Polychlorinated biphenyls in respirable particulate matter from different industrial areas in northern China

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HIGHLIGHTS

- First report of PCBs detection in PM from Linfen and Datong in China.
- Trichlorobiphenyls were the dominant PCBs in the various media.
- The PCB distributions in PM_{2.5} and PM_{2.5–10} were quite different in the two cities.
- Toxic equivalency concentrations based on ten dioxin-like PCBs were reported.
- The major PCB source may be associated with unintentional release of PCBs.

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ABSTRACT

As two typical industrial bases of China's great metropolises, Lingfen and Datong are affected by the steel industry, chemical plants, coal-fired power plants, and several coking plants, and face pollution from polychlorinated biphenyls (PCBs). Therefore, this study was conducted to determine the PCB concentrations in PM_{2.5} and PM_{2.5–10} samples obtained in Lingfen and Datong. We collected 22 respirable particulate matter samples (11 of PM_{2.5} and 11 of PM_{2.5–10}) from Lingfen and Datong, and measured a total of 144 PCB congeners. The total PCB concentrations were 5.92–38.7 pg m^{−3} (median: 21.58 pg m^{−3}) in PM_{2.5} and 1.83–40.8 pg m^{−3} (median: 24.3 pg m^{−3}) in PM_{2.5–10} in Linfen, and 4.33–18.5 pg m^{−3} (median: 11.9 pg m^{−3}) in PM_{2.5} and 13.0–47.4 pg m^{−3} (median: 17.4 pg m^{−3}) in PM_{2.5–10} in Datong. Of the PCB homologues, the dominant PCBs detected in the various media were all trichlorobiphenyls (tri-CBs). Moreover, the PCB distributions in PM_{2.5} and PM_{2.5–10} samples were quite different in the two cities. This may be caused by the differences of the industrial structures, and their relatively unintentional release of PCBs in these cities. Source analysis revealed that the major PCB contaminants in Linfen and Datong were tri-CBs and di-CBs, which were possibly associated with unintentional release of PCBs. Toxic equivalency concentrations based on ten dioxin-like PCBs ranged from 4.0×10^{-5} to 2.3×10^{-3} pgWHO-TEQ m^{−3} in Linfen, and 4.5×10^{-4} to 2.6×10^{-4} pgWHO-TEQ m^{−3} in Datong. The presence of PCB pollution is a potential threat to the residents of Datong and Linfen.

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1. Introduction

The potential effects of polluted air on human health has been a hot issue that has triggered numerous investigations in recent years (Mandalakis and Stephanou, 2007; Bartoš et al., 2009; Baek et al., 2011; Sheng et al., 2013). Fine and ultrafine particles can reach lung alveoli in humans (Tasdemir et al., 2004a; Kampa and Castanas, 2008). The inhalation of polluted air is one important

exposure pathway. For example, respirable particulate matter (PM) is the vector by which polychlorinated biphenyls (PCBs) enter the upper respiratory tract. Research results show that air PM and air flow are the main environmental pollutant and migration path, respectively, especially for persistent organic pollutants (POPs) (Kaupp and McLachlan, 1999; Lohmann et al., 2000; Ma et al., 2007).

PCBs are important and widespread POPs in the atmosphere, and because of their persistence, toxicity, bioaccumulation and long-distance migration, they can also be passed on to offspring through the cellular matrix, causing deformities (Priha et al.,

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2005). PCBs readily accumulate on particles, and respirable PM have a direct effect on public health, and increase the risk of human exposure to PCBs via inhalation and ingestion (Tasdemir et al., 2004a; Kampa and Castanas, 2008). Thus, PCBs severely threaten human health and ecosystems. PCBs were intentionally produced by industry as technical mixtures for use as the dielectric fluid in transformers and large capacitors, heat transfer fluids and hydraulic fluids (WHO/IPCS, 1993). Although the production and use of PCBs has been banned for many years in China, they are still widespread pollutants in the air, soil, sediments and biota. Most research on environmental contamination from PCBs in China has focused on typical polluted areas such as Taizhou (Han et al., 2010) and Guiyu (Xing et al., 2009). However, the contamination status in urban environments, and especially in industrialized regions, should not be ignored. While there is sufficient data available on the levels of PCBs in soils, sediments and biological tissue (Ren et al., 2007; Wang et al., 2008; Wang et al., 2010), much less is known about its levels in respirable PM, especially in industrialized regions in China. Therefore, it is difficult to estimate the exposure of the population in these regions to PCBs.

In the present study, PM_{2.5} and PM_{2.5–10} samples were collected in two typical industrial cities in Shanxi, northern China. There are several potential sources of PCB contamination in the city of Linfen, including iron and steel industries, cement and chemical plants. In contrast, Datong is home to distribution and freight, coal transportation & sales, coal-fired power plants, paint processing, and several coking plants. Linfen and Datong are not only two of China's great metropolises, but also two types of important industrial bases in China, with populations of approximately 3.4 and 1.1 million urban residents, respectively. Rapid economic growth and urbanization in recent years have sharply aggravated their pollution, and raised a series of related problems. However, the environmental behavior of PCBs in PM_{2.5} and PM_{2.5–10} samples of these industrialized areas remains unclear.

Because of the paucity of data on PCB levels of various respirable PM samples from the Chinese industrial environment, we undertook this study to determine both the concentration and profile of PCBs in respirable PM samples from two different types of industrialized areas in Shanxi. The main objectives were to establish the contamination status of each industrial area, explore the interaction of PCBs among PM_{2.5} and PM_{2.5–10} samples, and identify possible sources of pollution. The results from this study are discussed to further understand the source, transport and distribution of these contaminants in different industrialized areas.

2. Materials and methods

2.1. Samples

Linfen is located in southwest Shanxi, China, and covers an area of 20275 km². The central urban area of Linfen has 3.4 million urban residents. The area has a temperate semi-wet monsoon climate, with a mean annual temperature of 12.2 °C. China clay is the main representative soil type in Linfen. There are many industrial plants within a few kilometers of the urban area of Linfen.

Datong is located in north Shanxi, China, and occupies an area of 14112 km². The central urban area of Datong has 1.1 million urban residents. The area has a temperate semi-wet monsoon climate, with a mean annual temperature of 5.5 °C. China clay is the main representative soil type in Datong. There are several coal-fired power plants and coking plants around the urban area of Datong.

Sampling sites were set to represent the areas of Linfen and Datong. The sampling locations were chosen using a symmetrical grid (about 25 km² per grid square), in an attempt to evenly distribute sampling over the region (Fig. 1). According to consider

the atmosphere was a more uniform environmental media, one sampling point was selected to represent each corresponding grid. From the corresponding grid for respirable PM samples (sites LF1–5 and DT1–6) in Linfen and Datong, respectively, 22 respirable PM (PM_{2.5} and PM_{2.5–10}) samples were taken in winter. The detail information of sampling was listed in Table 1.

The PM samples were obtained with a modified medium-volume TH-150 sampler (Wuhan Tianhong Instrument Factory, Wuhan, China) which was a kind of classification sampler. PM_{2.5} and PM_{2.5–10} were collected by this sampler in the same period. The overall average volume was approximately 24 m³ (average flow rate: 100 L min^{−1}) and each sample was a 4-h composite. The suspended particulate matters were collected onto quartz fiber filters (Ø90 mm, Whatman Company, UK). There were 11 PM_{2.5} and 11 PM_{2.5–10} samples obtained. Before the experiment, the quartz fiber filters were annealed for 4 h at 550 °C to remove organic material and equilibrated in desiccators. After sampling, the filters were removed from the inlet, folded in half, returned to pre-cleaned aluminium envelopes and stored at −18 °C before analysis.

2.2. Chemicals

Five standard solutions of PCB congeners (Accustandard, New Haven, CT, USA) were used to quantify 144 congeners. 2,4,5,6-Tetrachloro-*m*-xylene (TCMX, as a surrogate) was purchased from Supelco (Bellefonte, PA, USA). *n*-Hexane, dichloromethane, and toluene were pesticide grade (Fisher Scientific, Fair Lawn, NJ, USA). Nonane was GC grade (Fluka, Sigma-Aldrich, Munich, Germany). Anhydrous sodium sulfate, sodium hydroxide, silver nitrate, and sulfuric acid were guaranteed reagent grade (Sinopharm Chemical, Beijing, China). Silica gel (60–100 mesh) for chromatography was analytical grade (Qingdao Haiyang Chemical, Qingdao, China). The solvents used were pesticide grade (J.T. Baker, Phillipsburg, NJ, USA).

2.3. Analysis

Each PM sample was extracted with 30 mL of hexane/dichloromethane (1:1, vol/vol) by ultrasonication for 4 min and then centrifuged at 3000g. This process was repeated three times and the extracts were combined. The concentrated extracts were evaporated to 1 mL for cleanup. The concentrated extracts were cleaned by using a chromatography column containing the various silica. The PCB fraction was eluted with 100 mL of hexane. The elution was then evaporated with a rotary evaporator and then reduced to 50 µL under a gentle N₂ stream for analysis. PCBs were measured with an Agilent 6890 series gas chromatograph (GC) coupled with an Agilent 5973 mass spectrometer (MS) using electron impact ionization source in SIM mode. Gas chromatographic separation was performed on a DB-5MS capillary column (30 m × 0.25-mm internal diameter; 0.25-µm film thickness). Cleanup and analysis of PCBs followed the modified methods described in our previous report (Fu et al., 2009).

2.4. Quality control

A laboratory control group was analyzed to demonstrate lack of interference and cross-contamination. A procedural blank in parallel with each set of six samples was also run to further check for interference and cross-contamination. Method repeatability was examined by regular analysis of duplicate samples (Fu et al., 2009).

An external standard method was used to quantify the concentration of PCBs. The measures taken to ensure the integrity of the results are described in our previous report (Fu et al., 2009). Under optimum conditions, the limit of detection (LOD, signal-to-noise ratio = 3) for samples was in the range of 0.01–0.05 ng g^{−1} (dry

Fig. 1. Sampling sites of respirable PM from Datong and Linfen in northern China.

weight) for PCBs. The matrix spike recoveries for the 144 PCB congeners (including some co-eluting PCB congeners) ranged from 70% to 110%, with a standard deviation of 15%. The recovery of TCMX surrogate in all samples was within the range of 70–95%.

A standard reference material sample (GBW 08307, National Research Center for Certified Reference Materials, China) was analyzed to validate the analytical method used. The results were satisfactory, with a z score of ≤ 1 for all congeners (range of 0.02–0.64 for PCBs; $p < 0.05$). Recovery of CB-209 surrogate was 85% with the GBW 08307 sample.

2.5. Data analysis

Statistical analysis was performed using PASW statistics 18.0 (IBM, Armonk, NY, USA). We used principal-component analysis

(PCA), a multivariate statistical technique, to derive new principal components (PCs) as a linear combination of the original variables, where PCs attempt to preserve the statistical relationships of the original data. In this study, we investigated interspecies variations in PCB congeners using PCA to deduce the possible sources of PCBs around three industrial sites.

3. Results and discussion

3.1. PCB concentrations in respirable PM

PCBs (144 congeners, including some coeluting PCB congeners) were identified in the 22 respirable PM samples (11 of $PM_{2.5}$ and 11 of $PM_{2.5-10}$) in Linfen and Datong. The total PCB concentrations

Table 1

The information of sampling in Datong and Linfen.

City	Sampling number	Sampling ID	Weather	Air temperature	Wind direction	Wind force	Sampling date
Linfen	LF1	LF1-PM2.5 LF1-PM10	Fine	−1 °C/−10 °C	No sustained wind direction	Breeze	4th January, 2012
	LF2	LF2-PM2.5 LF2-PM10	Fine	2 °C/−9 °C	No sustained wind direction	Breeze	5th January, 2012
	LF3	LF3-PM2.5 LF3-PM10	Fine	3 °C/−6 °C	West	Breeze	6th January, 2012
	LF4	LF4-PM2.5 LF4-PM10	Cloudy	2 °C/−6 °C	No sustained wind direction	Breeze	7th January, 2012
	LF5	LF5-PM2.5 LF5-PM10	Cloudy	4 °C/−7 °C	No sustained wind direction	Breeze	9th January, 2012
Datong	DT1	DT1-PM2.5 DT1-PM10	Cloudy	0 °C/−12 °C	South	Breeze	15th January, 2012
	DT2	DT2-PM2.5 DT2-PM10	Fine	−1 °C/−16 °C	Northwester	Breeze	12th January, 2012
	DT3	DT3-PM2.5 DT3-PM10	Cloudy	0 °C/−14 °C	South	Breeze	16th January, 2012
	DT4	DT4-PM2.5 DT4-PM10	Fine	−2 °C/−16 °C	Northwester	Breeze	13th January, 2012
	DT5	DT5-PM2.5 DT5-PM10	Cloudy	−2 °C/−15 °C	Northwester	Breeze	17th January, 2012
	DT6	DT6-PM2.5 DT6-PM10	Fine	−1 °C/−12 °C	Northwester	Breeze	18th January, 2012

Table 2Total concentrations of PCB homologues in each sample (pg m^{−3}).

Sampling number	Sampling ID	Mono-CBs	Di-CBs	Tri-CBs	Tetra-CBs	Penta-CBs	Hexa-CBs	Hepta-CBs	Octa-CBs	Nona-CBs	ΣPCBs
LF1	PM _{2.5}	N.D. ^a	N.D.	12.4	7.56	N.D.	1.25	0.42	N.D.	N.D.	21.6
	PM _{2.5–10}	N.D.	8.31	6.56	1.38	2.60	3.96	N.D.	1.46	N.D.	24.3
	PM ₁₀	N.D.	8.31	18.9	8.94	2.60	5.21	0.42	1.46	N.D.	45.9
LF2	PM _{2.5}	N.D.	8.17	12.5	4.04	N.D.	1.83	N.D.	0.94	N.D.	27.5
	PM _{2.5–10}	N.D.	12.1	8.85	1.17	0.58	N.D.	0.54	2.29	N.D.	25.5
	PM ₁₀	N.D.	20.3	21.4	5.21	0.58	1.83	0.54	3.23	N.D.	53.0
LF3	PM _{2.5}	N.D.	0.48	6.31	1.58	11.8	17.9	N.D.	N.D.	N.D.	38.1
	PM _{2.5–10}	N.D.	N.D.	10.5	N.D.	1.63	0.50	N.D.	N.D.	N.D.	12.7
	PM ₁₀	N.D.	0.48	16.8	1.58	13.4	18.4	N.D.	N.D.	N.D.	50.8
LF4	PM _{2.5}	N.D.	N.D.	8.48	6.08	3.48	N.D.	N.D.	N.D.	N.D.	18.0
	PM _{2.5–10}	N.D.	5.21	18.9	8.17	4.98	1.25	N.D.	2.31	N.D.	40.8
	PM ₁₀	N.D.	5.21	27.4	14.3	8.46	1.25	N.D.	2.31	N.D.	58.8
LF5	PM _{2.5}	N.D.	N.D.	5.92	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	5.92
	PM _{2.5–10}	N.D.	N.D.	N.D.	1.04	N.D.	N.D.	N.D.	0.79	N.D.	1.83
	PM ₁₀	N.D.	N.D.	5.92	1.04	N.D.	N.D.	N.D.	0.79	N.D.	7.75
DT1	PM _{2.5}	N.D.	3.52	3.10	1.35	N.D.	2.35	1.23	2.04	N.D.	13.6
	PM _{2.5–10}	N.D.	N.D.	4.29	0.63	3.10	1.48	0.50	1.25	1.77	13.0
	PM ₁₀	N.D.	3.52	7.40	1.98	3.10	3.83	1.73	3.29	1.77	26.6
DT2	PM _{2.5}	N.D.	N.D.	8.60	0.83	N.D.	0.50	N.D.	N.D.	N.D.	9.9
	PM _{2.5–10}	N.D.	21.9	14.7	2.50	0.75	N.D.	N.D.	N.D.	N.D.	39.9
	PM ₁₀	N.D.	21.9	23.3	3.33	0.75	0.50	N.D.	N.D.	N.D.	49.8
DT3	PM _{2.5}	N.D.	3.27	9.56	4.77	N.D.	N.D.	N.D.	0.88	N.D.	18.5
	PM _{2.5–10}	N.D.	7.10	4.60	2.48	1.85	1.67	0.65	N.D.	N.D.	18.4
	PM ₁₀	N.D.	10.4	14.2	7.25	1.85	1.67	0.65	0.88	N.D.	36.8
DT4	PM _{2.5}	N.D.	N.D.	8.08	0.88	0.81	0.40	N.D.	N.D.	N.D.	10.2
	PM _{2.5–10}	N.D.	20.6	21.6	1.15	N.D.	1.21	0.60	2.25	N.D.	47.4
	PM ₁₀	N.D.	20.6	29.7	2.02	0.81	1.60	0.60	2.25	N.D.	57.6
DT5	PM _{2.5}	N.D.	N.D.	13.3	0.81	N.D.	N.D.	N.D.	N.D.	N.D.	14.1
	PM _{2.5–10}	N.D.	5.31	4.69	1.46	N.D.	N.D.	1.15	0.54	N.D.	13.2
	PM ₁₀	N.D.	5.31	18.0	2.27	N.D.	N.D.	1.15	0.54	N.D.	27.2
DT6	PM _{2.5}	N.D.	N.D.	1.31	1.88	N.D.	0.40	N.D.	0.75	N.D.	4.33
	PM _{2.5–10}	N.D.	N.D.	10.9	2.92	1.85	0.67	N.D.	N.D.	N.D.	16.4
	PM ₁₀	N.D.	N.D.	12.2	4.79	1.85	1.06	N.D.	0.75	N.D.	20.7

^a N.D. was calculated assuming non-detected measurements were equal to LOD.

(defined as the sum of 144 congeners) were 5.92–38.7 pg m^{−3} (median: 21.58 pg m^{−3}) in PM_{2.5} and 1.83–40.8 pg m^{−3} (median: 24.3 pg m^{−3}) in PM_{2.5–10} and 7.75–58.8 pg m^{−3} (median: 50.8 pg m^{−3}) in PM₁₀ samples in Linfen, and 4.33–18.5 pg m^{−3} (median: 11.9 pg m^{−3}) in PM_{2.5} and 13.0–47.4 pg m^{−3} (median: 17.4 pg m^{−3}) in PM_{2.5–10} and 20.7–57.6 pg m^{−3} (median: 32.0 pg m^{−3}) in PM₁₀ samples in Datong (Table 2).

In comparison with other areas of China, the median PCB concentrations in the present study were lower than those in the urban area of Beijing (78.7 pg m^{−3} in PM_{2.5} and 89.2 pg m^{−3} in PM₁₀ samples) (Xu et al., 2005), an industrial zone of Taiyuan (46 pg m^{−3} in PM_{2.5} and 49 pg m^{−3} in PM₁₀ samples) (Fu et al., 2009), and a major e-waste dismantling area in Taizhou (1227 ± 433 pg m^{−3} in PM_{2.5} samples) (Han et al., 2010).

Compared with air from other countries, the PCB levels were similar to those in the atmosphere of the Lake Michigan area $20 \pm 15 \text{ pg m}^{-3}$ (Miller et al., 2001). The levels were lower than those in Chicago (90 pg m^{-3}) (Tasdemir et al., 2004b), a rural site in Melpitz in eastern Germany ($110 \pm 80 \text{ pg m}^{-3}$) (Mandalakis and Stephanou, 2007), an urban area of Bursa, Turkey ($491.8 \pm 189.4 \text{ pg m}^{-3}$) (Siddik Cindoruk and Tasdemir, 2007), and wetlands in India ($120\text{--}320 \text{ pg m}^{-3}$) (Zhang et al., 2008). In contrast, the levels were much higher than those in the Arctic (4.9 pg m^{-3}) (Hung et al., 2010), and the Antarctic (12.2 pg m^{-3}) (Baek et al., 2011).

The ratio of highest to lowest concentrations of PCBs in $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ samples exceeded 3, and obvious regional difference was found in the present study (Table 3). The concentrations of PCBs in $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ were no obvious differences in Linfen. However, the concentration of PCBs in $\text{PM}_{2.5-10}$ samples was higher than those in $\text{PM}_{2.5}$ samples in Datong. The distributions of ΣPCBs in $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ were shown in Fig. 2. They revealed an increasing trend in $\text{PM}_{2.5-10}$ towards the mideastern area of Datong. On the other hand, there was no significant difference in

contamination of $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ in Linfen. In Datong, this might be due to the fact that the coal-fired power plant and heating company were located in the mideastern portion of the city. These results indicated that $\text{PM}_{2.5-10}$ was the most polluted media of PCBs in Datong. Furthermore, the contamination status of ΣPCBs might be caused by cement plant and iron-steel industry, which was located in the middle of Linfen. It could be concluded that the PCB distributions in $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ were quite uniform in Linfen. The different typical industries could discharge different sizes of respirable particulate matter. The differences of contamination status should be mainly caused by the different types of industries in these two cities (see Table 3).

3.2. PCB congener profiles

In this study, the dominant PCBs in $\text{PM}_{2.5}$ samples were similar to those in $\text{PM}_{2.5-10}$ ones. The dominant PCBs detected in $\text{PM}_{2.5}$ and PM_{10} samples were trichlorobiphenyls (tri-CBs), with medians of 49% and 42% in Linfen and Datong, respectively, followed by di-CBs and tetra-CBs (CB is chlorobiphenyl), as shown in Fig. 3.

Fig. 2. Distribution of ΣPCBs from various respirable PM samples obtained in Datong and Linfen.

Higher-chlorinated congeners were detected at relatively low concentrations. This profile was expected because the lower volatility of higher-chlorinated congeners means that they become more firmly bound in heavily polluted areas (Chu et al., 1995). In other areas in China, tri-CBs were also the main PCB homologues detected in air samples (36.03–42.73%) obtained from the Pearl River Delta close to Guangzhou (Li et al., 2007). In urban air samples measured in Europe, the major PCB congeners were tetra-PCBs and tri-PCBs (Howel, 2007). The above results for Linfen and Datong are reasonable because lower-chlorinated congeners are firmly bound to fine and ultrafine particles owing to their low volatility.

3.3. Spatial distribution

There were some spatial distribution characteristics observed for the PM_{2.5} and PM_{2.5–10} samples (Fig. 2). The concentration of Σ PCBs from various respirable PM samples showed some

difference between Linfen and Datong. No significant differences of the spatial distribution were discovered from PM_{2.5} and PM_{2.5–10} samples collected in Linfen. However, the central area was the most polluted region in Linfen. According to PM_{2.5} samples from Datong, the differences in concentration over the whole city were small. Compared with PM_{2.5–10} samples obtained in Datong, an obvious increasing trend was found from west to east. These results indicate that in Linfen and Datong, the PCB distributions in PM_{2.5} and PM_{2.5–10} samples were quite different. This may be related to the different industrial structures and their relatively unintentional release of PCBs in these cities.

3.4. Contribution to TEQ

Because coplanar PCB congeners exhibit toxicological similarity to dioxins, risk assessment of PCBs has aroused great concerns (Giesy and Kannan, 1998). In this study, toxic equivalency (TEQ)

Table 3

Total concentrations of PCB homologues from PM_{2.5}, PM_{2.5–10} and PM₁₀ in Datong and Linfen (pg m⁻³).

PCBs	Linfen PM _{2.5} (n = 5)			Linfen PM _{2.5–10} (n = 5)			Linfen PM ₁₀ (n = 5)		
	Range	Ave ^b ± Sd ^c	Med ^d	Range	Ave ± Sd	Med	Range	Ave ± Sd	Med
Mono-CBs	N.D. ^a	–	–	N.D.	–	–	N.D.	–	–
Di-CBs	0–8.17	1.73 ± 3.6	–	0–12.1	5.13 ± 5.28	5.21	0–20.3	6.85 ± 8.25	5.21
Tri-CBs	5.92–12.5	9.12 ± 3.19	8.48	0–18.9	8.96 ± 6.83	8.85	5.92–27.4	18.1 ± 7.86	18.9
Tetra-CBs	0–7.56	3.85 ± 3.11	4.04	0–8.17	2.35 ± 3.29	1.17	1.04–14.3	6.2 ± 5.5	5.21
Penta-CBs	0–11.8	3.06 ± 5.12	–	0–4.98	1.96 ± 1.96	1.63	0–13.4	5.02 ± 5.77	2.60
Hexa-CBs	0–17.9	4.2 ± 7.72	1.25	0–3.96	1.14 ± 1.66	0.50	0–18.4	5.35 ± 7.57	1.83
Hepta-CBs	0–0.42	0.08 ± 0.19	–	0–0.54	0.11 ± 0.24	–	0–0.54	0.19 ± 0.27	–
Octa-CBs	0–0.94	0.19 ± 0.42	–	0–2.31	1.37 ± 0.99	1.46	0–3.23	1.56 ± 1.26	1.46
Nona-CBs	N.D.	–	–	N.D.	–	–	N.D.	–	–
∑PCBs	5.92–38.1	22.2 ± 11.9	21.58	1.83–40.8	21.0 ± 14.7	24.3	7.75–58.8	43.3 ± 20.4	50.8
	Datong PM _{2.5} (n = 6)			Datong PM _{2.5–10} (n = 6)			Datong PM ₁₀ (n = 6)		
	Range	Ave ± Sd	Med	Range	Ave ± Sd	Med	Range	Ave ± Sd	Med
Mono-CBs	N.D.	–	–	N.D.	–	–	N.D.	–	–
Di-CBs	0–3.52	1.13 ± 1.76	–	0–21.94	9.16 ± 9.81	6.21	0–21.9	10.3 ± 9.15	7.84
Tri-CBs	1.31–13.3	7.32 ± 4.39	8.34	4.29–21.6	10.1 ± 7.03	7.80	7.4–29.7	17.5 ± 8.04	16.1
Tetra-CBs	0.81–4.77	1.75 ± 1.54	1.11	0.63–2.92	1.85 ± 0.91	1.97	1.98–7.25	3.61 ± 2.08	2.80
Penta-CBs	N.D. ^a	0.14 ± 0.33	–	0–3.1	1.26 ± 1.23	1.30	0–3.1	1.4 ± 1.1	1.33
Hexa-CBs	0–2.35	0.61 ± 0.88	0.40	0–1.67	0.84 ± 0.73	0.94	0–3.83	1.44 ± 1.33	1.33
Hepta-CBs	0–1.23	0.2 ± 0.5	–	0–1.15	0.48 ± 0.44	0.55	0–1.73	0.69 ± 0.67	0.63
Octa-CBs	0–2.04	0.61 ± 0.81	0.38	0–2.25	0.67 ± 0.92	0.27	0–3.29	1.28 ± 1.23	0.81
Nona-CBs	N.D.	–	–	0–1.77	0.3 ± 0.72	–	0–1.77	0.3 ± 0.72	–
∑PCBs	4.33–18.5	11.8 ± 4.8	11.9	13.0–47.4	24.7 ± 15.0	17.4	20.7–57.6	36.5 ± 14.5	32.0

^a N.D. was calculated assuming non-detected measurements were equal to LOD.

^b Ave was average value.

^c Sd was standard deviation.

^d Med was median value.

Fig. 3. Distribution of PCB homologues from respirable PM in Datong and Linfen.

was determined based on 10 dioxin-like PCBs, PCB-77, PCB-81, PCB-123, PCB-105, PCB-114, PCB-118, PCB-156, PCB-157, PCB-167 and PCB-189. These ten dioxin-like PCBs accounted for 6.9% and 4.5% of the total of 144 PCBs in PM₁₀ from Linfen and Datong, respectively. In Linfen, PCB-118 (accounting for 50% of the total TEQ of PM₁₀) was the predominant dioxin-like PCB, followed by PCB-156 (accounting for 15% of the total TEQ of PM₁₀). In Datong, PCB-81 (accounting for 21% of the total TEQ in PM₁₀) was the predominant dioxin-like PCB, followed by PCB-189 (accounting for 19% of the total TEQ in PM₁₀). Although dioxin-like PCBs was a low proportion of the total PCBs, PCB-81, PCB-118, PCB-156, and PCB-189 were the main contributing analogues.

TEQ concentrations in respirable PM₁₀ (including PM_{2.5} and PM_{2.5–10}) samples were calculated using World Health Organization Toxic Equivalency Factors (WHO-TEFs) (Bhavsar et al., 2008; Van den Berg et al., 2013). In Linfen city, the concentrations of TEQ ranged from 4.0×10^{-5} to 2.3×10^{-3} pg-WHO TEQ m⁻³ in PM₁₀, N.D. – 1.7×10^{-3} pg-WHO TEQ g⁻¹ in PM_{2.5}, N.D. – 1.1×10^{-3} pg-WHO TEQ g⁻¹ in PM_{2.5–10}, respectively. In Datong, the concentrations of TEQ ranged from 1.5×10^{-4} to 8.8×10^{-4} pgWHO-TEQ m⁻³, N.D. – 2.6×10^{-4} pg-WHO TEQ g⁻¹ in PM_{2.5}, N.D. – 7.9×10^{-4} pg-WHO TEQ g⁻¹ in PM_{2.5–10}, respectively. These

result indicated that the distribution of the TEQ of dioxin-like PCBs in PM_{2.5} and PM_{2.5–10} existed obvious differences in Linfen and Datong. PM_{2.5} was relatively the most polluted media in Linfen. On the other hand, PM_{2.5–10} was relatively the most polluted media in Datong (Fig. 4). The main emission source of PCBs might be from coal combustion-related processes in Datong and industrial processes in Linfen. It could be concluded that the different emission sources influenced the TEQ distribution of PCBs in PM_{2.5} and PM_{2.5–10}.

Regarding total daily intake (TDI), almost 95% of the total daily intake (TDI) of PCBs is taken up by the food contamination. The inhalation intake doses have been reported to contribute approximately 2.61% of the TDI (Ministry of the Environment, 2003). Moreover, dioxin-like PCBs were only a part of dioxin-like POPs (such as PCDD/Fs, PBDD/Fs) which also could be found in air, these dioxin-like POPs could also be emitted by industrial and coal combustion-related sources. Because of the lack of data about dioxin-like PCB diet exposure, we cannot provide precise TDIs of dioxin-like PCBs by Datong and Linfen citizens. However, it could be concluded that there was a potential threat of exposure of the urban residents of Datong and Linfen to PCBs.

Fig. 4. Total concentrations of PCBs and TEQs in respirable PM from Linfen and Datong.

Fig. 5. Two-dimensional principal-component score plot and loading plots obtained from the data correlation matrix of 11 PM_{2.5} samples and 11 PM_{2.5–10} samples obtained in Datong and Linfen.

3.5. Source analysis

As a source apportionment method, PCA is a useful approach to elucidate probable source factors of POPs (Kim et al., 2004; Kim and Masunaga, 2005; Mari et al., 2008; Li et al., 2011; Hogarh et al., 2012). To evaluate the profiles of the PCB homologue patterns between PM_{2.5} and PM_{2.5–10}, we performed PCA on data normalized to percentage of Σ PCBs. PCB 3[#] and PCB 5[#] samples were also individually normalized to their percentage compositions and then subjected to PCA. Two extracted PCs explained by processing 79% and 86% of the data variance in Linfen and Datong, respectively. The loading plots and score plots were obtained after varimax rotation. Component 1 accounted for 55% and 57% of the total variance and was characterized by higher-chlorinated homologues, whereas component 2 accounted for 24% and 29% was characterized by lower-chlorinated homologues in Linfen and Datong, respectively. The score plot (Fig. 5) indicated that the compositions of PCBs in PM_{2.5} and PM_{2.5–10} samples were similar in Linfen and Datong, possibly originating from the same sources. The PCBs found in Linfen could therefore be classified into two main groups that were relatively highly contaminated by tri-CBs and di-CBs. There was also two clear clustering of samples, showing that tri-CBs and di-CBs were the dominant contaminants in Datong. It could be concluded that tri-CBs and di-CBs were the dominant contaminants from PM_{2.5} and PM_{2.5–10} samples in Linfen and Datong.

In China, approximately 10000 t of PCBs were produced in 1965–1974, 9000 t of trichlorobiphenyl (PCB 3[#]) and 1000 t of pentachlorobiphenyl (PCB 5[#]) (Xing et al., 2005). PCB 3[#] mainly used

for power capacitor impregnant, its composition is similar to Aroclor1242, PCB 5[#] was used for paints, insulation materials and other industrial products, its composition is similar with Aroclor1254 in China (Xing et al., 2006). The major homologues produced and used in China was tri-CBs, the major homologue profile of global PCB products was also composed of tri-CBs, and the composition of tri-CBs (40.4% of total) was higher in Chinese products than in globally (25.2% of total) (Breivik et al., 2002). Therefore, tri-CBs should be the dominant PCBs in PM_{2.5} and PM₁₀ of Linfen and Datong. All these samples as well as the major commercial PCB were characterized by a higher proportion of tri-CBs in the PCB profiles.

Solid fuel combustion, steel production and other industrial processes could produce PCBs and release lower-chlorinated congeners (Lee et al., 2005; Cetin et al., 2007). The different profiles of PCBs between PM_{2.5} and PM_{2.5–10} were fully embodied that pollution characteristics in Linfen and Datong. According to the highly polluted sampling points in this study, the PM_{2.5–10} samples obtained from LF4 (near a refractory factory) indicated that levels of di-CBs were relatively high in this points, while those measured for DT6 (located near a full carbon plant) was located in areas with relatively high concentrations of tri-CBs. Moreover, the PM_{2.5} samples obtained from LF3 (near an cement plant) indicated that levels of penta-CBs were relatively high in this points, while those measured for DT6 (located near a full carbon plant) was located in areas with relatively high concentrations of tri-CBs. It indicated that the sources of PCBs for these sampling locations might be associated with the unintentional release of the different typical industries.

4. Conclusions

The present study was the first to report contamination by PCBs in PM_{2.5} and PM_{2.5–10} from different typical industrial cities in China. In general, concentrations of PCBs in this study were lower than those reported in Germany, India, Turkey and US. The PCB levels in this study than reported elsewhere might suggest lower polluted status of PCBs in China. However, this was based on 22 samples of Linfen and Datong which might not be representative of the Chinese population overall. Despite this, this study determined both the concentration and profile of PCBs in respirable PM (PM_{2.5} and PM_{2.5–10}) samples from Linfen and Datong, explored the interaction of PCBs among different sizes of respirable particulate matter and identify possible sources of pollution. Against this backdrop, the presence of PCB pollution was a potential threat to the residents of Datong and Linfen.

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