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Estimation of physicochemical properties of 52 non-PBDE brominated flame retardants and evaluation of their overall persistence and long-range transport potential

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HIGHLIGHTS

- First estimation of physicochemical properties of 52 non-PBDE BFRs using two methods
- Evaluation of estimation performance of both methods by comparing with measured values
- First estimation of overall persistence and long-range transport potential (LRTP) of 52 non-PBDE BFRs
- Selection of POP-like non-PBDE BFRs on the basis of the persistence and LRTP
- Priority in properties of the selected POP-like BFRs to be measured in the future

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ABSTRACT

Non-PBDE (polybromodiphenyl ether) brominated flame retardants (BFRs) used as alternatives to PBDEs should be evaluated in terms of their environmental contamination potential. We first used two well-known estimation tools, EPI Suite and SPARC, to estimate the physicochemical properties of 52 non-PBDE BFRs. We assessed the dependence of the properties on the molecular weight and chemical structure of the compounds. The accuracy of the estimates was evaluated by comparing results with previous experimental data. In the case of EPI Suite, we have recommended an appropriate calculation method for the air–water partition coefficient. Half-lives in each environmental medium were also estimated with EPI Suite. Based on the estimated properties and half-lives, the overall persistence (P_{ov}) and long-range transport potential (LRTP) of the BFRs were calculated using the Organization for Economic Cooperation and Development P_{ov} and LRTP Screening Tool. We selected some POP-like chemicals from among the non-PBDE BFRs on the basis of their P_{ov} and LRTP. From a Monte Carlo analysis of the calculated results for the selected BFRs, we suggest physicochemical properties to be measured in the future.

1. Introduction

Some polybromodiphenyl ethers (PBDEs), such as commercial pentabromodiphenyl ether and octabromodiphenyl ether, were listed as persistent organic pollutants (POPs) in the Stockholm Convention in May 2009 (http://chm.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx). In addition, decabromodiphenyl ether (BDE-209) has been phased out of electric and electronic equipment in the EU since 1 July 2008 (European Court of Justice, 2008). Similarly, in the United States, BDE-209 will be phased out for most uses by 2013 (Hess, 2010). Research and development of non-PBDE flame retardants as alternatives to PBDEs has therefore received increasing attention. Other brominated flame retardants (BFRs), namely non-PBDE BFRs, have been used as alternatives to PBDEs. There are more than 50 non-BFRs, classified in some cases as "novel BFRs," "emerging BFRs," etc., as discussed by Bergman et al. (2012). The commercial use, volume of production, and physicochemical properties of selected non-PBDE BFRs have been reviewed by de Wit et al. (2010) and Covaci et al. (2011). Unfortunately, environmental contaminations caused by novel and emerging BFRs have been observed, as reported by various research groups (de Wit et al., 2010; Covaci et al., 2011; Yang et al., 2012; Nyholm et al., 2013; etc). Understanding the environmental fate and mechanism of contamination of

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non-PBDEs requires knowledge of their physicochemical properties, such as vapor pressure (p_i), water solubility (S_w), and 1-octanol–water partition coefficient (K_{ow}). Even if such data are available, most of the values are estimates. Moreover, not all properties are available. In other words, there are few experimental data on the properties of non-PBDE BFRs. In our previous work (Kuramochi et al., 2004a, 2004b, 2007, 2008), we have measured the properties of some novel BFRs as well as conventional BFRs. However, it is very time consuming to measure the properties of all emerging BFRs and novel BFRs. We should therefore know the approximate value of each property and then select some of the BFRs to be the foci of studies concerned with environmental contamination issues such as persistence and long-range transport. In addition, we should determine which of the physicochemical properties of the selected BFRs should be given priority.

In this work, we used EPI Suite (http://www.epa.gov/opptintr/exposure/pubs/episuite.htm) and SPARC (http://www.archemcalc.com/sparc.html) to estimate the physicochemical properties of 52 non-PBDE BFRs. We discuss the estimates in terms of the properties and partitioning characteristics of the compounds as well as their estimated performance. Furthermore, we used EPI Suite to estimate the degradation half-lives of the compounds in each environmental medium. From the combination of estimated properties and half-lives, the overall persistence (P_{ov}) and long-range transport potential (LRTP) of all the BFRs were calculated with the Organization for Economic Cooperation and Development (OECD) P_{ov} and LRTP Screening Tool (http://www.oecd.org/document/24/0,3746,en_2649_34379_45373336_1_1_1_1,00.htm; Wegmann et al., 2009). Some compounds were selected as POP-like BFRs on the basis of their high persistence and LRTP. Finally, we used a Monte Carlo analysis of the calculated results to propose the physicochemical properties of selected BFRs to be measured.

2. Methods

2.1. Chemicals

In this study, we selected 52 non-PBDE BFRs (Table 1) from previous work on non-PBDE BFRs (Bergman et al., 2012). Previous studies (Kuramochi et al., 2004a, 2008, and submitted) have reported some properties of five compounds: 2,4-dibromophenol (DBP), 2,4,6-tribromophenol (TBP), hexabromobenzene (HBB), tetrabromobisphenol A (TBBPA), and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE).

Moreover, we calculated the properties of some PBDEs and brominated chemicals similar to the non-PBDE BFRs and then compared those calculated properties with the measured properties (Kuramochi et al., 2004a, 2004b, 2008; Howard and Meylan, 1997; Fu and Suuberg, 2011) to evaluate the accuracy of the physicochemical properties estimated with the two calculation tools (Table 2).

2.2. Estimation of physicochemical properties

The physicochemical properties calculated in this study included vapor pressure (p_i), water solubility (S_w), the 1-octanol–water partition coefficient (K_{ow}), and the air–water partition coefficient (K_{aw}), which is a dimensionless form of Henry's Law constant. The last two partition coefficients, in particular, are required for the evaluation of overall persistence and long-range transport potential (vide infra). We used SPARC (release w4.6.1691–s4.6.1687) or EPI Suite (version 4.11) as the estimation tool, because the tools were freely available, and validated or reviewed by U.S.-EPA (e.g. Hilal et al., 2003; USEPA SAB, 2007). Unfortunately, the former is just now not open-accessed. For both tools, the CAS number of a chemical, or its SMILES code, which is a well-known line notation of a compound, is required as input. The principles of estimation differ between the tools. SPARC is based on linear free energy relationships. Since SPARC does not estimate K_{aw} with software specific for K_{aw} estimation, the K_{aw} value is derived from the following equation:

$$K_{aw} = p_i/(S_w RT) \quad (1)$$

EPI Suite is composed of various calculation tools. p_i, K_{ow}, and S_w are calculated by the modified Grain method, KOWWIN (version 1.68), and WSKOW (version 1.41), respectively. EPI Suite provides two estimates of K_{aw}, one obtained with built-in software (HENRYWIN version 3.20) for K_{aw} estimation, and the other with Eq. (1). In the calculation with HENRYWIN, the bond contribution method or the contribution group method must be selected. In the present calculation, the group method was preferentially used according to early evaluation (Dearden and Schüürmann, 2003). To suggest a more appropriate tool for estimating physicochemical properties, we calculated the deviation between measured values and the values estimated with each tool.

2.3. Estimation of half-lives in the environment

Half-lives in each environmental medium ($t_{air,\ 1/2}$, $t_{water,\ 1/2}$, and $t_{soil,\ 1/2}$) were also required for the estimation of P_{ov} and LRTP. Unfortunately, SPARC cannot provide such parameters, and thus all half-lives were calculated with EPI Suite. In estimating half-lives, EPI Suite equated the $t_{air,\ 1/2}$ value to the half-life of the hydroxyl radical reaction, whereas $t_{water,\ 1/2}$ and $t_{soil,\ 1/2}$ were calculated according to a correction table of biodegradation BIOWIN3 score estimated by EPI Suite (Aronson et al., 2006) and the assumption $2 \cdot t_{water,\ 1/2}$ (Fenner et al., 2005), respectively.

2.4. Estimation of P_{ov} and LRTP

Given the two estimated partition coefficients and three half-lives, the OECD P_{ov} and LRTP Screening Tool (version 2.2, freely downloadable) calculated the P_{ov} (days) and LRTP of a chemical. The tool provided two kinds of LRTPs as output: a characteristic travel distance (CTD) in kilometers and a transfer efficiency (TE) as a percent value. The P_{ov} is a measure of time scale for degradation of the chemical in the environment. The CTD is the distance from the source point to the point at which the concentration of the chemical is 37% of the concentration at the source. The TE is equated to the ratio of the flux (deposition) onto a target region to the flux (emission) from the source region. Non-PBDE BFRs with high P_{ov} and LRTP values were extracted and identified as POP-like BFRs by comparing their P_{ov} and LRTP values with the analogous values of some POP-PBDEs and the reference lines indicating POP-like (Klasmeier et al., 2006). The tool can use a Monte Carlo analysis to propagate uncertainty of the input parameters to uncertainty of the estimated results. For the selected POP-like non-PBDEs, the effect of individual physicochemical properties on the output was investigated in this way. We consider that influential parameters should be measured in the future.

3. Results and discussion

The estimated physicochemical properties are summarized in Table 1. Even though all properties are estimates, this is the first time that such a complete data table is provided. Figs. 1–4 show plots of individual properties estimated by both tools, with the compounds sorted on the basis of molecular weight. With the exception of K_{aw}, the properties were normally affected by molecular weight. The values of p_i and S_w decreased with an increase in molecular weight (Figs. 1 and 2). It should be noted that BFRs with an OH group or N have much lower p_i and higher S_w values. This pattern indicates that the partitioning potential from water to air of such chemicals is quite low. In contrast, K_{ow} increased at higher molecular weights. Most of the BFRs with molecular weights higher than 470 g/mol had log K_{ow} values greater than 5 (Fig. 3) and thus may be bioaccumulative.