



Brominated flame retardants in the urban atmosphere of Northeast China: Concentrations, temperature dependence and gas–particle partitioning



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HIGHLIGHTS

- Both PBDEs and alternative BFRs were analyzed in the atmosphere of Northeast China.
- Partial pressure of BFRs was significantly correlated with the ambient temperature.
- A strong temperature dependence of gas–particle partitioning was found.
- Absorption into organic matter was the control mechanism for G–P partitioning.

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ABSTRACT

57 pairs of air samples (gas and particle phases) were collected using a high volume air sampler in a typical city of Northeast China. Brominated flame retardants (BFRs) including 13 polybrominated diphenyl ethers (PBDEs, including BDEs 17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183, and 209) and 9 alternative BFRs (p-TBX, PBBZ, PBT, PBEB, DPTE, HBBZ, γ -HBCD, BTBPE, and DBDPE) were analyzed. The annual average total concentrations of the 13 PBDEs and the 9 alternative BFRs were 69 $\mu\text{g}/\text{m}^3$ and 180 $\mu\text{g}/\text{m}^3$, respectively. BDE 209 and γ -HBCD were the dominant congeners, according to the one-year study. The partial pressure of BFRs in the gas phase was significantly correlated with the ambient temperature, except for BDE 85, γ -HBCD and DBDPE, indicating the important influence of ambient temperature on the behavior of BFRs in the atmosphere. It was found that the gas–particle partitioning coefficients ($\log K_p$) for most low molecular weight BFRs were highly temperature dependent as well. Gas–particle partitioning coefficients ($\log K_p$) also correlated with the sub-cooled liquid vapor pressure ($\log P_p^L$). Our results indicated that absorption into organic matter is the main control mechanism for the gas–particle partitioning of atmospheric PBDEs.

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1. Introduction

Brominated flame retardants (BFRs) are organic flame retardants that are produced and used widely to prevent the spread of fire. It has been estimated that BFRs accounted for 39% of the global flame retardant market as of the year 2000, and their use in the electronics industry, specifically, accounted for 35–40% of total flame retardant use (Wang et al., 2009). With high octanol–water partition coefficients (K_{ow}), meaning their highly lipophilic and hydrophobic property, BFRs

easily accumulated in fat tissue and can be passed through the food chain into humans. Some BFRs are toxic and persistent in the environment, such as polybrominated dibenzo-p-dioxins (PBDDs) and dibenzofurans (PBDFs) (Thoma et al., 1987). In China, 10^4 tons of BFRs was produced in 2000, and the demand for BFRs is increasing every year at the rate of 8% (Mai et al., 2005).

Polybrominated diphenyl ethers (PBDEs) are a type of BFR that have commonly been used in plastics, foams, textiles and other materials for decades. The usage of PBDEs has increased over the last 20 years and as a result, large quantities of these compounds have been released into the environment during their production and use. In China, Deca-BDE (one type of PBDE) has been produced by more than 20 enterprises since the 1980s and became the dominant BFR product, with 30 000 tons used in 2005 (Zou et al., 2007) and 15 000 tons in 2006 (Hu et al., 2010). PBDEs were the most widely used BFR in history; after their phase-out, several

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other commercial products were introduced into the market. For example, 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE) was used as a replacement for Octa-BDE (Hoh and Hites, 2005), and decabromodiphenylethane (DBDPE) was used to replace Deca-BDE (Kierkegaard et al., 2004). Currently, many new alternative BFRs have been introduced and produced for commercial usage, such as 2,3,5,6-tetrabromo-p-xylene (p-TBX), pentabromotoluene (PBT), 1,2,3,4,5-pentabromobenzene (PBBZ), petabromoethylbenzene (PBEB), 2,3-dibromopropyl 2,4,6-tribromophenyl ether (DPTE), hexabromobenzene (HBBZ), and 1,2,5,6,9,10-hexabromocyclododecane (HBCD).

Gas-particle partitioning is an important factor in the transformation and transport of semi-volatile organic compounds (SVOCs) in the air. Therefore, it is essential to deeply understand the behavior of BFRs in the air, especially as it pertains to the development and evaluation of new alternative BFRs. In this study, both PBDEs and alternative BFRs were analyzed in the atmosphere surrounding Harbin, a typical city in Northeast China, for a 14-month period. The purpose of this study was to increase our current knowledge regarding the temperature dependence and gas-particle partitioning displayed by PBDEs and alternative BFRs. It is our understanding that this is the first study focused on both PBDEs and alternative BFRs to occur in Northeast China.

2. Materials and methods

2.1. Chemicals and reagents

The pesticide analysis grade organic solvents, including acetone, hexane, dichloromethane, and isooctane were purchased from J. T. Baker Co., USA. ACS grade silica gel (100–200 mesh) was purchased from Merck Co., Germany. The stock standard solution, which included 13 PBDEs (BDEs 17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183, and 209), along with γ -HBCD (an isomer of HBCD), PBEB, BTBPE, and DBDPE, were provided by the National Water Research Institute of Environment Canada. Other alternative BFRs were purchased from Wellington Laboratories Inc. (Guelph ON, Canada). BDE 71 and CB 155 were purchased from Accustandard Inc. (New Haven, CT, USA). These two compounds were used as an internal standard and as a surrogate, respectively.

2.2. Sampling

Harbin, with a population of 5 millions, is the capital city of Heilongjiang Province in Northeast China. The ambient temperature in Harbin ranges from $-30\text{ }^{\circ}\text{C}$ to $30\text{ }^{\circ}\text{C}$, providing a suitable opportunity to study the influence of temperature on SVOCs in the atmosphere. In this study, 57 pairs of samples (gas and particle phases) were collected using a high volume air sampler (KB-1000, Kingstar Electronic Technology Co., China) positioned on the roof of a building in a typical residential region of Harbin with the sampling rate of $0.8\text{ m}^3/\text{min}$. The samples were collected for a 14-month period from August 2007 to September 2008. During each month, 4–5 consecutive 24-hour days were chosen for sampling. Two attached polyurethane foams (PUFs, each measuring 9.5 cm in diameter and 5.0 cm in length) and one glass fiber filter (GFF, measuring 20 cm \times 25 cm, Kingstar Electronic Technology Co., China) were used to collect gas and particle phase air samples, respectively. Before sampling, the PUFs were extracted with a mixture of acetone and hexane (3:1, V:V) for 24 h. A different mixture of acetone and hexane (1:3, V:V) was then applied for 24 h for cleaning purposes. The GFFs were baked for 6 h at $450\text{ }^{\circ}\text{C}$ to remove any organic contaminants. After collection, the samples were frozen at $-20\text{ }^{\circ}\text{C}$ until further treatment.

2.3. Treatment

The details regarding the sample treatment and analysis can be found in our previous study (Ma et al., 2010). Briefly, after the surrogate

(CB 155) was added, all of the gas and particle phase air samples were Soxhlet-extracted with a mixture of acetone and hexane (1:1, V:V) and dichloromethane for 24 h with 4–6 extraction circles per hour, respectively. Then, the extracts were purified with a silica gel column, and the final extract volume was concentrated to 1.0 mL by evaporation and a gentle stream of nitrogen. The internal standard (BDE 71) was applied for quantization before analysis to remove matrix effects.

2.4. Analysis

All congeners, except for BDE 209 and DBDPE, were analyzed using Agilent 6890-5975B gas chromatography mass spectrometry (GC-MS) in an electron capture negative ionization mode equipped with an HP5-MS column (30 m \times 0.25 mm \times 0.1 μm , J&W Scientific). The chromatographic conditions for the 12 PBDE congeners (BDEs 17, 28, 47, 49, 66, 85, 99, 100, 138, 153, 154, and 183) and 8 alternative BFRs (p-TBX, PBBZ, PBT, HBBZ, DPTE, BTBPE, PBEB, and γ -HBCD) were as follows: $110\text{ }^{\circ}\text{C}$ for 2 min, $110\text{ }^{\circ}\text{C}$ to $220\text{ }^{\circ}\text{C}$ ($25\text{ }^{\circ}\text{C}/\text{min}$), $220\text{ }^{\circ}\text{C}$ to $290\text{ }^{\circ}\text{C}$ ($5\text{ }^{\circ}\text{C}/\text{min}$), and held for 15 min. The temperatures were set at $150\text{ }^{\circ}\text{C}$, $230\text{ }^{\circ}\text{C}$, and $250\text{ }^{\circ}\text{C}$ for the quadrupole, ion source, and interface, respectively. For BDE 209 and DBDPE analysis, a shorter DB5-MS column (15 m \times 0.25 mm \times 0.1 μm , J&W Scientific) was used with 6890-5975B GC-MS, with the following temperature program: $110\text{ }^{\circ}\text{C}$ for 0.5 min, $5\text{ }^{\circ}\text{C}/\text{min}$ to $220\text{ }^{\circ}\text{C}$, $20\text{ }^{\circ}\text{C}/\text{min}$ to $310\text{ }^{\circ}\text{C}$, and held for 15 min. In this case, the temperatures were $106\text{ }^{\circ}\text{C}$, $200\text{ }^{\circ}\text{C}$, and $270\text{ }^{\circ}\text{C}$ for the quadrupole, ion source, and interface, respectively. A high-purity helium was used as the carrier gas with the flow rates of 1.4 mL/min and 1.7 mL/min for the HP5-MS column and DB5-MS column, respectively. For identification purposes, the peaks for each sample were selected on the basis of retention time with standards. For quantification purposes, the five-point calibration curves (with the ranges of 50–1000 ng/mL for BDE 209, 1–25 ng/mL for other PBDEs, 8–400 ng/mL for DBDPE, and 1–50 ng/mL for other alternative BFRs) were applied, which were established with the authentic standard/internal standard concentration ratios and corresponding peak area ratios.

2.5. QA/QC

Field blanks and method blanks were performed during the sampling and sample treatment to check any background contaminations. The major contaminant observed in blanks was BDE 47, with concentrations less than 10% of the concentration in real samples. All of the reported concentrations were corrected with blanks. For the surrogate, the average recovery ranged from 75% to 102%. For the spiked samples, the recoveries of 13 PBDEs and 9 alternative BFRs ranged from 88.9% to 135%. All of the reported concentrations were corrected with surrogate recoveries. At the beginning of the program, we completed a preliminary experiment for checking the breakthrough of BFRs with the high volume active air sampler. Details can be found in our previous study (Ma et al., 2010). Our results indicated that the two attached 5.0 cm-long PUFs (10.0 cm in total) have enough capacity for adsorbing gaseous BFRs for a 24-hour sampling period. The instrumental limit of detection (LOD) was calculated as 3 times the signal to noise (S/N) ratio, which gave a range from $0.017\text{ pg}/\text{m}^3$ for p-TBX to $2.9\text{ pg}/\text{m}^3$ for γ -HBCD in air samples. If the concentration was lower than the LOD in real samples, half of the LOD was used for statistical analysis in this study.

3. Results and discussions

3.1. Concentration

The concentrations of various BFRs in the atmosphere surrounding Harbin are summarized in Table 1 and Fig. 1. Among 13 PBDEs, BDE 209 was the most abundant congener with a mean concentration of

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