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Five-year trends of selected halogenated flame retardants in the atmosphere of Northeast China

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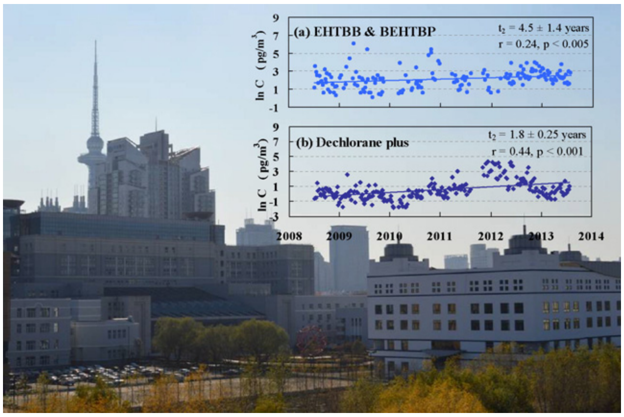
HIGHLIGHTS

- Five-year air samples were analyzed for four alternative HFRs.
- BEHTBP and DP were frequently detected in the particle phase.
- Local and nearby city sources of these HFRs were suggested.
- Concentrations of these HFRs were significantly increased in the five-year period.

GRAPHICAL ABSTRACT



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ABSTRACT

This study collected 227 pairs of gas phase and particle phase air samples in a typical urban city of Northeast China from 2008 to 2013. Four alternative halogenated flame retardants for polybrominated diphenyl ethers (PBDEs) were analyzed, namely 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EHTBB), bis (2-ethylhexyl) tetrabromophthalate (BEHTBP), syn-dechlorane plus (syn-DP) and anti-dechlorane plus (anti-DP). The average concentrations for EHTBB and BEHTBP were 5.2 ± 20 and 30 ± 200 pg/m^3, respectively, while for syn-DP and anti-DP were 1.9 ± 5.1 and 5.8 ± 18 pg/m^3, respectively. Generally, they were frequently detected in the particle phase, and the gas/particle partitioning suggested they were the maximum partition chemicals. The fractional abundance of EHTBB (f_{EHTBB}) and syn-DP (f_{syn}) were comparable with those in other studies. Strong local sources were identified based on the air parcel backward trajectories and the potential source contribution function. The concentrations of these chemicals were significantly increased during this sampling campaign, possibly suggesting their increasing usages from 2008 to 2013 in China.

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1. Introduction

Halogenated flame retardants (HFRs) are added to consumer products such as electronic circuitry, textiles, polyurethane foam, thermoplastics, construction materials and other products, to prevent and/or slow the spread of fire (Cequier et al., 2013). In the past 50 years, the use of HFRs in consumer products and electronics has increased exponentially (Kolic et al., 2009), and hundreds of compounds have been developed for the use as flame retardants (International Programme on Chemical Safety). Brominated flame retardants (BFRs) and chlorinated flame retardants (CFRs) accounted for 39% and 23% of the total amounts of flame retardants produced in 1997, respectively (Kolic et al., 2009). The total world production volume of BFRs was estimated at around 150,000 tonnes/year in 1992 (de Wit, 2002), which increased to more than 200,000 tonnes/year in 2007 (Bergman et al., 2012). The estimated consumption of three commercial polybrominated diphenyl ethers (PBDEs) mixtures, i.e. Penta-BDE, Octa-BDE and Deca-BDE, from 1970 to 2020 in in-use products were approximately 46,000, 25,000 and 380,000 tonnes, respectively (Abbasi et al., 2015).

Due to their lipophilic, toxic and persistent properties, PBDEs and some other HFRs have been considered as a risk to human and environmental health, and were partially banned by Stockholm Convention (UNEP, 2009). As a signatory to the Stockholm Convention, China had officially banned the usage of commercial Penta-BDEs and Octa-BDEs since 2006 (Zhang et al., 2009), and their atmospheric concentrations were decreased from 2005 to 2010 (Li et al., 2015a). However, several new or unregulated HFRs are still used as alternative flame retardants. For instance, three commercial products called DP-45, Firemaster 550, and Firemaster BZ-54 are used to replace commercial PBDE mixtures (Covaci et al., 2011). The major constituent of these three products are 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EHTBB) and bis (2-ethylhexyl) tetrabromophthalate (BEHTBP). It was demonstrated that these two chemicals have endocrine disrupting potentials (Saunders et al., 2013). BEHTBP can be metabolized by porcine esterases to a potentially toxic metabolite and thus cause rodent thyroid, liver, and fetal testis toxicity in a rat model study (Springer et al., 2012).

The levels of EHTBB and BEHTBP were increasing rapidly with the doubling time of 0.86–3.2 years in the Great Lakes atmosphere during 2008–2010 (Ma et al., 2012a). More recently, these chemicals were frequently detected in the indoor dust (Qi et al., 2014b) and sediment samples (Liu et al., 2014) in China, and in the house dust in Germany (Fromme et al., 2014), Egypt (Hassan and Shoeib, 2015) and USA (Johnson et al., 2013). The detection frequencies of these two compounds in paired human maternal serum and breast milk in nursing women from Québec, Canada were higher than that of decabromodiphenyl ethane (Zhou et al., 2014), another replacement of PBDEs. In atmospheric particles from a European Arctic site, the levels of EHTBB and BEHTBP contributed to ~46% and 17% of Σ_{45}BFRs concentration, respectively (Salamova et al., 2014). According to the results of these studies, it can be concluded these two compounds have been widely used in the world.

Another alternative to commercial DecaBDE mixtures is dechlorane plus (DP) (The European Commission report on potential alternatives to deca-BDE), a highly chlorinated flame retardant. DP has two isomers called syn-DP and anti-DP. They are used in cable coating, plastic roofing material, computer monitors and furniture (Betts et al., 2006; Sverko et al., 2011). Biological effect and the hepatic alkoxyresorufin O-dealkylase activity in quail exposure to DP were revealed in a recent study (Li et al., 2013). In China, DP has been frequently detected in air (Ren et al., 2008), soil (Ma et al., 2014, 2011), river water and sediment (Qi et al., 2010), indoor dust (Li et al., 2015b), and coastal environmental samples (Jia et al., 2011).

Due to the lack of long-term monitoring program, the temporal trend of these chemicals was still unclear in China. To accomplish this goal, weekly air samples were collected during 2008 and 2013 in a typical urban city in Northeast China. The main objectives were to measure concentrations of the four alternatives in the air samples, and to assess the temporal trend of these chemicals during the period.

2. Material and methods

2.1. Sample collection, preparation and analysis

All solvents used were of pesticide grade purity (J.T. Baker, USA). Silica gel (100–200 mesh) was purchased from Merck (Merck, Germany). Four target chemicals, namely syn-dechlorane plus (syn-DP), anti-dechlorane plus (anti-DP), 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EHTBB) and bis (2-ethylhexyl) tetrabromophthalate (BEHTBP) were acquired from Wellington Laboratories (Guelph, Canada). Chlorinated biphenyl 155 (CB-155) and Octachloronaphthalene (OCN) were purchased from AccuStandard Inc. (New Haven, CT, USA). $^{13}C_{10}$-syn-DP and $^{13}C_{10}$-anti-DP were purchased from Cambridge Isotope Laboratories Inc. (Massachusetts, USA).

A total of 227 pairs of gas and particle phases air samples were collected weekly from July 2008 to July 2013 on a roof top of a building in Harbin, the capital city in Heilongjiang Province, China (Fig. S1). The detail of sampling and pretreatment can be found in our previous study (Qi et al., 2014a; Yang et al., 2013). Briefly, gas and particle phases were collected using a high volume air sampler (KB-1000, Kingstar Electronic Technology Co., Ltd. Qiangdao) for 24 h. Polyurethane foam (PUF) plugs and glass fiber filters (GFFs) were used to collect gas and particle phases samples, respectively. In order to remove any organic contaminant, the PUF plugs were Soxhlet extracted for 24 h with acetone and for another 24 h with hexane, and GFFs were baked at 450 °C for 7 h. After sampling, the PUF plugs and GFFs were stored at −20 °C until extraction.

After being spiked with a mixed surrogate standard containing CB-155, $^{13}C_{10}$-syn-DP and $^{13}C_{10}$-anti-DP, the GFFs and PUF plugs were Soxhlet extracted for 24 h with dichloromethane and acetone: hexane (1:1, v/v), respectively. Extracts were purified with silica gel columns (0.40 m length × 10 mm i.d.) filled with 7.0 g of active silica gel. The extract was eluted with 70 mL of n-hexane:dichloromethane (1:1, v/v). The elution was concentrated by a rotary evaporator, then gently blown down to 0.8 mL with purified nitrogen (99.999%) and solvent exchanged into iso-octane. Then the internal standard with 250 ng of OCN was added before the final volume was adjusted to 1.0 mL.

The target chemicals were analyzed by Agilent 6890 series GC coupled to 5975 MS under negative ion chemical ionization conditions. Chromatographic resolution was achieved with a DB-5 MS capillary chromatographic column (15 m × 0.25 mm × 0.10 μm, J&W Scientific). The flow rate of carrier gas (helium) was set at a constant of 1.7 mL/min. Two microliter samples were injected in the splitless mode. The temperature of injection port was 250 °C. The following GC oven temperature program was used: 110 °C for 0.5 min, 5.0 °C/min to 220 °C, 20 °C/min to 310 °C, and hold for 5.0 min. The transfer line temperature was maintained at 280 °C. For the mass spectrometer, the ion source and quadrupole temperatures were both set at 150 °C. Target chemicals were analyzed with the following ions (m/z): 356.7/79/81 for EHTBB, 383.7/79/81 for BEHTBP; 653.7/651.7/649.7 for syn-DP and anti-DP.

2.2. Quality control and data analysis

Field blanks were taken seasonally during the sampling campaign. One method blank and one method spike were pretreated along with 10 samples. The mean recoveries of CB-155, $^{13}C_{10}$-syn-DP and $^{13}C_{10}$-anti-DP in the samples were 86% ± 12%, 82% ± 18% and 83% ± 19%, respectively. The mean recoveries of the target chemicals were 85 ± 13% in the method spikes. Concentrations of syn-DP and anti-DP were corrected for the recoveries of $^{13}C_{10}$-syn-DP and $^{13}C_{10}$-anti-DP, respectively, and the recoveries of CB-155 were