Chemosphere 150 (2016) 465–471

Contents lists available at ScienceDirect

Chemosphere

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

Characterization and human exposure assessment of organophosphate flame retardants in indoor dust from several microenvironments of Beijing, China

Min Wu [a], Gang Yu [a, *], Zhiguo Cao [a, b], Dongkui Wu [c], Kai Liu [a], Shubo Deng [a], Jun Huang [a], Bin Wang [a], Yujue Wang [a]

[a] School of Environment, Beijing Key Laboratory for Emerging Organic Contaminants Control, State Key Joint Laboratory of Environment Simulation and Pollution Control (SKLESPC), Tsinghua University, Beijing 100084, China
[b] School of Environment, Henan Normal University, Xinxiang 453007, China
[c] School of Chemical and Environmental Engineering, China University of Mining and Technology, Beijing, Beijing 100083, China

HIGHLIGHTS

- PFRs exposure assessment via dust ingestion for different populations was presented.
- Office dust showed much higher levels of PFRs than home and daycare center dust.
- Significant correlations were observed for TCEP, TCIPP and TBOEP in paired dust.
- Toddlers suffered higher degree to PFRs by dust ingestion but much lower than RfDs.

ARTICLE INFO

Article history:
Received 5 October 2015
Received in revised form
22 December 2015
Accepted 24 December 2015
Available online 12 January 2016

Handling Editor: J. de Boer

Keywords:
Organophosphate flame retardants (PFRs)
Indoor dust
Human exposure
Vulnerable population

ABSTRACT

Ten target organophosphate flame retardants (PFRs) were measured from floor dust samples collected from homes (n = 21), offices (n = 23) and daycare centers (room n = 16) located in Beijing, China, and paired elevated surface dust and floor dust from the same daycare centers (room n = 9) were analyzed in this study. Most PFRs were detected in analyzed dust samples, and detection frequency up to 100% was observed on tris (2-chloroethyl) phosphate (TCEP), tris (2-chloroisopropyl) phosphate (TCIPP), triphenyl phosphate (TPHP) and tris (2-butoxyethyl) phosphate (TBOEP). Among studied microenvironments, office samples showed significantly ($p < 0.05$) higher PFRs contamination level (1687–200,489 ng/g), followed by homes (4571–67,450 ng/g), and daycare centers (1489–33,316 ng/g). TCEP was the predominant PFR in both home and daycare center samples, while TCIPP was dominant in floor dust from offices. TCEP, TCIPP and TBOEP showed positive correlations ($p < 0.05$) between their levels in elevated surface dust and corresponding floor dust, and the mean concentrations of TPHP (1116 ng/g) and tricresyl phosphate (TMPP) (336 ng/g) were significantly higher ($p < 0.05$) in floor dust than those in elevated surface dust (269 and 93 ng/g, respectively). Estimated exposures of toddlers, average adults and the elderly to PFRs via dust ingestion were 38, 6 and 5 ng/kg bw/day, respectively (assuming the average daily time spent are 62.5% home and 37.5% daycare center for toddlers, 62.5% home and 37.5% office for average adults, and 100% home for the elderly; assuming median concentrations and average dust ingestion rate).

1. Introduction

Polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs) and tetrabromobisphenol A (TBBPA) are three of the most extensively used brominated flame retardants (BFRs) by the industry to improve the flame resistance of consumer products (Ali et al., 2012a). Because of their wide usage and/or relative persistence in the environment, these flame retardants have been ubiquitously detected (Law et al., 2008; Harrad et al., 2009; Li et al., 2011; Birgul et al., 2012). Moreover, *in-vitro* experiments suggested that many BFRs are bioaccumulative and

* Corresponding author.
E-mail address: yg-den@mail.tsinghua.edu.cn (G. Yu).

http://dx.doi.org/10.1016/j.chemosphere.2015.12.111
0045-6535/

may cause a variety of adverse effects to the living body (Rauert et al., 2014). In addition, certain PBDEs (i.e., Penta-BDE and Octa-BDE mixtures) and HBCDs have been listed under the Stockholm Convention in 2009 and 2013, respectively. With the banning/phasing out of PBDEs, the marketing demand for alternative flame retardants, such as organophosphate flame retardants (PFRs), has increased rapidly in recent years (Van den Eede et al., 2011).

PFRs are commonly used as flame retardants, plasticizers and antifoaming agents which are added in many products including furniture, textiles, cables, building materials, paints, floor polishes and electronics (Marklund et al., 2003). Since they are mostly employed as additives without chemical bonding, leaching from the products into the surrounding environments may easily occur throughout their entire lifetime. And PFRs' toxicological effects on animals and humans have been already reported (WHO, 1991, 1998, 2000; Kanazawa et al., 2010; Meeker and Stapleton, 2010; Van der Veen and de Boer, 2012). For example, tris (2-chloroethyl) phosphate (TCEP) is neurotoxic and carcinogenic to rats, tris (1,3-dichloro-2-propyl) phosphate (TDCIPP) can be absorbed through human skin and reduce thyroid hormone levels, while tri-n-butyl phosphate (TNBP) has been linked with sick building syndrome. In particular, tris (2-chloroisopropyl) phosphate (TCIPP) is structurally similar to TCEP, which has been identified as a possible carcinogen by the World Health Organization (WHO, 1998). In addition, TDCIPP, an analog of TCIPP, is now listed as a carcinogen under California Proposition 65 (California EPA, 2011). Furthermore, several studies showed that the concentrations of PFRs seem to be much higher than those of PBDEs in many environmental media, especially in indoor dust (Ali et al., 2013; Cao et al., 2014a,b; Cequier et al., 2014; Salamova et al., 2014).

Indoor dust plays an important role in human exposure to environmental pollutants since it can be ingested incidentally from different microenvironments, and people spend most of their time indoors (Zheng et al., 2015). It is known that intakes via dust ingestion contributes considerably to the total exposure of PBDEs (Wu et al., 2007; Harrad et al., 2008), but the pathway of PFRs intakes has not been examined in detail. Several studies have reported the occurrence of PFRs in dust samples in the indoor environments (Ali et al., 2012a,b, 2013; Cao et al., 2014a,b; Cequier et al., 2014). However, previous studies addressing human exposure to PFRs have been mostly focused on a single type of microenvironment, which may underestimate or overestimate the exposure (Ali et al., 2012a,b; Dirtu et al., 2012; Zheng et al., 2015). In addition, even though toddlers and the elderly are known to be particularly vulnerable to the exposure of contaminants from surrounding environments, PFRs contamination in indoor dust have rarely been investigated in microenvironments that are relevent to them, e.g., daycare centers (reviewed by Fromme et al., 2014). Worse still, as one of the largest PFRs manufacturer and consumer in the world, China has received few attention on the occurrence of PFRs in its indoor environment (Yang et al., 2013; Cao et al., 2014a,b; Lu et al., 2014).

In this study, toddlers, average adults and the elderly were selected as representative groups to estimate PFR exposure through dust ingestion. Therefore, homes, offices and daycare centers in Beijing, China were selected to collect indoor dust samples based on the particular lifestyle of these aforementioned groups. The primary objectives of the present study were (1) to evaluate the contamination level and congener profiles of PFRs between three different microenvironments; (2) to compare the similarities and differences of PFRs levels between paired elevated surface dust and floor dust in daycare centers; and (3) to present a estimation of PFRs exposure from indoor dust in China in the aforementioned three typical population.

2. Materials and methods

2.1. Materials

Standards of triethyl phosphate (TEP), tri-n-propyl phosphate (TPP), tri-iso-butyl phosphate (TIBP), tri-n-butyl phosphate (TNBP), tris (2-chloroethyl) phosphate (TCEP), tris (2-butoxyethyl) phosphate (TBOEP), triphenyl phosphate (TPHP), tris (1,3-dichloro-2-propyl) phosphate (TDCIPP) and tricresyl phosphate (TMPP) (mixture of 4 isomers) were purchased from Chiron AS (Trondheim, Norway). While standard of tris (2-chloroisopropyl) phosphate (TCIPP) (mixture of 3 isomers) was purchased from Pfaltz & Bauer (Waterbury, CT, USA). Surrogate standard triamyl phosphate (TAP) was purchased from TCI Europe (Zwijndrecht, Belgium), while another surrogate standard triphenyl phosphate-d_{15} (TPHP-d_{15}) was also purchased from Chiron AS (Trondheim, Norway). Recovery standard decachlorobiphenyl (PCB-209) was obtained from CSD IDEA (Beijing) Environmental Test & Analysis Co., Ltd. All organic solvents used during analysis were of HPLC grade.

2.2. Sample collection

Indoor dust samples (n = 69) were taken from different microenvironments in urban areas of Beijing between spring 2012 and summer 2013. Floor dust samples (n = 60) were collected from twenty-one homes, twenty-three offices and sixteen daycare center rooms. Elevated surface (surface of furniture, tables, and etc.) dust samples were collected from nine of the sixteen daycare center rooms. All samples were collected using a commercial vacuum cleaner. Dust sample collected from a 25 μm nylon sampling sock (Guangzhou Qi Xin filter Ltd., China) was placed in the suction nozzle of the vacuum cleaner. At private home, floor dust sample was collected from main living areas, i.e., living room, bedroom, and dining room. In offices and daycare centers, dust samples were collected from the whole floor/elevated surface. The home and daycare center dust were gathered by scientific people, while the floor dust in offices were obtained from the building cleaner. Collected dust samples were wrapped with aluminum foil, sealed in polyethylene zip bags, and stored at −20 °C until analysis.

2.3. Sample preparation and analysis

Indoor dust samples were sieved through a stainless steel sieve (500 μm) to remove large debris and hair before analysis. Sample extraction and clean-up were performed based on the method developed by Van den Eede et al. (2012), details were provided in the Supporting Information.

Quantitative analysis of PFRs was performed by a Shimadzu 2010 gas chromatograph coupled with a single quadrupole mass spectrometer (GC–MS) operated in electron impact ionization (EI) mode. A DB-5MS column (30 m × 0.25 mm × 0.25 μm, Agilent) was employed for separation and the MS was deployed in selected ion monitoring (SIM) mode. TAP was used as a surrogate standard for TEP, TPP, TIBP, TNBP, TCEP, TCIPP and TBOEP, while TPHP-d_{15} was used for TDCIPP, TPHP and TMPP, respectively. PCB-209 was employed as a recovery standard for quantification of TAP and TPHP-d_{15}.

2.4. Quantification and quality assurance

As part of the quality assurance protocol, validation experiments on analytical method were conducted before samples analysis, and detailed parameters (recoveries of target PFRs and so on) were provided in Table S-1. Two procedural blanks and one control sample (pre-analyzed dust with high contamination level) were