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Occurrence and impact of polychlorinated dibenzo-p-dioxins/dibenzofurans in the air and soil around a municipal solid waste incinerator

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ABSTRACT

To assess the influence of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) on the environment in the vicinity of municipal solid waste incinerators (MSWIs), we determined the levels of PCDD/Fs in air and soil samples collected around a MSWI, which is the largest in China. The International Toxicity Equivalency Quantity (I-TEQ) concentrations of PCDD/Fs in air samples were from 0.0300 to 1.03 pg I-TEQ/m³ (0.445–13.6 pg/m³), with an average of 0.237 pg I-TEQ/m³, while in soil samples they ranged from 0.520 to 3.40 pg I-TEQ/g (2.41–88.7 pg/g) with an average of 1.49 pg I-TEQ/g. The concentrations of PCDD/Fs in air and soil samples were comparable to other areas, and PeCDFs were the dominant contributors, which was different from stack gas homologue patterns. Multivariate statistical analysis showed that PCDD/Fs emission from the MSWI did not directly affect the profiles of PCDD/Fs in air and soils, so that vehicles and unidentified emission sources should be considered. The daily inhalation levels of PCDD/Fs for children (0.0110 to 0.392 pg I-TEQ/(kg·day) and adults (0.00600 to 0.221 pg I-TEQ/(kg·day) near the MSWI were lower than the tolerable daily intake of 1.00 to 4.00 pg WHO-TEQ/(kg·day), but in winter the values were higher than in summer. These results can be used as basic data for assessing the risk of PCDD/Fs exposure in residents living around this MSWI, and more monitoring programs and studies should be carried out around MSWIs.

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Introduction

Due to the rapid economic development and urbanization occurring over the last three decades, China is facing growing environmental pressure. For example, the quantity of various wastes has increased at an increasing rate, whose disposal

has already had impacts on the environment and public health. To dispose off huge amounts of solid waste at low cost and in an environmentally friendly manner, many incinerators have been set up in China. It is estimated that China will build up to 262 new municipal solid waste incinerators (MSWI) by 2015. Although MSWIs offer many advantages, such as

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significant volume and mass reduction of solid wastes, some secondary pollution occurs with the release of compounds such as heavy metals (Jung et al., 2004; Yao et al., 2012), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (Ni et al., 2009; Shibamoto et al., 2007).

Historic accidents have aroused public awareness of PCDD/Fs contaminations near incinerators. Many studies have evaluated the PCDD/Fs levels near emission sources and their effects on the environment in other countries (Joaquim et al., 2015; Lolita et al., 2015; Mi et al., 2014; Zhang et al., 2014; Liu et al., 2013). In China, the first national survey on the emission sources of PCDD/Fs was launched in 2005. However, the survey was mainly focused on the emission sources without investigating the influence on the environment.

Consequently, the objectives of this study are to: (1) investigate the concentrations and profiles of PCDD/Fs in ambient air and soil around the MSWI; (2) use homologue pattern comparison and multivariate statistical analysis to determine the relationship between PCDD/Fs emissions and the environment; and (3) to assess the health impact of people near the MSWI, via daily inhalation doses calculated for children and adults.

1. Materials and methods

1.1. Sampling sites

Fig. 1 shows the air and soil sampling sites near the MSWI. The MSWI, located in a valley, began operation in 2012 and was the largest incinerator in China as well as in Asia. Fourteen air samples (A1–A14) at seven sites were sampled from February to November 2014 (Table 1), and ambient air samples were collected using a SIBATA HV-1000F sampler according to HJ 77. 2-2008 (Environmental Protection Standard of China). The sampler was equipped with a quartz fiber filter (QFF), followed by a glass cartridge containing two polyurethane foam (PUF) plugs. Before

sampling, the PUF plugs were spiked with 1 ng of $^{37}\text{Cl}_4$ -TCDD as a sampling surrogate standard. About 1008 m³ ambient air was collected during a 24 hr period, with a flow rate of 0.700 m³/min. The samples were subsequently placed in a glass container wrapped with aluminum foil.

Based on the height of the chimney of the MSWI, we evaluated the potentially affected areas, and according to the results, 11 soil samples (S1–S11) were sampled around the MSWI. All soil samples were collected at a depth of 0–10 cm.

1.2. Sample pre-treatment and analysis

All the organic solvents were pesticide residue grade from J.T. Baker (PA, USA). Silica gel was purchased from Wako (Osaka, Japan). Calibration standard solutions, $^{37}\text{Cl}_4$ -TCDD, $^{13}\text{C}_{12}$ -labeled clean-up standards and $^{13}\text{C}_{12}$ -labeled injection standards were purchased from Wellington Laboratories (Guelph, Canada).

Analysis of the seventeen 2,3,7,8-substituted PCDD/Fs followed the method of HJ 77. 2-2008 (Environmental Protection Standard of China). Prior to a 24 hr Soxhlet extraction with toluene, the filters and PUFs were spiked with $^{13}\text{C}_{12}$ -labeled clean-up standards. The extract was then concentrated in a rotary evaporator to substitute n-hexane for toluene, followed by H₂SO₄ and H₂O liquid/liquid-extraction. Afterwards, the volume was adjusted to 100 mL with n-hexane, and then half of the solution was used for determination of PCDD/Fs. Subsequently, the extract was purified by silica gel and activated carbon. The PCDD/Fs were eluted from the carbon column with 200 mL toluene. After volume reduction to 20 μL , the injection standards were added.

A high resolution gas chromatograph interfaced with a high resolution mass spectrometer (HRGC-HRMS) (Agilent 6890 N-Waters AutoSpec Ultima NT) was used for identification and quantification of PCDD/Fs. Samples were injected in splitless mode at an injector temperature of 270°C. For separation of PCDD/Fs, a DB-5 column 60 m \times 0.250 mm (film thickness 0.250 μm) was used. The column temperature program was: start 160°C held for 2 min, 160–220°C at 5°C/min

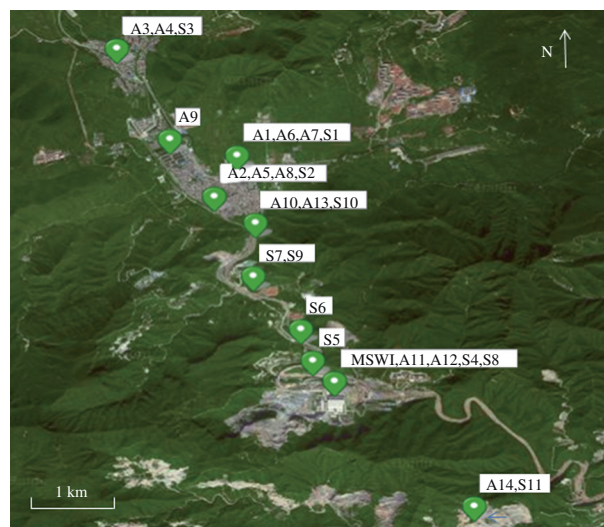


Fig. 1 – Air and soil sampling sites and location of the MSWI. MSWI: municipal solid waste incinerator.

Table 1 – Air sampling periods and PCDD/Fs concentration in the air samples (pg I-TEQ/m³).

Isomer	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12	A13	A14
	Feb 25–26, 2014			Apr 20–21, 2014				Jul 1–2, 2014				Oct 15–16, 2014		
2,3,7,8-TeCDF	0.028	0.043	0.032	0.008	0.009	0.003	0.002	0.003	0.004	0.004	0.005	0.003	0.003	0.004
1,2,3,7,8-PeCDF	0.022	0.032	0.024	0.001	0.005	0.002	0.002	0.001	0.002	0.002	0.003	0.002	0.002	0.003
2,3,4,7,8-PeCDF	0.290	0.410	0.295	0.010	0.070	0.025	0.030	0.008	0.030	0.025	0.035	0.025	0.025	0.030
1,2,3,4,7,8-HxCDF	0.083	0.110	0.087	0.015	0.012	0.005	0.007	0.004	0.007	0.006	0.009	0.008	0.008	0.009
1,2,3,6,7,8-HxCDF	0.059	0.081	0.062	0.014	0.012	0.005	0.006	0.004	0.006	0.006	0.007	0.007	0.006	0.007
1,2,3,7,8,9-HxCDF	0.007	0.011	0.006	0.0003	0.001	0.001	0.000	0.000	0.0003	0.0003	0.0003	0.0003	0.001	0.0003
2,3,4,6,7,8-HxCDF	0.069	0.096	0.074	0.007	0.016	0.006	0.008	0.004	0.008	0.008	0.010	0.007	0.007	0.008
1,2,3,4,6,7,8-HpCDF	0.021	0.028	0.024	0.004	0.004	0.002	0.002	0.001	0.002	0.002	0.003	0.003	0.003	0.003
1,2,3,4,7,8,9-HpCDF	0.004	0.005	0.006	0.001	0.001	0.0003	0.0004	0.0002	0.0003	0.0004	0.0002	0.0004	0.0005	0.0005
OCDF	0.001	0.002	0.001	0.0005	0.0002	0.0001	0.0001	0.0001	0.0001	0.000	0.0002	0.0002	0.0002	0.0002
2,3,7,8-TeCDD	0.021	0.043	0.025	0.010	0.010	0.0004	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
1,2,3,7,8-PeCDD	0.060	0.090	0.050	0.010	0.015	0.004	0.001	0.002	0.001	0.001	0.007	0.004	0.004	0.005
1,2,3,4,7,8-HxCDD	0.012	0.016	0.008	0.002	0.003	0.001	0.0004	0.001	0.0004	0.0004	0.0004	0.000	0.000	0.001
1,2,3,6,7,8-HxCDD	0.021	0.031	0.018	0.007	0.008	0.002	0.002	0.001	0.001	0.001	0.003	0.001	0.001	0.002
1,2,3,7,8,9-HxCDD	0.016	0.022	0.014	0.003	0.005	0.001	0.001	0.001	0.0004	0.001	0.002	0.001	0.0004	0.001
1,2,3,4,6,7,8-HpCDD	0.008	0.011	0.009	0.002	0.003	0.001	0.001	0.0004	0.001	0.001	0.002	0.001	0.001	0.001
OCDD	0.001	0.001	0.001	0.0005	0.0003	0.0002	0.0002	0.0001	0.0001	0.0001	0.0003	0.0001	0.0001	0.0001
TeCDF	0.028	0.043	0.032	0.008	0.009	0.003	0.002	0.003	0.004	0.004	0.005	0.003	0.003	0.004
PeCDF	0.312	0.442	0.319	0.011	0.075	0.027	0.032	0.008	0.032	0.027	0.038	0.027	0.027	0.033
HxCDF	0.218	0.298	0.229	0.036	0.041	0.016	0.021	0.012	0.021	0.020	0.026	0.022	0.022	0.024
HpCDF	0.025	0.033	0.030	0.005	0.004	0.002	0.003	0.001	0.003	0.003	0.003	0.003	0.003	0.003
OCDF	0.001	0.002	0.001	0.0005	0.0002	0.0001	0.001	0.0002	0.0004	0.001	0.0004	0.0002	0.0002	0.0002
TeCDD	0.021	0.043	0.025	0.010	0.010	0.0004	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
PeCDD	0.060	0.090	0.050	0.010	0.015	0.004	0.001	0.002	0.001	0.001	0.007	0.004	0.004	0.005
HxCDD	0.049	0.069	0.040	0.012	0.016	0.005	0.004	0.002	0.002	0.003	0.005	0.002	0.001	0.004
HpCDD	0.008	0.011	0.009	0.002	0.003	0.001	0.001	0.0004	0.001	0.001	0.002	0.001	0.001	0.001
OCDD	0.001	0.001	0.001	0.0005	0.0003	0.0002	0.0002	0.0001	0.0001	0.0001	0.0003	0.0001	0.0001	0.0001
I-TEQ	0.722	1.032	0.735	0.095	0.174	0.057	0.065	0.030	0.065	0.059	0.086	0.063	0.061	0.074

PCDD/F: polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofuran; I-TEQ: International Toxicity Equivalency Quantity.

held for 16 min, 220–235°C at 5°C/min held for 7 min, 235–330°C at 5°C/min held for 1 min. The ion source was operated at 220°C, the electron energy was 45 eV, and the mass spectrometer was tuned to a mass resolution >10,000. The most abundant signals of the molecular ion clusters of the tetra- to octa-chlorodibenzo-p-dioxins and -dibenzofurans were recorded in selected ion mode (SIM). The PCDD/Fs were quantified using fifteen ¹³C₁₂-labeled internal standards and two ¹³C₁₂-labeled recovery standards. The labeled PCDD/F internal standards and their response factors were used for quantification of unlabeled PCDD/Fs of homologous groups. Detection limits were calculated as three times the signal to noise ratio, and were 0.500–8.60 fg/m³ for 2,3,7,8-TCDF; 0.400–13.2 fg/m³ for 1,2,3,7,8-PeCDF; 0.900–14.6 fg/m³ for 2,3,4,7,8-PeCDF; 0.300–12.1 fg/m³ for 1,2,3,4,7,8-HxCDF; 0.300–14.4 fg/m³ for 1,2,3,6,7,8-HxCDF; 0.300–18.7 fg/m³ for 2,3,4,6,7,8-HxCDF; 0.200–21.9 fg/m³ for 1,2,3,7,8,9-HxCDF; 0.500–7.80 fg/m³ for 1,2,3,4,6,7,8-HpCDF; 0.400–9.80 fg/m³ for 1,2,3,4,7,8,9-HpCDF; 0.300–13.6 fg/m³ for OCDF; 0.600–5.70 fg/m³ for 2,3,7,8-TCDD; 1.10–12.3 fg/m³ for 1,2,3,7,8-PeCDD; 0.500–5.70 fg/m³ for 1,2,3,4,7,8-HxCDD; 0.500–6.20 fg/m³ for 1,2,3,6,7,8,9-HxCDD; 0.500–6.00 fg/m³ for 1,2,3,7,8,9-HxCDD; 0.200–9.50 fg/m³ for 1,2,3,4,6,7,8-HpCDD; and 0.300–19.2 fg/m³ for OCDD. Surrogate recoveries ranged from 40 to 110% for TCDD/Fs, 45 to 130% for PeCDD/Fs, 35 to 89% for HxCDD/Fs, 37 to 96% for HpCDD/Fs, and 41 to 85% for OCDD. One field and one laboratory blank were analyzed for every ten samples to eliminate interferences and laboratory

contaminations, and these values were all below the detection limits (LODs) in the blanks.

1.3. Statistical analysis

In order to identify the potential emission sources of PCDD/Fs, and to compare the differences and similarities in the congener profiles, principal component analysis (PCA) was performed on the homologue patterns in air, soil, and stack gas samples using SPSS software (version 17.0, IBM Inc.). The PCDD/Fs homologue levels were normalized with respect to the total PCDD/Fs concentration in the relevant sample.

2. Results and discussion

2.1. Levels and profiles of PCDD/Fs in air samples

The mass and I-TEQ concentrations of PCDD/F congeners for 14 air samples are summarized in Table 1. Concentrations below the detection limits were regarded as zero. In addition to 2,3,7,8-substituted PCDD/Fs, total native PCDD/Fs (tetra to octa) homologues including 2,3,7,8-PCDD/Fs and non-2,3,7,8-PCDD/Fs congeners, were also calculated.

Generally, similar homologue patterns were found among the different monitoring sites throughout the year.

For all samples, the mass concentrations of 2,3,7,8-substituted PCDD/Fs were 0.445 to 13.6 pg/m³ with an average of 3.30 pg/m³. The highest concentration was observed for sample A5 in February 2014 and the lowest for sample A8 in July 2014. The main contributors were 1,2,3,4,6,7,8-HpCDF, OCDF and OCDD, which accounted for 23%, 19% and 14% on average. For the I-TEQ concentration of PCDD/Fs, however, the range was from 0.0300 to 1.03 pg I-TEQ/m³, with an average of 0.237 pg I-TEQ/m³. The dominant contributor to total I-TEQ value was 2,3,4,7,8-PeCDF, with an average contribution of 38%. Other important contributors were 1,2,3,4,7,8-HxCDF (11%), 2,3,4,6,7,8-HxCDF (10%), 1,2,3,6,7,8-HxCDF (9%) and 1,2,3,7,8-PeCDD (6%). In winter, the concentrations of 2,3,7,8-substituted PCDD/Fs in some air samples were even higher than the ambient air standard in Japan (0.600 pg I-TEQ/m³) (MOE, Japan), but in other seasons, the concentrations were below 0.600 pg I-TEQ/m³. The levels of PCDD/Fs from three MSWIs in Italy were found to be in the range of 0.0100–0.337 pg I-TEQ/m³ (Caserini et al., 2004). In Korea, the PCDD/Fs level varied from 0.195 to 0.301 pg I-TEQ/m³ in the vicinity of an IWI (Kim et al., 2005). Compared with the above data, the PCDD/Fs levels in our study appear to be much higher in winter and lower in other seasons.

Based on our calculations, the area within 1 km of the MSWI was most likely to be affected by the PCDD/Fs emission, while the PCDD/Fs at the sampling sites did not show obvious spatial variation. However, PCDD/Fs concentrations in the atmosphere showed seasonal variations (Fig. 2): the highest concentration was observed in winter (1.03 pg I-TEQ/m³), and the lowest observed concentration was in summer (0.0300 pg I-TEQ/m³). Domestic burning and heavy haze might account for the observed high concentration in winter; in addition, wet deposition by precipitation was likely to play a key role in the low levels of atmospheric PCDD/Fs seen during the summer. Other environmental factors, such as several loss processes including photolysis, chemical reactivity, temperature inversion conditions, and scavenging by vegetation might also explain this phenomenon (Lohmann and Jones, 1998). The results were similar to previous investigations on the PCDD/Fs in the Beijing atmosphere; the reason may be that the MSWI was newly built, and environment around it did not have time to fully reflect its influence (Zhou et al., 2014).

2.2. Levels and profiles of PCDD/Fs in soil samples

The concentrations of soil samples are listed in Table 2. Many studies have shown that MSWIs had an influence on the soil around them. In our survey, the concentrations were from 0.520 to 3.40 pg I-TEQ/g (2.41–88.7 pg/g) with an average of 1.49 pg I-TEQ/g. In general terms, the current levels of PCDD/Fs in soils were lower than those in other studies near MSWIs. Deng reported a range of concentrations between 0.640 and 64.2 pg I-TEQ/g in the vicinity of a MSWI in Shanghai (China), whereas in Taiwan the levels ranged between 0.850 and 4.50 pg I-TEQ/g (Deng et al., 2011; Chen et al., 2011). The levels in our current study were also lower than for other types of soil reported by Nadal and Turgut (Nadal et al., 2009; Turgut et al., 2012). Regarding homologue patterns, OCDD accounted for 43.0%, and next was 1,2,3,4,6,7,8-HpCDF, accounting for 16.4%. For I-TEQ concentration profiles, 2,3,4,7,8-PeCDF accounted for 33.7%, and the next highest contributor was 2,3,4,6,7,8-HxCDF (10.4%). High levels of low-chlorinated furans indicate the presence of potential combustion sources of PCDD/Fs, but in this study, we should consider gaseous transmission and emission sources together, such as automobiles and incinerators.

Wind direction is an important factor to be considered in studying the effects of an incinerator on the environment. In the study area, the major winds blew in southern–northern directions. The highest sample was S1, and the lowest was S5; this was not consistent with our calculations, therefore we could not clearly observe a trend of declining PCDD/Fs levels as the distance increased. This conclusion was not consistent with other reports, and the reason might be that the MSWI had been operated for only two years.

2.3. Comparison of homologue patterns in air, soil and stack gas samples

In addition to comparing total concentration levels among different types of samples, we used homologue pattern comparisons to investigate the relationships between the incinerator and the environment. To compare the homologue patterns of each sample, soil and air data were normalized to the total PCDD/Fs ([PCDDs] + [PCDFs] = 1).

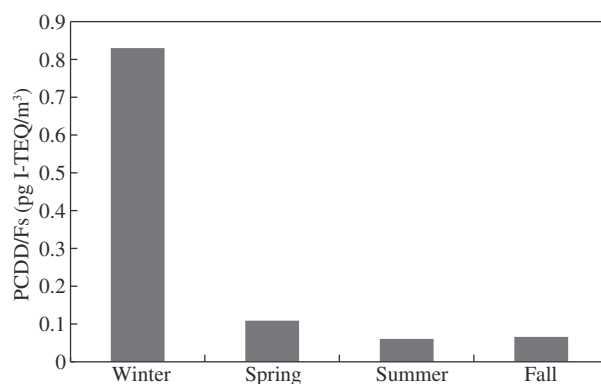


Fig. 2 – Seasonal changes of the average PCDD/F concentrations during the study period. PCDD/F: polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofuran.

Table 2 – PCDD/Fs concentration in the soil samples (pg I-TEQ/g).

Isomer	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11
2,3,7,8-TeCDF	0.130	0.170	0.100	0.051	0.011	0.057	0.440	0.003	0.003	0.350	0.150
1,2,3,7, 8-PeCDF	0.090	0.060	0.030	0.030	0.008	0.035	0.075	0.008	0.040	0.075	0.085
2,3,4,7, 8-PeCDF	1.000	0.500	0.250	0.250	0.250	0.250	0.500	0.250	0.250	1.000	1.000
1,2,3,4,7,8-HxCDF	0.300	0.100	0.050	0.050	0.050	0.100	0.200	0.050	0.100	0.300	0.300
1,2,3,6,7,8-HxCDF	0.240	0.140	0.070	0.090	0.010	0.090	0.140	0.050	0.120	0.210	0.250
1,2,3,7,8,9-HxCDF	0.020	0.015	0.010	0.015	0.010	0.010	0.010	0.015	0.015	0.010	0.015
2,3,4,6,7,8-HxCDF	0.270	0.140	0.070	0.120	0.030	0.100	0.130	0.080	0.150	0.240	0.320
1,2,3,4,6,7,8-HpCDF	0.065	0.043	0.030	0.032	0.007	0.030	0.046	0.018	0.062	0.083	0.110
1,2,3,4,7,8,9-HpCDF	0.022	0.002	0.004	0.004	0.002	0.004	0.008	0.002	0.002	0.008	0.002
OCDF	0.006	0.004	0.009	0.001	0.001	0.001	0.004	0.001	0.005	0.004	0.006
2,3,7,8-TeCDD	0.150	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025
1,2,3,7,8-PeCDD	0.600	0.150	0.050	0.075	0.050	0.050	0.050	0.075	0.075	0.050	0.200
1,2,3,4,7,8-HxCDD	0.120	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020
1,2,3,6,7,8-HxCDD	0.150	0.025	0.025	0.070	0.025	0.025	0.025	0.025	0.025	0.025	0.025
1,2,3,7,8,9-HxCDD	0.130	0.040	0.015	0.040	0.015	0.015	0.015	0.020	0.020	0.015	0.040
1,2,3,4,6,7,8-HpCDD	0.058	0.034	0.023	0.044	0.006	0.023	0.032	0.014	0.015	0.031	0.036
OCDD	0.049	0.034	0.030	0.007	0.001	0.006	0.023	0.008	0.004	0.013	0.015
TeCDF	0.130	0.170	0.100	0.051	0.011	0.057	0.440	0.003	0.003	0.350	0.150
PeCDF	1.090	0.560	0.280	0.280	0.258	0.285	0.575	0.258	0.290	1.075	1.085
HxCDF	0.830	0.395	0.200	0.275	0.100	0.300	0.480	0.195	0.385	0.760	0.885
HpCDF	0.087	0.045	0.034	0.036	0.009	0.034	0.054	0.020	0.064	0.091	0.112
OCDF	0.006	0.004	0.009	0.005	0.003	0.005	0.012	0.001	0.005	0.004	0.006
TeCDD	0.150	0.025	0.025	0.026	0.026	0.026	0.029	0.025	0.025	0.025	0.025
PeCDD	0.600	0.150	0.050	0.075	0.050	0.050	0.050	0.075	0.075	0.050	0.200
HxCDD	0.400	0.085	0.060	0.130	0.060	0.060	0.060	0.065	0.065	0.060	0.085
HpCDD	0.058	0.034	0.023	0.044	0.006	0.023	0.032	0.014	0.015	0.031	0.036
OCDD	0.049	0.034	0.030	0.007	0.001	0.006	0.023	0.008	0.004	0.013	0.015
I-TEQ	3.400	1.502	0.811	0.929	0.522	0.846	1.755	0.662	0.930	2.459	2.599

Different homologue patterns were observed between the MSWI and ambient air samples (Fig. 3a). The HxCDFs were the most dominant homologues in stack gas samples, and the others were PeCDFs and TeCDFs. Of all, the OCDD level was the lowest. PCDF levels were higher than those of PCDDs, and many studies have reported the same conclusions among the various thermal processes in flue gases (Lohmann and Jones,

1998; Oh et al., 1999; Mamontov et al., 2000). The homologue patterns found in the air samples were different from those found in stack gas. The dominant homologues were PeCDFs, others were HxCDFs and TeCDFs, and the OCDD level was also the lowest. Background air tends to have a typical homologue pattern of high levels of chlorinated dioxins (*e.g.*, OCDD) and generally low levels of chlorinated furans (Fiedler et al., 1996).

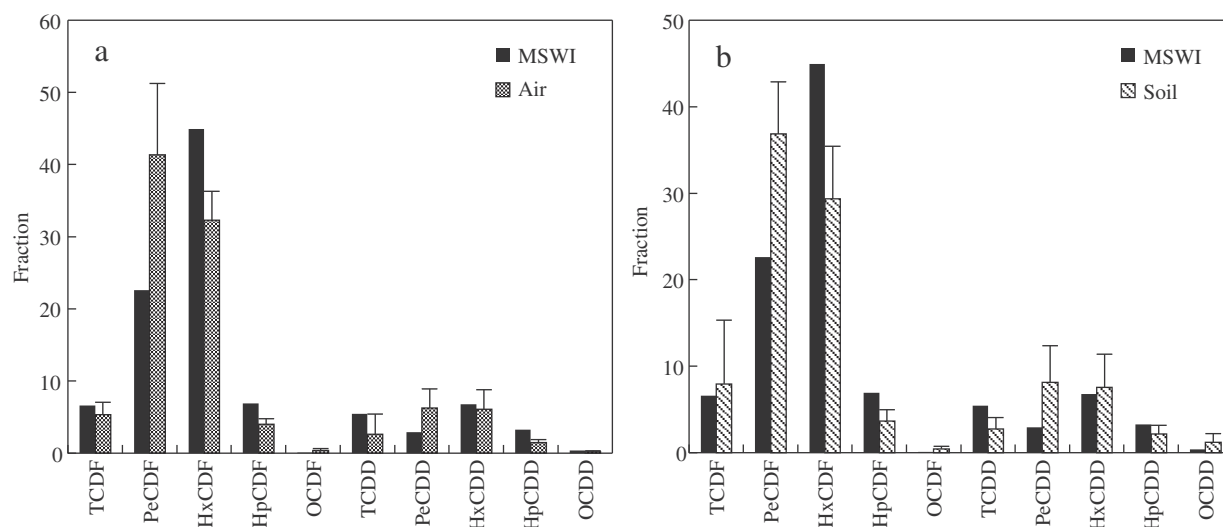


Fig. 3 – (a) PCDD/F homologue patterns in each type of sample in the MSWI and ambient air samples, (b) in the MSWI and soil samples.

As described previously, high levels of low-chlorinated furans indicate the presence of potential combustion sources of PCDD/Fs, such as an incinerator, but the different homologue distributions in stack gas and air indicated that the PCDD/Fs in air were influenced by different emission sources.

The homologue distribution in soil samples was also different from that in stack gas samples, but the same as that in air samples (Fig. 3b). This could be explained by the fact that the PCDD/Fs in soil were mostly from dry and wet deposition and also affected by multiple emission sources.

2.4. Multivariate analysis

In order to identify the potential emission sources of PCDD/Fs, and to compare the differences and similarities in the congener profiles, principal component analysis (PCA) was performed on the ten homologues of samples using SPSS software (version 17.0, IBM Inc.) (Fig. 4). Two main factors (FAs) were extracted. The first factor (FA 1) was found to account for 38.4% of the total variance; we could see that FA 1 was strongly and positively correlated with HpCDF, HxCDF and HpCDD, but negatively correlated with PeCDF and TCDF. Highly chlorinated PCDD/Fs can be considered an indicator for automobile exhaust emissions (U.S. EPA, 2001) and fossil fuel combustion emission (Lin et al., 2007). The second factor (FA 2) accounted for 23.8% of the total variance. FA 2 was positively correlated with OCDF and PeCDD, but negatively correlated with PeCDF. The PCA results also showed that these two FAs (Eigenvalue >1) accounted for 62.2% of total variability among the samples; therefore, most of the PCDD/Fs variation in the data set could be explained by the two factors. All the data points were clustered into two groups: group one contained the air samples and soil samples, and group two contained the flue gas samples. These findings indicated that PCDD/Fs in air and soil were from the same emission sources and might be affected by multiple emission sources, and that the MSWI was not the only one. Moreover, other factors, such as other

combustion facilities or motor vehicles, should also be considered (Gullet and Ryan, 1997).

2.5. Inhalation risk assessment

Direct inhalation of atmospheric pollutants may be a pathway of exposure to PCDD/Fs, thus emphasizing the need to evaluate the chemical risk posed to humans by daily respiration. We calculated the average daily intake of TEQs per unit body weight with the assumption that individuals were exposed to polluted air 24 hr/day and that indoor air pollution was equal to outdoor air pollution. Daily PCDD/Fs exposure doses were computed using the following equation:

$$\text{Inh} = \frac{t_f V_f f_r C_{\text{air}}}{\text{BW}}$$

Inh is the inhalation exposure in pg I-TEQ/(kg-day), t_f is the exposed time fraction and was assumed conservatively as 1, V_f is the ventilation rate with a value of 20 m³/day for adults and 7.60 m³/day for children, f_r is the alveolar fraction retained in the lungs, with a value of 0.750 for both adults and children, C_{air} is the average air concentration of dioxin in pg I-TEQ/m³, BW is the body weight (70 kg for adults and 15 kg for children) (Yu et al., 2006).

Table 3 lists the estimated daily intakes of PCDD/Fs for humans by inhalation in the sampling periods. It is evident that residents in all sampling sites around the MSWI were exposed to PCDD/Fs, with daily inhalation doses ranging from 0.00600 to 0.221 pg I-TEQ/(kg-day) for adults and 0.0110 to 0.392 pg I-TEQ/(kg-day) for children. In winter, the daily inhalation doses were higher (A1, A2, A3), but the values were lower in other seasons. From comparison with other cities, the exposure values were higher than those in Guangzhou (Li et al., 2011) and Shanghai (Li et al., 2008) in winter, but lower than those of the two cities in summer. The WHO European Centre for Environment and Health recommended a tolerable daily intake (TDI) of 1 to 4 pg of WHO-TEQ/(kg-day) weight (including twelve dioxin like PCBs) in 1998 (WHO, 1998). In previous studies, it was estimated that >90.0% of exposure of the general population to PCDD/Fs occurs through diet, and the inhalation intake doses of PCDD/Fs have been reported to contribute approximately 2.61% to the total daily intake (Yu et al., 2006). Compared with the TDI, the daily intakes by inhalation for citizen around the MSWI in this study were lower. We cannot give precise total daily PCDD/Fs intake doses for citizens around the MSWI; however, according to our results for inhalation, we could infer that the intake of residents around the MSWI was considerably higher in winter and lower in summer. The present data is still insufficient to reflect the total status of the PCDD/Fs around the MSWIs in China, since the pollutants from emission resources were continuous. Consequently, it is necessary to control and reduce the contaminant emission by stable combustion and advanced gas cleaning systems with the enforcement of stricter pollutant emission standards. In addition, more monitoring programs and studies should be carried out around the MSWI, in which other dioxin-like compounds, such as polybrominated dibenzo-p-dioxins and

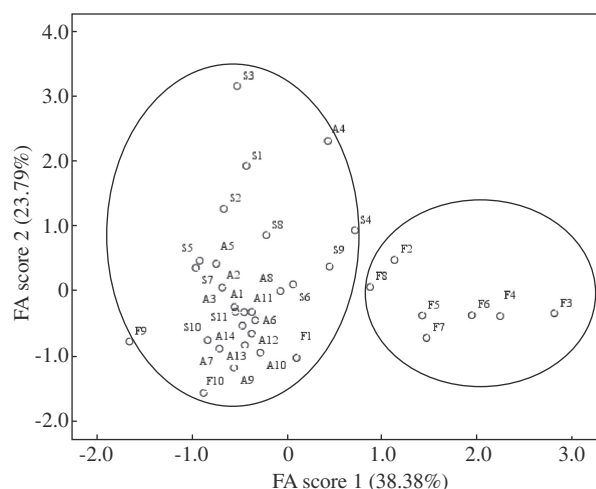


Fig. 4 – Principal component analysis for the incinerator (MSWI), air (A1–A14), and soil samples (S1–S11).

Table 3 – Inhalation risk evaluation of PCDD/Fs near the MSWI.

Samples name	Inhalation exposure dose (pg I-TEQ/(kg·day))		Samples name	Inhalation exposure dose (pg I-TEQ/(kg·day))	
	Adults	Children		Adults	Children
A1	0.155	0.274	A8	0.006	0.011
A2	0.221	0.392	A9	0.014	0.025
A3	0.157	0.279	A10	0.012	0.022
A4	0.020	0.036	A11	0.013	0.024
A5	0.037	0.066	A12	0.013	0.023
A6	0.012	0.022	A13	0.013	0.023
A7	0.014	0.025	A14	0.016	0.028

dibenzofurans (PBDD/Fs), and dioxin-like polychlorinated biphenyl (DL-PCBs) should also be considered.

3. Conclusions

We herein reported a comprehensive analysis of PCDD/Fs levels in a complex, MSWI-containing residential area in China for the first time. The PCDD/Fs levels in soil did not show the typical decrease with increasing distance from the MSWI reported by other investigators. Homologue pattern analysis revealed that the most dominant homologues in stack gas samples were HxCDFs, while in air and soil samples they were PeCDFs. Our results indicated that PCDD/Fs in air and soil were affected by many emission sources besides the MSWI. For instance, vehicles and unidentified combustion sources, such as heaters used in winter, might affect the environment. The results from SPSS showed the same conclusions. The daily inhalation doses in winter should arouse public concern. These results can be used as basic data for assessing the risk of PCDD/Fs exposure in residents living near this MSWI and will form the basis for our future human risk assessment studies, which will seek to confirm the quantitative influence of this MSWI on the nearby residential area.

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