



Novel flame retardants: Estimating the physical–chemical properties and environmental fate of 94 halogenated and organophosphate PBDE replacements



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HIGHLIGHTS

- Physical–chemical properties, degradation rates of 94 flame retardants estimated.
- Most estimates within 10^2 – 10^3 , compounds >800 g/mol or polar could differ by 10^{12} .
- Using OECD Screening Model, 50% of FRs have high to medium persistence.
- About half of FRs have LRTP potential, which is likely an underestimation.

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ABSTRACT

In the wake of the listing by the Stockholm Convention of PBDEs, an increasing number of “novel” flame retardants (NFRs) are being used in products. The properties that make for desirable flame retardants can also lead to negative health effects, long environmental residence times and an affinity for organic matrices. While NFRs are currently in use, little information is available regarding their physical–chemical properties and environmental fate. In this study, 94 halogenated and organophosphate NFRs were evaluated for their persistence and long-range transport potential. Physical–chemical properties (namely liquid sub-cooled vapor pressure P_l and solubility S_l , air–water (K_{AW}), octanol–water (K_{OW}), and octanol–air (K_{OA}) partition coefficients) of the NFRs were predicted using three chemical property estimation tools: EPI Suite, SPARC and Absolv. Physical–chemical properties predicted using these tools were generally within 10^2 – 10^3 for compounds with molecular weight < 800 g/mol. Estimated physical–chemical properties of compounds with >800 g/mol, and/or the presence of a heteroatom and/or a polar functional group could deviate by up to 10^{12} . According to the OECD P_{OV} and LRTP Screening Tool, up to 40% of the NFRs have a persistence and/or long range transport potential of medium to high level of concern and up to 60% have persistence and or long range transport potential similar to the PBDEs they are replacing. Long range transport potential could be underestimated by the OECD model since the model under-predicts long range transport potential of some organophosphate compounds.

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1. Introduction

Flame retardants (FRs) are used to reduce the flammability of a product or to slow down the spread of the flames once it is burning. Halogenated FRs have been in use since the 1940's with a sharp increase in demand and production since then due to the implementation of flammability standards and increased use of synthetic materials. The increasing demand has been met by

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the synthesis of new chemicals with more desirable properties in terms of flame retardancy (Hindersinn, 1990). Polybrominated diphenyl ethers (PBDEs) were one of the most widely used organic FRs that were added to a variety of polymers used in numerous consumer products, building materials, and vehicles (Darnerud et al., 2001; Abbasi et al., 2015). Following the discontinuation of penta-, octa- and decabrominated diphenyl ethers (BDEs), other “novel” FRs (NFRs), are being used in higher quantities in order to meet flammability standards (Babrauskas et al., 2011; Covaci et al., 2011). These chemicals are now being found in house dust (Ali et al., 2011), Arctic air (de Wit et al., 2010; Möller et al., 2011; Jantunen et al., 2014), urban air and streams (Salamova and Hites, 2011), and sediments (Klosterhaus et al., 2012; Yang et al., 2012). However, we have limited understanding of their potential risks and persistence, including their physical–chemical properties used for assessment.

NFRs replace their banned predecessors by sharing similar properties: fire retardancy, resistance to weathering, polymer compatibility, etc. (Hindersinn, 1990). These desirable qualities of FRs can cause them to be of environmental concern. The flame retardancy of halogenated FRs is given by the easily released halogen group, a chemical structure which is recognized for its potential mutagenic effects (Blum and Ames, 1977; Darnerud, 2003). Non-halogenated FRs such as certain organophosphate FRs (OPFRs) confer fire retardancy through char formation. Both groups react with radicals produced by fire (Lewin and Weil, 2001). FRs must be inherently stable (i.e., persistent) during the lifetime of the product to which they have been added. Polymer compatibility for additive and reactive FRs is provided by their non-polar structure, which also makes them compatible with other non-polar organic matrices, such as lipid-rich animal tissue. If the FR meets the criteria of persistence, bioaccumulation, and toxicity (PBT), it could be classified as a persistent organic pollutant (POP) under Annex D of the Stockholm Convention. As such, it is of utmost importance to determine if the alternative FRs that have replaced PBDEs also exhibit POP-like, PBT behavior.

Several government and non-governmental organizations such as Canada's Chemical Management Plan, REACH and the Stockholm Convention have assessed compounds in commerce against PBT criteria (Government of Canada a; European Commission; Stockholm Convention, 2008). Recently, Stieger et al. (2014) assessed the PBT properties of 36 NFRs but found that the quality and quantity of measured physical–chemical properties were insufficient to conduct a reliable hazard assessment. Kuramochi et al. (2014) conducted an evaluation of the estimated overall persistence (P_{OV}) and long-range transport potential (LRTP) of 52 brominated NFRs and found that at least 19 NFRs require closer monitoring and further study as they exhibited estimated P_{OV} and LRTP similar to that of POPs or PBDEs. Liagkouridis et al. (2015) reviewed 57 NFRs by providing “best estimates” of physical–chemical properties and evaluating P_{OV} and LRTP. They found that some low molecular weight compounds had lower P_{OV} and LRTP and, as such, could be viewed as better alternatives to the higher molecular weight FRs, noting significant uncertainties in the analysis. Selected NFRs are now being assessed under Canada's Chemical Management Plan (Table S1, Government of Canada b, http://www.chemicalsubstanceschimiques.gc.ca/group/flame_retardant-ignifuges/index-eng.php).

High quality physical–chemical property data are needed not only because of their use in environmental modeling exercises to inform on the potential fate and hazards of pollutants, but because they also provide the foundation in regulatory risk assessment for data interpretation of all endpoints (e.g., fate and behavior, toxicity and exposure). The importance of physical–chemical properties extends to their use in regulatory risk assessment for read-across in the structure–activity relationship toxicity assessments of com-

pounds (Wu et al., 2010; Patlewicz et al., 2013; Blackburn and Stuard, 2014). Read across, the use of chemical analogue information to fill data gaps, is a useful tool but its effectiveness depends on high quality comparative information, is endpoint specific, and requires expert judgment (ECHA, 2008). As such, high uncertainty related to the information used in the read-across will lead to high uncertainty in data estimates (Blackburn and Stuard, 2014).

The goal of this paper was to compare NFRs according to the similarity of P_{OV} and LRTP to that of PBDEs and other POPs. In order to do this, we first compiled a list of 94 halogenated (HFRs) and organophosphate flame retardants (OPFRs) used or marketed as PBDE replacements for which we obtained estimated physical–chemical properties using EPI Suite v4.1 (USEPA, 2013), SPARC (ARC, 2013), and Absolv (ACD/Labs, 2013). Environmental degradation rates were estimated using EPI Suite (USEPA, 2013), PBT profiler and CATALOGIC (LMC, 2011), as well as data reported in previous studies. We used half-lives of compounds with similar properties for the 12 compounds for which no data on environmental half-lives could be obtained. Second, we modeled P_{OV} and Characteristic Travel Distance (CTD), as defined by Beyer et al. (2000), as a proxy for LRTP using the OECD P_{OV} and LRTP Screening Tool v2.2 (OECD, 2013). Because NFRs are PBDE replacements, we used the overall persistence and LRTP of PBDEs, as well as other POPs, to guide our assessment. In contrast to previous work on the environmental persistence of NFRs (Kuramochi et al., 2014; Liagkouridis et al., 2015), our work includes an extensive list of HFRs, as well as halogenated and non-halogenated OPFRs. Additionally, we used the more advanced CATALOGIC model (Dimitrov et al., 2011) to estimate the biodegradation rate of NFRs.

2. Methods

The list of HFRs was assembled using the FR list compiled by Bergman et al. (2012) as PBDE replacements (note that physical–chemical properties listed by Bergman et al. were obtained using Absolv). To this list, we added six HFRs (OEHHA, 2008) and seven non-halogenated OPFRs (Stapleton et al., 2009; Brommer et al., 2014). Finally, we added five additional OPFRs, C12-30 α -bromo chloro alkenes, C12-30 α -chloro alkenes, and melamine, compounds that may be considered under the Canadian Chemical Management Plan, phase 3. Thus, in total 94 chemicals were studied, of which 71 were HFRs and 23 were non-halogenated (Table S2).

A full description of methods can be found in SI. Briefly, the U.S. Environmental Protection Agency's EPI Suite v4.1 (USEPA, 2013) and SPARC Performs Automated Reasoning in Chemistry's online calculator (ARC, 2013) were used to estimate: liquid sub-cooled vapor pressure (P_l) and liquid sub-cooled solubility (S_l); Henry's Law Constant (HLC), which can be converted into the air–water partition coefficient (K_{AW}) by dividing by temperature (298 K) and gas constant, R (8.314 Pa/K/mol); octanol–water (K_{OW}) and octanol–air (K_{OA}) partition coefficients at 25 °C. Estimates of partition coefficients were also obtained using Absolv (ACD/Labs, 2013).

In order to assess the efficacy of the three estimation programs, goodness-of-fit and root mean square error (RMSE) were evaluated between P_l , S_l , K_{AW} , K_{OW} and K_{OA} measured and estimated values for seven polycyclic aromatic hydrocarbons (PAHs), six polychlorinated biphenyls (PCBs), five PBDEs, and p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT). Additionally, measured P_l values for 11 OPFRs (Brommer et al., 2014) were also compared to estimated values obtained from EPI Suite and SPARC.

Air and water half-lives ($t_{air, 1/2}$ and $t_{wat, 1/2}$) were obtained using EPI Suite's Atmospheric Oxidation Program (AOP), AOPWIN v1.92, and HYDROWIN v2.00, respectively (USEPA, 2013). Compounds with no or extremely high $t_{water, 1/2}$, denoted as “no or high $t_{water, 1/2}$ ”, were assessed separately for their P_{OV} and LRTP, taking

note of the high uncertainty of the results (see S1.3, S5 for more details).

The half-lives for primary and ultimate biodegradation in soil ($t_{\text{soil}, 1/2}$) were obtained using EPI Suite's BIOWIN v4.10 model (USEPA, 2013) and CATALOGIC 301C model (LMC, 2011). See Table S3 for conversions used between BIOWIN's rank and assigned quantitative value (Aronson et al., 2006). In some cases, the chemicals were out of the domain for the different physical-chemical properties and degradation estimation models. However, when faced with having no estimates for these NFRs we chose to use the estimated values, taking note of this uncertainty.

P_{OV} and LRTP of the NFRs were assessed using the P_{OV} and LRTP Screening Tool v.2.2 (OECD, 2013). Using each pair of partition coefficients obtained from EPI Suite (including literature and PBT-profiler data), SPARC, and Absolv, the Screening Tool was run using ultimate and primary $t_{\text{soil}, 1/2}$ from CATALOGIC and EPI Suite for a total of 12 runs plus an additional four runs for the set of substances with "no or high $t_{\text{water}, 1/2}$ " (for a breakdown of each run's specifications see Figs. S11–13). Each run consisted of three emission scenarios, where the chemical was directly emitted to air, water or soil.

NFRs were screened for their POP-like environmental behavior by comparing their estimated P_{OV} and CTD values to those of the original 12 POPs under the Stockholm Convention provided by the Screening Tool. We used the estimate of P_{OV} of hexachlorocyclohexane (HCH) of 195 days and the estimate of CTD of PCB-28 of 5097 km as these limits (OECD, 2013). Similarly, PBDE-like behavior was categorized into three classes by comparing the NFRs' maximum estimated P_{OV} and CTD values from all three emission scenarios to the maximum estimated P_{OV} and CTD of the congeners in the penta- and octa-BDE mixtures that have been designated as POPs under the Stockholm Convention (Stockholm Convention, 2008; UNEP, 2009). Finally, LRTP of the NFRs was assessed using the CTD values based on emission into air according to the following ranges: if <700 km, low LRTP; if 700 km–2000 km, medium LRTP; and, if >2000 km, high potential for LRT (Beyer et al., 2000).

3. Results and discussion

3.1. Comparison of measured and modeled properties

Model predicted and measured partition coefficients were generally within one order of magnitude (Fig. S1–S3); DDT was the notable exception for which measured values of K_{AW} were overestimated by the three programs. EPI Suite estimates best approximated measured K_{AW} values with a RMSE of 0.43 for log K_{AW} , compared to SPARC's 0.51 and Absolv's 0.89. Predicted K_{OW} was generally overestimated (Fig. S2). K_{OW} estimated by Absolv using ppLFR best approximated measured values with a RMSE of 0.34 for log K_{OW} , compared to EPI Suite's 0.52 and SPARC's 0.63 (Fig. S2). Finally, K_{OA} estimates had no distinguishable over- or underestimation, with RMSE of 0.65, 0.51 and 0.56 for log K_{OA} predicted by EPI Suite, SPARC and Absolv, respectively (Fig. S3). Heavier PCBs were the exceptions as they were progressively overestimated with increasing molecular weight (or more likely molar volume). The "true" values of the K_{OA} of high molecular weight PCBs are difficult to know since measured values could be in error given the difficulty of the measurements.

EPI Suite tended to overestimate the measured values of P_l of PCBs and PBDEs by 10 – 10^2 times (Fig. S4). In comparison, SPARC tended to underestimate measured P_l by 10^2 , with the exception of PAHs which were generally well estimated. Overall, EPI Suite estimates showed the best fit to the measured log values with an RMSE of 0.81 for log P_l , compared to SPARC's 1.46.

In contrast to P_l , S_l estimates fitted less well with measured values (Fig. S5). Of the two EPI Suite models used, WSKOWWIN esti-

mates approximated measured values best, with a RMSE of 0.79 for log S_l , but the measured values of S_l for all the compounds except PAHs, were underestimated by 10 – 10^3 . The heavier PBDEs were especially problematic. WATERNT produced estimates with a higher RMSE of 1.18 than WSKOWWIN and the latter did not show bias. Estimated and measured S_l of PAHs and lower molecular weight PBDEs were closely approximated whereas S_l of PCBs and DDT were underestimated by 10 – 10^2 . Finally, S_l from SPARC, with a RMSE of 1.22 for log S_l , showed more variation in the estimates than the EPI Suite models. While SPARC tended to overestimate the S_l of PAHs by a factor of 10, its estimated values fitted the lighter PCBs but underestimated the heavier PCBs and PBDEs by 10 – 10^2 . Again, it is difficult to know the "true" values of S_l for sparingly soluble chemicals.

Measured values of P_l of TCEP, TPhP, TBEP, and EHDPP were underestimated by 10 – 10^2 by EPI Suite, while values of TCIPP, ToCP, and TDCIPP were overestimated by one order of magnitude (Fig. S6). The RMSE for EPI Suite was 1.01 for log P_l . SPARC tended to overestimate P_l by 10 – 10^2 with a RMSE of 1.15 for log P_l , except for the P_l of TCIPP and TBEP, which showed a good fit, and TCEP, which was underestimated by one order of magnitude. Similarly, Brommer et al. (2014) found the Modified Grain Method used by EPI Suite's MPBPVP model provided closer approximations to measured values of P_l than SPARC.

3.2. Estimated physical-chemical properties of NFRs

Table S4 lists values of logs of S_l , P_l , K_{AW} , K_{OW} , and K_{OA} of NFRs while Table S5 contains values for $t_{\text{air}, 1/2}$, $t_{\text{wat}, 1/2}$, and primary and ultimate $t_{\text{soil}, 1/2}$.

Log P_l (Pa) ranged from 4.24 (SPARC) for TMP (140 g/mol) to -27 (SPARC) for BPBTB (1451 g/mol) (Fig. S7). The largest variation was for BPBTB with estimated log P_l between -15 (EPI Suite) and -27 (SPARC). The average difference was $<10^4$ (RMSE of log P_l was 3.86). However, the average difference in P_l was over 10^8 (RMSE of log P_l was 8.47) for NFRs with molecular weight > 800 g/mol (see S2.1 for the list of compounds) in comparison to $<10^3$ difference for NFRs <800 g/mol (RMSE of log P_l was 2.72). Chemicals with higher molecular weight generally have lower vapor pressures, the measurement values of which are subject to larger bias. When these data are used as a training set for the regression based QSAR model such as EPI Suite, the predicted values tend to have larger bias.

TMP and BPBTB had the maximum (6, EPI Suite WATERNT) and minimum (-17.5 , EPI Suite WSKOWWIN estimate) log S_l (mg/L) values (Fig. S8). Generally, the three estimates differed by 10^2 – 10^3 for a given compound (RMSE of log S_l ranged 1.9–2.7). The largest discrepancy was for 4'-PeBPOBDE208, which had an estimated log S_l from -17.5 (EPI Suite WSKOWWIN) to -6 (EPI Suite WATERNT), and BPBTB with -17.5 (EPI Suite WSKOWWIN) and -6 (EPI Suite WATERNT). As with P_l , estimates of S_l of compounds with molecular weight > 800 g/mol differed by 10^7 between the estimates from WSKOWWIN and WATERNT of EPI Suite, 10^2 between WSKOWWIN and SPARC estimate and 10^5 between WATERNT and SPARC. The average difference was 10^2 for those compounds having molecular weight < 800 g/mol.

Log K_{AW} ranged from 1.2 (SPARC) for TiPP (224 g/mol) to -18.8 (EPI Suite) for EBTEBPI (952 g/mol) (Fig. S9). Among the three partition coefficients, K_{AW} had the largest variation among estimates. Generally, K_{AW} differed by 10^3 between the three estimates (RMSE of log K_{AW} ranged 2.1–3.6). OPFRs had the largest variations of 10^3 – 10^8 (see S2.2 for the list of compounds). The largest variation was for BCMP-BCEP (583 g/mol) with log K_{AW} of -12.2 (Absolv) to -5.4 (SPARC). TBBPA also exhibited large variation with log K_{AW} of -11.03 (EPI Suite) to -5.26 (SPARC). The variation was most

pronounced between SPARC and the other two programs, which are based on a fragment method.

Log K_{OW} ranged from -1.9 (Absolv) for melamine (126 g/mol) to 16.5 for BPBTB (1451 g/mol, Absolv) (Fig. S10). Variability in K_{OW} was within 10^{-2} (RMSE range 1.1–1.9). The largest variations in K_{OW} was $>10^5$ for BCMP-BCEP (583 g/mol) of log K_{OW} of 3.3 (EPI Suite) and 8.8 (SPARC). The variation between the estimates for other OPFRs tended to be greater than the average, particularly between SPARC and the other two programs (see S2.3 for the list of compounds).

Log K_{OA} ranged from 2.5 (SPARC) for TMP (140 g/mol) to 30.2 (EPI Suite) for BPBTB (1451 g/mol) (Fig. 1). Each compound's three estimates typically differed by $<10^2$ (RMSE ranged 1.8–1.9). The largest variation was for BDBP-TAZTO with log K_{OA} of 21.2 (EPI Suite) and 14.4 (SPARC). Discrepancies in estimates of 10^4 – 10^8 occurred for compounds that have a heteroatom N in the structural backbone and molecular weights varying from <400 to >800 g/mol. No program was performed better than another.

The difference among all the model estimates was consistently greater for compounds >800 g/mol, compared to those with <800 g/mol. This is not surprising given that the training sets used to develop these models are predominantly composed of lower molecular weight compounds (Arp et al., 2006; Zhang et al., 2010). Compounds ≥ 800 g/mol are typically beyond the models' parametric and structural domains and their estimated properties should be used with caution. Beyond the model domain, other factors also impact the large differences in estimated properties. First among these is the training set used; if the molecular structure of the compound of interest is not well represented among the training set compounds then a higher level of uncertainty is associated with the estimate. This is especially true for EPI Suite's HENRYWIN and WSKOWWIN models which predict partitioning behavior using a fragment method (Meylan and Howard, 1991, 1995; Zhang et al., 2010). Among NFRs, the phosphine oxide (P=O) structure of the OPFRs is not well represented in EPI Suite's training sets. Likewise, the theory used, and therefore assumptions made, when developing the algorithms used to calculate the estimated properties play a significant role in the overall variation among estimates. For example, although EPI Suite does contain polar chemicals in its training set, its inability to accurately account for the effect of polar functional groups to the overall partitioning of organic compounds is generally acknowledged (Zhang et al., 2010). In contrast, partition coefficients calculated using solute descriptors

emphasize the polar sections of the molecular structure (Japertas et al., 2007). This may explain the large variation among EPI Suite, SPARC and Absolv for K_{AW} with the more polar OPFRs. Arp et al. (2006) found EPI Suite most poorly estimated the partitioning behavior of slightly polar highly fluorinated compounds relative to measured data, in comparison to SPARC and a pp-LFER technique similar to the one used in this work, that had more accurate predictions. The source(s) of the large variation in the estimation of NFR physical–chemical properties is likely an aggregate of all these model characteristics, but mostly the lack of structural representation in the training sets. What is clear from these results is that there is a growing need for estimation programs that can more accurately and precisely predict the physical–chemical properties of NFRs.

3.3. Estimated environmental half-lives

Half-life estimates, in general, varied widely between different models and literature. Estimates for $t_{water, 1/2}$ in particular were uncertain. For the 82 NFRs with $t_{water, 1/2}$ estimated using HYDROWIN, PBT profiler or literature data (see S1.3, Table S5), $t_{water, 1/2}$ ranged from 208 h for TnBP to 581 d for PBB-Acr. Compounds with extreme values of $t_{water, 1/2}$ from HYDROWIN were as high as 2.9×10^{14} h (HBCYD, see S2.5 for the list of compounds). Estimated $t_{water, 1/2}$ ranged from 912 h for DBP-TAZTO, DBS, TDMPP, TPPP and TTMN to 180 d for 4'-PeBPOBDE208, HBCYD, OBPB, OBTMPI, PBB, TBBPS-BME and TTBP-TAZ for the 12 compounds with no $t_{water, 1/2}$ estimates in either HYDROWIN, PBT profiler or literature.

Primary $t_{soil, 1/2}$ estimates from CATALOGIC ranged from 1.7 h for MC 984, TDBPP, TmCP and TTBNPP to 164 d for TBP-DBPE (Table S5). EPI Suite estimates of primary $t_{soil, 1/2}$ ranged from 12 h (BDPP, TCP, TTBP) to 3650 d (considered recalcitrant) for compounds >500 g/mol. No compounds were considered recalcitrant according to CATALOGIC estimates. Even for low molecular weight compounds, CATALOGIC and EPI Suite estimates of primary $t_{soil, 1/2}$ differed unsystematically by up to two orders-magnitude. This variation increased by up to four orders-of-magnitude for some compounds >650 g/mol (EBTEBPI, BPBTB/PBTBPE).

Ultimate $t_{soil, 1/2}$ estimates were more variable than primary because of greater complexity of degradation pathways. CATALOGIC's estimates of ultimate $t_{soil, 1/2}$ varied from 11 to 14 h for Br-Cl-Alkene, Cl-Alkene, PIP, TiPP and TXP to 3650 d for 9 com-

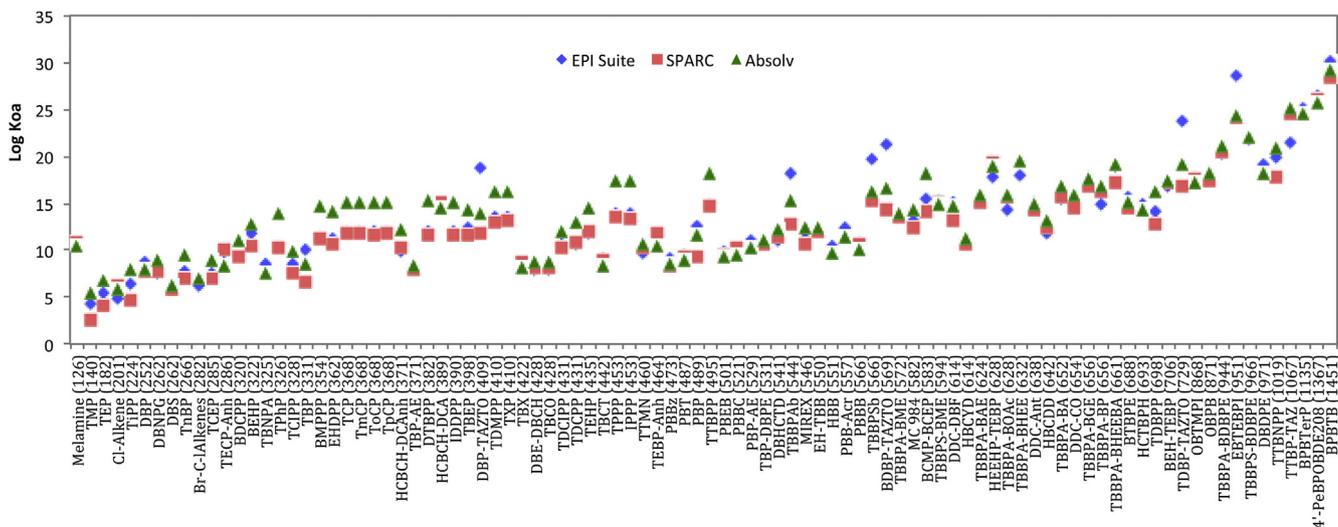


Fig. 1. Estimated log K_{OA} of NFRs, listed by increasing molecular weight (g/mol). EPI Suite estimates are represented by the blue diamonds, SPARC's by the red squares, and Absolv's by the green triangles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

pounds (4'-PeBPOBDE208, BCMP-BCEP, DBDPE, DBNPG, HCTBPH, OBTMP, PBP-AE, TCEP and TTBP-TAZ). Compounds with molecular weight < 400 g/mol generally had the shortest $t_{\text{soil}, 1/2}$, with EPI Suite and CATALOGIC estimates ≤ 1000 d (with several exceptions that were longer). EPI Suite estimated that compounds of >400 g/mol were predominantly recalcitrant while CATALOGIC estimates of ultimate $t_{\text{soil}, 1/2}$ showed no discernable pattern as a function of molecular weight. Using CATALOGIC, the potential degradation pathways of OBPB, TBBPS-BME, EH-TBB, BEH-TEBP, OBTMPI, and TBP-DBPE were identified as having stable degradation products of potential environmental concern given their bioaccumulation and bioconcentration factors, as estimated by EPI Suite's BCFBAF model (Arnot et al., 2009). Further work regarding the potential for toxicity and/or bioaccumulation of these degradation products is warranted but is beyond the scope of this work.

3.4. Estimated overall persistence and long range transport

The minimum P_{OV} and CTD of the 82 compounds with reliable values of $t_{\text{water}, 1/2}$ (S1.3, Table S5) and using primary $t_{\text{soil}, 1/2}$ was 14 h (TEHP) and <1 km (melamine, 126 g/mol), respectively. The maximum P_{OV} and CTD for this group was 216 d (BTBPE, EBTEBPI, OBTMPI and TTBP-TAZ) and 21,197 km (PBBz, 473 g/mol), respectively. When ultimate $t_{\text{soil}, 1/2}$ was used, P_{OV} ranged from 19 h (TEP and TMP) to 218 d (TBBPA-BHEEBA). P_{OV} for the group "no or extremely high $t_{\text{water}, 1/2}$ " (S1.3, Table S5) ranged from 40 d (DBS) to 34 years (HBCDD). CTDs were not impacted by changes in soil degradation rates. Fig. 2 shows the results from model runs 1–3, using K_{AW} and K_{OW} estimates from EPI Suite, SPARC, and Absolv and CATALOGIC's ultimate $t_{\text{soil}, 1/2}$. Results for the 16 runs are shown in Figs. S11–S13.

NFRs were categorized into three classes according to their POP-like and PBDE-like behavior based on model runs using CATALOGIC's ultimate $t_{\text{soil}, 1/2}$ (aggregate of runs 1–3 using physical-chemical properties from EPI Suite, SPARC and Absolv) and EPI Suite's ultimate $t_{\text{soil}, 1/2}$ (aggregate of runs 4–6 obtained using physical-chemical properties from each program). Classification

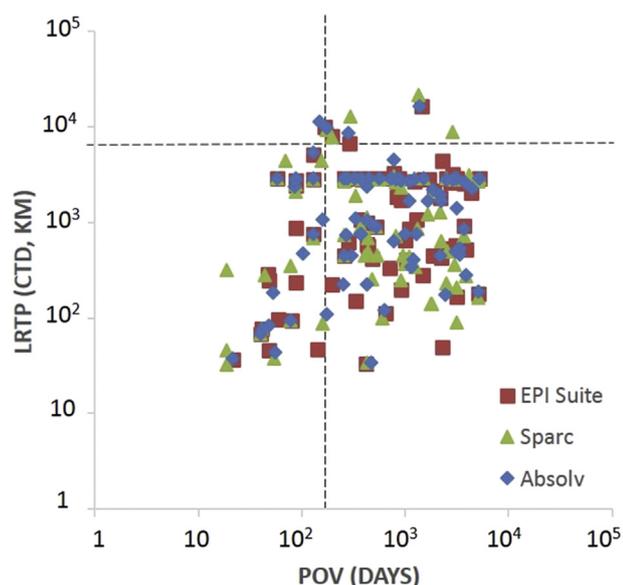


Fig. 2. P_{OV} and L RTP results from runs 1–3 obtained assuming using CATALOGIC's ultimate $t_{\text{soil}, 1/2}$ and K_{AW} and K_{OW} estimates from EPI Suite (red square), SPARC (green triangle), and Absolv (blue diamond). The dashed lines represent the limits for the POP-like comparison. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

differed significantly between results based on CATALOGIC versus EPI Suite estimates. Using CATALOGIC's ultimate $t_{\text{soil}, 1/2}$, 0% fell into Class I (POP-like behavior), 12% fell into Class II (POP-like P_{OV} or CTD), and 88% fell into Class III (do not exhibit POP-like behavior). Using EPI Suite's ultimate $t_{\text{soil}, 1/2}$, 2% exhibited POP-like behavior (Class I), 40% fell into Class II, and 58% fell into Class III. Using PBDE-like behavior as the criterion and CATALOGIC's ultimate $t_{\text{soil}, 1/2}$, 7% fell into Class I (exhibit PBDE-like behavior), 38% fell into Class II (PBDE-like P_{OV} or CTD), while 55% fell into Class III (do not exhibit PBDE-like behavior). Using EPI Suite's ultimate $t_{\text{soil}, 1/2}$, 29% fell into Class I, 30% into Class II, and 41% into Class III.

LRTP of NFRs was assessed using the emission-to-air scenario. Out of the three emission scenarios offered by the *Screening Tool*, this is most representative of NFRs' entrance into the environment via indoor-air to outdoor-air transfer or industrial emissions to air. CTD of the 94 NFRs ranged from <1 km for melamine (126 g/mol, EPI Suite, SPARC and Absolv partition coefficients, EPI Suite ultimate $t_{\text{soil}, 1/2}$) to >20,000 km for PBBz (473 g/mol, SPARC partition coefficients, EPI Suite ultimate $t_{\text{soil}, 1/2}$). Overall, 47–50% of NFRs had a CTD <700 km or low LRTP; 12–20% had a CTD of 700–2000 km or a medium LRTP; and, 30–41% had a CTD >2000 km or high LRTP (Beyer et al., 2000).

The results from the *Screening Tool* need to be interpreted in light of evidence of long range transport of some NFRs and the model's strengths and weakness. Recent studies have measured TDCIPP, TCEP, TCIPP, TPhP, TnBP, TBEP, TEHP and EHDPP in Arctic air at concentrations 10–10² higher than that of other BFRs and even higher than PBDEs at their peak usage (Jantunen et al., 2014; Salamova et al., 2014). In addition, Möller et al. (2011) measured PBBz, HBB, TBP-DBPE, PBT and BEH-TEBP in Arctic air at concentrations exceeding those of PBDEs. The measurements were taken from remote Arctic locations which do not suggest local sources of contamination (e.g., Hale et al., 2008). In comparison, the *Screening Tool* estimated that all OPFRs measured in Arctic air had low-to-medium LRTP except for TEHP for which LRTP ranged between low and high (runs 1–6). The *Screening Tool* did, however, estimate high LRTP for 9 of the tested OPFRs (IDDPP, MC 984, PIP, TEHP, TTBNPP, TTBP, TPPP, TDMPP and TXP).

The *Screening Tool* estimated that OPFRs would partition mainly to the water compartment (68–99% of the mass of TCEP and TCIPP, respectively). The chemical mass in air of about half of the OPFRs was estimated to be predominantly in the gas phase that reacts rapidly with the OH radical. However, measurements show OPFRs sorb to particles (Jantunen et al., 2014; Salamova et al., 2014) where they are not subject to OH radical reaction, thereby greatly increasing their atmospheric life span and making long-range transport viable (Liu et al., 2014). The *Screening Tool* was better able to predict the LRTP of other NFRs measured in the Arctic at elevated concentrations. PBBz, PBT, HBB and TBP-DBPE measured by Möller et al. (2011) were estimated by the *Screening Tool* to have a high LRTP except for TBP-DBPE, which was estimated to have a medium LRTP. In spite of Möller et al. (2011) detecting these compounds in the gas phase, the *Screening Tool* predicted that most PBT and TBP-DBPE mass in air would be particle-sorbed.

Scheringer and co-workers who developed the *OCED Screening Tool* model noted several sources of uncertainty in the model such as its inability to capture the episodic transport to the Arctic of particle-sorbed compounds (Scheringer, 2009; Scheringer et al., 2009). They also commented that the model's reliance on K_{OA} to estimate gas-particle partitioning could potentially be a source of error. Another explanation for the misclassification of LRTP of OPFRs may come from the very high variability, and presumably uncertainty, in K_{AW} as noted here. This uncertainty, together with potentially underestimating the fraction of particle-sorbed chemical, may explain the model's estimate of most OPFRs partitioning to water and underestimation of atmospheric transport.

4. Implications

Of the 94 NFRs identified here as PBDE replacements, up to 30% exhibited an environmental fate similar to PBDEs while 2% showed a P_{OV} and LRTP similar to other POPs. Furthermore, when released into the air, upwards of 40% have the potential to undergo LRTP. These results are not surprising given the tendency to replace banned substances with the next-best-alternative; chemicals that have a similar function and that can be used in a similar way in products as controlled substances are likely to have a similar environmental fate. For this reason, the one-by-one regulatory approach is problematic for ensuring that alternative FRs to the (mostly) controlled PBDEs will be less hazardous than their predecessors. Rather, NFRs, as a class, need to be evaluated for their “environmental acceptability” as well as environmental hazard. For example, the Government of Canada’s action on a grouping of Certain Organic Flame Retardants under the Chemicals Management Plan is intended to assist with informed substitution (http://www.chemicalsubstanceschimiques.gc.ca/group/flame_retardant-ignifuges/profile-eng.php).

The screening results presented here for NFR persistence and LRTP require a more critical assessment because of the wide variability in many physical–chemical property estimates obtained from EPI Suite, SPARC and Absolv, and potentially erroneous results obtained for some compounds using these estimation programs and the OECD *Screening Tool*. Although the EPI Suite models showed the best overall performance when judged relative to measured physical–chemical properties, the same cannot be said for NFRs until more empirical data become available for comparison. Furthermore, EPI Suite provided unreasonable estimates for the environmental degradation rates of several compounds. If used without further review, these estimates could dramatically affect the results of the assessment of environmental fate of these compounds. These results underscore the urgent need to update the programs’ training sets with compounds more representative of those in use as FRs. The environmental and health hazards associated with these compounds can only be properly assessed if the environmental fate and read-across toxicological assessments are based on trustworthy and reliable information, notably physical–chemical properties.

Selecting which estimation program to use depends on the purpose they serve. CATALOGIC can be useful when conducting an in-depth assessment of the degradation of chemicals. The OECD Toolbox provides much of the same functionality as CATALOGIC and is publicly available (<http://www.oecd.org/chemicalsafety/risk-assessment/theoecdqsartoolbox.htm>). When screening compounds for their persistence and LRTP, our results show that using EPI Suite is an acceptable alternative, even though estimated data on environmental fate should be used with caution and re-evaluated where necessary. As an added bonus, EPI Suite is publicly available. Finally, the seeming misclassification of LRTP of OPFRs should remind us to exercise caution when interpreting results from the OECD *Screening Tool*, which is intended to be just that – a screening tool.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2015.11.017>.

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