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Levels, distribution and human exposure of new non-BDE brominated flame retardants in the indoor dust of China

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ABSTRACT

Indoor environment is an important source of human exposure to several toxicants, such as brominated flame retardants. This study presents the concentrations of 22 Non-BDE brominated flame retardants (NBFRs) in 81 indoor dust samples from 23 provinces across China in the winter of 2010. The concentrations of ΣNBFRs ranged from 6.3 to 20,000 ng/g, with a median concentration of 720 ng/g. DBDPE was the dominated compound, followed by HBCD and BEHTBP. Significant differences of concentrations were found between samples from rural and urban areas, and between family and public houses, indicating different applications of NBFRs. The geographical distribution of NBFRs highlighted several hotspots in North China, suggesting the influence of room temperature (heating). The exposure via dust ingestion of NBFRs was 3.8–14 times higher than that of dermal absorption. The toddlers demonstrated the highest exposure dose (9.6 ng/kg-bw/day) of NBFRs through indoor dust among all life stages.

1. Introduction

Brominated flame retardants (BFRs) were added to consumer products to slow the spread of fire in items such as electronic circuitry, furniture, textiles, polyurethane foam, thermoplastics, construction materials and other products (Covaci et al., 2011). Polybrominated diphenyl ethers (PBDEs) were formerly one of the most common BFRs in daily life. Due to mounting environmental concerns, worldwide commercial production of Penta-BDE and Octa-BDE was phased-out between 2004 and 2010, and Deca-BDE is now phased-out in Canada and the United States since 2013 (Gentes et al., 2012). New and alternative brominated flame retardants (NBFRs) have been produced and used as PBDE replacements. For example, Firemaster 550, 1, 2-Bis (2, 4, 6-tribromophenoxy)-ethane (BTBPE) and Decabromodiphenylethane (DBDPE) were used as replacements for Penta-BDE, Octa-BDE and Deca-BDE (Hoh and Hites, 2005; Hu et al., 2010; Ma et al., 2011b). These flame retardants were reported as “new” non-BDE flame retardants in the global atmosphere under the global atmospheric passive sampling (GAPS) network (Lee et al., 2010). The production and application for these NBFRs has been increasing due to the enhanced market demand. Recently, NBFRs have been drawing considerable attention due to frequent detection in the environment (Ma et al., 2011a, 2011b; Shoeib et al., 2012).

Human spend more than 80% of the day in indoor environment (Johnson-Restrepo and Kannan, 2009; Mitra and Ray, 1995); thus, the quality of indoor environment is important to human health. Indoor dust exposures via ingestion and inhalation have been reported to be the major human exposure pathways to BFRs along with dietary exposure (Allen et al., 2007). For example, in North America, dust exposures accounted for 82% of the overall total estimated intake of PBDEs (Lorber, 2007). Ingestion of inadvertent house dust was the main pathway for human exposure to PBDEs for all life stages except for infants in the USA (Jones-Otazo et al., 2005).

Elevated concentrations of NBFRs were found in indoor dust worldwide (Ali et al., 2011; Shoeib et al., 2012; Wang et al., 2010). However, limited information on NBFRs was reported regarding indoor dust in China. In this study, 22 NBFRs were analyzed in the indoor dust samples collected across China in the winter of 2010. The objectives of this study are: to investigate the pollution levels and spatial distributions of NBFRs, and to assess the human exposure to NBFRs for general population in China.

2. Material and methods

2.1. Sampling

A total of 81 indoor dust samples, including 45 domestic (family) samples and 36 public samples, were collected in 23 provinces across China in the winter of 2010.

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The spatial distribution of the 81 indoor dust sampling sites can be found in Fig. S1 in Supporting Information (SI). For the family houses, dust was collected in living rooms, bedrooms, and kitchens. For the public houses, dust was collected in libraries, offices, classrooms, supermarkets, and laboratories. The dust samples were collected by trained volunteers using pre-cleaned brushes and stored using aluminum foil. Dust samples were collected by sweeping the floor with brushes under desks, shelves and beds, avoiding the influences of resident activities and sunlight. For family houses, dust sample was combination of dust from living rooms, kitchens, and bedrooms for obtaining one representative sample. Among the 81 samples, 55 can be considered as urban samples and 26 as rural samples base on their locations. Therefore, all the samples can be divided into 4 types: urban public, urban family, rural public and rural family. Corresponding information, such as room temperature, locations, house construction information, cooking habits, floor coverings, types of heating, furniture, presence of smoke, distance to main roads and nearby factories, was recorded during sampling. The dust samples were stored at −20 °C before further treatment.

2.2. Standards

Three mixing NBFR standards (FRMIX-A, FRMIX-B, FRMIX-C) were obtained from Wellington Laboratories Inc. (Guelph ON, Canada). FRMIX-A includes the following compounds: ATE (Allyl 2,4,6-tribromophenyl ether), p-TBX (2,3,5,6-Tetrabromo-p-xylene), BATE (2-Bromoallyl 2,4,6-tribromophenyl ether), PBBZ (1,2,3,4,5-Pentabromobenzene), TBCT (Tetrabromo-o-chlorotoluene), PBT (Pentabromotoluene), PBEB (Petabromoethylbenzene), DPTE (2,3-Dibromopropyl 2,4,6-tribromophenyl ether), HBBZ (Hexabromobenzene), TBEP (Tris (2-butoxyethyl) phosphate). FRMIX-B includes the following compounds: PBBA (Pentabromobenzyl acrylate), EHTBB (2-Ethylhexyl 2,3,4,5-tetrabromobenzoate), BEHTBP (Bis (2-ethylhexyl) tetrabromophthalate), OBIND (Octabromotrimethylphenylindane), DBDPE (Decabromodiphenylethane). FRMIX-C includes the following compounds: α,β-TBECH (α,β-Tetrabromoethylcyclohexane), α,β-TBCO (α,β-1,2,5,6-Tetrabromocyclooctane), HCDBCO (Hexachlorocyclopentenyl-dibromocyclooctane), T23BPIC (Tris (2,3-dibromopropyl) isocyanurate). Two other mixing standards, γ-HBCD (γ-l,2,5,6,9,10-Hexabromocyclododecan) and (BTBPE) (1,2-Bis(2,4,6-tribromophenoxy) -ethane), were provided by the National Water Research Institute of Environment Canada. Chlorinated biphenyl 155 (CB 155) and BDE 71 were used as recovery standard (surrogate) and internal standard, respectively; both were purchased from AccuStandard Inc. (New Haven, CT, USA).

2.3. Treatment

The method for the treatment of dust sample can be found in our previous study (Qi et al., 2014). Briefly, 0.2 g dust samples were transferred to a 10 mL glass centrifuge tube. After being spiked with a known amount of recovery standard (CB 155), dust samples were ultrasonically extracted with 10 mL of n-hexane/acetone (1:1, v/v, J.T. Baker, USA) for 20 min. The solvent mixture was centrifuged and the supernatant was transferred into a new glass tube. The extraction step was repeated three times. The extraction solvent was combined together and concentrated to 2 mL. Then the extracts were cleaned-up in a glass column (0.4 m length, 10 mm i.d.) with 7 g of active silica gel covered with 2 g of anhydrous sodium sulfate. The target compounds were eluted with 70 mL of n-hexane/dichloromethane (1:1, v/v). Then the eluate was concentrated to 0.8 mL by soft nitrogen gas flow and the internal standard (BDE 71) was added. Finally, the volume was adjusted to 1.0 mL in isooctane for analysis.

2.4. Analysis

All NBFRs were analyzed by Agilent 6890-5975B gas chromatography–mass spectrometry (GC–MS) in electron capture negative ionization mode using a DB-5MS capillary column (15 m × 0.25 μm × 0.10 μm film thickness, J&W Scientific, USA). The oven temperature program was: 110 °C for 0.5 min, 5 °C/min to 220 °C, 20 °C/min to 310 °C, and held for 15 min. 2 μL extracts were injected in splitless mode at an injector temperature of 250 °C. Selected ion monitoring (SIM) mode was used for MS. The selected ions (m/z) were as follows: 290.8/79/81 for ATE, 159.9/79/81 for TBECH, TBCO and BATE, 441.6/79/81 for TBCT, 485.6/79/81 for PBT, 159.7/79/81 for DPTE, 551.5/79/81 for HBBZ, 71/79/81 for PBBA, 236.8/79/81 for HCDBCO, 356.7/79/81 for EHTBB, and 383.7/79/81 for BEHTBP, 647.7/79/81 for T23BPIC. The ions at m/z of 79 and 81 were used for other target compounds.

2.5. Quality assurance and quality control

One method blank sample and one standard spiked blank sample (with anhydrous sodium sulfate) were included with every 10 real samples. Only PBT can be detected in the method blanks with levels less than 5% of those in real dust samples. The recovery of CB 155 (recovery standard) was in the range of 70%–130% (mean: 89.2%). The recoveries of NBFRs in the spiked blank samples ranged from 65% to 114%. The reported concentrations in this study were not blank and recovery corrected. The instrument detection limitation (IDL) was set as the standard concentration, which had the instrument response with a signal-to-noise of 3:1. The method detection limitation (MDL) was estimated as 3.3 times of the IDL. In this study, the final volume of extraction was set to 1.0 mL; therefore, the MDLs were calculated by dividing by the dust amount of 0.2 g for unit transfer. All the MDLs are listed in Table 1.

2.6. Data analysis

For statistical analysis, the concentrations in real samples below MDLs were replaced with half of MDL. The Nonparametric Mann–Whitney *U* Test and Spearman correlation were applied to test differences and correlations between two sets of data. Results were considered statistically significant if the *p*-value was less than 0.05 for correlation analysis. The Kruskal–Wallis Test was applied to test differences with more than two groups of variables. All the statistical analysis was performed using SPSS Software (Version 22).

In order to study the potential sources of EHTBB and BEHTBP, the fractional abundance of EHTBB in dust samples was compared with values from commercial products. The fractional abundance of EHTBB was calculated with the following equation (Ma et al., 2011b),

$$f_{EHTBB} = \frac{[\mathrm{EHTBB}]}{[\mathrm{EHTBB}] + [\mathrm{BEHTBP}]}$$

where, [EHTBB] and [BEHTBP] are the concentrations in dust samples. When calculating f_{EHTBB}, data points were excluded if only one compound was detected.

3. Results and discussion

3.1. Concentrations of NBFRs

Our results indicated that ATE, α-TBECH, β-TBECH, BATE, α-TBCO and T23BPIC were not detected (with concentration lower than MDL) in any of the dust samples. β-TBCO, TBCT, p-TBX, PBBA, HCDBCO and OBIND were found in less than 10% of the 81 samples. The low detection rate of those compounds in indoor dust indicated their less usage in China. Other 10 compounds (PBBZ, PBT, PBEB, DPTE, HBBZ, EHTBB, HBCD, BTBPE, BEHTBP, and DBDPE) were detected with higher detection rates (>33%), the statistical descriptions of which are presented in Table 1. The concentrations of ΣNBFRs ranged from 7.3 to 20,000 ng/g, with a median concentration of 720 ng/g in the indoor dust samples in China. In the following sections, only these 10 compounds are discussed.

3.1.1. DBDPE

As a highly brominated flame retardant, DBDPE has been produced as an alternative to BDE 209, with a production capacity of approximately 11,000 tons in China in 2006 (Hu et al., 2010). DBDPE was the dominant compound (with a median concentration of 280 ng/g), which contributed to 50% of the total concentration of NBFRs (Table 1). The results indicated that a large amount of DBDPE had been used and/or released in China. The highest concentration (16,000 ng/g) was found in a family dust sample, followed by 13,000 ng/g in a mushroom factory, 9500 ng/g in a dormitory, 7000 ng/g in an office, 6200 ng/g in a bank, and 5300 ng/g in an office. All of these sampling sites were classified as urban sites, and most of them were located in North and Northeast China.

3.1.2. HBCD

HBCDs have been widely used as additive brominated flame retardants in extruded and high-impact polystyrene foams for thermal insulation of buildings and the upholstery textiles, and in a lesser extent in enclosures for electronic equipment (Alaee et al., 2003; Covaci et al., 2011). The occurrence of HBCDs had been reported in both abiotic and biotic environment (Covaci et al., 2006; Morris et al., 2004; Shoeib et al., 2012; Stapleton et al., 2008); furthermore, studies have pointed significantly increasing concentration of HBCD in guillemot eggs and the sea lions during the observed time period (Covaci et al., 2006). In this study, HBCD was the second dominant compound with a median concentration of 120 ng/g (Table 1), contributing to 31% of the total concentration of NBFRs. The concentration of HBCD in indoor dust samples in China was about 2 times lower than that in the house dust of Canada