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Multi-year air monitoring of legacy and current-use brominated flame retardants in an urban center in northeastern China

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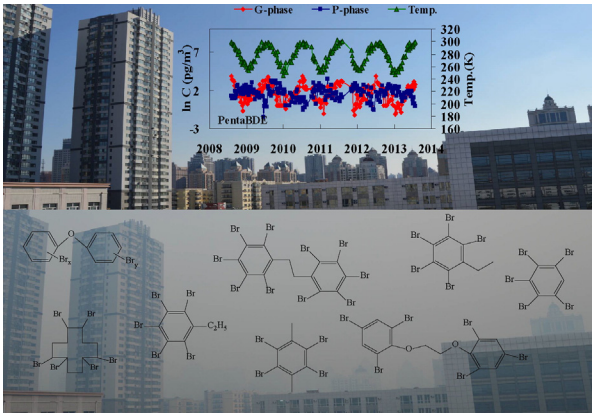
HIGHLIGHTS

- High mass BFRs were the dominant compounds in the air samples.
- Concentrations of BDE-209 and NBFRs were significantly increasing.
- Meteorological conditions could significantly affect the levels of BFRs.
- Atmospheric partitioning behaviors of NBFRs were similar to that of PBDEs.

GRAPHICAL ABSTRACT



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ABSTRACT

The occurrence and temporal trends of polybrominated diphenyl ethers (PBDEs) and non-PBDE brominated flame retardants (NBFRs) were investigated in an urban atmosphere of Northeast China in consecutive six years (2008–2013). Among all chemicals, BDE-209, l,2,5,6,9,10-hexabromocyclododecane (HBCD), and decabromodiphenylethane (DBDPE) were the three most dominant compounds. During the period, the levels of pentabromodiphenyl ethers in the gas-phase and octabromodiphenyl ethers in the particle-phase significantly decreased, while the levels of BDE-209 and NBFRs increased in either the gas-phase or particle-phase. Ambient temperature was the most significant variable that influenced the gas-phase and particle-phase concentrations of BFRs, followed by wind speed and relative humidity. A stronger temperature dependence of the atmospheric concentrations was found for lower mass BFRs. Gas-particle partitioning studies suggested PBDEs in the urban atmosphere of Northeast China were at steady-state. Steady-state equation can also well describe the

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Gas-particle partitioning
Northeast China

partitioning behavior for NBFRs, suggesting that the atmospheric partitioning behaviors of NBFRs were similar to those of PBDEs.

1. Introduction

Brominated flame retardants (BFRs) are added to consumer products of various materials such as furniture, electronic circuitry, textiles, construction materials and other products to reduce the risk from fatal fires (Alaee et al., 2003; Covaci et al., 2011; de Wit, 2002). Polybrominated diphenyl ethers (PBDEs) are a typical group of BFRs used for decades. Due to their persistence and ubiquitous occurrence in the environment, commercial pentabromodiphenyl ethers (PentaBDE) and octabromodiphenyl ethers (OctaBDE) are listed under the Stockholm Convention and have been banned worldwide (Renner, 2004; UNEP, 2009). Since the phase-out of PBDE products, several non-PBDE BFRs (NBFRs) including decabromodiphenylethane (DBDPE), 1,2,5,6,9,10-hexabromocyclododecane (HBCD), pentabromoethylbenzene (PBEB), and 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE) have been introduced as alternatives. However, many selected NBFRs are considered to be POP-like (Kuramochi et al., 2014). HBCD and BTBPE have been proven to be highly bioaccumulative, suggesting a potentially high environmental risk (Wu et al., 2011), while PBEB has been considered as persistent, toxic, and bioaccumulative (Covaci et al., 2011).

Recent evidence indicates that BFRs have entered the environment in large amounts. They were frequently detected in the air (Lee et al., 2016; Li et al., 2015a; Qi et al., 2014a; Takeuchi et al., 2014; Venier et al., 2012b), indoor dust (Ali et al., 2013; Qi et al., 2014b; Rauert and Harrad, 2015), soil (Law et al., 2014; Li et al., 2016b; Zehra et al., 2015; Zheng et al., 2015), and other environmental media (Eulaers et al., 2014; Lee et al., 2013; Lee et al., 2014; Malarvannan et al., 2013). It is essential to measure the atmospheric concentrations of BFRs as a function of time after the implementation of regulations on PBDEs. These measurements will provide important information on effectiveness of the regulations and on how fast the concentration in the atmosphere is changing (Salamova et al., 2015). Some PBDE and NBFR concentrations were still increasing in the Great Lakes atmosphere after the phase-out of PBDEs production (Ma et al., 2013b). There have been short-term monitoring programs limited to one to two years on BFRs in the atmosphere of China. For instance, the atmospheric concentrations of halogenated flame retardants were analyzed at the Tibetan Plateau during October 2006 and February 2008 (Xiao et al., 2012). However, longer period measurements are required to determine the temporal trends of atmospheric levels of BFRs. Data in the temporal trends of PBDEs in the atmosphere remain limited in China. It would be interesting to study the change in atmospheric levels of BFRs since the phase out of PBDEs.

Meteorological conditions such as temperature and wind speed could significantly affect the concentrations of BFRs in the atmosphere. Temperature dependence of various hazardous air pollutants including polychlorinated biphenyls (PCBs), PBDEs and polycyclic aromatic hydrocarbons (PAHs) have been suggested (Qi et al., 2014a; Simcik et al., 1999; Su et al., 2007). Previous research suggested that higher relative humidity leads to lower particle phase concentrations of semivolatile organic-compounds, which may be explained by the following mechanisms: the blocking of H_2O on the surface of particle, and/or phase material can become more hydrated and less hospitable to hydrophobic organic compounds as relative humidity increases (Pankow et al., 1993). The multi-year air samples with various meteorological conditions in Northeast China is suitable to test the relationship between atmospheric BFRs concentrations and meteorological conditions.

Gas-particle (G-P) partitioning is an important factor for environmental fate of BFRs in atmosphere, such as long-range atmospheric transport and deposition. Most of the studies described the G-P partitioning of PBDEs use the equilibrium state approach (Harner and Bidleman, 1998). However, the results indicated that the equilibrium approach was unable to accurately describe the relationship between gas-phase and particle-phase PBDEs in many cases, suggesting that the partitioning behavior of PBDEs should be based on a steady state instead of an equilibrium state in many cases (Li et al., 2015b; Li and Jia, 2014). Furthermore, the wide-range temperature with a span of 56 °C means great variations of octanol–air partition coefficients ($\log K_{OA}$), making this study suitable to research the temperature dependence of G-P partitioning.

The objectives of the present study are: (1) to quantify the pollution levels of BFRs in air samples in consecutive 6 years (2008–2013), (2) to investigate the temporal trends of BFRs since the phase out of PBDEs, which could provide valuable information on the sources, and thus could support the regulation of these pollutants (3) to test the meteorological influence on the atmospheric behaviors of BFRs, and (4) to study the G-P partitioning behaviors for both PBDEs and NBFRs using a steady-state approach under a wide range of temperatures.

2. Materials and methods

2.1. Chemicals and reagents

The samples were analyzed for the following BFRs: PentaBDE (including BDE-17, −28, −47, −66, −85, −99 and −100), OctaBDE (including BDE-138, −153, −154 and −183), DecaBDE (BDE-209), 2,3,5,6-tetrabromo-p-xylene (pTBX), 1,2,3,4,5-pentabromobenzene (PBBZ), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), 1,2,5,6,9,10-hexabromocyclododecane (HBCD), 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE) and decabromodiphenylethane (DBDPE) (Table S1, Supplementary data). The surrogate standards containing 1,3,5-tribromobenzene, $^{13}C_{10}$-dechlorane plus and PCB-155 were purchased from AccuStandard Inc. (New Haven, CT, USA). PBDEs were purchased from AccuStandard Inc. (New Haven, CT, USA). NBFRs were acquired from Wellington Laboratories (Guelph, Canada). Pesticide residue grade organic solvents were used in this study (J.T. Baker, Phillipsburg, NJ, USA).

2.2. Sample collection and pretreatment

Harbin (44°04′–46°40′N, 125°41′–130°13′E) is the capital city of Heilongjiang Province in the Northeastern China (Fig. 1). Harbin City is the 8th largest city in China with a population of 5.3 million in 2010. Table S2 shows the meteorological data including daily average temperature, dew point, wind speed, wind direction, duration of sunshine, relative humidity, visibility, atmospheric pressure and precipitation during the sampling period (2008–2013). The daily average temperature ranged from −27 °C to 29 °C during the sampling campaign, providing a suitable opportunity to study the influence of temperature on BFRs levels.

Detailed descriptions on the sample collection and pretreatment procedures for the samples were available in previous studies (Li et al., 2016a; Ma et al., 2013a; Yang et al., 2013). Generally, samples were collected nearly every week with high-volume air samplers between August 2008 and July 2013. Glass fiber filters (GFFs) and polyurethane foam (PUF) plugs were applied to collect the particle-phase and gas-phase compounds, respectively. A total of 222 pairs of gas-phase and particle-phase samples were collected. All the samples were transported to the laboratory and stored frozen (−20 °C) until extraction.

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