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Novel and legacy flame retardants in paired human fingernails and indoor dust samples

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ABSTRACT

In this study, the occurrence of 8 polybrominated diphenyl ethers (PBDEs), 5 alternative flame retardants (AFRs), and 7 organophosphate flame retardants (OPFRs) was determined in 50 pairs of human fingernail and indoor dust samples. The concentrations in fingernail were 9.79–242 ng/g, 17.7–926 ng/g, and 58.0–590 ng/g for PBDEs, AFRs, and OPFRs. Male fingernail showed significantly ($p < 0.05$) higher Σ_8PBDE concentrations than female fingernails, while no significant gender differences were observed for AFRs and OPFRs. Lower ratios of BDE209 to Σ_8PBDE and DBDPE to Σ_5AFRs were found in fingernails than in dust. Due to their relatively rapid *in vivo* debromination, BDE 209 and DBDPE in fingernails were most likely from external sources rather than internal exposure (such as through blood circulation). Similar composition profiles between fingernail and dust were observed for PBDEs (excluding BDE209), AFRs (excluding DBDPE), and OPFRs, indicating that indoor dust may be a significant source for these FRs in human fingernails. Significant correlations between fingernail and dust were observed for BDE 47 ($p < 0.01$; r = 0.50), TBPH ($p < 0.01$; r = 0.37) and TBOEP ($p < 0.01$; r = 0.53). Results in this study provided information about contamination levels and exposure sources of FRs, which is important for long-term biomonitoring and health risk assessment of FRs.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) were widely used as flame retardants (FRs) in a variety of commercial and household products over the past three decades. However, given their bioaccumulation, persistence and potential toxic effects, PBDEs were gradually phased out or restricted from the global market since the mid-2000s (Ali et al., 2011; Rauert et al., 2018). To maintain compliance with flammability standards, alternative flame retardants (AFRs) and organophosphate flame retardants (OPFRs) were introduced to substitute the discontinued PBDEs (Covaci et al, 2011; Van der Veen et al., 2012). FRs are used as additives rather than chemically bonded to the original materials, making them readily releasing into the environment via abrasion or volatilization. Likewise PBDEs, AFRs and OPFRs ubiquitously occurred in indoor dust, air, water, food, and sediment (Cequier et al., 2014; Covaci et al., 2011; Li et al., 2014; Sun et al., 2016; Yu et al., 2012).

Considering the abundant occurrence of FRs in the environment, human exposure to these chemicals is widespread. Growing toxicological studies have showed the adverse effects of exposure to FRs, such as neurotoxicity, carcinogenicity and thyroid endocrine disruption (Dingemans, et al., 2011; Van der Veen et al., 2012; Wang et al., 2019). Hence, human exposure to FRs deserve more attention to accurately determine potential health risks. There is an increasing number of studies using biomarkers, including blood, urine, breast milk, and hair, to monitor FR levels in humans (Carrizo et al., 2007; Fromme et al., 2014; Kim et al., 2012). Due to the advantages of being easy and inexpensive to collect and convenient to transport and store, fingernails are becoming a popular non-invasive alternative biomarker for serum and urine. Fingernails have low metabolic activities, resulting in that the chemicals are relatively unchanged in levels once absorbed into keratin of fingernails (Liu et al., 2016). Several studies have reported the levels of organic pollutants (e.g. phthalates and perfluoroalkyl compounds) in fingernails (Alves et al., 2016; Liu et al., 2011). Recent study observed the significantly positive correlation of several PBDE congeners between fingernails and serum samples, showing fingernails can be used as a non-invasive biomarker for FRs (Liu et al., 2016). However, the data about FR occurrence in human fingernails are very

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limited, and this information clearly can provide essential benefits for developing long-term biomonitoring and understanding the adverse effect of FRs.

On the other hand, widespread use of FRs in household products resulted in their accumulation in indoor dust. Growing studies have showed that indoor dust was a significant sink and exposure source of FRs (Ali et al., 2011; Huang et al., 2010; Jiang et al., 2014). Dust-associated FRs represent a considerable risk to humans, since they can enter the body via absorption through the skin, and unintentional ingestion or inhalation. Significant associations of TDCIPP and TPhP concentrations between indoor dust and urine/serum have been observed, indicating that dust was the major source for these OPFRs in human body (Carignan et al., 2013). However, the correlation between dust and human internal FRs has not been always found for all FRs (Tan et al., 2018), suggesting that the major exposure pathway may be variable among FRs. Therefore, investigating the association of FRs between paired human fingernail and indoor dust samples in the current study may provide some insight for understanding exposure pathways for different FR compounds.

In the present study, 50 pairs of human fingernail and household dust samples were collected during 2016 in Nanjing, China. The main objectives were to 1) determine the occurrence of FRs (namely PBDEs, AFRs, and OPFRs) in fingernail samples; and 2) investigate the association between FR levels in fingernail and dust samples. Results in the current work can provide a more in-depth assessment on human exposure pathways to FRs.

2. Materials and methods

2.1. Fingernail and dust sampling

Totally 50 paired dust and fingernail samples were collected from resident houses (n = 27) in Nanjing, China as well as undergraduate/graduate student dormitories (n = 23) in Nanjing University, Xianlin Campus, during June-September 2016. Fifty fingernail samples (no nail polish) were collected from apparently healthy individuals in each sampling site. None of the participants worked in the production of FRs or FR-related products. The participants were asked to wash their hands before clipping fingernails of ten fingers with a stainless steel nail clipper. The fingernail samples were packed in clean aluminum foil and stored at −20 °C until analysis. Information about age, weigh, height, and gender of fingernail donors was collected by questionnaire (Detailed information is listed in Table S1 of supporting information). Dust samples were collected from floors of living rooms and bedrooms by vacuum cleaner, which was pre-cleaned before each sampling. To avoid the variation among different sampling procedures, all the dust samples were collected by the same person (one of the authors) using the same vacuum cleaner. About 1–2 g dust samples were obtained from vacuum cleaner bags for each sampling site, packed in clean aluminum foil, and sent to laboratory immediately after sampling. Dust samples were homogenized, sieved through a 150 μm stainless sieve, and stored at −20 °C until analysis.

2.2. Chemicals and reagents

In this study, 8 PBDEs, 5 AFRs, and 7 OPFRs were investigated as the target FRs. Detailed information about the analytes of interest is found in *"Chemicals"* of the Supporting Information. Surrogate standards, including $^{13}C_{12}$-BDE 28, $^{13}C_{12}$-BDE 47, $^{13}C_{12}$-BDE 99, $^{13}C_{12}$-BDE 100, $^{13}C_{12}$-BDE 153, $^{13}C_{12}$-BDE 154, $^{13}C_{12}$-BDE 183, $^{13}C_{12}$-BDE 209, d_{12}-TCEP and d27-TBP were obtained from Cambridge Isotope Laboratories (Andover, MA). Organic solvents including n-hexane, dichloromethane, and methanol were HPLC grade and purchased from J.T. Baker (Phillipsburg, NJ, USA). Milli-Q water was generated by Millipore ultrapure water system (Dubuque, IA, USA). Stock solutions were prepared in n-hexane (for PBDEs and AFRs) and in methanol (for OPs) at a concentration of 100 μg/mL for further dilution.

2.3. Sample treatment and analysis

In our preliminary test, the washing efficiency of external contamination was conducted for fingernails. Briefly, 9 fingernails samples (out of the 50 fingernail samples used in the current study) were randomly collected from graduate students and professors at the School of the Environment, Nanjing University. These fingernail samples were divided into 3 treatments, i.e., non-washed, and washed in ultrasound with water or washed with 1% Triton-100, respectively. The results showed that the removal efficiency varied among OPFRs and washing reagents, while for PBDEs and AFRs, no statistical differences was found among the 3 treatments (Table S2). No washing procedure was therefore conducted before fingernail extraction. The extraction for fingernail and dust samples was performed based on the previously published procedure with slight modifications (Kucharska et al., 2015). Fingernail samples were cut into pieces < 1 mm by stainless steel scissors before extraction. Briefly, around 50 mg of dust or fingernails were accurately weighted into a 15-mL glass tube and spiked with 50 ng mixture of internal standards. The samples were soaked overnight in 5 mL of dichloromethane/n-hexane (3:1, v/v) to improve the extraction efficiency. The mixture was then sonicated for 30 min in sonication bath and centrifuged at 3000 rpm for 10 min. The supernatant was transferred into a 15-mL glass tube. Each sample was extracted for two more times with 5 mL of dichloromethane/n-hexane (3:1, v/v). The extracts were combined, concentrated to near-dryness under nitrogen gas stream, and reconstituted with 0.5 mL of n-hexane. An aliquot of 200 μL reconstituted solution was solvent changed to methanol/H_2O (1:1, v/v) for analysis of OPFRs, and the hexane fraction was analyzed by GC/MS for PBDEs and AFRs. The detailed information about instrumental analysis is found in Supporting Information. All the PBDEs were quantified through their corresponding labeled compounds as internal standards (IS, i.e., $^{13}C_{12}$-BDE 28, $^{13}C_{12}$-BDE 47, $^{13}C_{12}$-BDE 99, $^{13}C_{12}$-BDE 100, $^{13}C_{12}$-BDE 153, $^{13}C_{12}$-BDE 154, $^{13}C_{12}$-BDE 183 and $^{13}C_{12}$-BDE 209). For AFRs and OPFRs, HBB was quantified with $^{13}C_{12}$-BDE47 as IS; TBB was quantified with$^{13}C_{12}$-BDE 99; TBPH and DP were quantified with $^{13}C_{12}$-BDE 183; DBDPE was quantified with $^{13}C_{12}$-BDE 209; TCIPP and TPrP were quantified with d_{12}-TCEP; TPHP, TDCIPP, TBOEP and TBP were quantified with d_{27}-TBP.

2.4. Quality assurance and quality control

For each batch of 20 samples, a procedural blank and a duplicate sample were analyzed. The levels of target analytes in procedural blanks were below the limit of detection and the relative standard deviation of duplicate samples was less than 10%. Recoveries of all target chemicals (50 ng for each individual standard) in spiked blanks (replacing dust or fingernail with sodium sulfate) ranged from 90 ± 8.1% for BDE 28 to 112 ± 5.4% for TBPH. Recoveries of matrix spiked samples (50 ng for each standard) through the analytical procedure in fingernail and dust samples ranged from 64 ± 4.6% for TCEP to 115 ± 8.3% for TBPH, and 69 ± 5.8% for TCEP to 121 ± 2.9% for TBB, respectively (Table S3). The recoveries of the internal standards ranged from 61 ± 7.4% for d_{12}-TCEP to 117 ± 19% for $^{13}C_{12}$-BDE 183 for all fingernail and dust samples. A standard solution of medium concentration (5 ng/mL) was injected to check the stability of instrumental response with each batch of 20 samples. A calibration curve for all analytes was prepared at concentrations ranging from 0.5 to 200 ng/mL (totally nine level points, including 0.5, 1, 2, 5, 10, 20, 50, 100, 200 ng/mL), and the regression coefficients of calibration standards were all > 0.99. The limit of quantitation (LOQ) was determined based on signal-to-noise ratio of 10:1 (Table S3).

Table 1
Summary of PBDE, AFR, and OPFR concentrations in fingernail and indoor dust samples (ng/g).

	Fingernails (n = 50)				Dust (n = 50)			
	Median	GM	Range	DF[c]	Median	GM[a]	Range	DF
BDE28	1.13	0.63	< 0.03–19.7	66	3.61	2.19	0.12–73.4	98
BDE47	4.45	3.65	0.78–26.3	76	5.44	7.59	0.17–188	96
BDE100	1.02	1.52	< 0.05–29.7	18	1.86	1.93	0.15–1160	72
BDE99	2.23	2.95	< 0.06–39.4	56	5.91	5.44	0.22–624	92
BDE154	0.78	0.97	< 0.17–9.33	26	2.66	3.00	0.54–43.1	68
BDE153	1.63	2.52	0.44–186	62	17.9	16.2	0.67–698	88
BDE183	1.19	1.52	0.36–28.3	22	4.75	4.98	1.34–60.8	94
BDE209	12.7	13.2	1.67–199	88	415	401	60.4–3870	100
Σ_8PBDEs[b]	36.3	38.8	9.79–242	–	531	548	71.1–4035	–
HBB	25.5	18.8	0.32–177	98	71.2	54.4	3.11–619	98
TBB	26.7	18.9	1.67–258	92	81.1	77.4	1.91–3131	96
TBPH	28.1	36.2	4.21–689	100	85.1	76.8	3.17–652	100
DP	1.22	1.75	< 0.30–48.7	8	19.8	12.8	0.99–457	56
DBDPE	7.47	10.1	3.43–409	54	108	95.9	5.07–2301	86
Σ_5AFRs[b]	119	126	17.7–926	–	392	458	48.5–3915	–
TCEP	34.3	42.5	13.03–141	100	286	450	54.1–3692	100
TCIPP	52.4	70.5	16.67–298	100	520	671	72.1–2461	100
TPhP	19.6	33.4	3.50–232	100	184	365	58.3–4097	100
TPrP	0.08	0.25	< 0.02–1.83	90	0.30	1.00	< 0.02–7.35	94
TDCIPP	3.58	7.55	< 0.11–54.4	100	74.5	138	22.2–1078	100
TBOEP	2.25	7.94	0.49–87.3	100	40.3	90.4	6.18–582	100
TBP	12.7	18.5	4.81–101	100	19.8	38.2	6.47–334	100
Σ_7OPFRs[b]	150	181	58.0–590	–	1218	1753	331–6362	–

[a] Geometric mean.
[b] Σ_8PBDEs, Σ_5AFRs, Σ_7OPFRs: the sum concentrations of PBDEs, AFRs, and OPFRs, respectively.
[c] Detection frequency.

2.5. Data analysis

All statistical data analysis was performed with SPSS 20.0 (SPSS Inc., Chicago, IL, USA). When the concentrations were below LOQs, half of the LOQ values were used for calculation and statistical analysis. Mann–Whitney *U* test (for non-normally distributed data) and one-way ANOVA (for normally distributed data) were used to investigate the differences in the FR levels in fingernail samples between different gender and age groups. Spearman correlation coefficient was used to assess the association between FR concentrations in fingernail and dust samples. The statistical significance level was set as $p < 0.05$.

3. Results and discussion

3.1. Occurrence of flame retardants in fingernails

The statistical descriptions for the concentrations of FRs in fingernails samples (median, range and detection frequency (DF)) are shown in Table 1. PBDEs were frequently detected (DF = 56–88%) in fingernail samples, except BDE 100, BDE 154 and BDE 183 with DF of < 26%. The total concentrations of eight PBDEs varied greatly and ranged from 9.79 to 242 ng/g (median: 36.3 ng/g). Among the analyzed PBDEs, BDE 209 (DF = 88%, 12.7 ng/g) exhibited the highest median level, followed by BDE 47 (4.45 ng/g), BDE 99 (2.23 ng/g), BDE 153 (1.63 ng/g), BDE 183 (1.19 ng/g), BDE 28 (1.13 ng/g), BDE 100 (1.02 ng/g) and BDE 154 (0.78 ng/g). The levels of individual PBDEs were compared with those reported in American fingernail samples. The BDE 47 and BDE 99 concentrations were considerably lower than those in U.S. (fingernails: 23 and 14 ng/g for BDE 47 and 99), which can be attributed to the large amount use of Penta-BDE in U.S (Liu et al., 2016). It was reported that North America was the largest consumer market of Penta-BDE mixture, accounting for about 95% of sales in 2001 (Birnbaum and Staskal, 2004). BDE 209 was the most abundant congener in fingernails samples, which was different from the previously reported results for serum samples. For example, both concentrations and DF of BDE 209 were relatively low (< 10% for DF) in serum samples (Kim et al., 2012; Johnson et al., 2010), which may be ascribed to the rapid debromination of BDE 209 (Thuresson et al., 2005). Contaminants in fingernail can be from both internal and external sources, i.e., contaminants can accumulate in fingernails through the blood stream following inhalation or ingestion, or absorbed/deposited from external contamination (Esteban and Castaño, 2009). Therefore, the relatively higher BDE 209 levels in fingernails here may mainly be attributed to external sources rather than to internal exposure through the blood.

For AFRs, a relatively low DF (54%) was found for DBDPE with median level of 7.47 ng/g. DBDPE was extensively used as a substitution for Deca-BDE in electronics, the relatively lower DF of DBDPE may be attributed to its lower bioaccumulation potential and uptake rate constants (Li et al., 2014). In addition, DBDPE is more resistant to dermal uptake than BDE 209 due to its higher log Kow (Frederiksen et al., 2016). TBPH, TBB and HBB were the most frequently detected AFRs (DF > 92%), with median values of 28.1, 26.7 and 25.5 ng/g, respectively. The concentrations of TBPH were significantly positively correlated with those of TBB ($r = 0.35$, $p < 0.05$), suggesting that these two compounds may share similar sources. TBPH, together with TBB, is commonly used in commercial products Firemaster 550 (ratio 1:4) as a substitute for Penta-BDE in polyurethane foam (Covaci et al., 2011). The concentration of TBPH was slightly higher than that of TBB (ratio 1:0.95) in present study. This may be explained by the different metabolism potentials for TBPH and TBB. For example, TBPH was resistant to metabolic degradation, but TBB was more readily metabolized to 2,3,4,5-tetrabromobenzoic acid in humans and rat subcellular hepatic fractions (Roberts et al., 2012). In addition, there may be other sources of TBPH, including Firemaster BZ-54 (TBPH:TBB, 1:2.5), DP-45 (100% TBPH), and plasticizer in polyvinyl chloride and neoprene (Zheng et al., 2015). As a replacement for Penta-BDE, the sum of TBB and TBPH was 70.31 ng/g in median, and 7 times higher than those of penta-BDE congeners (sum of BDE 47, 99, 100, 153 and 154 with median of 13.8 ng/g) in fingernails samples ($p < 0.001$). This suggests, to some extent, the gradual replacement of Penta-BDE by Firemaster 550 in the market consumption. Of course, the different concentrations

observed here may also be attributed to the variation of exposure sources and metabolism rates between Firemaster 550 and Penta-BDE, which imply the necessity of further studies to identify the *in vivo* biotransformation characteristics of these compounds.

OPFRs were detected in almost all fingernail samples (DF > 90%), and the Σ_7OPFRs concentration ranged from 58.0 to 590 ng/g, with a median of 150 ng/g. Levels of individual OPFR compounds were much lower than those reported in America (Liu et al., 2016). TCIPP was the primary OPFRs with a median level of 52.4 ng/g. TCIPP was widely used in flexible polyurethane foams and polyisocyanate insulation and, for some applications, also as a replacement for TCEP (van der Veen et al., 2012). In fingernail samples, TCEP was present at the secondly high median level of 34.3 ng/g, followed by TPhP (19.6 ng/g), TBP (12.7 ng/g), TDCIPP (3.58 ng/g), TBOEP (2.25 ng/g), and TPrP (0.08 ng/g). In general, OPFRs were the dominant FRs, and the Σ_7OPFRs concentrations (150 ng/g) were significantly higher than the other two classes of FRs (PBDE = 36.3 ng/g, AFR = 119 ng/g) in fingernail samples ($p < 0.05$). Liu et al. (2016) have reported similar results in fingernail and hair samples collected from the USA. In a study conducted in the global atmospheric samples, OPFR concentrations were at least one order of magnitude higher than the PBDEs (Rauert et al., 2018). These results suggested the historical changes of FR application in household and commercial products, i.e., OPFRs are the gradual replacement for PBDEs.

3.2. Gender- and age-related patterns of flame retardants

Gender and age are considered as two important factors affecting organic pollutants levels in the human body (Kim et al., 2012; Schiavone et al., 2010). Mann-Whitney *U* test was conducted to examine gender-related patterns of FR concentrations (Fig. 1). No significant difference was observed between male and females for both AFRs and OPFRs ($p > 0.05$), while significantly higher Σ_8PBDE concentrations were found in fingernail samples from males than females ($p < 0.05$). Information on PBDE levels in fingernail samples is rather limited in the literature. Previous studies both from Korea and New Zealand reported that males also had higher PBDE concentrations than females in serum samples collected from general population (Kim et al., 2012; Harrad et al., 2007). The differences were explained by the different physiological characteristic between males and females. Females have the ability to excrete PBDEs via breast feeding and placenta transfer, as well as menstruation (Strandman et al., 2000). For example, PBDE concentrations in the sera of 4 year old children fed with maternal milk were reportedly higher than those with baby formula (Carrizo et al., 2007). On the other hand, the different dermal uptake efficiency can be another explanation. Females use more personal care

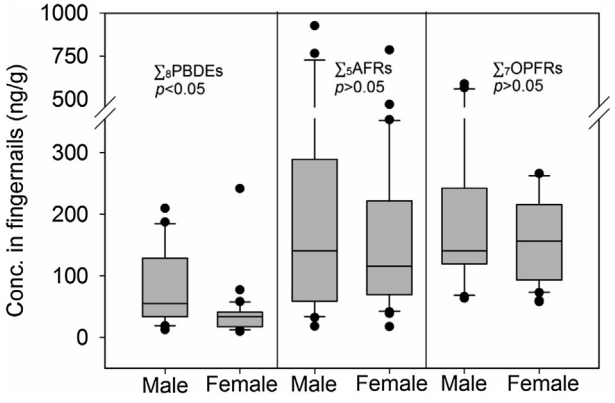

Fig. 1. Concentrations of Σ_8PBDEs, Σ_5AFRs, and Σ_7OPFRs in fingernail samples (n = 50) for different gender groups (ng/g). The horizontal lines represent 10th, 50th, and 90th percentiles and the boxes represent 25th and 75th percentiles. Outliers are shown as individual points.

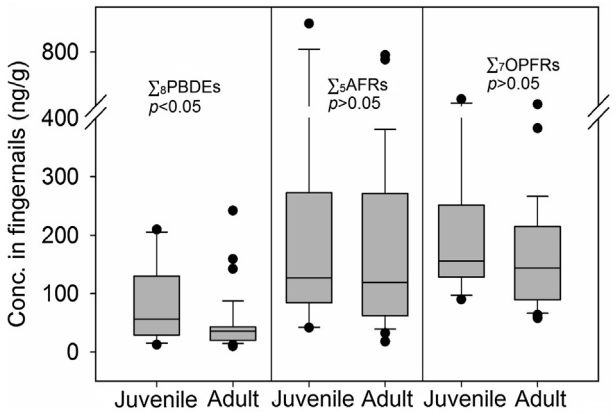

Fig. 2. Concentrations of Σ_8PBDEs, Σ_5AFRs, and Σ_7OPFRs in fingernail samples (n = 50) for different age groups (juvenile: 4–18 years old; adult: > 18 years old) (ng/g). The horizontal lines represent 10th, 50th, and 90th percentiles and the boxes represent 25th and 75th percentiles. Outliers are shown as individual points.

products than males, and these products may decrease the dermal uptake of FRs. For example, hand cream decreased the levels of BDE 100, 154, 209 in hand wipes (Tay et al., 2018), possibly due to the retain of lipophilic chemicals by lipids in hand cream (Pawar et al., 2017). In addition, for very lipophilic compounds, decreased dermal uptake was observed with increasing log Kow (6.43–11.96) (Frederiksen et al., 2016). The most efficient dermal uptake of human skin has been proved for compounds with a moderate hydrophilicity (WHO, 2006). When compared with PBDEs, relatively higher lipophilicity of AFRs may inhibit their dermal uptake, which may be the reason that no significant gender difference observed for AFRs.

To explore the influence of age, the sample providers were divided into two age groups, i.e., juvenile (4–18 years old, n = 11), and adult (> 18 years old, n = 39). As shown in Fig. 2, the PBDE levels in the juvenile group were significantly higher than those in adult group ($p < 0.05$), but no significant difference with age was found for AFRs and OPFRs ($p > 0.05$). Similar age-related patterns were previously found also in other matrices. Sjödin et al. (2008) investigated PBDE exposure in the American population and observed a linear decrease in PBDE concentration from 12 to 19 year group to 40–59 year group, and then increased quadratically for the > 60 year group. In the present study, all participants, except for one aged at 62 years, were younger than 40, and the decrease of PBDEs with age observed here was consistent with the previous reports. The negative correlations of PBDEs levels with age may be associated with the lifestyle and activity differences, including elevated hand-mouth contact behavior and increased dust exposure of children. Since AFRs and OPFRs are both relatively novel compounds as the substitution of PBDEs, the effect of age on AFRs and OPFRs levels may not have been apparent. In addition, OPFRs were readily metabolized and excreted in the form of dialkyl or diaryl phosphate metabolites after entering the human body (van der Veen et al., 2012). The higher metabolic rate of children than adults may also diminish age-dependent accumulation of OPFRs (Miller et al., 2002). Of note is that relatively small sample size and age span in the current study may also affect statistical analysis.

3.3. Occurrence of flame retardants in dust samples

The concentrations of Σ_8PBDEs in dust samples varied greatly and ranged from 71.1 to 4035 ng/g (Table 1). The median levels of PBDEs (531 ng/g) in the present study were considerably lower than those from other regions in China, such as Guangzhou (2686 ng/g), Haikou (1088 ng/g), Wuhan (844 ng/g), but higher than that from Hangzhou (239 ng/g) (Huang et al., 2010; Sun et al., 2016). BDE 209 was the most

abundant PBDE with the median level of 415 ng/g, which was the same order of magnitude with that in Hangzhou (229 ng/g), Shanghai (summer: 794 ng/g), and Wuhan (831 ng/g) of China (Huang et al., 2010; Sun et al., 2016; Yu et al., 2012).

For AFR congeners, the concentration of Σ_5AFRs ranged from 48.5 to 3915 ng/g, with the median level of 392 ng/g. The highest concentration was found for DBDPE (108 ng/g), followed by TBPH (85.1 ng/g), TBB (81.1 ng/g), HBB (71.2 ng/g), and DP (19.8 ng/g). It is not surprising because DBDPE was widely used as a replacement for Deca-BDE in China, and its application rate was growing at an annual rate of 80% in recent years (Qi et al., 2014). The median level of DBDPE in present study was comparable to those reported in the house dusts collected from UK (98 ng/g), Belgium (150 ng/g), Czechia (140 ng/g), the US (140 ng/g), and China (280 ng/g; 23 provinces) (Ali et al., 2011; Dodson et al., 2012; Kalachova et al., 2012; Qi et al., 2014). In addition, we also found the associations between the level of PBDEs and the corresponding substitutes. TBPH exhibited significant correlations with individual Penta-BDE (99, 100, 154 and 153; $p < 0.05$, r = 0.35–0.66). Similarly, significant correlations were observed for TBB with BDE 154 ($p < 0.01$; r = 0.50), and DBDPE was significantly correlated with BDE 209 ($p < 0.01$; r = 0.45). This suggested that the substitutes are gradually replacing the use of PBDE in household products in Chinese market.

Levels of Σ_7OPFRs ranged from 331 to 6362 ng/g. The most abundant OPFRs in dust were TCIPP, TCEP, and TPhP found at median levels of 520, 286, and 184 ng/g, respectively. The median level of Σ_7OPFRs in dust samples was significantly higher than that of Σ_8PBDEs ($p < 0.01$) and Σ_5AFRs ($p < 0.01$), which was consistent with the results in fingernail samples. Similar result was also reported in household dusts from South China, and the concentration of ΣOPFRs (9200 ng/g) was one order of magnitude greater than that of ΣPBDEs (800 ng/g) (Tan et al., 2017). These studies indicated that OPFRs may be more widely used than PBDEs and AFRs. Albeit the data on consumption was lacking in China, the market consumption of OPFRs exceeded that of PBDE mixtures in Europe (Tan et al., 2017). Moreover, some non-halogenated OPFRs, such as TPhP and TBOEP, are not only used as FRs, but also used as plasticizers in PVC, rubber, and lubricants (van der Veen et al., 2012).

3.4. Comparison of flame retardant composition profiles between fingernail and dust

The composition profiles of FRs between fingernail and dust samples are shown in Fig. 3. For PBDEs, BDE 209 was predominant analogue in dust samples, accounting for 90.8% of the Σ_8PBDEs, followed by BDE 153 (3.9%), BDE 99 (1.3%), and BDE 47 (1.2%). However, BDE 209 only contributed 50.5% of the total PBDEs in fingernails samples, followed by BDE 47 (17.7%), BDE 99 (8.9%), BDE 153 (6.5%). *In vivo* studies have reported that BDE 209 has a relatively short half-life (about 15 days), and be readily debrominated to form low brominated congeners in the human body (Thuresson et al., 2005). Moreover, the absorption of BDE 209 in the human digestive system was less effective than other lower brominated PBDEs (Munschy et al., 2011). For example, only about 10% of the BDE 209 dose was absorbed in rats and 90% of the exposure dose was excreted through feces, suggesting its lower bioaccumulation potential (Morck et al., 2003). This is consistent with previous results in serum samples, where BDE 209 made only a small contribution to total PBDEs (< 21%) even with the median levels being lower than the LOD (Johnson et al., 2010; Kim et al., 2012; Liu et al., 2016). Therefore, the BDE 209 found in fingernails may mainly be from external sources, such as contacting dusts or products containing BDE 209, instead of deposition through blood circulation. When excluding BDE 209, similar distribution pattern between fingernail and dust samples was found for all the other BDE congeners except BDE 47 and 153 (Fig. 3). BDE 47 contributed 35.8% to Σ_7PBDEs in fingernail samples, but only accounted for 12.9% in dust samples. The higher

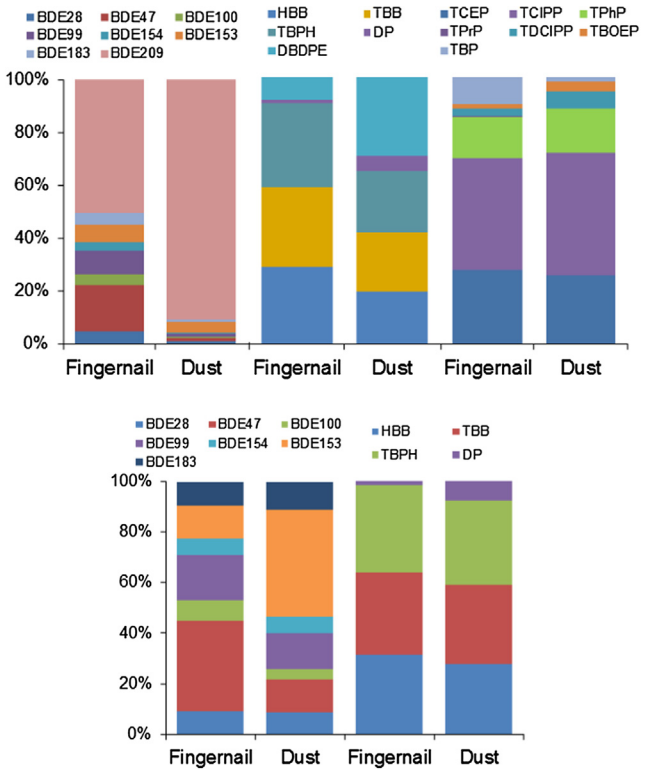

Fig. 3. Composition profiles of PBDEs, AFRs, and OPFRs (up), and composition profiles of PBDEs and AFRs when not considering BDE 209 and DBDPE in fingernail and indoor dust samples (down) (fingernails: n = 50; dust: n = 50).

proportion of BDE 47 in fingernail samples may be attributed to the fact that BDE 47 is the *in vivo* debromination product of higher brominated PBDEs. For examples, an animal study showed that BDE 47 contributed > 50% in the debromination products of BDE 153 in different tissues (Zhang et al., 2014).

For AFRs, the most abundant compound was DBDPE in dust samples, representing 29.5% of Σ_5AFRs, whereas in fingernail samples DBDPE only accounted for 8.4%. Similar with BDE 209, DBDPE was not detected in any serum samples from Tianjin, China, neither from Norway (Cequier et al., 2015; Zhu et al., 2009). BDE 209 and DBDPE have similar chemical structures, but the inclusion of the ethane bridge between the aromatic rings makes DBDPE more hydrophobic and less bioaccumulative than BDE 209 in the oligochaete (Li et al., 2014). DBDPE has high molecular weight and log Kow, which limit its dermal absorption (Frederiksen et al., 2016). The lower bioaccumulation and limited dermal uptake of DBDPE can explain the lower DF and levels in fingernail compared to BDE 209. The distribution pattern in fingernail samples was similar to that in dust samples when excluding DBDPE, indicating that dust may be a significant source for the other four AFRs (namely TBPH, TBB, HBB, and DP) in fingernail (Fig. 3). TBPH and TBB were the dominant compounds in fingernail samples, accounting for 31.5% and 29.9% of the Σ_5AFRs, respectively. Human data for TBPH and TBB were scarce, except for one study in which TBPH and TBB were detected in 16.7% and 56.9% serum samples with a low median level of 1.6 ng/g lipid weight (Zhou et al., 2014).

OPFRs shared a similar distribution pattern in fingernail and dust samples, in which TCIPP, TCEP, and TPhP were the most abundant compounds. TCIPP, TCEP and TPhP accounted for 46.2%, 25.4% and 16.4% of the Σ_7OPFRs in the dust samples, and 41.9%, 27.5% and 15.7% in fingernail samples, respectively. This result indicated that OPFRs in fingernail are most likely from external exposure (absorbed into keratin of nails) to environmental media, such as dust and air. Given short half-lives (several hours) and the rapid metabolism in the

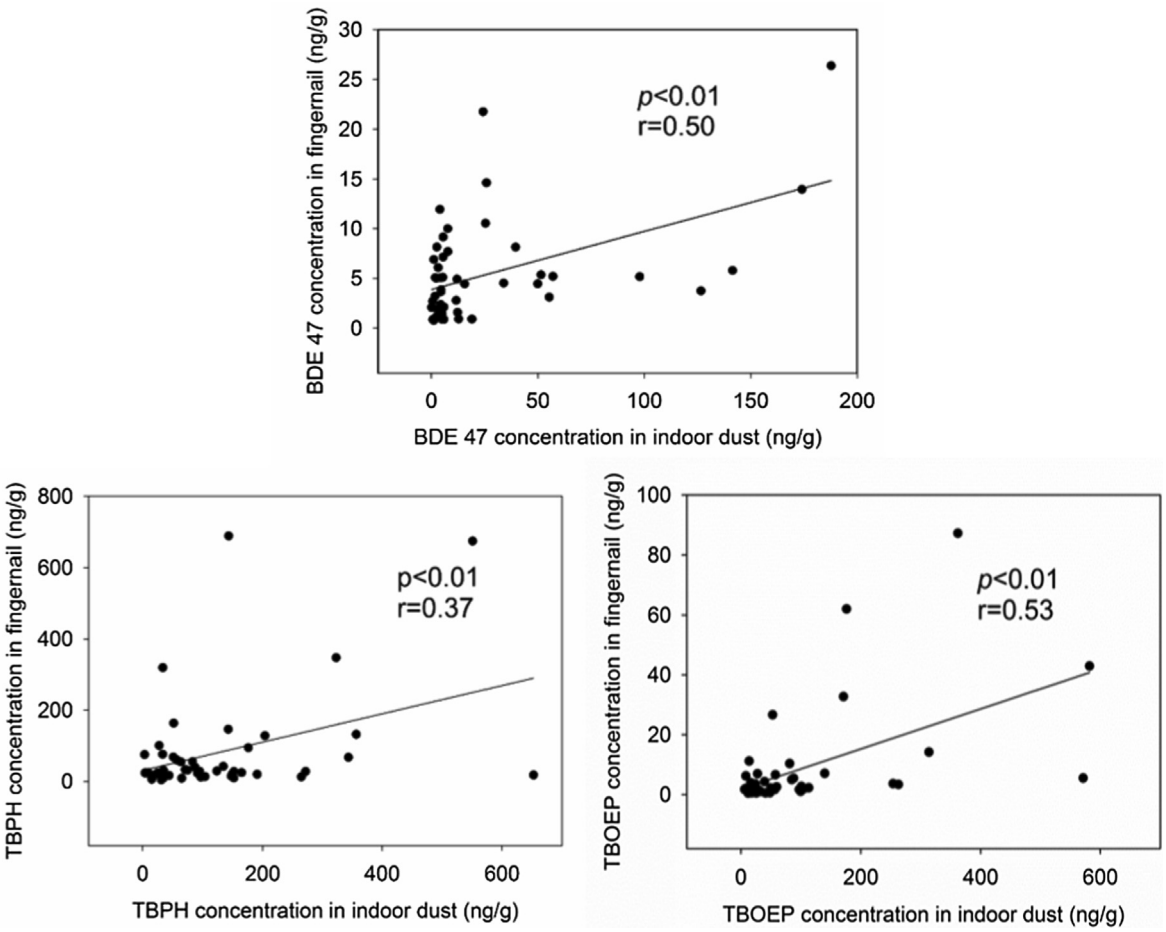

Fig. 4. Correlation analysis of BDE47, TBPH and TBOEP concentrations in fingernail samples versus those in indoor dusts.

body, it is difficult for OPFRs to be transported through the body and reach the nails. Liu et al. (2016) collected nail, hair, and serum samples from 50 healthy participants, but could not detect OPFRs in serum samples, suggesting OPFRs are readily undergo hydrolysis and are excreted (Kim et al., 2012). It is interesting that only TBP was much less abundant in dust samples (1.7%) than in fingernail samples (10.2%). The relatively high volatility allows TBP to volatilize out of products containing TBP and to rapidly diffuse into the air (van der Veen et al., 2012), indicating that air and product containing TBP, besides dust, may be another important sources for TBP detected in fingernail samples.

3.5. Correlation between levels of flame retardants in fingernail and dust samples

The Spearman's rank correlation coefficient was used to investigate the relationships between paired fingernail and dust samples for FRs. Significant correlations were obtained between FR levels in fingernail and dust samples for BDE 47 ($p < 0.01$; r = 0.50), TBPH ($p < 0.01$; r = 0.37), and TBOEP ($p < 0.01$, r = 0.53) (Fig. 4). Similar results were observed in previous studies, even very limited, for dust and human samples. For example, a previous study in Poland found significant positive correlation between the concentration levels for BDE 47 ($p = 0.05$) in dust and hair samples (Król et al., 2014). For OPFRs, significant correlations were only found between TBOEP levels in dust and the bis-(2-butoxyethyl) phosphate (BBOEP, the metabolite of TBOEP) levels in urine from German children (Fromme et al., 2014). Compared to other PBDE congeners, BDE 47 was not readily metabolized, and was excreted mainly as parent compound in both urine and feces in mice (Staskal et al., 2006). In *vitro* and *in vivo* studies showed that TBPH was resistant to metabolic degradation (Bearr et al., 2010; Roberts et al., 2012). Among the target OPFRs, TBOEP has a relatively high log K_{ow} (3.65) and the highest bioaccumulation factor (1080), suggesting that TBOEP can stay for a longer time in human body (van der Veen et al., 2012). As a result, the significant correlations showed that indoor dust played an important role in the exposure of BDE 47, TBPH, and TBOEP via pathways, such as dust ingestion/inhalation and dust contact.

No statistically significant correlations could be found between levels of other FRs in fingernail and dust samples, possibly due to several reasons. First, indoor dust may be not the major source for some FRs in fingernails. For example, dietary ingestion, particularly rice ingestion, was reported to be a more important exposure pathway for OPFRs than dust in China (Zhang et al., 2016). Consumption of high-fat foods like meat, fish and breast milk was also considered to be a significant route for human exposure to PBDEs and AFRs due to their high hydrophobicity (Daso et al., 2010). For the FRs with relatively high volatility, such as TBP, air may contribute more to the human exposure than dust. Secondly, the bioaccessibility of FRs in dust may be one of the most important constraints for accurate exposure assessment when considering the hydrophobicity of FRs. Therefore, the bioaccessibility of FRs in dust samples were also measured by Tenax-assisted physiologically based extraction test (TA-PBET, Li et al., 2016). Due to the very limited dust mass, only 12 dust samples with relatively large quantity was adopted to measure the FR bioaccessibility (Fig. S1). Stronger correlations between fingernail versus dust samples were observed for in 12 of 20 target FRs if using bioaccessible instead of total concentrations in dust samples (Table S5). For example, the correlation coefficient for BDE 183 increased from 0.18 ($p > 0.05$) to 0.64 ($p < 0.05$) when considering the bioaccessibility in dust. This result

indicated that it may be more accurate to analyze the correlation of FRs in fingernail and dusts based on their bioaccessibility in dust, if available. However, more studies with larger sample size are needed to confirm this hypothesis. Finally, only dust samples from living place were collected, but people are active at different microenvironments (e.g., workplace, school, and automobiles). On the other hand, FRs in fingernail reflect exposure not solely at home/dormitory, but the integrated exposure from multiple microenvironments. This may also be one of the reasons for not observing correlations between fingernail and indoor dust for some FRs. However, it should be noted that the inclusion of more dust from multiple microenvironments is challenging for sampling and may introduce additional uncertainty for statistics analysis.

In this study, the extensive occurrence and high levels of FRs in fingernails imply the potential health risks associated with FR exposure. On the other hand, the results also suggest, to some extent, the feasibility of fingernails used as biomarker for human exposure to FRs, which is beneficial for long-term epidemiological studies. The comparison between paired fingernail and dust samples in present study can reflect the sources of exposure to FRs. For example, compounds with rapid metabolism and low bioaccumulation potential, such as BDE 209, DBDPE and OPFRs, may mainly from external sources (e.g., contacting with dust or FR-containing products), while for other FRs, both external and internal sources (e.g., dust ingestion/inhalation) contributed to the levels in fingernails. This result here can also inform potential interventions aimed at reducing exposures and health risks associated with FRs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article include chemicals, instrumental analysis, bioaccessibility measurement, Tables S1, S2, S3, S4, S5, and Fig. S1. Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2019.105227.

References

Ali, N., Harrad, S., Goosey, E., Neels, H., Covaci, A., 2011. "Novel" brominated flame retardants in Belgian and UK indoor dust: implications for human exposure. Chemosphere 83, 1360–1365.
Alves, A., Covaci, A., Voorspoels, S., 2016. Are nails a valuable non-invasive alternative for estimating human exposure to phthalate esters? Environ. Res. 151, 184–194.
Bearr, J.S., Stapleton, H.M., Mitchelmore, C.L., 2010. Accumulation and DNA damage in fathead minnows (Pimephales promelas) exposed to 2 brominated flame-retardant mixtures, Firemaster® 550 and Firemaster® BZ-54. Environ. Toxicol. Chem. 29, 722–729.
Birnbaum, L.S., Staskal, D.F., 2004. Brominated flame retardants: cause for concern? Environ. Health. Persp. 112, 9–17.
Carrizo, D., Grimalt, J.O., Ribas-Fito, N., Sunyer, J., Torrent, M., 2007. Influence of breast feeding in the accumulation of polybromodiphenyl ethers during the first years of child growth. Environ. Sci. Technol. 41 (14), 4907–4912.
Carignan, C., McClean, M.D., Cooper, E.M., Watkins, D.J., Fraser, A.J., Heiger-Bernays, W., Stapleton, H.M., Webster, T.F., 2013. Predictors of tris(1,3-dichloro-2-propyl) phosphate metabolite in the urine of office workers. Environ. Int. 55, 56–61.
Cequier, E., Ionas, A.C., Covaci, A., Marcé, R.M., Becher, G., Thomsen, C., 2014. Occurrence of a broad range of legacy and emerging flame retardants in indoor environments in Norway. Environ. Sci. Technol. 48 (12), 6827–6835.
Cequier, E., Marcé, R.M., Becher, G., Thomsen, C., 2015. Comparing human exposure to emerging and legacy flame retardants from the indoor environment and diet with concentrations measured in serum. Environ. Int. 74, 54–59.
Covaci, A., Harrad, S., Abdallah, M.A.E., Ali, N., Law, R.J., Herzke, D., de Wit, C.A., 2011. Novel brominated flame retardants: A review of their analysis, environmental fate and behaviour. Environ. Int. 37 (2), 532–556.
Daso, A.P., Fatoki, O.S., Odendaal, J.P., Okonkwo, J.O., 2010. A review on sources of brominated flame retardants and routes of human exposure with emphasis on polybrominated diphenyl ethers. Environ Rev. 18, 239–254.
World Health Organization (WHO), 2006. Dermal absorption. Environ. Health Criteria 235.
Dingemans, M.M.L., van den Berg, M., Westerink, R.H.S., 2011. Neurotoxicity of brominated flame retardants: (In)direct effects of parent and hydroxylated polybrominated diphenyl ethers on the (developing) nervous system. Environ. Health Perspect. 119 (7), 900–907.
Dodson, R.E., Perovich, L.J., Covaci, A., Van den Eede, N., Ionas, A.C., Dirtu, A.C., Brody, J.G., Rudel, R.A., 2012. After the PBDE phase-out: a broad suite of flame retardants in repeat house dust samples from California. Environ. Sci. Technol. 46, 13056–13066.
Esteban, M., Castaño, A., 2009. Non-invasive matrices in human biomonitoring: A review. Environ. Inter. 35, 438–449.
Frederiksen, M., Vorkamp, K., Jensen, N.M., Sørensen, J.A., Knudsen, L.E., Sørensen, L.S., Webster, T.F., Nielsen, J.B., 2016. Dermal uptake and percutaneous penetration of ten flame retardants in a human skin ex vivo model. Chemosphere 162, 308–314.
Fromme, H., Lahrz, T., Kraft, M., Fembacher, L., Mach, C., Dietrich, S., Burkardt, R., Voelkel, W., Goeen, T., 2014. Organophosphate flame retardants and plasticizers in the air and dust in German daycare centers and human biomonitoring in visiting children (LUPE 3). Environ. Int. 71, 158–163.
Harrad, S., Porter, L., 2007. Concentrations of polybrominated diphenyl ethers in blood serum from New Zealand. Chemosphere 66 (10), 2019–2023.
Huang, Y.M., Chen, L.G., Peng, X.C., Xu, Z.C., Ye, Z.X., 2010. PBDEs in indoor dust in South-Central China: characteristics and implications. Chemosphere 78, 169–174.
Jiang, H., Lin, Z.K., Wu, Y.Y., Chen, X.P., Hu, Y.B., Li, Y.Y., Huang, C.J., Dong, Q.X., 2014. Daily intake of polybrominated diphenyl ethers via dust and diet from an e-waste recycling area in China. J. Hazard. Mater. 276, 35–42.
Johnson, P.I., Stapleton, H.M., Sjodin, A., Meeker, J.D., 2010. Relationships between polybrominated diphenyl ether concentrations in house dust and serum. Environ. Sci. Technol. 44 (14), 5627–5632.
Kalachova, K., Hradkova, P., Lankova, D., Hajslova, J., Pulkrabova, J., 2012. Occurrence of brominated flame retardants in household and car dust from the Czech Republic. Sci. Total. Environ. 441, 182–193.
Kim, J., Kang, J.H., Park, H., Baek, S.Y., Kim, Y.H., Chang, Y.S., 2012. Assessment of polybrominated diphenyl ethers (PBDEs) in serum from the Korean general population. Environ. Pollut. 164, 46–52.
Król, S., Namiesnik, J., Zabiegala, B., 2014. Occurrence and levels of polybrominated diphenyl ethers (PBDEs) in house dust and hair samples from Northern Poland; an assessment of human exposure. Chemosphere 110, 91–96.
Kucharska, A., Cequier, E., Thomsen, C., Becher, G., Covaci, A., Voorspoels, S., 2015. Assessment of human hair as an indicator of exposure to organophosphate flame retardants. Case study on a Norwegian mother-child cohort. Environ. Int. 83, 50–57.
Li, C., Sun, H.J., Juhasz, A.L., Cui, X.Y., Ma, L.Q., 2016. Predicting the relative bioavailability of DDT and its metabolites in historically-contaminated soils using a Tenax-improved physiologically-based extraction test (TI-PBET). Environ. Sci. Technol. 50, 1118–1125.
Li, H.Z., Zhang, B.Z., Wei, Y.L., Wang, F., Lydy, M.J., You, J., 2014. Bioaccumulation of highly hydrophobic organohalogen flame retardants from sediments: Application of toxicokinetics and passive sampling techniques. Environ. Sci. Technol. 48, 6957–6964.
Liu, W., Xu, L., Li, X., Jin, Y.H., Sasaki, K., Saito, N., Sato, I., Tsuda, S., 2011. Human nails analysis as biomarker of exposure to perfluoroalkyl compounds. Environ. Sci. Technol. 45, 8144–8150.
Liu, L.Y., He, K., Hites, R.A., Salamova, A., 2016. Hair and nails as noninvasive biomarkers of human exposure to brominated and organophosphate flame retardants. Environ. Sci. Technol. 50, 3065–3073.
Miller, M.D., Marty, M.A., Arcus, A., Brown, J., Morry, D., Sandy, M., 2002. Differences between children and adults: implications for risk assessment at California EPA. Int. J. Toxicol. 21, 403–418.
Morck, A., Hakk, H., Orn, U., Klasson Wehler, E., 2003. Decabromodiphenyl ether in the rat: Absorption, distribution, metabolism, and excretion. Drug. Metab. Dispos. 31 (7), 900–907.
Munschy, C., Héas-Moisan, K., Tixier, C., Olivier, N., Gastineau, O., Le Bayon, N., Buchet, V., 2011. Dietary exposure of juvenile common sole (Solea solea L.) to polybrominated diphenyl ethers (PBDEs): Part 1. Bioaccumulation and elimination kinetics of individual congeners and their debrominated metabolites. Environ. Pollut. 159, 229–237.
Pawar, G., Abdallah, M.A.E., de Saa, E.V., Harrad, S., 2017. Dermal bioaccessibility of flame retardants from indoor dust and the influence of topically applied cosmetics. J. Expo. Sci. Environ. Epidemiol. 27 (1), 100–105.
Qi, H., Li, W.L., Liu, L.Y., Zhang, Z.F., Zhu, N.Z., Song, W.W., Ma, W.L., Li, Y.F., 2014. Levels, distribution and human exposure of new non-BDE brominated flame retardants in the indoor dust of China. Environ. Pollut. 195, 1–8.
Rauert, C., Schuster, J.K., Eng, A., Harner, T., 2018. Global atmospheric concentrations of brominated and chlorinated flame retardants and organophosphate esters. Environ. Sci. Technol. 52, 2777–2789.
Roberts, S.C., Macaulay, L.J., Stapleton, H.M., 2012. In vitro metabolism of the brominated flame retardants 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB) and bis(2-ethylhexyl) 2,3,4,5-tetrabromophthalate (TBPH) in human and rat tissues. Chem. Res. Toxicol. 25 (7), 1435–1441.
Schiavone, A., Kannan, K., Horii, Y., Focardi, S., Corsolini, S., 2010. Polybrominated

diphenyl ethers, polychlorinated naphthalenes and polycyclic musks in human fat from Italy: comparison to polychlorinated biphenyls and organochlorine pesticides. Environ. Pollut. 158, 599–606.
Sjödin, A., Wong, L.Y., Jones, R.S., Park, A., Zhang, Y., Hodge, C., Dipietro, E., McClure, C., Turner, W., Needham, L.L., Patterson, D., 2008. Serum concentrations of polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyl (PBB) in the United States population: 2003–2004. Environ. Sci. Technol. 42 (4), 1377–1384.
Staskal, D.F., Hakk, H., Bauer, D., Diliberto, J.J., Birnbaum, L.S., 2006. Toxicokinetics of polybrominated diphenyl ether congeners 47, 99, 100, and 153 in mice. Toxicol. Sci. 94, 28–37.
Sun, J.Q., Wang, Q.W., Zhuang, S.L., Zhang, A.P., 2016. Occurrence of polybrominated diphenyl ethers in indoor air and dust in Hangzhou, China: Level, role of electric appliances, and human exposure. Environ. Pollut. 218, 942–949.
Strandman, T., Koistinen, J., Vartiainen, T., 2000. Polybrominated diphenyl ethers (PBDEs) in placenta and human milk. Organohalogen Compound 47, 61–64.
Tay, J.H., Sellström, U., Papadopoulou, E., Padilla-Sánchez, J.A., Haug, L.S., de Wit, C.A., 2018. Assessment of dermal exposure to halogenated flame retardants: Comparison using direct measurements from hand wipes with an indirect estimation from settled dust concentrations. Environ. Int. 115, 285–294.
Tan, H.L., Chen, D., Peng, C.F., Liu, X.T., Wu, Y., Li, X., Du, R., 2018. Novel and traditional organophosphate esters in house dust from South China: Association with hand wipes and exposure estimation. Environ. Sci. Technol. 52, 11017–11026.
Tan, H.L., Peng, C.F., Guo, Y., Wang, X.D., Wu, Y., Chen, D., 2017. Organophosphate flame retardants in house dust from South China and related human exposure risks. Bull. Environ. Contam. Toxicol. 99, 344–349.
Thuresson, K., Bergman, Å., Jakobsson, K., 2005. Occupational exposure to commercial decabromodiphenyl ether in workers manufacturing or handling flame-retarded rubber. Environ. Sci. Technol. 39, 1980–1986.
van der Veen, I., de Boer, J., 2012. Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis. Chemosphere 88, 1119–1153.
Wang, X.C., Ling, S.Y., Guan, K., Luo, X.J., Chen, L.G., Han, J., Zhang, W., Mai, B.X., Zhou, B.S., 2019. Bioconcentration, biotransformation, and thyroid endocrine disruption of decabromodiphenyl ethane (DBDPE), a novel brominated flame retardant, in zebrafish larvae. Environ. Sci. Technol. 53, 8437–8446.
Yu, Y.X., Pang, Y.P., Li, C., Li, J.L., Zhang, X.Y., Yu, Z.Q., Feng, J.L., Wu, M.H., Sheng, G.Y., Fu, J.M., 2012. Concentrations and seasonal variations of polybrominated diphenyl ethers (PBDEs) in in- and out-house dust and human daily intake via dust ingestion corrected with bioaccessibility of PBDEs. Environ. Int. 42, 124–131.
Zhang, F.H., Lu, J.H., Liu, J.C., Yan, J.H., Zhang, Z.H., 2014. Bioaccumulation, distribution and metabolism of BDE-153 in the freshwater fish carassius auratus after dietary exposure. Ecotox. Environ. Safe. 108, 16–22.
Zhang, X.L., Zou, W., Mu, L., Chen, Y.M., Ren, C.X., Hu, X.G., Zhou, Q.X., 2016. Rice ingestion is a major pathway for human exposure to organophosphate flame retardants (OPFRs) in China. J. Hazard. Mater. 318, 686–693.
Zheng, X.B., Xu, F.C., Chen, K.H., Zeng, Y.H., Luo, X.J., Chen, S.J., Mai, B.X., Covaci, A., 2015. Flame retardants and organochlorines in indoor dust from severale-waste recycling sites in South China: Composition variations and implications for human exposure. Environ. Int. 78, 1–7.
Zhou, S.N., Buchar, A., Siddique, S., Takser, L., Abdelouahab, N., Zhu, J.P., 2014. Measurements of selected brominated flame retardants in nursing women: implications for human exposure. Environ. Sci. Technol. 48, 8873–8880.
Zhu, L.Y., Ma, B.L., Hites, R.A., 2009. Brominated flame retardants in serum from the general population in northern China. Environ. Sci. Technol. 43, 6963–6968.