Science of the Total Environment 618 (2018) 48–59

Contents lists available at ScienceDirect

Science of the Total Environment

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

Legacy and novel brominated flame retardants in indoor dust from Beijing, China: Occurrence, human exposure assessment and evidence for PBDEs replacement

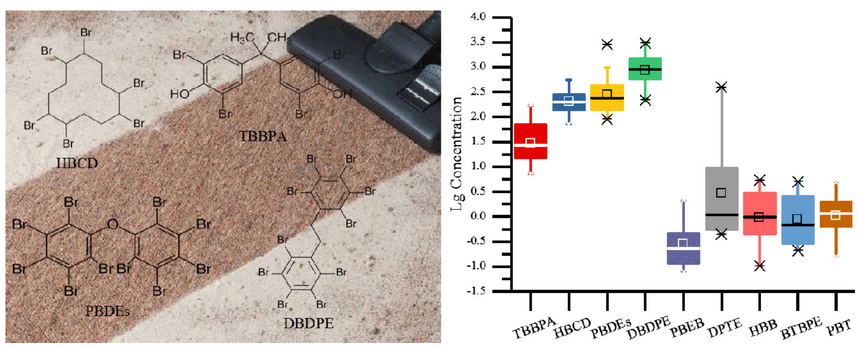
Jiandi Wang [a,b,1], Yuwei Wang [b,1], Zhixiong Shi [b,*], Xianqing Zhou [b], Zhiwei Sun [b]

[a] Shunyi Women and Children's Hospital of Beijing Children's Hospital, Capital Medical University, Beijing 110113, China
[b] School of Public Health and Beijing Key Laboratory of Environmental Toxicology, Capital Medical University, Beijing 100069, China

HIGHLIGHTS

- BFRs were measured in house dust and office dust collected from Beijing, China.
- Levels of DBDPE were higher than those of any other BFRs in this study.
- The consumption pattern of BFRs in China may have shifted from PBDEs to non-PBDE BFRs.
- The daily intake of BFRs is unlikely to raise significant health concerns.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 August 2017
Received in revised form 14 October 2017
Accepted 4 November 2017
Available online xxxx

Editor: Adrian Covaci

Keywords:
Brominated flame retardants
Decabrominated diphenyl ether
Polybrominated diphenyl ethers
Indoor dust
Exposure assessment

ABSTRACT

Levels of legacy brominated flame retardants (BFRs), including tetrabromobisphenol A (TBBPA), hexabromocyclododecane isomers (HBCDs) and polybrominated diphenyl ethers (PBDEs), and six currently used novel BFRs were determined in house dust and office dust collected from a community in Beijing, China. This is the first study where the three kinds of legacy BFRs and novel BFRs were all measured in dust samples from China. HPLC-MS/MS was used for the detection of TBBPA and HBCDs, and the other BFRs were tested on a GC-NCI/MS. Decabromodiphenyl ethane (DBDPE), PBDEs, HBCD and TBBPA were found to be the main BFRs in the dust samples, with median levels of 709, 241, 199 and 26.7 ng/g dust, respectively. Due to the high density of electronic equipment used in offices, levels of BFRs in office dust were found to be higher than those in house dust. DBDPE, as a replacement of PBDEs, was the predominant BFR, and the median level of DBDPE was not only several orders of magnitude higher than that of other novel BFRs but also 3 to 27 times higher than that of the three legacy BFRs, indicating that the consumption pattern of BFRs in the Chinese market has shifted from PBDEs to PBDE alternatives. Median estimated daily intakes (EDIs) of BFRs through dust ingestion for adults (>20 years) and toddlers (<2 years) were in the range of 2.8×10^{-5}–0.201 ng/kg body weight (bw)/day and 5.7×10^{-4}–2.52 ng/kg bw/day, respectively. The body burden of BFRs for toddlers was far higher than that for adults; however, a comparison between EDIs and threshold values suggested that daily intakes of BFRs for both adults and toddlers were unlikely to raise significant health concerns.

* Corresponding author.
E-mail address: szx0127@ccmu.edu.cn (Z. Shi).

[1] Jiandi Wang and Yuwei Wang contributed equally to this work.

https://doi.org/10.1016/j.scitotenv.2017.11.049
0048-9697/

1. Introduction

Brominated flame retardants (BFRs) are a series of chemicals designed to inhibit or reduce the propagation of fire. BFRs have been widely used in electrical devices and electronics, foams, padding materials, building materials and other products. BFRs are mainly produced and consumed in China, known as "The World's Factory" (Yu et al., 2016). Additionally, e-waste used for recycling from developed countries such as the United States, has increased BFR detection and concentration in China (UNU, 2015). BFRs with various physical and chemical properties are produced and used in the Chinese market. Tetrabromobisphenol-A (TBBPA), hexabromocyclododecane (HBCD) and polybrominated diphenyl ethers (PBDEs) are the three kinds of BFRs mainly used in China in the past forty years, and they are described as "legacy BFRs" (Covaci et al., 2011; Yu et al., 2016). TBBPA is used as a reactive BFR, and in a few cases, it is also used as an additive BFR. Since the European Union reported in 2006 that the use of TBBPA is unlikely to raise health risks, the production and application of TBBPA jumped sharply (EU, 2006). However, a recent study based on a rat model suggested that TBBPA should be classified as an endocrine disruptor to mammals (Dunnick et al., 2017). PBDEs and HBCD are both additive BFRs and can therefore leach or volatilize from products, resulting in environmental contamination and potential health risks such as neurodevelopmental effects. There are three types of commercial PBDEs: penta-BDE, octa-BDE and deca-BDE. Penta-BDE and octa-BDE were added to the list of POPs under the Stockholm Convention in 2009. According to the announcement of the Ministry of Environmental Protection of China, the production, import and use of penta-BDE and octa-BDE have been phased out in China since 2014 without special immunity (China MEP, 2014), whereas the production and application of deca-BDE (mainly composed of BDE-209) continues in China, although deca-BDE was also listed as a POP in 2017 (Stockholm Convention, 2017). HBCD was listed as a POP in 2013, and its use has been reduced in China since 2016; however, the application of HBCD in special building materials, extruded polystyrene (XPS) and expanded polystyrene (EPS), is still permitted in China (China MEP, 2016). Hence, the production and application of HBCD also continues in China. Due to the regulation of legacy BFRs, the production and usage of "novel" BFRs (NBFRs) increased sharply in Asia (Covaci et al., 2011). Decabromodiphenyl ethane (DBDPE), as a replacement for deca-BDE, has been produced only since 2005 in China; however, the production of DBDPE increases 80% per year (Covaci et al., 2011). The production volume of DBDPE, with 25,000 t in 2012, may have exceeded that of PBDEs and other NBFRs, indicating that DBDPE has become the most popular NBFR in China (Zhang and Gu, 2013; Zhang and Lu, 2011). For other NBFRs, BTBPE, as a replacement for octa-BDE, has been used in ABS, HIPS, thermoplastics, etc. since the 1970s. The worldwide production/usage of BTBPE was estimated to be 16,710 tons in 2001 (Ren et al., 2017); 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) is less frequently studied but also currently used as a BFR (Vetter et al., 2017). Pentabromotoluene (PBT), pentabromoethylbenzene (PBEB) and hexabromobenzene (HBB) belong to polybromobenzenes that have one phenyl ring with several bromine atom substituents. PBT is used mostly in unsaturated polyesters with a production volume estimated between 1000 and 5000 tons per year. PBEB is an additive FR mainly used in thermoset polyester resins, and HBB was primarily used in Japan and China as an additive FR to paper and woods. Polybromobenzenes are currently produced and used but at lower volumes; however, polybromobenzenes have higher vapor pressures than PBDEs and DBDPE, and thus, they are more likely to evaporate and enter into the surrounding environment (Covaci et al., 2011; Li et al., 2015). Due to long-term and wide use, BFRs have been found to be ubiquitous in various environmental matrices such as sediment, soil, air, indoor dust, foods and human milk (Fromme et al., 2016; Yu et al., 2016). Thus, the general population could be exposed to BFRs by various routes, including dust ingestion, air inhalation, and food consumption. Indoor dust ingestion was found to be the primary exposure pathway in some studies; for example, in a Swedish study, the daily intake of deca-BDE by Swedish mothers via dust ingestion was found to be three times higher than intake via food consumption (Sahlstrom et al., 2015).

Indoor dust ingestion is thought to be one of the primary pathways for human exposure to various organic contaminants and risk posed to human health by indoor contaminants (Fromme et al., 2016). The objective of this study is to measure all the legacy BFRs and some novel BFRs in house dust and office dust samples collected from a community in Beijing, China. This is the first study where the three kinds of legacy BFRs and novel BFRs were all measured in dust samples from China. On the basis of the concentration of BFRs in dust, the daily intakes of the measured BFRs via dust ingestion were calculated for risk assessment, and a comparison between EDI via dust ingestion and EDI via food consumption, which was calculated in our previous study, is presented. In addition, a comparison between the contamination levels of the legacy and novel BFRs is also presented.

2. Materials and methods

2.1. Sample collection

Dust samples ($n = 57$) were collected from 30 houses and 27 offices in a community in Beijing, China. The community (39°81′ N, 116°40′ E) is representative of the residential and work areas in Beijing without specific BFR point sources nearby. House and office dust samples were collected between June to August in 2014 in residential buildings and office buildings located in this community. The average temperature of Beijing in June to August in 2014 was 26.5 °C. Indoor dust samples were collected following the standardized protocol described by (Ali et al., 2011). In offices (including meeting room), 5–8 m^2 bare floor was sampled for 2 min. In houses, 10–15 m^2 bare floor was vacuumed for 5 min (carpet is rarely used in China), a combined dust sample per house was collected from living room, bedroom, kitchen and study. The collection was performed using nylon sock fitted within the nozzle of the vacuum cleaner. After the sampling, all the socks were closed and packed with aluminum foil and zipped plastic bags. Of course, the sampling instruments would be cleaned thoroughly by water and a hexane-impregnated disposable wipe before and after sampling different rooms. Each sample was sieved through a pre-cleaned 500 μm mesh and stored at −18 °C until analysis. During collection time, the presence and type of electronic products (including computer, printer, TV, air conditioner, and refrigerator) that might have been treated with flame retardants were recorded by questionnaires in each sampling site, the questionnaires showed that the average number of electronic devices (TV, computer, air conditioner, etc.) recorded from the sampling houses was 4.5 per house, whereas offices contained a higher density of electronic equipment (average 9.3 per office), detail information of electronic equipment recorded by questionnaires has been listed in Supplementary Table S1.

2.2. Analysis of dust

2.2.1. Reagents and chemicals

All solvents used were of HPLC grade from Merck (Darmstadt, Germany). Reagent-grade sulfuric acid was obtained from Tianjin Fuchen Chemical Factory (Tianjin, China). The individual PBDE standards, including BDE 28, 47, 77, 99, 100, 128,153, 154, 183, and 209, were purchased from AccuStandard Inc. (New Haven, CT, USA). The individual NBFRs standards, including DBDPE, DPTE, PBT, HBB, PBEB and BTBPE, were also from AccuStandard Inc. The standard solutions of α- , β- and γ-HBCD and TBBPA as well as isotopic internal standards of $^{13}C_{12}$-labeled α- , β- and γ-HBCD, $^{13}C_{12}$-labeled TBBPA and $^{13}C_{12}$-labeled BDE-209 were obtained from Wellington Laboratories (Guelph, Ontario, Canada). Indoor dust reference material SRM 2585 was