

Evaluation of Long-Range Transport Potential of Selected Brominated Flame Retardants with Measured 1-Octanol–Air Partition Coefficients

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Various alternative flame retardants are used in many countries since polybrominated diphenyl ethers (PBDEs) were classified as persistent organic pollutants (POPs). However, difficulties in the evaluation of the long-range transport potential (LRTP) of the alternatives are related to the lack of information on their physicochemical properties, which govern their environmental fates and transport. Based on the simulation of LRTP using OECD P_{OV} and LRTP Screening Tool, five alternative brominated flame retardants (BFRs) (hexabromobenzene [HBB], 2,3,4,5,6-pentabromotoluene [PBT], 2,3,4,5,6-pentabromoethyl benzene [PBEB], 2-ethylhexyl 2,3,4,5-tetrabromobenzoate [TBB], and 1,2,4,5-tetrabromo-3,6-dimethylbenzene [TBX]), and 3 PBDEs (BDE-28, BDE-47, and BDE-99) were chosen to perform a refined assessment. This was done using an experimentally measured 1-octanol–air partition coefficient (K_{OA}) for the calculation of the air–water partition coefficient (K_{AW}) required for the model. The four selected alternative BFRs (HBB, PBT, PBEB, TBX) have K_{OA} values close to the *in silico* estimation used in the screening evaluation. On the other hand, the measured K_{OA} value for TBB was two orders of magnitude lower than the estimated value used in the screening simulation. The refined simulation showed that characteristic travel distance (CTD) and transfer efficiency (TE) for HBB, PBT, PBEB, and TBX were greater than those for BDE-28, whereas CTD and TE for TBB were lower than those for BDE-28. This suggested that TBB has a lower LRTP than BDE-28, considering the refined partition coefficients.

Keywords: Long-range transport potential, Environmental fate, Partition coefficient, Degradability, Alternatives

Flame retardants have been used for decades to prevent the progress of a fire.¹ Brominated flame retardants (BFRs) have been the most widely used for many applications. Their chemical stability makes them persistent in the environment and, consequently, causes harmful effects on humans and wildlife.^{2,3} In 2009, tetra- and pentabromodiphenyl ethers (2,2',4,4'-tetrabromodiphenyl ether [BDE-47], 2,2',4,4',5-pentabromodiphenyl ether [BDE-99], and other tetra- and pentabromodiphenyl ethers present in commercial pentabromodiphenyl ether) were listed, and a commercial mixture of decabromodiphenyl ether is under consideration of being listed, in Annex A of the Stockholm Convention.⁴

With the international regulation of polybrominated diphenyl ethers (PBDEs), alternative flame retardants have been developed, and the number of substitutes for PBDEs has greatly increased.^{5–9} According to a recent report by the Norwegian Institute for Air Research (NILU), inorganic flame retardants such as aluminum hydroxides are mainly used in the United States and Europe, whereas brominated organic compounds are mainly used in Asian countries including China, Japan, and Korea.¹ There are many alternative BFRs including tetrabromobisphenol A (TBBPA), allyl 2,4,6-tribromophenyl ether (ATE), 1,2-bis(2,4,6-

tribromophenoxy)ethane (BTBPE), and 2,3,4,5,6-pentabromotoluene (PBT).^{1,5} Because alternative BFRs have chemical structures similar to those of the already banned PBDEs, they are also suspected to be persistent in the environment after release.¹⁰ Indeed, several researchers have reported the environmental occurrence of alternative BFRs.^{6,11–13} However, the chemicals monitored in those studies were limited to a few substances, and there is still much to be revealed before we can judge the environmental persistence and long-range transport potential (LRTP) of the many alternatives in use.

Conclusive evidence by field monitoring requires extensive studies around the world after the chemical substances in question have been released for a long time. For alternatives, and new chemicals recently developed, models are often the only available tools for assessing environmental persistence and LRTP. Several models such as ELPOS,¹⁴ TaPL III,¹⁵ and Globo-POP¹⁶ have been developed to evaluate the persistence and LRTP of organic chemicals. Those simple models require only a few input parameters (molecular weight [MW], partition coefficients, and half-lives in environmental media). More sophisticated models, such as Globo-POP, may adapt non-steady-state mass-balance equations, and include thermodynamic parameters such as

enthalpies of phase transfer, to include temperature effects.¹⁷ The Organization for Economic Cooperation and Development (OECD) reviewed the existing models and developed the OECD P_{OV} and LRTP Screening Tool, a fugacity-based steady-state multimedia model, in which the overall persistence (P_{OV}), characteristic travel distance (CTD), and transfer efficiency (TE) are used as output values for environmental persistence and LRTP.^{18,19}

Because partition coefficients are essential parameters in those models, reliable input values are required to obtain a reliable evaluation of the LRTP. Partition coefficients used in those screening models are inter-related. The value of the air–water partition coefficient (K_{AW}) can be estimated using the ratio of the vapor pressure to water solubility or the ratio of the octanol–air partition coefficient (K_{OA}) to the octanol–water partition coefficient (K_{OW}).²⁰ The model outcomes could be greatly improved by providing experimentally measured partition coefficients.

The main purpose of this study was to refine the evaluation of the LRTP with experimentally measured K_{OA} values for BFR alternatives that are suspected to have LRTP. Based on the preliminary evaluation of the LRTP using the OECD P_{OV} and LRTP Screening Tool Version 2.2, five BFR alternatives for which the CTD was greater than or equal to that of already restricted BDE-28 were chosen.

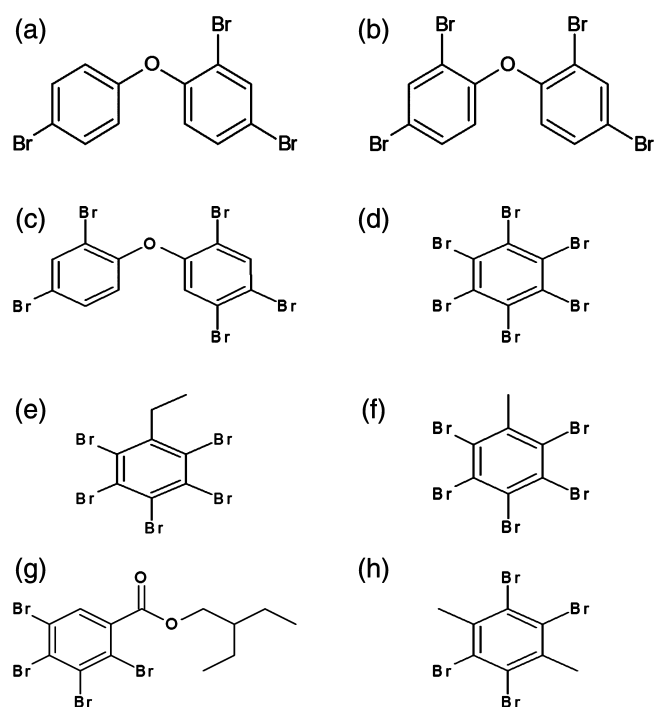


Figure 1. Chemical structures of selected chemicals: (a) 2,4,4'-tribromodiphenyl ether (BDE-28), (b) 2,2',4,4'-tetrabromodiphenyl ether (BDE-47), (c) 2,2',4,4',5-pentabromodiphenyl ether (BDE-99), (d) hexabromobenzene (HBB), (e) 2,3,4,5,6-pentabromoethylbenzene (PBEB), (f) 2,3,4,5,6-pentabromotoluene (PBT), (g) 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB), (h) 1,2,4,5-tetrabromo-3,6-dimethylbenzene (TBX).

The values of $\log K_{OA}$ were determined using the air–boundary layer diffusion method. Refined assessment was conducted with experimental $\log K_{OA}$ values, and the results were compared with the initial screening.

Experimental

Chemicals. High-purity 1-octanol ($\geq 98\%$) was purchased from Sigma-Aldrich (St. Louis, MO, USA). The experimental method was verified using 2,4,4'-tribromodiphenyl ether (BDE-28), BDE-47, and BDE-99 because their partition coefficients have already been reported.^{21–24} 2,2',3,4,4',5',6-heptabromodiphenyl ether (BDE-183) was employed as internal standard. All standards of PBDE congeners (50 $\mu\text{g/mL}$ in isooctane) were obtained from Accustandard (New Haven, CT, USA). Five alternative BFRs were chosen for the experimental determination of the 1-octanol–air partition coefficient (K_{OA}). The compounds hexabromobenzene (HBB, $>98\%$; CAS Reg. no. 87-82-1), 2,3,4,5,6-pentabromotoluene (PBT, $>98\%$; CAS Reg. no. 87-83-2), 2,3,4,5,6-pentabromoethylbenzene (PBEB, 99.8%; CAS Reg. no. 85-22-3), 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB, $>98\%$; CAS Reg. no. 183658-37-7), and 1,2,4,5-tetrabromo-3,6-dimethylbenzene (TBX, $>95\%$; CAS Reg. no. 23488-38-2) were purchased from Sigma-Aldrich, Tokyo Chemical Industry (Tokyo, Japan), Fluka (Buchs, Switzerland), Toronto Research Chemical (Toronto, Canada), and Oxchem Corporation (Irwindale, CA, USA), respectively. The chemical structures of all selected BDEs and BFR alternatives are presented in Figure 1.

Evaluation of Environmental Persistence Using the OECD P_{OV} and LRTP Screening Tool Version 2.2. The OECD P_{OV} and LRTP Screening Tool Version 2.2 (OECD Tool), a fugacity-based steady-state multimedia mass-balance model, was used for evaluating the environmental persistence and LRTP of BFR alternatives. This model was designed to assess environmental persistence and LRTP using a few physicochemical properties that are essential in the evaluation of the environmental fate of organic chemicals.¹⁹ These properties are the half-lives in the three environmental media (*i.e.*, air, seawater, and soil), molar mass, air–water partition coefficient, and the octanol–water partition coefficient (K_{OW}). Outputs of the model include LRTP and P_{OV} . LRTP is further expressed in terms of CTD and TE.¹⁹ CTD is defined as the distance from the point of emission to the point where the concentration has decreased to 37% of the emission concentration, and TE is described as the ratio of deposition mass flux to emission mass flux. It is calculated for emission via air, water, and soil.^{15,25,26}

For running the model, the parameters obtained by reliable experimental values were of priority. Whereas the experimental partition coefficients (K_{OW} , K_{OA} and K_{AW}) for BDE-28, BDE-47, and BDE-99 were available,^{21–24} no experimental values were reported for the selected

alternatives (PBT, PBEB, TBB, and TBX). The K_{OW} and K_{OA} values for HBB were reported by Kuramochi and coworkers.^{27,28} Thus, the K_{OW} and K_{OA} values were estimated using KOWWIN²⁹ and HENRYWIN,²⁹ respectively. The air–water partition coefficients (K_{AW}) obtained in this study using experimental or estimated K_{OW} and experimental K_{OA} were used in the refined assessment. Because the half-lives in environmental media were not available for all selected chemicals, the half-lives in air were estimated using AOPWIN²⁹ and those in water were estimated using the expert judgment model of BIOWIN.²⁹ Because a range of aqueous half-life are estimated by BIOWIN,²⁹ it was converted to half-life according to Aronson *et al.*³⁰ Soil half-lives were assumed to be double those of the water, as was done in a previous study.³¹ All the input and output values used are summarized in Table 1.

Determination of 1-Octanol–Air Partition Coefficients (K_{OA}). The values of K_{OA} were determined by the method described by Ha and Kwon,³² in which the measured mass transfer rate in the air–boundary layer is used for the derivation of K_{OA} . Detailed theory and procedure for the determination of K_{OA} is presented elsewhere.³³ In short, the diffusive mass transfer of vaporized substances from the octanol solution to a drop of octanol hanging from a syringe needle is described by a simple one-compartment model as follows:

$$\frac{dC_{\text{drop}}}{dt} = k_a C_a - k_d C_{\text{drop}} \quad (1)$$

where C_{drop} and C_a are the concentrations of a test chemical in the octanol drop and in air, respectively, and k_a and k_d are absorption and desorption rate constants, respectively. Because the volume of air in the headspace of the vial was approximately $2.0 \times 10^{-6} \text{ m}^3$, and the volume of the octanol solution in the vial was $2.00 \times 10^{-7} \text{ m}^3$, it was assumed that the headspace was rapidly equilibrated with the test chemical from the octanol solution and that the concentration in the air did not change with time. Thus, C_a is approximated by $C_{\text{octanol}}/K_{OA}$. The octanol–air partition coefficient is also expressed as the ratio of k_a to k_d , and Eq. (1) becomes

$$\frac{dC_{\text{drop}}}{dt} = k_d (C_{\text{drop}} - C_{\text{octanol}}) \quad (2)$$

Integration of Eq. (2) gives

$$\ln \left(1 - \frac{C_{\text{drop}}(t)}{C_{\text{octanol}}} \right) = k_d t \quad (3)$$

Thus, k_d is experimentally determined by measuring changes in C_{drop} with time. Using a two-film steady diffusion model, k_d is expressed as

$$k_d = \frac{D_a}{K_{OA} \delta_a} \frac{A}{V_{\text{drop}}} \quad (4)$$

where D_a is the diffusion coefficient of the test chemical, δ_a is the thickness of the air diffusion–boundary layer, A is the surface area of the drop, and V_{drop} is the volume of the drop. A spacer was used to provide a constant gap of 3 mm between the octanol solution and the octanol drop. The value of δ_a was estimated in a previous study³² and found to be 0.000725 m. From the volume of the hanging octanol drop (V_{drop}), *i.e.*, $1.00 \times 10^{-9} \text{ m}^3$, the surface area of a sphere (A) was estimated to be $4.84 \times 10^{-6} \text{ m}^2$. The value of the diffusion coefficient in air was calculated using the Fuller–Schettler–Giddings correlation method.³³

$$D_a = \frac{10^{-3} \times T^{1.75} \times \left[\left(\frac{1}{M_a} \right) + \left(\frac{1}{M_{\text{BFRs}}} \right)^{\frac{1}{2}} \right]}{p \times \left[(\nu_a)^{\frac{1}{3}} + (\nu_{\text{BFRs}})^{\frac{1}{3}} \right]^2} \quad (5)$$

where M_a and M_{BFR} are the MW of air and the test BFR, respectively; and ν_a and ν_{BFR} are the molar volume of air and the BFR, respectively. The molar volume was calculated using the Abraham and McGowan method.³⁴ The temperature (T) was maintained at 298 K and the pressure (p) was ambient (*i.e.*, 1 atm). The experiments were conducted using three mixtures (mixture A: BDE-28 and BDE-47; mixture B: PBEB, TBB, and TBX; mixture C: BDE-99 and HBB) and a single chemical (PBT), assuming that there were negligible interactions between the solutes at

Table 1. Reported physicochemical properties for selected chemicals used as model input values.

Abbreviation	Molar mass (g/mol)	Log K_{AW}	Log K_{OW}	Half-life in air (h) ²⁹	Half-life in water (h) ²⁹	Half-life in soil (h) ^a
BDE-28	406.90	−2.71 ²²	5.94 ²¹	90.8	2880	5760
BDE-47	365.7	−3.46 ²²	6.81 ²³	128	5760	11500
BDE-99	374.52	−4.01 ²²	7.39 ²³	233	17300	34600
HBB	551.49	−3.01 ²⁸	6.07 ²⁷	11200	17300	34600
PBEB	500.65	−2.49 ²⁹	7.48 ²⁹	112	5760	11500
PBT	486.62	−2.60 ²⁹	6.99 ²⁹	694	5760	11500
TBB	549.92	−3.59 ²⁹	8.75 ²⁹	11.8	2880	5760
TBX	421.75	−2.17 ²⁹	6.65 ²⁹	270	5760	11500

^a Twice water half-lives.

sufficiently low concentration. The initial concentrations in the octanol dosing solutions were 25 $\mu\text{g/mL}$ for BDE-99; 50 $\mu\text{g/mL}$ for BDE-28 and BDE-47; 100 $\mu\text{g/mL}$ for HBB, PBEB, TBB, and TBX; and 1000 $\mu\text{g/mL}$ for PBT. The same concentration of the internal standard (0.50 $\mu\text{g/mL}$) was spiked to both the octanol dosing solution and to the hanging drop. The potential experimental errors with the volume and the surface area were corrected by the measured concentration of the internal standard. The experimental results were excluded when the measured concentration of the internal standard deviated by more than 10% from the expected value for the derivation of k_d .

Instrumental Analyses. All BDEs and BFR alternatives were quantified using an Agilent 5890 gas chromatograph (GC) (Palo Alto, CA, USA) equipped with a split/splitless injector and an electron capture detector (ECD). The octanol drop from which analytes were extracted was directly injected without dilution to the GC-ECD, and the octanol dosing solution was diluted appropriately before the GC-ECD analysis. Analytes were separated on a 30-m HP-5 column (J&C Scientific, Folsom, CA, USA) with 0.25 mm i.d. and 0.25 μm film thickness, and with nitrogen as a carrier gas. The injector temperature was maintained at 240 and 250°C for BFR alternatives (HBB, PBEB, TBB,

TBX, and PBT) and PBDEs, respectively, and the detector temperature was 300°C. The GC oven temperature program for PBT was as follows: the initial temperature of 100°C was held for 2 min, followed by increase at the rate of 25°C/min to 260°C; at 1.5°C/min to 280°C; and at 25°C/min to 320°C, where it was held for 15 min. For PBDEs, PBEB, TBB, and TBX, a simpler oven temperature program was used as follows: the initial temperature of 90°C was ramped to 300°C at 15°C/min, and then held for 5 min. The oven program for HBB and BDE-99 consisted of the initial temperature at 140°C (1 min), 20°C/min to 220°C held for 5 min, 15°C/min to 300°C maintained for 10 min.

Results and Discussion

Choice of BFR Alternatives and Their Octanol–Air Partition Coefficients. Many BFR alternatives showed CTD and TE values greater than that of BDE-28, which has already been restricted under the Stockholm Convention.⁴ Among them, five substances of interest (HBB, PBT, PBEB, TBB, and TBX) were chosen for the precise determination of K_{OA} and derivation of the K_{AW} value using K_{OA} for the OECD Tool because (1) their LRTP is greater

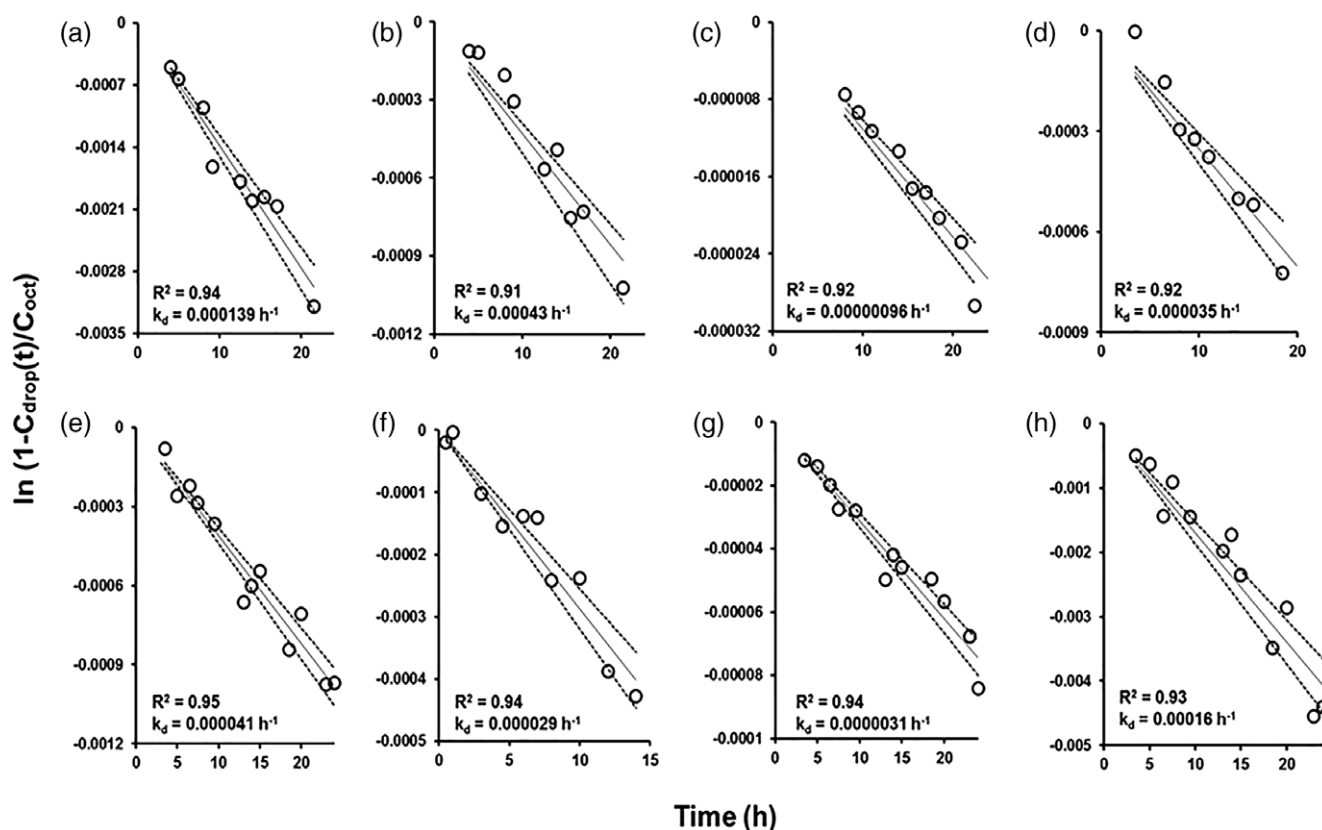


Figure 2. Determination of desorption rate constants for (a) 2,4,4'-tribromodiphenyl ether (BDE-28), (b) 2,2',4,4'-tetrabromodiphenyl ether (BDE-47), (c) 2,2',4,4',5-pentabromodiphenyl ether (BDE-99), (d) hexabromobenzene (HBB), (e) 2,3,4,5,6-pentabromoethylbenzene (PBEB), (f) 2,3,4,5,6-pentabromotoluene (PBT), (g) 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB), (h) 1,2,4,5-tetrabromo-3,6-dimethylbenzene (TBX). Solid lines represent regression lines using Eq. (3), and dashed lines show the 95% confidence interval.

or similar to that of BDE-28 (already regulated as a POP), (2) the properties used for the evaluation are not highly reliable without experimental values, (3) they are widely used and commercially available, and (4) their expected log K_{OA} values are below 13.0, and so can be determined by the experimental method.³²

Figure 2 shows the determination of desorption rate constants for BDEs and BFR alternatives using Eq. (3). For all test chemicals, the coefficients of determination (R^2) were greater than 0.9, indicating that the uptake of chemicals by the hanging drop was well explained by the model. The highest k_d values were measured for TBB, followed by BDE-28, HBB, BDE-47, PBEB, PBT, TBX, and BDE-99.

Table 2 summarizes the experimentally obtained k_d and log K_{OA} values for the selected BDEs and alternatives, as well as the log K_{OA} values reported in the literature. Harner and Shoeib²² reported log K_{OA} values for BDE-28, BDE-47, and BDE-99 as 9.50, 10.53, and 11.31, respectively, using a generator column method. Their values are consistently higher than those obtained in this study. This difference might have originated from a difference in the experimental methods used. In the generator column method, chemicals in the air that passed through a column containing glass beads coated with octanol solution were captured by an absorbent trap and quantified. Thus, the measured air concentration might be lower than the equilibrated concentration with octanol coating due to (1) insufficient equilibration between octanol coating and passing air, and (2) low absorption efficiency using a trap. Thus, the generator column method might overestimate the K_{OA} . On the other hand, the desorption rate constants might be influenced by small dust particles that could accelerate the overall transfer of BDEs from the octanol solution to the hanging drop. As presented in Eq. (4), an overestimated k_d might lead to an underestimation of K_{OA} .

In order to support the validity of the method, the internal consistency between three partition coefficients (*i.e.*,

Table 3. Comparison of deviation of reported log K_{OA} for and measured log K_{OA} for BDEs.

Abbreviation	Deviation of log K_{OA} ³⁵	
	Literature log K_{OA} values	This study
BDE-28	0.45 ^a	−0.18 ^b
BDE-47	0.37 ^c	−0.78 ^d
BDE-99	0.25 ^c	−0.03 ^d

^a Values of log K_{OW} , log K_{AW} , and log K_{OA} are from Refs 21,22,24, respectively.

^b Values of log K_{OW} , log K_{AW} , and log K_{OA} are from Refs 21,22 and measured in this study, respectively.

^c Values of log K_{OW} , log K_{AW} , and log K_{OA} are from Refs 22,23,24, respectively.

^d Values of log K_{OW} , log K_{AW} , and log K_{OA} are from Refs 22,23, respectively.

K_{OW} , K_{OA} , and K_{AW}) was checked (Table 3). The deviation of log K_{OA} , defined as log K_{OA} + log K_{AW} —log K_{OW} ,³⁵ was −0.18 and −0.03 for BDE-28 and BDE-99, respectively. For BDE-47, it was more negative (−0.78), but still the deviation was within one order of magnitude, supporting the validity of the experimental method.

For BFR alternatives except for TBB, the experimental log K_{OA} values agreed well with the values estimated using KOAWIN.²⁹ However, the experimental values of log K_{OA} for TBB were lower than those estimated by KOAWIN, by approximately two orders of magnitude. KOAWIN calculates K_{OA} using K_{AW} and K_{OW} values estimated using the bond-contribution method.^{36,37} However, the K_{AW} value for TBB calculated using vapor pressure and water solubility was estimated by the EPISuite program, and was greater by two orders of magnitude than that obtained by HENRY-WIN, indicating an inconsistency. This inconsistency might be due to limitations of the bond-contribution method, namely the exclusion of specific intermolecular and intramolecular interactions³⁸ and the limited size of the training set.

Table 2. Summary of reported physicochemical properties and experimentally obtained k_d and log K_{OA} values for selected flame retardants.

Chemicals	Molar volume ³⁴ (cm ³ /mol)	Diffusion coefficient in air ³³ (D_a ; m ² /h)	Desorption rate constant ^a (k_d ; h ^{−1})	Measured log K_{OA} ^b	Measured log K_{AW} ^c	Literature log K_{OA}	Literature log K_{AW}
BDE-28	348.2	0.01555	1.39 (1.26, 1.51) × 10 ^{−4}	8.87 (8.78, 8.97)	−2.93	9.50 ²⁴	−2.71 ²²
BDE-47	365.7	0.01511	4.30 (3.70, 4.80) × 10 ^{−5}	9.38 (9.27, 9.48)	−2.57	10.53 ²⁴	−3.46 ²²
BDE-99	374.52	0.01487	9.60 (9.00, 10.2) × 10 ^{−7}	11.01 (10.92, 11.11)	−3.62	11.31 ²⁴	−4.01 ²²
HBB	255.36	0.01785	3.50 (3.10, 4.00) × 10 ^{−5}	9.53 (9.43, 9.64)	−3.46	9.13 ²⁹	−3.01 ²⁸
PBEB	305.4	0.01645	4.10 (3.80, 4.40) × 10 ^{−5}	9.43 (9.34, 9.52)	−1.95	9.97 ²⁹	−2.49 ²⁹
PBT	271.6	0.01740	2.90 (2.50, 3.63) × 10 ^{−5}	9.61 (9.50, 9.71)	−2.60	9.60 ²⁹	−2.61 ²⁹
TBB	531.7	0.01253	3.10 (2.90, 3.30) × 10 ^{−6}	10.43 (10.34, 10.52)	−1.68	12.34 ²⁹	−3.59 ²⁹
TBX	287.9	0.01701	1.60 (1.50, 1.80) × 10 ^{−4}	8.85 (8.75, 8.94)	−2.20	8.82 ²⁹	−2.17 ²⁹

^a Values in parentheses represent 95% confidence interval of regression.

^b Values in parentheses are the corresponding ranges obtained by error propagation.

^c Measured log K_{AW} = log K_{OW} —measured log K_{OA} in this study.

Table 4. Comparison of overall persistence (P_{OV}), characteristic travel distance (CTD), and transfer efficiency (TE) values based on K_{OA} values from the literature and values measured in this study.

Chemicals	P_{OV} (days)		CTD (km)		TE (%)	
	Using literature value	Using measured value	Using literature value	Using measured value	Using literature value	Using measured value
BDE-28	340	340	1700	1700	1.2	1.5
BDE-47	690	690	690	2400	3.8	2.0
BDE-99	2100	2100	2100	2800	10	9.3
HBB	2000	2100	21 000	10 000	260	92
PBEB	690	690	2100	2200	1.7	0.7
PBT	690	690	8200	8200	25	25
TBB	350	350	1800	290	5.0	0.03
TBX	670	670	5100	5100	4.2	4.4

LRTP of Selected BFRs. Table 4 compares the LRTP of five alternative BFRs and three PBDEs using the experimentally measured $\log K_{OA}$ values and $\log K_{AW}$ values estimated in the literature. P_{OV} was determined by the soil emission scenario. Because P_{OV} is known to rely more on environmental degradability,⁷ the refinement of the partition coefficients did not change the calculated P_{OV} values significantly. Because the measured $\log K_{OA}$ values were close to those estimated from $\log K_{OW}$ and $\log K_{AW}$ in the literature, the calculated CTD and TE values were not very different from each other, except for TBB. The calculated CTD and TE values for TBB changed from 1800 to 290 km and from 5.0 to 0.03%, respectively, using the experimentally measured $\log K_{OA}$. Although the LRTP calculated using the estimated partition coefficients were greater than those for BDE-28, the refined simulation with measured $\log K_{OA}$ values.

TBB, based on its partitioning properties, is classified as a single hopper that predominantly adsorbs to the aerosols in the air and irreversibly deposits in water and soil.³⁹ TBB has a relatively short half-life in the atmosphere among the selected chemicals,²⁹ because the photolysis rate of TBB in the gas phase is high. With the larger $\log K_{OA}$ value for TBB, almost all TBB is adsorbed on aerosols in the atmosphere, preventing photolysis and resulting in greater CTD and TE values.

Although environmental degradability was not refined in this study, half-lives in environmental media are also very important in determining environmental persistence.^{7,8} The degradability of synthetic organic chemicals in water and soil is usually estimated based on ready or inherent biodegradability data,⁷ and degradability in air is estimated using hydroxyl-radical rate constants.⁷ Most of the reported hydroxyl-radical rate constants were measured or estimated in the gas phase. However, a significant proportion of persistent organic pollutants (POPs) tend to adsorb the atmospheric-particle partition due to high $\log K_{OA}$ values, and this partitioning explains differences in the LRTP. The reaction rate of those chemicals with atmospheric oxidants, such as hydroxyl radicals, should be influenced by heterogeneous chemistry. Thus, it is also required to develop

laboratory methods to evaluate the reactivity of POPs on atmospheric particles if we are to refine the estimation of LRTP indicators.

Modeling studies provide valuable screening assessment results for newly developed chemicals or alternatives to chemicals under regulations, because it has not been long enough for them to be released to the environment. Field observation is required to confirm the environmental persistence and LRTP for those substances. Monitoring suspected POPs in the Arctic region would give us affirmative results about their LRTP screened by modeling studies.

Conclusion

1-Octanol–air partition coefficients were determined for selected BFR alternatives, and their LRTPs were evaluated using the OECD Tool ver. 2.2. All selected BFR alternatives were found to be more persistent than BDE-28 except for TBB. Indicators of LRTP for TBB were lowered by the refined assessment using the experimentally determined K_{OA} value. The refined value was two orders of magnitude lower than the previously estimated value, suggesting that TBB has limited LRTP, although other partition coefficients also need to be precisely determined.

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