



Brominated flame retardants in the indoor environment – Comparative study of indoor contamination from three countries



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ARTICLE INFO

Article history:

Received 8 January 2016

Received in revised form 15 April 2016

Accepted 16 April 2016

Available online xxxx

Keywords:

Brominated flame retardants

Indoor

Air

Dust

Window film

ABSTRACT

Concentrations of more than 20 brominated flame retardants (FRs), including polybrominated diphenyl ethers (PBDEs) and emerging FRs, were measured in air, dust and window wipes from 63 homes in Canada, the Czech Republic and the United States in the spring and summer of 2013. Among the PBDEs, the highest concentrations were generally BDE-209 in all three matrices, followed by Penta-BDEs. Among alternative FRs, EHTBB and BEHTBP were detected at the highest concentrations. DBDPE was also a major alternative FR detected in dust and air. Bromobenzenes were detected at lower levels than PBDEs and other alternative FRs; among the bromobenzenes, HBB and PBEB were the most abundant compounds. In general, FR levels were highest in the US and lowest in the Czech Republic – a geographic trend that reflects the flame retardants' market. No statistically significant differences were detected between bedroom and living room FR concentrations in the same house ($n = 10$), suggesting that sources of FRs are widespread indoors and mixing between rooms. The concentrations of FRs in air, dust, and window film were significantly correlated, especially for PBDEs. We found a significant relationship between the concentrations in dust and window film and in the gas phase for FRs with $\log K_{OA}$ values < 14 , suggesting that equilibrium was reached for these but not compounds with $\log K_{OA}$ values > 14 . This hypothesis was confirmed by a large discrepancy between values predicted using a partitioning model and the measured values for FRs with $\log K_{OA}$ values > 14 .

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1. Introduction

Because the indoor environment is an important human exposure route for semi-volatile organic compounds (SVOCs), such as brominated flame retardants (BFRs), knowledge of their levels and partitioning between different indoor matrices is essential for evaluating their impact on human health. Most studies on BFRs in the indoor environment have focused on their presence in dust because of its putative contribution to exposure [e.g., Harrad et al. (2008b); Wilford et al. (2004)]. Although, some studies have documented air concentrations indoors (Abdallah et al., 2008; Dodson et al., 2015), significantly fewer studies have dealt with accumulation of BFRs on surfaces such as window films (Bennett et al., 2015; Butt et al., 2004; Cetin and Odabasi, 2011). Of these studies, only Bennett et al. (2015) compared indoor film concentrations with those of other indoor matrices, i.e. air and dust.

Indoor air can be sampled using passive or active techniques, and each has its advantages and disadvantages. Passive samplers are easy

to deploy and are unobtrusive, which is important in an indoor setting. These samplers do not require electricity, but they need to be deployed for several weeks, providing an integrated measurement over this time period. In comparison, active samplers are bulky and noisy, which is particularly problematic indoors. They require trained personnel to be deployed, but they can be left at the site for shorter periods. The most common passive air sampling design uses a polyurethane foam (PUF) disk enclosed in a stainless steel bowl (Shoeb and Harner, 2002). With knowledge of sampling rates, one can calculate time-integrated air concentrations for compounds mainly present in the gas phase (Bohlin et al., 2014a, 2014b; Saini et al., 2015). Recent studies have shown that these samplers can also provide reliable results for higher molecular weight compounds that are found mainly in the particulate phase (Bohlin et al., 2014a; Harner et al., 2013; Harrad and Abdallah, 2008a; Peverly et al., 2015).

Indoor dust is a complicated, heterogeneous matrix for which different sampling approaches have been used. The most common technique is to collect floor dust, although in some circumstances undisturbed settled dust on other surfaces can be used (Björklund et al., 2012; de Wit et al., 2012; Liroy et al., 2002). Comparisons between different studies

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can be confounded by differences in sampling methods, within room spatial variability, and by the presence in the room of specific products (e.g. electronics) (Harrad et al., 2009; Muenhor and Harrad, 2012). Recently, Li et al. (2015) found a strong positive correlation between the power consumption of electronics and PBDE levels in air and dust in a large room, which they attributed to heat generated from in-use electronics promoting the release of these compounds. The least common medium studied in the indoor setting is the film formed on hard surfaces by condensation and deposition of gas-phase chemicals and particles respectively (Diamond et al., 2000; Gingrich et al., 2001). Windows are convenient to use for sampling the film because the glass is inert, because of the lack of contamination that could arise from other surfaces, and because the film can be removed quantitatively from this surface. The most common approach to windows film sampling employs pre-cleaned wipes (Butt et al., 2004).

With the control and subsequent decline and cessation of production of polybrominated diphenyl ethers (PBDEs) in the last decade in many countries, other brominated flame retardants (BFRs) have risen in importance. Even though some of these alternative flame retardants have been produced for a long time, most of them have only come to the attention of the public and the global scientific community in the past few years. While levels of PBDEs in the environment are generally stable or decreasing (Crimmins et al., 2012; Ma et al., 2013), concentrations of “new” brominated flame retardants, notably 2-ethylhexyl tetrabromobenzoate (EHTBB) and bis(2-ethylhexyl)tetrabromophthalate (BEHTBP), are increasing as more products containing these compounds are introduced to the market to replace products containing PBDEs (Dodson et al., 2012; Ma et al., 2012; Stapleton et al., 2011). In spite of this change in the flame retardant market, data regarding the presence of these replacements of alternative compounds in the environment are limited.

In this paper, we report the concentrations of newer and legacy flame retardants in the indoor environments in three different countries (United States, Canada, and the Czech Republic). We collected air, dust, and windows films in 63 private homes, and we measured about 20 brominated flame retardants and Dechlorane Plus, a chlorinated flame retardant. In this paper, we compare concentrations in these three countries, and we put them in the context of their usage in North America and Europe. We also look at differences between rooms in the same home to elucidate possible sources. Finally, we evaluate how these compounds partition between phases (air, dust, and window film) and evaluate which sampling media provide the most comprehensive characterization of indoor levels.

2. Materials and methods

2.1. Study population

Samples were collected in three different locations: Bloomington, Indiana, United States, Toronto, Canada, and Brno, Czech Republic in May–August 2013. Air, dust, and window film samples were collected from a total of 63 houses and apartments: 20 homes each from the Czech Republic and the U.S. and 23 from Canada. At least one room was sampled in each home (i.e. the main bedroom), and a second room was sampled in 10 houses per country (i.e. the living room). Participation in the campaign was voluntary and did not include any compensation.

On day 1, passive samplers were deployed, and selected windows were cleaned with Kimwipes moistened with 2-propanol until no dirt was visible on the Kimwipes. Participants were asked not to vacuum the room where the sampler was located until completion of the campaign, if at all possible. Participants were interviewed by a field technician to gather information about the house and the household (e.g. electronic equipment and furniture in the sampled rooms, number of occupants, and cleaning and ventilation habits).

2.2. Sample collection

Before sampling, all matrices (PUF disks, nylon vacuum socks, and Kimwipes) were pre-cleaned by Soxhlet extraction (8 h in acetone, then 8 h in toluene), dried, wrapped in aluminum foil, and transported to the site. PUF disks for passive air sampling were exposed to indoor air for 28 days using a single (U.S. and Canada) or double-bowl shaped housing (Czech Republic) (see Fig. S1). Sampling rates for each sampler configuration were calculated in a separate experiment by simultaneously deploying single bowl and double bowl samplers (see Supporting Information for details and Fig. S2). For this study, we used a sampling rate of 1.6 m³/day for the double bowl sampler and 2.9 m³/day for the single bowl sampler. These values are consistent with previously reported sampling rates indoors (Zhang et al., 2011). Window film samples were collected after 28 days using pre-cleaned Kimwipes moistened with 2-propanol. Windows were wiped with a succession of Kimwipes until no dirt was visible on the Kimwipes, and all Kimwipes from one window were composited. The sampled area averaged at 0.32 m² for Canada, 0.93 m² for the U.S., and 1.8 m² for the Czech Republic. Floor dust samples from each room were taken using pre-cleaned polyester socks inserted on a vacuum cleaner hose attachment, by vacuuming the largest possible area and recording it. All collected samples were wrapped in clean aluminum foil, sealed, labeled, and subsequently stored at –20 °C until analysis. Pre-cleaned PUF, Kimwipes, and polyester socks, which had been exposed by unsealing the aluminum foil wrap during sample retrievals, were treated as field blanks.

2.3. Target compounds

In this paper, we have focused on the following compounds: polybrominated diphenyl ethers (congeners 28, 47, 66, 85, 99, 100, 153, 154, 183, and 209), hexabromobenzene (HBB), *p*-tetrabromoxylene (*p*-TBX), pentabromobenzene (PBBz), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB), bis(2-ethylhexyl)tetrabromophthalate (BEHTBP), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenylethane (DBDPE), and Dechlorane Plus (*syn* and *anti*). All the analytical standards [except BDE-118, which was purchased from AccuStandard (AccuStandard, New Haven, CT)], were purchased from Wellington Laboratories, Guelph, Canada.

2.4. Sample analysis

The U.S. samples were analyzed in Bloomington, Indiana, U.S. (Indiana University, IU), and the Canadian and Czech samples were analyzed in Brno, Czech Republic (RECETOX). Details of the analytical protocols are given in the SI and are summarized here. Before extraction, all samples were spiked with known amounts of recovery standards. Socks with dust were weighed, the dust was sieved to <500 μm, approximately 100 mg were weighed, and the excess dust was stored in an aluminum foil packet for future use. The sock was rinsed with solvent (30 mL hexane in acetone, 1:1), and the solvent was combined with weighed dust. Dust was sonicated in 30 mL of acetone in hexane 1:1 (v:v); left to settle for 30 min, and the supernatant was decanted. The procedure was repeated 2 additional times with 10 mL of solvent, and the extracts were combined. At IU, the extract was rotary evaporated to 2 mL and then fractionated on a silica column (3.5% water deactivated) using 25 mL of hexane, 25 mL hexane in dichloromethane 1:1 (v:v), and 25 mL of dichloromethane in acetone 3:7 (v:v) as eluting solvents. At RECETOX, the volume of the combined extracts were reduced under a N₂ stream and separated by weight to two aliquots. The first aliquot was 70% of the extract, and it was treated with sulfuric acid-modified silica. The remaining 30% of the extract was cleaned using a standard non-modified silica column. PUF and Kimwipes samples were Soxhlet extracted with 400 mL of acetone in hexane 1:1 (v:v) for 24 h at IU (Peverly et al., 2015) and with 250 mL

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