



Test chamber and forensic microscopy investigation of the transfer of brominated flame retardants into indoor dust via abrasion of source materials



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HIGHLIGHTS

- HBCD contamination of dust via source material abrasion reproduced in test chamber
- Fragments of plastic with elevated BDE-209 content identified in dust samples
- Results suggest high BFR concentrations in dust due to source material abrasion.

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ABSTRACT

Brominated flame retardants (BFRs) have been detected in indoor dust in many studies, at concentrations spanning several orders of magnitude. Limited information is available on the pathways via which BFRs migrate from treated products into dust, yet the different mechanisms hypothesized to date may provide an explanation for the range of reported concentrations. In particular, transfer of BFRs to dust *via* abrasion of particles or fibers from treated products may explain elevated concentrations (up to 210 mg g⁻¹) of low volatility BFRs like decabromodiphenyl ether (BDE-209). In this study, an indoor dust sample containing a low concentration of hexabromocyclododecane, or HBCD, (110 ng g⁻¹ ΣHBCDs) was placed on the floor of an in-house test chamber. A fabric curtain treated with HBCDs was placed on a mesh shelf 3 cm above the chamber floor and abrasion induced using a stirrer bar. This induced abrasion generated fibers of the curtain, which contaminated the dust, and ΣHBCD concentrations in the dust increased to between 4020 and 52 500 ng g⁻¹ for four different abrasion experiment times. The highly contaminated dust (ΣHBCD at 52 500 ng g⁻¹) together with three archived dust samples from various UK microenvironments, were investigated with forensic microscopy techniques. These techniques included Micro X-ray fluorescent spectroscopy, scanning emission microscopy coupled with an energy dispersive X-ray spectrometer, Fourier transform infrared spectroscopy with further BFR analysis on LC-MS/MS. Using these techniques, fibers or particles abraded from a product treated with BFRs were identified in all dust samples, thereby accounting for the elevated concentrations detected in the original dust (3500 to 88 800 ng g⁻¹ ΣHBCD and 24 000 to 1 438 000 ng g⁻¹ for BDE-209). This study shows how test chamber experiments alongside forensic microscopy techniques, can provide valuable insights into the pathways via which BFRs contaminate indoor dust.

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1. Introduction

Brominated flame retardants (BFRs) are incorporated in numerous textile, plastic and foam products with extensive indoor applications.

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They are incorporated into consumer products in two main ways: (a) via an “additive” process where the BFR is physically mixed with the molten polymer, and (b) via a “reactive” process where the BFR is covalently bound to the polymer. BFRs incorporated via the additive process are considered loosely bound to the product and more available for re-release into the environment than those incorporated into materials in a “reactive” manner. Owing to their extensive indoor application and their low vapour pressures that favor air-to-dust partitioning, BFRs such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) are ubiquitous and substantial contaminants of indoor dust

(Besis and Samara, 2012; Covaci et al., 2006; Harrad et al., 2010a). Contact with indoor dust has thus been identified as an important human exposure pathway, particularly for young children who spend extended time periods crawling over surfaces and display extensive hand-to-mouth contact (Jones-Otazo et al., 2005). Consequently, improved understanding of the pathways via which BFRs migrate to dust from treated products can inform strategies to reduce exposure. To date however, limited experimental evidence is available about such migration pathways. Currently hypothesized pathways include: (1) volatilization of BFRs from the treated product with subsequent partitioning to dust; (2) abrasion via physical wear and tear of the treated product (likely enhanced by UV degradation of the polymer), resulting in the transfer of particles or fibers of the treated product directly to dust; and (3) transfer via direct contact between the treated product and dust. Pathway (1) appears particularly relevant for more volatile BFRs incorporated additively into the product, and is expected to result in a homogeneous bromine distribution within the dust. In contrast, pathway (2) appears more applicable to the product-to-dust migration of less volatile BFRs, and/or those BFRs incorporated reactively into products. A non-uniform, or heterogeneous, bromine distribution is anticipated to result from this migration pathway. Finally, pathway (3) also appears more relevant for additive BFRs for which migration from the product matrix to the surface and uptake by surface dust occurs via sorption or other physical processes such as capillary forces. A homogeneous bromine distribution is hypothesized for this pathway.

Emission chamber studies to date have focused largely on measurement of emissions to air of BFRs and related semivolatile organic compounds (SVOCs) from treated products (Rauert et al., 2014). In contrast, very few studies have investigated the migration of SVOCs from products to dust, with – to the authors' knowledge – no such studies existing for BFRs. Specifically, the migration to dust of phthalates (a class of SVOCs) has been simulated in test chamber experiments that investigated migration pathways (1) and (3) (Clausen et al., 2004; Schripp et al., 2010). Moreover, while we reported recently (Rauert et al., 2014) on test chamber experiments examining volatilization with subsequent partitioning to dust of HBCDs (pathway (1)); controlled test chamber experimental studies of the migration of BFRs from products to dust via pathway (2), or abrasion, have yet to be reported in the literature for any SVOC.

Forensic microscopy techniques such as energy dispersive Micro X-ray fluorescence spectroscopy (Micro XRF) and scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) have been utilized previously to provide information on the origins of dust contamination with BFRs. Suzuki et al. (2009) used Micro XRF to map dust samples, identifying particles of high bromine content, with isolated particles analyzed by GC-HRMS to determine their PBDE content. In a parallel study, Webster et al. (2009) utilized Micro XRF for identification of areas of high bromine content in dust samples containing high concentrations of decabromodiphenyl ether (BDE-209), followed by SEM/EDS to provide compositional and morphological information. However, the XRF and SEM/EDS techniques used in these preliminary studies can only confirm the existence of bromine, so additional confirmation is required of the presence of BFRs. Using GC-HRMS, Suzuki et al. (2009) were able to identify and quantify the content of PBDEs (pg per bromine rich fragment) contained within individual bromine (Br)-rich particles isolated from a dust sample, with BDE-209 quantified in each isolated fragment. However, due to the uncertainty associated with the gravimetric determination, the mass of the particles themselves could not be measured. Subsequent studies by Ghosal and Wagner (2013) and Wagner et al. (2013) reported the use of Raman micro-spectroscopy to study Br-rich particles, after identification with SEM/EDS, for non-destructive confirmation of the presence of PBDEs. Collectively, studies to date have all identified in dust samples the presence of particles or fibers originating from a product treated with BFRs, suspected to migrate via abrasion or pathway (2). This pathway may provide an explanation for the high concentrations, up to 210 mg g⁻¹

(Batterman et al., 2009), reported of the relatively non-volatile BDE-209 in some dust samples.

This study for the first time mimics experimentally the abrasion of a BFR source material and the subsequent migration of the abraded material into dust. The dust sample generated by this experiment was analyzed with a combination of forensic microscopy techniques to identify the abraded material. To further show the applicability of these selected microscopy techniques to providing information on BFR migration pathways to dust, three 'real' dust samples, previously sampled from indoor microenvironments in the UK and containing high levels of BFRs, were analyzed with the same sequence of techniques. This augmented further, the existing evidence that such highly contaminated dusts are due to the presence of a small proportion of fibers and/or particles abraded from BFR-treated materials.

2. Materials and methods

2.1. Test chamber experiments

2.1.1. Experimental design for investigating the abrasion migration pathway

An in-house designed and built test chamber was utilized to investigate migration pathway (2). The experimental design of the chamber is illustrated in Fig. 1. Briefly, the chamber design consisted of a cylindrical stainless steel chamber (20 cm height, 10 cm diameter), with a removable aluminium mesh shelf. In this experiment, the shelf was placed 3 cm above the chamber floor and a magnetic stirrer bar, 40 mm × 8 mm, (Fisher Scientific, Leicestershire, UK) placed on the shelf to mimic abrasion. A piece of product treated with BFRs (the BFR source) was placed on the shelf and a known mass of dust placed on a glass fiber filter (GFF), situated on the chamber floor. The dust contained low concentrations of HBCDs and PBDEs (Σ HBCDs = 110 ng g⁻¹ and Σ PBDEs = 280 ng g⁻¹). The chamber was sealed and placed on a magnetic stirrer plate, operated at 200 rotations per minute. In this way, abrasion was mimicked via direct contact between the rotating stirrer bar and the treated product, with the fibers and particles thus generated, falling through the mesh shelf and incorporated into the dust sample below. This process was conducted at room temperature, and repeated for four durations of 2, 3, 21, and 48 hours. Dust generated from 48 hours of certain abrasion was analyzed further with forensic microscopy techniques.

2.1.2. BFR source

Fabric curtains treated with technical HBCD were obtained from the National Institute for Environmental Studies (NIES), Tsukuba, Japan. Concentrations of HBCDs in these curtains were: 18 000 mg/kg for α -HBCD, 7500 mg/kg for β -HBCD and 17 000 mg/kg for γ -HBCD (Kajiwara et al., 2013).

2.1.3. Archived dust samples

Three UK dust samples were chosen for detailed analysis via forensic microscopy. These samples were previously identified as containing highly elevated concentrations of BDE-209 and HBCDs (Harrad et al., 2008, 2010b) with the concentrations listed in Table 1. Each dust originated from a different microenvironment category (a residential living room, office and primary school for Dusts 1, 2, and 3 respectively) however little other information was available on microenvironment characteristics or putative sources for these samples.

2.2. Forensic microscopy

2.2.1. Sample preparation for forensic microscopy

The bulk dust sample to be examined was mixed thoroughly before use with a vortex mixer before use. A small quantity of dust (1 mg) was evenly distributed in a monolayer, with tweezers, onto a 25 × 25 mm square area of double sided carbon tab attached to a glass sample plate for analysis with Micro XRF.

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