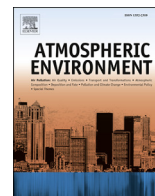




Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Brominated flame retardants in Chinese air before and after the phase out of polybrominated diphenyl ethers



Wen-Long Li ^a, Hong Qi ^a, Wan-Li Ma ^a, Li-Yan Liu ^a, Zhi Zhang ^b,
 Mohammed O.A. Mohammed ^a, Wei-Wei Song ^{a,*}, Zifeng Zhang ^{a,**}, Yi-Fan Li ^a

^a International Joint Research Center for Persistent Toxic Substances (IJRC-PTS), State Key Laboratory of Urban Water Resource and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China

^b School of Agricultural Resource and Environment, Heilongjiang University, Harbin 150080, China

H I G H L I G H T S

- Twelve PBDEs and six NBRs were investigated in Chinese air.
- The distribution of BFRs showed a typical primary fractionation pattern.
- Temperature and GDP were the major factors affecting the levels of BFRs.
- An evolving commercial usage of BFRs was found since the phase out of PBDEs.

A R T I C L E I N F O

Article history:

Received 9 February 2015

Received in revised form

12 July 2015

Accepted 13 July 2015

Available online 15 July 2015

Keywords:

Brominated flame retardants

Air

Seasonal variation

Temporal trend

China

A B S T R A C T

Brominated flame retardants (BFRs), including polybrominated diphenyl ethers (PBDEs) and novel non-BDE flame retardants (NBRs), were analyzed in Chinese air during China's POPs Soil and Air Monitoring Program Phase I (SAMP-I) and Phase II (SAMP-II). The levels of Σ_{12} PBDEs and Σ_6 NBRs in urban sites were significantly higher than those in rural sites and background sites. The higher detection rate and concentrations of high molecular weight PBDEs and NBRs in Phase II indicated the changing of the commercial pattern of BFRs after the phase out of PBDEs in China. Temperature was the major factor affecting the seasonal variations of molecular weight BFRs in atmosphere. A significant correlation between BFRs concentration and gross domestic product (GDP) was observed, with the GDP parameter explained 59.4% and 72.7% of the total variability for Octa-BDEs and low molecular weight NBRs, respectively. Our findings indicated an evolving commercial usage of BFRs from SAMP-I to SAMP-II, i.e. shifting from lower molecular weight to higher molecular weight congeners in China.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Brominated flame retardants (BFRs), including polybrominated diphenyl ethers (PBDEs) and novel non-BDE flame retardant

(NBRs), have been used widely in electronic devices, furniture, construction materials and other commercial products to prevent the spread of fire (Alaee et al., 2003). BFRs accounted for 39% of the flame retardants worldwide in 1998 (European Flame Retardants Association, 2005). In China, 10^4 tons of BFRs were produced in 2000, and the demand for BFRs was increased every year at the rate of 8% (Mai et al., 2005).

Both Penta-BDEs and Octa-BDEs, two of the commercial mixtures of PBDEs, have been banned by the Stockholm Convention on Persistent Organic Pollutants (UNEP, 2009). Deca-BDEs, another commercial mixture of PBDEs, has been produced since the 1980s and became the dominant BFR product, with a production of 30 000 tons in 2005 (Zou et al., 2007) and 15 000 tons in 2006 in China (Hu et al., 2010). The production, importation, and sales of

* Corresponding author. International Joint Research Center for Persistent Toxic Substances (IJRC-PTS), State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, 202 Haihe Road, Nangang District, Harbin 150090, Heilongjiang, China.

** Corresponding author. International Joint Research Center for Persistent Toxic Substances (IJRC-PTS), State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, 202 Haihe Road, Nangang District, Harbin 150090, Heilongjiang, China.

E-mail addresses: wwwsong@hit.edu.cn (W.-W. Song), zifeng_zhang@aliyun.com (Z. Zhang).

Deca-BDEs has been voluntarily phased-out in Canada and the United States since the end of 2013 (U.S.E.P.A., 2009).

Alternative BFRs were reported as “new” non-BDE brominated flame retardants or novel brominated flame retardants (NBFRs). Among which pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), 1,2,3,4,5-pentabromobenzene (PBBZ), 1,2,5,6,9,10-hexabromocyclododecan (HBCD) and decabromodiphenylethane (DBDPE) was commonly detected in the global atmosphere under the global atmospheric passive sampling network (Lee et al., 2010). Some NBFRs have been produced to replace PBDEs for commercial application. For example, BTBPE is a replacement for the Octa-BDEs mixture (Hoh and Hites, 2005). DBDPE has been reported to be a replacement for Deca-BDEs with a production volume of approximately 11 000 tons in 2006 in China (Hu et al., 2010).

The polyurethane foam (PUF) disk passive air sampler (PAS) (Harner et al., 2003, 2004; Shoeib and Harner, 2002) has been widely used for monitoring of PCBs on a national scale in China (Zhang et al., 2008a), as well as for PCBs and PCNs across East Asia (Hogarh et al., 2012) and PCBs, PBDEs, and OCPs across Asia (Jaward et al., 2005) and Europe (Jaward et al., 2004). PUF-PAS is a cost-effective and simple sampler to collect airborne contaminants, especially in a large scale study when electricity is unavailable (Zhang et al., 2008b). This capability makes it be better suitable for sampling in remote areas and providing higher spatial resolution data (Hayward et al., 2010). Reliable estimation of atmospheric concentration and semi quantitative comparison of levels and patterns of POPs in large scale can be achieved by PUF-PAS. Furthermore, the PUF-PAS is helpful in identifying source/sink regions and underlying temporal trends through long-term monitoring (Jaward et al., 2004).

In this study, twelve PBDEs and six NBFRs were analyzed in air samples collected by PUF-PAS under the Chinese air during China's POPs Soil and Air Monitoring Program (SAMP) Phase I (2005–2007) and Phase II (2008–2010). The aims of this study were: (1) to gather information regarding the pollution levels and distribution of BFRs in atmosphere in China; (2) to discuss the differences of BFRs levels in urban, rural and background sites for figuring out the influence of human activities; (3) to study the seasonal variation of BFRs; (4) and to evaluate the changing of BFRs in atmosphere in China before and after the official ban of Penta-BDEs and Octa-BDEs in 2006 (Zhang et al., 2009a).

2. Materials and methods

2.1. Sampling

China's POPs Soil and Air Monitoring Program Phase I (SAMP-I) and Phase II (SAMP-II) were conducted in 2005–2007 and 2008–2010, respectively (Yang et al., 2012, 2013; Zhang et al., 2008a; Zhang et al., 2008b). Ninety-seven passive air samples were collected in 4 background sites, 69 rural sites, and 24 urban sites across China from mid-July to mid-October in 2005 (SAMP-I), and 38 passive air samples were collected in 11 Chinese large cities for four seasons from June 2009 to June 2010 (SAMP-II). The sampling sites across China in 2005 are shown in Fig. S1. The 11 urban sampling sites in 2009–2010 include: Harbin (HRB), Shihezi (SHZ), Beijing (BJ), Lanzhou (LZ), Xi'an (XA), Lasha (LS), Chengdu (CD), Nanchang (NC), Kunming (KM), Dalian (DL) and Guangzhou (GZ). Detailed information regarding the sampling sites and sampling procedures can be found in our previous studies (Yang et al., 2012, 2013; Zhang et al., 2008a; Zhang et al., 2008b). Briefly, PUF-PASs were deployed for 3 months for each site. After sampling the PUF disks were retrieved and resealed in their original jars, and returned to the IJRC-PTS laboratories, where they were kept at -20°C before extraction.

2.2. Analysis

PASs air samples were treated and analyzed according to the methods established in the Hazardous Air Pollutants (HAPs) Laboratory and the National Laboratory for Environmental Testing (NLET), Science and Technology Branch, Environment Canada. After being spiked with a recovery standards (surrogates) containing 1,3,5-tribromobenzene (TBB) and polychlorinated biphenyl 155 (CB-155) (Accustandard, New Haven, CT), samples were Soxhlet extracted for 24 h using acetone and hexane (1:1, v:v). Extracts were cleaned using a glass column which consisted of 5 g silica gel. Finally, extracts were solvent exchanged into isooctane and concentrated under a gentle stream of ultra high purity nitrogen. Before analysis, BDE-71 and octachloronaphthalene were added as internal standards for establishing the calibration curves.

BFRs were quantified using Agilent 6890A series gas chromatograph and Agilent 5975C mass spectrometer (GC/MS) with an electron capture negative ionization (ECNI) ion source. DB-5 MS (15 m \times 0.25 mm \times 0.1 μm , J&W Scientific) column with a constant flow rate of 1.7 mL/min was used for the separation of target chemicals. Injections (2 μL) were made in the splitless mode. The oven temperature program was as follows: held at 110°C for 0.5 min; $5^{\circ}\text{C}/\text{min}$ to 220°C ; $20^{\circ}\text{C}/\text{min}$ to 310°C , and then held for 9 min. The temperatures were set at 270°C , 150°C , and 150°C for the transmission line, quadrupole and ion source, respectively. Target BFRs were monitored with the following ions (m/z): 79, 81 and 471.6 for PBBZ; 79, 81 and 485.6 for PBT; 484.3, 486.3 and 488.5 for BDE-209; and 79 and 81 for the other compounds (Table S1). The standard of isomer γ -HBCD was applied to quantify the total concentration of HBCDs due to their co-elution of the three isomers (α -HBCD, β -HBCD and γ -HBCD).

2.3. QA/QC

Analytical procedures were undertaken using strict quality assurance and quality control methods. One method blank and one spiked blank were treated in each batch of 10 samples. The chromatographic peaks were integrated only when the signal-to-noise ratio was higher than 3, which were treated as the instrumental limit of detection (LOD) with the range of 0.018–0.057 ng/sample for PBT, PBEB, BTBPE and PBDEs (without BDE-209), and 0.9–2.4 ng/sample for BDE-209, HBCD and DBDPE. The mean recoveries of the two surrogates were $77.5 \pm 8.6\%$ and $85.2 \pm 11.4\%$ for TBB and CB-155, respectively. The recoveries for BFRs in the spiked blanks ranged from 75.2% to 103.5%, with a mean of 83.7%. Low levels of target compounds (BDE-28, BDE-47, BDE-209 and PBT) in blanks were detected, which was less than 5% of the levels in real air samples. Therefore, the reported results were not corrected with blanks and surrogate recoveries.

3. Results and discussion

3.1. Summary of BFRs concentration in SAMP-I and SAMP-II

BFRs concentrations in Chinese air in SAMP-I are summarized in Table 1 and Table S2. The total concentrations of BFRs ($\Sigma_{18}\text{BFRs}$) ranged from 0.10 to 1500 ng/sample. The 5th and 95th percentile of $\Sigma_{12}\text{PBDEs}$ varied about three orders of magnitude from 0.2 to 81 ng/sample. As a result of the high production and consumption of Deca-BDEs in China, BDE-209 is the dominant congener in most samples, followed by BDE-47, BDE-99 and BDE-28. For NBFRs, PBBZ, PBT and PBEB were frequently detected (detection rate $> 80\%$), while DBDPE was only detected in 11% of the samples. The concentrations of $\Sigma_{12}\text{PBDEs}$ were generally higher than those of $\Sigma_6\text{NBFRs}$, with the median level of $\Sigma_{12}\text{PBDEs}$ being 5 times higher

Download English Version:

<https://daneshyari.com/en/article/6337733>

Download Persian Version:

<https://daneshyari.com/article/6337733>

[Daneshyari.com](https://daneshyari.com)