



Distribution of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in the Atmosphere of Beijing, China

Zhi-Guang Zhou^{1,2}, Bin Zhao^{1*}, Li Qi², Peng-Jun Xu², Yue Ren², Nan Li², Sen Zheng², Hu Zhao², Shuang Fan², Ting Zhang², Ai-Min Liu², Ye-Ru Huang², Li Shen³

¹ State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

² State Environmental Protection Key Laboratory of Dioxin Pollution Control, National Research Center for Environmental Analysis and Measurement, 1 South Yuhui Rd, Chaoyang District, Beijing 100029, China

³ Ontario Ministry of the Environment, 125 Resources Road, Toronto, ON M9P 3V6, Canada

ABSTRACT

Air samples were collected from six locations during the periods of February, 2011–March, 2012 in Beijing city. Samples were analyzed using HRGC-HRMS according to HJ 77. 2-2008. The concentrations, congener profiles, seasonal variation, spatial distribution, and sources identified were investigated. The mass concentrations of 2,3,7,8-substituted PCDD/Fs is 1750 to 10380 fg/m³ with an average of 3670 fg/m³. The highest concentration was observed at site DS in February 2011 and the lowest was at site NS in July 2011. The TEQ concentrations of PCDD/Fs ranged from 35.0 to 751 fg I-TEQ/m³, with an average of 251 fg I-TEQ/m³. The dominant contributor to total TEQ value is 2,3,7,8-PeCDFs, with an average contribution of 40%. Low-chlorinated PCDDs were observed in all samples in winter. The concentration and profiles exhibit obvious seasonal variation. The PCDD/Fs at six sampling sites did not show obvious spatial variation. Seasonal variation of PCDD/F concentrations indicated that the emission sources may be different. Fossil fuel combustion and automobiles may be the main dioxins emission sources during the heating period, whereas, in non-heating period, the automobiles alone are the main emission sources.

Keywords: PCDD/Fs; Atmosphere; Beijing; Seasonal and spatial variation; Sources.

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) have aroused big concerns of the public and government for a few decades. More attention is paid than any other persistent organic pollutant (POPs) due to the fact that they are highly toxic and bioaccumulative in ecosystem, especially 17 congeners of 2,3,7,8-substituted PCDD/Fs in developing countries. The main sources of PCDD/Fs to the environment are from high temperature burning processes, e.g., incineration of municipal, clinical and industrial wastes, vehicle emissions, accidental fires, and combustion of biomass and biogenic fuels and unwanted by-products in various chemical manufacturing processes such as chlorine production, paper and pulp bleaching, petroleum refining processes (De Assunção and Pesquero, 1999; Kouimtzis *et al.*, 2002). In

2004, China released PCDD/Fs emission inventory from nine emission sources for the first time (Jia H *et al.*, 2011). Moreover, PCDD/Fs can transport over long distances from their sources of emission. Ambient air is the most important pathway for PCDD/Fs to transfer. Many countries (including China) have conducted PCDD/Fs monitoring studies in ambient air (Bakoglu *et al.*, 2005; De Assunção *et al.*, 2005; Coutinho *et al.*, 2007; Kim *et al.*, 2007; Ren *et al.*, 2007; Li *et al.*, 2008 a, b).

Beijing is the capital of China, located on Huabei plain with area of 16,410 km². It is also the biggest city throughout the country. Beijing belongs to sub-humid warm temperate continental monsoon climate zone. The main industries include electronics, automobile manufacture, pharmaceutical synthesis and petroleum refining. Rapid economic growth and urbanization in recent years have sharply increased annual fossil fuel consumption in Beijing, which result in air pollution and sometimes severe air pollution episodes. According to the statistic data, the whole city consumed 6.90×10^9 m³ natural gas, and 2.63×10^7 tons coal from the year of 2011 to 2012. Up to 2012, the number of automobiles reached 5.01×10^6 . Before and after the Olympic Games in 2008, government has invested lots of

* Corresponding author.

Tel.: 86-10-62842865; Fax: 86-10-62849339
E-mail address: binzhao@rcees.ac.cn

money to improve the environment. For example, Capital Iron and Steel Company which is the largest emission source of PCDD/Fs, has been moved out from Beijing. As a result, there is no large industrial emission source in Beijing city, and the automobiles have become the significant source.

This study was the first one conducted after Olympic Games in 2008, and the goal is to monitor the 2,3,7,8-substituted PCDD/Fs at six different functional zones in urban of Beijing and to evaluate the emission sources after the strict control measures for Olympic Games. Monitoring was carried out in winter, spring and summer, fall from February 2011 to March 2012. PCDD/Fs concentrations, profiles and their relationship with meteorological conditions, seasonal variations, as well as the potential emission sources are also discussed.

MATERIALS AND METHODS

Sampling Sites

Six sampling sites that cover six different functional zones were selected to evaluate the atmospheric levels and profiles of PCDD/Fs in Beijing. They were: Dongsì Road (DS: newly developed commercial area), Beisì Road (BS: culture area), Xisì Road (XS: old industrial area), Nansì Road (NS: traffic center), Changqiao (CQ: residential area), Tiantan (TT: urban resort area). The sampling locales, as well as the relevant landmarks, are indicated in Fig. 1. Site DS was about seven kilometers to the power plant of municipal solid waste burning, and site XS was about three kilometers to the Babaoshan funeral parlour. Details about sampling date, sites, volume and target analytes in each sample are listed in Table 1.

Sample Collection

Ambient air samples were collected using a SIBATA HV-1000F sampler according to HJ 77. 2-2008 (Environmental Protection Standard of China), equipped with quartz fiber filter (QFF), and followed by a glass cartridge containing

two polyurethane foam (PUF) plugs. Before sampling, the PUF were spiked with 1 ng of $^{37}\text{Cl}_{35}$ -TCDD as sampling surrogate standard. About 2160 m³ ambient air were collected during a 72-hour period, with a flow rate of 0.500 m³/min and sampled twice at one site. The samples were subsequently placed in a glass container wrapped with aluminum foil. The QFF was weighed before and after sampling to obtain total suspended particle (TSP) weight.

Meteorological parameters revealed air dispersion and stagnant atmospheric conditions, and therefore meteorological conditions were also recorded during sampling period (Table 1). Haze and snow occurred on 22–28, February 2011. On July 6–8 2011, there was light rain during the sampling period. It was sunny during half of total sampling days.

Sample Pre-Treatment and Analysis

All the organic solvents are pesticide residue grade from J.T. Baker (PA, USA). Silica gel was purchased from Wako (Osaka, Japan). Calibration standard solutions, $^{37}\text{Cl}_{35}$ -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 h 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 100ml with n-hexane. And then half of 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 spikes were added.

A high-resolution gas chromatograph interfaced with a high-resolution mass spectrometer (HRGC-HRMS) were used for identification and quantification of PCDD/Fs. An Agilent 6890 N gas chromatograph connected with a Waters AutoSpec Ultima NT high-resolution mass spectrometer was employed. 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 programs were: start 160°C held for 2 min, 160–220°C at 5 °C/min 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 $^{13}\text{C}_{12}$ -labeled internal standards and two $^{13}\text{C}_{12}$ -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 by three times of signal- to-noise ratio, which were 0.500–8.60 fg/m³ for



Fig. 1. Maps of sampling sites in Beijing.

Table 1. Summary of PCDD/Fs in the atmosphere of Beijing.

PCDD/Fs (fg/m ³)	February 22–28, 2011						June 8–14, 2011						November 7–13, 2011						February 29–March 5, 2012					
	DS	BS	XS	NS	CQ	TT	DS	BS	XS	NS	CQ	TT	DS	BS	XS	NS	CQ	TT	DS	BS	XS	NS	CQ	TT
2,3,7,8-TCDF	201	167	202	119	154	156	54.0	45.0	36.0	80.0	49.0	65.0	154	110	75.0	82.0	59.0	154	224	211	138	176	121	111
1,2,3,7,8-PeCDF	247	253	270	144	227	223	70.0	53.0	53.0	98.0	54.0	81.0	199	150	105	95.0	88.0	199	253	264	171	208	152	148
2,3,4,7,8-PeCDF	325	325	320	165	255	265	95.0	58.0	65.0	135	75.0	130	255	218	160	140	120	255	400	410	235	315	220	215
1,2,3,4,7,8-HxCDF	415	425	400	205	375	375	140	107	95.0	175	125	175	260	203	145	120	130	260	385	425	270	325	240	230
1,2,3,6,7,8-HxCDF	356	355	370	185	301	302	141	120	98.0	172	123	181	248	232	157	129	128	248	368	412	239	305	229	220
1,2,3,7,8,9-HxCDF	21.0	34.0	31.0	16.0	23.0	31.0	14.0	13.0	6.00	13.0	9.00	22.0	24.0	23.0	16.0	17.0	14.0	24.0	17.0	28.0	18.0	16.0	12.0	13.0
2,3,4,6,7,8-HxCDF	361	374	400	190	323	325	152	158	116	210	151	240	253	245	176	139	137	253	428	472	258	340	246	240
1,2,3,4,6,7,8-HpCDF	1154	1240	1304	595	1062	1083	541	505	429	686	503	816	647	585	423	315	355	647	1143	1378	780	1000	730	683
1,2,3,4,7,8,9-HpCDF	217	246	220	106	196	194	97.0	92.0	80.0	127	90	156	125	123	78.0	62.0	66.0	125	198	260	141	166	124	113
OCDF	960	1075	1200	480	900	955	515	553	440	615	560	790	480	428	310	225	295	480	725	1002	515	635	480	440
2,3,7,8-TCDD	13.0	0.00	12.0	9.00	10.0	9.00	2.00	2.00	1.00	0.00	1.00	1.00	47.0	10.0	22.0	9.00	16.0	47.0	15.0	11.0	8.00	8.00	4.00	2.00
1,2,3,7,8-PeCDD	38.0	45.0	40.0	22.0	35.0	34.0	12.0	0.00	0.00	8.00	3.00	3.00	84.0	30.0	47.0	20.0	45.0	84.0	54.0	43.0	29.0	39.0	27.0	26.0
1,2,3,4,7,8-HxCDD	29.0	27.0	34.0	13.0	23.0	22.0	10.0	0.00	0.00	12.0	4.00	4.00	37.0	27.0	23.0	17.0	19.0	37.0	43.0	35.0	25.0	34.0	23.0	23.0
1,2,3,6,7,8-HxCDD	63.0	50.0	71.0	35.0	55.0	60.0	30.0	18.0	10.0	30.0	20.0	30.0	60.0	42.0	40.0	30.0	30.0	60.0	85.0	75.0	50.0	70.0	40.0	45.0
1,2,3,7,8,9-HxCDD	46.0	36.0	54.0	25.0	37.0	43.0	21.0	8.00	7.00	24.0	13.0	25.0	44.0	33.0	33.0	22.0	24.0	43.0	61.0	53.0	38.0	49.0	30.0	29.0
1,2,3,4,6,7,8-HpCDD	277	319	340	160	262	275	199	168	131	240	169	272	244	173	245	119	150	244	409	325	233	298	199	232
OCDD	485	470	550	288	395	510	385	382	320	390	380	540	455	335	920	210	865	455	650	575	358	508	330	1068
ΣPCDD/ΣPCDF	0.224	0.210	0.234	0.187	0.214	0.244	0.362	0.339	0.330	0.305	0.339	0.330	0.367	0.280	0.809	0.321	0.877	0.367	0.318	0.230	0.268	0.288	0.258	0.591
ΣPCDD/Fs	5203	5439	5818	2611	4631	4859	2474	2282	1883	3015	2326	3530	3611	2968	2972	1748	2539	3611	5456	5979	3505	4489	3205	3838
ΣI-TEQ	380	375	388	207	323	328	129	104	84.0	163	105	163	345	243	207	154	163	200	434	443	264	342	240	233
Meteorological conditions	Haze to snowing						Sunny to weaken raining						Sunny						Cloudy					

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 40–110% for TCDD/Fs, 45–130% for PeCDD/Fs, 35–89% for HxCDD/Fs, 37–96% for HpCDD/Fs, and 41–85% for OCDD. One field and one laboratory blank were analyzed for every ten samples to check for interferences and laboratory contamination, the values were all below the detection limits (LODs) in the blanks.

RESULTS AND DISCUSSION

Concentrations and Profiles of PCDD/Fs

The mass and International Toxicity Equivalency Quantity (I-TEQs) concentrations of PCDD/F congeners for Beijing air in six different districts were summarized in Table 1. The mean values were adopted as the representative concentrations of each sample sites. 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 approximately calculated.

For all samples, the concentrations of 2,3,7,8-substituted

PCDD/Fs is 1750 to 10380 fg/m³ with an average of 3670 pg/m³. The highest concentration were observed at site DS in February 2011 and the lowest was at site NS in July 2011. The main contributors to the ΣPCDD/Fs were 1,2,3,4,6,7,8-HpCDF, OCDF and OCDD, which account for 23%, 20% and 15% on average, respectively. Considering homologue groups, an decrease in the concentration was observed as chlorination level increased (Cl₄ > Cl₅ > Cl₆ > Cl₇ > Cl₈) for PCDFs. However, the variation of PCDDs concentration was not consistent with the degree of chlorination (Fig. 2). It is interesting to note that the distribution of homologues in this study is different from that observed in 2006 in Beijing (Li *et al.*, 2008), and São Paulo City (De Assunção *et al.*, 2005), this could ascribe to different sources, meteorology, air mass movement and atmospheric degradation process.

A haze occurred on February 22–24 in 2011 during the sample period, which suggest heavy air pollution according to the data released by Beijing Environmental Monitor Station, PM₁₀ ranged from 160 to 270 μg/m³ (the second class air quality value: 150 μg/m³). During the haze period, the level of PCDD/Fs increased dramatically with the highest mass concentration of 10380 fg/m³, which is about ten times higher than those during non-haze periods. In the following four days, the concentration of PCDD/Fs decreased to about one tenth of the highest concentration with snow occurring. When haze occurred, the TSP concentration increased by two times, while the concentration of PCDD/Fs increased by 4–10 times (Table 2). This indicated that fine particles increase in haze, and fine particles have larger specific surface area and therefore absorbed more PCDD/Fs, so the concentration of PCDD/Fs increased more than TSP (Oh *et al.*, 2002; In and Park, 2003).

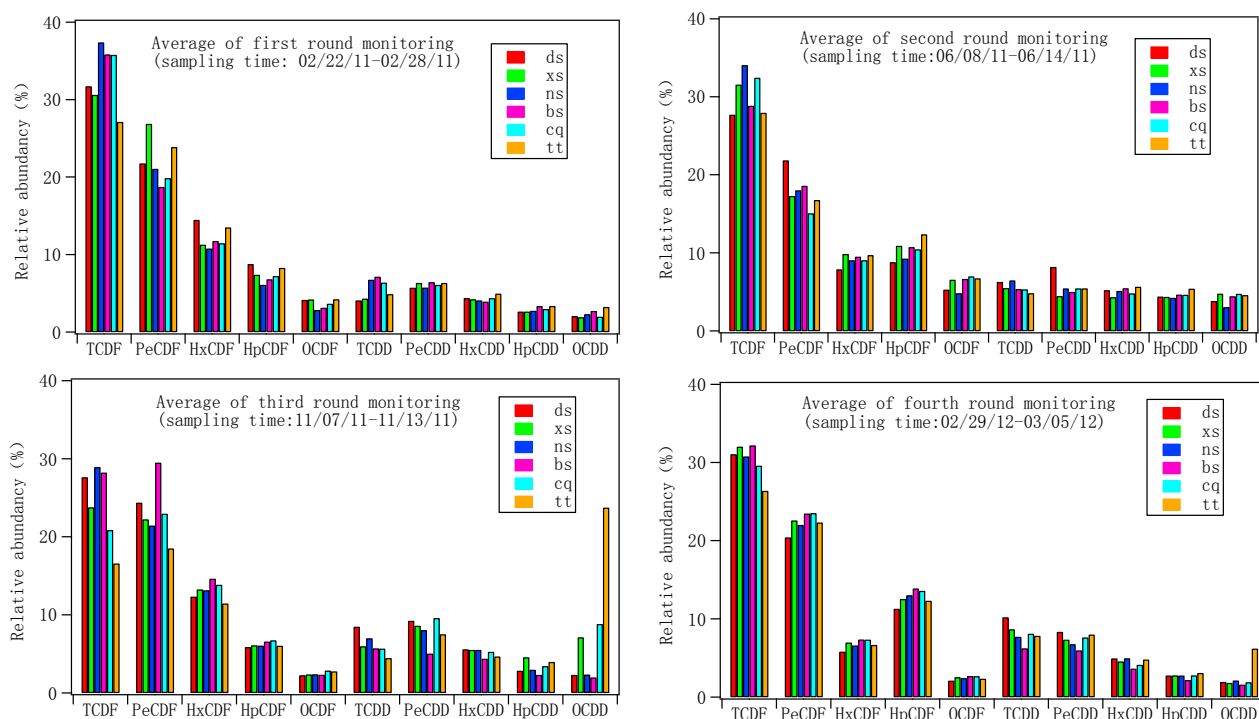


Fig. 2. Comparison of the PCDD/Fs homologues groups in the six sites during sampling periods (mass concentration).

Table 2. Average TSP and PCDD/Fs concentrations.

	Site DS	Site BS	Site XS	Site NS	Site CQ	Site TT
February 22–25 2011 with haze						
Average TSP (mg/m ³)	0.599	0.736	0.565	0.654	0.570	0.754
Average PCDD/Fs (fg/m ³)	8736	10380	8411	10072	5870	4548
February 25–28 2011 without haze						
Average TSP (mg/m ³)	0.350	0.309	0.295	0.421	0.647	0.417
Average PCDD/Fs (fg/m ³)	670	1228	1472	972	1240	1112
Difference between with and without haze in TSP (mg/m ³)	0.249	0.427	0.256	0.233	0.244	0.337
PCDD/Fs (fg/m ³)	8066	9152	6939	9100	4630	3436

I-TEQ Concentrations of PCDD/Fs

For all the samples, the I-TEQ concentrations were calculated by multiplying 2,3,7,8-substituted PCDD/Fs mass concentration by I-TEF (International Toxicity Equivalency Factor). The I-TEQ concentration of PCDD/Fs ranged from 35.0 to 751 fg I-TEQ/m³, with an average of 251 pg I-TEQ/m³. The dominant contributor to total I-TEQ value is 2,3,4,7,8-PeCDF, with an average contribution of 40% (Fig. 3). Other important contributors were 2,3,4,6,7,8-HxCDF (10%), 1,2,3,6,7,8-HxCDF (10%), 1,2,3,4,7,8-HxCDF (9%), 1,2,3,7,8-PeCDD (6%). OCDD and OCDF contribute < 1% to the I-TEQ concentration. The ΣPCDF concentrations were higher than that of ΣPCDDs and all the ΣPCDDs/ΣPCDFs ratios were < 1. The concentrations of 2,3,7,8-substituted PCDD/Fs in Beijing air in winter exceeded some countries ambient air standard for some samples, such as, Japan: 0.600 pg I-TEQ/m³ (<http://www.env.go.jp/en/air/aq/aq.html>), but in summer the concentrations were below 0.600 pg I-TEQ/m³.

The I-TEQ concentration of PCDD/Fs in China and other countries were summarized in Table 3. Compared with other cities, the average I-TEQs were similar to Korea (Park and Kim, 2002), São Paulo City (De Assunção *et al.*,

2005), and were lower than some cities, such as, Guangzhou (Yu *et al.*, 2006), Chengdu (Chen, *et al.*, 2011), Huangshi (Chen, *et al.*, 2011), Japan (Government of Japan, 2005), but higher than some Chinese, European and American cities, such as, Shanghai (Chen, *et al.*, 2011), Fuzhou (Chen *et al.*, 2011), Taiwan (Chang *et al.*, 2003), Thessaloniki (Kouimtzis *et al.*, 2002), Oporto (Coutinho *et al.*, 2007), Lancaster (Lohmann *et al.*, 1999), Phoenix (Hunt *et al.*, 1997). Samples in haze weather increased the I-TEQ concentration in Beijing air, but the extreme pollution weather does not usually happen (two to three times in one year), so the high concentration sample cannot represent the general concentration of PCDD/Fs in Beijing air.

Spatial Variation

As shown in Fig. 1, the sampling sites could be divided into different functional zones. Fig. 2 compared the PCDD/Fs homologues groups in the six sites during sampling periods.

Site CQ was residential area and site TT was urban resort area, but the concentration of PCDD/Fs at these two sites had no difference with other sampling sites. This indicated that PCDD/Fs came from the same sources, such as, heavy traffic.

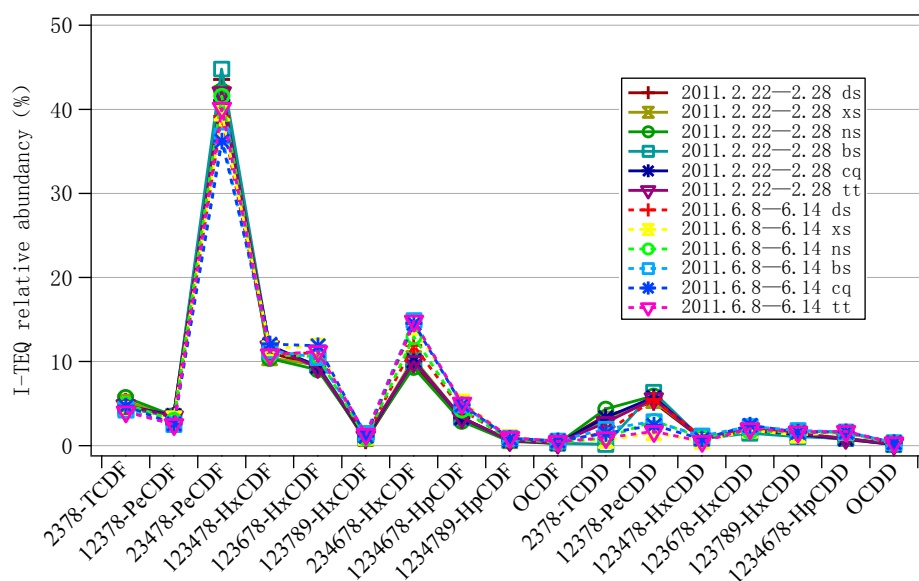


Fig. 3. Relative Contribution (%) of the individual 2,3,7,8-congeners to the total I-TEQ concentrations at six sites in winter and summer.

Table 3. Comparison of PCDD/Fs levels with other urban studies.

Site	Period	Type	I-TEQ (fg/m ³)	Reference
Beijing, China	February–July 2011	Center	75.0–751	This study
Beijing, China	February–December 2006	Urban	180–644	Li <i>et al.</i> (2008)
Chengdu China	December 2007	outskirt	1930	Chen <i>et al.</i> (2011)
Huangshi China	November 2008	Industrial	1150	Chen <i>et al.</i> (2011)
Shanghai China	September 2008	Residential	70.0	Chen <i>et al.</i> (2011)
Fuzhou China	July 2009	Countryside	80.0	Chen <i>et al.</i> (2011)
Nanchong China	August 2009	Outskirt	40.0	Chen <i>et al.</i> (2011)
Guangzhou China	July–September 2004	Urban	128–570	Yu <i>et al.</i> (2006)
Taiwan China	November 1999–July 2000	Urban	348–560	Chang <i>et al.</i> (2003)
HongKong China	January–August 2000	Urban	180–430	Sin <i>et al.</i> (2002)
Korea	June 2000–March 2001	Urban	169–882	Park and Kim (2002)
Japan	2004	Urban	550–830	Government of Japan (2005)
Houston USA	September 2002–April 2003	Urban	400–550	Correa <i>et al.</i> (2004)
Phoenix USA	1994	Urban	94.0–448	Hunt <i>et al.</i> , 1997
Thessaloniki Greece	March–October 1999	Urban	119–400	Kouimtzi <i>et al.</i> (2002)
Athens Greece	July 2000	Urban	42.0	Mandalakis <i>et al.</i> (2002)
Lancaster U K	1997	Urban	7.00–18.0	Lohmann <i>et al.</i> , 1999
São Paulo Brazil	2000–2001	Urban	47.0–751	Assunção <i>et al.</i> (2005)
Berlin Germany	1986–1987	Urban	20.0–40.0	Christman <i>et al.</i> , 1989
Catalonia Spain	1994–2004	Industrial	5.00–1196	Abad <i>et al.</i> (2007)
Oporto Portugal	1998–1999	Suburban	24.0–547	Coutinho <i>et al.</i> (2001)
Rome Italy	2000	Urban	65.0	Menichini <i>et al.</i> (2007)

Site XS was in Shijingshan district where Capital Iron and Steel Company and Babaoshan funeral parlour were located, previous research indicated that the concentration of PCBs in this district was two times higher than the background (Sun *et al.*, 2009). But from 2008, the steel factory was moved out of city, the concentration of PCDD/Fs in this study was comparable to other sample sites, which indicated the air quality improved since 2008. PCDD/Fs in the atmosphere within Babaoshan funeral parlour region was analyzed in November 2010, the I-TEQ concentration ranged 390 fg I-TEQ/m³ to 520 fg I-TEQ/m³. The sampling period and meteorological conditions corresponded to this study in November 2011, and confirmed Babaoshan funeral parlour had no significant influence on the air.

Site DS was about 7 kilometers from the municipal solid waste incinerator (MSWI). The concentration of PCDD/Fs in the exhaust was 0.0350 ng I-TEQ/m³, and was below the European Union limit (0.100 ng I-TEQ/m³), which suggest the MSWI had limited influence on the surrounding air. The deduction was also corroborated by comparing the homologue profiles between the flue gas and ambient air samples.

In conclusion, there was no major industry activity in Beijing city from the year of 2008, moreover, the air circulation in this area is typically quick, which facilitate the mixing of ambient pollutants, and thus the concentration and congener profile for PCDD/Fs in six functional zones show similar characteristics in the same sampling periods.

Seasonal Variation

The concentration and profiles of PCDD/Fs in the atmosphere are expected to vary with season because there were different emission sources in different seasons, and the conditions for dispersion were also different. Spring

and autumn were short, so this paper only compared the PCDD/Fs in winter (February 22–28 2011, heating period) and in summer (June 8–14 2011, non-heating period).

Seasonal variations were observed in this study, and higher PCDD/F concentrations in winter and lower levels in summer were found. Similar results had also been reported in other studies (Lohmann and Jones, 1998; Lee *et al.*, 1999; Oh *et al.*, 2006). The ratios of total PCDD/Fs in winter and summer were 2.00 to 4.60 as shown in Table 1, and the ratio was 3 in Portugal (Coutinho *et al.*, 1999). PCDF homologue distributions were quite similar in different seasons, most of the seven PCDD congeners were detected in winter, while some highly-chlorinated PCDDs were observed in summer only; this indicated that emission sources might vary in winter and summer. For single sample, the ratio for $\Sigma\text{PCDDs}/\Sigma\text{PCDFs}$ was 0.220 in winter and 0.330 in summer. Domestic heating in winter might contribute to the higher PCDD/Fs concentrations. Although, PCDDs in gas phase react more easily with OH radicals and O₃ than PCDFs, PCDFs had weak stability than PCDDs, and thus PCDFs can degrade more easily than PCDDs, so photolysis might be another reason for lower PCDD/Fs concentration in summer (Kwok and Atkinson, 1995).

Source 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 average relative intensity of ten homologues of two samples for each sampling period using SPSS software (version 17.0, IBM Inc.) (Fig. 4(A)). Relative intensity of mass concentration of ten homologues were taken as variables, large percentages mean highly

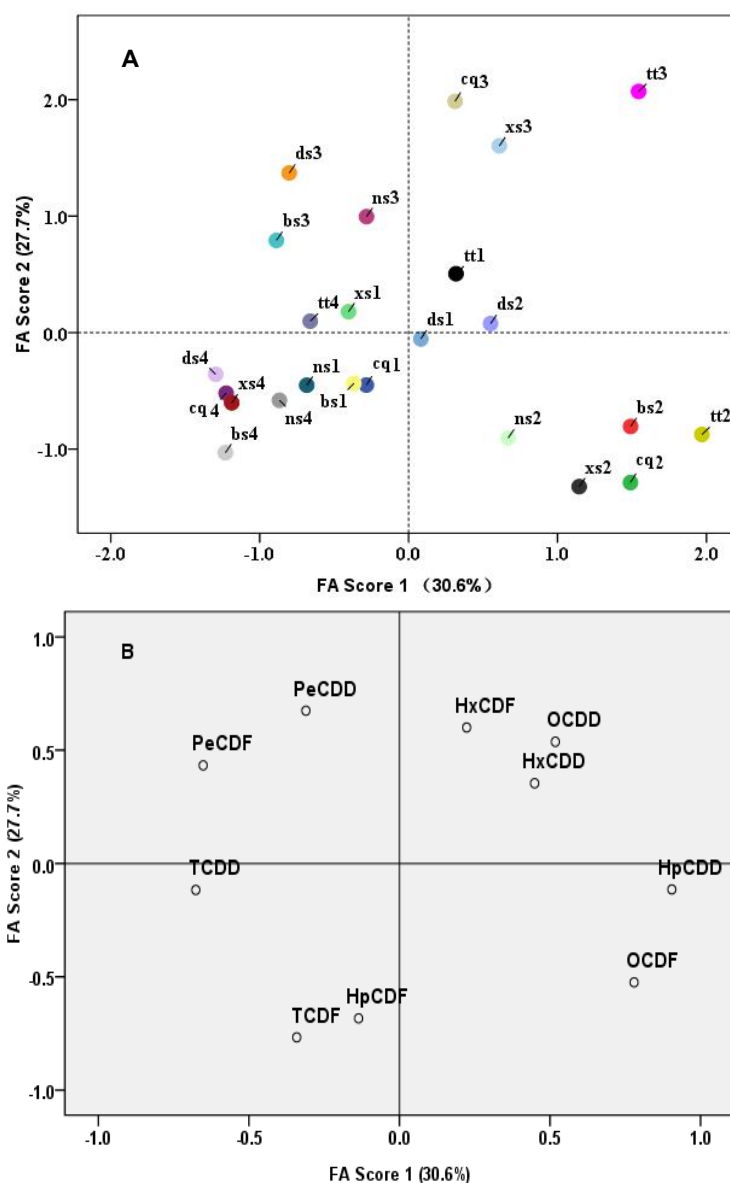


Fig. 4. Principal components analysis for all samples (A) and FA Score1-FA Score2 loading plot (B).

correlated. Two main factors (FAs) were extracted. The first factor (FA1) was found to account for 30.6% of the total variance; the second factor (FA2) accounted for 27.7% of the total variance. The PCA results showed that these two FAs (Eigenvalue > 1) accounted for 58.3% 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 three groups: the first sampling period and the fourth sampling period (heating period), the second sampling period (non-heating period), the third sampling period (between heating period and non-heating period), the points in the same group might have the same sources. During heating period, Beijing and around Beijing area consumed more fossil fuel, such as natural gas, coal etc. In recent years, with dramatically increased automobiles, the exhaust gas aroused big concerns. Fossil fuel combustion and automobiles may be the main dioxin emission sources

in heating period, whereas in non-heating period, the automobiles, were the main emission sources. In addition to emission sources, meteorological conditions, air mass movement and atmospheric degradation process can also affect congener profiles of PCDD/Fs in the atmosphere. For example, in summer the strong photolysis can influence the congener profile, which may be another reason to distinguish heating and non-heating period (Kwok and Atkinson, 1995). However, further investigations are still needed to validate the speculations. As the Fig. 4(A) showed, the first round and the fourth round samples were overlapped. The possible reason could be that the emission sources are similar since the two sampling periods are close although at different years. We also made the FA1–FA2 loading plot. From Fig. 4(B), we could see that FA1 and FA2 were both in proportion to HxCDD, HxCDF and OCDD. FA1 were also in proportion to HpCDD and OCDF, but was negatively correlated to TCDD. Highly chlorinated

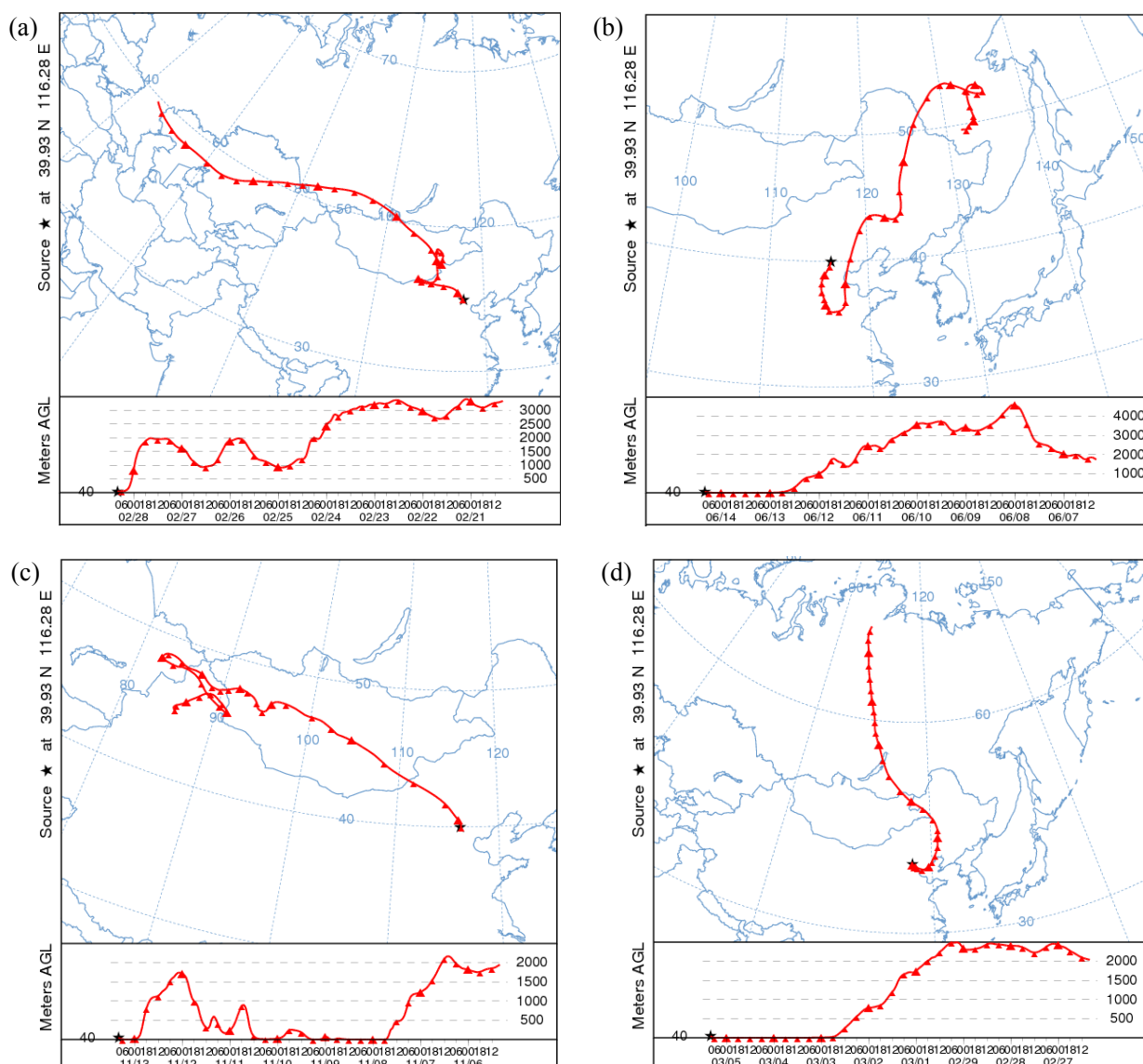


Fig. 5. The backward trajectory of air mass at specific elevation during sampling periods.

PCDD/Fs can be deemed as indicator for automobile exhausts emissions (US EPA, 2001) and fossil fuel combustion emission (Lin *et al.*, 2007). FA2 was positively correlated to PeCDD and PeCDF, but negatively correlated to TCDF and HpCDF, this could be as indicator for other waste combustion emissions (Lohmann *et al.*, 2006).

Air masses transferring from different directions contain different pollutants, and thus may contribute to the concentrations in studied area. The backward trajectory of air mass at specific elevation during given time period was simulated using Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model in order to evaluate the effect of air mass movement on the ambient concentration of PCDD/Fs. The start location and elevation for trajectory simulation was set at N39.93°, E116.28° (geographic coordinate of Beijing) and 40m (approximate height for air sampling), respectively. The start time for simulation was 192 h before the end of each sampling. Fig. 5 showed the backward trajectory of air mass for the four sample periods.

The air mass for first, third and fourth sample periods came from west-north, mainly from Inner Mongolia, Russia (66.0 fg I-TEQ/m³) (Maystrenko *et al.*, 1998) and Mongolia. There were few inhabitants and industrial activities around these areas. The air mass barely contained pollutants, and should not contribute to the sampling sites as import sources, in other words the PCDD/Fs emission sources were local. The air mass during the second sampling periods came from east-north, via Heilongjiang, Jilin, Liaoning and Hebei provinces and then entered Beijing area. The dioxin emission sources for second samples period were mainly from local sources accompanied with import contributor. The concentration of dioxins in the atmosphere in Shenyang (57.0 to 140 fg I-TEQ/m³), Liaoning Province was also monitored in our lab and found to be lower than Beijing. If taken as representative of east-north area to Beijing, the air mass from east-north area contributed to the concentration of PCDD/Fs in Beijing atmosphere to some extent, but the contribution fraction need further investigation.

CONCLUSIONS

In this study, except for extreme weather, the concentrations of PCDD/Fs were comparable or lower than other Chinese cities being reported, but higher than some European and American cities. Since the year of 2008, there are hardly industrial activities in Beijing, and thus spatial variation was not obvious. Higher concentration was found in winter and lower concentration was found in summer, so seasonal variation does exist. The dominant contributor to total TEQ value is 2,3,7,8-PeCDFs, which was the typical combustion-influenced fingerprint. The main emission sources were combustion of natural gas, coal and gasoline, diesel by automobiles. There were no import sources in winter. In contrast, the main emission source was exhaust gas from automobiles in summer, and the import source has contribution to the concentration of PCDD/Fs in the atmosphere in Beijing.

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