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# Seasonality in polybrominated diphenyl ether concentrations in the atmosphere of the Yangtze River Delta, China



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#### HIGHLIGHTS

• Seasonal atmospheric PBDE concentrations in the Yangtze River Delta are reported.

• PBDE concentrations in the atmosphere ranged from 0.20 to 43 pg/m<sup>3</sup>.

• Higher PBDE concentrations were detected mainly in summer and winter.

- BDE28, 47, 99, 153, and 183 were the main congeners during the four seasons.
- Potential sources were penta-BDE products from the satellite cities.

#### ARTICLE INFO

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#### ABSTRACT

Polybrominated diphenyl ether (PBDE) concentrations in the atmosphere in rapidly developing parts of China have been studied little. In this study, polyurethane foam disk passive air samplers were used to comprehensively investigate PBDE concentrations in the atmosphere of the Yangtze River Delta in different seasons in 2010 and 2011. The mean sum of the concentrations of 13 PBDE congeners was 3.3 pg/m<sup>3</sup> in spring, 7.3 pg/m<sup>3</sup> in summer, 1.0 pg/m<sup>3</sup> in autumn, and 12 pg/m<sup>3</sup> in winter. Higher PBDE concentrations were found in urban areas than in rural areas. The PBDE concentrations were comparable to concentrations that have been found in cities around the world. BDE28, BDE47, BDE99, BDE153, and BDE183 were the dominant PBDE congeners in all seasons. High PBDE concentrations were found in satellite cities, such as Changshu, Wujiang, and Zhangjiagang, suggesting that commercial PBDEs (including pentabromodiphenyl ether products) are produced and/or used in those cities. The PBDE concentrations in the atmosphere were used to estimate daily doses through the inhalation of outdoor air. The most severe risks posed by exposure to PBDEs were found to occur in winter, for both adults and children, but the PBDE concentrations were found not to pose appreciable risks to human health.

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#### 1. Introduction

The Yangtze River Delta (YRD), in eastern China, covers an area of 99,600 km<sup>2</sup>. More than 80 million people live in the YRD, approximately 50 million of them in urban areas (Zhang et al., 2011). The YRD is one of the three largest regional economic zones in China. The YRD has quickly become industrialized and urbanized over the last three decades. This economic boom has led to a general decline in environmental quality in the YRD. Air

http://dx.doi.org/10.1016/j.chemosphere.2016.01.001 0045-6535/© 2016 Elsevier Ltd. All rights reserved. pollution is perhaps the greatest environmental problem faced by China (Fang et al., 2009; Li et al., 2011; Shao et al., 2006; Zhou et al., 2010).

Polybrominated diphenyl ethers (PBDEs) are semi-volatile organic compounds that are ubiquitous environmental pollutants. Certain PBDEs have properties allowing them to be classed as persistent organic pollutants (Stapleton et al., 2011; Voorspoels et al., 2006). Two major commercial PBDE products (penta-BDE and octa-BDE) have been classed as persistent organic pollutants under the Stockholm Convention and have been banned in many countries, including China, because of the risks they pose to human and ecological health.

Polyurethane foam (PUF) disk passive air samplers (PASs) are cost-effective and simple samplers that can be used to collect



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airborne contaminants, especially in large-scale studies in which electricity is not available to power electronic sampling equipment at every sampling site. PBDE concentrations in the atmosphere across China have been measured using PUF-PASs in previous studies (Jaward et al., 2005; Li et al., 2015; Zhao et al., 2013). To the best of our knowledge, PBDE concentrations in the atmosphere in the YRD region have been measured in very few studies. PBDE concentrations in the atmosphere at Taihu Lake in different seasons have been reported by Qiu et al. (2010). The tribromodiphenyl ether, tetrabromodiphenyl ether, pentabromodiphenyl ether, and hexabromodiphenyl ether concentrations in the gas phase through all seasons in 2004–2005 were 79, 180, 66, and 9.2 pg/m<sup>3</sup>, respectively. PBDE concentrations in the atmosphere of Shanghai were found to range from 34.4 to 108 pg/m<sup>3</sup> in 2006 (Yu et al., 2011). PBDE concentrations in the YRD atmosphere in 2009–2010 were recently reported by Zhang et al. (2013a), and concentrations of the tribromodiphenyl ethers to the heptabromodiphenyl ethers ranged from below the limit of detection to 275 pg/m<sup>3</sup>. However, these PBDE concentrations were acquired using high volume active air samplers, so the data cannot fully reflect the PBDE concentrations in the YRD atmosphere because of the limited sampling sites and sampling periods that were used.

In this study, duplicate PUF-PASs were deployed at 31 sites in the YRD to collect gas phase PBDEs in 2010–2011. The results are used to investigate the concentrations and seasonal distributions of PBDEs in the YRD atmosphere. The potential sources of PBDEs are assessed, and an inhalation exposure assessment is performed. These resultscan help in the management of urban environmental pollution in megacities that have undergone rapid economic development.

#### 2. Materials and methods

#### 2.1. Materials

A mixed standard containing native PBDEs and  $^{13}C_{12}$ -labeled PBDEs (MBDE-MXFS, "mass-labeled PBDE surrogate stock") was obtained from Wellington Laboratories (Guelph, Canada). All solvents were of pesticide grade, and were obtained from Tedia (Fairfield, OH, USA). Anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and sodium hydroxide (NaOH) were "guaranteed reagent" grade, and were obtained from Beijing Chemical Factory (Beijing, China). Sodium sulfate was baked at 450 °C and stored in a sealed container. Silica gel was washed twice with n-hexane in a glass flask and then activated at 160 °C overnight before use.

#### 2.2. Sample collection

Detailed sampling information is presented in Table S1 and our previous publications (Zhang et al., 2013b, 2013c). Briefly, duplicate PASs were deployed for four 3-month periods (i.e., covering the meteorological seasons spring, summer, autumn, and winter) between June 2010 and June 2011. The sample collection dates and the number of days in each sampling period were given in our previous publication (Zhang et al., 2013b). Samples were collected at 31 sites across the YRD region (120.2°–121.0° E, 29.9°–32.1° N; see Fig. 1), including in nine cities, Changshu, Jiangyin, Kunshan, Nantong, Suzhou, Tongzhou, Wujiang, Wuxi, and Zhangjiagang. Each PAS was a PUF disk in a domed stainless steel chamber that was designed to decrease the influence of the wind speed on the uptake rate and to protect the PUF disk from precipitation. Once collected, each PUF disk was wrapped in aluminum foil and stored in a sealed plastic bag at –20 °C until it was extracted.

#### 2.3. Sample pretreatment and analysis

Before being deployed, each PUF disk was rinsed with hot water, then extracted with a 1:1 (v/v) mixture of hexane and dichloromethane in an accelerated solvent extraction instrument (ASE 300; Dionex, Sunnyvale, CA, USA), and then dried under vacuum in a desiccator. Previously published polycyclic aromatic hydrocarbon data for the PUF-PASs showed that the duplicate PUF disks gave consistent results (Zhang et al., 2013c). Therefore, we combined the duplicate PUF samples from each site to give one sample for PBDE analysis.

Each sample was extracted with a 1:1 (v/v) mixture of hexane and dichloromethane in a Dionex ASE 300 accelerated solvent extraction instrument, then the extract was split into two equal aliquots, one of which was used for PBDE analysis. The extract for PBDE analysis was cleaned up by passing it through a multi-layer silica column (12 mm i.d., containing, from bottom to top, 1 g anhydrous sodium sulfate, 2 g Florisil, 1 g activated silica gel, 3 g basic silica (deactivated to 1.3% w/w with deionized water), 1 g activated silica gel, 8 g silica gel containing 44% (w/w) concentrated sulfuric acid, 1 g activated silica gel, and 2 g anhydrous sodium sulfate), which was a slightly modified version of the columns used in Chinese Environmental Monitoring Standard method HJ 77.2–2008 and the United States Environmental Protection Agency method 1614. The multi-layer column was eluted with 150 mL of a 4:1 (v/v) mixture of hexane and dichloromethane. The cleaned extract was concentrated to approximately 1 mL, then <sup>13</sup>C-labeled PBDEs were added to act as internal standards. The extract was then analyzed for 13 PBDE congeners (BDE17, BDE28, BDE47, BDE66, BDE71, BDE85, BDE99, BDE100, BDE138, BDE153, BDE154, BDE183, and BDE190) by isotope dilution high resolution gas chromatography (using an Agilent 6890 instrument; Agilent Technologies, Santa Clara, CA, USA) and high resolution mass spectrometry (using a Micromass Autospec Ultima instrument; Waters, Milford, MA, USA). The concentrations of the individually resolved PBDE congeners were summed to give total PBDE concentrations.

#### 2.4. Data processing and analysis

The amounts of chemicals retained by the PUF (in nanograms per sampler) had to be converted into concentrations in the air (in picograms per cubic meter) to allow the data to be compared with previously reported PBDE concentrations in air. The concentrations in the air were estimated using Equation (1) (Baek et al., 2008):

$$C_{\text{PAS}} = C_{air} \cdot R \cdot t \tag{1}$$

where C<sub>PAS</sub> is the amount of chemical in the PAS (ng/sampler), C<sub>air</sub> is the PBDE concentration in ambient air  $(pg/m^3)$ , R is the sampling rate  $(m^3/d)$ , and t is the sampling period (d). It has been recommended that depuration compounds should be added to PASs before the PASs are deployed so that the wind and temperature dependencies of the sampling rates for gas-phase compounds can be taken into account (Klanova et al., 2008). This is particularly useful for obtaining comparable data from samplers deployed in different environments and subject to different meteorological conditions. The sampling area in this study was, however, relatively small, and the wind speeds, temperatures, and other meteorological parameters were similar at all of the sampling sites (Zhang et al., 2013b, 2013c). Moreover, sampling rates for compounds that are mainly found in the gas phase in the atmosphere are expected to vary relatively little (within a factor of about two) (Klanova et al., 2008). Using an average sampling rate of 3.5 m<sup>3</sup>/d, which was used in studies published by Jaward et al. (2005) and Li

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