Mass transfer of PBDEs from plastic TV casing to indoor dust via three migration pathways - A test chamber investigation

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DOI:

[10.1016/j.scitotenv.2015.07.050](https://doi.org/10.1016/j.scitotenv.2015.07.050)

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Document Version

Peer reviewed version

Citation for published version (Harvard):

Rauert, C & Harrad, S 2015, 'Mass transfer of PBDEs from plastic TV casing to indoor dust via three migration pathways - A test chamber investigation', *Science of the Total Environment*, vol. 536, pp. 568-574.
<https://doi.org/10.1016/j.scitotenv.2015.07.050>

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1 **TITLE**

2 Mass Transfer of PBDEs from plastic TV casing to Indoor Dust via Three Migration
3 Pathways - a Test Chamber Investigation

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Abstract

Polybrominated diphenyl ethers (PBDEs) are widely detected in humans with substantial exposure thought to occur in indoor environments and particularly via contact with indoor dust. Despite this, knowledge of how PBDEs migrate to indoor dust from products within which they are incorporated is scarce. This study utilises an in-house designed and built test chamber to investigate the relative significance of different mechanisms via which PBDEs transfer from source materials to dust, using a plastic TV casing treated with the Deca-BDE formulation as a model source. Experiments at both room temperature and 60 °C revealed no detectable transfer of PBDEs from the TV casing to dust via volatilisation and subsequent partitioning. In contrast, substantial transfer of PBDEs to dust was detected when the TV casing was abraded using a magnetic stirrer bar. Rapid and substantial PBDE transfer to dust was also observed in experiments in which dust was placed in direct contact with the source. Based on these experiments, we suggest that for higher molecular weight PBDEs like BDE-209; direct dust:source contact is the principal pathway via which source-to-dust transfer occurs.

Keywords

Brominated flame retardants, PBDEs, Migration pathways to dust, Test chambers

44 **Research Highlights**

- 45 • Transfer from a TV casing to dust of high molecular weight PBDEs examined
- 46 • Direct source:dust contact effected rapid and most substantial transfer
- 47 • Substantial source:dust transfer also occurred via abrasion of source

1. Introduction

Brominated flame retardants (BFRs) have numerous applications in indoor environments and are found ubiquitously in indoor air and dust, leading to human exposure and resultant concerns about adverse health impacts. As the majority of BFRs in current use are incorporated into the product using an additive process they are considered loosely bound to the product and are hence available for possible migration from the treated product to dust in particular, via different mechanisms. Hypothesised pathways of BFR migration to dust include: (1) volatilisation of BFRs from the treated product with subsequent partitioning to dust; (2) abrasion via physical wear and tear of the treated product, resulting in the transfer of particles or fibres of the treated product directly to dust (Wagner et. al., 2013, Webster et. al., 2009); and (3) transfer via direct contact between the treated product and dust (Takigami et. al., 2008).

One of the principal classes of additive BFRs are polybrominated diphenyl ethers (PBDEs), which have been in use since the 1970s (ATSDR, 2004) primarily as additives in polyurethane foam (PUF); printed circuit boards and microprocessor packaging in computers; thermoplastics, such as high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS) copolymers; and textiles (La Guardia et. al., 2006, Harrad et. al., 2008). Despite their presence at elevated concentrations in indoor dust (up to 210 mg g⁻¹ of BDE-209 (Batterman et. al., 2009)), relatively little is known about how PBDEs transfer to dust from goods within which they are incorporated. Combined with evidence about the potential adverse health impacts of PBDEs (USEPA 2008a, USEPA 2008b) this is of concern as dust has been shown to be an important exposure pathway of PBDEs for toddlers who spend extended time periods crawling over surfaces and display extensive hand-to-mouth contact ((Jones-Otazo et. al., 2005); Stapleton et al., 2012). Moreover, it is estimated that US children (1-5 years) have higher PBDE intakes than adults, and that a combination of ingestion and dermal contact with indoor dust contributes 82% of overall total adult exposure of tri to deca PBDEs (Lorber, 2008).

Emission chamber studies to date have focused largely on measurement of emissions to air of BFRs and other semivolatile organic compounds (SVOCs) from treated products (Rauert et. al., 2014c). The authors previous work has investigated the migration of hexabromocyclododecane (HBCD) from a textile treated with the HBCD technical formulation via migration pathways (1) and (2) (Rauert et. al., 2014a and 2014b), however to their knowledge the migration of PBDEs via any migration pathway has yet to be studied. 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 partitioning to dust, and via direct transfer as a result of contact between the source material and dust. This study for the first time investigates experimentally, the migration of higher molecular weight PBDEs (particularly BDE-209) from a model source to dust *via* three different migration pathways, using an in-house test chamber. The contribution of each pathway to total PBDE dust contamination is discussed, highlighting areas for future chamber experiments.

2. Materials and Methods

2.1. *PBDE treated plastic TV casing and low concentration dust procurement*

The model source used in this study consisted of plastic TV casing, treated with PBDEs. It was received as small triangular pieces each weighing ~100 mg from the National Institute for Environmental Studies (NIES), Tsukuba, Japan. The sample was a composite of 50 cathode ray tube (CRT) back casings (high impact polystyrene) that had been melted and remoulded to form a material for interlaboratory tests. Four replicate analyses of the TV casing by NIES using methods reported previously (Takigami et al, 2008), determined the concentrations of PBDEs in the sample, listed in Table 1. The higher RSDs (> 20%) of some congeners suggest a degree of inhomogeneity in the distribution of these compounds throughout the TV casing.

In order to more easily detect increments in PBDE concentrations in dust as a result of emissions from the model source, all experiments in this study used a dust sample containing low concentrations of PBDEs (Σ PBDEs = 280 ng g⁻¹). This was derived from a vacuum cleaner bag taken from a private residence in Belgium in 2012 and stored at -18 °C thereafter. The dust was sieved at <500 µm before homogenisation

via vortexing. Concentrations of PBDEs in this dust, determined from repeat (n=9) analyses are provided in Table 2. The low concentration dust showed a level of inhomogeneity for BDE-209 ($230 \pm 180 \text{ ng g}^{-1}$) and this may pose a limitation to this study, yet due to the low concentrations present, this dust was judged suitable for this study.

2.2. Test Chamber Experiments

Chamber experimental designs for investigating the migration of HBCDs *via* the first two proposed migration pathways have been reported previously (Rauert et. al., 2014a, Rauert et. al., 2014b). The experimental details are summarised in the following section.

2.2.1 Experimental design for investigating volatilisation with subsequent partitioning to dust.

A cylindrical in-house designed and built test chamber was utilised for these investigations; 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. This air flow provided an air exchange rate (400 times per hour) that would exceed that viewed in a 'real world' scenario (in general 4 times per hour) but was used due to equipment restrictions. The higher air flow may have resulted in removal of more volatile congeners before partitioning to dust, thereby leading to capture on the PUF plug. 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 suspended 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. The inclusion of an aluminium mesh shelf situated approximately 10 cm above the chamber floor, allowed physical separation of a 2 cm x 2 cm portion of the model source placed on the shelf from an aliquot of low concentration dust (200 mg) placed on a glass fibre filter (GFF, Whatman,

Loughborough, UK) on the chamber floor. The chamber was sealed, with air flow, and experiments run for: (a) 24 hours at 60 °C, and (b) 1 week at room temperature (22 ± 1 °C). The 60 °C maximum temperature scenario was chosen to represent a high emission case of an electronic item heated during operation (Kemmllein et. al., 2003). Post experiment, the dust was analysed for concentrations of PBDEs.

2.2.2 *Experimental design for investigating abrasion.*

The test chamber was next utilised to investigate migration via abrasion of particles to dust. The experimental configuration employed for this purpose is illustrated in Figure 2. The removable aluminium shelf was placed 3 cm above the chamber floor and a magnetic stirrer bar, 40 mm x 8 mm, (Fisher Scientific, Leicestershire, UK) placed on the shelf to act as the abrading mechanism. The model source was placed on the shelf and a known mass of low concentration dust (200 mg) placed on a glass fibre filter (GFF), situated on the chamber floor. The chamber was sealed (with air flow attached to collect emissions on polyurethane foam (PUF) plugs attached to the exit air vent) and placed on a magnetic stirrer plate, operated at 200 rotations per minute. In this way, abrasion was replicated via direct contact between the rotating stirrer bar and the treated product, with any particles thus generated, falling through the mesh shelf and incorporated into the dust sample below. This process was conducted at room temperature (22 ± 1 °C) to minimise volatilisation, and repeated for four experimental durations of 2, 3, 24, and 48 hours. This chamber abrasion process does not map directly on to real time abrasion of rigid polymeric materials like TV casing; instead it is aimed at mimicking long-term abrasion from repeated wiping/moving/bumping of the source product; all of which processes are likely accentuated by weathering (e.g. by sunlight) over time. Consequently, results from our chamber experiments were extrapolated to ‘real world’ abrasion. It was assumed that the PBDE mass transferred in 5 seconds of chamber abrasion equated to mass transfer occurring during 5 seconds of ‘real world’ abrasion. A ‘maximum transfer’ scenario of 5 seconds of abrasion per day was used in further calculations to determine the PBDE mass transferred per year from abrasion.

Post experiment the dust aliquot was analysed for concentrations of BFRs.

2.2.3 Experimental design for investigating transfer via direct contact between source and dust particles

The chamber experimental design was modified to investigate migration pathway (3) and the experimental design is illustrated in Figure 3. The aluminium mesh shelf was now placed 10 cm above the chamber floor. The model source was placed on top of a clean GFF situated on the shelf, and a thin layer of dust (~150 mg) placed evenly on the top surface of the BFR treated product. The dust was lightly and carefully sprinkled over the surface of the product using laboratory tweezers. The chamber was sealed (with no air flow, to minimise disturbance of the dust) and left at room temperature (22 ± 1 °C) for either 24 hours or 1 week. Post experiment the dust was removed by gently agitating the source, homogenised through vortex mixing, and analysed. Each time period was repeated in duplicate with the entire dust sample analysed for BFRs.

2.3. Determination of concentrations of PBDEs

2.3.1. Chemicals

All solvents used for extraction and analysis were of HPLC grade quality (Fisher Scientific, Loughborough, UK). Standards of PBDEs (BDE-47, 85, 99, 100, 153, 154, 183, 209), labelled ^{13}C -PBDEs (^{13}C -BDE 47, 99, 100, 153, 209), were acquired from Wellington Laboratories (Guelph, ON, Canada). Florisil (60-100 mesh) and silica gel (60Å, 60-100 mesh) were provided from Sigma Aldrich (Dorset, UK). Concentrated sulfuric acid (95-97%) was obtained from Merck (Darmstadt, Germany). Glass fibre filters (GFF, 12.5 cm diameter, 1 µm pore size, Whatman, UK) were purchased from Agilent (UK).

2.3.2. Sample analyses

PUF and dust samples generated by test chamber experiments were extracted and analysed using modified in-house methods as reported previously (Rauert et. al., 2014a, Rauert et. al., 2014b). Briefly, samples were spiked with ^{13}C -PBDE analogues as internal (surrogate) standards prior to pressurised liquid extraction (ASE, Dionex Europe, UK, ASE 350) with hexane:dichloromethane (1:1 v/v). After clean-up of the crude extracts via elution through sulfuric acid-impregnated silica (44% w/w), the eluates were evaporated and made up to 100 µL using ^{13}C -BDE 100 in methanol, as a

recovery determination (or syringe) standard. Analyte separation was achieved with a Varian Pursuit XRS3 (Varian, Inc., Palo Alto, CA) C18 reversed phase analytical column (250 mm x 4.6 mm i.d., 3 μ m particle size). Analysis was conducted with 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 ion source, operated in negative ion mode.

2.4. Quality Assurance

Samples were analysed using established QA/QC procedures. Method blanks were conducted by extracting a pre-cleaned 66 mL cell filled with Hydromatrix and were run with each batch of samples, and a clean PUF was extracted for a PUF blank. Concentrations of all target PBDEs in all blanks were <LOQs. Method LOQs were calculated assuming 0.2 g of dust (calculated as ng g⁻¹) or as ng per PUF/chamber rinse and was calculated as the concentration relating to a 10:1 signal to noise ratio. For ¹³C BDE-47, 99, 153 and 209, average recoveries ranged from 80 to 85%. Accuracy and precision of the analytical method was assessed via replicate analyses (n=15) of NIST SRM 2585 (organics in house dust). The results of these analyses compared with certified values as appropriate are supplied as supplementary data (Table SD-1). Experimental data is presented as mean values of replicate experiments $\pm$ standard deviations.

3. Results and Discussion

3.1. Test chamber experiments examining source-to-dust transfer via volatilisation and subsequent partitioning to dust

For the experiments conducted to examine transfer of PBDEs to dust via volatilisation from the model source and subsequent partitioning to dust, concentrations of PBDEs in the dust both pre and post experiment combined with masses detected on air exit PUFs and in chamber inner surface solvent rinses are given in Table 2. A clear increase in PBDE concentrations in dust, post experiment, was not observed in these experiments, with the exception of experiment 2 conducted over 24 h at 60 °C. Moreover, PBDEs were not detected above LOQs (0.8 to 4.5 ng per PUF) on the PUF,

at either temperature, and only minor quantities were detected in the chamber surface rinses. These PUF and chamber rinse results further suggest that the PBDEs are not volatilising from the TV casing in this chamber configuration. We have previously reported on experiments (Rauert et. al., 2014a) using the same experimental configuration but in which the model source was a filter paper spiked with 100 ng each of BDEs 47, 99 and 100. In contrast to our observations when TV casing material was the model source, these earlier experiments revealed clear increments in post-experiment concentrations of these congeners in dust, even though lower concentrations were studied in the chamber in these filter paper experiments. Specifically, the masses of BDE-47, 99 and 100 present in the model source in the current experiments were 390, 960 and 330 ng respectively (up to ~10 times higher concentration than in the spiked filter paper experiments). A plausible explanation for these different outcomes is that PBDEs are more strongly bound to the TV casing than they are to the GFF, and are hence less available for volatilisation. Moreover, the melting and remoulding process used to produce the material tested may also have influenced the strength with which the PBDEs are bound to the polymer. In addition, the greater surface area:volume ratio of the GFF will likely contribute in more facile volatilisation of PBDEs.

Although BDE-209 was detected in dust post-experiment in each experiment; in 3 out of 4 cases, concentrations were not substantially different to those present in the dust pre-experiment. This suggests that migration of BDE-209 from the TV casing to dust via this pathway was minimal. However, the second chamber experiment conducted for 24 hours at 60 °C reveal a sizeable increment in the BDE-209 concentration in the dust post-experiment (4800 ng g⁻¹) compared to the starting concentration (230 ± 180 ng g⁻¹). A possible explanation is that the dust in this experiment was contaminated as a result of abrasion of the model source brought about by the air flow within the chamber. Although an increment was only observed for BDEs 183 and -209 in this specific experiment, this is likely because of the much lower concentrations of other target PBDEs in the TV casing, such that any casing particles transferred would make a negligible impact on dust concentrations. We have reported a similar effect in chamber experiments examining HBCD transfer from a fabric source to dust (Rauert et al., 2014b). However, we recognise that such air flow induced abrasion is less likely for the TV casing studied here. In conclusion, these chamber experiments

suggest that migration from plastic TV casing to dust, of PBDEs consistent with treatment with the Deca-BDE formulation via volatilisation and subsequent partitioning to dust is minimal. We emphasise however, that our earlier work (Rauert et al., 2014b) suggests strongly that such migration will likely be substantial from source materials containing elevated concentrations of PBDEs more volatile than those present in the material tested here, in which BDE-209 predominated.

3.2. Test chamber experiments for abrasion of particles to dust

Table 3 shows the concentrations of target PBDEs detected in dust following the experiments described in section 2.1.2, in which source-to-dust transfer via source abrasion was examined. Post experiment there was a clear increase in concentrations of BDE-183 and BDE-209 in dust in each experiment conducted over all time intervals studied. Discernible increases in concentration were also observed for BDEs-153 and 154 in 2 out of 4 experiments. Concentrations of other target PBDEs were not discernibly higher post-experiment in any instance.

In contrast to the outcome of our previously reported abrasion experiments using HBCD treated curtains as the source (Rauert et. al., 2014b); there was no apparent relationship between abrasion duration and concentration of either BDE-183 or -209. This is likely attributable to the inherently inconsistent nature of the abrasion process. Specifically, it was particularly difficult in our experiments to abrade the TV casing pieces in a reproducible fashion, as they had a tendency to ‘flick’ around the chamber. Evidence that the increment observed in concentrations of some PBDEs in dust during these experiments is attributable to abrasion of the TV casing source is provided by comparison of congener patterns in the TV casing and the dust both pre- and post experiment. To facilitate this, the concentrations of PBDEs detected in each sample were log-transformed (to permit clearer visual comparison of the contributions of less abundant congeners) and expressed as percentage contributions to the sum of PBDEs. Figure 4 compares the relative contributions of BDE-209 and BDE-183 in each sample in all four experiments, showing a similar pattern in the chamber generated abrasion dust samples to that in the TV casing, that differs from that in the dust pre-experiment. The similarity between congener profiles in the TV casing and post-experiment dust samples, that both differ from that observed in the dust pre-

experiment, provide strong evidence that PBDEs have entered dust as a result of abrasion of small particles of the TV casing.

Our results also indicate that abrasion of the plastic material will not result in a linear relationship between abrasion time and PBDE concentration transferred to dust. The resultant PBDE mass transferred will be highly dependent on the size and PBDE concentration of the particles transferred during the abrasion process. As reported in our previous findings (Rauert et. al., 2014b) BDE-209 containing polymer particles observed in sampled indoor dust varied in measurable size from 30 to 250 μm in length. When coupled with the forensic microscopy investigation of 'real' dust samples reported previously (Rauert et. al., 2014b), our results suggest that abrasion of plastic fragments into dust is a feasible and important migration pathway.

As highlighted earlier in 2.2.2, the abrasion induced in these test chamber experiments does not represent realistic abrasion from e.g 24 hour use of a TV, as this method is highly rigorous. However, we have interpreted these results as an acceleration test to mimic long-term abrasion. To achieve this aim an estimate of possible abrasion time of a TV casing needs to be made. Abrasion can occur from wiping/cleaning the product but it is likely that for TV casing abrasion would be further encouraged from degradation of the polymer due to high product operation temperatures (at least 60 $^{\circ}\text{C}$ (Kemmlen et. al., 2003)), or UV degradation encouraged by direct sunlight exposure, hence relating chamber results to the 'real world' is difficult.

In the maximum PBDE mass transferred abrasion scenario, it was assumed TV abrasion occurred for about 5 seconds a day, which included cleaning (such as wiping) and enhanced polymer degradation leading to increased abrasion. The 2 hour chamber abrasion experiment may thus represent house dust concentration increment from abrasion over 1440 days (~4 years), where dust is contaminated with 22 000 μg of BDE-209 (the mass transferred during the 2 hour abrasion experiment), equating to 5400 μg of BDE-209 contamination per year. Other product uses of BFR treated plastics (such as computer keyboards) that have higher user contact time periods would be expected to suffer even more extensive abrasion. There are many uncertainties associated with these calculations, including the assumption that

abrasion via contact with a rotating stir bar is representative of ‘real world’ abrasion. While acknowledging such uncertainties, the abrasion induced in these chamber experiments represents a first attempt to imitate migration via abrasion from a product treated with BFRs into dust and relate the migration to a ‘real world’ scenario. Abrasion will also depend on factors such as: the product material (e.g. plastic or fabric), how and how often the product is used, as well as its age and extent to which it is exposed directly to UV light and consequent weathering. We conclude from our studies that the ease with which abrasion can be replicated in these chamber experiments, suggests it is a feasible migration pathway.

3.3. Test chamber experiments for direct contact between source:dust

Table 4 presents the concentrations of PBDEs detected in dust both before and after experiments examining source-to-dust transfer as a result of direct contact (section 2.1.3). The average BDE-209 concentration present in dust after the two different exposure durations examined, reveal greater mass transfer after 1 week (4,900 ng g⁻¹), than after 24 hours (820 ng g⁻¹). This suggests that BDE-209 has not reached source:dust equilibrium after 1 day of source:dust contact. While more detailed work is required to characterise the kinetics of such transfer, this observation has practical implications, as it implies that frequent cleaning to remove dust from source surfaces will minimise contamination of dust. Also of interest, replicate experiments for each exposure duration show large variations in concentrations of PBDEs in dust (590-1000 and 1000-8700 ng g⁻¹ for 24 hours and 1 week of exposure respectively). This may be due to an inhomogeneous distribution of PBDE concentration across the surface of the source in contact with dust; and/or as a consequence of an inhomogeneous distribution of the organic carbon content of the exposed dust.

Figure 5 shows the PBDE congener pattern (expressed as percentage contributions to log-normalised Σ BDEs) in the dust post-experiment compared with that in the TV casing and in the dust pre-experiment. Due to the lower concentrations in the second 24 hour duration experiment, only BDE-209 was detected, hence this experiment is not included in this comparison. A similar congener profile was seen in post-experiment dust and the TV casing, that differed from that in the dust pre-experiment.

380 These findings provide further evidence of substantial source-to-dust transfer of
381 PBDEs in these experiments.

382
383 The physical processes effecting migration of SVOCs between source and dust via
384 direct contact are not completely understood. However, Schripp et. al. (2010)
385 suggested SVOC transfer occurs as a result of contact between dust and gas phase
386 contaminants present in the boundary layer directly above the source. Compounds
387 with lower vapour pressures will be less abundant in this layer (and experience a
388 slower release into the boundary layer to replace mass sorbed by dust) leading to
389 lower mass transfer. Such a transfer mechanism would lead to congener ratios in post-
390 experiment dust that would be enriched in more volatile PBDEs compared to the
391 pattern present in the source. While more evidence is required to fully evaluate the
392 mechanisms via which source-to-dust transfer of PBDEs occurs via direct source:dust
393 contact, inspection of Figure 5 presents it is not consistent with the hypothesis of
394 Schripp et. al. (2010). An alternative explanation – advanced by Clausen et. al. (2004)
395 - is that transfer may occur as a consequence of direct contact between the source and
396 dust particles. In this scenario, the role of the boundary layer is replaced by the dust
397 particles, and the influence of vapour pressure is minimised. This explanation appears
398 more consistent with our experimental observations.

399
400 Only a few studies have investigated BFR concentrations in dust samples removed
401 from putative sources in indoor microenvironment studies. Prominent amongst these,
402 the study by Takigami et. al. (2008) reported elevated concentrations of BDE-209 in
403 dust sampled directly from the back casings of various TVs compared to that in the
404 surrounding floor dust. The components of the TV were also analysed for PBDEs,
405 with BDE-209 the dominant congener in the rear plastic cabinets of the TVs and in all
406 dust samples. As the congener profile in the dust sampled from the TV was similar to
407 that in the TV components it was strongly suggested that extensive PBDE transfer
408 occurred directly from the components in the TV casing to the dust, a similar finding
409 to that seen in these chamber experiments. The rapid transfer and high PBDE masses
410 transferred to dust further confirm that direct contact between dust and source
411 materials is a potentially important pathway of BFR migration to dust, particularly for
412 the low volatility BDE-209.

413

3.4. Comparison of three migration pathways

The migration of BDE-209 to dust in indoor microenvironments is strongly influenced by the abrasion and direct contact migration pathways. In contrast, volatilisation with subsequent partitioning to dust appears to exert little influence over mass transfer. This result is expected as the very low vapour pressure of BDE-209 implies it will undergo minimal volatilisation. The abrasion chamber configuration was successful in abrading a plastic matrix containing PBDEs, with elevated concentrations detected in dust after as little as 2 hours of abrasion. The direct contact experiments transferred highly elevated concentrations to dust and the majority of the transfer was achieved in the first 24 hours of exposure.

In conclusion, while further experiments are required, this study provides evidence that under ‘real world’ scenarios, migration of BDE-209 to dust is likely due to a combination of the three migration pathways reported here. Our study highlights areas requiring future research. We recognise that the experimental conditions examined here do not necessarily represent ‘real-world’ scenarios and hence results are presented as a preliminary indication of the relative importance of different pathways via which BDE-209 undergoes source-to-dust transfer. Future studies should also investigate a range of organic flame retardants, both those of higher volatility as well as those incorporated reactively as the relative importance of the pathways examined here will likely vary substantially from that observed here for additive, low volatility PBDEs.

Acknowledgements

The research leading to these results has received funding from the European Union Seventh Framework Program (FP7/2007-2013) under grant agreement No 264600 (INFLAME project). We also thank Natusuko Kajiwara and Hidetaka Takigami from the National Institute for Environmental Studies, Japan, for supplying the PBDE-treated plastic TV casing.

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Figures and Tables

Figure 1: Schematic of test chamber configuration for volatilisation with subsequent partitioning to dust experiments.

Figure 2: Schematic of test chamber configuration for abrasion experiments

Figure 3: Schematic of test chamber configuration for direct contact between source and dust experiments.

Pre characterised dust
layered on top of BFR
source material

Figure 4: Relative contributions (%) of BDE-209 and 183 in the four chamber generated abrasion dust samples, the original TV casing and the low concentration dust pre-experiment, derived from log-normalised concentrations

Figure 5: Relative contributions (%) of BDE-209 and 183 in direct contact experiment generated dust samples, the original TV casing and the low concentration dust pre-experiment, derived from log-normalised concentrations

Table 1: PBDE concentrations ($\mu\text{g g}^{-1}$) and %RSD of 4 analyses of the Plastic TV back casing used as the model source in this study

Analyte	Concentration ($\mu\text{g g}^{-1}$)	%RSD
BDE-47	1.3	15
BDE-85	N/A	N/A
BDE-99	3.2	27
BDE-100	1.1	39
BDE-153	520	26
BDE-154	59	22
BDE-183	3 700	21
BDE-209	90 000	19

* N/A = not analysed

547 *Table 2: Concentrations of PBDEs (ng g⁻¹) in dust pre (n=9) and post volatilisation experiments and mass of PBDEs (ng) collected on PUFs*
548 *and in chamber solvent rinses, under two temperature scenarios*

		BDE-47	BDE-85	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209
	<i>Pre experiment (ng g⁻¹)</i>	<i>10 ± 11</i>	<i>2 ± 2</i>	<i>27 ± 31</i>	<i>5 ± 5</i>	<i>6 ± 6</i>	<i>3 ± 3</i>	<i>2 ± 2</i>	<i>230 ± 180</i>
24 Hours at 60 °C									
Experiment 1	Dust (ng g ⁻¹)	<4.5	<0.8	1.8	<0.7	4.1	<1.8	14	210
	PUF (ng)	<4.5	<0.8	<0.8	<0.7	<1.3	<1.8	<1.0	<1.2
	Chamber Rinse (ng)	<4.5	<0.8	2.2	<0.7	3.8	<1.8	11	270
Experiment 2	Dust (ng g ⁻¹)	<4.5	<0.8	2.1	<0.7	<1.3	<1.8	<1.0	4800
	PUF (ng)	<4.5	<0.8	<0.8	<0.7	<1.3	<1.8	<1.0	<1.2
	Chamber Rinse (ng)	<4.5	<0.8	<0.8	<0.7	1.8	<1.8	5.6	55
1 week at 22 °C									
Experiment 1	Dust (ng g ⁻¹)	<4.5	<0.8	1.5	<0.7	<1.3	<1.8	<1.0	230
	PUF (ng)	<4.5	<0.8	<0.8	<0.7	<1.3	<1.8	<1.0	<1.2
	Chamber Rinse (ng)	<4.5	<0.8	<0.8	<0.7	<1.3	<1.8	6.8	340
Experiment 2	Dust (ng g ⁻¹)	<4.5	<0.8	1.5	<0.7	<1.3	<1.8	2.0	120
	PUF (ng)	<4.5	<0.8	<0.8	<0.7	<1.3	<1.8	<1.0	<1.2
	Chamber Rinse (ng)	<4.5	<0.8	<0.8	<0.7	<1.3	<1.8	3.7	150

549 *NB: LOQs calculated as the concentration relating to a 10:1 signal:noise ratio*

Table 3: Concentrations (ng g⁻¹) in dust pre experiment and post experiment for four different abrasion experimental durations

	Pre-experiment (ng g ⁻¹)	2 hours (ng g ⁻¹)	3 hours (ng g ⁻¹)	24 hours (ng g ⁻¹)	48 hours (ng g ⁻¹)
BDE-47	10 ± 11	<4.5	<4.5	<4.5	<4.5
BDE-85	2 ± 2	<0.8	<0.8	<0.8	<0.8
BDE-99	27 ± 31	3.2	1.9	17	2.5
BDE-100	5 ± 5	<0.7	<0.7	<0.7	<0.7
BDE-153	6 ± 6	120	<1.3	520	7.5
BDE-154	3 ± 3	12	<1.8	93	<1.8
BDE-183	2 ± 2	1100	41	3100	240
BDE-209	230 ± 180	37 000	1300	91 000	15 000

Table 4: Mean ± SD concentrations (ng g⁻¹) of PBDEs in dust pre experiment and maximum and minimum concentrations (ng g⁻¹) in dust post direct contact experiment for 24 hours and 1 week exposure (n=2)

	Pre experiment (ng g⁻¹)	24 hours (ng g⁻¹)	1 week (ng g⁻¹)
BDE-47	10 ± 11	<4.5	<4.5
BDE-85	2 ± 2	<0.8	<0.8
BDE-99	27 ± 31	<0.8	<0.8
BDE-100	5 ± 5	<0.7	<0.7
BDE-153	6 ± 6	(<1.3, 20)	(29, 65)
BDE-154	3 ± 3	<1.8	<1.8
BDE-183	2 ± 2	(<1.0, 220)	(140, 500)
BDE-209	230 ± 180	(590, 1000)	(1000, 8700)

*Table SD-1: Mean $\pm$ standard deviation of PBDEs in SRM 2585, %RSD and
Certified values*

Analyte	Measured mean $\pm$ Standard Deviation (n = 15)	% RSD	Certified Value (SRM2585, NIST)
BDE-47	438 $\pm$ 59	13.6	498 $\pm$ 46
BDE-85	37.7 $\pm$ 5.0	13.3	43.8 $\pm$ 1.6
BDE-99	817 $\pm$ 61	7.4	892 $\pm$ 53
BDE-100	140 $\pm$ 12	8.6	145 $\pm$ 11
BDE-153	124 $\pm$ 15	12.0	119 $\pm$ 1
BDE-154	76.7 $\pm$ 10	13.6	83.5 $\pm$ 2.0
BDE-183	42.4 $\pm$ 5.9	14.0	43.0 $\pm$ 3.5
BDE-209	2410 $\pm$ 300	12.3	2510 $\pm$ 190

Reference:

SRM 2585, *Organic Contaminants in House Dust*; National Institute of Standards and
Technology, U.S. Department of Commerce: Gaithersburg, MD (2014).