



# 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.

## ARTICLE INFO

### Article history:

Received 3 July 2015

Received in revised form 4 November 2015

Accepted 5 November 2015

Available online 22 November 2015

Handling editor: Ian Cousins

### Keywords:

Flame retardants

Physical–chemical properties

EPI suite

Absolv

SPARC

POP screening

OECD  $P_{OV}$  and LRTP screening tool

Long range transport potential

Chemical persistence

## 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](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  $\alpha$ -bromo chloro alkenes, C12-30  $\alpha$ -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.

$P_{\text{OV}}$  and LRTP of the NFRs were assessed using the  $P_{\text{OV}}$  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  $P_{\text{OV}}$  and CTD values to those of the original 12 POPs under the Stockholm Convention provided by the Screening Tool. We used the estimate of  $P_{\text{OV}}$  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  $P_{\text{OV}}$  and CTD values from all three emission scenarios to the maximum estimated  $P_{\text{OV}}$  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  $K_{\text{AW}}$  were overestimated by the three programs. EPI Suite estimates best approximated measured  $K_{\text{AW}}$  values with a RMSE of 0.43 for log  $K_{\text{AW}}$ , compared to SPARC's 0.51 and Absolv's 0.89. Predicted  $K_{\text{OW}}$  was generally overestimated (Fig. S2).  $K_{\text{OW}}$  estimated by Absolv using ppLFR best approximated measured values with a RMSE of 0.34 for log  $K_{\text{OW}}$ , compared to EPI Suite's 0.52 and SPARC's 0.63 (Fig. S2). Finally,  $K_{\text{OA}}$  estimates had no distinguishable over- or underestimation, with RMSE of 0.65, 0.51 and 0.56 for log  $K_{\text{OA}}$  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  $K_{\text{OA}}$  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  $P_i$  of PCBs and PBDEs by  $10$ – $10^2$  times (Fig. S4). In comparison, SPARC tended to underestimate measured  $P_i$  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  $P_i$ , compared to SPARC's 1.46.

In contrast to  $P_i$ ,  $S_i$  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  $S_i$ , but the measured values of  $S_i$  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  $S_i$  of PAHs and lower molecular weight PBDEs were closely approximated whereas  $S_i$  of PCBs and DDT were underestimated by  $10$ – $10^2$ . Finally,  $S_i$  from SPARC, with a RMSE of 1.22 for log  $S_i$ , showed more variation in the estimates than the EPI Suite models. While SPARC tended to overestimate the  $S_i$  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  $S_i$  for sparingly soluble chemicals.

Measured values of  $P_i$  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  $P_i$ . SPARC tended to overestimate  $P_i$  by  $10$ – $10^2$  with a RMSE of 1.15 for log  $P_i$ , except for the  $P_i$  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  $P_i$  than SPARC.

#### 3.2. Estimated physical-chemical properties of NFRs

Table S4 lists values of logs of  $S_i$ ,  $P_i$ ,  $K_{\text{AW}}$ ,  $K_{\text{OW}}$ , and  $K_{\text{OA}}$  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  $P_i$  (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  $P_i$  between  $-15$  (EPI Suite) and  $-27$  (SPARC). The average difference was  $<10^4$  (RMSE of log  $P_i$  was 3.86). However, the average difference in  $P_i$  was over  $10^8$  (RMSE of log  $P_i$  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  $P_i$  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  $S_i$  (mg/L) values (Fig. S8). Generally, the three estimates differed by  $10^2$ – $10^3$  for a given compound (RMSE of log  $S_i$  ranged 1.9–2.7). The largest discrepancy was for 4'-PeBPOBDE208, which had an estimated log  $S_i$  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  $P_i$ , estimates of  $S_i$  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  $K_{\text{AW}}$  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,  $K_{\text{AW}}$  had the largest variation among estimates. Generally,  $K_{\text{AW}}$  differed by  $10^3$  between the three estimates (RMSE of log  $K_{\text{AW}}$  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  $K_{\text{AW}}$  of  $-12.2$  (Absolv) to  $-5.4$  (SPARC). TBBPA also exhibited large variation with log  $K_{\text{AW}}$  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  $\geq 800$  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  $2.9 \times 10^{14}$  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 TBNPP to 164 d for TBP-DBPE (Table S5). EPI Suite estimates of primary  $t_{soil, 1/2}$  ranged from 12 h (BDDP, 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-

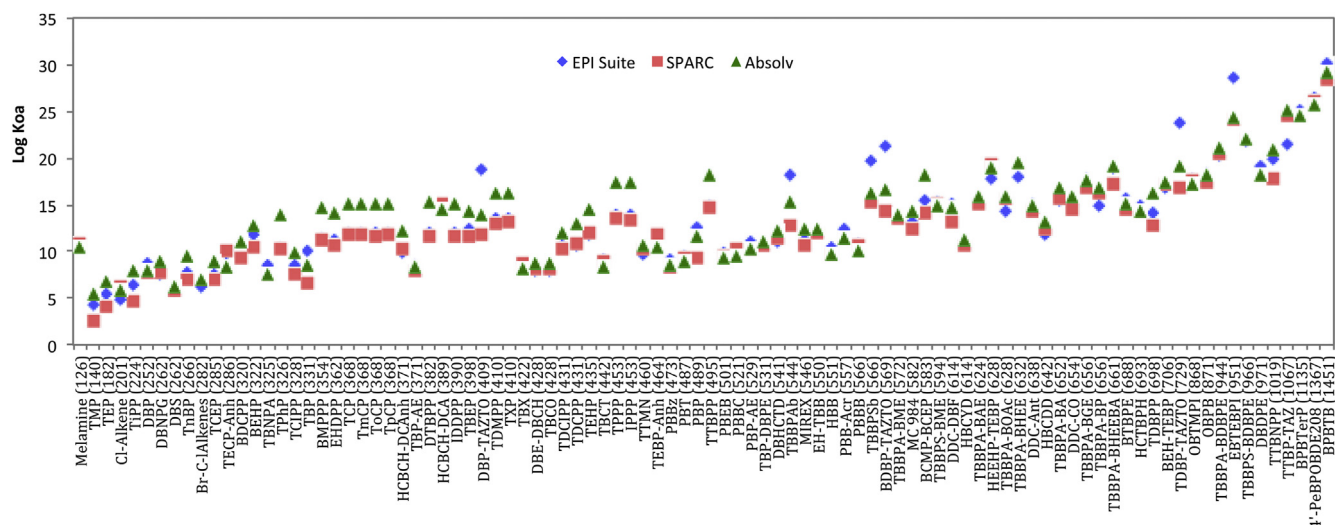


Fig. 1. Estimated log  $K_{OA}$  of NFRs, listed by increasing molecular weight (g/mol). EPI Suite estimates are represented by the blue diamonds, SPARC's by the red squares, and Absolv's by the green triangles. (For interpretation of the references to color in this figure legend, the reader is referred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

pounds (4'-PeBPOBDE208, BCMP-BCEP, DBDPE, DBNPG, HCTBPH, OBTMP, PBP-AE, TCEP and TBBP-TAZ). Compounds with molecular weight < 400 g/mol generally had the shortest  $t_{\text{soil}, 1/2}$ , with EPI Suite and CATALOGIC estimates  $\leq 1000$  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  $P_{\text{OV}}$  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  $P_{\text{OV}}$  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,  $P_{\text{OV}}$  ranged from 19 h (TEP and TMP) to 218 d (TBBPA-BHEEBA).  $P_{\text{OV}}$  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  $K_{\text{AW}}$  and  $K_{\text{OW}}$  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

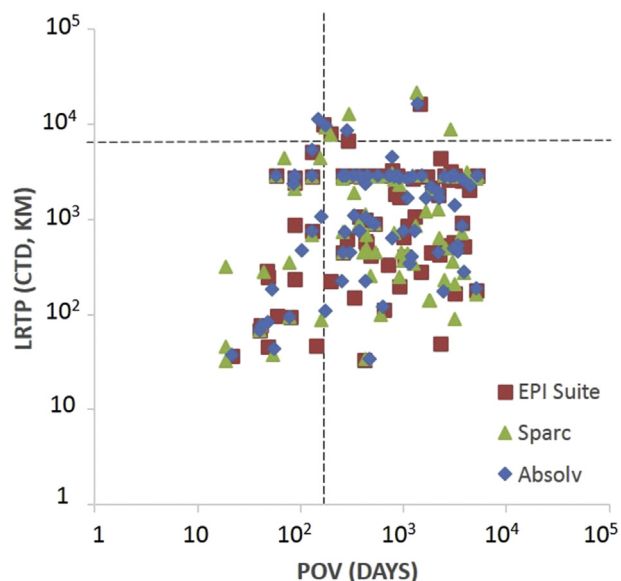
differed significantly between results based on CATALOGIC versus EPI Suite estimates. Using CATALOGIC's ultimate  $t_{\text{soil}, 1/2}$ , 0% fell into Class I (POP-like behavior), 12% fell into Class II (POP-like  $P_{\text{OV}}$  or CTD), and 88% fell into Class III (do not exhibit POP-like behavior). 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  $P_{\text{OV}}$  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  $10\text{--}10^2$  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  $K_{\text{OA}}$  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  $K_{\text{AW}}$  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.



**Fig. 2.**  $P_{\text{OV}}$  and LRTP results from runs 1–3 obtained assuming using CATALOGIC's ultimate  $t_{\text{soil}, 1/2}$  and  $K_{\text{AW}}$  and  $K_{\text{OW}}$  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).

#### 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  $P_{OY}$  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](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.

#### Acknowledgments

Funding to DS was provided by the Natural Sciences and Engineering Research Council of Canada (124042-12) and the University of Toronto, Department of Earth Sciences. Thanks to Dr. Arlene Blum of Green Science Policy Institute for starting the project.

#### 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>.

#### References

- Abbasi, G., Buser, A.M., Soehl, A., Murray, M., Diamond, M.L., 2015. Stock and flows of PBDEs in products from use to waste in U.S. and Canada from 1970 to 2020. *Environ. Sci. Technol.* 49 (3), 1521–1528.
- ACD/Labs, 2013. ACD/Absolv. Advanced Chemistry Development Toronto, Canada <http://www.acdlabs.com/>.
- Ali, N., Harrad, S., Goosey, E., Neels, H., Covaci, A., 2011. “Novel” brominated flame retardants in Belgian and UK indoor dust: Implications for human exposure. *Chemosphere* 83, 1360–1365.
- Aronson, D., Boethling, R., Howard, P., Stiteler, W., 2006. Estimating biodegradation half-lives for use in chemical screening. *Chemosphere* 63, 1953–1960.
- ARC, 2013. SPARC Performs Automated Reasoning in Chemistry. Automated Reasoning in Chemistry, Athens, USA.
- Arnot, J.A., Meylan, W., Tunkel, J., Howard, P.H., Mackay, D., Bonnell, M., Boethling, R.S., 2009. A quantitative structure–activity relationship for predicting metabolic biotransformation rates for organic chemicals in fish. *Environ. Toxicol. Chem.* 28, 1168–1177.
- Arp, H.P.H., Niederer, C., Goss, K.U., 2006. Predicting the partitioning behavior of various highly fluorinated compounds. *Environ. Sci. Technol.* 40, 7298–7304.
- Babrauskas, V., Blum, A., Daley, R., Birnbaum, L.S., 2011. Flame retardants in furniture foam: benefits and risks. *Fire Saf. Sci.* 10, 265–278.
- Bergman, A., Ryden, A., Law, R.J., de Boer, J., Covaci, A., Alae, M., Birnbaum, L., Petreas, M., Rose, M., Sakai, S., Van den Eede, N., van der Veen, I., 2012. A novel abbreviation standard for organobromine, organochlorine and organophosphorus flame retardants and some characteristics of the chemicals. *Environ. Int.* 49, 57–82.
- Beyer, A., Mackay, D., Matthies, M., Wania, F., Webster, E., 2000. Assessing long-range transport potential of persistent organic pollutants. *Environ. Sci. Technol.* 34, 699–703.
- Blackburn, K., Stuard, S.B., 2014. A framework to facilitate consistent characterization of read across uncertainty. *Regul. Toxicol. Pharmacol.* 68, 353–362.
- Blum, A., Ames, B.N., 1977. Flame-retardant additives as possible cancer hazards. *Science* 195, 17–23.
- Brommer, S., Jantunen, L.M., Bidleman, T.F., Harrad, S., Diamond, M.L., 2014. Determination of vapor pressures for organophosphate esters. *J. Chem. Eng. Data* 59, 1441–1447.
- Covaci, A., Harrad, S., Abdallah, M.A.-E., Ali, N., Law, R.J., Herzke, D., de Wit, C.A., 2011. Novel brominated flame retardants: a review of their analysis, environmental fate and behaviour. *Environ. Int.* 37, 532–556.
- Darnerud, P.O., 2003. Toxic effects of brominated flame retardants in man and in wildlife. *Environ. Int.* 29, 841–853.
- Darnerud, P.O., Eriksen, G.S., Johannesson, T., Larsen, P.B., Viluksela, M., 2001. Polybrominated diphenyl ethers: occurrence, dietary exposure, and toxicology. *Environ. Health Perspect.* 109, 49–68.
- de Wit, C.A., Herzke, D., Vorkamp, K., 2010. Brominated flame retardants in the Arctic environment – trends and new candidates. *Sci. Total Environ.* 408, 2885–2918.
- Dimitrov, S., Pavlov, T., Dimitrova, N., Georgieva, D., Nedelcheva, D., Kesova, A., Vasilev, R., Mekenyan, O., 2011. Simulation of chemical metabolism for fate and hazard assessment. II CATALOGIC simulation of abiotic and microbial degradation. *SAR QSAR Environ. Res.* 22, 719–755.
- ECHA European Chemicals Agency, 2008. Guidance on Information Requirements and Chemical Safety Assessment, Chapter R.6: QSARs and Grouping of Chemicals.
- European Commission. REACH – Registration, Evaluation, Authorisation and Restriction of Chemicals. [http://ec.europa.eu/enterprise/sectors/chemicals/reach/index\\_en.htm](http://ec.europa.eu/enterprise/sectors/chemicals/reach/index_en.htm) Last updated 2013-09-17.
- Government of Canada. Chemicals Management Plan. a. <http://www.chemicalsubstanceschimiques.gc.ca/approach-approche/categor-eng.php>.
- Government of Canada. Chemicals Management Plan. b. <http://www.chemicalsubstanceschimiques.gc.ca/plan/index-eng.php> Last updated 2014-07-17.
- Hale, R.C., Kim, S.L., Harvey, E., La Guardia, M.J., Mainor, T.M., Bush, E.O., Jacobs, E.M., 2008. Antarctic research bases: local sources of polybrominated diphenyl ether (PBDE) flame retardants. *Environ. Sci. Technol.* 42, 1452–1457.
- Hindersinn, R.R., 1990. Historical aspects of polymer fire retardance. *Fire and Polymers*. American Chemical Society, Washington, D.C., p. 627.
- Jantunen, L.M., Gawor, A., Wong, F., Bidleman, T., Wania, F., Stern, G.A., Pucko, M., Hung, H., 2014. Organophosphate Ester Flame Retardants and Plasticizers in the Canadian Arctic. Workshop on Brominate & Other Flame Retardants (Indianapolis, USA).
- Japert, P., Sazonovas, A., Clarke, E.D., Delaney, J.S., 2007. Prediction of Abraham Descriptors for Agrochemicals. *PhysChem Forum* 4, Brussels, Belgium. Accessed from <http://www.acdlabs.com/company/events/eventinfo.php?id=268>.
- Klosterhaus, S.L., Stapleton, H.M., La Guardia, M.J., Greig, D.J., 2012. Brominated and chlorinated flame retardants in San Francisco Bay sediments and wildlife. *Environ. Int.* 47, 56–65.
- Kuramochi, H., Takigami, H., Scheringer, M., Sakai, S.-I., 2014. Estimation of physicochemical properties of 52 non-PBDE brominated flame retardants and evaluation of their overall persistence and long-range transport potential. *Sci. Total Environ.* 491, 108–117.
- Lewin, M., Weil, D.D., 2001. Mechanisms and modes of action in flame retardancy of polymers. In: Horrocks, A.R., Price, D. (Eds.), *Fire Retardant Materials*. Woodhead Publishing Ltd, Cambridge, p. 429.



- Liagkouridis, I., Palm Cousins, A., Cousins, I.T., 2015. Physical-chemical properties and evaluative fate modelling of 'emerging' and 'novel' brominated and organophosphorus flame retardants in the indoor and outdoor environment. *Sci. Total Environ.* 524–535, 416–426.
- Liu, Y., Liggio, J., Harner, T., Jantunen, L., Shoeib, M., Li, S.-M., 2014. Heterogeneous OH initiated oxidation: a possible explanation for the persistence of organophosphate flame retardants in air. *Environ. Sci. Technol.* 48, 1041–1048.
- LMC, 2011. CATALOGIC. Laboratory of Mathematical Chemistry, Burgas, Bulgaria <http://catalogicsoftware.com/>.
- Meylan, W.M., Howard, P.H., 1991. Bond contribution method for estimated Henry's law constants. *Environ. Toxicol. Chem.* 10, 1283–1293.
- Meylan, W.M., Howard, P.H., 1995. Atom fragment contribution method for estimating octanol–water partition-coefficients. *J. Pharm. Sci.* 84, 83–92.
- Möller, A., Xie, Z., Cai, M., Zhong, G., Huang, P., Cai, M., Sturm, R., He, J., Ebinghaus, R., 2011. Polybrominated diphenyl ethers vs alternate brominated flame retardants and dechloranes from East Asia to the Arctic. *Environ. Sci. Technol.* 45, 6793–6799.
- OECD, 2013. OECD Pov and LRTP Screening Tool. [OECD] Organization for Economic Co-Operation and Development, Paris, France <http://www.oecd.org/chemicalsafety/risk-assessment/oecd-pov-and-lrtp-screening-tool.htm>.
- OEHHA, 2008. Proposal 65 safe harbor levels development. In: C.E.P.A. (Ed.). Office of Environmental Health and Hazard Assessment (Sacramento, USA).
- Patlewicz, G., Ball, N., Booth, E.D., Hulzebos, E., Zvinavashe, E., Hennes, C., 2013. Use of category approaches, read-across and (Q)SAR: general considerations. *Regul. Toxicol. Pharmacol.* 67, 1–12.
- Salamova, A., Hermanson, M.H., Hites, R.A., 2014. Organophosphate and halogenated flame retardants in atmospheric particles from a European arctic site. *Environ. Sci. Technol.* 48, 6133–6140.
- Salamova, A., Hites, R.A., 2011. Discontinued and alternative brominated flame retardants in the atmosphere and precipitation from the Great Lakes Basin. *Environ. Sci. Technol.* 45, 8698–8706.
- Scheringer, M., 2009. Long-range transport of organic chemicals in the environment. *Environ. Toxicol. Chem.* 28, 677–690.
- Scheringer, M., Jones, K.C., Matthies, M., Simonich, S., van de Meent, D., 2009. Multimedia partitioning, overall persistence, and long-range transport potential in the contexts of POPs and PBT chemical assessments. *Integr. Environ. Assess. Manag.* 5, 557–576.
- Stapleton, H.M., Klosterhaus, S., Eagle, S., Fuh, J., Meeker, J.D., Blum, A., Webster, T.F., 2009. Detection of organophosphate flame retardants in furniture foam and U.S. house dust. *Environ. Sci. Technol.* 43, 7490–7495.
- Stieger, G., Scheringer, M., Ng, C.A., Hungerbühler, K., 2014. Assessing the persistence, bioaccumulation potential and toxicity of brominated flame retardants: data availability and quality for 36 alternative brominated flame retardants. *Chemosphere* 116, 118–123.
- Stockholm Convention, 2008. The New POPs Under the Stockholm Convention. Secretariat of the Stockholm Convention, Châtelaine, Switzerland <http://chm.pops.int/Implementation/NewPOPs/TheNewPOPs/tabid/672/Default.aspx>.
- UNEP, 2009. Conference of the parties of the Stockholm convention on persistent organic pollutants fourth meeting. In: (UNEP), U.N.E.P. (Ed.). UNEP/POPS/COP4/17. Secretariat of the Stockholm Convention, Geneva Accessed from <http://chm.pops.int/Convention/ConferenceoftheParties%28COP%29/Meetings/COP4/COP4Documents/tabid/531/Default.aspx>.
- USEPA, 2013-1-15. (EPI Suite) Estimation Programs Interface Suite. United States Environmental Protection Agency, Washington, D.C., USA <http://www.epa.gov/oppt/exposure/pubs/episuite.htm> Last updated 2013-1-15.
- Wu, S.D., Blackburn, K., Amburgey, J., Jaworska, J., Federle, T., 2010. A framework for using structural, reactivity, metabolic and physicochemical similarity to evaluate the suitability of analogs for SAR-based toxicological assessments. *Regul. Toxicol. Pharmacol.* 56, 67–81.
- Yang, R.Q., Wei, H., Guo, J.H., Li, A., 2012. Emerging brominated flame retardants in the sediment of the Great Lakes. *Environ. Sci. Technol.* 46, 3119–3126.
- Zhang, X.M., Brown, T.N., Wania, F., Heimstad, E.S., Goss, K.U., 2010. Assessment of chemical screening outcomes based on different partitioning property estimation methods. *Environ. Int.* 36, 514–520.

## Supplemental Information

### NOVEL FLAME RETARDANTS: ESTIMATING THE PHYSICAL-CHEMICAL PROPERTIES AND ENVIRONMENTAL FATE OF 94 HALOGENATED AND ORGANOPHOSPHATE PBDE REPLACEMENTS

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## **S1. Methods**

The list was compiled as described in the text, starting with the list from Bergman et al. (2012).

The additional HFRs from OEHHA (2008) were MC984, OBPB, BPBTB, BPBTerP, TTMN and PBBz. Seven additional OPFRs from Stapleton et al. (2009) and Brommer et al (2014) were OPFRs BDCPP, TPPP, TDMPP, TTBPP, BEHP, IDDPP and EHDPP.

The list of OPFRs used to evaluate goodness-of-fit and root mean square error (RMSE) between measured (Brommer et al., 2014) and modelled  $P_f$  values were TCEP, TCIPP, ToCP, TmCP, TpCP, TEHP, TPPP, TPHP, TBEP, TDCIPP, and EHDPP.

### **S1.1 Estimation of Physical-Chemical Properties**

Pl and Sl at 25 °C were obtained using EPI Suite's MPBPVP v1.43, WSKOWWIN v1.42 and WATERNT models (USEPA, 2013). MPBPVP uses the Modified Grain Method (Lyman, 1985) to estimate Pl. WSKOWIN uses regression models based on KOW and melting point, as outlined by Meylan et al. (1996). WATERNT was developed using the Atom/Fragment Contribution (AFC) Method first developed for KOWWIN (Meylan and Howard, 1995). SPARC calculates Pl and Sl using intermolecular interaction models, based on dispersion, induction, dipole-dipole, and H-bonding interactions (Hilal et al., 2007).

EPI Suite's HENRYWIN v3.20 model (USEPA, 2013) was used to calculate HLC using the Bond Contribution Method adapted by Meyland and Howard (1991) from Hine and Mookerjee (1975). HENRYWIN (as well as KOWWIN and WATRNT) provides an option called Experimental Value Adjustment (EVA) which allows the user to correct property estimates based on structural differences between the target chemical and a structural analogue. The EVA procedure was conducted for HLC for the brominated FRs using DDT as a structural analogue

(since DDT is used to calibrate vapour pressure and KOA using the GC retention time method, e.g., Brommer et al. 2014) to obtain the HLC of compounds outside of the model's domain, as described by Meylan and Howard (1991); DDT is not an appropriate structural analogue for OPFRs and so in the absence of a suitable structural analogue, EVA was not conducted for the OPFRs. SPARC calculates HLC as per Equation S1, where  $VP_{io}$  is the PI of pure solute (i) and  $\gamma_{ij\infty}$  is the activity coefficient of solute (i) in liquid phase (j) at infinite dilution (Hilal et al., 2007).

EPI Suite's KOWWIN v1.68 model (USEPA, 2013) was used to calculate KOW using the Atomic Fragment Contribution (AFC) Method (Equation S2) (Meylan and Howard, 1995). EVA was conducted for compounds outside the model's domain following the same method used for the EVA of HENRYWIN HLC estimates. SPARC estimates KOW by calculating the activities of the chemical in octanol and water separately, determined by the calculated intermolecular interactions of the compound in each phase (Hilal et al., 2007).

Second, Absolv (ACD/Labs, 2013) was used to estimate KAW and KOW by obtaining estimated solute (i) descriptors to be applied to poly-parameter linear free energy relationships (pp-LFER). The solute descriptors: Hydrogen bonding acidity ( $A_i$ ) and basicity ( $B_i$ ) parameters, dipolarity/polarizability ( $S_i$ ), gas phase and hexadecane logarithmic partitioning coefficient ( $L_i$ ), McGowan volume ( $V_i$ ), and excess molar refraction ( $E_i$ ) were used in pp-LFER (Equations S3 and S4), adapted by Goss (2005) from Abraham's (1993) linear solvation energy relationships (LSERs) method at 298K. The pp-LFER method was tested on FRs by Stenzel et al. (2013).

Absolv does not specify domain applicability directly. The training set for Absolv was largely derived from the pharmaceutical sector and does contain some brominated aromatic and

phosphate-based compounds. However, expert judgement is needed to evaluate whether a chemical of interest has sufficient structural coverage within the Absolv training set.

For all three estimation programs used, octanol-air partition coefficient ( $K_{OA}$ ) was calculated by subtracting  $\log K_{OW}$  from  $\log K_{AW}$ .

## **S1.2 Comparison of Estimates of Physical-Chemical Properties**

Measured values for PAHs were taken from Bamford et al. (1999) for HLC, which were converted to  $K_{AW}$ ; Sangster (1989) for  $K_{OW}$ ; Odabasi et al. (2006) for  $P_l$  and  $K_{OA}$ ; and May et al. (1978) for  $S_l$ . All measured values for PCBs ( $P_l$ ;  $S_l$ ; HLC, converted to  $K_{AW}$ ;  $K_{OW}$ ; and  $K_{OA}$ ) were taken from Li et al. (2003). Measured values of PBDEs were taken from Cetin and Odabasi (2005) for HLC, which were converted to  $K_{AW}$ ; Braekevelt et al. (2003) for  $K_{OW}$ ; Harner and Shoeib (2002) for  $K_{OA}$ ; and Tittlemier et al. (2002) for  $P_l$  and  $S_l$ . All measured values for p,p'-DDT ( $P_l$ ;  $S_l$ ; HLC, converted to  $K_{AW}$ ;  $K_{OW}$ ; and  $K_{OA}$ ) were taken from Shen and Wania's (2005) compilation of physical-chemical properties of selected organochlorine pesticides.

## **S1.3 Degradation Rates**

AOPWIN estimates  $t_{air,1/2}$  from the daylight reaction of a compound to hydroxyl radicals in the troposphere. It takes into account all known OH reaction pathways, as described by Atkinson (1988) and later improved by Meyland and Howard (1993). Though the model is capable of providing the rate constant estimates for the reaction between certain organic compounds and ozone, this was not included in  $t_{air,1/2}$ . HYDROWIN estimates  $t_{wat, 1/2}$  from the overall hydrolysis half-life of the compounds, composed of acid-catalyzed, base-catalyzed, and neutral hydrolysis. Since HYDROWIN v2.00 is only capable of estimating neutral hydrolysis for phosphate esters

(Mill et al., 1987), missing values were obtained from PBT profiler, literature, or estimated from compounds with similar properties.

BIOWIN provides a rank for primary (BIOWIN4) and ultimate (BIOWIN3) aerobic biodegradation based on the structural similarities of the compound of interest to the compounds in the training set which were ranked according to semi-qualitative expert opinion. The estimated rank of 5 to > 1.75, is related to a rate estimate in the range of hours, days, weeks, months, or recalcitrance (Boethling et al., 1994). It is the responsibility of the user to convert the ranks into a quantitative value within the appropriate range; our conversion values listed in Table S3, follow those of Aronson et al. (2006). CATALOGIC 301C, a kinetic biodegradation model based on the CATABOL method, simulates all possible biodegradation pathways from parent molecule to metabolite to calculate biological oxygen demand (BOD), from which is  $t_{\text{soil},1/2}$  is derived (Dimitrov et al., 2011). The CATALOGIC model has recently been used to estimate biodegradation in a study of the persistence of cyclical sesquiterpenes (Jenner et al., 2011) and its predecessor, CATABOL, has been recommended as a suitable alternative to experimental measurements to characterize degradation when assessing potential POPs (Boethling et al., 2009).

Obtaining representative half-life estimates for  $t_{\text{water},1/2}$  proved challenging. HYDROWIN only provided  $t_{\text{water},1/2}$  for 16 of the 94 target analytes. Furthermore, five of these differed by several orders of magnitude from literature data (ECHA; Liagkouridis et al., 2015; Muir et al., 1984; Biomonitoring California, 2012; UK EA, 2009a,b,c,d; EC, 2009; WHO, 2000) or data provided by the PBT profiler, indicating that these estimates might be flawed (DBE-DBCH, HBCDD, HBCYD, TBBPA-BGE and TBCO). Estimates of  $t_{\text{water},1/2}$  for 82 compounds could be obtained using values from the PBT profiler as well as literature values. For the remaining 12 compounds



(4'-PeBPOBDE208, DBP-TAZTO, DBS, HBCYD, OBPB, OBTMPI, PBBC, TBBPS-BME, TDMPP, TPPP, TTBP-TAZ and TTMN),  $t_{\text{wat},1/2}$  was estimated from compounds with similar properties.

The *P<sub>OV</sub> and LRTP Screening Tool* v.2.2 tool is a steady-state, fugacity-based multimedia model used to screen chemicals for POP-like behavior (Scheringer et al., 2009, Wegmann et al. 2009). The *Screening Tool* requires six input parameters: molecular weight;  $K_{\text{OW}}$ ,  $K_{\text{AW}}$ ,  $t_{\text{air},1/2}$ ,  $t_{\text{wat},1/2}$  and  $t_{\text{soil},1/2}$ . It provides estimates for  $P_{\text{OV}}$ , characteristic travel distance in kilometers (CTD or the time over which 67% of the parent compound degrades and 33% is transported in the model environment, which is used as a proxy for LRTP), and transfer efficiency.

NFRs were organized into three different classes according to the similarity of their environmental behavior to that of POPs. The NFRs' maximum estimated  $P_{\text{OV}}$  and CTD values from all three emission scenarios were compared to  $P_{\text{OV}}$  and CTD limits that denote the lowest necessary values required for a compound to exhibit similar  $P_{\text{OV}}$  and LRTP to POPs. We used the estimated  $P_{\text{OV}}$  of octa-BDE of 4060 hours and the estimated CTD of penta-BDE of 2510 km as the PBDE limits. Class I compounds have estimated  $P_{\text{OV}}$  and CTD values equal to or greater than the limits and therefore exhibit POP-like or PBDE-like behavior (higher risk compounds); Class II compounds have only one value, either estimated  $P_{\text{OV}}$  or estimated CTD, beyond the limit, but not both (medium risk compounds); while Class III compounds have both estimated  $P_{\text{OV}}$  and CTD values below the limits and therefore do not exhibit POP-like or PBDE-like behavior (lower risk compounds).

## **S2. Results**

**S2.1** The average difference in  $P_l$  of seven orders of magnitude for NFRs with molecular weight >800 g/mol were for OBTMPI, OBPB, TBBPA-BDBPE, EBTEBPI, TBBPS-BDBPE, DBDPE, TTBNPP, BPBTerP, 4'-PeBPOBDE208, and BPBTB.

**S2.2** Discrepancies in Log  $K_{AW}$  of three to eight orders of magnitude was greatest for TMP, TiPP, TPhP, EHDPP, TCP, TpCP, TmCP, ToC, IDDPP, TDMPP, TPPP, and BCMP-BCEP.

**S2.3** Log  $K_{OW}$  variations were greatest for the OPFRs TMP, TiPP, TPhP, TCP, TpCP, TmCP, ToCP, and IDDPP.

**S2.4** The greatest differences in log  $K_{OA}$  were for TBBPA<sup>b</sup>, TBBPS<sup>b</sup>, BCMP-BCEP, EBTEBPI, PIP, and TDBP-TAZTO that have a heteroatom N in the structural backbone and molecular weights varying from < 400 to > 800 g/mol.

**S2.5** The following compounds had estimated  $t_{water,1/2}$  from HYDROWIN with extreme values as high as  $2.9 \times 10^{14}$  h (HBCYD): DBE-DBCH, HBCDD, HBCYD, TBBPA-BGE and TBCO.

**Table S1.** Listing of Novel Flame Retardants (NFRs) under Canadian Regulation

[http://www.chemicalsubstanceschimiques.gc.ca/group/flame\\_retardant-ignifuges/index-eng.php](http://www.chemicalsubstanceschimiques.gc.ca/group/flame_retardant-ignifuges/index-eng.php)

Compound	CAS ID	Canadian Status
<b>Bromides - Aromatic</b>		
OBTMPI	155613-93-7	no results
	893843-07-7	no results
	1084889-51-9	no results
	155613-93-7	no results
TBP	118-79-6	DSL
TTBP-TAZ	25713-60-4	NDSL
TBP-AE	3278-89-5	CMP2 - FR groupings
TBP-DBPE	35109-60-5	NDSL
TBX	23488-38-2	NDSL
DBS	31780-26-4	no results
OBPB	31977-87-4	no results
EBTEBPI	32588-76-4	CMP2 - FR grouping
HCTBPH	34571-16-9	NDSL
DBP	615-58-7	NDSL
PBP	608-71-9	DSL
PBP-AE	01/11/3555	NDSL
PBBz	608-90-2	no results
PBEb	85-22-3	NDSL
PBBB	38521-51-6	no results
PBBC	58495-09-3	no results
PBB-Acr	59447-55-1	no results
PBT	87-83-2	NDSL
HBB	87-82-1	NDSL
BTBPE	37853-59-1	DSL
TBCT	39569-21-6	no results
TBBPS <sup>b</sup>	39635-79-5	NDSL
TBBPS-BDBPE	42757-55-1	DSL
TBBPS-BME	70156-79-5	no results
DBDPE	84852-53-9	CMP2-FR grouping
DBDBE	497107-13-8	no results
DBP-TAZTO	57829-89-7	no results
TDBP-TAZTO	52434-90-9	DSL
4'-PeBPOBDE208	58965-66-5	DSL
TTMN	855992-98-2	no results
	855993-01-0	no results

<b>Compound</b>	<b>CAS ID</b>	<b>Canadian Status</b>
<b>Bromides - Phthalates</b>		
EH-TBB	183658-27-7	CMP2 - FR groupings
HEEHP-TEBP	20566-35-2	DSL
BEH-TEBP	26040-51-7	CMP2 -FR groupings
TEBP-Anh	632-79-1	DSL
	72625-95-7	no results
BDBP-TAZ	75795-16-3	no results
BPBTB	82001-21-6	no results
BPBTerP	90075-91-5	no results
<b>Bromides - TBBPAs</b>		
TBBPA <sup>b</sup>	79-94-7	DSL
TBBPA-BDBPE	21850-44-2	NDSL
TBBPA-BA	55205-38-4	no results
TBBPA-BAE	25327-89-3	DSL
TBBPA-BGE	3072-84-2	NDSL
TBBPA-BP	37419-42-4	no results
TBBPA-BME	37853-61-5	NDSL
TBBPA-BHEE	4162-45-2	DSL
TBBPA-BHEEBA	66710-97-2	NDSL
TBBPA-BOAc	33798-02-6	NDSL
<b>Bromides - Aliphathic (cyclic and non-cyclic)</b>		
HBCYD	25495-98-1	no result
HBCDD	3194-55-6	DSL
TBCO	3194-57-8	NDSL
DBE-DBCH	3322-93-8	DSL
TBNPA	1522-92-5	no results
	36483-57-5	DSL
DBNPG	3296-90-0	DSL
<b>Chlorinated - Aliphatic (cyclic and non-cyclic)</b>		
HCBCH-DCA	115-28-6	DSL
HCBCH-DCA <sup>anh</sup>	115-27-5	DSL
DDC-CO	13560-89-9	CMP2-FR grouping
MIREX	2385-85-5	no results
DDC-DBF	31107-44-5	NDSL
DBHCTD	51936-55-1	NDSL
<b>Chlorinated - Other</b>		
DDC-Ant	13560-92-4	no results
TCP-Anh	117-08-8	DSL
<b>Phosphates</b>		
TDBPP	126-72-7	NDSL
TBNPP	19186-97-1	DSL
TCEP	115-96-8	DSL
TCIPP	13674-84-5	CMP2-FR grouping
TDCIPP	1367487-8	CMP2-FR grouping



<b>Compound</b>	<b>CAS ID</b>	<b>Canadian Status</b>
	78-43-3	
BCMP-BCEP	38051-10-4	DSL
MC 984	66108-37-0	NDSL
BDCPP	72236-72-7	no results
TPPP	64532-95-2	no results
TDMPP	9006-37-5	no results
TTBPP	78-33-1	DSL
BEHP	298-07-7	DSL
IDDP	29761-21-5	DSL
TBEP	78-51-3	DSL
TEP	78-40-0	
TXP	25155-23-1	
BMPPP	26446-73-1	
BPD	56803-37-3	
PIP	68937-41-7	
TPhP	115-86-6	DSL
EHDPP	1241-94-7	DSL
TEHP	78-42-2	DSL
TCP	1330-78-5	CMP2 - FR groupings
TpCP	78-32-0	DSL
TmCP	78-30-8	DSL
ToCP	563-04-2	DSL
TMP	512-56-1	DSL
TiPP	513-02-0	no results
TnBP	126-73-8	DSL
<b>Other</b>		
Br-Cl-Alkene	68527-02-6	
Cl-Alkene	68937-41-7	
Melamine	108-78-1	

**Table S2.** Abbreviations (PRAbs), names and CAS ID numbers of 94 novel flame retardants

Abbreviation	Chemical Name	CAS #
4'-PeBPOBDE208	Benzene, 1,2,4,5-tetrabromo-3,6-bis(2,3,4,5,6-pentabromophenoxy)-	58965-66-5
BCMP-BCEP	Tetrakis(2-chloroethyl)dichloroisopentyldiphosphate or bis[bis(2-chloroethyl)phosphate] or Phosphoric acid, P,P'-[2,2-bis(chloromethyl)-1,3-propanediyl] P,P,P',P'-tetrakis(2-chloroethyl) ester	38051-10-4
BDBP-TAZTO	1,3,5-Triazine-2,4,6(1H,3H,5H)-trione, 1,3-bis(2,3-dibromopropyl)-5-(2-propen-1-yl)-	75795-16-3
BDCPP	bis(1,3-dichloro-2-propyl) phosphate	72236-72-7
BEHP	Bis(2-ethylhexyl) phosphate	298-07-7
BEH-TEBP	1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, 1,2-bis(2-ethylhexyl) ester	26040-51-7
BPBTB	Bis(pentabromobenzyl) tetrabromophthalate	82001-21-6
BPBTerP	Bis(pentabromobenzyl) terephthalate	90075-91-5
BTBPE	1,2-Bis(2,4,6-tribromophenoxy)ethane	37853-59-1
DBDBE	Benzene, 1,1'-[oxybis(methylene)]bis[2,3,4,5,6-pentabromo- (9CI)	497107-13-8
DBDPE	Decabromodiphenylethane	84852-53-9
DBE-DBCH	Cyclohexane, 1,2-dibromo-4-(1,2-dibromoethyl)-	3322-93-8
DBHCTD	hexachlorocyclopentadienyl-dibromocyclooctane	51936-55-1
DBNPG	1,3-Propanediol, 2,2-bis(bromomethyl) OR 2,2-Bis(bromomethyl)-1,3-propanediol	3296-90-0
DBP	Phenol, 2,4-dibromo-	615-58-7
DBP-TAZTO	1,3,5-Triazine-2,4,6(1H,3H,5H)-trione, 1-(2,3-dibromopropyl)-3,5-di-2-propen-1-yl-	57829-89-7
DBS	Benzene, dibromoethenyl-	31780-26-4
DDC-Ant	1,4:5,8:9,10-Trimethanoanthracene, 1,2,3,4,5,6,7,8,12,12,13,13-dodecachloro-1,4,4a,5,8,8a,9,9a,10,10a-decahydro-	13560-92-4
DDC-CO	1,4:7,10-Dimethanodibenzo[a,e]cyclooctene, 1,2,3,4,7,8,9,10,13,13,14,14-dodecachloro-1,4,4a,5,6,6a,7,10,10a,11,12,12a-dodecahydro-	13560-89-9
DDC-DBF	1,4:6,9-Dimethanodibenzofuran, 1,2,3,4,6,7,8,9,10,10,11,11-dodecachloro-1,4,4a,5a,6,9,9a,9b-octahydro-	31107-44-5
EBTEBPI	N-N-Ethylene-bis(tetrabromophthalimide	32588-76-4
EHDPP	ethylhexyldiphenyl phosphate	1241-94-7
EH-TBB	Benzoic acid, 2,3,4,5-tetrabromo-, 2-ethylhexyl ester	183658-27-7
HBB	Benzene, 1,2,3,4,5,6-hexabromo-	87-82-1
HBCDD	1,2,5,9,10-Hexabromocyclodecane	3194-55-6
HBCYD	Cyclodecane, hexabromo-	25637-99-4
		25495-98-1

Abbreviation	Chemical Name	CAS #
HCBCH-DCA	1,4,5,6,7,7-hexachloro-Bicyclo 2.2.1 hept-5-ene-2,3-dicarboxylic acid, aka Chlorendic acid	115-28-6
HCBCH-DCAnh	4,7-Methanoisobenzofuran-1,3-dione, 4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro- aka Chlorendic anhydride	115-27-5
HCTBPH	Bicyclo[2.2.1]hept-2-ene, 1,2,3,4,7,7-hexachloro-5-(2,3,4,5-tetrabromophenyl)-	34571-16-9
HEEHP-TEBP	1,2-Benzenedicarboxylic acid, 3,4,5,6-tetrabromo-, 1-[2-(2-hydroxyethoxy)ethyl] 2-(2-hydroxypropyl) ester	20566-35-2
IDDPP	Isodecyl diphenyl phosphate	29761-21-5
MC 984	Tris(2,3-dichloro-1-propyl)phosphate	66108-37-0
MIREX	1,3,4-Metheno-1H-cyclobuta[cd]pentalene,	2385-85-5
OBPB	1,1a,2,2,3,3a,4,5,5,5a,5b,6-dodecachlorooctahydro-1,4,-Bis(2,4,6-tribromophenoxy)-2,3-dibromobutene	31977-87-4
		1025956-65-3
OBTMPI	1H-Indene, 4,5,6,7-tetrabromo-2,3-dihydro-1,1,3-trimethyl-3-(2,3,4,5-tetrabromophenyl)-	893843-07-7 1084889-51-9 <b>155613-93-7</b>
PBB-Acr	2-Propenoic acid, (2,3,4,5,6-pentabromophenyl)methyl ester	59447-55-1
PBBB	Benzene, 1,2,3,4,5-pentabromo-6-(bromomethyl)-; 2,3,4,5,6-PENTABROMOBENZYL BROMIDE	38521-51-6
PBBC	Benzene, 1,2,3,4,5-pentabromo-6-(chloromethyl)-	58495-09-3
PBBz	Pentabromobenzene	608-90-2
PBEb	Benzene, 1,2,3,4,5-pentabromo-6-ethyl-	85-22-3
PBP	Phenol, 2,3,4,5,6-pentabromo-	608-71-9
PBP-AE	Benzene, 1,2,3,4,5-pentabromo-6-(2-propen-1-yloxy)-	3555-11-1
PBT	Benzene, 1,2,3,4,5-pentabromo-6-methyl-	87-83-2
TBBPA <sup>b</sup>	Phenol, 4,4'-(-methylethylidene)bis[2,6-dibromo-]	79-94-7
TBBPA-BA	2-Propenoic acid, 1,1'-[(1-methylethylidene)bis(2,6-dibromo-4,1-phenylene)] ester	55205-38-4
TBBPA-BAE	Benzene, 1,1'-(1-methylethylidene)bis[3,5-dibromo-4-(2-propen-1-yloxy)-	25327-89-3
TBBPA-BDBPE	Benzene, 1,1'-(1-methylethylidene)bis[3,5-dibromo-4-(2,3-dibromopropoxy)-	21850-44-2
TBBPA-BGE	Oxirane, 2,2'-[(1-methylethylidene)bis[(2,6-dibromo-4,1-phenylene)oxymethylene]]bis-	3072-84-2
TBBPA-BHEE	Ethanol, 2,2'-[(1-methylethylidene)bis[(2,6-dibromo-4,1-phenylene)oxy]]bis-; 4,4'-Isopropylidenebis[2-(2,6-dibromophenoxy)ethanol	4162-45-2
TBBPA-BHEEBA	2-Propenoic acid, 1,1'-[(1-methylethylidene)bis[(2,6-dibromo-4,1-phenylene)oxy-2,1-ethanediyl]] ester	66710-97-2

Abbreviation	Chemical Name	CAS #
TBBPA-BME	TETRABROMOBISPHENOL A DIMETHYL ETHER; Benzene, 1,1'-(1-methylethylidene)bis[3,5-dibromo-4-methoxy-	37853-61-5
TBBPA-BOAc	Phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo-, 1,1'-diacetate	33798-02-6
TBBPA-BP	Phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo-, dipropionate (9CI)	37419-42-4
TBBPS <sup>b</sup>	Phenol, 4,4'-sulfonylbis[2,6-dibromo-	39635-79-5
TBBPS-BDBPE	Benzene, 1,1'-sulfonylbis[3,5-dibromo-4-(2,3-dibromopropoxy)-	42757-55-1
TBBPS-BME	Benzene, 1,1'-sulfonylbis[3,5-dibromo-4-methoxy-	70156-79-5
TBCO	Cyclooctane, 1,2,5,6-tetrabromo-	3194-57-8
TBCT	Benzene, 1,2,3,4-tetrabromo-5-chloro-6-methyl-	39569-21-6
TBEP	tris(2-butoxyethyl) phosphate	78-51-3
TBNPA	1-Propanol, 2,2-dimethyl-, tribromo derive. (Tribromoneopentylalcohol)	36483-57-5 1522-92-5
TEP	Triethylphosphate	78-40-0
TXP	Phenol, dimethyl-, phosphate (3:1); Trixylyl phosphate	25155-23-1
BMPPP	Bis(methylphenyl) phenyl phosphate	26446-73-1
BPDP	Di-tert-butylphenyl diphenyl phosphate	56803-37-3
PIP	Isopropylphenyl phosphate	68937-41-7
TBP	Phenol, 2,4,6-tribromo-	118-79-6
TBP-AE	Benzene, 1,3,5-tribromo-2-(2-propen-1-yloxy)-	3278-89-5
TBP-DBPE	Benzene, 1,3,5-tribromo-2-(2,3-dibromopropoxy)-	35109-60-5
TBX	Benzene, 1,2,4,5-tetrabromo-3,6-dimethyl-	23488-38-2
TCEP	Ethanol, 2-chloro-, phosphate (3:1)	115-96-8
TCIPP	Tris(1-chloro-2-propyl)phosphate	13674-84-5
TCP	tris(cresyl) phosphate	1330-78-5
TDBPP	1-Propanol, 2,3-dibromo-, 1,1',1''-phosphate	126-72-7
TDBP-TAZTO	1,3,5-Triazine-2,4,6(1H,3H,5H)-trione, 1,3,5-tris(2,3-dibromopropyl)-; 1,3,5-Tris(2,3-dibromopropyl)-2,4,6-trioxohexahydrotriazine	52434-90-9
TDCIPP	2-Propanol, 1,3-dichloro-, phosphate (3:1)	13674-87-8 78-43-3
TDMPP	tris(3,5-dimethyl phenyl) phosphate	9006-37-5
TEBP-Anh	Tetrabromophthalic anhydride	632-79-1 72625-95-7
TECP-Anh	1,3-Isobenzofurandione, 4,5,6,7-tetrachloro- AKA TETRACHLOROPHTHALIC ANHYDRIDE	117-08-8
TEHP	tris(2-ethylhexyl) phosphate	78-42-2
TiPP	Triisopropyl phosphate	513-02-0



Abbreviation	Chemical Name	CAS #
TmCP	tris(m-cresyl) phosphate	78-30-8
TMP	Trimethyl phosphate	512-56-1
TnBP	Tri <i>n</i> butyl phosphate	126-73-8
ToCP	tris(o-cresyl) phosphate	563-04-2
TpCP	tris(p-cresyl) phosphate	78-32-0
TPhP	triphenyl phosphate	115-86-6
TPPP	tris(2-isopropyl phenyl) phosphate	64532-95-2
TTBNPP	1-Propanol, 3-bromo-2,2-bis(bromomethyl)-, 1,1',1''-phosphate	19186-97-1
TTBPP	tris(4-tert-butylphenyl) phosphate	78-33-1
TTBP-TAZ	1,3,5-Triazine, 2,4,6-tris(2,4,6-tribromophenoxy)-	25713-60-4
TTMN	1,2,3,9-Tetrabromo-1,2,3,4-tetrahydro-1,4-methanonaphthalene	855992-98-2 855993-01-0
Br-Cl-Alkene	Alkenes, C12-30 alpha-, bromo chloro	68527-01-5
Cl-Alkene	Alkenes, C12-24-chloro	68927-02-6
iPPP	Isopropylphenyl phosphate	68937-41-7
Melamine	1,3,5-Triazine-2,4,6-triamine	108-78-1

**Table S3.** Conversion of BLOWIN output to quantitative values (Aronson et al. 2006)

Rank (BLOWIN output)	Qualitative Range	Quantitative value
4.75-5	hours	6 h
4.25-4.75	hours-days	12 h
3.75-4.25	days	2 d
3.25-3.75	days-weeks	7 d
2.75-3.25	weeks	14 d
2.25-2.75	weeks to months	1.5 m
1.75-2.25	months	6 m
<1.75	recalcitrant	10 y

The following equation is used by SPARC to calculate the Henry's Law Constant, HLC, Bond Contribution Method, expanded:

$$(S1) \quad HLC = VP_i^0 \gamma_{ij}^\infty$$

Where  $VP_i^o$  is the  $P_i$  of pure solute (i) and  $\gamma_{ij}^\infty$  is the activity coefficient of solute (i) in liquid phase (j) at infinite dilution (Meylan and Howard 1991; Hine and Mookerjee 1975).

$K_{OW}$  was calculated using the atom/fragment contribution (AFC) method of Meylan and Howard (1995):

$$(S2) \quad \log K_{OW} = \sum (f_i n_i) + \sum (c_j n_j) + 0.229$$

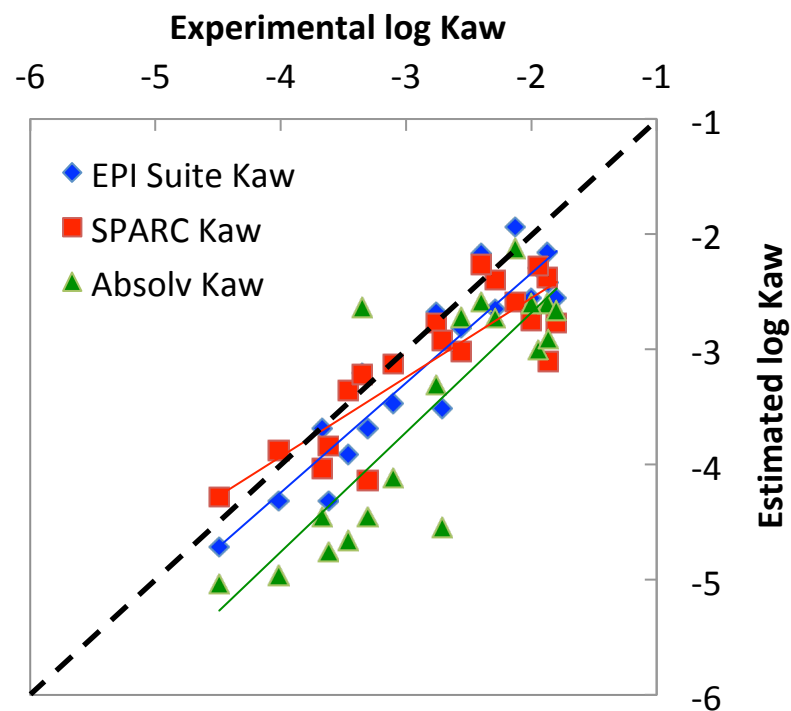
Where  $\sum (f_i n_i)$  is the sum of the coefficients assigned to each atom/fragment multiplied by the number of times it occurs in the molecule, and  $\sum (c_j n_j)$  is the sum of each correction factor times the number of times it is applied to the molecule (Meylan and Howard 1995).

Polyparameter linear free energy relationships (pp-LFER) used by Absolv to calculate  $K_{AW}$  and  $K_{OW}$  (Goss 2005):

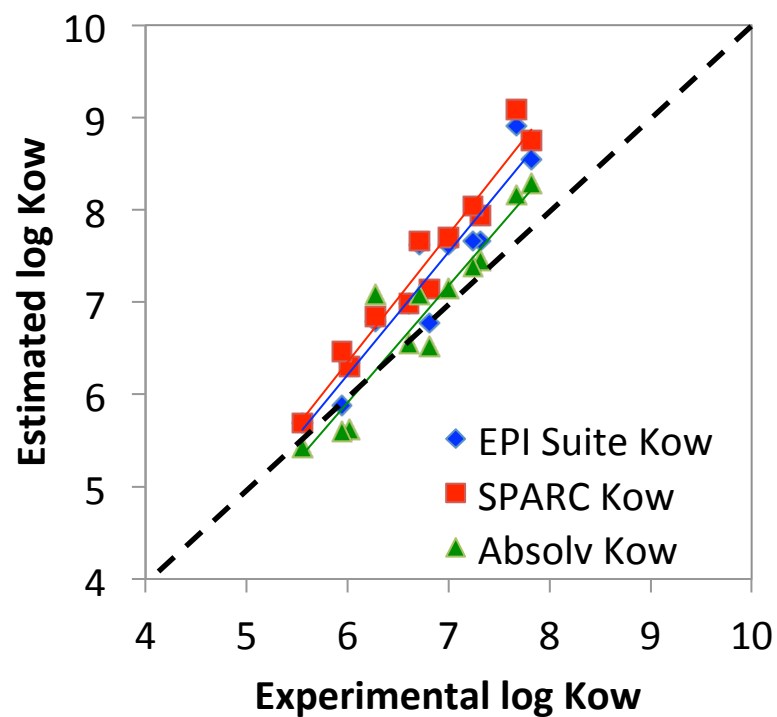
$$(S3) \quad \log K_{AW} = - (2.07S_i + 3.67A_i + 4.87B_i + 0.48L_i - 2.55V_i - 0.59)$$

$$(S4) \quad \log K_{OW} = -1.41S_i - 0.18A_i - 3.45B_i + 0.43L_i + 2.41V_i + 0.34$$

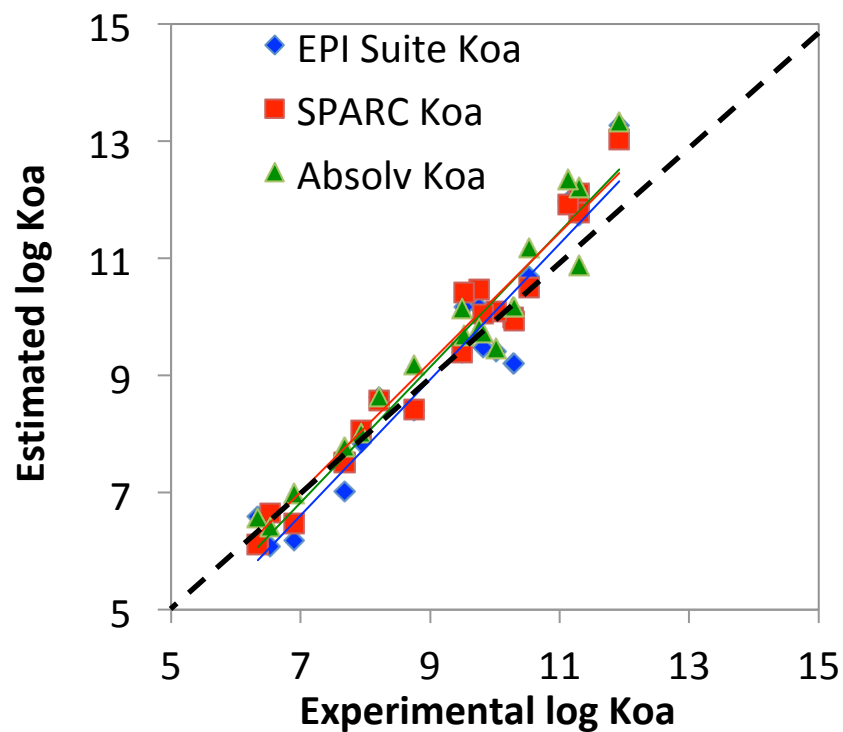
Where  $A_i$  and  $B_i$  are the solute descriptors for hydrogen bonding acidity and basicity parameters,  $S_i$  is the descriptor for dipolarity/polarizability,  $L_i$  is the gas phase and hexadecane logarithmic partitioning coefficient,  $V_i$  is the McGowan volume, and  $E_i$  is the excess molar refraction descriptor.



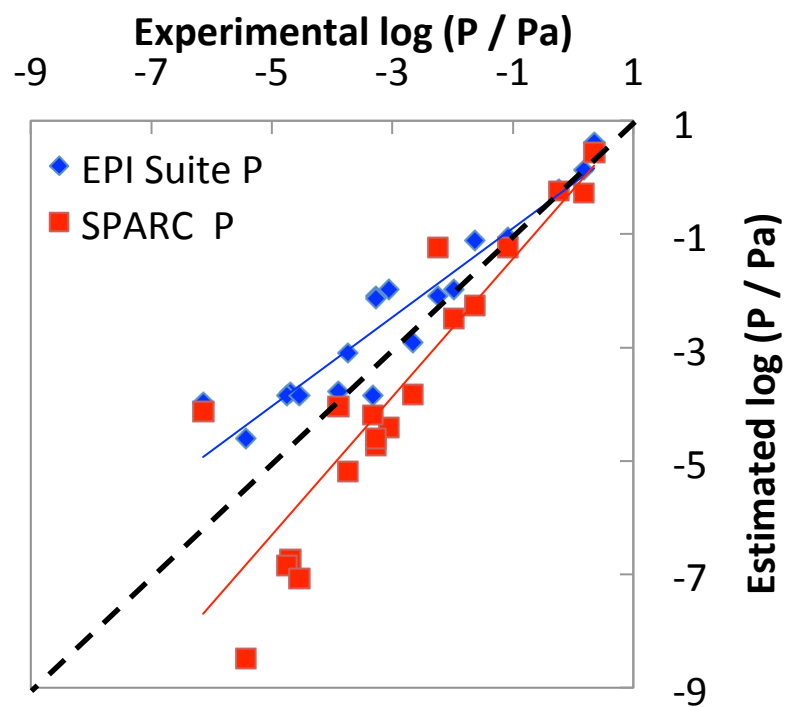
**Figure S1.**  $K_{AW}$  goodness-of-fit. Estimated  $K_{AW}$  values of select PAHs, PCBs, PBDEs, and DDT were compared to measured data. EPI Suite estimates are represented by the blue diamonds, SPARC's by the red squares, and Absolv's by the green triangles. Root mean square errors (RMSE) were 0.43, 0.51 and 0.89 for EPI Suite, SPARC and Absolv, respectively.



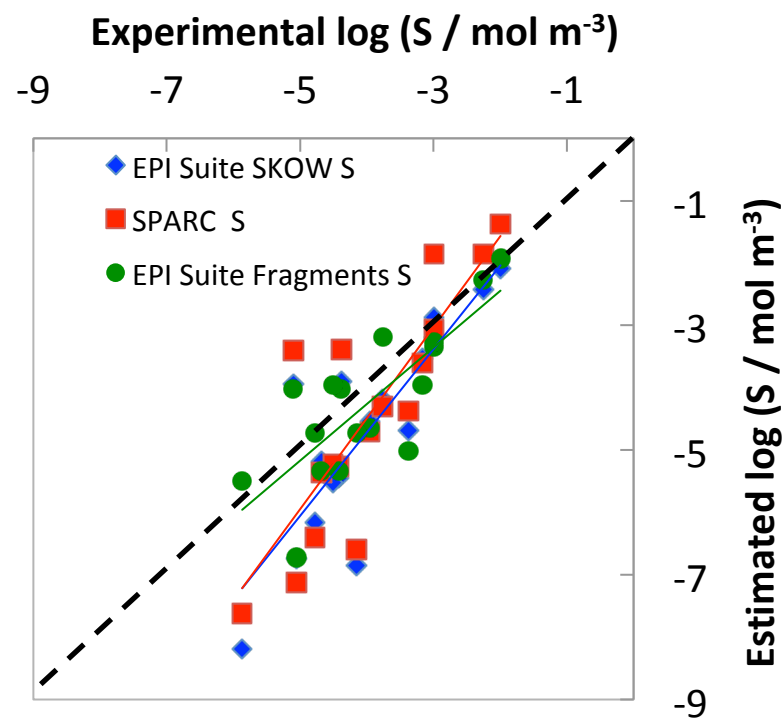
**Figure S2.** K<sub>ow</sub> goodness-of-fit. Estimated K<sub>ow</sub> values for select PCBs, PBDEs, and DDT were compared to measured data (PAHs were omitted). EPI Suite estimates are represented by the blue diamonds, SPARC's by the red squares, and Absolv's by the green triangles. RMSE were 0.52, 0.63 and 0.34 for EPI Suite, SPARC and Absolv, respectively.



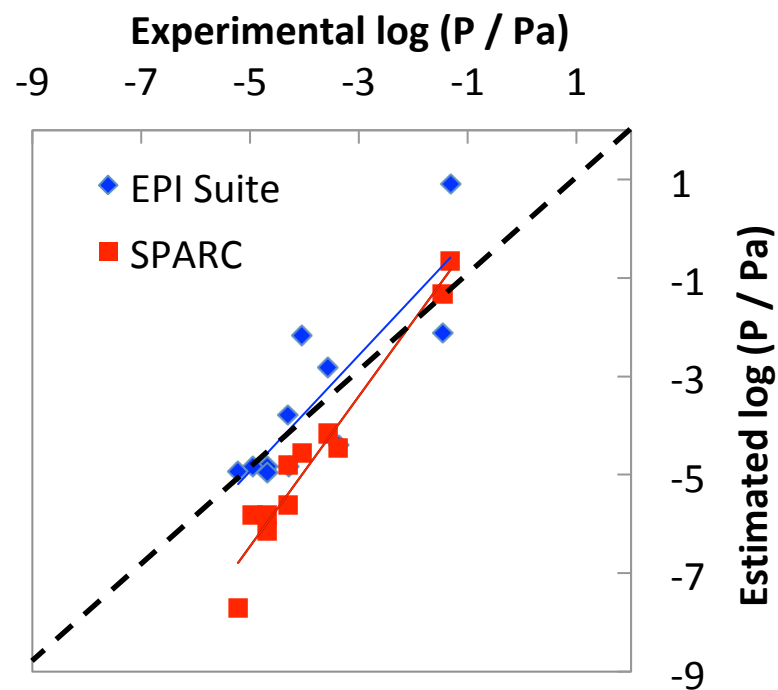
**Figure S3.**  $K_{OA}$  goodness-of-fit. Estimated  $K_{OA}$  values for select PAHs, PCBs, PBDEs, and DDT were compared to measured data. EPI Suite estimates are represented by the blue diamonds, SPARC's by the red squares, and Absolv's by the green triangles. RMSE were 0.65, 0.51 and 0.56 for EPI Suite, SPARC and Absolv, respectively.



**Figure S4.**  $P_i$  goodness-of-fit. Estimated  $P$  values for select PAHs, PCBs, PBDEs, and DDT were compared to measured data. EPI Suite estimates are represented by the blue diamonds and SPARC's by the red squares. RMSE were 0.81 and 1.46 for EPI Suite and SPARC, respectively.



**Figure S5.**  $S_l$  goodness-of-fit. Estimated  $S$  values for select PAHs, PCBs, PBDEs, and DDT were compared to measured data. EPI Suite SKOW estimates are represented by the blue diamonds, EPI Suite Fragments estimates by the blue asterisks, and SPARC's by the red squares. RMSE were 0.79 and 1.18 for EPI Suite SKOW  $S$  (WSKOWWIN) and Fragment  $S$  (WATERNT). RMSE for SPARC was 1.22.



**Figure S6.**  $P_l$  goodness-of-fit for OPFRs. Estimated  $P$  values for select OPFRs were compared to measured data of Brommer et al. (2014). EPI Suite estimates are represented by the blue diamonds and SPARC's by the red squares. RMSE were 1.01 and 1.15 for EPI Suite and SPARC, respectively.



**Table S4.** Physical-chemical properties of novel flame retardants.

Compound	MW / g mol <sup>-1</sup>	log (SI / mg L <sup>-1</sup> )		log (PI / Pa)			log K <sub>AW</sub>			log K <sub>OW</sub>			log K <sub>OA</sub>		
		EPI Suite		SPARC	EPI Suite	Absolv	EPI Suite	SPARC	Absolv	EPI Suite	SPARC	Absolv	EPI Suite	SPARC	Absolv
		WSKOWWIN	WATERNT												
4'-															
PeBPOBDE208	1367	-17.4	-5.9	-17.4	-13.6	-26.1	-9.6	-8.9	-9.2	16.9*	17.2	16.5	26.5	26.1	25.7
BCMP-BCEP	583	-0.5	1.5	-4.0	-4.9	-8.8	-12.2	-5.4	-14.0	3.3	8.8	4.2	15.5	14.2	18.2
BDBP-TAZTO	569	-3.2	-3.6	0.4	-8.0	-8.8	-14.6	-9.8	-12.2	6.6	4.5	4.4	21.2	14.4	16.6
BDCPP	320	2.1	3.3	2.5	-4.9	-2.7	-8.8	-6.0	-9.2	2.2	3.4	1.9	11.0	9.4	11.1
BEH-TEBP	706	-8.7	-5.7	-6.3	-6.4	-12.0	-4.9	-6.3	-5.1	12.0	10.9	12.4	16.9	17.2	17.5
BMPPP	354	-1.2	-0.3	-3.2	-4.5	-5.3	-5.7	-3.0	-10.2	5.8	8.3	4.5	11.5	11.3	14.7
BPBTB	1451	-17.5	-5.8	-13.9	-15.2	-26.5	-13.9	-12.9	-12.6	16.3*	15.5	16.5	30.2	28.4	29.1
BPBTerP	1135	-13.4	-5.9	-10.7	-11.8	-21.6	-11.2	-11.3	-10.8	14.0*	13.2	13.7	25.2	24.6	24.5
BPDP	382	-0.8	-1.0	-3.9	-3.1	-5.6	-5.4	-2.6	-10.0	6.6	9.1	5.3	12.0	11.7	15.3
Br-Cl-Alkene	282	-1.4	-1.1	-1.3	-0.1	-0.9	0.3	-0.6	-0.3	6.6	6.5	6.8	6.2	7.1	7.1
BTBPE	688	-6.2	-3.7	-5.4	-5.5	-9.9	-6.5*	-5.1	-6.4	9.2	9.4	8.6	15.7	14.5	15.1
Cl-Alkene	201	-0.6	-0.6	-1.0	0.3	0.1	1.2	0.0	0.4	6.1	6.2	6.1	4.9	6.2	5.8
DBDPE	971	-11.9	-6.0	-9.7	-8.0	-15.3	-5.6	-6.0	-5.6	13.6*	12.2	12.6	19.2	18.2	18.2
DBE-DBCH	428	-1.2	0.0	0.7	-1.1	-2.3	-2.8	-3.8	-2.8	5.2	4.4	6.0	8.0	8.2	8.8
DBHCTD	541	-4.2	-3.9	-2.9	-3.3	-5.5	-3.1	-3.2	-3.9	7.9	8.2	8.4	11.1	11.4	12.3
DBNPG	262	3.4	5.0	5.4	-2.2	-1.5	-6.8	-7.9	-6.7	0.9	-0.1	2.2	7.6	7.8	8.9
DBP	252	2.2	3.5	3.5	0.4	-0.1	-5.4	-4.7	-4.7	3.3	3.1	3.2	8.7	7.8	7.9
DBP-TAZTO	409	-1.6	-2.4	1.7	-6.2	-5.7	-12.8	-8.2	-10.8	5.9	3.6	3.1	18.7	11.8	13.9
DBS	262	1.3	1.9	0.8	0.0	0.3	-2.3	-1.5	-2.4	3.6	4.4	3.9	5.9	5.9	6.2
DDC-Ant	638	-7.6	-6.2	-5.5	-4.7	-8.3	-4.0	-3.4*	-4.8	11.2	10.8	10.1	15.2	14.3	14.9
DDC-CO	654	-7.8	-6.2	-6.4	-5.1	-8.8	-3.5	-3.0*	-5.1	11.3	11.6	10.7	14.8	14.5	15.8
DDC-DBF	614	-4.8	-5.3	-4.2	-4.2	-7.0	-7.0	-3.4	-6.8	8.1	9.8	7.9	15.0	13.2	14.8
EBTEBPI	951	-8.5	-5.1	-5.9	-15.8	-20.0	-18.8	-14.6	-16.8	9.8	9.7	7.5	28.6	24.2	24.3
EHDPP	362	-1.2	-0.7	-3.6	-2.2	-4.6	-5.0	-1.8	-8.6	6.3	8.8	5.6	11.3	10.6	14.1
EH-TBB	550	-4.9	-2.5	-3.4	-3.8	-6.5	-3.6	-3.7	-3.6	8.8	8.3	8.8	12.3	12.0	12.4
HBB	551	-2.7	-0.6	-2.5	-2.2	-4.7	-3.1	-2.8*	-3.2	7.3	6.8	6.4	10.4	9.6	9.6

Compound	MW / g mol <sup>-1</sup>	log (SI / mg L <sup>-1</sup> )		log (PI / Pa)			log K <sub>AW</sub>			log K <sub>OW</sub>			log K <sub>OA</sub>		
HBCDD	642	-4.7	-2.5	-2.5	-2.7	-7.1	-4.2	-5.2	-4.2	7.7	7.2	8.9	11.9	12.4	13.2
HBCYD	614	-3.8	-2.8	-2.1	-3.2	-5.2	-4.4	-3.7	-2.4	6.9	6.9	8.9	11.3	10.6	11.3
HCBCH-DCA	389	1.3	0.9	2.5	-3.8	-9.1	-11.9	-12.4*	-11.3	3.1	2.8	3.2	15.0	15.2	14.5
HCBCH-DCA <sub>nh</sub>	371	-0.1	0.7	3.4	-1.8	-4.0	-5.4	-8.2	-11.0	4.4	2.2	1.3	9.8	10.3	12.2
HCTBPH	693	-7.4	-5.3	-4.8	-4.9	-9.3	-4.3*	-5.0	-4.6	10.6*	9.4	9.8	14.9	14.4	14.4
HEEHP-TEBP	628	-1.2	2.9	0.1	-9.3	-14.2	-14.0	-14.9	-14.1	3.8	4.5	4.9	17.8	19.4	19.0
IDDPP	390	-1.1	-1.8	-4.7	-4.6	-5.7	-4.7	-1.8	-8.4	7.3	9.8	6.6	12.0	11.6	15.0
MC 984	582	-2.0	-0.4	-2.2	-4.9	-7.1	-8.1	-5.5	-8.1	5.0	7.0	6.3	13.2	12.5	14.4
Melamine	126	6.0	3.0	4.5	-4.2	-6.2	-11.1	-12.0	-12.3	-0.4	-1.0	-1.9	10.7	10.9	10.5
MIREX	546	-3.3	-4.2	-3.5	-2.7	-3.8	-4.3*	-1.0	-5.3	7.0	9.7	7.0	11.3	10.7	12.3
OBPB	871	-8.7	-5.1	-7.6	-8.0	-13.1	-7.7	-6.0	-7.8	10.7*	11.4	10.4	18.4	17.4	18.3
OBTMPI	868	-10.7	-6.1	-8.4	-7.3	-13.8	-4.7*	-5.8	-4.1	13.0*	11.7	13.2	17.8	17.6	17.3
PBB-Acr	557	-3.4	-0.9	-1.5	-3.2	-5.9	-5.5	-5.0	-4.7	6.9	6.5	6.7	12.4	11.5	11.4
PBBB	566	-3.8	-1.2	-2.2	-2.7	-5.7	-3.6	-4.1	-3.1	7.3	6.5	7.0	10.9	10.7	10.1
PBBC	521	-3.5	-0.9	-1.9	-2.5	-5.1	-3.1	-3.9	-2.8	7.2	6.4	6.8	10.3	10.3	9.6
PBBz	473	-2.5	0.1	-1.2	-1.5	-3.0	-2.7	-2.5	-2.8	6.4	5.9	5.8	9.1	8.4	8.5
PBEB	501	-3.5	-1.0	-2.2	-2.1	-4.2	-2.5	-2.8	-2.4	7.5	6.8	7.0	10.0	9.5	9.3
PBP	489	-1.6	1.5	-1.2	-3.0	-4.1	-6.6	-3.6	-5.5	6.0	5.7	6.1	12.6	9.3	11.6
PBP-AE	529	-3.6	-1.3	-2.6	-2.6	-4.9	-3.8	-2.9	-3.2	7.4	7.3	7.1	11.1	10.2	10.3
PBT	487	-3.0	-0.5	-1.8	-1.8	-4.0	-2.6	-2.8	-2.5	7.0	6.4	6.4	9.6	9.2	8.9
PIP	453	-4.6	-3.3	-6.2	-4.9	-7.6	-4.9	-2.2	-9.5	9.1	11.2	8.0	14.0	13.4	17.5
TBBPAb	544	-3.0	-0.5	-3.1	-6.7	-7.7	-11.0	-5.3	-6.6	7.2	7.5	8.6	18.2	12.8	15.2
TBBPA-BA	652	-5.0	-3.6	-3.1	-5.9	-10.2	-7.5	-7.7	-8.0	8.1	8.0	8.9	15.5	15.7	16.9
TBBPA-BAE	624	-6.5	-5.5	-5.7	-5.7	-9.8	-5.3*	-4.6	-5.7	10.0	10.4	10.1	15.3	15.0	15.8
TBBPA-BDBPE	944	-9.9	-6.0	-8.6	-9.2	-16.3	-8.8	-8.2	-8.3	11.5*	12.2	12.8	20.3	20.4	21.1
TBBPA-BGE	656	-4.5	-2.9	-3.9	-6.6	-11.6	-10.3	-8.3	-8.6	7.4	8.5	9.0	17.7	16.8	17.6
TBBPA-BHEE	632	-3.8	-1.6	-3.2	-10.5	-14.3	-11.1	-11.7	-11.8	6.8	7.9	7.6	17.9	19.6	19.4
TBBPA-BHEEBA	661	-5.2	-4.6	-4.0	-7.0	-11.5	-10.7	-8.0	-10.2	8.2	9.2	8.9	18.9	17.2	19.1
TBBPA-BME	572	-4.7	-3.4	-4.2	-4.5	-8.2	-5.5	-4.7	-5.2	8.3	8.8	8.7	13.8	13.5	13.9

Compound	MW / g mol <sup>-1</sup>	log (SI / mg L <sup>-1</sup> )		log (PI / Pa)			log K <sub>AW</sub>			log K <sub>OW</sub>			log K <sub>OA</sub>		
TBBPA-BOAc	628	-4.3	-2.6	-2.5	-5.4	-10.2	-6.9	-8.3	-7.3	7.4	7.3	8.6	14.3	15.6	15.9
TBBPA-BP	656	-5.3	-3.6	-3.5	-6.0	-10.8	-6.7	-7.9	-7.1	8.3	8.4	9.7	15.0	16.3	16.8
TBBPSb	566	-1.4	0.5	-0.6	-8.5	-10.4	-14.6	-10.5	-10.5	5.2	4.8	5.7	19.8	15.3	16.2
TBBPS-BDBPE	966	-8.4	-6.0	-6.4	-10.8	-18.2	-12.3	-12.1	-12.2	9.5	9.9	9.9	21.8	22.0	22.1
TBBPS-BME	594	-3.2	-2.3	-1.9	-6.0	-9.9	-9.0	-8.6	-9.1	6.3	6.6	5.8	15.4	15.1	14.9
TBCO	428	-1.2	0.2	0.8	-1.3	-2.3	-2.8	-3.9	-2.8	5.2	4.4	6.0	8.0	8.3	8.8
TBCT	442	-2.5	-0.4	-1.6	-1.5	-3.4	-2.3	-2.6	-2.2	6.7	6.3	6.2	9.1	8.8	8.4
TBEP	398	0.3	2.8	0.1	-3.8	-4.8	-9.3	-5.6	-8.9	3.0	6.0	5.4	12.3	11.6	14.3
TBNPA	325	2.5	2.9	4.0	-1.7	-0.9	-6.3	-5.8	-3.9	2.3	1.9	3.7	8.5	7.7	7.6
TBP	331	1.0	2.9	1.1	-0.7	-0.7	-5.8	-2.6	-4.3	4.2	4.0	4.3	10.0	6.7	8.6
TBP-AE	371	-1.1	0.1	-0.3	-1.1	-1.8	-3.0	-2.3	-3.2	5.6	5.6	5.1	8.6	7.9	8.3
TBP-DBPE	531	-2.8	-1.1	-1.6	-2.8	-5.1	-4.7*	-4.1	-4.5	6.3	6.5	6.4	11.1	10.6	11.0
TBX	422	-2.3	-0.3	-1.2	-1.3	-3.2	-2.2	-2.8	-1.8	6.7	6.0	6.3	8.8	8.8	8.1
TCEP	285	2.9	3.7	1.1	0.9	-0.7	-6.0	-2.7	-6.9	1.6	4.3	2.0	7.6	7.0	8.9
TCIPP	328	1.7	2.9	-0.7	-2.1	-1.3	-5.6	-1.5	-6.7	2.9	6.1	3.3	8.5	7.6	10.0
TCP	368	-0.7	-0.9	-3.5	-4.1	-5.9	-5.7	-3.2	-9.9	6.3	8.6	5.1	12.0	11.8	15.1
TDBPP	698	-2.1	0.0	-2.4	-1.6	-7.7	-9.9	-5.8	-11.0	4.2	7.1	5.4	14.1	12.9	16.3
TDBP-TAZTO	729	-4.9	-4.9	-1.1	-9.8	-11.9	-16.3	-11.4	-13.5	7.4	5.4	5.7	23.7	16.9	19.2
TDCIPP	431	0.2	1.5	-0.9	-4.4	-4.4	-7.0	-4.3	-7.6	3.7	6.1	4.4	10.6	10.3	12.0
TDCPP	431	0.2	1.5	-1.1	-3.9	-4.9	-7.0	-4.5	-9.1	3.7	6.3	3.9	10.6	10.8	13.0
TDMPP	410	-3.4	-2.4	-5.2	-4.9	-7.1	-5.5	-2.6	-9.2	8.0	10.3	7.0	13.5	12.9	16.2
TEBP-Anh	464	-1.7	1.8	1.4	-2.8	-6.7	-5.2	-8.8	-6.3	5.6	3.0	4.2	10.8	11.8	10.5
TECP-Anh	286	0.2	1.9	2.3	-1.7	-4.4	-4.1	-7.6	-5.0	4.7	2.5	3.3	8.8	10.2	8.3
TEHP	435	-4.8	-3.6	-5.9	-5.0	-6.1	-2.4	-0.9	-4.4	9.5	11.1	10.1	11.9	12.0	14.5
TEP	182	4.0	5.1	1.2	1.7	2.6	-4.6	0.2	-6.0	0.9	4.2	0.9	5.5	4.0	6.9
TiPP	224	2.7	4.2	-0.5	1.2	1.8	-4.3	1.2	-5.8	2.1	5.9 <sup>a</sup>	2.1	6.4	4.6	7.9
TmCP	368	-1.7	-0.9	-3.7	-4.8	-5.8	-5.7	-2.9	-9.9	6.3	8.9	5.1	12.0	11.8	15.1
TMP	140	5.5	6.0	2.5	2.1	4.2	-5.0	0.5	-6.3	-0.6	3.1 <sup>a</sup>	-0.7	4.4	2.6	5.6
TnBP	266	0.9	2.0	-1.2	-0.8	-0.7	-3.9	-0.4	-5.4	3.8	6.6	4.1	7.7	7.0	9.5
ToCP	368	-1.7	-0.9	-3.7	-4.8	-5.6	-5.7	-2.7	-9.9	6.3	8.9	5.1	12.0	11.6	15.1
TpCP	368	-1.7	-0.9	-3.7	-4.8	-5.8	-5.7	-2.9	-9.9	6.3	8.9	5.1	12.0	11.8	15.1

Compound	MW / g mol <sup>-1</sup>	log (SI / mg L <sup>-1</sup> )		log (PI / Pa)			log K <sub>AW</sub>			log K <sub>OW</sub>			log K <sub>OA</sub>		
TPhP	326	0.0	0.7	-2.1	-2.8	-4.2	-5.8	-2.9	-10.7	4.7	7.4	3.3	10.5	10.3	14.0
TPPP	453	-4.6	-3.3	-5.7	-4.9	-7.7	-4.9	-2.7	-9.5	9.1	10.8	8.0	14.0	13.5	17.5
TTBNPP	1019	-7.5	-4.9	-5.3	-4.9	-13.7	-12.0	-8.8	-10.1	8.1	9.1	10.8	20.0	17.9	21.0
TTBPP	495	-6.0	-4.4	-7.3	-4.9	-9.0	-4.6	-2.3	-8.6	10.4	12.3	9.5	15.0	14.7	18.1
TTBP-TAZ	1067	-10.7	-6.0	-10.5	-12.5	-21.9	-10.0	-11.7	-14.1	11.5	12.8	11.1	21.5	24.5	25.2
TTMN	460	-1.1	-1.5	-0.4	-2.5	-4.5	-4.7	-4.9	-4.7	5.0	5.3	6.0	9.6	10.2	10.6
TXP	410	-3.4	-2.4	-5.1	-4.5	-7.4	-5.5	-3.1	-9.2	8.0	10.1	7.0	13.5	13.2	16.2

<sup>a</sup> Identified as statistically significant outliers through the use of Grubb's Test.

\*Estimates obtained with the EVA method, using DDT as a structural analogue

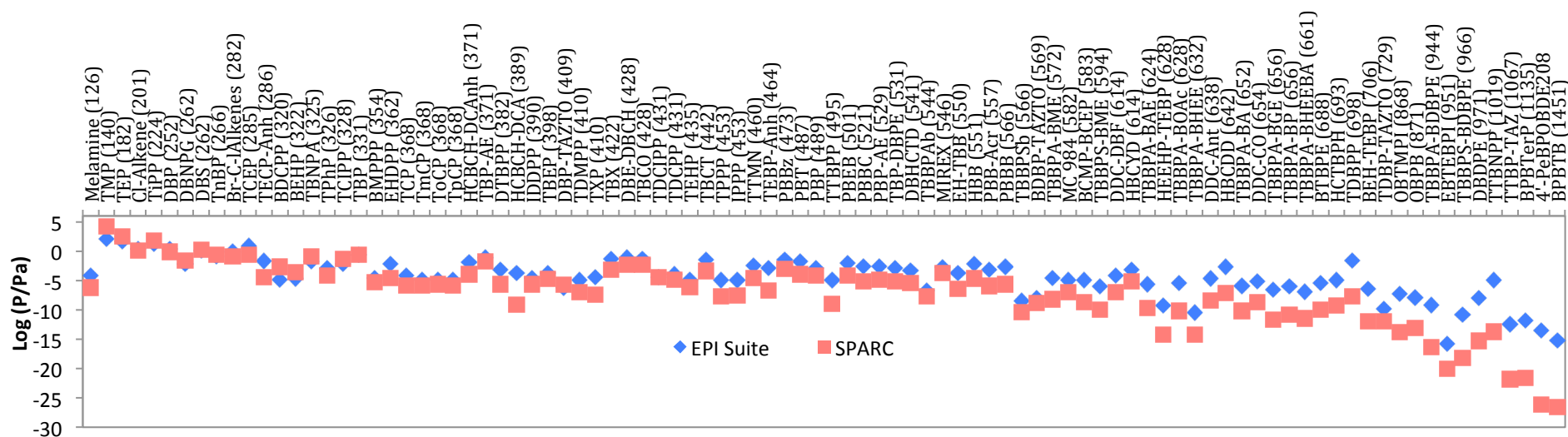
**Table S5.** Environmental degradation half-lives (h) of 94 novel flame retardants

	$t_{\text{air},1/2}$	$t_{\text{wat},1/2}$	$t_{\text{wat},1/2}$	$t_{\text{wat},1/2}$	Primary $t_{\text{soil},1/2}$		Ultimate $t_{\text{soil},1/2}$	
	EPI Suite	EPI Suite	Literature	PBT profiler	EPI Suite	CATALOGIC	EPI Suite	CATALOGIC
4'-PeBPOBDE208	2351			4320	87600	768	87600	87600
BCMP-BCEP	2	2705			336	912	87600	46440
BDBP-TAZTO	4			1440	336	624	4320	8448
BDCPP	11		8760		336	1968	4320	7968
BEHP	2		8760	360	48	1968	336	7416
BEH-TEBP	6	701			336	4	4320	816
BPBTB	68	750			87600	4	87600	5424
BPBTerP	40	2006			87600	4	87600	1224
BTBPE	9			4320	4320	2328	87600	87600
DBDPE	54			4320	87600	456	87600	68712
DBE-DBCH	26	7.6E+05*		912	168	1464	1080	37656
DBHCTD	12			4320	4320	1512	87600	87600
DBNPG	14			360	168	12	336	5496
DBP	45			912	336	2448	1080	14568
DBP-TAZTO	2			912	168	768	1080	9408
DBS	17			912	168	3288	1080	13608
DDC-Ant	8			4320	87600	768	87600	42240
DDC-CO	6			4320	87600	768	87600	54168
DDC-DBF	9			4320	87600	744	87600	36792
EBTEBPI	3			4320	87600	113	87600	4632
EHDPP	3		780	360	48	1488	336	15336
EH-TBB	12	819			336	8	4320	1032
HBB	11207			4320	4320	864	87600	61896
HBCDD	26	1.6E+10*		1440	336	792	4320	87600
HBCYD	17	2.9E+14*		4320	1080	1296	87600	61824
HCBCH-DCA	16			4320	336	8	87600	65976
HCBCH-DCA <sub>nh</sub>	38			4320	4320	2	87600	7080
HCTBPH	25			4320	87600	1488	87600	48684
HEEHP-TEBP	4	327			336	3	4320	840
IDDPP	3		2256	912	48	1248	1080	12912
	$t_{\text{air},1/2}$	$t_{\text{wat},1/2}$	$t_{\text{wat},1/2}$	$t_{\text{wat},1/2}$	Primary $t_{\text{soil},1/2}$		Ultimate $t_{\text{soil},1/2}$	

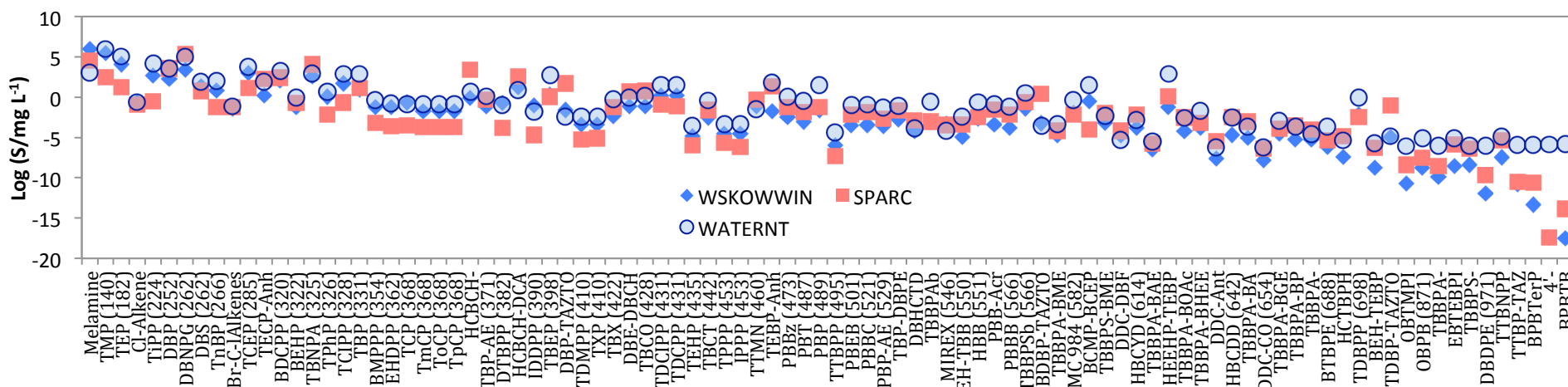
	EPI Suite	EPI Suite	Literature	PBT profiler	EPI Suite	CATALOGIC	EPI Suite	CATALOGIC
MC 984	3			4320	336	1464	87600	24600
MIREX	4320			4320	87600	792	87600	31896
OBPB	7			4320	4320	1032	87600	76512
OBTMPI	75			4320	87600	792	87600	87600
PBB-Acr	12	23563		4320	1080	19	87600	2112
PBBB	447			4320	1080	3	87600	3216
PBBC	337			4320	4320	3	87600	3216
PBBz	3212			4320	1080	1032	87600	49920
PBEB	112			4320	1080	792	87600	50184
PBP	285			4320	1080	1224	87600	25248
PBP-AE	4			4320	1080	840	87600	20328
PBT	694			4320	1080	744	87600	52200
TBBPAb	43			4320	1080	288	87600	6288
TBBPA-BA	6	4596			1080	9	87600	2160
TBBPA-BAE	2			4320	1080	26	87600	12312
TBBPA-BDBPE	12			4320	4320	288	87600	18456
TBBPA-BGE	7	1.1E+06*		4320	1080	12	87600	3288
TBBPA-BHEE	5			4320	1080	12	87600	2160
TBBPA-BHEEBA	3	18113		4320	336	8	87600	1776
TBBPA-BME	26			4320	1080	5	87600	2664
TBBPA-BOAc	44	928			1080	4	87600	1752
TBBPA-BP	34	1099			1080	4	87600	1176
TBBPSb	253			4320	1080	1560	87600	11136
TBBPS-BDBPE	17			4320	4320	3936	87600	63120
TBBPS-BME	66			4320	1080	5	87600	2160
TBCO	38	1.6E+10*		912	168	1152	1080	87600
TBCT	673			4320	1080	912	87600	47520
TBEP	1		704	208.8	12	816	168	6264
TBNPA	25			912	168	2	1080	5568
TBP	270			1440	336	1968	4320	28200
TBP-AE	4			1440	336	960	4320	21096
TBP-DBPE	32			4320	336	1440	87600	51912
	t <sub>air, 1/2</sub>	t <sub>wat, 1/2</sub>	t <sub>wat, 1/2</sub>	t <sub>wat, 1/2</sub>	Primary t <sub>soil, 1/2</sub>		Ultimate t <sub>soil, 1/2</sub>	
	EPI Suite	EPI Suite	Literature	PBT	EPI Suite	CATALOGIC	EPI Suite	CATALOGIC

	profiler							
TBX	270			4320	1080	1344	87600	65040
TCEP	6		2904	1440	168	1464	4320	44304
TCIPP	3		5100	1440	168	1464	4320	15168
TCP	9		906	912	168	10	1080	13.677
TDBPP	5		1440	1440	168	2	4320	6192
TDBP-TAZTO	20			1440	336	1464	4320	21840
TDCIPP	7		3600	4320	336	480	87600	8112
TDCPP	6		4320	4320	336	1464	87600	16848
TDMPP	2			912	168	1464	4320	21840
TEBP-Anh	5263			4320	1080	9	87600	20.913
TECP-Anh	4061			4320	336	2	87600	6192
TEHP	1		272	208.8	12	1464	168	12072
TiPP	1		360	360	48	1464	336	10248
TmCP	9		906	912	168	10	1080	14
TMP	15		360	360	48	1464	336	7224
TnBP	2		208	208.8	12	1464	168	7200
ToCP	4		906	912	168	10	1080	11
TpCP	9		906	912	168	10	1080	14
TPhP	12		678	912	48	10	1080	13
TPPP	6			912	168	25	4320	5016
TTBNPP	2		4320		1080	1464	87600	51432
TTBPP	9			4320	336	576	87600	71472
TTBP-TAZ	87			4320	87600	1632	87600	87600
TTMN	20			912	336	1224	4320	72384
TEP	2		360	360	48	2760	336	7224
TXP	3			1440	168	220	4320	720
BMPPP	10			912	168	234	1080	326
DBDP	8			912	168	1080	1080	8304
Br-Cl-Alkene	4			912	168	2424	1080	9192
Cl-Alkene	1			912	168	388	1080	1080
PIP	4			1440	168	558	4320	28512
Melamine	195			912	168	121	1080	1176

\*Compounds with high HYDROWIN estimates, that were assessed separately

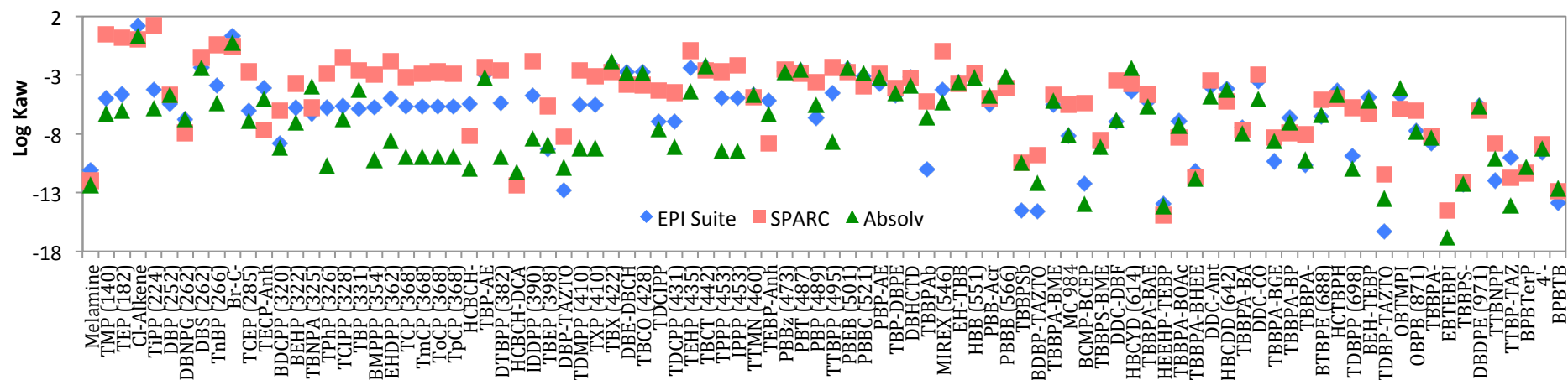


**Figure S7.** Estimated  $P_l$  of NFRs, listed by increasing molecular weight. EPI Suite estimates are represented by the blue diamonds and SPARC's by the red squares.

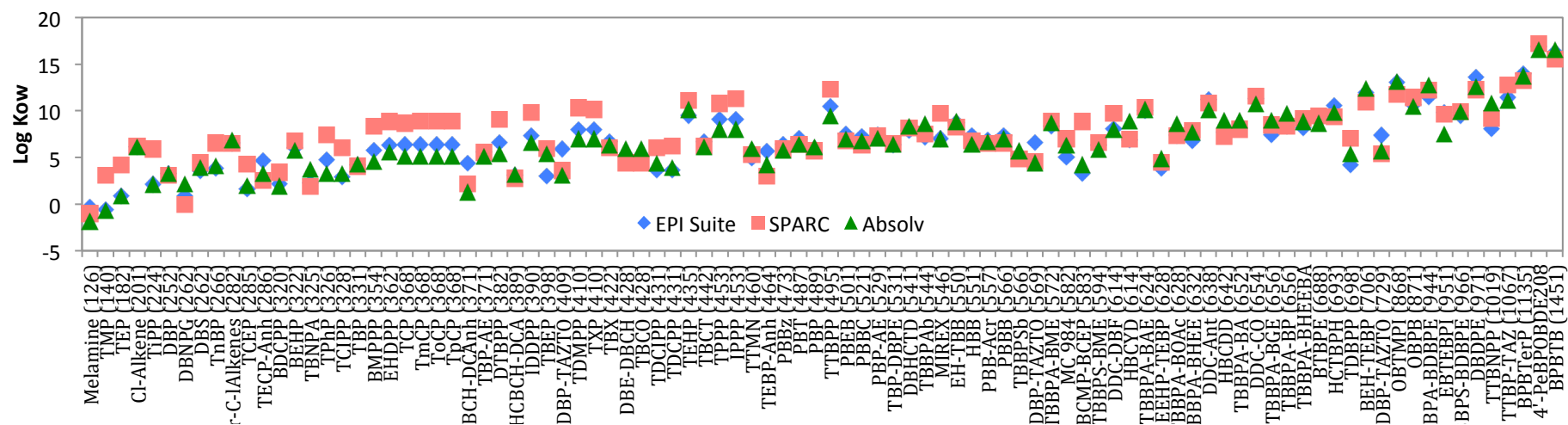


**Figure S8.** Estimated  $S_l$  of NFRs, listed by increasing molecular weight. EPI Suite SKOW estimates are represented by the blue diamonds, EPI Suite Fragment estimates by the blue circles, and SPARC's by the red squares.



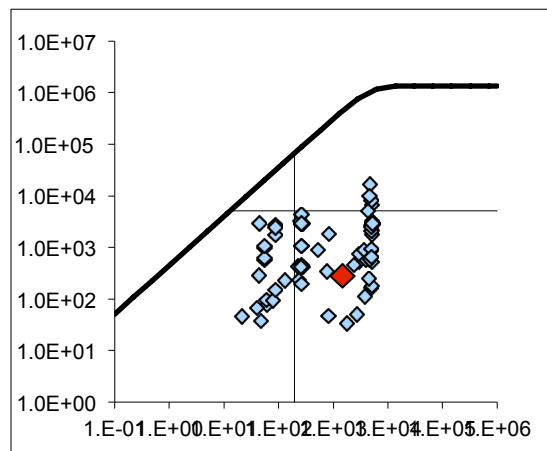


**Figure S9.** Estimated log  $K_{AW}$  of NFRs, listed by increasing molecular weight (g/mol). EPI Suite estimates are represented by the blue diamonds, SPARC's by the red squares, and Absolv's by the green triangles.

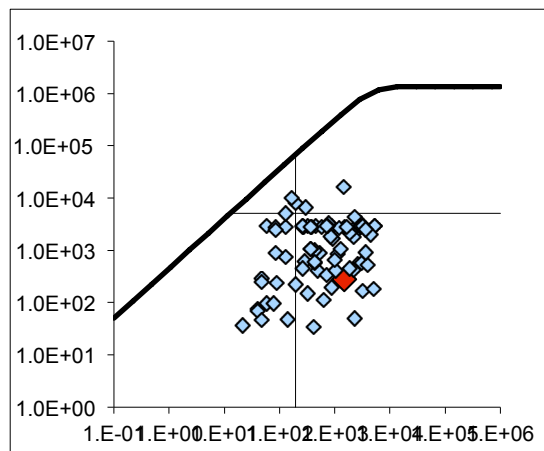


**Figure S10.** Estimated log K<sub>ow</sub> of NFRs, listed by increasing molecular weight (g/mol). EPI Suite estimates are represented by the blue diamonds, SPARC's by the red squares, and Absolv's by the green triangles.

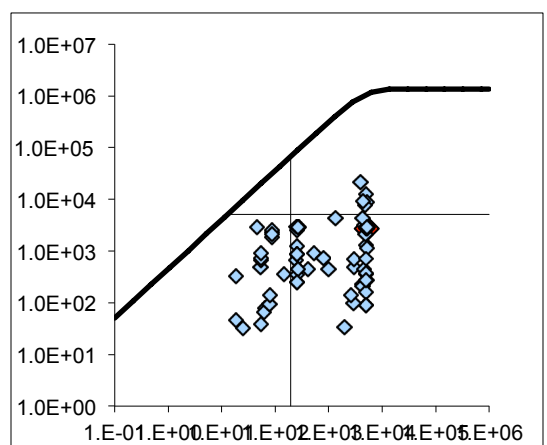
a. Run 1:



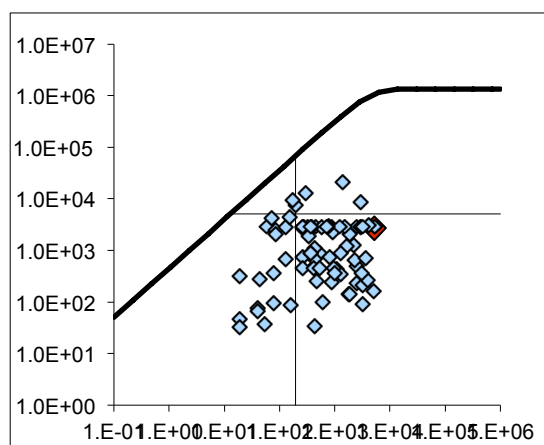
d. Run 4:



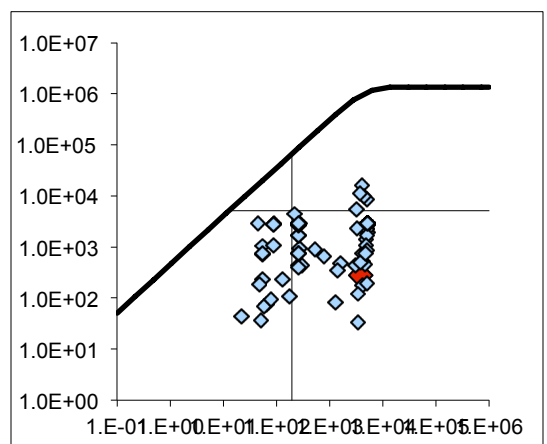
b. Run 2:



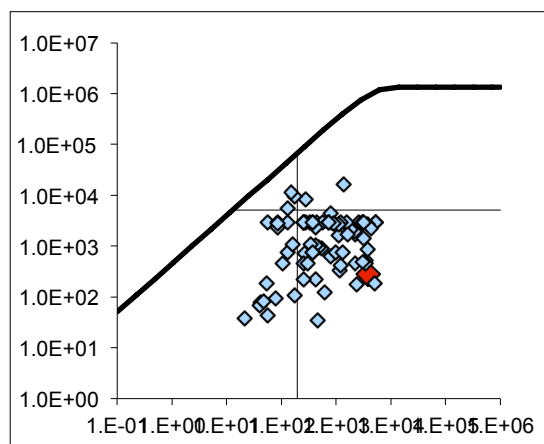
e. Run 5:



c. Run 3:

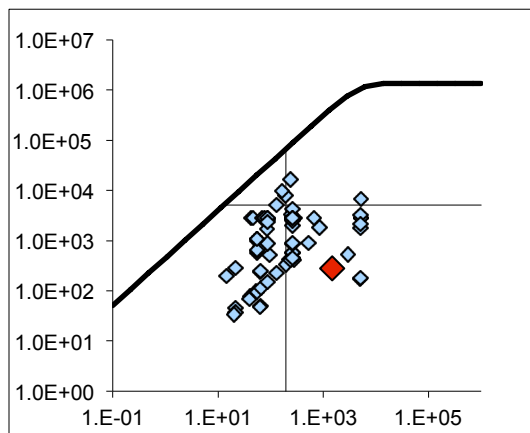


f. Run 6:

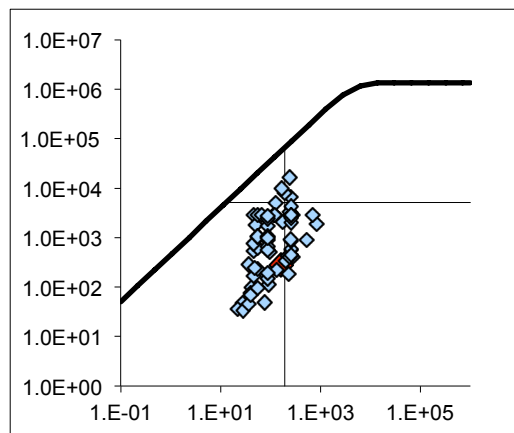


**Figure S11.** Output from  $P_{OV}$  (x axis, days) and LRTP (y axis, km) Screening Tool (Run 1-6). Model run with:  $K_{AW}$  and  $K_{OW}$  from EPI Suite (first row), SPARC (second row), and Absolv (third row) and ultimate  $t_{soil,1/2}$  from EPI Suite (a, b, c) and CATALOGIC (d, e, f).

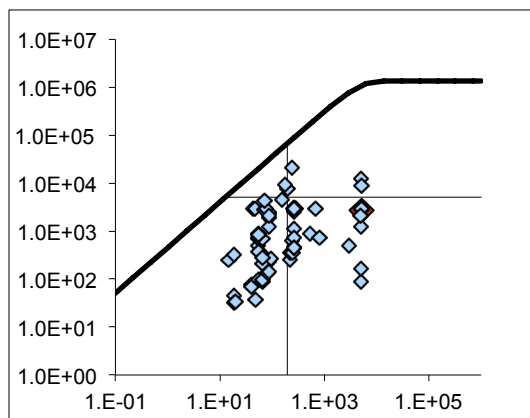
a. Run 7:



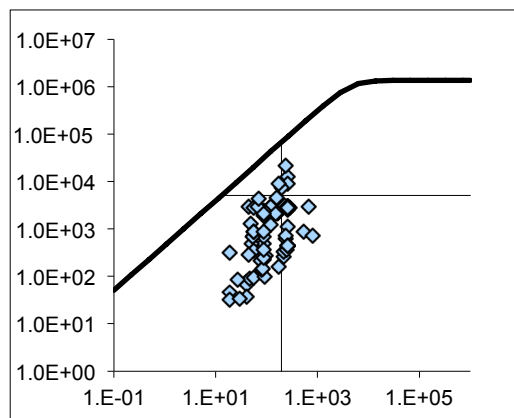
d. Run 10:



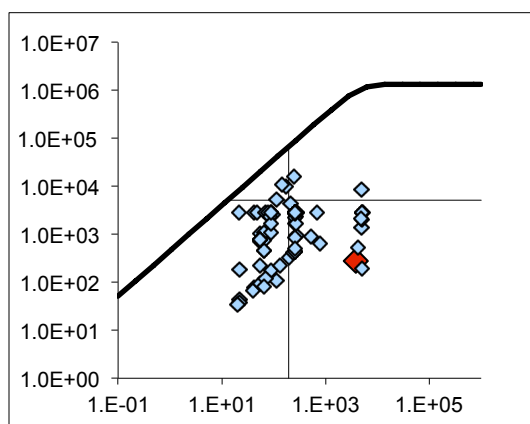
b. Run 8:



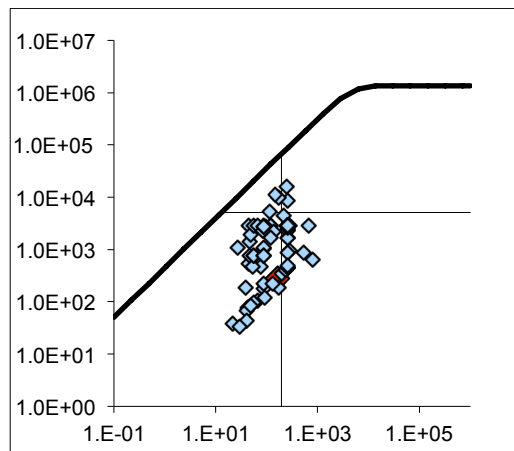
e. Run 11:



c. Run 9:

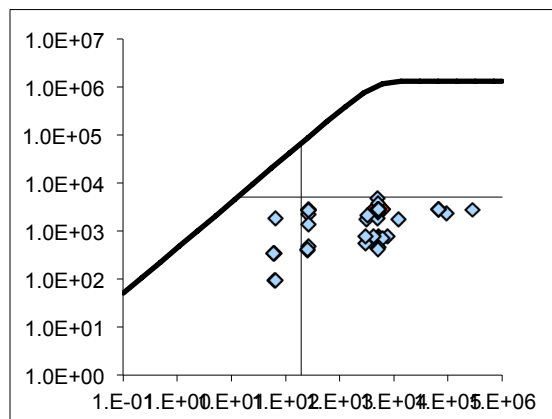


f. Run 12:

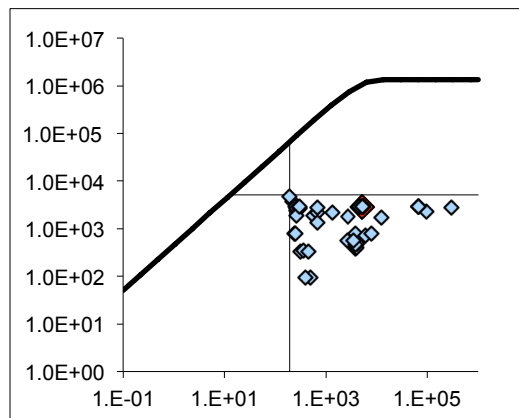


**Figure S12.** Output from  $P_{OV}$  (x axis, days) and LRTP (y axis, km) Screening Tool (Run 7-12). Model run with:  $K_{AW}$  and  $K_{OW}$  from EPI Suite (first row), SPARC (second row), and Absolv (third row) and primary  $t_{soil,1/2}$  from EPI Suite (a, b, c) and CATALOGIC (d, e, f).

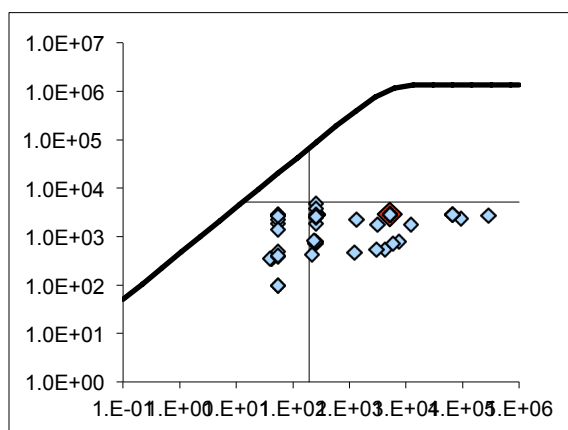
a. Run 13:



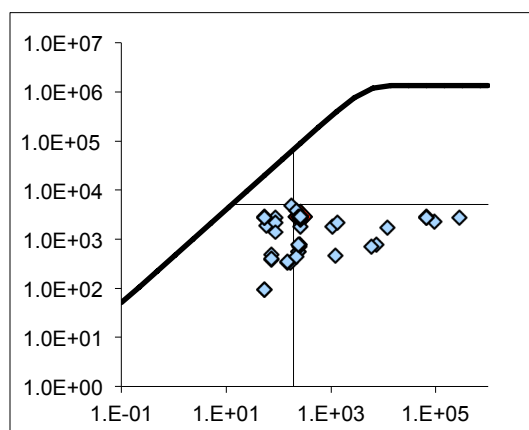
c. Run 15:



b. Run 14:



d. Run 16:



**Figure S13.** Output from  $P_{OV}$  (x axis, days) and LRTP (y axis, km) Screening Tool (Run 13-16). Model run for compounds with high  $t_{water,1/2}$  estimates from HYDROWIN or estimated  $t_{water,1/2}$  from compounds with similar properties. Ultimate  $t_{soil,1/2}$  (first row) and primary  $t_{soil,1/2}$  (second row) from EPI Suite (a, b) and CATALOGIC (c,d).

## REFERENCES

- Abraham, M.H., 1993. Scales of solute hydrogen-bonding: Their construction and application to physicochemical and biochemical processes. *Chemical Society Reviews* 22, 73-83.
- ACD/Labs, 2013. ACD/Absolv. Advanced Chemistry Development, Toronto, Canada.  
<http://www.acdlabs.com/>
- Aronson, D., Boethling, R., Howard, P., Stiteler, W., 2006. Estimating biodegradation half-lives for use in chemical screening. *Chemosphere* 63, 1953-1960.
- Atkinson, R., 1988. Estimation of gas-phase hydroxyl radical rate constants for organic chemicals. *Environmental Toxicology & Chemistry* 7, 435-442.
- Bamford, H.A., Poster, D.L., Baker, J.E., 1999. Temperature dependence of Henry's law constants of thirteen polycyclic aromatic hydrocarbons between 4 degrees C and 31 degrees C. *Environmental Toxicology & Chemistry* 18, 1905-1912.
- Bergman, A., Ryden, A., Law, R.J., de Boer, J., Covaci, A., Alaee, M., Birnbaum, L., Petreas, M., Rose, M., Sakai, S., Van den Eede, N., van der Veen, I., 2012. A novel abbreviation standard for organobromine, organochlorine and organophosphorus flame retardants and some characteristics of the chemicals. *Environment International* 49, 57-82.
- Biomonitoring California, 2012. Materials for: March 16, 2012 Meeting of Scientific Guidance Panel (SGP). Non-halogenated Aromatic Phosphates.  
<http://oehha.ca.gov/multimedia/biomon/pdf/031612NhArP.pdf>; accessed 10.08.2015
- Boethling, R.S., Howard, P.H., Meylan, W., Stiteler, W., Beauman, J., Tirado, N., 1994. Group-contribution method for predicting probability and rate of aerobic biodegradation. *Environmental Science & Technology* 28, 459-465.
- Boethling, R., Fenner, K., Howard, P., Klecka, G., Madsen, T., Snape, J.R., Whelan, M.J., 2009. Environmental persistence of organic pollutants: Guidance for development and review of POP risk profiles. *Integrated Environmental Assessment & Management* 5, 539-556.
- Brommer, S., Jantunen, L.M., Bidleman, T.F., Harrad, S., Diamond, M.L., 2014. Determination of vapor pressures for organophosphate esters. *Journal of Chemical & Engineering Data* 59, 1441-1447.
- Cetin, B., Odabasi, M., 2005. Measurement of Henry's law constants of seven polybrominated diphenyl ether (PBDE) congeners as a function of temperature. *Atmospheric Environment* 39, 5273-5280.

Braekevelt, E., Tittlemier, S.A., Tomy, G.T., 2003. Direct measurement of octanol-water partition coefficients of some environmentally relevant brominated diphenyl ether congeners. *Chemosphere* 51, 563-567.

Dimitrov, S., Pavlov, T., Dimitrova, N., Georgieva, D., Nedelcheva, D., Kesova, A., Vasilev, R., Mekenyan, O., 2011. Simulation of chemical metabolism for fate and hazard assessment. II CATALOGIC simulation of abiotic and microbial degradation. SAR and QSAR in *Environmental Research* 22, 719-755.

European Communities (EC), 2009. European Union Risk Assessment Report, TRIS (2-CHLOROETHYL) PHOSPHATE, TCEP; <http://echa.europa.eu/documents/10162/2663989d-1795-44a1-8f50-153a81133258>

Goss, K.-U., 2005. Predicting the equilibrium partitioning of organic compounds using just one linear solvation energy relationship (LSER). *Fluid Phase Equilibria* 233, 19-22.

Harner, T., Shoeib, M., 2002. Measurements of octanol-air partition coefficients ( $K_{oa}$ ) for polybrominated diphenyl ethers (PBDEs): Predicting partitioning in the environment. *Journal of Chemical & Engineering Data* 47, 228-232.

Hilal, S.H., Saravanaraj, A.N., Whiteside, T., Carreira, L.A., 2007. Calculating physical properties of organic compounds for environmental modeling from molecular structure. *Journal of Computer-Aided Molecular Design* 21, 693-708.

Hine, J., Mookerjee, P.K., 1975. Structural effects on rates and equilibria. XIX. Intrinsic hydrophilic character of organic compounds. Correlations in terms of structural contributions. *The Journal of Organic Chemistry* 40, 292-298.

Jenner, K.J., Kreutzer, G., Racine, P., 2011. Persistency assessment and aerobic biodegradation of selected cyclic sesquiterpenes present in essential oils. *Environmental Toxicology & Chemistry* 30, 1096-1108.

Li, N.Q., Wania, F., Lei, Y.D., Daly, G.L., 2003. A comprehensive and critical compilation, evaluation, and selection of physical-chemical property data for selected polychlorinated biphenyls. *Journal of Physical & Chemical Reference Data* 32, 1545-1590.

Lyman, W.J., 1985. Estimation of physical properties. Chapter 2. In: *Environmental exposure from chemicals*. Volume I., Neely, W.B., Blau, G.E. (Eds.). CRC Press, Inc., Boca Raton, USA.

Mackay, D., Shiu, W.-Y., Ma, K.-C., Lee, S.C., 2006. *Handbook of physical-chemical properties and environmental fate for organic chemicals*. CRC Press, Inc., Boca Raton, USA

May, W.E., Wasik, S.P., Freeman, D.H., 1978. Determination of the solubility behavior of some polycyclic aromatic hydrocarbons in water. *Analytical Chemistry* 50, 997-1000.

- Meylan, W.M., Howard, P.H., 1991. Bond contribution method for estimated Henry's law constants. *Environmental Toxicology & Chemistry* 10, 1283-1293.
- Meylan, W.M., Howard, P.H., 1993. Computer estimation of the atmospheric gas-phase reaction-rate of organic-compounds with hydroxyl radicals and ozone. *Chemosphere* 26, 2293-2299.
- Meylan, W.M., Howard, P.H., 1995. Atom fragment contribution method for estimating octanol-water partition-coefficients. *Journal of Pharmaceutical Sciences* 84, 83-92.
- Meylan, W.M., Howard, P.H., Boethling, R.S., 1996. Improved method for estimating water solubility from octanol water partition coefficient. *Environmental Toxicology & Chemistry* 15, 100-106.
- Mill, T., Haag, W., Penwell, P., Pettit, T., Johnson, H., 1987. Environmental fate and exposure studies development of a PC-SAR for hydrolysis: Esters, alkyl halides and epoxides. SRI International, Menlo Park, USA.
- Muir, D.C.G., 1984. Phosphate esters. In: Hutzinger O, ed. *Anthropogenic compounds. The handbook of environmental chemistry 3C*. Germany, Berlin: Springer-Verlag. pp. 41-66
- Odabasi, M., Cetin, E., Sofuoglu, A., 2006. Determination of octanol-air partition coefficients and supercooled liquid vapor pressures of PAHs as a function of temperature: Application to gas-particle partitioning in an urban atmosphere. *Atmospheric Environment* 40, 6615-6625.
- OEHHA, 2008. Proposal 65 Safe Harbor Levels Development. In: Office of Environmental Health and Hazard Assessment, C.E.P.A. (Ed.), Sacramento, USA.
- Sangster, J., 1989. Octanol-water partition coefficients of simple organic compounds. *Journal of Physical & Chemical Reference Data* 18, 1111-1229.
- Scheringer, M., Jones, K.C., Matthies, M., Simonich, S., van de Meent, D., 2009. Multimedia partitioning, overall persistence, and long-range transport potential in the contexts of POPs and PBT chemical assessments. *Integrated Environmental Assessment & Management* 5, 557-576.
- Shen, L., Wania, F., 2005. Compilation, evaluation, and selection of physical-chemical property data for organochlorine pesticides. *Journal of Chemical & Engineering Data* 50, 742-768.
- Stapleton, H.M., Klosterhaus, S., Eagle, S., Fuh, J., Meeker, J.D., Blum, A., Webster, T.F., 2009. Detection of organophosphate flame retardants in furniture foam and U.S. house dust. *Environmental Science & Technology* 43, 7490-7495.
- Stenzel, A., Goss, K.-U., Endo, S., 2013. Determination of polyparameter linear free energy relationship (pp-LFER) substance descriptors for established and alternative flame retardants. *Environmental Science & Technology* 47, 1399-1406.



Tittlemier, S.A., Halldorson, T., Stern, G.A., Tomy, G.T., 2002. Vapor pressures, aqueous solubilities, and Henry's law constants of some brominated flame retardants. *Environmental Toxicology & Chemistry* 21, 1804-1810.

UK Environment Agency (UK EA, 2009a). Environmental risk evaluation report: 2-Ethylhexyl diphenyl phosphate (CAS No. 1241-94-7). Environment Agency. United Kingdom. Available at: <http://publications.environmentagency.gov.uk/PDF/SCHO0809BQTY-E-E.pdf>

UK Environment Agency (UK EA 2009b). Environmental risk evaluation report: Isodecyl diphenyl phosphate (CAS no. 29761-21-5). Environment Agency. United Kingdom. Available at: <http://publications.environmentagency.gov.uk/PDF/SCHO0809BQUF-EE.pdf>

UK Environment Agency (UK EA 2009c). Environmental risk evaluation report: Tricresyl phosphate (CAS no. 1330-78-5). Environment Agency. United Kingdom. Available at: <http://publications.environment-agency.gov.uk/PDF/SCHO0809BQUJ-E-E.pdf>

UK Environment Agency (UK EA, 2009d). Environmental risk evaluation report: Tetraphenyl resorcinol diphosphate (CAS nos. 57583-54-7). Environment Agency. United Kingdom. Available at: <http://publications.environmentagency.gov.uk/PDF/SCHO0809BQUL-E-E.pdf>

USEPA, 2013. (EPI Suite) Estimation Programs Interface Suite. United States Environmental Protection Agency, Washington, D.C., USA.  
<http://www.epa.gov/oppt/exposure/pubs/episuite.htm>. Last updated 2013-1-15.

Wegmann, F., Cavin, L., MacLeod, M., Scheringer, M., Hungerbuhler, K., 2009. The OECD software tool for screening chemicals for persistence and long-range transport potential. *Environmental Modelling Software* 24, 228-237.

World Health Organization Geneva (WHO), 2000. Flame retardants: tris(2-butoxyethyl) phosphate, tris(2-ethylhexyl) phosphate and tetrakis(hydroxymethyl) phosphonium salts. *Environmental Health Criteria* 218,  
[http://apps.who.int/iris/bitstream/10665/42248/1/WHO\\_EHC\\_218.pdf](http://apps.who.int/iris/bitstream/10665/42248/1/WHO_EHC_218.pdf)