

PCDD/Fs CONCENTRATIONS IN THE ATMOSPHERE OF BEIJING, CHINA

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1. 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. Moreover, PCDD/Fs can transport over long distances from their sources of emission. Ambient air is the most important pathway for PCDD/Fs transfer. Many countries (including China) have conducted PCDD/Fs monitoring studies in ambient air^[1].

Beijing, as the capital of China, is one of the largest cities throughout the country. It is characterized with a high population density and heavy traffic. Industries mainly consist of electronics, automobile manufacture, pharmaceutical synthesis, petroleum refining and waste burning. As a result, traffic and waste burning may be the primary source for PCDD/Fs in Beijing. The goal of this paper is to report the atmospheric PCDD/Fs pattern in Beijing. Measurements of these toxic pollutants were carried out in winter, and summer. Four sample sites were chosen near the Fourth Ring Road with intense traffic, where the traffic flow comprises heavy duty diesel buses and light duty gas vehicles. Vehicular emissions are expected to make significant contributions since there are no industrial activities in the immediate vicinity. Additional two sample sites, one in Tian Tan Park and the other in residential area, are selected as comparisons to those along the Fourth Ring Road. PCDD/Fs concentration, and their relationship with meteorological conditions, seasonal variations, as well as the potential emission sources are also discussed.

2. Materials and Methods

2.1 Sampling

Ambient samples were collected according to US EPA Method TO-9A using a SIBATA HV-1000F sampler, equipped with quartz fiber filter (QFF), and followed by a glass cartridge containing two polyurethane foam (PUF) plugs. Before sampling, the PUF plugs were spiked with 1 ng of ¹³C₁₂ labeled surrogate standards. About 2160 m³ ambient air were sampled during a 72 h sampling period, with a flow rate of 0.5 m³ min⁻¹. After sampling, the samples were placed in a glass container wrapped with aluminum foil. The QFF was weighed before and after sampling to obtain total suspended particle (TSP) mass concentration. The sample period was between February 22-28 in winter and between July 7-13 in summer in 2011.

2.2 Analysis

All the organic solvents are pesticide residue grade from J. T Baker (USA). Silica was purchased from Wako (Osaka Japan). Calibration standard solutions, ¹³C₁₂ labeled surrogate standards and ¹³C₁₂ labeled injection standards were purchased from Wellington Laboratories (Guelph, Canada).

Analysis of PCDD/Fs followed HJ 77.2-2008 in China.

3. Results and discussion

3.1 PCDD/Fs mass concentrations

The highest mass concentration of total seventeen 2,3,7,8-substituted PCDD/Fs was found at site with the concentration of 10.38 pg/m^3 in winter. The lowest concentration is 1.31 pg/m^3 at site 16 in summer. Similar homologue profiles were observed in both winter and summer for all the sampling sites that HpCDF predominated furan concentrations. The main contributors to the PCDD/Fs were HpCDF, followed by HxCDF and OCDF, which account for 27%, 22% and 20% of PCDD/Fs mass concentration on average, respectively. Additionally, an increase in the concentration was observed as chlorination level increased ($\text{Cl}_4 < \text{Cl}_5 < \text{Cl}_6 < \text{Cl}_7 < \text{Cl}_8$) for PCDDs. The same trend was also found for PCDFs, with an exception of OCDF whose concentrations were between PeCDFs and HxCDFs ($\text{Cl}_4 < \text{Cl}_5 < \text{Cl}_8 < \text{Cl}_6 < \text{Cl}_7$).

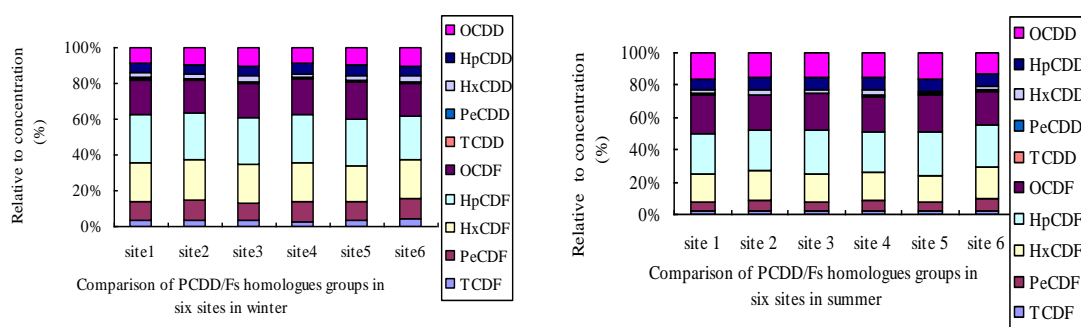


Fig. 1 Comparison of the PCDD/Fs congeners in samples

3.2 Toxicity equivalency (TEQ) concentrations of PCDD/Fs

The TEQ concentrations of the seventeen congeners of PCDD/Fs are calculated using I-TEF (International Toxicity Equivalency Factor). The I-TEQ concentrations of PCDD/Fs range from 0.062-0.751 $\text{pg I-TEQ} \cdot \text{m}^{-3}$ with the highest concentration found in a haze day in winter and the lowest found in summer. PeCDF contributed most to the total TEQ concentration, with an average contribution of 45.5%. Other important contributors were HxCDF (30%), PeCDD (5%), TCDF (4.5%), and HxCDD (4.0%). OCDD and OCDF contribute <1% to the TEQ concentration. The $\sum\text{PCDF}$ concentrations were higher than that of $\sum\text{PCDDs}$ and all the $\sum\text{PCDDs}/\sum\text{PCDFs}$ ratios were <1. The concentrations of 2,3,7,8-substituted PCDD/Fs in Beijing air in winter were higher than those reported by Joao et al. (2005) and exceeded the ambient air standard of 0.6 $\text{pg TEQ} \cdot \text{m}^{-3}$ regulated in Japan (<http://www.env.go.jp/en/air/aq/aq.html>) for some samples, but in summer the concentrations were lower than other cities and below 0.6 $\text{pg-TEQ}/\text{m}^{-3}$.^[2]

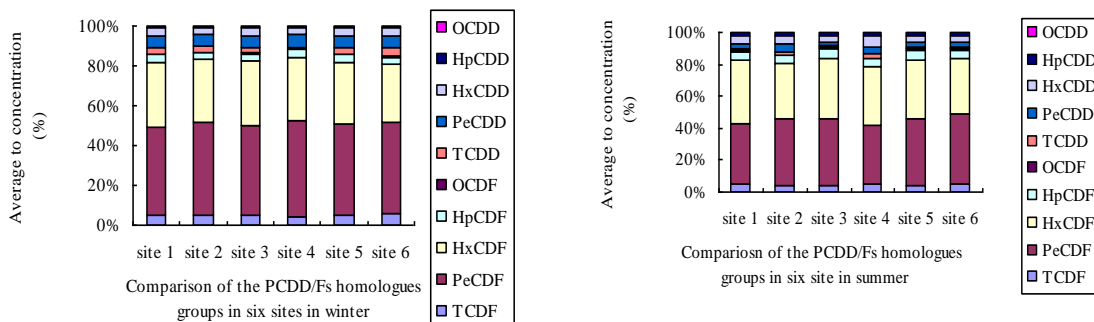


Fig. 2 Comparison of the PCDD/Fs homologues in samples

3.3 Seasonal variation

Seasonal variation was characterized with higher concentrations in winter and lower concentrations in the summer, which was consistent with observations in previous studies^[3]. The seasonal variation can be explained by the extensive fossil fuel combustion for heating and haze weather resulting in worse dispersion in winter. During summer sampling period, light rains and good dispersion conditions during the whole sampling period were observed. Lower concentrations of PCDD/Fs were found when compared to those in winter samples. As wet deposition is the major removal mechanism for suspended particles, rainfall lead to a lower environmental concentration of PCDD/Fs^[4]. And low TSP concentrations were also observed during the same sampling period.

3.4 TSP vs. PCDD/Fs

A haze occurred on February 22-24 in 2011 during the sample period, which indicated heavy air pollution by the data released by Beijing Environmental Monitor Station. During the haze period, the level of PCDD/Fs increased dramatically with the highest mass concentration of 10.38 $\mu\text{g}/\text{m}^3$, 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, but the concentration of PCDD/Fs increased by 4-10 times. This indicted that fine particles were increase in haze, and fine particles absorbed PCDD/Fs, so the concentration of PCDD/Fs increased more than TSP.

Table 1 Average TSP and PCDD/Fs concentrations

		February 22- 25 2011 with haze					
		Site1	Site2	Site3	Site4	Site5	Site6
Average	TSP($\mu\text{g}/\text{m}^3$)	0.599	0.736	0.565	0.654	0.570	0.754
Average	PCDD/Fs(pg/m^3)	8.736	10.380	8.411	10.072	5.870	4.548
		February 25- 28 2011 without haze					
		Site1	Site2	Site3	Site4	Site5	Site6
Average	TSP($\mu\text{g}/\text{m}^3$)	0.350	0.309	0.295	0.421	0.647	0.417
Average	PCDD/Fs(pg/m^3)	0.670	1.228	1.472	0.972	1.240	1.112

PCDD/Fs(pg/m3)						
Difference between with and without haze in TSP(ug/m3)	0.249	0.427	0.256	0.233	0.244	0.337
PCDD/Fs(pg/m3)	8.036	9.152	6.940	9.100	4.630	3.436

3.5 Principal component 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 relative intensity of ten homologues of each sample. The first principal component (PC1, explaining 56% of the total variance) was strongly and positively correlated with HxCDF, TeCDF, and PeCDF, yet strongly and negatively with OCDF. The second principal component (PC2, explaining 18% of the total variance) was negatively correlated with OCDF, yet positively with OCDD. All the samples were divided into three groups. Combining with the meteorological conditions, we found that: The samples in group 1 were collected in haze day in winter, and group 2 were sampled after snowing in winter, and group 3 were sampled in summer. The analysis indicated that PCDD/Fs in haze day were attributable to multiple emission sources, such as waste burning, vehicle exhaust and domestic heating. The pattern in group 2 differed due to the washout effect by snow. The profiles for group 3, of which the samples were collected in summer without domestic heating, were expected to be mainly influenced by waste burning and vehicle exhaust.

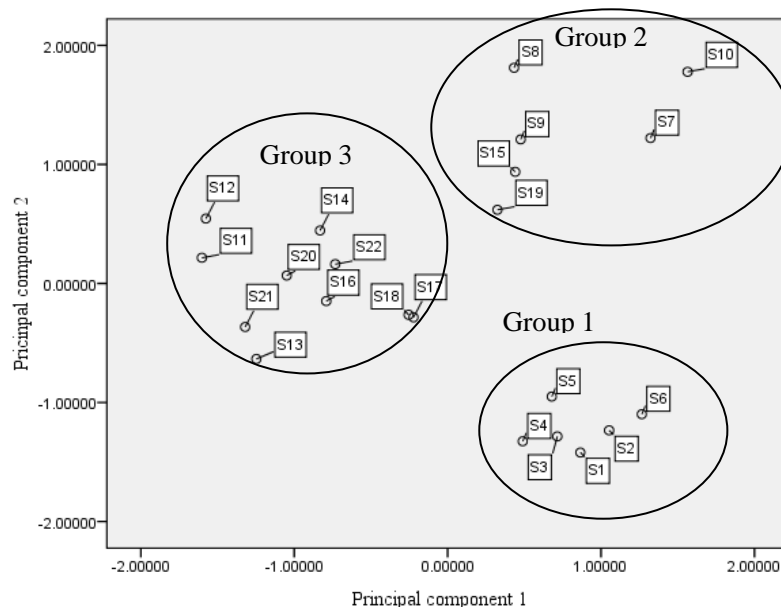


Fig.3 Principal component analysis for samples

4. Acknowledgements

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