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CONTENTS

Seasonal trend of ambient PCDD/Fs in Tianjin City, northern China using active sampling strategy

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Abstract

The spatial concentrations, seasonal trends, profiles and congener pairs of ambient polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were investigated within a seasonally active sampling scheme during Jun 2008 and Jan 2009 in Tianjin City, northern China. The PCDD/F concentrations ranged 14.2–172 fg I-TEQ/m^3 (average 69.3 fg I-TEQ/m^3) in summer and $(89.8–1.01) \times 10^3$ fg I-TEQ/m^3 (average 509 fg I-TEQ/m^3) in winter, respectively, except for the E-waste dismantling site where much higher values were observed (1.04×10^3 fg I-TEQ/m^3 in summer and 7.123×10^3 fg I-TEQ/m^3 in winter). The results indicated a significantly seasonal trend with higher TEQ values in winter as compared with summer, which could be related to increased emission sources and seasonal variations of the atmospheric boundary layer height. 2,3,4,7,8-PeCDF was the dominant contributor to the total PCDD/F toxic equivalents, and 2,3,7,8-TCDD was detected at almost all the sampling sites in winter. Most of the similarly substituted PCDD/F congener pairs exhibited high correlations, suggesting that they might have similar environmental fate or sources. But different seasonal and spatial distributions of PCDD/F concentrations indicated that the emission sources might be intermittent.

Key words: PCDD/Fs; seasonal trend; Tianjin; high-volume air sampling

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) were classified as Persistent Organic Pollutants (POPs) under the 1998 UNECE Protocol and 2001 Stockholm UNEP Convention. In 2004, the National Implementation Plan (NIP) on POPs was ratified and PCDD/Fs were officially under supervisory in China. Several artificial activities, such as combustion (e.g., waste incineration, burning of coal, wood, etc.), the refining of petroleum, metallurgy production, and synthesis procedures for certain chlorinated chemicals (e.g., pentachlorophenol), are related with PCDD/F formation (Lohmann and Jones, 1998; Lee et al., 2005; Lohmann et al., 2000; National Atmospheric Emission Inventory, 2011). Due to their persistence, bioaccumulation and long-range atmospheric transport in the environment, PCDD/Fs have attracted much attention since the 1970s, when organizations and institutes began funding studies on PCDD/Fs to evaluate the effectiveness of source reduction measures and give a basis for assessing aspects of human exposure (Meijer et al., 2008).

Under the NIP guidance, the ambient atmosphere concentrations of PCDD/Fs in big cities in China, including

Guangzhou, Beijing and Shanghai, were studied to evaluate the impact of PCDD/Fs on the local residents, and the results showed that the PCDD/F contamination levels in the investigated atmospheres were comparable or slightly higher than those in many other urban cities around the world (Yu et al., 2006; Li et al., 2008a, 2008c). However, further investigations must be continued in China, not only because the levels and trends of PCDD/Fs in urban and rural locations are not clear due to lack of historical records, but also because more and more artificial activities related to the formation of PCDD/Fs are becoming more active, especially in cities undergoing rapid urbanization and increasing industrial processes, where the PCDD/Fs emission sources and characteristics are also not clear.

Anthropogenic activities and human intensity have been increasing in recent decades in Tianjin City, a typical Chinese city with different functional zones mixing together. The eco-environmental risk must be considered for rapidly developing cities and real-time evaluation should also be undertaken to investigate the distributions of atmospheric POPs in different urban functional areas. In this work, the concentrations, congener profiles and seasonal variation of the seventeen 2,3,7,8-substituted PCDD/Fs in the ambient air were monitored. Besides urban zones, sampling was also conducted at a background area to evaluate the impact

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of different urban functional areas on the PCDD/F ambient air concentrations and the relevant potential risks to the local residents.

1 Materials and methods

1.1 Sample collection

Tianjin is one of the largest chemical bases, and is considered as a new economic growth center in China. It is subject to a warm continental monsoon climate. The average temperature is $-3 \sim 5$°C in winter and 26–27°C in summer. A total of 21 air samples were collected using three high-volume air samplers (GPS-1, Thermo Inc., USA) over a duration of 24 hr for each sample on 13–30 Jun 2008 and 1–5 Jan 2009 in different functional zones in Tianjin City. The sampling sites included one residential site (S1), four industrial sites (S2, S3, S4 and S5) and one background site (S6) which was far away from the city. Details of the sampling locations are shown in Fig. 1. The sampling process was conducted according to the revised US EPA Method TO-9A. Glass fiber filters (GFF, 10.16 cm diameter) and polyurethane foam (PUF, 6.3 cm diameter, 7.6 cm length) materials were used to absorb particle-bound and gaseous chemicals, respectively. Prior to sampling, the GFFs were baked at 450°C to remove organic contaminants and the PUFs were extracted with acetone in accelerated solvent extraction (ASE, ASE300, Dionex, USA) at 100°C and 1500 psi for 2 static extraction cycles, followed by an additional ASE extraction procedure with hexane. The sampling cartridges were vacuum-dried in desiccators and stored in sealed bags. The detailed sampling procedure strictly followed the previous reference (Li et al., 2008b).

1.2 Sample analysis

The analysis procedure of the seventeen 2,3,7,8-substituted PCDD/Fs was in accordance with the US EPA Method 1613B. Briefly, 1 ng of $^{13}C_{12}$-labeled PCDD/F surrogate standards (^{13}C-2,3,7,8-TCDF, ^{13}C-1,2,3,7,8-

PeCDF, ^{13}C-2,3,4,7,8-PeCDF, ^{13}C-1,2,3,4,7,8-HxCDF, ^{13}C-1,2,3,6,7,8-HxCDF, ^{13}C-2,3,4,6,7,8-HxCDF, ^{13}C-1,2,3,7,8,9-HxCDF, ^{13}C-1,2,3,4,6,7,8-HpCDF, ^{13}C-1,2,3,4,7,8,9-HpCDF, ^{13}C-2,3,7,8-TCDD, ^{13}C-1,2,3,7,8-PeCDD, ^{13}C-1,2,3,4,7,8-HxCDD, ^{13}C-1,2,3,6,7,8-HxCDD, ^{13}C-1,2,3,4,6,7,8-HpCDD, and ^{13}C-OCDD) were spiked into the air samples before an ASE extraction with organic solvents (hexane:dichloromethane = 1:1, (V/V)) using the same extraction procedures as mentioned above. The extracts were concentrated by a rotary evaporator and followed by a cleanup with acid silica gel and multilayer silica columns which consisted of 1 g silica, 4 g basic silica (1.2%, m/m), 1 g silica, 8 g acid silica (30%, m/m), 2 g silica, and 2 g anhydrous sodium sulfate. Prior to the injection, the final extract was spiked with 1 ng $^{13}C_{12}$-labeled injection standards ($^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD) for recovery quantification. A high resolution gas chromatograph combined with a high resolution mass spectrometer (HRGC/HRMS, Autospec Ultima, Waters, UK) was equipped with an electron impact ionization (EI) source and the electron emission energy was set to 35 eV, and VSIR mode was used for the analyte quantitation at resolution $\geqslant 10,000$. Exactly 1 μL of sample solution was injected into a 60 m DB-5MS column with a CTC PAL autosampler in splitless mode. Helium served as the carrier gas with a constant flow of 1.2 mL/min. The source temperature was 270°C and the oven temperature program was as follows: started at 160°C and held for 2 min, ramped from 160 to 220°C at 7.5°C/min and held for 16 min, raised from 220 to 235°C at 5°C/min and held for 7 min, and raised to the final temperature of 330°C at 5°C/min and held for 1 min.

1.3 Quality assurance/quality control (QA/QC)

A breakthrough test was performed using another PUF in series with the sampling PUF. None of the analyte was detected in the second PUF, indicating no breakthrough occurred in the sampling procedures. One field and one laboratory blank were routinely analyzed in each batch of seven samples and values were all below the detection limits (LODs) in the blanks. The LODs were defined as 3 times the signal/noise ratio, and were 0.055–0.086 pg/sample for TCDD/F, 0.069–0.087 pg/sample for penta-PCDD/Fs, 0.032–0.085 pg/sample for hexa-PCDD/Fs, 0.031–0.074 pg/sample for hepta-PCDD/Fs and 0.120–0.142 pg/sample for OCDD/F. Sample recoveries ($n = 21$) in this study varied between 32.9%–124% (average 69.5%) for PCDD/Fs, which meet the requirements of Method 1613B. All quantification results were not blank corrected and the concentrations below the LODs were set as zero.

2 Results and discussion

2.1 Concentration of 2,3,7,8-substituted PCDD/Fs in the atmosphere

In the present study, the I-TEQ scheme (North Atlantic Treaty Organization, 1988) was used to present the individ-
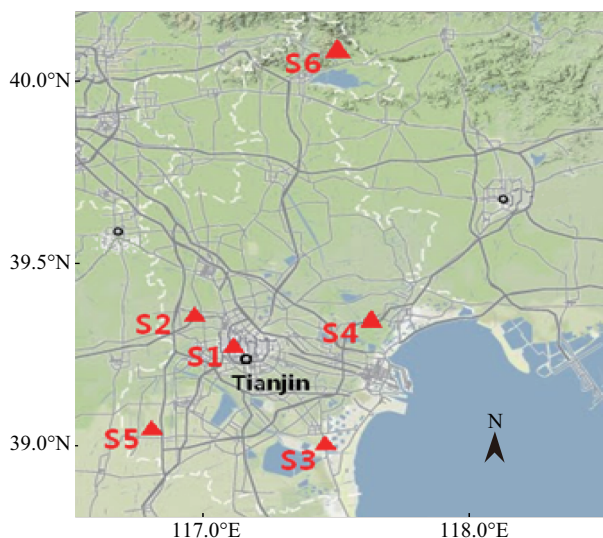

Fig. 1 Air sampling locations in Tianjin, Northern China.

ual and $\sum_{17}$PCDD/Fs concentrations in ambient air, which are listed in Table 1. All seventeen target congeners were detected with the spatial concentrations in the range of a few fg I-TEQ /m^3 to several pg I-TEQ /m^3 levels. As expected, the PCDD/F concentrations in the background site (S6) showed much lower levels compared with the other sites. Except for S5, the PCDD/F concentrations ranged from 14.2 to 172 fg I-TEQ/m^3 (average 69.3 fg I-TEQ/m^3) in summer, which were much lower than the ambient air standard of 600 fg TEQ/m^3 for dioxins proposed by Japan (Government of Japan, 2005) and fell within the lower limit of global urban areas (100–400 fg TEQ/m^3) reported by Lohmann and Jones (1998). However, it was notable that the average PCDD/F concentrations in winter (509 I-TEQ fg/m^3, range 89.8–1.01 × 10^3 fg I-TEQ/m^3) (Table 2) were significantly higher than those in summer, and close to the upper limit of the Japanese ambient air standard (Government of Japan, 2005). Compared with other Chinese cities, such as Beijing (18–644 fg I-TEQ/m^3) (Li et al., 2008b), Guangzhou (57–1.28 × 10^3 fg I-TEQ/m^3, Yu et al., 2006) and Shanghai (2.2–2.08 × 10^4 fg I-TEQ/m^3, Li et al., 2008a), the ambient PCDD/Fs in the sampling sites in Tianjin were at lower levels, except for sampling site S5. The PCDD/Fs concentrations in this study were also comparable to other Asian cities, such as Hong Kong (18–430 fg I-TEQ/m^3, Sin et al., 2002), Taiwan (56–348 fg I-TEQ/m^3, Chang et al., 2002), Korea (169–882 fg I-TEQ/m^3, Park and Kim, 2002) and Japan (83–550 fg I-TEQ/m^3, Government of Japan, 2005). However, the concentrations were several to a hundred times higher than those reported in relatively less contaminated European and North American countries and cities such as Greece (40–119 fg I-TEQ/m^3, Kouimtzis et al., 2002), Manchester (26–220 fg I-TEQ/m^3, Lohmann et al., 2000), London (62–180 fg I-TEQ/m^3, Coleman et al., 1997), Spain (10–357 fg I-TEQ/m^3, Abad et al., 1997), Rome (65 fg I-TEQ/m^3, Menichini et al., 2007) and Houston (40–55 fg I-TEQ/m^3, Correa et al., 2007). In the E-waste dismantling area (S5), The total ambient PCDD/F levels were 1.04 × 10^3 and

7.123 × 10^3 fg I-TEQ/m^3 in summer and in winter, respectively, which was even comparable to the observation in the Taizhou area in east China (Li et al., 2008c). These higher results suggested that the E-waste dismantling industry might contribute more to the ambient PCDD/F levels in the local area.

2.2 Seasonal trends of the ambient air PCDD/F concentrations

As shown in Fig. 2, seasonal variations were observed in the present study with higher PCDD/F concentrations in the winter and lower levels in the summer, which has been also widely reported in other studies (Lohmann and Jones, 1998; Lee et al., 1999). Generally, increased combustion (i.e., domestic space heating) and seasonal variations in the atmospheric boundary layer height might be likely causes. However, considering the different functional zones where the sampling sites were located, the diurnal variation of the height of the inversion base is evident in the city area (S1, S2 and S3), which significantly affects the diffusion of pollutants. It is therefore probable that increased combustion mainly leads to higher levels of PCDD/Fs in winter in the rural areas (S4), including background sites (S5), and the
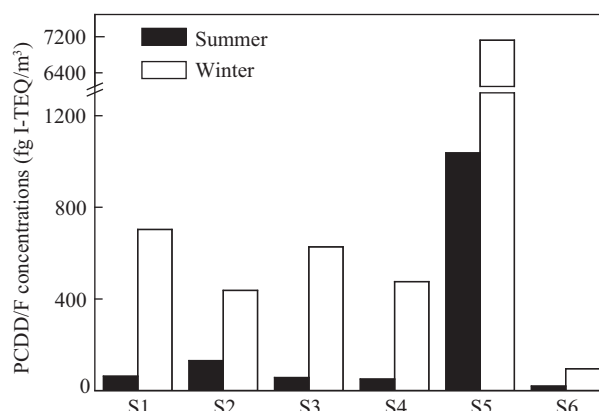

Fig. 2 Seasonal variation of PCDD/F concentrations at the sampling sites.

Table 1 Ambient air PCDD/F concentrations (fg I-TEQ/m^3) at the sampling sites during summer sampling period

Summer	S1[a]			S2			S3			S4			S5[b]	S6
	S1-1	S1-2	Average	S2-1	S2-2	Average	S3-1	S3-2	Average	S4-1	S4-2	Average	S5-1	S6-1
2378-TCDF	7.90	2.20	5.05	8.00	9.50	8.75	6.90	4.20	5.55	5.50	5.40	5.45	54.9	1.60
12378-PeCDF	2.50	< LOD[c]	1.25	2.10	2.90	2.48	4.40	< LOD	2.20	< LOD	0.58	1.15	46.8	< LOD
23478-PeCDF	54.0	< LOD	27.0	30.5	54.5	42.5	44.0	12.0	28.0	12.5	27.0	19.8	505	< LOD
123478-HxCDF	9.20	2.80	6.00	10.6	13.2	11.9	5.00	3.60	4.30	5.20	7.10	6.15	61.5	4.30
123678-HxCDF	8.30	2.40	5.35	10.6	12.4	11.5	6.40	4.20	5.30	4.40	7.90	6.15	69.8	3.90
234678-HxCDF	15.3	4.8	10.1	14.1	22.3	18.2	12.1	5.00	8.55	6.20	7.20	6.70	168	6.80
123789-HxCDF	2.50	< LOD	1.25	2.40	3.40	2.90	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	46.8	< LOD
1234678-HpCDF	2.88	1.02	1.95	3.72	5.13	4.43	1.83	1.12	1.48	1.14	4.32	2.73	22.9	1.62
1234789-HpCDF	0.40	0.09	0.24	0.36	0.62	0.49	0.28	0.12	0.20	0.15	0.71	0.43	3.15	0.27
OCDF	0.20	0.07	0.13	0.31	0.50	0.40	0.12	0.08	0.10	0.09	0.83	0.46	2.08	0.19
2378-TCDD	< LOD	< LOD	< LOD	21.0	10.5	10.5	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	26.0	< LOD
12378-PeCDD	< LOD	< LOD	< LOD	8.50	9.50	9.00	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
123478-HxCDD	1.40	< LOD	0.70	< LOD	2.00	1.00	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	5.70	< LOD
123678-HxCDD	2.50	< LOD	1.25	2.00	4.10	3.05	< LOD	< LOD	< LOD	0.90	< LOD	0.45	9.90	< LOD
123789-HxCDD	1.60	< LOD	0.80	1.10	3.60	2.40	1.20	< LOD	0.60	< LOD	< LOD	< LOD	8.30	< LOD
1234678-HpCDD	1.20	0.59	0.91	1.20	3.60	2.40	0.45	0.17	0.31	0.29	0.81	0.55	6.00	0.34
OCDD	0.45	0.20	0.33	0.22	4.05	2.14	0.11	0.07	0.09	0.09	0.25	0.17	1.12	0.09
I-TEQ	110	14.2	62.3	95.7	172	134	82.8	30.6	56.7	37.6	61.5	49.6	1.04 ×10^3	19.1

[a] S1-1 and S1-2: parallel samples obtained from the same site during the active sampling procedures. Average: the average value of the parallel samples.
[b] One of the parallel samples obtained at S5 was missing due to equipment failure, and thus S5-2 and average value were not given. [c] Limit of detection.

Table 2   Ambient air PCDD/F concentrations (fg I-TEQ/m^3) at the sampling sites during winter sampling period

Winter	S1[a]			S2			S3			S4			S5			S6
	S1-1	S1-2	Average	S2-1	S2-2	Average	S3-1	S3-2	Average	S4-1	S4-2	Average	S5-1	S5-2	Average	S6-1
2378-TCDF	61.8	29.3	45.6	53.3	21.5	37.4	43.0	50.5	46.8	48.3	46.6	47.5	30.3	699	365	7.50
12378-PeCDF	36.9	10.8	23.8	25.7	< LOD[b]	12.9	5.20	26.1	15.6	19.6	10.5	15.0	9.15	490	249	<LOD
23478-PeCDF	459	208	333	422	<LOD	211	167	397	282	0	289.5	145	207	6.90×10^3	3.55×10^3	30.5
123478-HxCDF	117	31.6	74.1	74.1	24.8	49.5	58.0	83.8	70.9	48.7	46.1	47.4	37.6	1.73×10^3	884	14.5
123678-HxCDF	67.8	19.4	43.6	37.0	6.10	21.6	33.7	48.4	41.1	47.9	48.1	48.0	27.3	909	468	14.7
234678-HxCDF	98.6	30.8	64.7	69.7	16.4	43.1	47.7	86.9	67.3	50	50.5	50.0	32.8	1.25×10^3	644	5.20
123789-HxCDF	24.1	12.2	18.2	14.9	<LOD	7.45	18.5	17.8	18.2	16.9	16.1	16.5	9.40	255	132	4.70
1234678-HpCDF	49.8	9.70	29.7	27.3	9.35	18.3	19.3	32.6	26.0	15.0	14.2	14.6	11.1	593	302	3.40
1234789-HpCDF	8.05	1.32	4.69	5.45	1.44	3.45	2.86	4.95	3.91	1.92	2.05	1.99	1.80	87.1	44.4	<LOD
OCDF	3.22	0.49	1.85	1.42	0.38	0.90	1.10	1.84	1.47	0.60	0.80	0.70	0.85	23.4	12.1	0.23
2378-TCDD	30.0	22.0	26.0	20.0	<LOD	10.0	<LOD	26.0	13.0	<LOD	37.0	18.5	28.0	342	185	9.00
12378-PeCDD	<LOD	<LOD	<LOD	13.5	4.50	9.00	<LOD	<LOD	<LOD	39.5	36.0	37.75	<LOD	< LOD	< LOD	<LOD
123478-HxCDD	7.10	4.10	5.60	3.70	<LOD	1.85	5.30	6.90	6.10	4.70	8.00	6.35	5.40	86.9	46.2	1.10
123678-HxCDD	18.0	7.60	12.8	6.10	<LOD	3.05	100	15.9	12.95	10.9	11.3	11.1	9.80	177	93.6	1.40
123789-HxCDD	14.7	6.50	10.6	5.50	3.60	4.55	8.80	14.3	11.6	9.30	9.10	9.20	6.50	143	74.5	<LOD
1234678-HpCDD	11.7	3.66	7.70	3.63	1.56	2.60	8.18	9.46	8.82	5.71	5.49	5.60	3.87	123	63.7	1.86
OCDD	1.65	0.52	1.08	0.97	0.16	0.57	2.52	1.64	2.08	0.70	0.76	0.73	1.12	17.0	9.06	0.68
I-TEQ	1.01×10^3	398	703	784	89.8	437	431	824	627	320	632	476	422	1.38×10^4	7.13×10^3	94.7

[a] S1-1 and S1-2: parallel samples obtained from the same site during the active sampling procedures. Average: the average value of the parallel samples.
[b] Limit of detection.

thicker inversion layer in winter increased the residence of pollutants in the city areas (S1, S2 and S3). Compared with a report showing average winter/summer ratios of 3 for sampling sites in Portugal (Coutinho et al., 1999), the ratios were up to about 10-fold in the urban sampling sites such as S1, S3 and S4, but relatively lower (3–7 fold) in the remaining rural sites. Katsoyiannis et al. (1999) reported that winter PCDD/F concentrations slightly higher than those of summer might imply the contribution of diffuse combustion sources such as domestic space heating. In many northern cities in China, scattered heating activities are still very active in winter, which might have an important impact on the high winter/summer PCDD/F ratios. On the other hand, the temperature effect might also be a possible explanation for the observed seasonal trends (Li et al., 2010).

2.3 PCDD/F profiles in the ambient air samples

Figure 3 presents the average homologue profiles for each site in summer and winter, respectively. It has been reported that 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD constituting the dominant congeners was the typical coal or wood combustion-influenced fingerprint (Lohmnan et al., 2006). In our investigation, 2,3,4,7,8-PeCDF was the single dominant contributor to the PCDD/F I-TEQs in both the summer and winter sampling period, accounting for

an average contribution of 64.5% to the toxic equivalents of PCDD/Fs, while the contribution of 1,2,3,7,8-PeCDD was much lower (average 5.98% of the total I-TEQs). This result was also consistent with the world average for ambient air (Lohmann and Jones, 1998). The other main contributors were 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF and 2,3,4,6,7,8-HxCDF, accounting for average contributions of 11.5%, 9.66%, and 13.7% to the PCDD/F I-TEQs, respectively. A lower contribution (< 8%) of 2,3,7,8-TCDD/Fs was observed at all the sites in Tianjin, which was comparable to the study by Lohmann and Jones (Lohmann and Jones, 1998) who suggested that 2,3,7,8-TCDD/Fs generally make a low contribution and account for 10%–15% of the overall toxicity. It should be noted that besides the PCDFs in all the samples, most of the seven PCDD congeners were detected in winter, while only some highly-chlorinated PCDDs were observed in summer. This probably indicated that enhanced emission sources of PCDD/Fs existed in winter.

2.4 PCDD/F congener pairs in the ambient air samples

It was reported that PCDD and PCDF congener pairs could be used to obtain useful information on the sources and fate of PCDD/Fs (Lohmnan et al., 2006). A Pearson linear correlation was performed in this study. Some pairs of congeners were identified with strong correlations. 1,2,3,6,7,8-
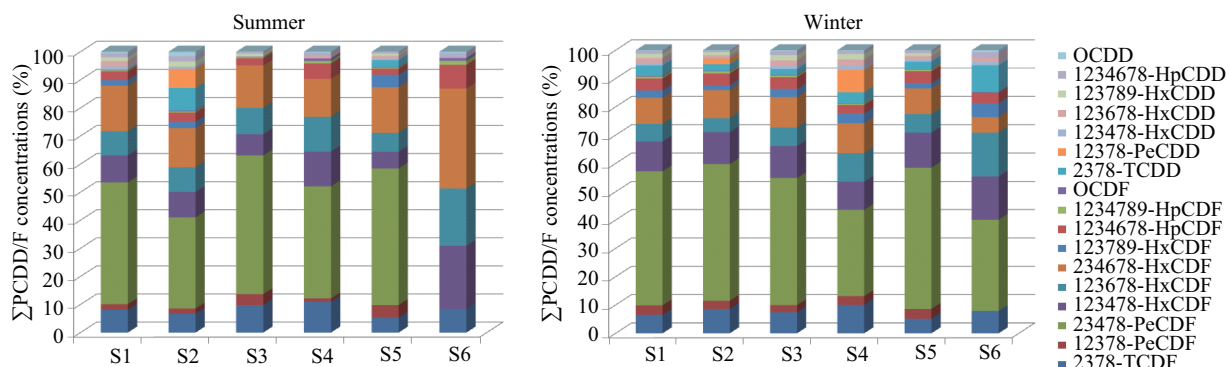

Fig. 3   Concentration profiles of individual PCDD/Fs in the ambient air samples.

Table 3 Pearson correlation coefficient between PCDD/F congener pairs

PCDD congener	PCDF congener	R^2	p^a (2-tailed)
2,3,7,8-TCDD	2,3,7,8-TCDF	0.994	< 0.01
1,2,3,7,8-PeCDD	1,2,3,7,8-PeCDF	0.151	0.517
1,2,3,4,7,8-HxCDD	1,2,3,4,7,8-HxCDF	0.996	< 0.01
1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxCDF	0.996	< 0.01
1,2,3,7,8,9-HxCDD	1,2,3,7,8,9-HxCDF	0.980	< 0.01
1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpCDF	0.994	< 0.01
OCDD	OCDF	0.939	< 0.01

[a] $n = 21$.

HxCDD was correlated with 1,2,3,6,7,8-HxCDF (R^2 = 0.996, $p < 0.01$) and there was also a significant correlation between 1,2,3,4,7,8-HxCDD and 1,2,3,4,7,8-HxCDF (R^2 = 0.996, $p < 0.01$). As shown in Table 3, it was found that most of the pairs of similarly substituted PCDD/Fs exhibited higher correlation, ranging from moderate to higher correlation, but no correlation was found between 1,2,3,7,8-PeCDD and 1,2,3,7,8-PeCDF. This suggested that the correlated congener pairs could follow similar environmental fates or they might have the same sources. It is hypothesized that the sources may have sufficiently similar conditions and the formation rates of congener pairs might be relatively constant.

3 Conclusions

In the present study, except for the E-waste dismantling area, the atmospheric PCDD/F concentrations in different functional zones in Tianjin City were found to be at a relatively lower level than those in some other Chinese cities, but higher than reported concentrations in Europe and the United States. Obvious seasonal trends with higher PCDD/F concentrations in winter and lower levels in the summer sampling period were also observed. PCDD/F profiles and congener pairs suggested that the more likely sources could be increased combustion (i.e., domestic space heating) and seasonal variations in the atmospheric boundary layer height, but different seasonal and spatial distributions indicated that release emission activities might be intermittent.

Acknowledgments

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