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.

ARTICLE INFO

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 $\sum$PBDEs (0.2–12.3 µg/g dry weight or dw) and $\sum$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

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 (HCBDCO), 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}-

TCEP, d$_{15}$-TDCPP, d$_{27}$-TBP, and M$_6$-TBEP) and extracted with 5 mL of a mixture of hexane and dichloromethane (1:1, v/v) under sonication. Sonication was conducted in three cycles each of which lasted for 5 min. After each cycle, the tube was centrifuged and the supernatant extract was collected. Combined extracts from three cycles were concentrated and cleaned through a SPE cartridge packed with 1 g of ammonium silica (Biotage, Charlotte, NC). The target OPFR analytes were eluted out with 4 mL of 20:80 (v/v) hexane:dichloromethane and 8 mL of dichloromethane. The resulting extract was concentrated and spiked with internal standard, coumaphos-d$_{10}$, for OPFR analysis.

2.3. Instrumental analysis

FRs excluding OPFRs and HBCDDs were analyzed on an Agilent 7890B gas chromatogram (GC) coupled to an Agilent 5977A mass spectrometer (MS; Agilent Tech., Palo Alto, CA). The GC was equipped with a 15 m DB-5HT column (0.35 mm i.d., 0.1 μm film thickness, J&W Scientific, Folsom, CA). The GC oven program and the MS parameters were introduced in Boyles et al. (2017). The initial column temperature was held at 50 °C for 4 min and then ramped to 300 °C at 10 °C/min (held for 15 min). Identification and quantification of FR substances was achieved via selected ion monitoring (SIM) of characteristic ions in electron capture negative ionization (ECNI) mode (Table S1). After GC-MS analysis, the same extract was solvent exchanged to methanol and determined for α-, β-, and γ-HBCDD on an Agilent 1260 HPLC interfaced with a 3200 Q Trap triple quadrupole/linear ion trap MS (AB Sciex; Toronto, Canada). The HPLC system was equipped with a Waters Xterra® phenyl column (2.1 mm × 100 mm, 3.5 μm particle size). The MS was equipped with a TurboIonSpray® electrospray ionization (ESI) probe operated in the multiple reaction monitoring (MRM) mode for quantitative measurement of HBCDD diastereomers (Table S1). The instrumental analysis protocol was discussed in the Supporting Information in detail. OPFRs were determined on the same LC-MS/MS system equipped with a Kinetex EVO C18 column (2.1 mm × 100 mm, 5 μm particle size; Phenomenex, Torrance, CA, USA). The mobile phase consisted of methanol (A) and water (B), both spiked with 0.1% formic acid (v/v). The mobile phase flow rate was 200 μL/min and the following gradient was employed: 5% B ramped to 70% B in 3 min (linear) and then ramped to 80% B in 12 min (linear), followed by a linear increase to 95% B in 3 min (held for 12 min) and then a change to 5% B in 1 min (held for 15 min). The SIM ions or MRM ion pairs of target FRs were summarized in Table S1.

2.4. Quality assurance and control

Quality assurance and control procedures included the evaluation of analyte recoveries in spiking experiments, procedural blanks and recoveries of surrogate standards in authentic samples. Flame retardants of interest (50 ng each) were spiked into a dust composite (n = 5) and analyzed using the above methods. The mean (±standard deviation) of recoveries of spiked individual analytes, after subtracting the original values in the dust composite, ranged from 74.2 ± 7.1% to 109 ± 5.2% for OPFRs and 63.1 ± 14.7% to 106 ± 11.1% for other FRs in five replicates. Procedural blanks contained no detectable analytes except TBP, TPhP or TBEP, which were present in blanks at concentrations of up to 8—16 ng/g dw. Blank contamination was subtracted from dust concentrations. Average recoveries of surrogate standards ranged from 68.5% to 92.3% for PBDE analysis and 61%—87.4% for OPFR analysis. Reported concentrations of analytes were corrected based on the recoveries of relevant surrogate standards. The limit of quantification (LOQ), defined as an analyte response 10 times the standard deviation of

the noise, ranged from 2 to 12 ng/g for OPFRs and 2—10 ng/g for other FRs.

2.5. Data analysis

All concentrations were expressed as ng/g dry weight (dw), unless otherwise noted. For an analyte with detection frequency above 60%, a regression plotting method was applied to assign values for its measurements below LOQs or non-detectable (nd) (Newman, 1995) Reported concentrations of analytes were corrected based on the recoveries of relevant surrogate standards. Non-normally distributed data were logarithmically transformed to approximate a normal distribution before the Kruskal-Wallis one-way analysis of variance (ANOVA) with Dunn's post-hoc analyses or the Pearson correlation analyses (PASW Statistics 18.0, IBM Inc.). The level of significance was set at α = 0.05 for all statistical tests.

3. Results and discussion

3.1. Occurrences of flame retardants in dust

To make the discussion convenient, we grouped the variety of target FR analytes into three classes: PBDEs, OPFRs, and all other alternative FRs (referred to as AFRs). Regardless of microenvironments, the total concentrations of OPFRs or $\sum$OPFRs were generally one order of magnitude greater than those of $\sum$PBDEs (including all detectable PBDE congeners) and $\sum$AFRs (including all detectable non-PBDE FRs excluding OPFRs) in indoor dust (Table 1, Fig. 1). Concentrations of $\sum$OPFRs ranged from 8.0 to 165.5 μg/g (median: 11.5 μg/g) in dust from bedrooms, while $\sum$PBDEs and $\sum$AFRs ranged from 0.2 to 11.2 μg/g (median: 1.0 μg/g) and 0.3—6.7 μg/g (median: 1.0 μg/g) in the same microenvironment, respectively. Dust from university computer labs contained 9.9—27.4, 0.4—3.8 and 1.3—18.6 μg/g of $\sum$OPFRs, $\sum$PBDEs and $\sum$AFRs, respectively. Vehicle dust contained these three groups of FRs with median concentrations of 15.4, 0.2, and 0.4 μg/g, respectively (Table 1). This common pattern suggested that OPFRs have become the dominant flame retardants in the indoor and vehicle environment from Shanghai, East China. OPFRs have been used not only as FRs, but also as plasticizers, anti-foam agents or in hydraulic fluids, lacquer, paint, glue and floor finish (Marklund et al., 2003). In addition to wide applications in various fiber types in textiles, OPFRs are also compatible with other processing materials and easy to use (van der Veen and de Boer, 2012). Available data showed that market demands on OPFRs have surpassed that for brominated flame retardants (BFRs) in Europe (Reemtsma et al., 2008). A number of OPFRs, such as TBP and TPhP, have been identified as potential substitutes for BFRs used in textile back-coatings (Horrocks et al., 2007) and may be subject to increased use following the discontinuation of PBDE mixtures. Although market demand data for OPFRs remain unclear in China, it was expected to follow the general pattern of FR usage in the rest of the world. Global studies revealed similar patterns of FR contamination in indoor dust, where OPFRs were consistently dominant (Ali et al., 2013; Cristale et al., 2016). Thus, OPFRs represent a major group of indoor chemicals worldwide, raising the attention of potential human exposure risks.

In addition to OPFRs and PBDEs, additional FRs in the group of AFRs, such as DBDPE (0.05—18.2 μg/g dw), BTBPE (nd — 0.09 μg/g dw), EH-TBB (nd — 0.3 μg/g dw), BEH-TEBP (nd — 0.9 μg/g dw), DPs (including *syn-* and *anti*-isomers; <LOQ — 0.1 μg/g dw) and HBCDDs (including α-, β- and γ-diastereomers; 0.05—1.4 μg/g dw) were also frequently detected in the present study (i.e. detection frequency ≥54.3%). In particular, DBDPE exhibited very comparable concentrations with PBDEs (mostly BDE-209 or DecaBDE). In fact, as the main component of commercial mixtures such as Saytex 8010

Table 1
Concentrations of most frequently detected flame retardants in dust samples from Shanghai, East China (μg/g dry weight).

	Living room (n = 15)			Bedroom (n = 15)			Balcony (n = 7)			Car (n = 4)			Computer lab (n = 7)		
	Median	Mean	Range	Median	Mean	Range	Median	Mean	Range	Median	Mean	Range	Median	Mean	Range
TCEP	1.2	4.3	0.2–38.0	1.0	1.1	0.1–3.1	0.4	0.6	0.2–1.3	2.0	16.6	0.3–62.1	2.4	4.0	0.4–12.0
TCPP	1.5	2.9	0.6–18.2	1.6	3.8	0.6–20.6	2.2	2.2	1.5–3.0	3.4	11.6	2.5–36.9	3.2	4.0	1.3–11.4
TDCPP	0.6	0.7	0.2–1.7	0.7	0.8	0.3–1.4	0.5	0.6	0.3–1.1	0.6	0.9	0.1–2.3	1.8	2.9	1.4–7.8
TBP	0.2	1.1	0.07–9.6	0.3	0.4	0.1–1.8	0.2	0.2	0.08–0.3	0.1	0.1	0.06–0.2	0.07	0.07	0.03–0.1
TEP	0.05	0.2	0.02–1.4	0.03	0.1	nd[a]-1.4	0.07	0.4	0.03–1.8	0.3	0.5	0.03–1.2	0.2	0.1	0.02–0.2
TPP	0.9	1.4	0.4–7.3	0.9	1.1	0.4–2.0	1.2	1.1	0.3–2.1	0.3	0.4	0.1–0.6	1.4	1.6	0.7–2.7
TCrP	0.3	0.6	0.1–3.2	0.3	0.4	0.2–0.6	0.3	0.3	0.1–0.6	0.3	0.5	0.1–1.3	0.4	0.6	0.4–1.2
TBEP	1.6	5.9	0.5–27.3	2.0	18.6	0.4–158.2	2.0	5.3	0.3–23.0	1.4	3.6	0.5–10.9	0.9	1.2	0.6–2.8
TEHP	1.2	1.1	0.2–1.9	1.4	1.4	nd-2.1	0.5	0.6	0.2–1.5	1.3	2.9	1.0–8.1	1.1	1.0	nd-1.7
EHDPP	0.9	0.9	0.3–1.4	0.9	0.9	0.4–1.3	0.3	0.4	0.1–0.7	1.3	2.2	0.5–5.8	0.8	0.9	0.4–1.3
∑OPFRs [c]	18.1	19.0	3.8–44.0	11.5	28.5	8.0–165.5	8.4	11.7	4.7–32.2	15.4	39.2	9.6–116.6	14.3	16.4	9.9–27.4
BTBPE	0.01	0.02	<LOQ[b]-0.06	0.01	0.01	nd-0.04	<LOQ	0.02	<LOQ -0.09	<LOQ	0.01	<LOQ-0.02	0.02	0.02	<LOQ-0.03
DBDPE	0.7	1.6	0.2–9.5	0.5	0.9	0.1–6.0	0.7	0.6	0.09–0.9	0.2	0.3	0.05–0.8	1.3	3.9	0.5–18.2
EH-TBB	0.04	0.05	nd-0.3	0.03	0.04	nd-0.1	0.01	0.01	nd-0.02	<LOQ	0.02	nd-0.09	0.04	0.04	nd-0.1
BEH-TBEP	0.05	0.1	nd-0.5	0.03	0.09	nd-0.6	0.02	0.03	nd-0.07	0.02	0.1	nd-0.5	0.1	0.3	0.04–0.9
∑DPs [d]	0.02	0.02	0.01–0.08	0.01	0.02	0.01–0.05	0.01	0.01	<LOQ-0.02	0.01	0.04	<LOQ-0.1	0.02	0.02	0.01–0.04
HBCDDs [e]	0.2	0.4	0.08–1.4	0.2	0.4	0.04–1.4	0.3	0.5	0.1–1.3	0.1	0.2	0.05–0.3	0.2	0.2	0.08–0.4
Other	0.01	0.04	<LOQ-0.2	<LOQ	0.07	nd-0.9	0.03	0.08	0.01–0.3	nd	nd	0–0.01	0.05	0.04	<LOQ-0.07
∑AFRs [f]	1.4	2.1	0.02–10.1	1.0	1.5	0.3–6.7	1.2	1.1	0.2–1.9	0.4	0.7	0.7–1.6	1.7	4.5	1.3–18.6
BDE-209	1.1	2.1	0.4–10.1	0.7	1.3	0.07–8.9	0.7	3.7	0.5–12.3	0.2	0.2	0.06–0.4	1.0	1.2	0.2–3.3
∑PBDEs [g]	1.9	3.1	0.8–12.3	1.0	1.7	0.2–11.2	0.9	4.3	0.6–14.2	0.2	0.3	0.07–0.6	1.5	1.5	0.4–3.8

[a] Not detectable.
[b] Less than limit of quantification.
[c] Summed concentration of all detectable organophosphate flame retardant (OPFR) substances.
[d] Including syn- and anti-DP isomers.
[e] Including α-, β-, and γ-HBCDD diastereomers.
[f] Summed concentration of all detectable flame retardant substances excluding OPFRs and polybrominated diphenyl ethers (PBDEs).
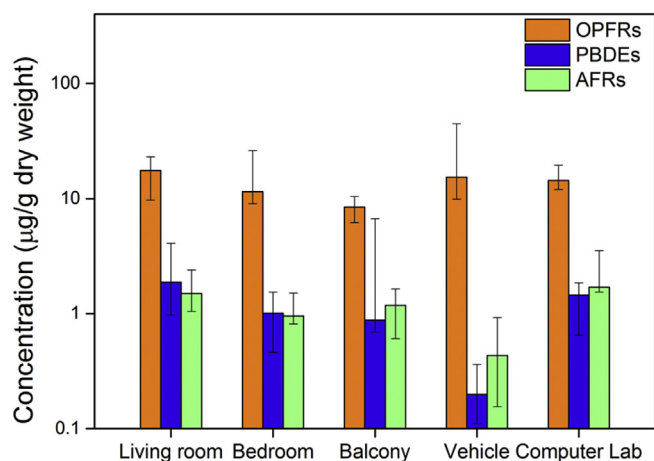[g] Summed concentration of all detectable PBDE congeners.

Fig. 1. Median concentrations (μg/g dry weight) of organophosphate flame retardants (∑OPFRs), polybrominated diphenyl ethers (∑PBDEs), and alternative flame retardants (∑AFRs) in dust collected from different microenvironments in Shanghai, East China. Error bars represent 75 and 25 percentiles, respectively.

(Albermarle Corp.) and Firemaster 2100 (Chemtura Corp.), DBDPE has become an alternative product to DecaBDE since 1990s (Covaci et al., 2011). It has almost the same applications as DecaBDE. Some other brominated FRs, such as EH-TBB, BEH-TEBP and BTBPE, were considered as potential PentaBDE or OctaBDE replacements (Covaci et al., 2011). EH-TBB and BEH-TEBP are major components of the commercial FR mixtures Firemaster 550, Firemaster BZ-54, and DP-45 (BEH-TEBP only) produced by Chemtura Corp (Farajzadeh and Mogaddam, 2012). BTBPE, marketed as FF-680 (Chemtura Corp.), has been used to replace OctaBDE since 2005 (Hoh et al., 2005). The discontinuation of PBDE mixtures may stimulate the industrial application of these major alternative flame retardants and result in

increasing concentrations in indoor environment. This has been supported by the increasing number of reports of these AFRs in global studies.

3.2. Compositions of FR groups

Concentrations of PBDEs in indoor dust were consistently dominated by BDE-209 with an average percentage of 69–82% in different microenvironments (Fig. 2). This pattern was observed globally in the indoor or outdoor dust, revealing the strong affinity of BDE-209 with organic contents in dust. Webster et al. (2009) suggested that BDE-209 could be transported to dust via physical processes such as abrasion or weathering of Deca-containing products. A similar migration mechanism may be predicted for DBDPE which has an even greater molecular weight and hydrophobicity than BDE-209. Similarly, DBDPE also dominated in the group of AFRs in indoor dust (Fig. 2), likely due to its strong affinity with dust particles along with great usage in household products. Semi-volatile or volatile chemicals may migrate to indoor environment via volatilization or physical processes and are more abundant in indoor air and suspended particles than less volatile or non-volatile chemicals (Blanchard et al., 2014; Salthammer et al., 2003). The concentration ratio of FRs between indoor air and settled dust increased significantly with their octanol-air partitioning coefficients (K_{oa}) (Cequier et al., 2014). Humans are exposed to chemicals associated with settled dust mainly through oral or dermal routes, whereas chemicals associated with airborne particles enter human bodies mainly through inhalative or oral pathways (Wensing et al., 2005). Thus, physicochemical properties of various FR substances greatly influence their migration and transport mechanisms in indoor environment and result in different exposure pathways.

Among the group of dechloranes, only syn- and anti-DP were frequently detected, whereas other dechlorane analogues were generable non-detectable. The only exception was chlordane plus
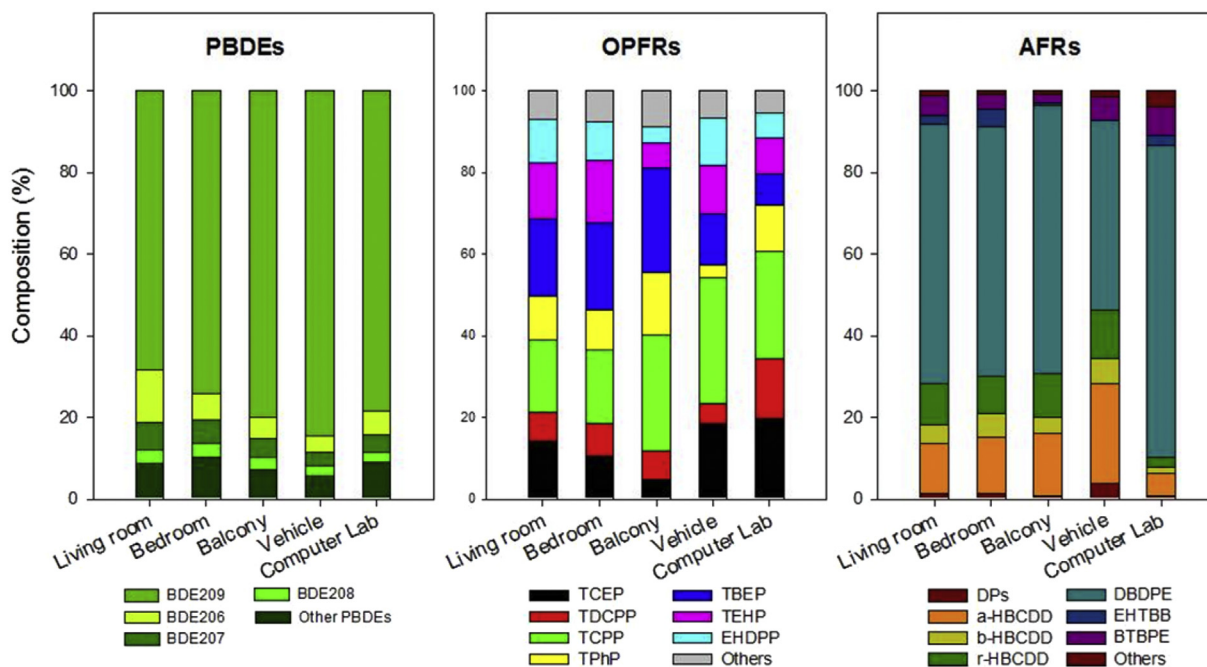
Fig. 2. Composition profiles (%) of PBDEs, OPFRs and AFRs in dust from Shanghai, East China.

which was detectable at two samples with concentrations below LOQ. The f_{anti} (defined as a concentration of anti-DP to ΣDPs) ranged from 0.64 to 0.95, with a mean (±standard deviation) value of 0.80 ± 0.05, close to the composition in technical DP mixtures where f_{anti} ranges from 0.65 to 0.75 (Qiu et al., 2007). Three main diastereomers of HBCDD, including α-, β-, and γ-HBCDD, were all detected in 100% of the samples, with compositions of 48 ± 18.3%, 16.8 ± 10.3%, and 35.2 ± 18.2%, respectively. The HBCDD composition profile was similar to that reported in many other countries (Abdallah et al., 2008) and the relative abundance of γ-HBCDD in dust was less than its composition in technical HBCDD mixtures (75−89%). This likely indicates the relative vulnerability of γ-HBCDD to degradation occurring during the production of consumer products or in indoor environment when compared with the other two diastereomers (Covaci et al., 2006).

OPFRs in indoor dust from Shanghai were dominated by chlorinated OPFRs including TDCPP, TCEP and TCPP, which in combination contributed to an average of 34−61% of ∑OPFR concentrations in different microenvironments (Fig. 2). TBEP was the main non-halogenated OPFRs in indoor dust, contributing to an average of 9−29% of ∑OPFRs. Fig. 3 provides a detailed description of the distribution of OPFRs in living rooms. This pattern resembled that observed in office and house dust from Beijing (North China) and house dust from the electronic-waste recycling sites in South China (Cao et al., 2014a, b; He et al., 2015; Zheng et al., 2015), as well as in indoor dust from Kuwait, Pakistan, Saudi Arabia, and Spain (Abdallah and Covaci, 2014; Ali et al., 2013, 2016; Cristale et al., 2016). However, different patterns were observed in dust from many other countries, where TBEP was generally predominant (Brommer and Harrad, 2015; Dodson et al., 2012; Mizouchi et al., 2015; Xu et al., 2016a). The discrepancy in OPFR composition profiles suggested country-specific applications of different OPFR chemicals. The dominance by chlorinated OPFRs is of concern, as most chlorinated OPFRs were suggested to be carcinogenic (van der Veen and de Boer, 2012). TDCPP could induce tumors in liver, kidney and

testes after oral exposure (van der Veen and de Boer, 2012). TDCPP and TCPP can exhibit concentration-dependent neuro-toxicity, inhibit DNA synthesis, and decrease cell number and alter neurodifferentiation (Dishaw et al., 2011). TCEP is toxic to aquatic organisms and can cause neurological and reproductive effects in rodents (Chapin et al., 1997; Tilson et al., 1990; Umezu et al., 1998). Human studies also revealed the association between TDCPP concentrations in house dust and altered hormone levels or decreased semen quality in men (Meeker and Stapleton, 2010). Thus, the dominance by chlorinated OPFRs in indoor dust may potentially elevate overall exposure risks from a toxicological standpoint.
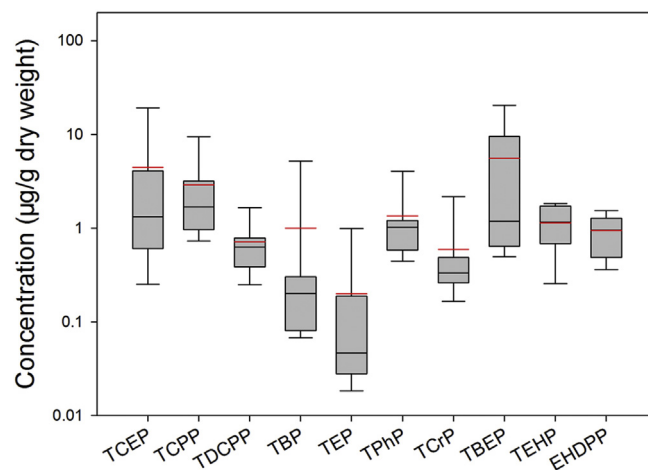

Fig. 3. Concentrations (μg/g dry weight) of frequently detected OPFRs in dust from living rooms in Shanghai, East China. TDBPP and TPrP were excluded from the graph as they were not detectable in any of the samples. The horizontal lines represent 10th, 50th, and 90th percentiles and the boxes represent 25th and 75th percentiles, respectively. Red lines represent mean concentrations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3. Comparison of microenvironments

The three microenvironments in dwellings (e.g. bedroom, living room and balcony) did not exhibit significant differences in concentrations of any group of FRs or major individual substances according to the Kruskal-Wallis one-way ANOVA with Dunn's post-hoc analyses ($p > 0.05$ in all comparisons). Given that most balconies in the sampled dwellings were semi-closed, which is typical in Chinese urban dwellings, dust from balcony may be coming from both indoor and outdoor environments and the signatures of contamination may be largely influenced by the frequency of opening of the balcony windows. Correlative analyses revealed that concentrations of the three groups of FRs as well as the major individual chemicals (except for TDCPP) in dust from living room and bedroom significantly correlated with each other (Table S2). By contrast, only $\sum$PBDEs or BDE-209, but not $\sum$AFRs, $\sum$OPFRs or other major individual chemicals (except for TCPP), revealed significant correlations between living room or bedroom with balcony (Table S2). The influences of indoor or outdoor environments on balcony appeared to vary for different groups of FRs, likely suggesting chemical-dependent exchanges between indoor and outdoor environments. However, a small sample size, particularly for balcony, may confound the findings.

University computer labs appeared to have significantly greater contamination of DBDPE compared with bedroom, balcony and vehicle, but not different from living rooms. DBDPE is applied to different polymer materials, such as high-impact polystyrene, acrylonitrile butadiene styrene, and polypropylene, some of which may be used in the thermoplastics of electronics including computers (Kierkegaard et al., 2004). The more abundance of computers enhanced the concentrations of DBDPE inside the university computer rooms. Living rooms usually contain more electronics (i.e., TV, refrigerator, and stereo systems) than other dwelling microenvironments, thus elevating DBDPE concentrations. Overall, the differences in the types and abundances of household products among microenvironments affected FR contamination levels and patterns. This may subsequently lead to different human exposure scenarios.

3.4. Comparison with domestic and international studies

In order to understand the contamination scenario in Chinese indoor environment on an international scale, we compared the concentrations of $\sum$PBDEs, $\sum$OPFRs and DBDPE between this study and other Chinese studies as well as international studies (Fig. 4). Only data from dwelling environment were used for comparison, given that most data were from home environment. As there were no statistical differences observed between bedrooms and living rooms in this study, we only used the living room data for inter-study comparison. The comparison demonstrated that $\sum$PBDEs data from the present study were very comparable to those reported in other regular dwelling environment from different regions of China (0.11–4.5 µg/g) (He et al., 2015; Wang et al., 2010, 2014; Xu et al., 2016b), but much lower than those reported in Chinese dwellings from electronic-waste (E-waste) regions (0.69–63.3 µg/g) (Table S3) (Wang et al., 2010; Zheng et al., 2015). However, $\sum$OPFRs from regular Chinese homes (i.e. 9.3–18.1 µg/g) were within the range of concentrations in homes from e-waste regions (2.2–33.1 µg/g) (Table S3). A dominance of $\sum$OPFRs over $\sum$PBDEs in house dust from Shanghai (this study) resembled the pattern observed in office and hotel dust from Beijing, North China (Cao et al., 2014a, b). However, OPFRs exhibited comparable concentrations with PBDEs in house dust from Beijing, both of which were lower than $\sum$AFRs (Cao et al., 2014a). A different pattern was also observed in house dust from e-waste recycling sites where
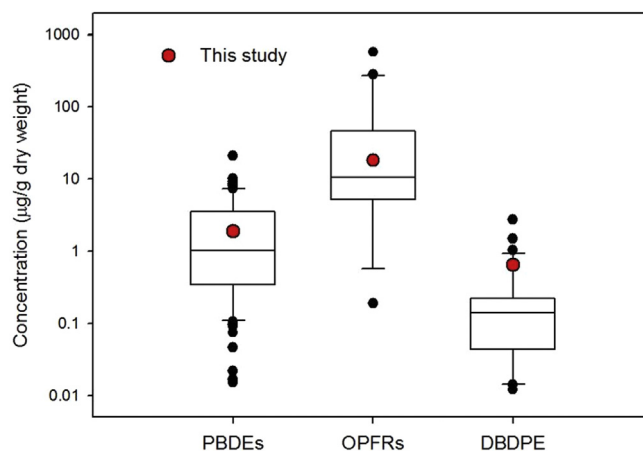
Fig. 4. Summary of concentrations of $\sum$OPFRs, $\sum$PBDEs, and DBDPE in house dust from global studies. Median concentrations are used wherever possible, whereas some other studies only report mean concentrations. Outliers are shown as individual black dots. Red dots represent data from our study. Literature data and corresponding references are summarized in Table S3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

PBDEs were generally found as the most dominant FRs (Zheng et al., 2015). These differences may indicate inter-regional difference in the usage patterns or environmental occurrences of FRs within China, but cautions are needed to draw any conclusion from a limited number of studies. Nevertheless, concentrations of $\sum$PBDEs and $\sum$OPFRs from Chinese dwellings (excluding those from e-waste regions) were generally in the middle of concentration ranges reported worldwide (Fig. 4, Table S3). For example, the median concentrations of $\sum$OPFRs in our study (i.e. 18.1 µg/g in living rooms) were lower than those from Japan (32.5–1611 µg/g), comparable with those from some studies in U.S., Canada, U.K., Sweden, Norway, and Belgium (6.1–59 µg/g), but generally one magnitude greater than those reported from Egypt, Philippines, Pakistan, Portugal and Saudi Arabia (0.19–3.8 µg/g) (Table S3). By contrast, DBDPE concentrations in Chinese dwelling dust, including data from this and previous studies (Chen et al., 2014; Wang et al., 2010), were overall at the high end of the concentration range reported, although the number of studies was fewer than that for PBDEs and OPFRs (Fig. 4, Table S3). DBDPE is the second highest in volume among the currently used additive FRs and its production is increasing at 80% per year (Covaci et al., 2011). Overall, the inter-regional differences in FR contamination levels and compositions reflect different market demands on FRs among countries or regions, which may be affected by fire regulations, economic levels, and regulations on FR applications. It is expected that the discontinuation of PBDE mixtures would increase the use of various existing or new substances as replacements to continuously meet flame retardancy needs. This would temporally change the compositions of FR contamination in indoor environment. It is noteworthy that a number of new BFR mixtures with high bromination and molecular weight (MW) have emerged in the market. For example, ethylene bis(tetrabromophthalimide (EBTEBPI, MW = 951.5) is a main component of Saytex BT-93 (Albermarle). The main component of FR-245 flame retardant, 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBP-TAZ), contains a total of 9 bromine atoms and has a MW of 1067. Another emerging FR substance, 1,2-bis(2,3,4,5,6-pentabromophenoxy)ethane (BPBPE) also has a MW greater than 1000. These heavily brominated FRs have log K_{ow} (octanol-water partition coefficient) comparable with or greater than of BDE-209 or DBDPE. Thus, a strong affinity with dust particles is expected for them, which indicates a potential human

Table 2
Estimated daily intake (EDI; ng/kg bw/day) of PBDEs, OPFRs and AFRs by toddlers and adults under different exposure scenarios.

	Home			Car			Office[c]			Total		
	PBDEs	OPFRs	AFRs	PBDEs	OPFRs	AFRs	PBDEs	OPFRs	AFRs	PBDEs	OPFRs	AFRs
Toddler (average dust ingestion[a])												
Median	16.1	156.1	11.7	0.08	6.3	0.2				16.2	162.4	11.9
Mean	26.7	163.6	18.0	0.1	16.1	0.3				26.9	179.7	18.3
5th	7.0	50.9	1.9	0.03	4.0	0.1				7.0	54.8	2.0
95th	66.3	329.1	48.1	0.2	41.9	0.6				66.6	371.0	48.7
Toddler (high dust ingestion[b])												
Median	64.3	624.4	46.7	0.3	25.2	0.7				64.6	649.6	47.4
Mean	107.0	654.5	72.1	0.5	64.3	1.1				107.4	718.8	73.2
5th	27.8	203.5	7.7	0.1	15.8	0.2				27.9	219.3	7.9
95th	265.3	1316.3	192.5	1.0	167.6	2.4				266.2	1483.9	194.9
Adult (average dust ingestion[a])												
Median	0.4	3.7	0.3	<0.001	0.2	0.01	0.1	1.0	0.1	0.5	4.9	0.4
Mean	0.6	3.9	0.4	<0.001	0.5	0.01	0.1	1.2	0.3	0.7	5.5	0.8
5th	0.2	1.2	0.1	<0.001	0.1	<0.001	0.03	0.7	0.1	0.2	2.0	0.1
95th	1.6	7.7	1.1	0.01	1.3	0.02	0.2	1.8	1.0	1.8	10.9	2.2
Adult (high dust ingestion[b])												
Median	1.0	9.2	0.7	0.01	0.5	0.01	0.3	2.5	0.3	1.2	12.2	1.0
Mean	1.6	9.6	1.1	0.01	1.3	0.02	0.3	2.9	0.8	1.89	13.8	1.9
5th	0.4	3.0	0.1	<0.001	0.3	<0.001	0.1	1.8	0.2	0.5	5.1	0.4
95th	3.9	19.4	2.8	0.02	3.3	0.05	0.6	4.5	2.5	4.5	27.2	5.4

[a] Assuming 20 mg/day for adults and 50 mg/day for toddlers.
[b] Assuming 50 mg/day for adults and 200 mg/day for toddlers.
[c] Not appropriate for toddlers.

exposure risks from oral or inhalative exposure via dust. Although analytical challenge may exist for these large MW substances, future studies are needed to investigate their migration and fate, as well as human exposure risks, in indoor environment.

3.5. Human exposure to FRs though indoor dust

Given that ingestion of indoor dust represents an important exposure pathway to flame retardants, we estimated the daily intake of FRs via indoor dust ingestion using the following equation (He et al., 2016):

$$EDI = \frac{DIR \times \sum(C_i \times IEF_i)}{BW} \qquad (1)$$

Where EDI is the estimated daily intake (ng/kg body weight/day), C_i is the concentration of a FR chemical in dust from the i microenvironment, IEF_i is the indoor exposure fraction (hours spent over a day in the i environment), DIR is the dust ingestion rate (g/day), and BW is the body weight. We assumed 100% absorption of FRs from ingested dust. The average and high DIR were assumed to be 20 and 50 mg/day for adults and 50 and 200 mg/day for toddlers, respectively (Abdallah and Covaci, 2014; Ali et al., 2013). We also assumed that the average body weights of toddlers and adults are 5 and 63 kg, respectively, based on the provincial average values of Shanghai (Shi et al., 2009). Given the similarity between offices and computer labs in the relative abundance of computers and other electronics, we used the data from computer labs to represent exposure in office environment. We assumed that the adults spend an average of 63.8% of their time at home, 22.3% office, and 4.1% car, whereas for toddlers 86.1% home and 4.1% car (Abdallah et al., 2008; Klepeis et al., 2001).

Therefore, the median daily intake by adults in the present study were estimated to be 0.5, 4.9 and 0.4 ng/kg bw/day for PBDEs, OPFRs, and AFRs under the average exposure scenarios, respectively, and 1.2, 12.2, and 1.0 ng/kg bw/day under the high exposure scenarios (Table 2). Toddlers appeared to be subject to elevated exposure than adults. Their median daily intake of PBDEs, OPFRs and AFRs were estimated to be 16.2, 162.4 and 11.9 ng/kg bw/day

under the average exposure scenarios and 64.6, 649.6, and 47.4 ng/kg bw/day under the high exposure scenarios, respectively. The EDIs of FRs in the present study, even under the high exposure scenarios, were generally 2–4 orders of magnitude lower than the reference doses (in a range of 100–333,000 ng/kg_bw/day) (Ali et al., 2013), indicating the low health risk to dust-associated FRs for general populations in Shanghai. However, potential health risks should not be neglected, given possible additive or synergistic effects among different FRs or between FRs and other toxic chemicals occurring in indoor dust, such as polychlorinated biphenyls (PCBs), perfluorinated chemicals (PFCs), plastic additives, or personal care products (Ali et al., 2013; Fromme et al., 2016; Harrad et al., 2010; Wang et al., 2016). Additionally, long-term exposure to even low dose of FRs may still represent a potential health risk.

4. Conclusions

In summary, our study determined a suite of emerging and legacy flame retardants in dust from dwellings, cars, and computer labs from Shanghai, East China. The results exhibited a consistent dominance of OPFRs over PBDEs and other alternative flame retardants in dust regardless of microenvironments. In addition to OPFRs, some emerging FRs such as DBDPE, BTBPE, EH-TBB, were also frequently detected. Among them, DBDPE was the main contaminant with concentrations comparable to PBDEs. Comparison with domestic and international studies indicated that concentrations of $\sum$PBDEs and $\sum$OPFRs from Chinese dwellings were generally in the middle of concentration ranges reported worldwide, whereas elevated DBDPE was observed in Chinese house dust compared with other countries or regions. OPFR composition profiles in house dust also differed between Chinese data and those from many other countries. These may suggest 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 estimated daily intake in our study was generally 2–4 orders of magnitude lower than the reference doses. Future studies are needed to better elucidate temporal variations of FR contamination levels and

compositions, the occurrence of additional emerging FRs, and potential health risks from co-exposure to FRs and other contaminants.

Acknowledgements

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2017.08.038.

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