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Polybrominated diphenyl ethers in atmosphere from three different typical industrial areas in Beijing, China

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HIGHLIGHTS

- First report of PBDEs detection in gaseous and PM from different industrial regions in China.
- Tri-BDEs were the dominant PBDEs in gaseous.
- Penta-, tetra-, and deca-BDEs were dominant PBDEs in particulate matter.
- The PBDE distributions in gaseous and particulate matter were quite different.
- Human exposure to PBDEs via gas and particles inhalation was reported.

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ABSTRACT

Three common industries that cause polybrominated diphenyl ethers (PBDEs) pollution in Beijing, China, are solid waste incineration, chemical manufacturing, and coal-fired thermal power generation. This study was conducted to determine both the concentrations and profiles of 42 PBDEs in gaseous and particulate matter (including $PM_{2.5}$, $PM_{2.5-10}$, and total suspended particulate (TSP)) from the major industries listed above at three sites in Beijing. The total concentration of PBDEs (defined as the sum of 42 congeners in gas and TSP) were 60.5–216 pg m^{-3} at the solid waste incineration plant, 71.8–7500 pg m^{-3} at the chemical plant, and 34.4–454 pg m^{-3} at the coal-fired thermal power plant. The results indicate that the components of PBDE in gas were similar between three industrial sites, and the dominant congener was tri-BDEs. However, in particulate matter, the dominant BDEs were different between the three sites, possibly because they originated from different sources. In particulate matter, the dominant PBDEs were penta-BDEs at the solid waste incineration plant, deca-BDE at the coal-fired thermal power plant, and tetra-BDEs and deca-BDE at the chemical plant. Source analysis revealed that PBDE contamination might be associated with the use of different commercial PBDE flame-retardant mixtures. Results from a previous risk assessment indicated that the risk to human health was low. However, results from this study suggest that there is a potential threat associated with human exposure to PBDEs for the residents near these industrial sites.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been used as additive flame retardants around the world for several decades (Romano et al., 2013; Yu et al., 2013). Because of their excellent flame retardant properties, PBDEs have been widely used in various consumer products such as electronic appliances, building materials, textiles, and furniture (Sellström et al., 1998; Nouira et al., 2013; Zhang et al., 2014). Because the additives in such products are not chemically bound to the compounds, they can be easily released to the surrounding environment over the entire life cycle of the products (Meironyte et al., 1999). There are 209 different congeners of PBDEs, and the commercial production of brominated flame retardants are based on mixtures of penta-, octa- and deca-BDE (La Guardia et al., 2006; Trudel et al., 2011; Pardo et al., 2014). Research has shown that the toxicity of lower brominated congeners is higher than that of higher brominated congeners (Birnbaum and Staskal, 2003). Penta-BDE and octa-BDE were voluntarily phased out in the United States since 2004 (Betts, 2008; Kemmlein et al., 2009). In 2005, European Union had already phased out the use of penta-BDE and octa-BDE.

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Because of this phase out, the use of deca-BDE mixture was increased in EU (Söderström et al., 2004). At last, all technical mixtures of PBDEs were banned in the EU (EU, 1976; EU, 2003; EU, 2008; Kemmlein et al., 2009). In 2006, the technical mixtures of PBDEs (besides deca-BDE) in electronic and electric equipment were controlled in China (PRC, 2006). In 2009, PBDEs were added to the list of persistent organic pollutants (POPs) under the Stockholm convention (UNEP, 2009). PBDEs have been widely studied by researchers as global persistent organic pollutants (Parera et al., 2013; Ondarza et al., 2014).

The occurrence of PBDE pollutants is widespread globally. The atmosphere plays a key role in the transport and transformation of PBDEs (Hoh and Hites, 2005; Choi et al., 2008; Li et al., 2009; Li et al., 2012). Moreover, PBDEs in the atmosphere can enter the human body through the respiratory tract (inhalation and dust ingestion), and become concentrated in the human body (Fitzgerald et al., 2012; Yu et al., 2012; Arellano et al., 2013; Krol et al., 2014). Previous studies have shown that high concentrations of PBDEs may be associated with their transport patterns (Sofuoglu et al., 2013), or may originate from emissions from products, especially electrical equipment (Zhang et al., 2011; Birgul et al., 2012). Moreover, many studies have demonstrated that PBDE pollution in industrial or urban areas is much higher than in rural areas (Zhang et al., 2008; Syed et al., 2013). In China, the contaminant status of PBDEs in the environment has been studied extensively, especially in areas of e-waste dismantling in southeast China (7980 pg m^{-3}) (Chen et al., 2011; Ma et al., 2012; Li et al., 2014). In recent years, there have been many reports about PBDE pollutants in the atmosphere in China, including the levels of PBDEs in several urban regions (Chen et al., 2006; Yang et al., 2012; Zhao et al., 2013; Wang et al., 2014), in indoor and outdoor dust (Ni et al., 2011; Yu et al., 2012), at typical e-waste recycling areas (Deng et al., 2007; Chen et al., 2009; Li et al., 2014; Ren et al., 2014), and several other industrial areas (Wang et al., 2010; Tu et al., 2011, 2012; Xiang et al., 2014). The characteristic, and transport and transformation patterns of PBDEs in industrial areas are closely related to the health of local populations. However, little is known about current levels of PBDEs in particulate matter (PM) of different sizes in industrial areas of Beijing, China.

The aim of this study is to obtain a better understanding of PBDE levels in gas and PM samples collected from three industrial sites in Beijing. Beijing, the capital city of China, covers 16410.54 square kilometers and has a population of 10000000. There are several industrial areas in Beijing, and the pollutant levels and effects on local residents are largely unknown. It is therefore necessary to investigate the current atmosphere contamination status of these industrial areas in Beijing. We chose three different potential pollution sources as research areas, including a solid waste incineration plant, a chemical plant, and a coal-fired thermal power plant.

Because of the paucity of data on PBDE levels from various environmental media in Chinese industrial regions, we undertook this study to determine both the concentration and profile of PBDEs in gaseous and PM ($PM_{2.5}$, $PM_{2.5-10}$, and total suspended particulate (TSP)) from three industrial plants in Beijing. The main objectives were to establish the contamination status of these industrial areas, explore the interactions of PBDEs between these environmental media in the atmosphere, identify possible sources of pollution, and conduct a risk assessment.

2. Materials and methods

2.1. Samples

We collected the 48 samples including 12 gas samples, 12 $PM_{2.5}$ samples, 12 $PM_{2.5-10}$ samples, and 12 TSP samples from three industrial sites in Beijing (Fig. 1). The solid waste incineration plant, located in the Chaoyang district of Beijing, is the largest modern solid waste incineration plant in the city, and began operating in 2010. The daily processing capacity of waste is about 3000 tons, which accounts for more than half of the municipal solid waste production of the Chaoyang district. The chemical plant, located in the Tongzhou district, began operating in 1978 and is currently the largest production base of acrylic and esters in China. The coal-fired thermal power plant is in the Shijingshan district of northwest Beijing, and has an installed capacity of 660 MW.

Beijing prevailing northwest wind in winter, which showed in the wind rose for the whole year in Beijing (Wang, 2010) (Fig. 1). In order to avoid the influences of wind as far as possible, the 48 samples were collected when there was no sustained wind or breeze in the sampling location. According to the prevailing wind direction and environmental conditions, respirable PM samples were taken with a modified medium-volume TH-150 sampler with a dual sampling module, which is in two main parts: a filter holder and glass fiber filters, located on the top of the sampler (Wuhan Tianhong Instrument Factory, Wuhan, China). The overall average volume was approximately 22.1 m^3 (average flow rate: 100 L min^{-1}) and each sample was a 4 h composite. There were 12 $PM_{2.5}$ samples and 12 $PM_{2.5-10}$ samples taken. Simultaneously, there were 12 gas and 12 TSP samples collected with a high-volume sampler (ECHO-PUF, Tecota, Italy) at a flow rate of 200 L min^{-1} for 4 h, and the average volume was approximately 66.4 m^3. Prior to the experiment, all the fiber filters (diameter 9.0 cm and 10.14 cm, Whatman Company, Maidstone, UK) were annealed for 4 h at 550 °C to remove organic material, and equilibrated in desiccators, weighed, and placed into aluminous envelopes that were pre-washed with acetone. Polyurethane foam plugs (PUFs) were pre-cleaned by Soxhlet extraction using n-hexane and dichloromethane (1:1) for 48 h. The PUFs were dried in a desiccator under vacuum, and then wrapped with pre-cleaned aluminum foil in a desiccator before sampling. After sampling, the filters and PUFs were removed from the inlet and folded in half and returned to the pre-cleaned aluminous envelopes and stored them at −18 °C before analysis.

2.2. Chemicals

The standard solutions of PBDE congeners (BDE-AAP-A) were purchased from AccuStandard Inc. (New Haven, CT, USA). The BDE-AAP-A mixtures provided 39 congeners including mono-BDEs 1, 2, and 3; di-BDEs 7, 8, 10, 11, 12, 13, and 15; tri-BDEs 17, 25, 28, 30, 32, 33, 35, and 37; tetra-BDEs 47, 49, 66, 71, 75, and 77; penta-BDEs 85, 99, 100, 116, 118, 119, and 126; hexa-BDEs 138, 153, 154, 155, and 166; and hepta-BDEs 181, 183, and 190. An analytical standard of BDE-205, 206, and 209 was purchased from AccuStandard Corporation. The ^{13}C-labled BDE-47, 99, 183, and 209 (Cambridge Isotope Laboratory, Andover, MA, USA) were used as internal standards. The solvents used were pesticide grade (J.T. Baker, Phillipsburg, NJ, USA). Anhydrous sodium sulfate, sodium hydroxide, silver nitrate, and sulfuric acid were guaranteed reagents (Sinopharm Chemical Reagent Corporation, Beijing, China). Silica gel (60–100 mesh) was chromatographic grade (Merck, Darmstadt, Germany) for chromatography.

2.3. Extraction and cleanup

All samples were extracted with 150 ml of n-hexane/dichloromethane (1:1, v/v) by Soxhlet extraction for 24 h. Before extraction, 50 μL of ^{13}C-BDE-47, 99, 183 and 209 (all at 100 ng mL^{-1}) was added to each sample as internal standards and balanced in a desiccator for 2 h. The extracts were then collected and this procedure was repeated three times. The extracts were reduced to