Environmental Research 162 (2018) 166–172

Contents lists available at ScienceDirect

Environmental Research

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

Impact of particle size on distribution and human exposure of flame retardants in indoor dust

Rui-Wen He[a], Yun-Zi Li[a], Ping Xiang[a], Chao Li[a], Xin-Yi Cui[a,*], Lena Q Ma[a,b,*]

[a] State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210046, People's Republic of China
[b] Soil and Water Science Department, University of Florida, Gainesville, FL 32611, United States

ARTICLE INFO

Keywords:
Flame retardants
Dust particle size
Bioaccessibility
Human exposure

ABSTRACT

The effect of dust particle size on the distribution and bioaccessibility of flame retardants (FRs) in indoor dust remains unclear. In this study, we analyzed 20 FRs (including 6 organophosphate flame retardants (OPFRs), 8 polybrominated diphenyl ethers (PBDEs), 4 novel brominated flame retardants (NBFRs), and 2 dechlorane plus (DPs)) in composite dust samples from offices, public microenvironments (PME), and cars in Nanjing, China. Each composite sample (one per microenvironment) was separated into 6 size fractions (F1–F6: 200–2000 μm, 150–200 μm, 100–150 μm, 63–100 μm, 43–63 μm, and < 43 μm). FRs concentrations were the highest in car dust, being 16 and 6 times higher than those in offices and PME. The distribution of FRs in different size fractions was Kow-dependent and affected by surface area (Log Kow = 1–4), total organic carbon (Log Kow = 4–9), and FR migration pathways into dust (Log Kow > 9). Bioaccessibility of FRs was measured by the physiologically-based extraction test, with OPFR bioaccessibility being 1.8–82% while bioaccessible PBDEs, NBFRs, and DPs were under detection limits due to their high hydrophobicity. The OPFR bioaccessibility in 200–2000 μm fraction was significantly higher than that of < 43 μm fraction, but with no difference among the other four fractions. Risk assessment was performed for the most abundant OPFR-tris(2-chloroethyl) phosphate. The average daily dose (ADD) values were the highest for the < 43 μm fraction for all three types of dust using total concentrations, but no consistent trend was found among the three types of dust if based on bioaccessible concentrations. Our results indicated that dust size impacted human exposure estimation of FRs due to their variability in distribution and bioaccessibility among different fractions. For future risk assessment, size selection for dust sampling should be standardized and bioaccessibility of FRs should not be overlooked.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been widely applied as flame retardants (FRs) in furniture, upholstery materials, and polymer resins (Brandsma et al., 2013; van der Veen and de Boer, 2012). Due to their health concerns, their use has been banned worldwide recently (Shaw et al., 2010). However, being persistent organic pollutants (POPs), PBDEs can be ubiquitously detected even after being banned for decades. On the other hand, the phase-out of PBDEs is concurrent with increasing use of alternative FRs. The common alternatives include organophosphate flame retardants (OPFRs), novel brominated flame retardants (NBFRs), and dechlorane Plus (DPs) (Stapleton et al., 2012).

Flame retardants can be released into the environment by abrasion or volatilization, leading to their accumulation in indoor dust (Abdallah and Covaci, 2014; van der Veen and de Boer, 2012). Growing evidence showed that indoor dust plays a significant role in human exposure to FRs (Mercier et al., 2011). As a complex mixture with particles from multiple sources, dust particle size varies from nanometer to millimeter level (Butte and Heinzow, 2002). Some studies reported that the concentrations of organic contaminants were related to particle size but with inconsistent conclusion (Lewis et al., 1999; Yu et al., 2013). For example, phthalate esters were mainly present in dust with particle size of 63–2000 μm (Wang et al., 2013a). On the other hand, Cao et al. (2014a) found that finer particles (~7 μm) showed no enrichment of PBDEs and NBFRs compared with larger particles. In addition, contaminant distribution among different particle size fractions is important for risk assessment since human exposure to contaminants in indoor dust is affected by particle size. For example, particles < 246 μm usually adhere to children's hands, and are therefore more likely to be ingested, while particles < 100–200 μm are retained by skin (Mercier et al., 2011), which may pose health threat through dermal uptake. However, studies regarding the distributions of FRs in different particle size fractions in dust are still poorly understood.

* Corresponding author.
E-mail addresses: lizzycui@nju.edu.cn (X.-Y. Cui), lqma@ufl.edu (L.Q. Ma).

https://doi.org/10.1016/j.envres.2017.12.014
Received 8 September 2017; Received in revised form 21 November 2017; Accepted 15 December 2017

Another critical issue in risk assessment is bioaccessibility because contaminants are not necessarily all available for uptake after oral ingestion (Rostami and Juhasz, 2011). In recent decades, some physiologically-based in vitro methods have been used to measure the bioaccessibility of organic contaminants in dust, such as PAHs, OCPs, and PBDEs (Kang et al., 2012; Yu et al., 2012). However, information about the bioaccessibility of novel flame retardants including NBFRs, OPFRs, and DPs is still rare. Their bioaccessibility in dust may also depend on particle size (USEPA, 1995), and has been investigated for some organic contaminants (e.g., PCBs; Wang et al., 2013b). To our knowledge, no information is available about the effect of particle size on FR bioaccessibility in dust so far.

To better estimate the potential risks associated with human exposure to FRs in dust, it is important to understand the impact of dust particle size on their distribution and bioaccessibility. To this end, the objectives of this study were to: (1) determine the distribution of FRs among particle size fractions in different indoor dust; and (2) investigate the effect of particle size on the bioaccessibility of FRs via physiologically-based extraction test (PBET); and (3) to estimate the oral exposure risk of FRs among different particle size fractions based on both total and bioaccessible concentrations.

2. Materials and methods

2.1. Chemicals and reagents

A total of 20 flame retardants were investigated, including 6 OPFRs (TCEP, TCPP, TDCPP, TBP, TPP, and EHDPP), 4 NBFRs (HBB, TBB, TBPH, and DBDPE), 8 PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209), and 2 DPs (syn-DP and anti-DP). The full name and detailed properties of all FRs are listed in supporting information as Table S1. Standard chemicals were purchased from Aladdin Industrial Corporation (Shanghai, China) and J&K Scientific (Shanghai, China) with purity > 98%. All solvents and chemicals were of HPLC or analytical grade. Stock solutions were prepared in n-hexane at concentrations of 100–1000 mg/L for each compound.

2.2. Indoor dust sampling

Three types of indoor dust samples were collected from offices (n = 12), public microenvironments (PME) (n = 7, 3 laboratories, 1 classroom, 1 lobby, 1 hotel, and 1 supermarket), and a car wash station (composite dust samples of > 100 cars) in Nanjing, China. The dust samples from offices and PME were collected from air-conditioner (AC) filters, while car dust was collected from carpet surface, seats, and dashboard by a vacuum cleaner. Dust samples from each category were mixed, homogenized, and sieved through nylon sieve to < 2000 μm. Each type of sample was separated into 6 fractions via sieving, including F1 (200–2000 μm), F2 (150–200 μm), F3 (100–150 μm), F4 (63–100 μm), F5 (43–63 μm), and F6 (< 43 μm). Different sampling methods (AC filter sampling for office and PME dust vs surface collection for car dust) may effect on the particles size distribution. AC filters usually retain smaller particles from the air, while larger size of dust can be observed in surface dust (He et al., 2016). However, the effect of different sampling methods on size distribution of dust was alleviated by manually sieving dust samples into 6 fractions. All dust samples were stored in aluminum foil at −20 °C until analysis. Total organic carbon (TOC) contents in dust were analyzed by element analyzer (vario TOC select, Elementar, Germany) after removing carbonate carbon by dissolving dust in 0.5 M HCl.

2.3. Total concentrations of flame retardants in dust

The dust samples were extracted according to He et al. (2016). Triplicates were used for each dust and procedural blanks were also included. Each dust sample (~0.2 g) was extracted in a sonicator (SCOENTZ, SB-800 DTD, China) with 20 mL n-hexane for 30 min three consecutive times. The combined extract was evaporated to near dryness (IKA® RV10, Germany) and re-dissolved in 2 mL n-hexane. The n-hexane solution was then transferred to 2 mL amber vials after filtration through a 0.45 mm PTFE filter (ANPEL, China) and stored at −20 °C until analysis.

2.4. Bioaccessible flame retardants in dust

Bioaccessible FRs in dust samples were measured using the physiologically-based extraction test (PBET) (Ruby et al., 2002; Tilston et al., 2011) in the way reported in our previous study (He et al., 2016). Briefly, ~0.2 g dust sample was extracted by gastric fluid at pH = 2.5 with being shaken at 37 °C in an incubator (HZP-250, China) at 150 rpm. After 1 h, the solution was converted to intestinal fluid by adjusting pH to 7 and adding 0.035 g bile salts and 0.01 g pancreatin. After shaking for 4 h at 37 °C and 150 rpm, the mixture was centrifuged at 3000 rpm for 5 min and the supernatant was filtrated through a 0.45 μm PTFE filter (SCAA-113, China) into a glass centrifuge tube. An aliquot of 10 mL supernatant was extracted by sonication with 10 mL n-hexane for 30 min three times. The extracts were combined into 150 mL flask bottle after dehydration by filtration with anhydrous sodium sulfate. The extracts were then condensed and reconstituted in 2 mL n-hexane. The final extract was filtered through a 0.45 μm PTFE filter (ANPEL, China) into 2 mL amber vial for analysis. The bioaccessibility of FRs was calculated based on the following equation:

$$\text{Bioaccessibility}\% = \frac{Extracted\,FRs}{Total\,FRs\,in\,dust} * 100\%$$

2.5. Risk assessment

The values of average daily dose (ADD) of FRs in the dust samples through non-dietary ingestion was determined according to the following equation. There are other exposure pathways that contribute to the overall exposure in addition to dust ingestion, namely inhalation and dermal pathway. However, in terms of dust samples, due to the relatively large particle size as well as high frequency of hand-mouth behavior, especially for young children, incidental dust ingestion can be considered as a significant exposure pathway. Therefore, we focused on the ADD_{ingest}.

$$ADD_{ingest} = \frac{IngR \times C}{BW}$$

Where C represents FR concentrations in cars, PME, or office dust (μg/g), IngR is the ingestion rate of indoor dust (g/day) at 0.11 for adults (Kang et al., 2012), and BW refers to the body weight (kg) at 61.5 kg for adults (Wang et al., 2013a). Bioaccessible FRs were also taken into consideration for non-dietary ingestion exposure:

$$ADD_{ingest-bio} = Bioaccessibility\% \times ADD_{ingest}$$

2.6. Chemical analysis

The analysis of OPFRs was conducted on gas chromatography (Agilent Technologies, 7890A) coupled with mass spectrometry with an electron ionization mode (Agilent Technologies, 5975) (GC-MS) in selective ion-monitoring mode. Temperature of the injector and ion source was 280 °C, and analyte separation was achieved using a TR-5MS column (30 m × 0.25 mm i.d with 0.25 μm film thickness). Helium (99.999%) was used as a carrier gas at a flow rate of 1 mL/min. The analysis of PBDEs, NBFRs, and DPs were conducted on GC (Agilent Technologies, 7890 A) coupled with MS (Agilent Technologies, 7000B) (GC-MS) under negative chemical ionization mode. Temperatures of the injector and ion source were 280 °C and 150 °C, and analyte separation was achieved using a DB-5MS column (10 m × 0.25 mm i.d with