Science of the Total Environment 524–525 (2015) 416–426

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Physical–chemical properties and evaluative fate modelling of 'emerging' and 'novel' brominated and organophosphorus flame retardants in the indoor and outdoor environment

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HIGHLIGHTS

- 'Best-estimates' of physical–chemical properties of alternative FRs are proposed.
- The 'SMURF' model and the OECD 'The Tool' are used to estimate the environmental fate.
- Many alternative BFRs and HOPFRs have similar environmental fate to PBDEs.
- Among alternative FRs, certain low MW NHOPFRs are the least persistent.
- Needs for experimental data for model evaluation are highlighted.

ARTICLE INFO

Article history:
Received 9 October 2014
Received in revised form 31 January 2015
Accepted 24 February 2015
Available online xxxx

Editor: Adrian Covaci

Keywords:
BFRs
OPFRs
Indoor fate
Persistence
Physical–chemical properties

ABSTRACT

Several groups of flame retardants (FRs) have entered the market in recent years as replacements for polybrominated diphenyl ethers (PBDEs), but little is known about their physical–chemical properties or their environmental transport and fate. Here we make best estimates of the physical–chemical properties and undertake evaluative modelling assessments (indoors and outdoors) for 35 so-called 'novel' and 'emerging' brominated flame retardants (BFRs) and 22 organophosphorus flame retardants (OPFRs). A QSPR (Quantitative Structure-Property Relationship) based technique is used to reduce uncertainty in physical–chemical properties and to aid property selection for modelling, but it is evident that more, high quality property data are required for improving future assessments. Evaluative modelling results show that many of the alternative FRs, mainly alternative BFRs and some of the halogenated OPFRs, behave similarly to the PBDEs both indoors and outdoors. These alternative FRs exhibit high overall persistence (P_{ov}), long-range transport potential (LRTP) and POP-like behaviour and on that basis cannot be regarded as suitable replacements to PBDEs. A group of low molecular weight alternative BFRs and non-halogenated OPFRs show a potentially better environmental performance based on P_{ov} and LRTP metrics. Results must be interpreted with caution though since there are significant uncertainties and limited data to allow for thorough model evaluation. Additional environmental parameters such as toxicity and bioaccumulative potential as well as functionality issues should be considered in an industrial substitution strategy.

1. Introduction

Modern life is linked with extensive use of chemicals in a wide range of applications. Flame retardants (FRs) constitute a broad and diverse group of such chemicals, the use of which saw a dramatic increase in the last two decades (Alaee et al., 2003; Covaci et al., 2011). During these years certain well-known brominated flame retardants (BFRs), the polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs) and tetrabromobisphenol A (TBBPA) were used widely resulting in their ubiquitous presence as contaminants in the environment (de Wit, 2002; Law et al., 2006). These BFRs, commonly referred to as 'established' BFRs, have been the subject of detailed risk assessment studies, which in turn have contributed towards the implementation of regional and international regulations on their use (BSEF, 2014).

Following the phase-out, restrictions and tight regulations on the production and use of PBDEs and more recently HBCDs, several alternate classes of FRs have been introduced or proposed as replacements. These include the 'novel' and 'emerging' BFRs (herein collectively referred to as 'alternative' BFRs), organophosphorus flame retardants

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http://dx.doi.org/10.1016/j.scitotenv.2015.02.106
0048-9697/

(OPFRs), as well as a number of inorganic FRs. Many of these chemicals have already been marketed for years not solely as FRs but for other uses as well (Covaci et al., 2011; van der Veen and de Boer, 2012). A key question that arises is; do these alternatives pose a lower risk to the environment than those they replace? As an example, using a "read across" assessment, one could argue that the environmental behaviour of decabromodiphenyl ethane (DBDPE), marketed as an alternative to decabromodiphenyl ether (DecaBDE) (Kierkegaard et al., 2004), will not be different than for DecaBDE given their structural similarities. Over the past few years an increasing number of studies, reviews and assessment reports on alternative FRs (e.g. see the following recent literature reviews by Covaci et al. (2011); van der Veen and de Boer (2012) and Waaijers et al. (2013)) is indicative of the growing research focus and regulatory interest in these chemicals. Although the information on the production volumes, use patterns and emissions as well as the environmental fate and toxicity profiles of most of the alternative FRs is often described as limited or inconclusive, there are worrying initial indications that some of them exhibit PBTL (persistence, bioaccumulation, toxicity and long-range transport) characteristics (de Wit et al., 2010; EFSA, 2012; Moller et al., 2012).

In this study we perform an evaluative modelling assessment of the likely indoor and outdoor fate of a large number of alternative brominated and organophosphorus FRs and benchmark the fate of alternatives against the relatively well-studied PBDEs. Special focus is given to the indoor environment which is less well studied despite its significance for human exposure to FRs (Jones-Otazo et al., 2005) and its role as a potential source to outdoors (Björklund et al., 2012). Two multimedia fate models are employed to assess the fate of the alternative BFRs and OPFRs in evaluative indoor and outdoor environments. Environmental fate is assessed in terms of the chemical distribution, persistence/residence time and long-range transport potential. The main goal of this study is to evaluate the environmental performance of the alternative FRs. Comparison with PBDEs will help to identify those alternatives that would potentially constitute favourable replacements. Furthermore, we aim to assess the influence of physicochemical properties of the selected FRs on their fate in the environment and the potential implications the latter has for human exposure in the indoor environment.

2. Selected FRs

A total of 67 FRs (see Table S1 in the Supplementary data) were selected and assessed in this study. These are divided into two groups; BFRs (n = 45) and OPFRs (n = 22). The selected BFRs include 8 PBDEs, HBCDs, TBBPA and 35 of the so called 'novel' and 'emerging' BFRs. OPFRs are divided into 15 non-halogenated OPFRs (NHOPFRs) and seven halogenated OPFRs (HOPFRs). Inorganic alternative FRs were not assessed here because current modelling approaches are not appropriate for these substances (Waaijers et al., 2013). Names, abbreviations and CAS numbers were taken from Bergman et al. (2012) and van der Veen and de Boer (2012).

2.1. Physical–chemical properties of selected FRs

Several key physical–chemical properties determine the environmental behaviour and fate of non-ionic, organic chemicals such as the BFRs and OPFRs of this study, namely; solubility in water (S_w), vapour pressure (P_s), the air–water (K_{aw}, which is closely related to the Henry's law constant, H), the octanol–water (K_{ow}), and the octanol–air (K_{oa}) partition coefficients (Mackay, 2001; Schwarzenbach et al., 2005). Degradation rates (often expressed as overall degradation half-lives for each environmental medium of interest) determine environmental persistence and are thus also fundamental input parameters to chemical fate models.

We performed a literature screening including published experimental studies, reviews and reports, and online databases to compile a database for K_{ow} and K_{aw} (or H) (see Tables S2 and S3 in the Supplementary data). Two software estimation tools, SPARC On-Line Calculator 4.6 (Hilal et al., 2003, 2004) and EPISuite 4.1 (USEPA, 2012), were used to provide additional values for K_{ow} and K_{aw}. For the calculation of K_{aw} (H) by EPISuite, the HENRYWIN v3.20 module was used. HENRYWIN predictions for EBTEBPI, TBBPS and TDBP-TAZTO were judged to be erroneous as they were largely different (greater than a factor of 10^5) from the P_s/S_w estimates. In those cases the P_s/S_w ratio calculated by EPIWIN was used to calculate K_{aw}. K_{ow} values calculated by a third estimation tool, ACD/Labs Software, were retrieved from the literature (Bergman et al., 2012) and included as additional data entries. Degradation half-lives in air ($t_{1/2,air}$), water ($t_{1/2,water}$) and soil ($t_{1/2,soil}$) (h) were calculated exclusively by the AOPWIN v1.92a and BIOWIN v4.10 modules of the EPISuite platform.

2.1.1. Data availability and variability

Unlike the 'established' BFRs (mainly PBDEs, and to a lesser extent, TBPPA and HBCD) for which a number of experimental studies of physical–chemical properties exist, there are either few or no measured data reported for the alternative BFRs. This serious paucity of measured K_{ow} and K_{aw} values signified the importance of software estimation tools for obtaining missing data. Fig. 1 summarizes K_{ow} and K_{aw} data availability for HBCD, TBPPA and the 35 alternative BFRs of this study. Availability of experimental K_{ow} and K_{aw} data is somewhat better in the case of OPFRs (Fig. 2a and b).

The screening for relevant physical–chemical property data revealed not only a scarcity in well-reported experimental values, but occasionally also a significant variability in experimental and calculated values. In some cases, more than 3 orders of magnitude differences were observed (see Figs. 1 and 2). Discrepancies in K_{ow} are typically larger for higher molecular weight compounds (more clearly shown in Figs. 3 and S1) for which solubilities in water reach extremely low levels. An analogous trend has been demonstrated for S_w and P_s for phthalate esters (Cousins and Mackay, 2000) and K_{ow} of PBDEs (Cousins, 2013). Agreement between software estimates was generally good for BFRs (values within the same order of magnitude), which is in line with the recent findings by Kuramochi et al. (2014). For OPFRs a systematic over-prediction of both K_{ow} and K_{aw} by SPARC was observed. Overall, both the limited availability of experimental physical–chemical properties and the variability in data can be attributed to i) the extreme properties of many FRs (e.g. low solubilities or high K_{OW} values) for which methods for determination (including the analytical methods needed) exceed their performance limits and, ii) differences in calculation methods employed by the software estimation tools (Arp et al., 2010a, 2010b; Zhang et al., 2010).

3. Methods/modelling tools

3.1. Chemical fate in the indoor environment

To assess the likely fate of the BFRs and OPFRs in the indoor environment we adapted the Stockholm Multimedia URban Fate (SMURF) model (Cousins, 2012). The SMURF model is a Level III (Mackay-type) fugacity-based chemical fate model that consists of an indoor and an outdoor module originally parameterised for the municipality of Stockholm. The indoor module of the SMURF model was 'disconnected' from the outdoor one and run as a 'stand-alone' model. The indoor environment comprises indoor air (gas + particle phase), vertical (walls + ceiling) and horizontal (floor areas) surfaces. Both surface types are assumed to be covered by an organic film layer consisting of condensated and deposited gas- and particle-phase organic compounds (Butt et al., 2004). A thin layer of dust is further assumed to cover the horizontal (floor) areas. Ventilation serves as a chemical removal mechanism from the indoors. The adapted model considers a single emission-to-air scenario and the input parameters required are K_{ow}, K_{aw} and $t_{1/2,air}$. The model automatically adjusts the half-life in air based on a typical indoor concentration of OH radicals. The SMURF model assumes degradation half-lives on indoor surfaces that are proportional to the degradation half-life in air. Model output includes the