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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.

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 transportion & 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 20 275 km^2. 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 14 112 km^2. 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 km^2 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 m^3 (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 (∅90 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 aluminous 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 3000*g*. 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 N_2 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