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Atmospheric PBDEs at rural and urban sites in central China from 2010 to 2013: Residual levels, potential sources and human exposure

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ABSTRACT

Atmospheric polybrominated diphenyl ethers (PBDEs) were monitored monthly from 2010 to 2013 at rural and urban sites near a large shallow Chinese lake (Lake Chaohu). The urban areas had higher air PBDEs than the rural areas because of endogenic pollution. The highest and lowest concentrations of Σ_{13}BDEs were observed in the winter and in the summer, respectively. A weak temperature dependence and significant positive correlations between certain PBDE congeners and the PM_{10} ($p < 0.01$) suggest transport with particulate matter. Using air-mass back-trajectories, we determined that the main sources of the PBDEs were the areas to the north, such as Shandong Province, and to the east, such as Zhejiang Province. PBDEs did not pose an appreciable risk to human health based on the inhalation exposure assessment. The residents in urban areas were exposed to higher levels of PBDEs, and wintertime exposures posed the greatest human health risk.

1. Introduction

Polybrominated diphenyl ethers (PBDEs), particularly tetra-, penta-, hexa-, and hepta-BDEs, were approved as newly listed persistent organic pollutants (POPs) in May 2009 after an investigation of their persistence, long-distance transport, bioaccumulation, and toxicity over recent decades (SCPOP, 2009; Wania and Dugani, 2003; Yu et al., 2011a). Because of the semi-volatility of PBDEs, these pollutants are easily released into the air due to manufacturing, daily production of polymers, waste combustion, municipal solid waste incinerators, electronic waste recycling sites, waste water treatment plants, and landfills (Deng et al., 2007; Martellini et al., 2012; Tian et al., 2011; Wang et al., 2010a; Weinberg et al., 2011a,b; Wyrzykowska-Ceradini et al., 2011). In addition to “product-use-treatment” emissions, some other daily combustion sources, including mobile sources, such as diesel engines of vehicles (Chang et al., 2014; Shi et al., 2012; Wang et al., 2011), and stationary sources, such as power plants (Wang et al., 2010b), are also non-negligible in urban and rural areas.

Due to their adsorption and absorption onto or into airborne particles, PBDEs will be present as a particle-bound phase (Chen et al., 2006; Strandberg et al., 2001). Certain particles are the primary constituents of atmospheric dust and constitute the major pathways of PBDE exposure, accounting for 56%–77% of the total daily intake (TDI) (Johnson-Restrepo and Kannan, 2009). However, direct exposure via outdoor air inhalation is quite small (Besis and Samara, 2012).

Because of the significant role that the atmosphere plays in transporting PBDEs from emission sources to uncontaminated areas, numerous studies of atmospheric PBDEs have been performed worldwide (Harrad et al., 2004; Hayakawa et al., 2004; Lee et al., 2004; Mandalakis et al., 2009; Strandberg et al., 2001). During the past 30 years, China's economy has grown rapidly, becoming the world's second largest economy in 2010. However, the environmental cost of this high-speed development has included serious contamination of atmospheric PBDEs in both urban and rural areas (Chen et al., 2006; Wang et al., 2012; Yu et al., 2011b; Zhang et al., 2009). To investigate the residual levels and transport mechanism of PBDEs in the atmosphere, Chinese researchers have conducted studies from southern to northern China (Deng et al., 2007; Wang et al., 2012), from the known source areas (i.e., e-waste plants and landfills) of PBDEs to remote rural areas (Tian et al., 2011; Wang et al., 2012) and from the coast to inland areas (Deng et al., 2007; Wang et al., 2012). Thus far, all of these studies were conducted based on only one year of monitoring, and it is unreasonable and unverified to deduce environmental occurrences and temporal variations based on a short-term study. For example, Tian et al. (2011) deduced seasonal variations from only a one year

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study; however, it is incredible to consider that seasonal variations in other years were similar to the investigated year. One or two more years of monitoring should be conducted to verify the seasonal variations. Sometimes, we found that seasonal variations were unclear from long-term air monitoring of PBDEs, for example, the seasonal variations of Σ_{14}BDE at Point Petre (Su et al., 2009). Moreover, multi-year measurements provided us with seasonal cycles and with multi-year trends. Source directions based on the multi-year monitoring of PBDE concentrations and air-mass back-trajectory models, such as the hybrid single-particle Lagrangian integrated trajectory (HYSPLIT) model, can also be determined (Draxler, 1999; Draxler and Hess, 1997; Hoh and Hites, 2005; Kong et al., 2013; Su et al., 2009). Additionally, few data were available for urban and rural areas in central China, where large electronic waste recycling plants are absent.

In this study, a program of long-term (40-month) atmospheric measurements in urban and rural areas extended our knowledge of residual PBDE levels near a large, shallow lake, Lake Chaohu, which is in central China. The objectives of this study were to (1) investigate urban–rural variations in the concentrations and congener profiles of PBDEs in central China, (2) identify the influence of meteorological factors on seasonal variations and on gas/particle partitioning, (3) identify the potential source regions during various seasons, and (4) assess the human exposure to urban and rural residents based on long-term monitoring.

2. Materials and methods

2.1. Sample collection

The sampling sites are shown in Fig. S1. The details of the sampling technology included in the Text S1 in the Supplementary materials (SM) have been reported elsewhere (Ouyang et al., 2012; Wang et al., 2012). Briefly, the monthly atmospheric measurements of PBDEs from May 2010 to July 2013 were performed to investigate the occurrence and temporal variations in the levels of PBDEs. The urban sampling site (117°53′16″ E, 31°37′22″ N) was at the government center of Chaohu City. The rural sampling site (117°27′56″ E, 31°34′55″ N) was on the lake shore in the town of Zhongmiao, which is 40 km west of the urban site. To obtain both particulate and gaseous samples, a medium-volume (~300 L/min) cascade impactor (PM10-PUF-300, Guangzhou, China) was used to draw air through glass-fiber filters (GFF) and through two polyurethane foam (PUF) plugs over a period of 48 h. Two PUF plugs were used to reduce the possibilities of breakthroughs of the more volatile congeners, particularly in summer when the temperatures exceed 25 °C over a 48-h sampling period. In total, 40 pairs of samples (particles and gas) from each site were collected. We noticed that most researchers employed conventional air collection devices similar to ours because of these devices are widely used and are commercially available products with low costs (Birgul et al., 2012; Tian et al., 2011; Wang et al., 2012). However, this device might overestimate or underestimate particulate concentrations of some chemicals in comparison with an annular diffusion denuder sampler (Ahrens et al., 2012). The comparison study of conventional devices and annular diffusion denuder samplers for atmospheric PBDEs will be investigated in a future study. The meteorological data obtained during the sampling period are summarized in Table S1. The average daily temperature, wind speeds, and relative humidity, ranged from −1.1–31.5 °C, from 1.2 to 5.7 m/s, and from 40.7% to 92.3%, respectively.

2.2. Sample extraction and cleanup

Before the extraction, 50 ng of ^{13}C-PCB 141 was added as a surrogate standard (SS) to determine the procedural recoveries. Samples were extracted from the PUF plugs using 150 mL of a 1:1 hexane/acetone mixture in a Soxhlet extractor for 12 h. Samples were extracted from the GFFs using microwaves in a Teflon microware extraction tank with 25 mL of a hexane/acetone (1:1) mixture. This tank was placed in a microwave-assisted extraction (MAE) system MARS 5 (CEM Corp., Matthews, NC, USA) under the following conditions: the working power was 1200 W, and the temperature was increased to 100 °C within 10 min, held at 100 °C for 10 min, and decreased to the ambient temperature within 30 min. After concentrated to a volume of 1 mL, the PUF and GFF extracts were transferred to chromatograph columns packed with neutral aluminum oxide (6 cm); neutral silica gel (2 cm); alkaline silica gel (5 cm); neutral silica gel (2 cm); acidic silica gel (6 cm); and anhydrous sodium sulfate (1 cm), listed from bottom to top. In total, 70 mL of a solvent mixture of hexane and dichloromethane (1:1) was used to elute the column. The eluate was collected and concentrated to 1 mL before 50 ng of an internal standard (^{13}C-PCB 208, Cambridge, USA) was added. The eluate with IS was further concentrated to 0.1 mL under a gentle stream of nitrogen and stored at −18 °C pending the GC–MS analysis. All of the glassware was cleaned in an ultrasonic cleaner and heated at 450 °C for 6 h.

2.3. Instrument analysis

The samples were analyzed using an Agilent 7890 gas chromatograph that was equipped with an Agilent 5975C mass spectrometer (GC–MS) (Agilent Technologies, Avondale, PA, US), which was operated in negative chemical ionization (NCI) and selective ion monitoring (SIM) modes, and an HP-5MS column (15 m × 0.25 mm internal diameter; 0.1 μm film thickness). The samples were injected by auto-sampling in splitless mode, with a venting time of 1 min. The oven temperature was programmed to an initial temperature of 110 °C for 5 min and then increased at a rate of 20 °C/min to 200 °C, where the temperature was maintained for 5 min; increased at a rate of 10 °C/min to 280 °C; and finally increased at a rate of 20 °C/min to 305 °C, where the temperature was maintained for 10 min. Helium was used as both the carrier (2 mL/min) and the makeup gas (20 mL/min). The temperatures of the inlet, quadrupole, and ion source were 265 °C, 150 °C and 230 °C, respectively. The quantitative ion fragment *m/z* 79 or 81 was used for individual PBDEs, with the exception of BDE 209. The quantitative ion fragment of BDE 209 was *m/z* 487. Quantitation was performed using the internal calibration method based on a six-point calibration curve for individual PBDEs. The order of the PBDE congeners in the rest of the study followed the eluting sequence on the GC column. The total organic carbon (TOC) of the PM_{10} particulate matter was analyzed using a TOC 5000A coupled with an SSM-5000A sampler (Shimadzu Corp., Japan). TOC analysis and correction were performed on a sub-sample of the filter from the sample used for the PBDE analysis.

2.4. Quality assurance and quality control

Field blanks (cleaned first and obtained by transporting PUF plugs and GFFs) and procedural blanks were analyzed along with each batch of samples. BDE-28, -47, and -209 were detected in the field blanks but were below the limit of quantity (LOQ). Accordingly, the reported concentrations in the samples were blank corrected. The amounts of PBDEs in the field blanks were not significantly higher than those amounts of the procedural blanks. The mean values of individual congeners' recoveries were 88%–105% for the spiked PUF plugs and 76%–103% for the spiked GFFs. Samples were added with SS for the method performance and for the matrix effect, and these average rates of recoveries were 72%–98% for the PUF plugs and 85%–93% for the GFFs. The reported data were not corrected using the SS values because most of the analytical results of the SSs were within an acceptable range of 70%–130%. The limits of detection (LOD, signal/noise ratio of 3) of BDE-209 and of other congeners were 0.30 pg/m^3 and 0.06 pg/m^3, respectively, and the limits of quantification (signal/noise ratio of 10) of BDE-209 and of other congeners were 1.0 pg/m^3 and 0.2 pg/m^3, respectively, based on an average volume of 800 m^3. The thermal degradation of BDE 209 was likely to occur in the GC injector (265 °C). Therefore, before analyzing the samples, we first analyzed standard PBDE mixtures to investigate the degradation of BDE-209. The samples were analyzed using GC–MS when the degradation rate of BDE-209 in the mixtures was less than 10%.

2.5. Statistical analysis

The data compilation was performed using Microsoft Excel 2010 software, and the statistical analyses, including a normal or log-normal distribution test; Spearman correlation analysis; linear regression analysis; cluster analysis (CA); and principal component analysis (PCA), were performed using SPSS v. 20 software. A level of significance of 0.05 was assigned. Because the multiple congener contributions to the total PBDEs in conventional two- and three-dimensional graphs were not sufficiently clear to provide for multivariate data analysis, CA and PCA were used to further evaluate the relations among the PBDE congeners and sampling events. To meet the requirements of CA and PCA, the "none-detected" analytical results were assigned a value of 1/2 of the LOD, and the data were log-transformed to conform to a normal distribution. The similarity coefficient was set as the classification criterion for CA. The varimax rotation method with Kaiser Normalization was employed to rotate the component matrix in the PCA, which made values positive in the component 1 (PC 1) column. This method helps to clarify the meaning of PC 1.

3. Results and discussion

3.1. Concentrations and congener profiles

3.1.1. Residual levels

The total atmospheric concentrations (gaseous and particle-bound phases) of the PBDEs are listed in Table 1. The arithmetic mean (AM) of Σ_{13}PBDEs (excluding BDE-209) and BDE-209 measured at the urban site were 27.6 pg/m^3, with a range of 3.5–201.0 pg/m^3, and 58.5 pg/m^3, with a range of 3.9–262.3 pg/m^3, respectively. High levels of Σ_{13}PBDEs and BDE-209 were also found at the rural site, although the concentrations were significantly