai, were among the first emission issues identified as concerns in China (Tian and Ouyang 2003). In this research area, there were no other industries. So PCP-Na, diesel-fueled vehicles and MSWIs had been identified as main emission sources in these study areas. To identify the pollution sources near the MSWIs, PCDD/F homologue profiles from the agricultural soil samples near the MSWIs and background soil samples, together with the three probable emission sources (PCP-Na, diesel-fueled vehicles, MSWI) were analyzed by PCA (Shigeki et al. 2001; USEPA 2001), and the results are shown in Fig. 4.

PCA has identified three main components, which account for 81.88% variability of the 45 samples, with the variables being the ten homologue families. Figure 4 shows the score plot for the PCA of PC1 and PC2. The data

points for the agriculture soils near the MSWIs appear to cluster into four groups. The score plot indicates that most of the soil samples are in group II, which displays similar patterns to the background soil samples. The average concentration of the soil samples in group II was  $210.35 \text{ pg g}^{-1}$  ( $1.63 \text{ pg I-TEQ g}^{-1}$ ), which is consistent with the concentration level in the soil samples from the background area of Shanghai (Li et al. 2009). The other three groups are clustered closer to the MSWI in the score plot, most particularly for group I, indicating these three groups of samples were influenced more by the MSWIs than sampling group II. Within groups I, III and IV, sites J2, J3, J12 and Y13 showed patterns divergent from the other samples. The homologue profiles of sites J3 and Y13 were similar to those for PCP-Na, suggesting that the agricultural soils from sites J3 and Y13 may be also influenced by the application of PCP-Na. Conversely, the homologue profiles of sites J2 and J12 are similar to those displayed by diesel-fueled vehicles. It is remarkable that the five agricultural soil samples (J2, J3, J12, J14, Y13) with extremely high concentrations are all related to specific emission sources. It is indicated the MSWIs were not the only emission source near the MSW incinerations and the influence of the MSWIs was limited to some extent. These results are acceptable, given that the half-life of PCDD/Fs in soils is thought to be more than 10 years (Domingo et al. 2002), and in the range of 25–100 years in the subsurface and the MSWIs were operating for no more than 4 years in Shanghai prior to the study.

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