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Research Highlights

- Uptake of BFRs by dust following volatilisation from a source shown experimentally
- Migration of HBCDs from curtains elevated concentrations in dust up to 10 fold
- Test chamber design and sink effects are important considerations

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TITLE

Test Chamber Investigation of the Volatilisation from Source Materials of Brominated Flame Retardants and their Subsequent Deposition to Indoor Dust

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Abstract

Numerous studies have reported elevated concentrations of brominated flame retardants (BFRs) in dust from indoor microenvironments. Limited information is available however on the pathways via which BFRs in source materials transfer to indoor dust. The most likely pathways hypothesised are: (a) volatilisation from the source with subsequent partitioning to dust, and (b) abrasion from everyday ‘wear and tear’ of the treated product that transfers microscopic fibres or particles to the dust. Test chambers are one method for investigating these pathways. This study reports on the development and application of an in-house test chamber for investigating BFR volatilisation from source materials and subsequent partitioning to dust. The performance of the chamber for such experiments was evaluated against that of a commercially available chamber, and inherent issues with such chambers were investigated, such as irreversible loss of BFRs to chamber surfaces (so-called “sink effects”). A sample of curtain fabric treated with hexabromocyclododecane (HBCD) was placed on a metal grid 10 cm above the chamber floor and subjected to emission testing. Concentrations of HBCD in dust placed on the chamber floor measured after the emission test, exceeded substantially those detected in the dust before the experiment. These results provide the first experimental evidence of HBCD volatilisation from a source material followed by deposition to dust.

Keywords

Brominated flame retardants, HBCDs, PBDEs, test chambers, transfer to dust, test chamber sink effects

1. Introduction

Brominated flame retardants (BFRs) are a class of chemicals used in numerous foam, material and plastic products in a variety of indoor microenvironments (Harrad et al., 2010). Often they are incorporated via an additive process, so are loosely bound to the polymer and available for release during normal use of the product. Alternatively, some BFRs are covalently bound to the polymer matrix, and referred to as "reactive" BFRs. Elevated concentrations of BFRs have been reported in indoor air and dust, with consequent implications for human exposure (Batterman et al., 2009; Harrad et al., 2008). Correlations have been reported between putative BFR sources and BFR concentrations in indoor air and dust in several studies (Allen et al., 2008; de Wit et al., 2012; Harrad et al., 2004); however, little is known about the pathways via which BFRs migrate from treated consumer products into air and dust. The principal pathways of migration or mass transfer from treated materials into dust are hypothesised to comprise: volatilisation with subsequent deposition (or partitioning) to dust, abrasion ('wear and tear') of the treated product leading to direct particle or fibre transfer to dust (Wagner et al., 2013; Webster et al., 2009), and migration via direct contact between source material and dust (Takigami et al., 2008). Actual migration is likely to be a combination of these pathways, with the relative significance of each, dependent on factors such as the physicochemical properties of the BFR and the mode via which it is incorporated into the product. For example, while abrasion is likely a viable pathway for both additive and reactive BFRs; the other two pathways are likely far less facile for reactive BFRs. The use of test chambers is a potentially important strategy for investigating migration pathways of FRs to dust.

Emission chambers have been utilised in studies for measurement of specific emission rates (SERs) of BFRs and organophosphorus flame retardants from consumer products, providing information on gas phase emissions (Rauert et al., 2014). In contrast, to the authors' knowledge the migration of BFRs to particulates and dust has not been investigated via emission chambers; however the mass transfer of phthalates, another class of semi-volatile organic compound (SVOC), from wall paint and vinyl flooring to dust has been investigated in modified chambers (Clausen et al., 2004; Schripp et al., 2010). These studies demonstrated the migration of phthalates to dust occurred via both volatilisation with subsequent deposition, and via direct transfer as a result of contact between the source material and dust.

The current study investigates the migration into dust *via* volatilisation and subsequent deposition of polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs). An in-house test chamber was designed and built at the University of Birmingham. Experiments to evaluate the optimum configuration of this chamber are described, alongside its validation against a commercially available micro-emission chamber. Following validation, the in-house chamber was used to study the transfer of HBCDs from treated curtains into dust.

2. Materials and Methods

2.1 Test chamber apparatus

A cylindrical in-house designed and built test chamber was utilised at the University of Birmingham (UoB chamber), constructed from stainless steel with dimensions of 10 cm diameter and 20 cm height to give a total chamber volume of 1570 cm^3, and internal surface area of 785 cm^2. Attachment of a Capex L2 Diaphragm Pump (Charles Austen Pumps Ltd, Surrey, UK) provided a constant air flow of 10 L min^{-1} through the chamber, that led to an air change rate of 400 times per hour. Polyurethane foam (PUF) plugs (140 mm diameter, 12 mm thickness, 360.6 cm^2 surface area, 0.07 g cm^{-3} density, PACS, Leicester, UK) were attached to the exit air vent to collect analyte emissions in both the gas and airborne particulate phases. The chamber was maintained at the desired temperature by immersion in a hot water bath with chamber internal temperature monitored using a LogTag TRIX-8 temperature data logger (LoggerShop Technology, Dorset, UK). The chamber configuration is illustrated in Figure 1. Note the inclusion of an aluminium mesh shelf situated approximately halfway down the chamber. As detailed later, this permitted separation of a BFR source from dust placed on the chamber floor.

2.2 Commercially-available micro-chamber

A Micro-Chamber/Thermal Extractor^{TM} (Markes International) located at VITO (Flemish Institute for Technological Research), Belgium consisting of 6 linked chambers (Figure 2) was used for comparison with the UoB chamber. Each linked chamber, internal surfaces constructed of electropolished stainless steel, had dimensions of 4.5 cm diameter and 2.8 cm height to give a total chamber volume of 44 cm^3, and internal surface area of 71 cm^2. A uniform heating system (20-120˚C) surrounded each chamber and adjustable airflow set at 0.5 L min^{-1} (air change rate of 682 times per hour) was provided to the chambers. The addition of a PUF plug (140 mm diameter, 12 mm thickness, 360.6 cm^2 surface area, 0.07 g cm^{-3} density, PACS, Leicester, UK) to the exit air line, facilitated collection of emitted analytes. The micro-chambers were also fitted with a shelf mid-way to facilitate separation of the BFR source from dust.

2.3 HBCD treated curtains and low level dust procurement

Fabric curtains treated with the HBCD technical formulation were obtained from the National Institute for Environmental Studies (NIES), Tsukuba, Japan. Concentrations of HBCDs in these curtains were 18,000 mg kg^{-1} for α-HBCD, 7,500 mg kg^{-1} for β-HBCD, and 17,000 mg kg^{-1} for γ-HBCD (Kajiwara et al., 2013).

Initial source-air-dust partitioning experiments were conducted using a bulk house dust sample obtained from a private residence in Birmingham. In common with many UK dust samples, this dust contained moderately elevated concentrations of HBCDs and of BDE-209, rendering it unsuitable for experiments studying these analytes. As a result, a further bulk dust sample containing lower concentrations of PBDEs and HBCDs was collected from a private residence in Belgium. Concentrations of PBDEs and HBCDs in both dusts are provided as supplementary data (Table SD-1).

2.4 Chemicals

All solvents used for extraction and analysis were of HPLC grade quality (Fisher Scientific, Loughborough, UK). Standards of individual PBDEs (BDEs 47, 85, 99, 100, 153, 154, 183, 209), HBCDs (α-HBCD, β-HBCD, γ-HBCD), labelled ^{13}C HBCDs (α-, β-, γ-), d_{18} γ-HBCD and labelled ^{13}C PBDEs (BDEs 47, 99, 100, 153, 209) were purchased from Wellington Laboratories (Guelph, ON, Canada). Florisil (60-100 mesh) and silica gel (60Å, 60-100 mesh) were obtained from Sigma Aldrich (Dorset, UK) with concentrated sulfuric acid procured from Merck (Darmstadt, Germany). Large glass fibre filters (GFF, 12.5 cm diameter, 1 µm pore size, Whatman, UK) and small GFFs (4.25 cm diameter, 0.7 µm pore size, Whatman, UK) were purchased from Agilent (UK).

2.5 Experimental Design for investigating BFR partitioning to dust after volatilisation

The chamber configuration for these experiments is illustrated in Figure 1b. It consists of a known mass of pre-characterised dust (200 mg) weighed onto a GFF and placed on the chamber floor. A piece of material known to contain BFRs (e.g. HBCD-treated curtain) was placed on the mesh shelf located half way down the chamber. Post experiment, the chamber was cooled at room temperature for 5 hours (with air flow still attached) to minimise loss of volatiles when opening the chamber. The dust, PUFs and GFFs were then extracted and analysed separately. All chamber inner wall surfaces were washed with 200 mL of hexane:dichloromethane (1:1 v/v) and collected for separate analysis.

2.6 Analytical protocols

2.6.1 Sample preparation and extraction

Sample extraction and purification was performed using slight modifications of in-house published methods (Abdallah et al., 2009; Abdallah et al., 2008). Dust, PUFs and GFFs were extracted with pressurised liquid extraction (ASE-350, Dionex Europe, UK). PUFs and GFFs were packed into precleaned 66 mL cells using precleaned Hydromatrix (Varian Inc., UK) to fill the void. Dust samples were loaded into pre-cleaned 66 mL cells containing 1.5 g of pre-cleaned Florisil and Hydromatrix. Each cell was spiked with 4 ng each of ^{13}C-labelled α-, β-, and γ-HBCD; 40 ng of ^{13}C-PBDE 47; 10 ng each of ^{13}C-labelled PBDE-99 and PBDE-153; and 20 ng of ^{13}C-PBDE 209 as internal (surrogate) standards prior to extraction with hexane:dichloromethane (1:1 v/v) at 90 ˚C and 1500 psi. The cell was heated for 5 min, held static for 4 min and purged for 90 s, with a flush volume of 50%, for 3 cycles.

2.6.2 Clean up

The ASE extracts and chamber inner surface solvent rinses were combined and concentrated to 0.5 mL using a Zymark Turbovap II (Hopkinton, MA, USA), then purified by loading onto SPE cartridges filled with 8 g of pre-cleaned acidified silica (44% concentrated sulfuric acid, w/w). The analytes were eluted with 30 mL of hexane:dichloromethane (1:1, v/v), with the eluate evaporated to dryness under a gentle stream of nitrogen. Samples were reconstituted to 100 μL with 2 ng of d_{18}-γ-HBCD and 20 ng of ^{13}C-PBDE 100 in HPLC grade methanol, used as recovery standards for internal standard recovery determination.

2.6.3 LC-MS/MS analysis

Target PBDEs and HBCDs were separated and analysed using modified, in-house published methods (Abdallah et al., 2009; Abdallah et al., 2008), using a dual pump Shimadzu LC-20AB Prominence liquid chromatograph (Shimadzu, Kyoto, Japan) equipped with a SIL-20A autosampler, and a DGU-20A3 vacuum degasser. Mass spectrometric analysis was performed using a Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA) equipped with an APPI (PBDEs) or ESI (HBCDs) ion source, operated in negative ion mode.

2.6.3.1 PBDE Analysis

A Varian Pursuit XRS3 (Varian, Inc., Palo Alto, CA) C18 reversed phase analytical column (250 mm x 4.6 mm i.d., 3 μm particle size) was used for separation of target PBDEs (47, 85, 99, 100, 153, 154, 183 and 209). A mobile phase programme based upon (mobile phase A) 1:1 methanol/water and (mobile phase B) 1:4 toluene/methanol at a flow rate of 0.4 mL min^{-1} was applied for elution of the target compounds; starting at 85% (mobile phase B), increased linearly to 100% (mobile phase B) over 20 min, and then held for 10 min. The column was equilibrated with 85% (mobile phase B) for 5 min between runs. MS/MS detection, operated in MRM mode, was used for quantitative determination of the PBDE congeners based on *m/z* 420.8→78.8, *m/z* 500.8→78.8, *m/z* 578.8→78.8, *m/z* 658.6→78.8, *m/z* 486.6→78.8. ^{13}C-labelled analogues were determined based on *m/z* 432.4→78.8, 512.4→78.8, 590.6→78.8, and *m/z* 494.7→78.8.

2.6.3.2 HBCD Analysis

A Varian Pursuit XRS3 C18 reversed phase analytical column (150 mm x 4.6 mm i.d., 3 μm particle size) was used for separation of target HBCDs (α-, β-, γ-). A mobile phase program based upon (mobile phase A) 1:1 methanol/water and (mobile phase B) methanol at a flow rate of 0.18 mL min^{-1} was applied for elution of the target compounds; starting at 50% (mobile phase B), then increased linearly to 100% (mobile phase B) over 4 min, held for 5 min before decreasing linearly to 88%

(mobile phase B) over 1 min. The column was equilibrated with 50% (mobile phase B) for 4 min between runs. MS/MS detection, operated in MRM mode, was used for quantitative determination of the HBCD diastereomers, ^{13}C-, and d_{18}-labelled analogues based on *m/z* 640.4→79.0, *m/z* 652.4→79.0, and *m/z* 657.7→79 respectively.

2.6.4 Quality Assurance

Samples were analysed using established QA/QC procedures. Method blanks were run with each batch of samples. For ^{13}C-α-, β-, and γ-HBCDs, average recoveries ranged from 64 to 97% while for ^{13}C-PBDE 47, 99, 153, and 209, average recoveries ranged between 69 and 80%. Accuracy and precision of the analytical method was assessed *via* replicate analyses (n=7) of NIST SRM 2585 (organics in house dust). The results of these analyses compared with indicative and certified values as appropriate are supplied as supplementary data (Table SD-2).

3. Results and Discussion

3.1 Experimental design development

3.1.1 Influence of exit air sampling train length

The influence of the length of polypropylene tubing carrying air exiting the chamber to the collection PUF was investigated in chamber experiments conducted at 60 ˚C for 24 hours, to promote volatilisation. In both experiments the BFR "source" was a small GFF (4.25 cm diameter) spiked with 100 ng of each of the target BFRs. Reducing the tubing length (pictured in Figure 1a) from 15 cm to 2 cm increased the mass of all BFRs collected on the PUFs by up to 7 times. Figure 3 and Table SD-3 compare the masses collected on the PUF for both tubing lengths – with results the average of 3 and 2 replicates for the 15 cm and 2 cm length tubing respectively. The substantially higher BFR masses detected on the PUF with shorter tubing length, suggests the analytes sorb strongly to the inner tubing surfaces thereby underestimating the extent of emissions via volatilisation. This is particularly relevant for chamber experiments conducted at above-ambient temperatures, which encourage volatilisation. Consistent with our data, Xu et al. (2012) reported that reducing the length of the stainless steel tube connecting their chamber to the sampling sorbent tube, increased apparent volatilisation of the phthalate DEHP from vinyl flooring. As a result of reducing the length of the connecting tube, Xu et al. (2012) found gas-phase concentrations reached steady state conditions in 20 rather than 40 days. We conclude therefore that the length of the connection between the chamber exit and the sampling sorbent should be kept to a minimum for studies of SVOCs like BFRs.

3.1.2 PUF Breakthrough

To test the sampling efficiency of the PUFs used to collect BFRs in chamber exit air; two PUFs were placed sequentially in a glass holder with the chamber-side end of the first collection PUF spiked with standards of native PBDEs and HBCDs (100 ng/analyte) before attachment to the chamber. The empty chamber was maintained at 60 ˚C to replicate an experimental scenario in which substantial losses might be expected (warm air passing through the system configuration), and air was pumped through the system for 24 hours. Post experiment, both PUFs were extracted separately and analysed. Analyte concentrations were below LOQs on the second "air-side" PUF while recoveries of analytes on the chamber-side PUF were 99±7 %. These data are clear evidence that there is no significant analyte loss via PUF breakthrough with the UoB chamber. Similar experiments were conducted with the micro-chamber and also revealed satisfactory analyte recoveries of 90±11 %. Recoveries of individual analytes are listed in Table 1.

3.1.3 Sink Effects

The lower vapour pressure of SVOCs affects their study in test chambers as it can lead to preferential sorption, following their volatilisation, to chamber surfaces rather than collection in gas phase emissions. The loss of analytes via sorption to chamber wall surfaces is referred to as sink effects and has been previously reported in chamber studies of SVOCs (Katsumata et al., 2008; Kemmlein et al., 2003; Uhde and Salthammer, 2006; Xu et al., 2012). We investigated the loss to such sink effects in both the UoB test chamber and the micro-chamber configurations. To do so, GFFs spiked with standards of the analytes (100 ng/analyte) were placed inside the completely sealed off chambers (no air flow), which were then heated to 60 ˚C for 24 hours. Post experiment, whilst still sealed, both the UoB chamber and the micro-chamber were cooled to room temperature (22 ˚C) for 5 hours. The inner chamber surfaces were then rinsed as described in section 2.5 to assess the proportion of analytes reversibly deposited to such surfaces, and the GFF analysed to determine non-volatilised mass. Total mass recoveries of individual BFRs were then calculated as the sum of masses detected in the chamber solvent rinses, and the GFF; with the mass unaccounted for assumed to be due to loss to irreversible sorption to internal chamber surfaces (i.e. “sink effects”).

Considerable levels of the more volatile analytes were recovered in the solvent washes of the chamber walls but 100% recovery was not obtained for any of the analytes. Table 2 lists the total % recovery of analytes in both the UoB and micro-chambers, with the proportions recovered from the chamber inner surface rinses and that remaining on the GFF reported separately. Liu et al. (2013) listed measures that can be undertaken to reduce such sink effects and minimise time for steady-state to be reached. These comprise: increasing the source surface area, decreasing the sink (i.e. chamber) surface area per volume ratio, using materials for chamber surfaces with lower sorptive capacity, and increasing the chamber air change rate. We therefore interpreted our data on loss to sink effects – which generally show a slightly greater loss for the micro-chamber - in this context.

As the same size GFF was used in both chambers and both chamber internal surfaces were stainless steel, no differences exist in the source area or the sorptive capacity of the internal surfaces of the two chambers. In contrast, the lower surface area-to-volume ratio for the UoB chamber (0.5 $m^2.m^{-3}$) compared to the micro-chamber (1.6 $m^2.m^{-3}$) should lead to a lower sink effects loss for the UoB chamber. However, this is offset to some extent by the lower air change rate for the UoB chamber (400 air changes per hour) compared to the micro-chamber (682 air changes per hour). The ratio of the differences between these two parameters for the two chambers suggests the loss to sink effects in the micro-chamber be about twice that of the UoB chamber. Our data are broadly consistent with this, suggesting that the factors listed by Liu et al (2013) are the principal parameters governing losses to sink effects and should be taken into account in future chamber design. However, the greater losses of BDE-209 in the UoB chamber highlights that other factors likely play a role.

Other efforts were made to minimise sink effects for the UoB chamber. We first explored the impact of the sorptive capacity of the internal chamber surface. To do so, experiments were repeated in a blown glass tube (20 cm length, 3 cm diameter) to compare sink effects using glass and stainless steel surfaces, and the impact of coating the chamber interior with a Teflon spray to reduce active sorption sites was also evaluated. Improvements in analyte recovery were not observed using either glass or Teflon coated surfaces. In an attempt to reverse any sorption to chamber walls, the chamber was also heated post experiment to 80 ˚C for 6 hours, to volatilise analytes sorbed to chamber surfaces, but this yielded only minor improvements in analyte recovery from the chamber (an increase of 2-22%, see Table SD-4), and left up to 60% of analyte mass still unaccounted for. Higher post-experiment temperatures were avoided to prevent analyte degradation or thermal stereoisomerisation of HBCDs (Heeb et al., 2008).

To ascertain the full extent of sink effects from the stainless steel surfaces of the chamber, longer experiments of the order of months are required for attainment of steady state conditions inside the chamber, due to the slow emission rates and strong partitioning to chamber surfaces associated with SVOCs like BFRs (Xu et al., 2012). If steady state conditions are not reached then gas phase emissions and the rate of partitioning to dust may be underestimated. Our investigations suggest the UoB chamber is not constructed of low sorptive material and that over the experimental durations employed in this study, it is likely that steady state conditions are not attained. Therefore, our results are presented as an indicator of the importance of sink effects when determining SERs of BFRs and studying their migration to dust, and of the factors influencing sink effects; rather than a detailed study of partitioning to chamber interior surfaces.

3.2 Partitioning of BFRs to dust using standards spiked on a GFF as the source

Initial experiments evaluating the partitioning of BFRs to dust following their emission to air were conducted in both the UoB and the micro-chamber. In these experiments, a known mass of house dust (100-200 mg) was placed on a GFF on the chamber floor. Another GFF was spiked with standards of the analytes and placed on the wire mesh shelf, separated from the dust (by 5 cm in the UoB chamber and 1 cm in the micro-chamber), as the BFR 'source'. To mimic operating conditions of electronic devices like PCs (Kemmlein et al., 2003), the chamber was operated at 60 ˚C for 24 hours; with the dust, spiked GFF and chamber surface rinses analysed separately post-experiment. BFR partitioning to dust was observed in both chambers and Figure 4 shows the post-experiment increase in PBDE concentrations in the dust.

Data for the HBCDs and BDE-209 is not included as the UK house dust used in these initial experiments contained substantial concentrations of these analytes pre-experiment. The incremental concentration detected post-experiment in the dust is greater in the UoB chamber, likely due to the lower air change rate resulting in increased contact time compared to the micro-chamber. Conversely, as depicted in Figure 5, in the micro-chamber a greater proportion of the target analytes appear on the PUF with a lower proportion remaining on the GFF. Figure 5 also shows the proportion of the BFRs initially present in the "source" that is recovered in the various components of each experiment including the solvent chamber interior surface rinse. The micro-chamber was again more efficient at promoting volatilisation of BFRs which were subsequently collected on the PUF, rather than partitioning to dust, due to the micro-chamber's comparatively higher air change rate (60% higher) and smaller volume. These result in a shorter distance between the "source" and air outlet leading to greater capture by the PUF. Note in Figures 4 and 5, the UoB chamber results are the average of 3 replicates and the micro-chamber data represent an average of 6 replicates.

3.3 Partitioning of HBCDs to dust using a HBCD treated curtain as the source

Following our initial experiments using spiked GFFs as the BFR "source", partitioning to dust was investigated as previously using a 2 x 2 cm square piece of HBCD treated curtain placed on the chamber shelf as the source. The curtains were not obtained 'new' from the manufacturer having been stored at -18 ˚C for 2-3 years prior to testing. This is relevant as other studies have reported that the age of the product tested can influence emissions of SVOCs, with emissions significantly reducing over time (Carlsson et al., 2000; Ni et al., 2007; Salthammer et al., 2003). Thus emissions from this small sub-sample may not be representative of this and similar materials generally.

Initial experiments with the treated curtains were conducted in the UoB chamber for 24 hours at 60 ˚C to promote volatilisation of the analytes (n=4). Further experiments (n=3) in this chamber were conducted at room temperature for 1 week, to better simulate 'real-world' conditions. The average increment in concentrations of HBCDs in dust under both scenarios (at 60 ˚C and room temperature) is depicted in Figure 6. Similarly substantial increases in HBCD concentrations in dust were observed at the end of both experiments, providing clear evidence of HBCD migration from the curtain to dust *via* volatilisation and subsequent partitioning.

Figure 6 also shows the pre- and post-experiment concentrations of HBCDs in dust when the 24 hour 60 ˚C experiments were conducted in the micro-chamber, using a sample of the same HBCD-treated curtain (n=6). Far greater variation in post-experiment concentrations was observed than those obtained under the same conditions using the UoB chamber. We believe this is because the source shelf in the micro-chamber placed the curtain only a very short distance (1 cm) from the entering airflow. Also the air change rate in the micro-chamber is 60% higher, resulting in a higher air velocity than in the UoB chamber. The resulting greater airflow turbulence, to which the curtain sample was exposed in the micro-chamber, caused abrasion of the curtain and the detection post-experiment of visible small fibres in the dust. Such abrasion was not reproducible and likely accounts for the more variable concentrations of HBCDs in the post-experiment dust samples. The importance of an appropriate experimental configuration is clearly shown by these results and the UoB chamber was more fit-for-purpose for these highly specific experiments.

4. Conclusions

Migration of HBCDs and PBDEs from source materials to dust *via* volatilisation and subsequent deposition was demonstrated for the first time in test chamber experiments, confirming that this pathway is an important contributor to the concentrations of BFRs widely observed in indoor dust. Experimental evidence is provided that confirms sink effects are an important issue associated with chamber studies of BFRs. Moreover, this study demonstrates that chamber configuration, dimensions, and operating conditions exert substantial influences on experimental outcomes, and that a thorough understanding of such factors is essential to facilitate correct interpretation of data generated by chamber studies. Notwithstanding these issues, the ease with which volatilisation from a source followed by deposition to dust can be reproduced in test chambers, both underlines the validity of this migration pathway, and the potential for similar chamber experiments to study the migration to dust of BFRs and other SVOCs from a range of source materials *via* this and other hypothesised pathways.

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Figures and Tables

Figure 1: (Top) Photograph of UoB test chamber configured for experiments monitoring emissions to air and (bottom) Schematic of experimental design for source-air-dust transfer experiments. For UoB chamber x,y =10 cm, for micro-chamber x = 1 cm, y = 2 cm.

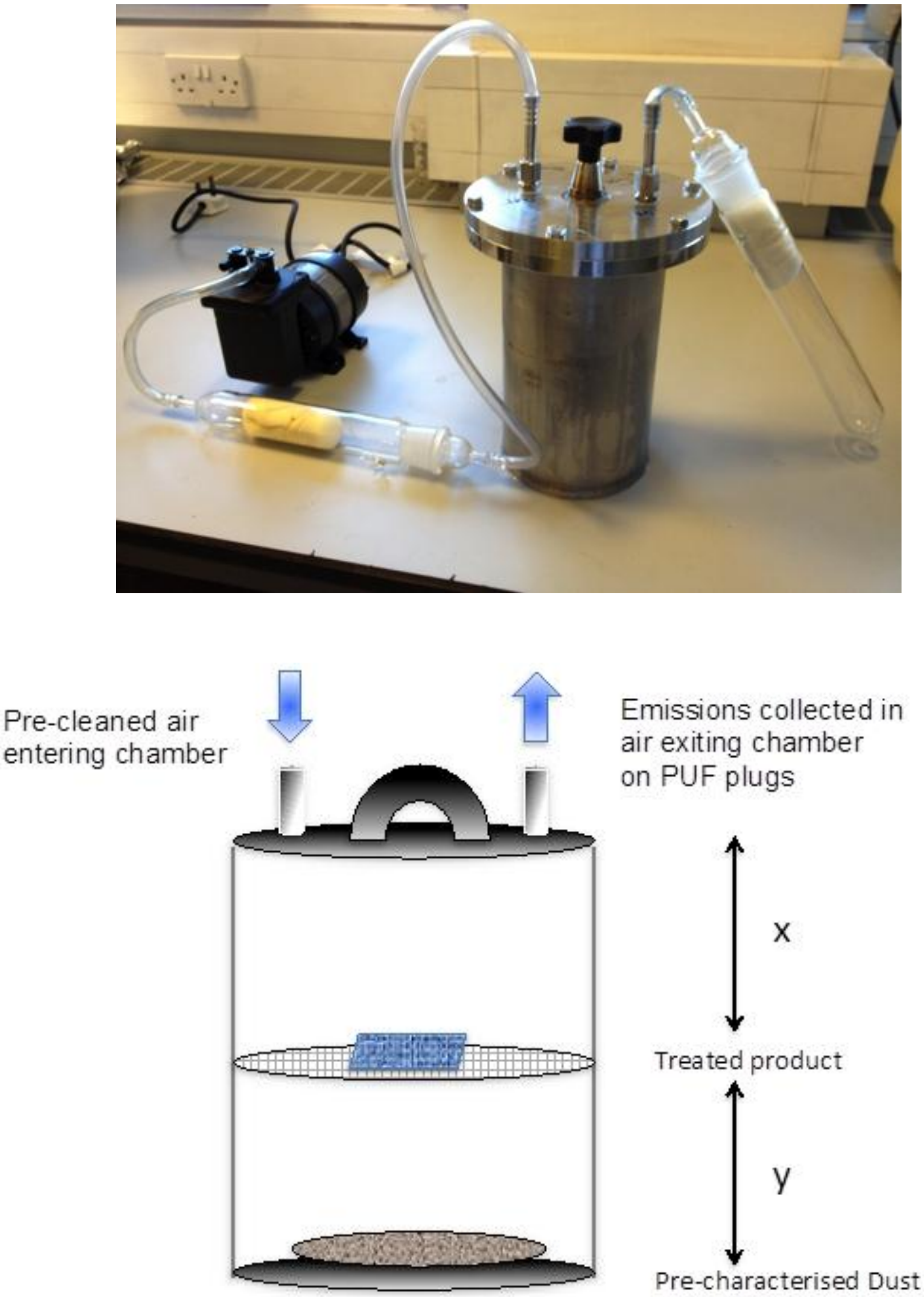

Figure 2: Photographs of the micro-chamber showing (top) Chamber modifications for the dust experiments, and (bottom) Experimental configuration of the 6 linked chambers configured for monitoring emissions to air.

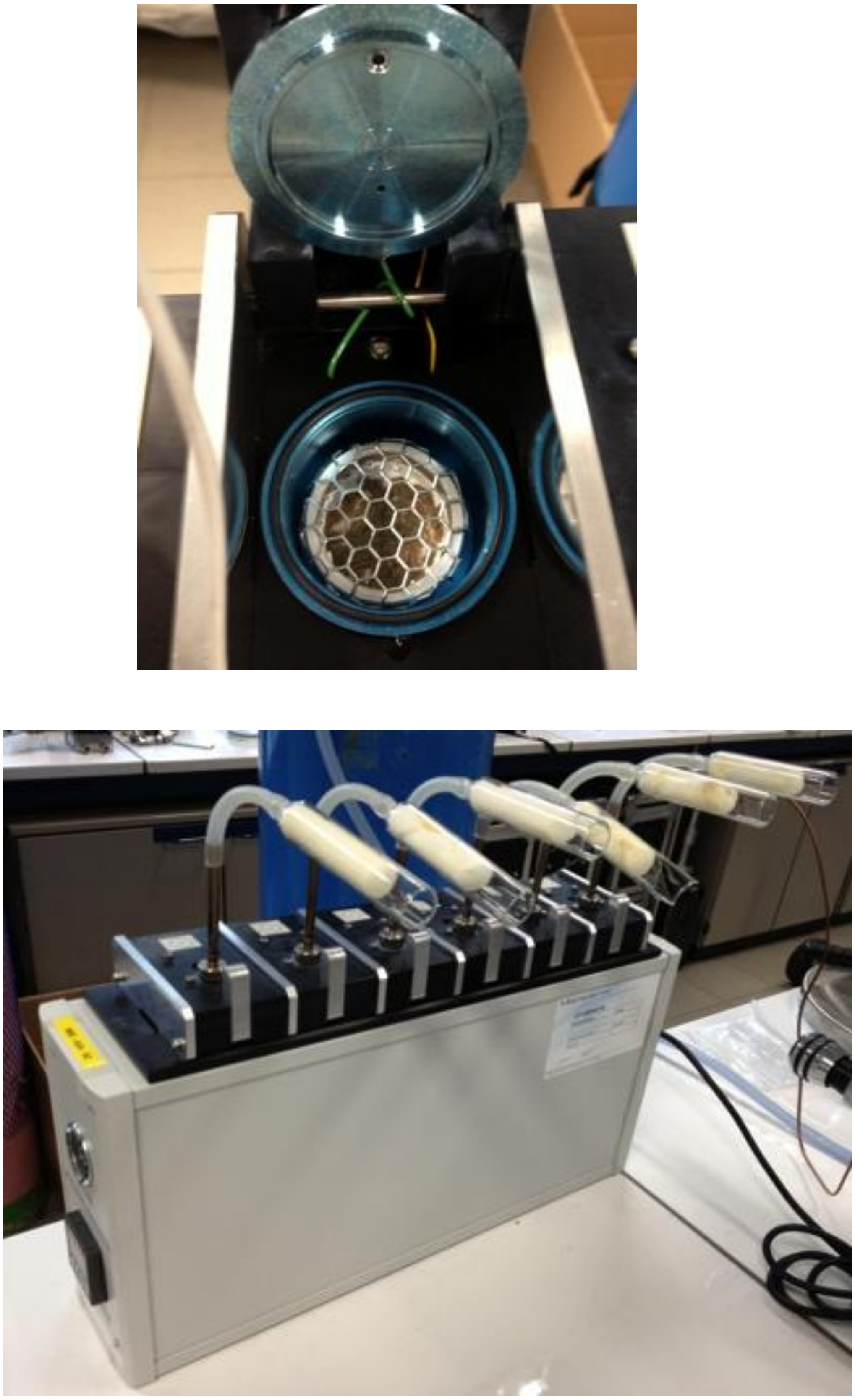

Figure 3: Mass of BFR (ng) collected on PUF plugs sampling chamber exit air for different exit air sampling train lengths

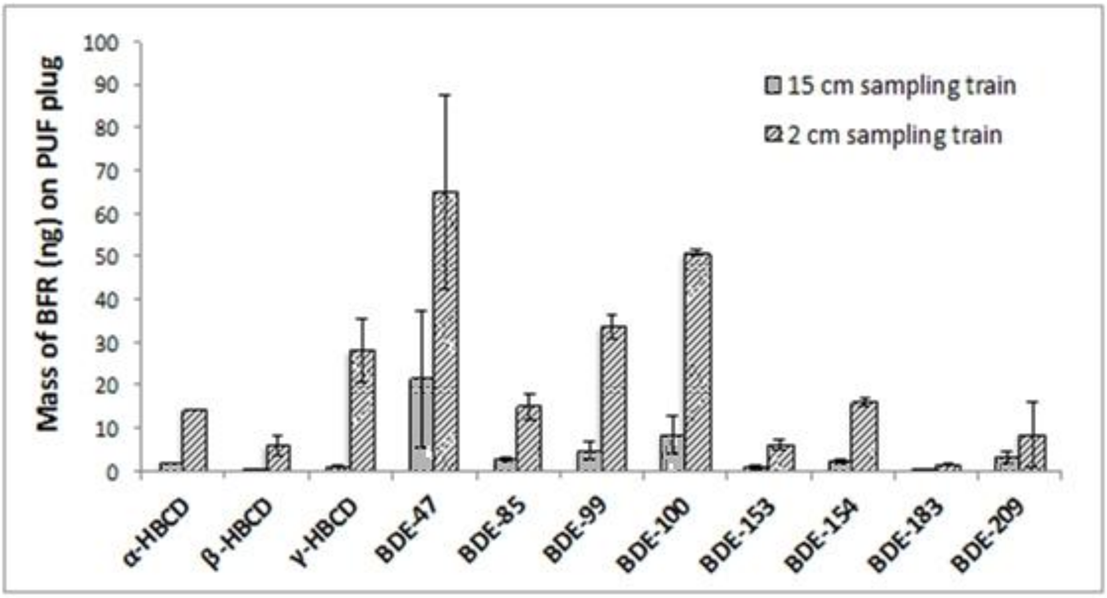

Figure 4: Concentrations (ng g^{-1}) of PBDEs in dust, pre and post partitioning experiment in the UoB chamber (n=3) and micro-chamber (n=6) using a spiked GFF as the source

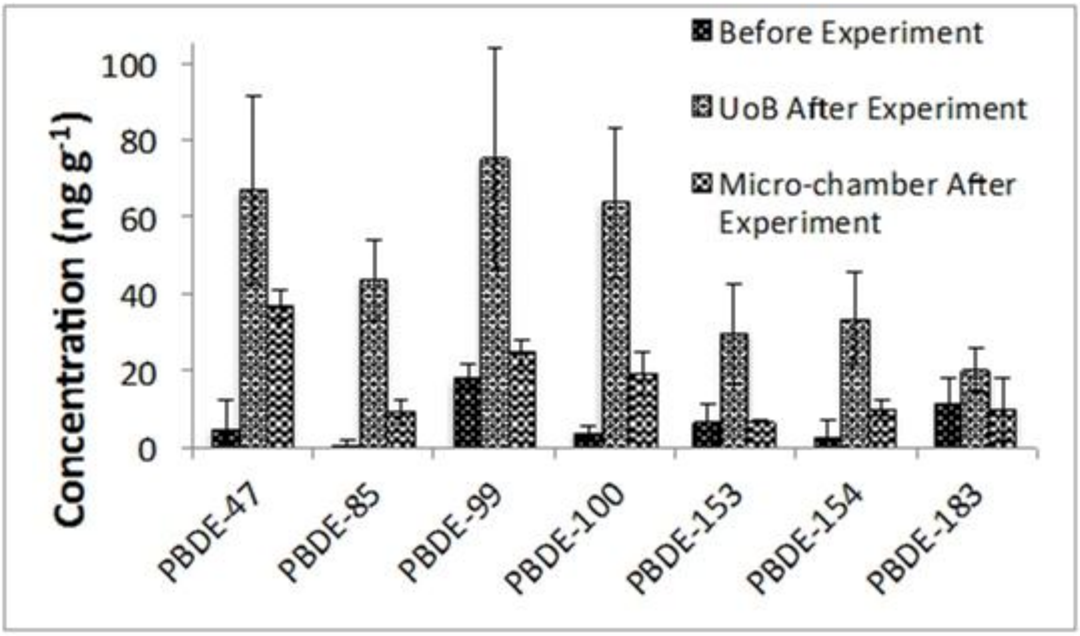

Figure 5: Average recovery (%) of PBDEs in various components in (top) the UoB chamber (n=3) and (bottom) the micro-chamber (n=6) using a spiked GFF as the source

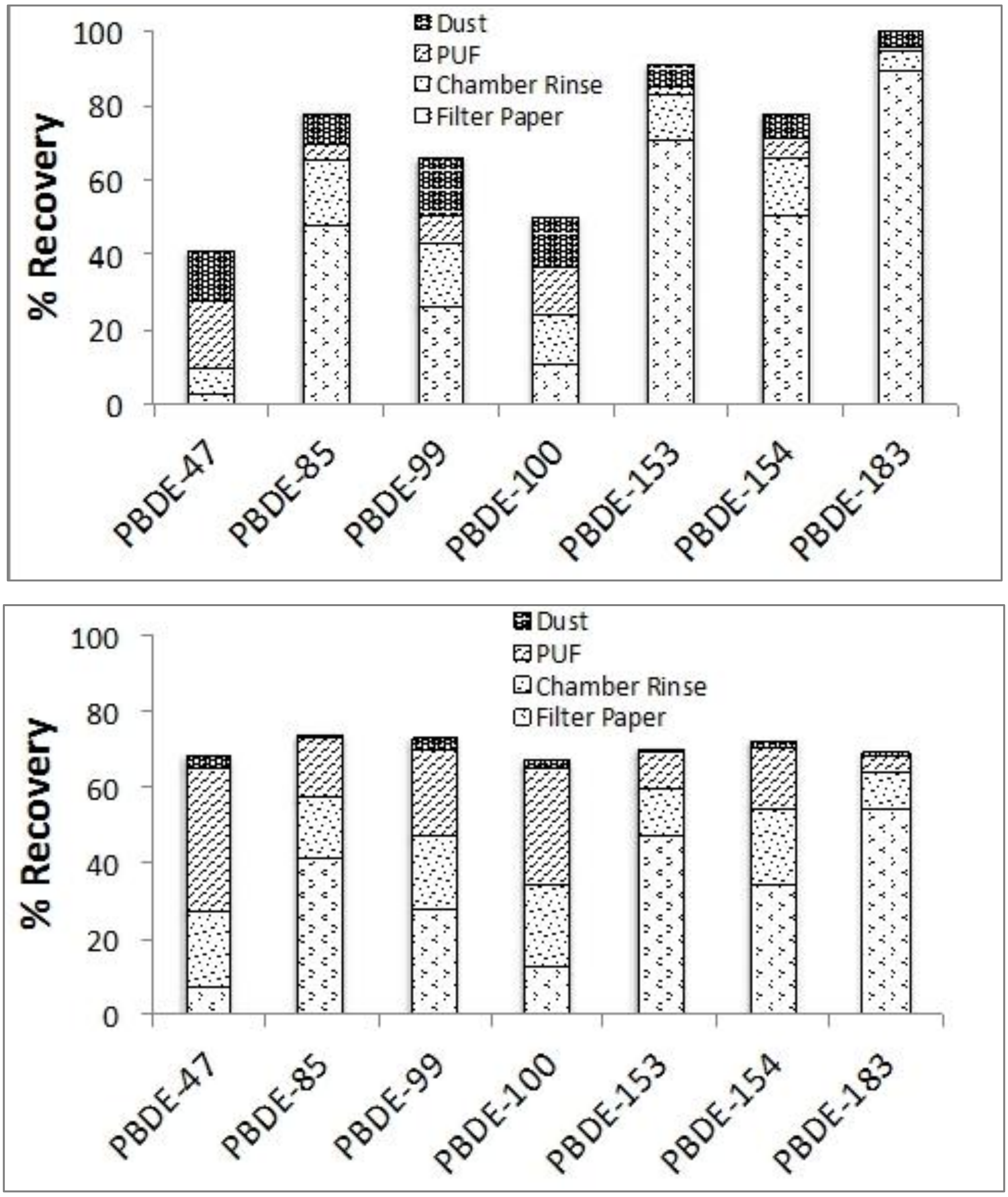

Figure 6: Concentrations of HBCDs in dust (ng g^{-1}) pre- and post-experiments using a HBCD-treated curtain as the source after: (top) 24 hours at 60 ˚C in the UoB chamber (n=4); (middle) 1 week at room temperature in the UoB chamber (n=3), and (bottom) 24 hours at 60 ˚C in the micro-chamber (n=6)

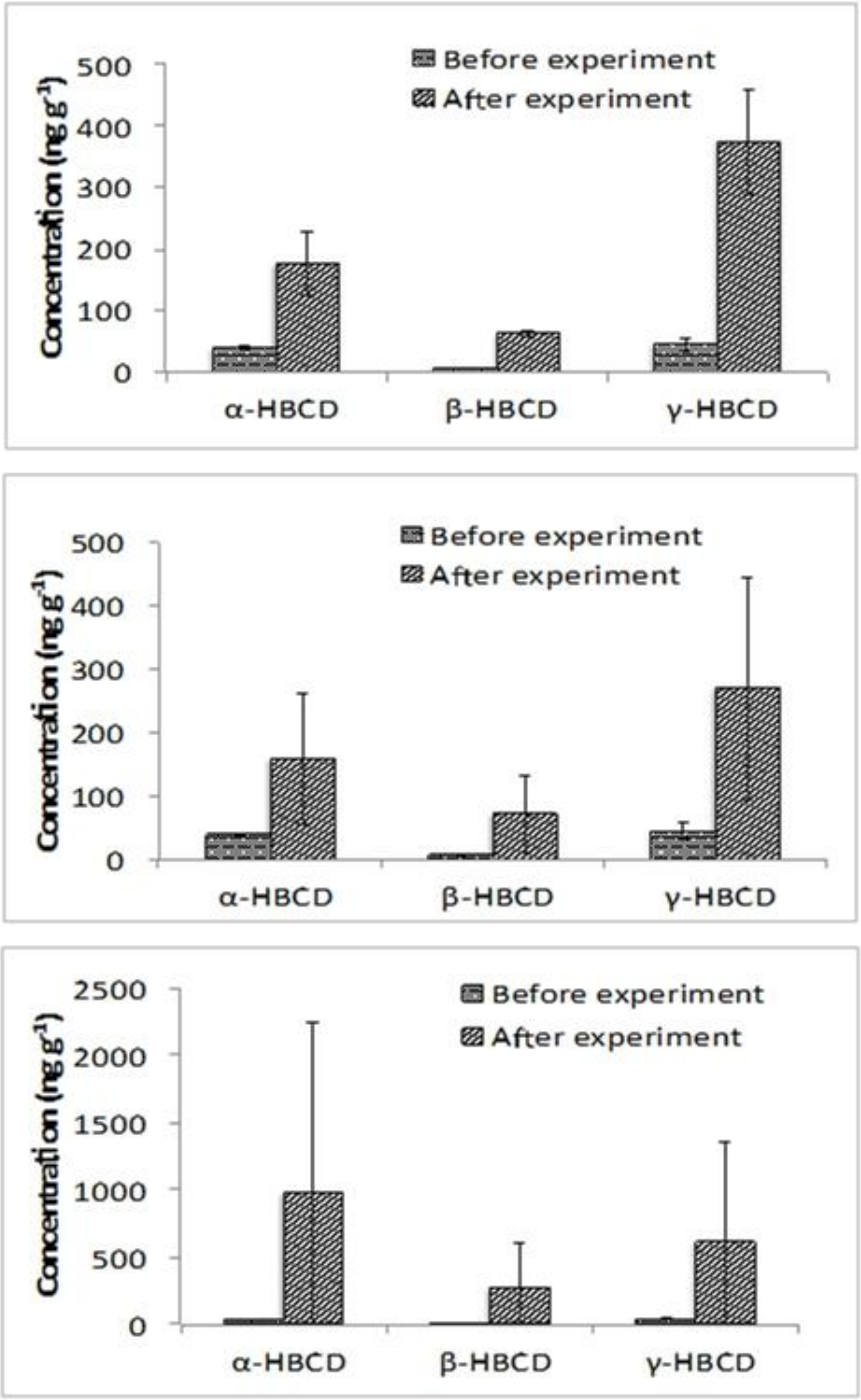

Table 1: Recoveries (%) of BFRs from PUF breakthrough experiments

	BDE-47	**BDE-85**	**BDE-99**	**BDE-100**	**BDE-153**	**BDE-154**	**BDE-183**	**BDE-209**	**α-HBCD**	**β-HBCD**	**γ-HBCD**
Birmingham Chamber	93	106	105	106	101	100	92	107	92	93	100
Micro-chamber	102	80	94	92	88	89	82	92	82	87	83

Table 2: Average (± standard deviation) recoveries of PBDEs and HBCDs from various components during experiments testing sink effects for the UoB and micro-chambers

	BDE-47	**BDE-85**	**BDE-99**	**BDE-100**	**BDE-153**	**BDE-154**	**BDE-183**	**BDE-209**	**α-HBCD**	**β-HBCD**	**γ-HBCD**
Total recovery (%) UoB chamber (n=1)	43	52	54	51	89	78	76	90	89	70	65
Total recovery (%) Micro-chamber (n=8)	47 ± 14	50 ± 6.1	49 ± 8.9	46 ± 13	53 ± 9.1	51 ± 12	60 ± 6.0	97 ± 14	55 ± 22	36 ± 21	25 ± 26
Recovery (%) GFF-UoB	5.3	21	13	10	59	35	71	85	86	69	63
Recovery (%) GFF - Micro	6.2 ± 5.9	13 ± 6.0	10 ± 5.4	8.0 ± 5.2	25 ± 14	15 ± 13	45 ± 11	96 ± 14	45 ± 21	32 ± 20	20 ± 23
Recovery (%) surface rinse - UoB	38	32	41	41	30	43	5.6	4.3	2.6	1.0	1.8
Recovery (%) surface rinse - Micro	41 ± 9.8	37 ± 4.0	39 ± 5.5	38 ± 8.5	28 ± 5.7	36 ± 5.0	15 ± 5.3	1.4 ± 0.8	10 ± 3.1	4.4 ± 1.5	5.1 ± 2.9

Supplementary Data

Table SD-1: Average starting concentrations of BFRs (ng g^{-1}) in bulk dust used for chamber experiments from 6 and 7 repeat analyses respectively

	BDE-47	**BDE-85**	**BDE-99**	**BDE-100**	**BDE-153**	**BDE-154**	**BDE-183**	**BDE-209**	**α-HBCD**	**β-HBCD**	**γ-HBCD**
Birmingham House Dust (n=6)	4.6 ± 7.8	0.6 ± 1.0	17 ± 4.1	4.1 ± 1.6	6.6 ± 4.6	2.5 ± 4.9	11 ± 6.7	2036 ± 551	393 ± 106	180 ± 45	2609 ± 3238
Belgian House Dust (n=7)	9.9 ± 11	2.0 ± 1.8	27 ± 31	4.6 ± 4.7	5.9 ± 6.1	3.1 ± 3.0	1.9 ± 2.1	230 ± 176	46 ± 19	13 ± 10	50 ± 39

Table SD-2: Average concentrations (ng g^{-1}) in 7 analyses of SRM 2585 and the reported certified PBDE (Stapleton et al., 2006) and indicative HBCD values (Keller et al., 2007)

	BDE-47	**BDE-85**	**BDE-99**	**BDE-100**	**BDE-153**	**BDE-154**	**BDE-183**	**BDE-209**	**α-HBCD**	**β-HBCD**	**γ-HBCD**
SRM Measured Value (n=7)	347 ± 39	35.1 ± 4.6	730 ± 93	133 ± 13	126 ± 13	78.6 ± 13	44.4 ± 5.0	2460 ± 400	19 ± 5.7	5.6 ± 2.2	98 ± 35
Certified/Indicative Values	*498 ± 46*	*43.8 ± 1.6*	*892 ± 53*	*145 ± 11*	*119 ± 11*	*83.5 ± 2.0*	*43.0 ± 3.5*	*2510 ± 190*	*19 ± 3.7*	*4.3 ± 1.1*	*120 ± 22*

Table SD-3: BFR mass collected on PUFs with different air sampling train lengths and analytes recovered (%) by heating the chamber post experiment

	BDE-47	**BDE-85**	**BDE-99**	**BDE-100**	**BDE-153**	**BDE-154**	**BDE-183**	**BDE-209**	**α-HBCD**	**β-HBCD**	**γ-HBCD**
PUF mass (ng) 15 cm tubing (n=3)	21 ± 16	2.8 ± 0.6	4.9 ± 1.9	8.4 ± 4.5	1.0 ± 0.3	2.3 ± 0.5	0.4 ± 0.1	3.2 ± 1.4	1.9 ± 0.2	0.7 ± 0.1	1.2 ± 0.4
PUF mass (ng) 2 cm tubing (n=2)	65 ± 23	15 ± 2.9	34 ± 2.6	51 ± 0.8	6.3 ± 1.0	16 ± 0.7	1.5 ± 0.2	8.4 ± 7.7	14 ± 0.1	5.9 ± 2.3	28 ± 7.7

Table SD-4: BFR recovery (%) on chamber exit PUF achieved by heating UoB chamber post-experiment to 80 ˚C for 6 hours

Recovery (%) (n=3)	2.1 ± 1.7	8.8 ± 4.7	9.0 ± 4.9	5.6 ± 3.3	4.5 ± 1.7	6.9 ± 3.5	1.7 ± 0.9	3.0 ± 1.0	12 ± 13	4.6 ± 6.3	22 ± 29

***Conflict of interest**

Conflict of Interest Declaration

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

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