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Emerging and legacy flame retardants in indoor dust from East China

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HIGHLIGHTS

- A large suite of emerging and legacy flame retardants was determined in indoor dust from East China.
- Organophosphate flame retardants were predominant in dust regardless of microenvironments.
- Dust from East China contained elevated DBDPE levels compared with that from most other countries.
- Limited human health risk from dust exposure was determined in East China.

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ABSTRACT

To understand human exposure to dust-associated flame retardants in the biggest metropolitan area (city of Shanghai) of East China, our study determined a suite of legacy and emerging flame retardants in dust from dwellings, cars, and university computer labs. The results exhibited a consistent dominance of organophosphate flame retardants (OPFRs) over polybrominated diphenyl ethers (PBDEs) and other alternative flame retardants (AFRs) regardless of microenvironments. In addition to OPFRs, some alternative flame retardants, such as decabromodiphenyl ethane (DBDPE), 2-ethylhexyltetrabromobenzoate (EH-TBB), bis(2-ethylhexyl)-3,4,5,6-tetrabromobenzoate (BEH-TEBP), and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), were also frequently detected. Among them, DBDPE exhibited concentrations comparable to those of PBDEs. Comparison with international studies indicated that concentrations of ∑PBDEs (0.2–12.3 μg/g dry weight or dw) and ∑OPFRs (3.8–165.5 μg/g dw) from Shanghai dwellings (bedroom and living room) were generally in the middle of concentration ranges reported worldwide, whereas elevated DBDPE concentrations (0.1–9.5 μg/g dw) was observed compared with most other countries or regions. OPFR compositions in house dust from this study also differed from those from many other countries. This suggested inter-regional differences in market demands on the quantities and types of flame retardants. Human intake estimation suggested elevated exposure for toddlers when compared with adults, although the daily intake estimations of individual flame retardants were generally 2–4 orders of magnitude lower than the reference doses. The findings from this preliminary study developed a baseline for future evaluation of the sources and fate of emerging flame retardants and related human exposure risks in East China.

1. Introduction

Flame retardants (FRs) are a group of anthropogenic chemicals added to consumer products in order to meet fire retardancy needs. Polybrominated diphenyl ethers (PBDEs) have been among the most widely used FRs since 1990s. Numerous PBDE studies have revealed their global distribution and demonstrated they are persistent, bioaccumulative and toxic (Darnerud, 2003; Law et al., 2014). Consequently, commercial PentaBDE and OctaBDE mixtures have been phased out from North American and European markets since 2004. Both were added to the persistent organic pollutants (POPs) list of the Stockholm Convention (www.pops.int). The production of DecaBDE mixture was also discontinued since the end of 2012 (United States Environmental Protection Agency, 2013). However, the discontinuation of PBDE mixtures has

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stimulated the increased use of existing chemicals or development of alternative chemicals to replace PBDEs while meeting flame retardancy needs. To date, more than 70 alternative FR chemicals have been reported for industrial applications (Covaci et al., 2011). These include a variety of brominated or chlorinated substances as well as organophosphate flame retardants (OPFRs). OPFRs represent a group of halogenated or non-halogenated compounds with tri-ester structures, including tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCPP), tributyl phosphate (TBP), triphenyl phosphate (TPhP), tris(2-butoxyethyl) phosphate (TBEP), and a few others (van der Veen and de Boer, 2012). Typical brominated FRs include 2-ethylhexyltetrabromobenzoate (EH-TBB), bis(2-ethylhexyl)-3,4,5,6-tetrabromobenzoate (BEH-TEBP), and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), as well as many others (Covaci et al., 2011). Chlorinated FRs mainly include Dechlorane Plus (DP) and its analogues, such as Dechlorane (or Dec-) 601, 602, 603, and 604 (Sverko et al., 2011). These various alternative FRs are different from PBDEs in physicochemical properties, environmental behavior and fate, thus likely representing different risks to the environment and human health.

Dust has been demonstrated as an important vector for human exposure to indoor chemicals released from household products or building materials. Chemicals associated with dust can enter the body via ingestion after hand-to-mouth contact, inhalation of resuspended dust, or direct absorption through the skin (Whitehead et al., 2011). Previous studies have demonstrated the universal presence of PBDEs in indoor dust (Harrad et al., 2010). Significant correlations in PBDE concentrations have been reported between indoor dust and human breast milk or placenta samples (Coakley et al., 2013; Vorkamp et al., 2011). Significant positive associations were also found between dust pentaBDE concentrations and serum levels of free T4, total T3, estradiol, or sex hormone binding globulin (SHBG), along with an inverse association with follicle stimulating hormone (Johnson et al., 2013). These studies suggested indoor dust as an important exposure pathway for PBDEs and very possibly for other FRs as well.

It was anticipated that indoor levels of non-PBDE FRs would be increasing as a result of the discontinuation of PBDEs. Available studies have reported a number of alternative FRs in indoor dust. However, the concentrations and compositions of alternative FRs varied largely among countries or regions, reflecting inter-regional differences in usage patterns. China has been one of the major countries manufacturing and using FR-containing consumer products. Although there existed a number of PBDE studies in indoor environment (Chen et al., 2014; Kang et al., 2011; Meng et al., 2015; Wang et al., 2015; Zhu et al., 2013), knowledge on the indoor contamination of alternative FRs remained limited in China compared to other regions. In the present study, we conducted a preliminary investigation of FR contamination in indoor dust from the city of Shanghai, the biggest metropolitan area in East China. Specific objectives were to: (1) determine a variety of alternative FRs and compare their concentrations with PBDEs; (2) compare the concentrations and compositions of dust-associated FRs from different indoor microenvironments (i.e., dwellings, vehicles and university computer labs) and with those from international studies; and, (3) estimate human exposure risks via dust ingestion.

2. Materials and methods

2.1. Chemicals and reagents

Reference standards of 20 PBDE congeners (BDE-28, -47, −49, −66, −85, −99, −100, −138, −153, −154, −183, −196, −197, −201, −202, −203, −206, −207, −208, −209) were purchased from AccuStandard (New Haven, CT). A total of 12 OPFRs, including TBEP, TBP, TCEP, TCPP, TDCPP, TPhP, 2-ethylhexyl-diphenyl phosphate (EHDPP), tricresyl phosphate (TCrP), tris(2,3-dibromopropyl) phosphate (TDBPP), tris(2-ethylhexyl) phosphate (TEHP), triethyl phosphate (TEP) and tripropyl phosphate (TPrP), were purchased from AccuStandard or Wellington Laboratories (Guelph, Canada). Reference standards of 10 Dechlorane analogues (i.e., syn-DP, anti-DP, monodechlorinated DP, didechlorinated DP, chlordane plus, Dec-601, Dec-602, Dec-603, Dec-604, and Dec-604 Component B) and 21 additional brominated FRs, including 2,4,6-tribromophenyl allyl ether (ATE), BEH-TEBP, BTBPE, DBDPE, EH-TBB, hexabromobenzene (HBBZ), α-, β-, and γ-hexabromocyclododecane (HBCDD), hexachlorocyclopentenyl-dibromocyclooctane (HCBD-CO), penttabromobenzyl acrylate (PBBA), pentabromobenzyl bromide (PBBB), pentabromobenzene (PBBZ), pentabromoethyl benzene (PBEB), pentabromotoluene (PBT), 1,3,5-tribromobenzene (TBB), tetrabromo-*o*-chlorotoluene (TBCT), α-, β-, and γ-1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH), and 2,3,5,6-tetrabromo-*p*-xylene (TBX), were purchased from AccuStandard or Wellington Laboratories. Surrogate standards, 4′-fluoro-2,3′,4,6-tetrabromodiphenyl ether (F-BDE69), 4′-Fluoro-2,3,3′,4,5,6-hexabromodiphenyl ether (F-BDE160), 2,2′,3,3′,4,5,5′,6,6′-nonabromo-4′-chlorodiphenyl ether (4PC-BDE208), d_{18}-α-hexabromocyclododecane (HBCDD), d_{15}-TPhP, d_{12}-TCEP, d_{15}-TDCPP, d_{27}-TBP, and tris(2-butoxy-[13C2]-ethyl) phosphate (M_6-TBEP), as well as internal standards, 3′-Fluoro-2,2′,4,4′,5,6′-hexabromodiphenyl ether (F-BDE154) and coumaphos-d_{10}, were purchased from AccuStandard, Wellington or Cambridge Isotope Laboratories (Andover, MA). High performance liquid chromatography (HPLC) grade solvents were purchased from Fisher Scientific (Hanover Park, IL).

2.2. Sampling and treatments

A total of 15 families living in the city of Shanghai voluntarily participated in this study. The dwellings of these families were scattered across the city. None of the dwellings was from the same building. A customized and pre-cleaned nylon bag with a pore size of ~25 μm was attached to the floor attachment of a commercial vacuum cleaner (Electrolux, ZMO1511, 1400 W). Floors of living room and bedroom(s) from each dwelling were vacuumed. Seven out of 15 dwellings have a semi-closed balcony, where its floor was also vacuumed. Four families had private vehicles from which dust was collected from car floor and surfaces. Seven computer laboratories from a university residing in the city were visited and vacuumed for floor dust. After dust from each microenvironment was collected, the nylon bag was detached, wrapped with clean aluminum foil, and transported back to the analytical laboratory on ice. Dust on the nylon bag was sieved through a 500-μm stainless cloth sieve (Hogentogler & Co., Inc., Columbia, MD) and stored at −20 °C. For the analysis of flame retardants of interest excluding OPFRs, approximately 20–50 mg of the sieved dust was spiked with surrogate standards (F-BDE69, F-BDE160, 4PC-BDE208, and d_{18}-α-HBCDD) and extracted with accelerated solvent extraction (ASE350; Thermo Scientific, Sunnyvale, CA, USA) with dichloromethane (DCM) at 100 °C and 1500 psi. The resulting extract was cleaned through a solid phase extraction (SPE) cartridge packed with 2 g Isolute® silica sorbent (Biotage, Charlotte, NC). After the SPE cartridge was rinsed with 10 mL hexane and the sample was loaded, the cartridge was eluted with 3.5 mL hexane (fraction 1), followed by 10 mL of 60:40 (v/v) hexane/dichloromethane (fraction 2). The latter fraction was concentrated and spiked with internal standard F-BDE154 for the determination of FRs excluding OPFRs. For the analysis of OPFRs, approximately 20–50 ng of sieved dust was spiked with surrogate standards (including: d_{15}-TPhP, d_{12}-