Vietnam Journal of Science and Technology ***61*** *(4) (2023) 666-680*

doi:10.15625/2525-2518/16449

Occurrence and human exposure risk assessment of brominated and organophosphate flame retardants in indoor dust in Ha Noi, Viet Nam

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Received: 20 August 2021; Accepted for publication: 29 November 2022

Abstract. The widespread use of flame retardants in commercial and industrial products has led to their increased presence in the environment. Recently, indoor dust has been identified as a major human exposure route for flame retardants. In the present study, brominated flame retardants (BFRs) and organophosphate flame retardants (OPFRs) were examined in indoor dust samples collected from apartments in Hanoi, Viet Nam. OPFRs were detected at the highest concentrations with the mean concentration ∑OPFRs of 8700 ng/g (ranged from 1400 to 18000 ng/g). Tris(1-chloro-2-propyl) phosphate and tris(2-butoxyethyl) phosphate were the most abundant OPFRs in all indoor dust samples, accounting for 50 % (ranged 22 - 69 %) and 33 % (ranged 16 - 63 %) of the total OPFRs levels, respectively. The mean concentrations of total polybrominated diphenyl ethers (PBDEs) and total novel brominated flame retardants (NBFRs) in these samples were 200 ng/g (ranged 67 - 480 ng/g) and 310 ng/g (ranged 56 - 1500 ng/g), respectively. Polybrominated diphenyl ether congener 209 and decabromodiphenyl ethane were the most predominant components in PBDEs and NBFRs, respectively. Other BFRs were only found in some samples at very low levels. The estimated daily intake doses of flame retardants (FRs) via dust ingestion were calculated for both adults and children. The results revealed that the estimated levels of compound exposure through dust ingestion, even under the high-exposure scenario were also below their reference dose values, indicating that human health risks from exposure to FRs via indoor dust ingestion are not significant.

Keywords: brominated flame retardants, polybrominated diphenyl ethers; organophosphate flame retardants; indoor dust; human exposure.

Classification numbers: 3.4.5, 3.6.2

1. INTRODUCTION

Flame retardants (FRs) are a group of chemicals widely used as additives in order to reduce flammability and comply with fire safety regulations of various materials and consumer products such as textiles, electric and electronic equipment, furniture, plastics, polyurethane foam, building materials, and vehicle interiors [1, 2]. Prior to 2004, polybrominated diphenyl ethers (PBDEs) were the most common flame retardants in commercial and consumer products worldwide [3, 4]. However, the extensive use of PBDEs has resulted in a rapid increase in these pollutants in the environment and adverse effects on human health as well as ecosystems because of their high persistence, potential for bioaccumulation, and toxicity [5, 6]. Numerous studies have demonstrated that exposure to PBDEs can also cause impairing the immune system, thyroid disorders, neurological effects, developmental disorders, and potentially carcinogenic [7, 8]. As a result, the manufacturing and use of PBDEs have been restricted or banned in most countries [9, 10]. This has led to increased production and usage of alternative flame retardants such as novel brominated flame retardants (NBFRs) and organophosphate flame retardants (OPFRs) [1, 11]. However, these alternative FRs also exhibit potential toxicity in organisms, wildlife, and humans. Numerous studies have shown that NBFRs such as decabromodiphenyl ethane (DBDPE) and 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) also pose potential risks to the environment and human health. These NBFRs have been observed to possess bioaccumulation and toxic properties comparable to PBDEs. [2, 12]. Similar to NBFRs, the increasing use of OPFRs has caused concerns about their adverse effects on the environment, the health of animals and humans because many of them are toxic and persistent Chlorinated OPFRs have been proved to be neurotoxic and carcinogenic [1, 13]. Tri(2-chloroethyl) phosphate (TCEP) and tri(1,3-dichloroisopropyl) phosphate (TDCPP), caused tumor growth in various organs in rodents after long-term exposure and thus are suspect carcinogens. TCEP has been classified as a “potential human carcinogen” (carcinogen category 3) by the EU in 2008 [14] and TDCPP was added to California's Proposition 65 List of Potential Carcinogens in 2011 [15]. Most of these flame retardants are semi-volatile organic compounds. They are used as chemical additives so they easily get out of products and release into the environment through volatilization and abrasion from FRs-containing products and materials during use and disposal [13, 16]. These compounds tend to accumulate in dust particles. Therefore, indoor dust could reflect the overall pollution status of these pollutants in the indoor environment and has been frequently used in environmental monitoring studies [17, 18].

Humans could be exposed to PBDEs, NBFRs, and OPFRs through various routes, including ingestion of dust, food consumption, inhalation of air, and absorption, permeation via dermal contact [12, 19]. Numerous studies have shown that ingestion of indoor dust is one of the main pathways of human exposure to these FRs because people spend most of their time in indoor environments and levels of these FRs in indoor dust were significantly greater than those in matching outdoor dust [20, 21]. However, studies on the presence and distribution of OPFRs and brominated flame retardants (BFRs) in the indoor environment as well as the health risks of exposure to these compounds in Viet Nam remain limited.

In the present study, we measured PBDEs, NBFRs, and OPFRs in indoor dust samples collected from apartments in 4 inner districts of Ha Noi city. The aims of the present study were to 1) determine the concentrations and profiles of PBDEs, NBFRs, and OPFRs in indoor dust to fill the information gap about the contamination status of these compounds in indoor environment from Viet Nam, and 2) assess the risk from exposure to these pollutants through dust ingestion on human health.

2. MATERIALS AND METHODS

2.1. Chemicals and materials

The standards of thirty-three PBDEs (including BDE-17, 28, 30, 47, 49/71, 66, 77, 85, 99, 100, 119, 126, 138, 139, 140, 153, 154, 156/169, 171, 180, 183, 184, 191, 196, 197, 201, 203, 204, 205, 206, 207, 208, and 209) and four NBFRs (DBDPE, BTBPE, PBEB, and BB-153) were purchased from AccuStandard Inc. (New Haven, CT, USA). Twelve OPFR standards were purchased from Wellington Laboratories (Ontario, Canada): TCEP; TDCPP; tris(1-chloro-2-propyl) phosphate (TCPP, mixture of 3 isomers); tri-n-butyl phosphate (TnBP); dibutyl phenyl phosphate (DBPP); triphenyl phospate (TPhP); tris(2-butoxyethyl) phosphate (TBOEP); 2-ethylhexyl diphenyl phosphate (EHDPP); tris(2-ethylhexyl) phosphate (TEHP); tris(2-methylphenyl) phosphate (TOCP); tris(3-methylphenyl) phosphate (TMCP); tris(4-methylphenyl) phosphate (TPCP).

The surrogate standards monofluorinated FBDE-15, FBDE-99, FBDE-183, FBDE-208 were purchased from AccuStandard Inc; $^{13}C_{12}$-BDE-209 was acquired from Wellington Laboratories (Guelph, Canada); TnBP-d27, TPhP-d15, and TCEP-d12 were purchased from Sigma-Aldrich (Germany). The internal standard monofluorinated FBDE-154 was purchased from AccuStandard Inc; Phenanthrene-d10 (Phen-d10) was purchased from Thermo Fisher Scientific (USA).

Supelclean^{TM} ENVI^{TM}-Florisil SPE cartridges (500 mg, 3 mL) were purchased from Supelco (Bellefonte, PA, USA). Silica gel, concentrated sulfuric acid (H_2SO_4), and anhydrous sodium sulfate (Na_2SO_4) were purchased from Merck (Darmstadt, Germany). All solvents used in this study were purchased from Merck and they were of analytical grade.

2.2. Sample collection

Twelve indoor dust samples (n = 12) were collected from 12 apartments in four districts (Hoan Kiem, Ba Dinh, Cau Giay, and Ha Dong) of Hanoi (Figure 1) from June to July 2018. The collection of indoor dust samples was carried out in the living room from the surface of the carpet, furniture; under the table, sofa; on top of the air conditioner, refrigerator, cabinet, and fan blades during the daytime. During sampling, the presence of consumer products, furniture, carpets, curtains, polymers, and textile products as well as room area, wall/floor material in the sampling locations were recorded. Prior to sampling, the houses were requested to not vacuum floors or surfaces of furniture and equipment for a minimum period of two weeks.

The household vacuum cleaner (D-530) with nylon socks (25 μm pore size) inserted into its nozzle was used to collect dust samples. Before and after each sampling event, the vacuum cleaner's nozzle was carefully cleaned with acetone to prevent potential cross-contamination across locations. Each sampling apartment was vacuumed for a total time of 12 min, including the floor; the surfaces of furniture, electrical and electronic appliances; and the upholstery with the ratio of vacuuming time for the floor, surfaces, and upholstery as 3:2:1 (min), respectively. After being collected, dust samples were carefully wrapped in aluminum foil that had been solvent-rinsed and kept in polyethylene zip bags to protect them from humidity, light, and other external influences that could potentially alter their composition. After being transported to the laboratory, the dust samples were sieved through a stainless-steel sieve (250 μm), homogenized, and stored at -20 °C until analysis.

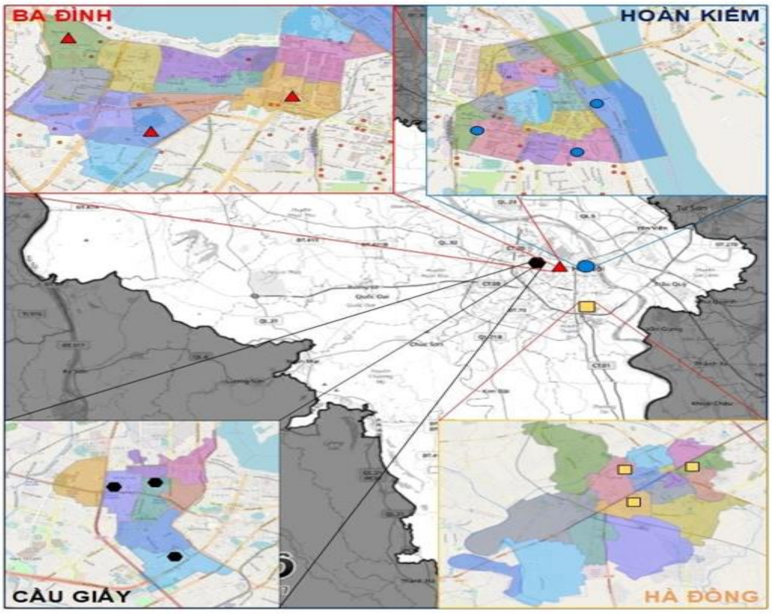

Figure 1. Map of study areas and sampling sites in Ha Noi, Viet Nam.

2.3. Sample preparation and analysis

The sample extraction and purification method were performed according to the report by Van den Eede *et al.* [22] with some modifications. An accurately weighed aliquot of dust (approximately 100 mg) was spiked with surrogate standards and extracted with 10 ml Hex: Ace (1:1, v/v) in an ultrasonic bath for 10 min. The extraction procedure was repeated three times. This combined extract was evaporated to dryness under a gentle nitrogen flow and redissolved in 1 mL Hex. The extracts were fractioned on Florisil SPE cartridges (cartridges were prewashed with 6 mL of Hex) by eluting with 8 mL of Hex (Fraction 1) and 10 mL of EtAc (Fraction 2), respectively. For PBDEs and NBFRs analysis, Fraction 1 was evaporated until 1 mL and transferred onto a 44 % Sulfuric Acid Silicagel column for a second clean-up. The extracts were eluted with 10 mL of Hex: DCM (1:1, v/v), and afterward evaporated to dryness under gentle nitrogen flow and redissolved in 100 μL nonane spiked with the internal standard (FBDE-154) prior to GC/MS analysis. For OPFRs analysis, Fraction 2 was evaporated to dryness under a gentle nitrogen stream and resolubilized in 100 μL hexane containing the internal standard (Phen-d10) to ready for GC/MS analysis.

Thirty-three PBDEs and four NBFRs were quantified by using a gas chromatograph coupled mass spectrometer (GC/MS-QP2010 Plus, Shimadzu). A DB-5ht capillary column (15 m × 0.25 mm × 0.10 µm; Agilent Technologies) was used to separate PBDEs and NBFRs. Temperature of injection port was 260 ^{o}C. Initial column oven temperature was 135 ^{o}C for 2 min, increased to 215 ^{o}C (10 ^{o}C/min), to 275 ^{o}C (5 ^{o}C/min), to 295 ^{o}C (20 ^{o}C/min, held 0.5 min) and finally raised at 20 ^{o}C/min to 310 ^{o}C and held for 4 min. The temperature of the interface and ion source was 310 ^{o}C and 250 ^{o}C, respectively. The analysis of twelve OPFRs was also performed by GC/MS-QP2010. A DB-5ms column (30 m × 0.25 mm × 0.25 µm, Agilent) was used to separate OPFRs. The injection temperature was set at 250 ºC. The column temperature program started at 40 °C and held for 2 min, then increased to 310 °C (8 °C/min) and held for 4 min. The temperature of the interface and ion source was 310 ^{o}C and 250 ^{o}C, respectively.

2.4. Quality assurance and quality control

Method validation was carried out to ensure the reliability of the analytical method. Procedural blanks (sodium sulfate) were analyzed to assess potential contamination during the analytical procedure. Native standards spiked samples (n = 5) and indoor dust Standard Reference Material® 2585 (SRM 2585, NIST, Gaithersburg, MD, US) (n = 5) were examined to assess the precision and accuracy of the method. In general, most of FRs were not detected in blank samples. Only TCEP, TCPP, and TBEP were detected in some of the blank samples, with average values of 1.16, 2.03 ng/g and 1.95 ng/g, respectively. However, levels of FRs in dust samples were blank-corrected by subtracting the mean values of FRs in blank samples.

The recoveries of native-spiked samples and SRM 2585 were 78.3 % to 114 % for BFRs and 76.2 to 106 % for OPFRs, respectively. The average recovery of surrogates ranged from 76.5 to 101 % and from 79.2 to 102 % for BFRs and OPFRs, respectively. The results showed that the method had good precision and accuracy and was suitable for the analysis of indoor dust samples. Method detection limits (MDLs) from 0.10 to 0.50 ng/g for PBDEs, except for BDE-209 (5.00 ng/g) and 0.76 to 3.12 ng/g for OPFRs.

2.5. Exposure assessment of BFRs and OPFRs via indoor dust ingestion

Indoor dust has been considered as one of the most important pathways of human exposure to FRs. Human exposure to PBDEs, NBFRs, and OPFRs via dust ingestion was estimated by the daily intake doses (ID, ng/kg-bw/day) using the following equation with some modification, published previously [22, 23].

$$ID = (C \times IR \times FT \times AF) / BW \qquad (1)$$

Human health risk assessment was assessed with hazard quotient (HQ) and hazard index (HI) values according to the following formula [24]:

$$HI = \Sigma\, HQi = \Sigma\, (IDi / RfDi) \qquad (2)$$

In the equations, C are the measured levels of BFRs and OPFRs in indoor dust (ng/g); IR is the daily dust ingestion rate (g/day); BW is the average body weight (kg); FT is the fraction of time spent indoor; AF is the absorption efficiency of the target compounds; HQi is the hazard quotient which used to estimate the human health risks from exposure to compounds; IDi is the daily intake dose of target compounds (ng/kg-bw/day); RfDi is the oral reference dose (ng/kg-bw/day). If the HI value is ≥ 1, it indicates that the cumulative daily intake may have a negative impact on health. Conversely, if the HI value is < 1, it suggests that the risks to human health via indoor dust ingestion are negligible.

3. RESULTS AND DISCUSSION

3.1. Concentrations and profiles of FRs in indoor dust

Information about the concentrations and detection frequency of studied PBDEs, NBFRs, and OPFRs in indoor dust samples is summarized in Table 1. Most of the target FRs were detected in all indoor dust samples, indicating widespread contamination by FRs in indoor environments. The levels of ΣPBDE, ΣNBFR, and ΣOPFR measured in all dust samples ranged from 67 to 480 (mean: 200) ng/g, 56 to 1500 (mean: 310) ng/g, and from 1400 to 18000 (mean: 8700) ng/g, respectively. OPFRs was the most abundant family of FRs, followed by NBFRs and PBDEs. The higher levels of OPFRs in indoor dust may be due to the cessation of PBDE usage, which may have led to increased use OPFRs in household products and subsequent release of these chemicals into the indoor environment.

Table 1. Descriptive statistics for concentrations (ng/g) of PBDEs, NBFRs, and OPFRs in indoor dust from Ha Noi, Viet Nam.

Compound	**Mean ± SD**	**Median**	**Range**	**DF (%)**
BDE-17	0.65 ± 0.25	0.61	0.37 - 1.2	100
BDE-28	1.9 ± 1.2	1.5	0.67 - 4.3	100
BDE-47	1.8 ± 0.53	1.9	0.76 - 2.4	100
BDE-49	1.5 ± 1.4	1.0	0.14 - 4.8	100
BDE-99	4.6 ± 11	1.4	0.25 - 62	100
BDE-100	0.46 ± 0.44	0.37	ND - 1.7	100
BDE-153	0.93 ± 2.3	0.29	ND - 8.1	92
BDE-154	0.33 ± 0.24	0.26	0.10 - 1.0	100
BDE-180	0.59 ± 1.4	ND	ND - 4.9	42
BDE-183	1.3 ± 2.6	0.55	0.21 - 9.5	100
BDE-196	0.66 ± 0.24	0.69	0.33 - 1.0	100
BDE-197	0.62 ± 0.16	0.65	0.27 - 0.87	100
BDE-203	0.72 ± 0.24	0.77	0.32 - 1.0	100
BDE-206	9.5 ± 5.4	8.7	2.9 – 20	100
BDE-207	8.3 ± 4.3	7.9	2.6 – 15	100
BDE-208	4.8 ± 2.5	4.6	1.3 - 8.9	100
BDE-209	160 ± 120	120	49 – 360	100
ΣPBDEs	200 ± 140	160	67 – 480	100
PBEB	0.24 ± 0.20	0.20	ND - 0.81	92
BB-153	0.09 ± 0.08	0.10	ND - 0.20	67
BTBPE	2.3 ± 3.6	1.2	0.52 - 13	100
DBDPE	310 ± 430	130	54 - 1500	100
ΣNBFRs	310 ± 430	130	56 - 1500	100
TBP	130 ± 240	47	16 – 870	83
TCEP	200 ± 190	100	39 – 580	100
TCPP	4500 ± 2500	4900	500 - 8900	100
TDCPP	220 ± 280	160	180 - 1000	75
TBOEP	2800 ± 1500	2500	340 - 6400	100
TPhP	470 ± 450	360	140 - 1800	100
EHDPP	160 ± 140	120	34 – 440	100
TEHP	120 ± 110	80	12 – 410	75
TOCP	240 ± 330	150	31 – 1200	92
ΣOPFRs	8700 ± 4300	8000	1400 - 18000	100

SD: Standard deviation (*n* = 24); DF: Detection frequency; ND: not detected.

Among the PBDE congeners, high-brominated PBDEs, such as BDE-206, -207, -208, and -209, showed the highest levels among PBDE congeners. In particular, BDE-209 was the most dominant congener detected in all indoor dust samples. The levels of BDE-209 varied from 49 to 360 ng/g (mean 160 ng/g), contributing 65 - 87 % (mean 76 %) of the total PBDE contents. The levels of BDE-209 were 1 to 3 orders of magnitude greater than those measured for the other PBDE congeners with a strong positive correlation observed between BDE-209 and total PBDE concentrations (Pearson's $r = 0.992$; $p < 0.001$). Similar results in indoor dust and road dust samples were also reported elsewhere in Viet Nam [25, 26]. This showed that deca-BDE was one of the PBDE mixtures that were most commonly used in consumer products, electronics, and electrical equipment in Viet Nam. Figure 2A displays the composition profiles of PBDEs in indoor dust samples. In addition to BDE-209, the next predominant congeners detected in all samples included BDE-206, BDE-207, BDE-208, BDE-99, BDE-28, and BDE-47 were also detected in all samples, contributing (mean ± SD) 5.3 ± 0.87 %, 4.5 ± 0.92 %, 2.5 ± 0.61 %, 2.4 ± 2.6 %, 1.2 ± 1.3 %, and 1.1 ± 1.2 % of the total PBDE content, respectively. The relatively high contribution of BDE-99 and BDE-47 may be due to emissions from materials treated with penta-BDE technical formulations [27]. In general, the four congeners (BDE-209, BDE-206, BDE-207, and BDE-208) were the dominant compounds in all indoor dust samples, accounting for over 90 % of the ΣPBDE levels. The distribution pattern of congeners indicates that deca-BDE products made a main contribution to the presence of PBDEs in house dust, followed by penta-BDE products.

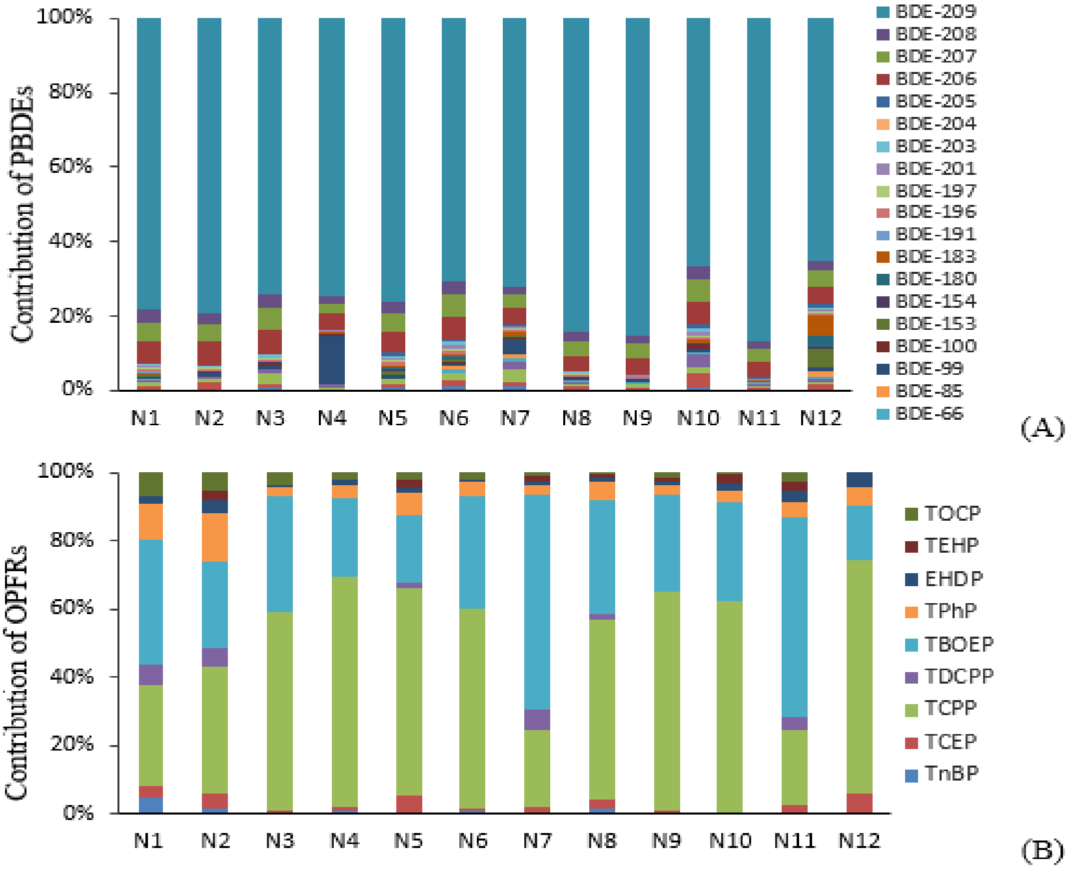

Figure 2. Compositional profiles of PBDEs (A) and OPFRs (B) in indoor dust from Ha Noi, Viet Nam.

Among NBFRs, DBDPE was the most dominant congener, detected in all samples with a mean level of 310 ng/g (range 55 - 1500 ng/g), contributing 98.3 % (range 94.8 - 99.9 %) of the total NBFR level. The concentrations of DBDPE in indoor dust samples suggested that this compound is widely used in consumer products. BTBPE was also detected in all samples with low concentrations (mean 2.3 ng/g, range 0.52 - 13 ng/g), accounting for 1.2 % of the ΣNBFRs levels. BTBPE was manufactured in the mid-1970s and is currently being used as a substitute for octa-BDE [12]. PBEB and BB-153 were detected at trace levels with detection frequencies of 83 % and 67 %, respectively. This could be attributed to the relatively limited usage of products containing PBEB and BB-153 in Viet Nam.

Among the target OPFR compounds, nine out of twelve OPFRs were detected at a frequency of 75 % - 100 % in indoor dust samples, including TCEP, TCPP, TDCPP, TnBP, TPhP, TBOEP, EHDPP, TEHP, and TOCP, demonstrating their widespread occurrence in the indoor environment. The concentrations and the composition profiles of OPFRs in indoor dust samples were presented in Table 1 and Figure 2B. Among the detected OPFRs, TCPP and TBOEP were the most abundant congeners detected in all indoor dust samples with concentrations ranging from 500 to 8900 ng/g (mean 4500 ng/g) and 340 to 6400 ng/g (mean 2800 ng/g), respectively. These compounds accounted for 22 - 69 % (mean 50 %) and 16 - 63 % (mean 33 %) of ∑OPFRs, respectively. Other OPFRs such as TPhP, TOCP, TDCPP, TCEP, EHDPP, TBP, and TEHP were detected at mean concentrations 470; 240; 220; 200; 160; 130 and 120 ng/g, accounting for 5.5; 2.7; 2.5; 2.3; 1.9; 1.5; and 1.4 % of the total of OPFRs, respectively. The predominance of TCPP and TBOEP suggests greater use of these chemicals in consumer products and materials in Viet Nam. The high level of TCPP in indoor dust samples of this study probably indicates the high usage of TCPP-containing products and materials indoors. Since TCPP and TCEP are mainly used as flame retardants in plastic products, polyurethane foams, textiles, insulation and furniture upholstery therefore furniture, sofas, mattress, curtains, baby products, spray foam insulation... are maybe the main source of these compounds to the indoor environment [13]. However, TCEP has not been used because of its carcinogenic potential and it has been gradually replaced by other flame retardants, primarily TCPP [28]. That may be the reason why TCPP accounted for high levels in indoor dust samples. TBOEP is used as a plasticizer in rubber and plastics and as a polisher in floor-finishing products (up to 0.5 % - 8 %) [29], which might be an important source in indoor environments. TPhP was used in the plastic material of computers, is most likely the source of TPhP found in the samples from computer covers and screens, T.V screens and sound systems. DBPP, TMCP, and TPCP were not detected in any of the samples, which is consistent with expectations since these substances are mainly used in industrial processes.

3.2. Comparison of FR concentrations in indoor dust with other studies

The accurate comparison of total PBDE concentrations across studies would be difficult as PBDE congeners investigated in dust differed from each other among studies. Therefore, in addition to the total PBDE levels, concentrations of BDE-209 were also used for comparison among studies because BDE-209 was generally the dominant congener in indoor dust samples across most studied sites [11, 30]. Among the selected NBFRs, DBDPE was the main dominant congener in indoor dust samples at most studied sites, so the concentrations of DBDPE were used for comparison across different studies. The comparison of median concentrations of BDE-209, DBDPE, and ΣOPFRs in indoor dust in Viet Nam and other countries was displayed in Table 2.

The median concentration of BDE 209 (120 ng/g) in indoor dust in this study was slightly lower than those detected in Spain (151 ng/g), Norway (160 ng/g) and Belgium (180 ng/g). The concentrations of BDE-209 in this study were also significantly lower than those in the studies from Italy (230 ng/g) and Brazil (425 ng/g), and much lower than those in the studies from Korea (640 ng/g), Japan (1280 ng/g), China (2050 ng/g), the USA (1300 ng/g), and the UK (3350 ng/g). The median concentration of DBDPE (130 ng/g) in our study was comparable to those reported in Italy (120 ng/g), Belgium (140 ng/g) and the UK (150 ng/g), but higher than those from the studies in Korea (64 ng/g) and Spain (86 ng/g). The level of PBDEs in this study was lower than the study conducted in Japan and much lower than studies conducted in China, Brazil and the UK.

The composition profiles of OPFRs among studies from various countries. This study and studies from Belgium, China, and the UK revealed the dominance by chlorinated OPFRs [31, 37, 39]. This is in contrast with the patterns observed in some other countries, such as Japan, Brazil, Norway, Italy and Spain, where non-chlorinated OPFRs such as TBOEP was usually dominant in indoor dust [33, 35, 37, 39]. The significant differences among concentrations of individual OPFR congeners in indoor dust reported in different studies more likely reflect differences in the extent to which OPFRs were used in consumer products and building materials. In general, the overall concentration of the major OPFRs in this study was comparable and higher than reported in Korea [34] and China [32] but lower than those in studies from Norway, Germany, Spain, Italy, Brazil, the UK, and Japan [33, 35, 37-39]. Differences in level and composition profile of FRs in indoor dust between places can be attributed to different types, features and qualities of consumer products and construction materials containing varying amounts of flame retardants and the flammability standards of each country.

Table 2. Comparison of median concentrations (ng/g) of BFRs and OPFRs in indoor dust from different study locations

Country	PBDEs	NBFRs	OPFRs						Reference
	BDE-209	DBDPE	TCPP	TCEP	TBOEP	TPhP	EHDPP	OPFRs	
Viet Nam (n = 12)	120	130	4900	100	2500	360	120	8000	This study
China (n = 15)	-	-	2290	1140	1520	600	257	7150	[31]
China (n = 30)	2050	730	-	-	-	-	-	-	[32]
Japan (n = 10)	1280	220	1700	2700	82000	820	200	97000	[33]
Korea (n = 111)	640	64	440	450	600	540	640	4900	[34]
Brazil (n = 10)	425	980	1870	237	22100	3830	1750	42600	[35]
USA (n = 10)	1300	150	4270	920	-	-	-	-	[36]
Belgium (n = 22)	180	140	4420	460	830	590	470	12800	[37]
Italy (n = 21)	230	120	1320	139	5658	429	608	12800	[37]
Spain (n = 21)	150	86	1615	88	2238	991	377	12800	[37]
Germany (n = 15)	-	-	4200	1100	4300	1200	-	14000	[38]
Norway (n = 10)	160	686	1960	120	18360	830	195		[39]
UK (10)	3350	1090	64550	870	8070	1510	2380		[39]

n = sample numbers analyzed; - : not analyzed.

3.3. Human exposure assessment and health risks

The IDs of selected BFRs and OPFRs through indoor dust ingestion for children and adults in Hanoi were calculated and displayed in Table 3. Two exposure scenarios were calculated using median and 95th percentile (high-end exposure) concentrations with high dust ingestion rates (50 mg/day for adults and 200 mg/day for children) and assuming 100 % absorption of contaminants from ingested dust [40]. Fractions of time spent indoor were evaluated to be 64 % for adults and 86 % for children [41]. The body weights (kg) were estimated to be 60 kg for Vietnamese adults and 18 kg for 5-year-old children (according to the survey report of Viet Nam National Institute of Occupational Safety and Health (2020) and the weight standards of Vietnamese children-oriented from the World Health Organization WHO).

Table 3. Exposure assessment for BFRs and OPFRs through indoor dust ingestion for adults and children.

Compound	RfD	Adults				Children			
		ID (ng/kg-bw/day)		HQ		ID (ng/kg-bw/day)		HQ	
		Median[c] Exposure	High[d] Exposure	Median[c] Exposure	High[d] Exposure	Median[c] Exposure	High[d] Exposure	Median[c] Exposure	High[d] Exposure
BBE-47	100[a]	1.0×10^{-3}	1.3×10^{-3}	1.0×10^{-5}	1.3×10^{-5}	0.02	0.02	1.9×10^{-4}	2.2×10^{-4}
BDE-99	100[a]	0.6×10^{-3}	1.5×10^{-3}	5.9×10^{-6}	1.5×10^{-5}	0.01	0.03	1.1×10^{-4}	2.7×10^{-4}
BDE-153	200[a]	0.2×10^{-3}	2.9×10^{-3}	7.7×10^{-7}	1.5×10^{-6}	2.8×10^{-3}	5.3×10^{-3}	1.4×10^{-5}	2.6×10^{-5}
BDE-209	7000[a]	6.2×10^{-2}	0.19	8.9×10^{-6}	2.7×10^{-5}	1.12	3.40	1.6×10^{-4}	4.9×10^{-4}
ΣPBDEs	-	1.08	1.68	-	-	19.2	30.1	-	-
BTBPE	200000[a]	6.8×10^{-2}	0.36	3.4×10^{-7}	1.8×10^{-6}	1.21	6.51	6.1×10^{-6}	3.3×10^{-5}
DBDPE	300000[a]	0.6×10^{-3}	1.8×10^{-3}	2.1×10^{-9}	6.1×10^{-9}	0.01	0.03	3.7×10^{-8}	1.1×10^{-7}
ΣNBFRs	-	1.26	1.86	-	-	22.6	33.4	-	-
TnBP	10000[b]	2.5×10^{-2}	6.8×10^{-2}	2.5×10^{-6}	6.8×10^{-6}	0.45	1.22	4.5×10^{-5}	1.2×10^{-4}
TCEP	7000[b]	5.6×10^{-3}	0.28	8.0×10^{-6}	4.0×10^{-5}	1.0	5.0	1.4×10^{-4}	7.1×10^{-4}
TCPP	10000[b]	2.64	3.57	2.6×10^{-4}	3.6×10^{-4}	47.2	64.1	4.7×10^{-3}	6.4×10^{-3}
TDCPP	20000[b]	8.3×10^{-2}	0.13	4.2×10^{-6}	6.3×10^{-6}	1.49	2.26	7.5×10^{-5}	1.1×10^{-4}
TBOEP	15000[b]	1.33	2.24	8.9×10^{-5}	1.5×10^{-4}	23.8	40.1	1.6×10^{-3}	2.7×10^{-3}
TPhP	70000[b]	0.19	0.31	2.7×10^{-6}	4.4×10^{-6}	3.40	5.51	4.9×10^{-5}	7.9×10^{-5}
TEHP	100000[b]	4.3×10^{-2}	0.22	4.3×10^{-7}	2.2×10^{-6}	0.76	3.93	7.6×10^{-6}	3.9×10^{-5}
ΣOPFRs	-	4.28	9.35	-	-	76.7	167.5	-	-
HI	-	-	-	4.0×10^{-4}	6.2×10^{-4}	-	-	7.1×10^{-3}	1.1×10^{-2}

RfD: The reference doses (ng/kg-bw/day) are suggested by US EPA ([a]) and Li et al. [42] ([b])

[c] Median dust concentrations used for calculating exposure.

[d] 95th percentile (P95) dust concentrations used for calculating exposure.

For normal (50th percentile) scenarios, the IDs via dust ingestion for adults and children were 1.08 and 19.2 ng/kg-bw/day for ΣPBDEs, 1.26 and 22.6 ng/kg-bw/day for ΣNBFRs, 4.29 and 76.7 ng/kg-bw/day for ΣOPFRs, respectively. In the worst scenario (95th percentile), the overall IDs of PBDEs, NBFRs, and OPFRs for children and adults were approximately two times higher than those for the normal (50th percentile) scenario. The IDs via dust ingestion for adults and children in the worst scenario (95th percentile) were 1.68 and 30.1 ng/kg-bw/day for

ΣPBDEs, 1.86 and 33.4 ng/kg-bw/day for ΣNBFRs, 9.35 and 167.5 ng/kg-bw/day for ΣOPFRs, respectively. In particular, BDE-209 and DBDPE contributed significantly to total PBDEs and NBFRs exposures, respectively. TCPP and TBOEP contributed significantly to total OPFRs exposure. Based on the IDs of all FRs through dust ingestion for both exposure scenarios, OPFRs were associated with the highest exposure levels to children and adults, followed by NBFRs and PBDEs. Regardless of scenarios, the exposure levels to BFRs and OPFRs through dust ingestion for children were much higher than those for adults. This could be a result of lower body weights and higher dust ingestion rates than those in adults. However, the IDs of all the selected FRs for both children and adults (even in the worst-case scenario with high dust intake rate and using 95th percentile concentrations) were also several orders of magnitude lower than their RfD. The results of HQ and HI of FRs for adults and children are presented in Table 3. Fortunately, all values of HI were far less than 1, indicating that the health risks of BFRs and OPFRs from indoor dust were negligible for both adults and children.

4. CONCLUSION

This study provides first insight into the occurrence and distribution of BFRs and OPFRs in urban indoor dust in Hanoi as well as the human health risks of exposure to these flame retardants. Results of the study showed that PBDEs, NBFRs and OPFRs were detected in all indoor dust samples, indicating widespread contamination of these flame retardants in indoor environments in Hanoi, Viet Nam. BDE-209 and DBDPE were the predominant BFRs, while TCPP and TBOEP were the most abundant OPFR congeners in all dust samples. Among studied compounds, OPFRs were present at the highest concentration, followed by PBDEs and finally NBFRs. ΣOPFRs concentration was about 20 times higher than ΣPBDEs and ΣNBFRs concentration in all dust samples collected in Hanoi indoor environments, which suggested that OPFRs are being used as an alternative to BFRs. The IDs for children were found to be notably higher than those for adults. However, IDs of all the selected FRs (even in the worst-case scenario) were far less than their RfDs with hazard index $\ll 1$, indicating that the health risks of FRs via indoor dust ingestion were negligible.

Acknowledgments: This research was funded by the Vietnam Academy of Science and Technology under grant number “TĐPCCC.05/21-23”.

CRediT authorship contribution statement. Hoang Thi Tue Minh: Manuscript writing, Methodology, Investigation, Formal analysis. Duong Thi Hanh: Formal analysis. Phan Quang Thang: Formal analysis. Trịnh Thu Ha: Manuscript editing, Methodology, Formal analysis, Supervision.

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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