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Physiochemical Properties and Environmental Levels of Legacy and Novel Brominated Flame Retardants

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<http://dx.doi.org/10.5772/intechopen.79823>

Abstract

Polybrominated diphenyl ethers (PBDEs) and 'novel' brominated flame retardants (NBFRs) are synthetic chemicals widely used in consumer products to enhance their ignition resistance. Since in most applications, these chemicals are used additively, they can transfer from such products into the environment. PBDEs have been classified as significant pollutants in the environment. Knowledge of PBDE and NBFR physicochemical properties provides information about their potential environmental fate and behaviour. This chapter highlights the most important physiochemical properties such as molecular weight, vapour pressure, octanol/air partitioning coefficient, octanol/water partition coefficient, water solubility and organic carbon/water partitioning coefficient that influence the distribution pattern of these contaminants in the environment. In addition, this chapter provides an evaluation of the concentrations of these chemicals in various environmental media such as indoor and outdoor air, indoor dust, soil and sediment, sewage sludge, biota and food, and human tissues.

Keywords: PBDEs, NBFRs, physiochemical properties, environmental levels, fate and behaviour

1. Introduction

Brominated flame retardants (BFRs) are a group of synthetic chemicals added to a wide range of polymers, foam, plastic, textile, and building materials to meet flame retardancy standards set by various jurisdictions worldwide, containing 50–85% bromine by weight [1]. Depending on their mode of incorporation into the polymers to which they are added, they are referred to as either reactive or additive BFRs. Reactive flame retardants, such as tetrabromobisphenol-A

(TBBPA), are chemically bonded to the polymer. Conversely, additive BFRs, such as PBDEs and hexabromocyclododecane (HBCD) are simply blended with the polymers and do not become a part of the base polymer. Additive BFRs are the most common because their application in consumer goods is less complicated than for reactive BFRs [2]. An extensive body of research has reported the presence of BFRs in air, dust, soil, sediment and biota samples. Evidence of their persistence and capacity for bioaccumulation, coupled with concerns about their adverse health effects has led to widespread bans and restrictions on the manufacture and use of PBDEs and their listing under the Stockholm Convention on Persistent Organic Pollutants (POPs) [3]. Such bans and restrictions on the use of BFRs without the relaxation of flammability standards has likely resulted in increased production and use of alternatives referred to collectively as 'novel' brominated flame retardants [4]. According to the empirical data, studies suggest that some NBFRs have the same hazard profiles as 'legacy' BFRs [5].

2. PBDEs and NBFRs

PBDEs are a family of chemicals with a common structure of a brominated diphenyl ether and have the chemical formula $C_{12}H_{(0-9)}Br_{(1-10)}O$. Any of the 10 hydrogen atoms of the diphenyl ether moiety can be exchanged with bromine, resulting in 209 possible congeners. Each individual PBDE is distinguished from others by both the number of bromine atoms and the placement of those atoms (**Figure 1**). These congeners are numbered using the International Union of Pure and Applied Chemistry (IUPAC) system [6].

Commercial products of PBDEs have been marketed in three main formulations, namely: pentabromodiphenyl ether (Penta-BDE), octabromodiphenyl ether (Octa-BDE) and decabromodiphenyl ether (Deca-BDE). The leading commercial Penta-BDE mixture is primarily comprised 28% BDE-47 and 43% BDE-99. A commercial Octa-BDE mixture is comprised of 13–42% BDE-183 and 11–22% BDE-197, while Deca-BDE mixture contains primarily >97% BDE-209 [7].

Bans and restrictions on the use of established BFRs have resulted in the production of alternatives to comply with flammability standards. The term NBFRs refer to brominated flame retardants, which 'are new to the market or recently observed in the environment due to the restrictions and bans on the use of some "legacy" BFRs'. Other terms such as 'alternate', 'emerging' or 'non-PBDEs' have also been used to refer to these BFRs [4]. It has been indicated that the NBFRs are urgently required because any non-halogenated substituting chemicals can involve significant costs, as industries must adapt their products for all required

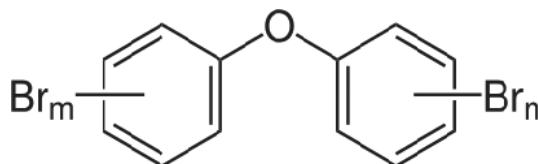


Figure 1. General structure of PBDEs ($n + m = 1-10$).

performances and product standards [1]. The most common NBFRs replacing PBDEs are: a mixture of 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) and bis (2-ethylhexyl)3,4,5,6-tetrabromophthalate (BEH-TEBP) under the trade name Firemaster 550 as a replacement for Penta-BDEs; 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) as a replacement for Octa-BDE; and decabromodiphenyl ethane (DBDPE) as a replacement for Deca-BDE [8]. **Figure 2** illustrates the chemical structure of selected NBFRs replacing PBDEs.

2.1. Physicochemical properties of PBDEs and NBFRs

PBDE commercial products are solids at room temperature, not flammable, and do not present a physiochemical hazard [7]. They are hydrophobic contaminants (highly water insoluble) and typically have high log octanol-water partition coefficients.

Similar to PBDEs, NBFRs are highly hydrophobic compounds and displaying low volatility. However, differences in molecular structure between PBDEs and their NBFR replacements result in specific differences in physicochemical properties. For example, the ethane bridge between the aromatic rings in the DBDPE molecule makes it more flexible and hydrophobic than BDE-209, with consequences for its environmental fate and behaviour [4]. In general, BTBPE, BEH-TEBP and DBDPE possess lower vapour pressures and higher log octanol-water partition coefficients compared with Octa-, Penta- and Deca-BDE, respectively. **Tables 1** and **2** and **Figure 3** illustrate the most important physicochemical properties: molecular weight (MW), vapour pressure (V_p), octanol/air partitioning coefficient (K_{OA}), octanol/water partition coefficient (K_{OW}), water solubility and organic carbon/water partitioning (K_{OC}) that influences the environmental fate and behaviour of PBDEs and NBFRs.

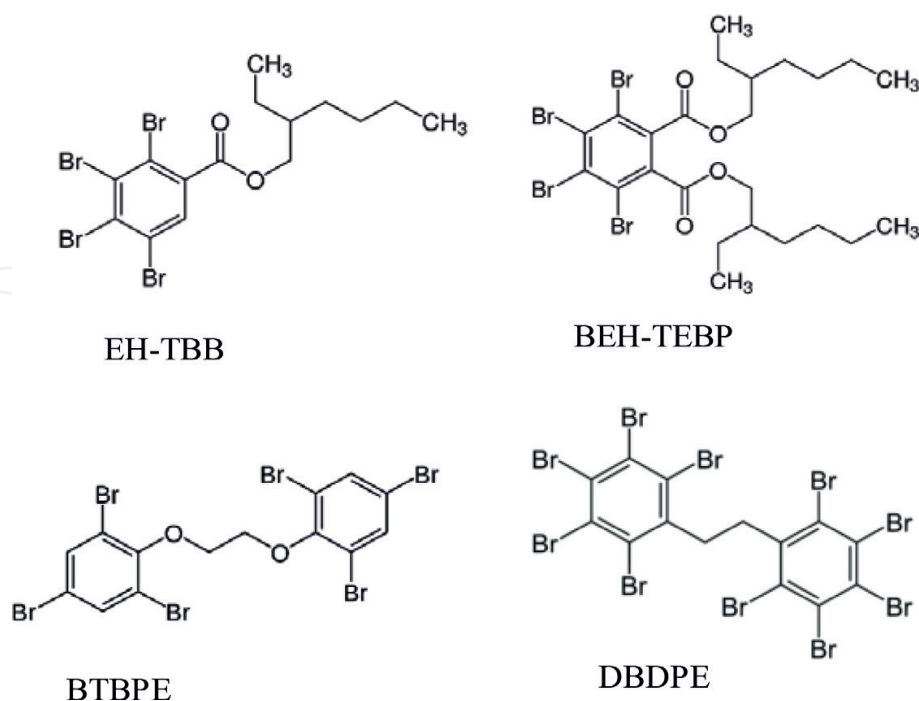


Figure 2. Chemical structure of selected NBFRs replacing PBDEs.

BDE	Molecular weight	Water solubility mg/L (@25°C)	Log K _{ow}	Log K _{OA} (@25°C)	Log K _{oc}	Vapour pressure (Pa) (@25°C)
BDE-28	407.1	0.07	5.94	9.5	3.91	6.51×10^{-4}
BDE-47	485.82	0.001–0.002	6.81	10.53	4.12	5.52×10^{-5}
BDE-99	564.75	0.009	7.32	11.31	4.34	7.94×10^{-6}
BDE-100	564.75	0.04	7.24	11.13	n.a	7.07×10^{-6}
BDE-153	643.62	0.001	7.9	11.82	n.a	5.80×10^{-6}
BDE-154	643.62	0.001	7.82	11.92	n.a	2.64×10^{-7}
BDE-183	722.4	0.002	8.27	11.96	n.a	n.a
BDE-209	959.17	<0.001	6.3–12.6	13.21	6.30	9.28×10^{-9}

Table 1. Physicochemical properties of selected BDEs [1, 7, 9].

NBFR	Molecular weight	Water solubility (mg/L @ 25°C)	Log K _{ow}	Log K _{OA} (@25°C)	Log K _{oc}	Vapour pressure (Pa) (@25°C)
EH-TBB	549.92	1.10×10^{-5}	7.73	12.34	5.59	4.57×10^{-6}
BTBPE	687.64	1.90×10^{-5}	8.31	15.67	5.89	3.88×10^{-10}
BEH-TEBP	706.14	1.60×10^{-6}	9.34	16.86	6.45	1.55×10^{-11}
DBDPE	971.22	2.10×10^{-7}	11.1	19.22	7.00	6.00×10^{-15}

Table 2. Physicochemical properties of selected NBFRs [8, 10, 11].

2.1.1. *Impact of physicochemical properties on the environmental behaviour of BFRs*

Knowledge of the physicochemical properties of substances provides information about their potential environmental fate and behaviour.

2.1.1.1. *Molecular weight (MW)*

Depending on their molecular weight, chemicals show diverse behaviour in environmental and biological systems. With specific regard to PBDEs, variations in the degree of bromination drive variations in physicochemical properties such as vapour pressure, hydrophobicity and lipophilicity, which in turn lead to congener-specific variations in environmental fate and behaviour. For example, while those less brominated congeners prevalent in the commercial Penta- and Octa-BDE formulations are more bioaccumulative in aquatic biota; higher brominated congeners, such as BDE-209, predominated in sediments. However, potential degradation of higher brominated compounds could yield lower brominated PBDEs that display stronger bioaccumulation characteristics than BDE-209 itself [12].

2.1.1.2. *Vapour pressure (V_p)*

V_p is a useful indicator to determine the potential of chemicals to volatilise from surfaces to the atmosphere. Inhalation is less likely to be a substantial pathway of exposure to chemicals

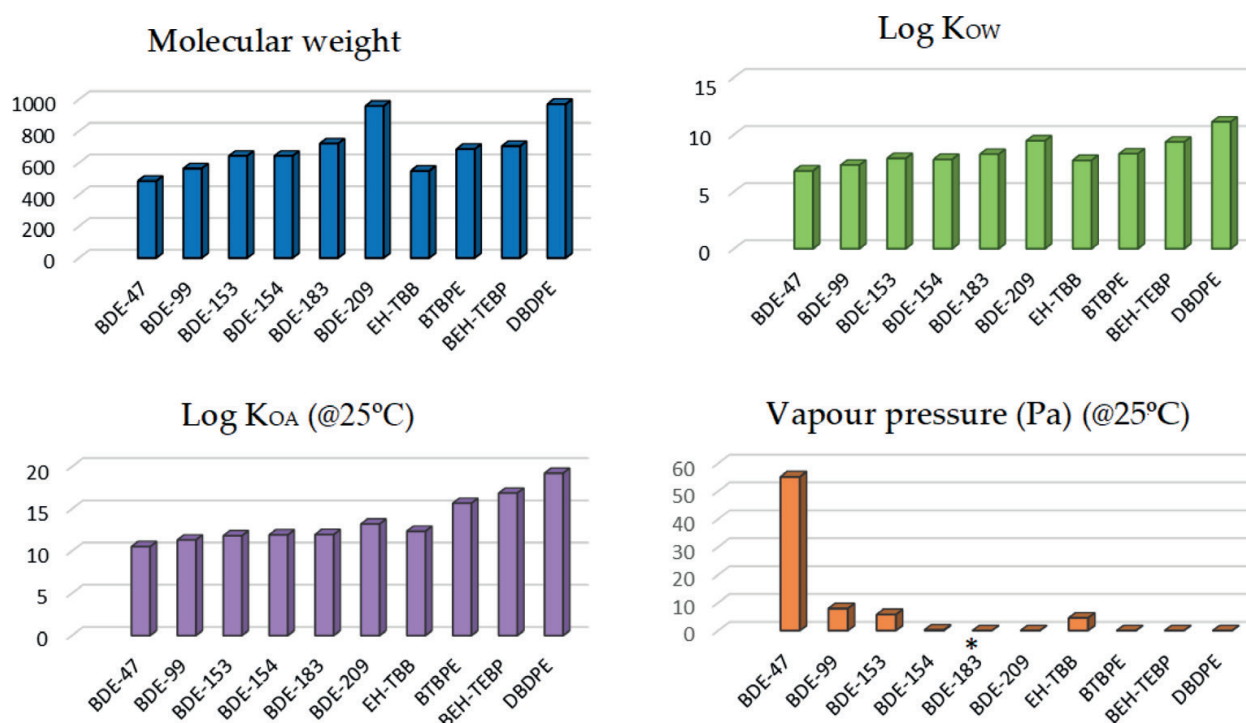


Figure 3. Molecular weight, Log K_{ow} (octanol/water partition coefficient), Log K_{OA} (octanol/air partitioning coefficient) and vapour pressure of selected PBDEs and NBFRs. *Octa-BDE.

with a $V_p < 10^{-6}$ mm Hg (10^{-4} Pa). Conversely, inhalation is likely significant for chemicals with a $V_p > 1 \times 10^{-4}$ mm Hg (10^{-2} Pa) [5]. Chemicals including many BFRs possess a V_p between 1×10^{-8} and 1×10^{-4} mm Hg partition between the gas and particulate phases and are thereby considered semi-volatile. The equilibrium between the two phases is controlled by the V_p , the surrounding air temperature, and the concentration and chemical composition of airborne particulate matter. V_p of PBDEs and NBFRs decrease with increasing molecular weight and degree of bromination [5, 7].

2.1.1.3. Octanol-air partition coefficient (K_{OA})

K_{OA} is a parameter that describes the partition of semi-volatile organic compounds (SVOCs) between the gas phase and organic matter such as that found in airborne particles. Commonly expressed as $\log K_{OA}$, it is the ratio between the concentration of the chemical in air and its concentration in octanol at the equilibrium state. As with V_p , $\log K_{OA}$ depends on the temperature. Higher $\log K_{OA}$ values imply stronger binding to the organic content of particles [13, 14]. As shown in **Tables 1** and **2**, $\log K_{OA}$ values fall between 9.5 and 13.2 for PBDEs and between 12.3 and 19.2 for NBFRs. This indicates that BFRs will deposit readily from the gas phase into indoor dust, soil and vegetative biomass. In addition, the wide range of $\log K_{OA}$ values implies a varying abundance of these pollutants in particulate phases [7].

2.1.1.4. Water solubility and octanol/water partition coefficient (K_{OW})

As shown in **Tables 1** and **2** and **Figure 3**, in general, PBDE water solubility values are higher than those of NBFRs. Water solubility is strongly inversely related to the K_{OW} . Commonly expressed as $\log K_{OW}$, this is an important property for assessing the environmental fate and

behaviour of chemicals. Generally, organic chemicals with a $\log K_{OW}$ value ≥ 5.0 are very hydrophobic, thereby displaying a high tendency to sorb organic carbon in sediments, soils, and indoor dust and—when combined with a resistance to metabolism—possess a marked capacity for bioaccumulation [7].

2.1.1.5. Organic carbon water partitioning coefficient (K_{OC})

Another important physiochemical property is K_{OC} , which provides an indication of a chemical to leach from soil to groundwater and to partition from the aqueous phase of water bodies to suspended solids and sediments. Chemicals with high K_{OC} values are strongly sorb to soil [5, 7]. In general, as shown in **Tables 1** and **2**, K_{OC} values for PBDEs (3.9–6.3) are slightly lower than by those of their replacements ($\log K_{OC}$ of NBFRs 5.8–7).

2.2. Environmental levels of PBDEs and NBFRs

PBDEs and NBFRs as additive flame retardants can be released from treated products and enter the environment via several ways. These include volatilisation and leaching from treated products, partitioning to indoor dust, leaching from landfills and recycling of waste products [15]. As a consequence of their persistence and potential for long-range atmospheric transport, PBDEs and NBFRs have been detected in Arctic media, transported on airborne particulates rather than the gas phase. The first detection of PBDEs was in 1979 in soil, and slug samples from the USA, with the first detection in vertebrates (fish and marine mammals collected from the Baltic Sea) were in the 1980s. By comparison with legacy BFRs, the occurrence of NBFRs in the environment is at lower levels; however, the last few years has seen a rise in contamination with NBFRs [16].

2.2.1. Levels of PBDEs and NBFRs in indoor and outdoor air

Depending on their V_p and K_{OA} , SVOC BFRs can volatilise from treated products and be abundant in both gaseous and particulate phases. The partitioning between the two phases is mainly driven by atmospheric temperature. It is expected that at a given temperature, lower brominated compounds are more abundant in the gas phase, while higher brominated congeners are more prevalent in the particle phase [14].

It is difficult to compare PBDEs levels in air samples between countries, due to the different number of individual congeners, sampling method (passive or active) and the atmospheric phase sampled (vapour, particle or both). PBDEs were detected in indoor air samples from the UK [17], Germany [18], Denmark [19], Sweden [20], USA [21], Canada [22], China [23], Japan [24], and Australia [25]. Concentrations were variable between countries. For the above-mentioned countries, PBDE concentrations were between 17 and 55 pg/m^3 in Japan and 210 and 3980 pg/m^3 in the USA. In Norway, the maximum concentration of BDE-209 in indoor air samples was 4150 pg/m^3 with a median concentration of 3.8 pg/m^3 ($n = 47$) [26].

In outdoor air samples, BFRs were detected at low levels compared with those in indoors. For each of BDE-47, BDE-99 and BDE-100, concentrations in indoor air were 100 times higher than

the outdoor in the UK [17]. In the USA, Σ PBDE concentrations ranged between 10 and 85 pg/m^3 , with BDE-47 predominant [27]. In China, concentrations of Σ tri-hepta-PBDEs ranged between 87.6 and 1941 pg/m^3 , with BDE-47 and BDE-99 predominant [28].

Recently, in addition to PBDEs, more attention has been paid to NBFRs. Low concentrations of NBFRs were detected in air samples. In Sweden, BEH-TEBP and DBDPE in indoor air ranged $<35\text{--}150 \text{ pg/m}^3$ and $< 90\text{--}250 \text{ pg/m}^3$ with detection frequencies of 15 and 8% for BEH-TEBP and DBDPE respectively [29]. In China, only EH-TBB and DBDPE were detected, at very low concentrations [30].

2.2.2. Levels of PBDEs and NBFRs in surface water

As a source of fresh water, lakes are important. In the UK, an average concentrations of tri-hexa-BDEs in nine English lakes was 61.9 pg/L . Spatial variation was found between lakes, however, no correlation was detected between PBDE concentrations and population density. In addition, no evidence a decline in concentrations during the sampling period [31]. Another study [32] in the USA, from 18 stations on the five Great Lakes' water, reported that the average concentrations of Σ tri-deca-BDEs (112 pg/L) were dominated by BDE-47 and BDE-99 with average concentrations of 26.8 and 26.4 pg/L respectively followed by BDE-209 (9.5 pg/L). Average concentrations of BEH-TEBP, EH-TBB and other NBFRs were 10.4, 5.6 and $<1.1 \text{ pg/L}$, respectively [32]. In sea water from the European Arctic, concentration of Σ_{10} PBDEs (tri-deca) in dissolved water and suspended phases of seawater ranged from 0.03 to 0.64 pg/L , with BDE-47 and BDE-99 predominant [33].

2.2.3. Levels of PBDEs and NBFRs in sediment and soil

PBDE congener profiles in sediments are dominated by higher brominated congeners such as BDE-209 and DBDPE. This is different from profiles in biota samples, which are dominated by lower brominated congeners, such as BDE-47 and BDE-99 [34]. In marine sediments, BFRs were detected in Canada [35], San Francisco Bay, USA [36], Gulf of Lion, France [37], Northern Arabian Gulf [38], East Java Province, Indonesia [39], Goseong Bay, Korea [40], South China [41], and the Scheldt estuary, the Netherlands [42]. With the exception of the Scheldt estuary, the Netherlands (where sediment concentrations ranged 14–22 ng/g dw for tri-hepta-BDEs and 240–1650 ng/g dw for BDE-209) and south China (for which sediment concentrations fell between 30 and 5700 ng/g dw for BDE-209); concentrations of PBDEs in other countries were very low. In surficial sediments sampled along cruise transects from the Bering Sea to the central Arctic Ocean, Σ_{24} PBDEs (without BDE-209) in the marine sediments ranged from $<\text{MDL}$ to 67.8 pg/g dw , with an average concentration of $9.8 \pm 11.9 \text{ pg/g dw}$ [43]. The study pointed that the Σ_{24} PBDE concentrations show a reduction from 2008 to 2012. In river sediment cores from China, PBDE concentrations ranged between 1.3 and 1800 ng/g dwt with the highest levels found at 4–6 cm depth [44].

Soil represents a major sink for many volatile organic pollutants operating during atmospheric transport. In Birmingham, UK, average concentrations of BDE-209 and Σ tri-hepta-BDEs in soil samples were 11 and 3.6 ng/g , respectively [45]. These concentrations were higher in sites

closest to Birmingham city centre [45]. In an e-waste recycling area in South China, PBDE and NBFR concentrations in rhizosphere soils and non-rhizosphere soils were 13.9–351 ng/g for PBDEs and 11.6–70.8 ng/g for NBFRs. BDE-209 and DBDPE were predominant compounds [46]. Another study in China emphasised that DBDPE and BDE-209 were the predominant compounds in the forest soil samples. The concentrations of DBDPE and BDE-209 ranged between 25–18,000 pg/g and <dl -5900 pg/g respectively. In the same study, the distribution of BEH-TEBP and most PBDEs were significantly correlated with population density. In addition, the correlation between PBDEs and their replacement products indicates similar environmental behaviour [47]. Possible debromination of BDE-209 to lower brominated congeners in soils and sediments is a major concern [48].

2.2.4. Levels of PBDEs and NBFRs in sewage sludge

Wastewater treatment plants may not be effective in removing PBDEs. About 52–80% and 21–45% PBDEs remained in effluent and dewatered sludge, respectively, post-sewage treatment [49]. On the other hand, both lower brominated PBDEs and BDE-209 could be successfully removed from contaminated sludge under aerobic conditions [50]. In Korea, concentrations of Σ PBDE in sludge ranged from 298 to 48,000 ng/g dry weight, and among 10 NBFRs, DBDPE and BTBPE were only detected in sludge samples. DBDPE and BTBPE concentrations ranged from <dl-3100 to <dl-21.0, with average concentrations of 237 and 1.57 ng/g dwt for DBDPE and BTBPE, respectively [40]. In Spain, the occurrence of eight PBDEs and NBFRs (EH-TBB, BTBPE, BEH-TEBP and DBDPE) was evaluated in wastewater from wastewater treatment plants. With the exception of BEH-TEBP, no PBDEs or NBFRs were detected in unfiltered influent samples. However, 279–2299 ng/g dwt of flame retardants were detected in primary sludge [51].

From 12 countries around the world, the highest levels of DBDPE in slug samples from wastewater treatment plants were found in Germany (216 ng/g dwt) compared with Europe (81 ng/g dwt) and North America (31 ng/g dwt). The highest concentrations of Deca-BDE were found in the UK and the USA with values of 12,000 ng/g dwt and 19,000 ng/g dwt, respectively [52]. In waste biological sludge and treated bio solids from wastewater treatment plants in Canada, BDE-209, BDE-99 and BDE-47 were the predominant compounds with concentrations of 230–82,000, 530–8800 and 420–6000 ng/g, for BDE-209, -99 and -47 respectively [53].

2.2.5. Levels of PBDEs and NBFRs in biota and food

During the last decade, in addition to PBDEs, their replacement of NBFRs has been shown to accumulate in biota. NBFR levels in seven animal species from the Arctic, specifically one fish species, three seabirds, and three mammalian species were investigated. BTBPE and DBDPE were not detected in any of these species, while EH-TBB was found in all species and BEH-TEBP in only five. Concentrations of EH-TBB ranged between 378 and 3460 pg/g wet wt, while those of BEH-TEBP ranged from 573 to 1799 in whole fish, liver, egg and plasma [54]. For PBDEs, Eulaers et al. [55] reported that PBDE concentrations in muscle, liver, adipose, preen gland and feathers in Barn Owls were 7.46–903 ng/g lw in 2008–2009, which were lower

than in those collected in 2003–2004 (46–11,000 ng/g lw). The authors tentatively ascribed the decline to the 2004 European ban of Penta- and Octa-BDE mixtures. By comparison, NBFRs were found to be poorly bioaccumulated (2.3%) [55].

PBDEs and NBFRs have been detected in human food, animal feed and baby food. In the UK, concentrations of Σ_{17} PBDEs in food samples ranged between 0.02 and 8.91 ng/g whole weight, and, in animal feed, samples ranged between 0.11 and 9.63 ng/g whole weight. The highest PBDE concentrations were detected in fish, processed foods and fish feeds [56]. In home produced eggs from e-waste sites in China, EH-TBB and BEH-TEBP were found in low concentrations in 50% of chicken egg samples, ranged between <dl-1.82 and 1.17–2.6 ng/g for EH-TBB and BEH-TEBP, respectively [57]. In the three categories of baby food (formula, cereal, and puree) from USA and Chinese stores, median concentrations of Σ PBDEs (sum of BDE-17, -28, -47, -49, -99, -100, -153, -183, and -209) were 21 and 36 pg/g for American and Chinese baby foods, respectively [58].

2.2.6. Levels of PBDE and NBFR in human tissues

As discussed above, numerous studies have shown the presence of PBDEs and NBFRs in many media pertinent for human exposure via inhalation, ingestion and dermal routes. Due to their persistent and bioaccumulative properties, PBDEs and NBFRs have been found in human milk, serum, hair and nail samples. EH-TBB, BEH-TEBP, BTBPE, DBDPE, BDE-209 and BDE-153 in paired human serum (n = 102) and breast milk (n = 105) samples from Canada were investigated. Only EH-TBB and BDE-153 (lower brominated degree and more bioaccumulative) had detection frequencies higher than 55% in both serum and human milk samples, while detection frequencies for other BFRs were lower than 30%. Concentrations in serum and human milk were 1.6 and 0.41 ng/g lw for EH-TBB, and 1.5 and 4.4 ng/g lw for BDE-153, respectively [59]. In the UK, the average concentrations of Σ tri-hexa-BDE and BDE-209 in human milk were 5.95 and 0.31 ng/g lw respectively. Concentrations of BDE congeners were BDE-47 > BDE-153 > BDE-99 [60]. BDE-47, -99, -100, and -183 were detected in most human hair samples from Hong Kong [61]. Concentrations of PBDEs in human hair samples in females were higher than males [62]. For NBFRs, EH-TBB and BEH-TEBP were detected in hair and nail samples at concentrations between 20 and 240 and 11 and 350 ng/g in hair samples and <17–80 ng/g and <9–71 ng/g in nail samples for EH-TBB and BEH-TEBP respectively [63].

2.2.7. Levels of PBDE and NBFR in indoor dust

As semi-volatile organic compounds (SVOCs) and additive flame retardants, PBDEs and NBFRs can be released from the products via volatilisation into surrounding air, depending on their V_p . Such volatilised pollutants may then undergo deposition to both suspended and settled indoor dust, with the relative partitioning between these two phases governed by the K_{OA} of the BFRs [13].

A large number of investigations around the world have reported high concentrations of BFRs in indoor dust. The highest levels of PBDEs were reported in US dust samples with

Country (media) [reference]	Median/range—indoor air (pg/m ³)				
	BDEs	EH-TBB	BEH-TEBP	BTBPE	DBDPE
USA [21]	760				
Germany [18]	37.8				
Sweden [20]	330				
Australia [25]	19				
China [23]	628				
UK [17]	128				
Sweden [29]			<35		<90
China [30]		7.2			40
Indoor dust (ng/g)					
Germany [78]	979.1	<3.0	343	<10	146
USA [79]		133	142	30	201
Canada [80]		120	99	30	
Pakistan [70]	143.8				
UK [64]	2862				
Kuwait [70]	339.4				
Iraq [72]	631.5	5.3	64.2	14.1	125
Egypt [71]	53.07	0.81	0.12	0.24	
Pakistan [81]		0.03	3.5	3.15	14
Surface water (pg/L)					
European Arctic [33]	0.03–0.64				
USA, Great Lakes [32]	117–623				
UK, lakes [31]	9.2–171.5				
Sediment and soil (pg/g dw)					
Arabian Gulf [38]	0.06–0.44				
Netherlands [42]	14,000–22,000				
China Marin sediment) [41]	30,000–5,700,000				
China (river sediment) [44]	1300–1800				
South China (soil) [46]	13,900–351,000				
China (forest soils) [47]	<dl-5900 (BDE-209)	<dl-1400	4–643		25–1800
Sewage sludge (ng/g dw)					
Korea [40]	298–48,000			<dl-21.0	<dl-3100
Spain [51]	279–2299 (BFRs)				
Canada (biological slug) [53]	230–82,000 (BDE-209)				

Country (media) [reference]	Median/range—indoor air (pg/m ³)				
	BDEs	EH-TBB	BEH-TEBP	BTBPE	DBDPE
Biota, food and human tissues (ng/g)					
The Arctic (fish and seabirds) [54]		0.378–3.460	0.573–1.799		
Belgium (Barn Owls) [55]	7.46–903				
UK (food samples) [56]	0.02–8.91				
UK (animal feed) [56]	0.11–9.63				
China (Egg) [57]		<dl-1.82	1.17–2.6		
Canada (serum) [59]	1.5(BDE-153)	1.6			
Canada (human milk) [59]	4.4 (BDE-153)	0.41			
UK (human milk) [60]	6.26				
Hong Kong (human hair) [61]	0.86–5.24 (BDE-47)				

Table 3. Concentrations of PBDEs and NBFRs in air, water, sediment, soil, indoor dust and human tissues from different countries around the world.

median concentrations of Σ PBDEs ranging between 1910 and 21,000 ng/g [21, 63]. The UK displayed the second highest PBDE indoor levels with concentrations ranging between 2900 and 10,000 ng/g [64]. For other parts of the world, Σ PBDE median concentrations were: 950 ng/g in Canada [65], 386 ng/g in Germany [18], 510 ng/g in Sweden [20], 1941 ng/g in China [61] and 1200 ng/g in Australia [66]. In the Middle East, the first study in Kuwait in 2006 reported a median concentration of Σ PBDEs of 90.6 ng/g [67], these levels increased in 2011 to a median concentration of 356 ng/g [68]. In Egypt, Iraq and Pakistan, Σ PBDE median concentrations were 46 [69], 635 [70] and 143 ng/g [68], respectively. Similar to the distribution of PBDE congeners in indoor dust from UK and China, BDE-209 was the major BFR detected in indoor dust from the Middle East. The PBDE congener profiles have changed, and Penta-BDE levels were about one-third those measured in previous studies in 2006 [71, 72].

Recently, studies have increasingly measured NBFRs in indoor dust. EH-TBB, BEH-TEBP, BTBPE and DBDPE represented the highest NBFR concentrations in house dust in the USA [73], with a distribution profile of EH-TBB > BEH-TEBP > DBDPE > BTBPE. The median concentrations were 337, 186, 22.3 and 82.8 for EH-TBB, BEH-TEBP, BTBPE and DBDPE respectively [74]. In Europe, NBFR concentrations and profiles differ from those in the USA. The major compounds in European indoor dust are DBDPE and BEH-TEBP, with EH-TBB and BTBPE present at lower levels. In the UK (classroom dust), median concentrations were 25, 96, 9 and 98 for EH-TBB, BEH-TEBP, BTBPE and DBDPE, respectively [75]. Meanwhile, in Sweden, median concentrations of EH-TBB, BEH-TEBP, BTBPE and DBDPE were 51, 47, 320, 2.6, 61, 6.3, and 150 ng/g, respectively [76].

In China, in addition to the elevated concentrations of PBDEs, high concentrations of NBFRs were detected in floor house dust as well. Σ PBDEs ranged between 685 and 67,500 ng/g, and Σ NBFRs ranged between 1460 and 50,010 ng/g in indoor dust from e-waste sites, with BDE-209 and DBDPE the major BFRs. DBDPE was predominant (nd–16,000 ng/g) followed by

BEH-TEBP (nd—1600), BTBPE (0.2–220 ng/g) and EH-TBB (nd—6300 ng/g) [77]. In addition to the mentioned studies, **Table 3** summarises concentrations of PBDEs and NBFRs in air, water, sediment, soil, indoor dust and human tissues from different countries around the world.

3. Conclusion

Depending on their physiochemical properties, PBDEs and NBFRs show diverse behaviour in various environmental media and the possibility of human exposure. Low molecular weight compounds (less brominated degree) possess lower vapour pressures and higher $\log K_{OA}$. This implies a high tendency of such chemicals to the gas phase of indoor air and consequently the exposure will occur via inhalation pathway. On the other hand, water solubility and octanol/water partition coefficient (K_{OW}) are important properties to assess the tendency of higher brominated compounds to organic carbon in sediment, soils, and indoor dust, in which the main exposure will occur via ingestion. This is different from profiles in biota samples which are dominated by lower brominated compounds such as BDE-47 and EH-TBB. The highest levels of PBDEs and NBFRs were reported in US, China and UK indoor dust samples, which were dominated by BDE-209, DBDPE and BEH-TEBP with a decline in PBDE levels and rise in NBFRs.

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