MICRO-EMISSION CHAMBER INVESTIGATIONS OF BROMINATED FLAME RETARDANTS: CHAMBER "SINK" EFFECTS

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Introduction

This project is part of the INFLAME Marie Curie Initial Training Network that consists of 14 different but linked projects. INFLAME's overall goal is to further understanding of how and to what extent flame retardants that are used in everyday consumer goods and construction materials migrate from these products, enter humans and the risk to health of such exposure. This particular project is focussing on the migration pathways of certain brominated flame retardants (BFRs) into indoor dust.

Brominated flame retardants (BFRs) are chemical additives found in many fabrics and electrical/electronic goods in homes and offices. They are added as part of the manufacturing process but as many are blended physically (rather than chemically bonded) into the polymeric product they can be released during normal use, migrating into the environment. Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) in particular have been found at measurable concentrations in many indoor environments[1], with concomitant potential for human exposure[2].

The levels of PBDEs in indoor dust have been of particular interest as high concentrations (up to 0.26% of BDE-209 (w/w) in UK dust[1]) have been reported[1,3,4]. The exact mechanistic pathways of this migration are not known, although the prominent theories are that the lower brominated, more volatile BFRs, volatilise into the surrounding atmosphere with subsequent gas phase deposition to dust; whilst the more heavily brominated (non-volatile) compounds migrate through abrasion of the materials/goods and/or adsorption to dust particles[2].

Previous studies with emission chambers have provided some insight into the migration of BFRs from treated goods'. Kemmlein et al[5] investigated area specific emission rates of PBDEs from certain treated consumer products in designed chamber studies and Wilford et al[6] conducted chamber emission studies of treated PUF products to investigate the rate of release of PBDEs. Through the use of a specially designed, built for purpose, in-house micro-emission chamber these migration pathways and the different hypotheses are being further investigated. This preliminary paper reports on progress to date during the first year of the project, addressing the chamber "sink" effects observed and efforts to understand their causes in order to develop strategies to minimise such effects.

Materials and methods

A micro-emission chamber has been designed and constructed for use in experiments investigating the migration pathways of certain BFRs, see Figure 1 below. The chamber consists of a 10 cm diameter, 20 cm height enclosed stainless steel cylinder. Attachments to the lid allow the system to become an active air sampler by the addition of a low volume pump. A pre-cleaning PUF (140 mm diameter, 12 mm thickness, 360.6 cm^2 surface area, 0.07 g cm^{-3} density, PACS, Leicester, UK) is attached between the pump and chamber and a collection PUF (140 mm diameter, 12 mm thickness, 360.6 cm^2 surface area, 0.07 g cm^{-3} density, PACS, Leicester, UK) is attached outside the chamber to collect volatilised BFRs.

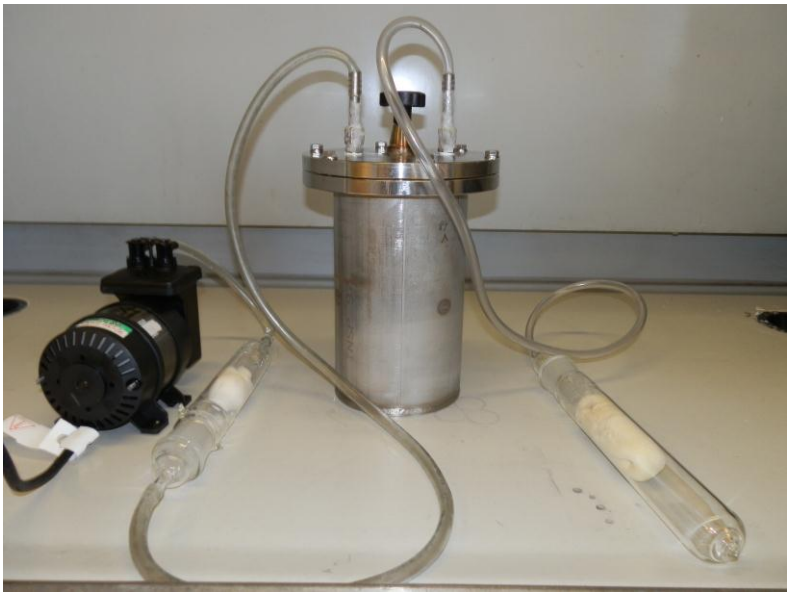

Figure 1: The micro-emission chamber configuration

Initial trials have investigated the emission profiles of the more volatile congeners using mass balance experiments. A piece of filter paper (47 mm PTFE membrane filter, 1.0 μm pore size, Whatman, UK) was spiked with standards of the analytes, placed inside the chamber, and a steady airflow is pumped through the system. PUF plugs, connected to the chamber, collect emissions of the volatiles. After the experiment has finished the filter paper, PUFs and solvent rinses of the empty chamber are analysed separately with recoveries summed to obtain a total % recovery.

The filter paper and PUFs were extracted using pressurised liquid extraction (ASE 350, Dionex Europe, U.K.) using hexane/dichloromethane (1:9, v/v) at 90^{o}C and 1500 psi with a heating time of 5 min, static 4 min, purge time 90 s, flush volume 50%, with three static cycles. The chamber walls were rinsed thoroughly with hexane/dichloromethane (1:1 v/v) for the chamber solvent rinse extracts. All extracts were concentrated and cleanup/purification was conducted with acidified silica (44% concentrated sulfuric acid, w/w). PBDE and HBCD analysis was conducted using a modified, in-house published method[7,8] utilising a dual pump Shimadzu LC-20AB Prominence liquid chromatograph (Shimadzu, Kyoto, Japan) equipped with a SIL-20A autosampler, a DGU-20A3 vacuum degasser, and 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) interfaced with a Sciex API 2000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA) equipped with an ESI ion source operated in negative ion mode for HBCD analysis and an APPI ion source operated in negative ion mode for PBDE analysis.

Results and discussion

Temperature investigations

The emission profiles of PBDEs and HBCDs were investigated at different temperatures (21^{o}C and 60^{o}C) to simulate differing operating conditions of treated products in indoor environments. The experiments show similar results to the study conducted by Kemmlein et al[5], with emissions of the lower molecular weight (more volatile) compounds greatly increased at 60˚C. Room temperature experiments saw little to no capture of PBDEs on the collection PUF. Heating the chamber for 24 hours however saw up to 20% (of total spiked concentration in the system) of BDE-47 and between 1 and 10% of other PBDE congeners retained on the collection PUF. The more volatile congeners also suffered greater total losses in the chamber system, possibly the result of sink effects where the analytes adhere to the chamber walls and are not removed in solvent washes.

Sink Effects

Sink effects are where volatilised analytes sorb onto the chamber wall surface rather than be captured on the PUF in the chamber exit air. The extent of such sink effects was investigated in enclosed chamber experiments where a piece of filter paper, spiked with standard solutions, was placed inside the chamber. The chamber wall washes and filter paper were analysed separately after heating the chamber at 60 ^{o}C for 24 hours. Considerable levels of the more volatile analytes were seen in the solvent washes of the chamber walls but 100% recovery of all analytes was not obtained. Figure 2 below shows the % recovery of analytes: 1) left on the filter paper after this experiment, 2) in the solvent rinse of the chamber walls. The more volatile compounds are found in greater concentration on the chamber walls, as expected. The HBCDs however (particularly β- and γ-HBCD) are not found on the filter paper or chamber wall washes. These results lead us to hypothesise that HBCDs are suffering larger sink effects and not being recovered in the solvent washes and/or the chamber is providing an environment for thermal degradation of these compounds. Experiments were also conducted to investigate possible volatilisation of analytes from the collection PUFs (PUF breakthrough). There were no significant losses, confirming effects inside the chamber are the primary cause of analyte losses.

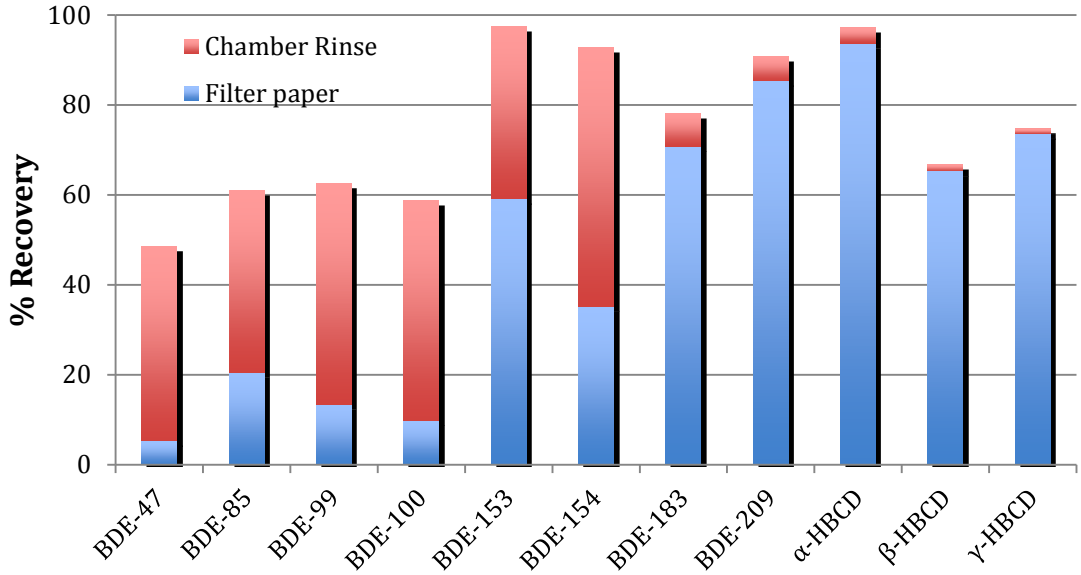

Figure 2: Component % Recoveries of analytes from the 'sink effects' investigation

Degradation products of HBCDs

The increased losses of the HBCD congeners, with temperature and time spent in the heated chamber (60^{o}C), are described in Figure 3 below. A glass chamber was also used for comparison with the stainless steel chamber and the losses are greater in this chamber indicating that photolytic processes may be important. The α-HBCD appears to be less volatile than the other two diastereomers, as greater proportions remain on the filter paper, but it still suffered substantial losses with increased time in the heated chamber. The possibility of within-chamber degradation of HBCDs, accounting for some proportion of the observed losses, is also under investigation. Degradation products of the HBCDs, namely pentabromocyclododecenes (PBCDs) have been observed in preliminary investigations suggesting thermal degradation of the HBCD congeners could be a significant effect in the chamber. The losses in the glass chamber of α-HBCD are noticeably lower than for β- and γ-HBCD. This is consistent with the previously reported greater thermal stability of α-HBCD[9].

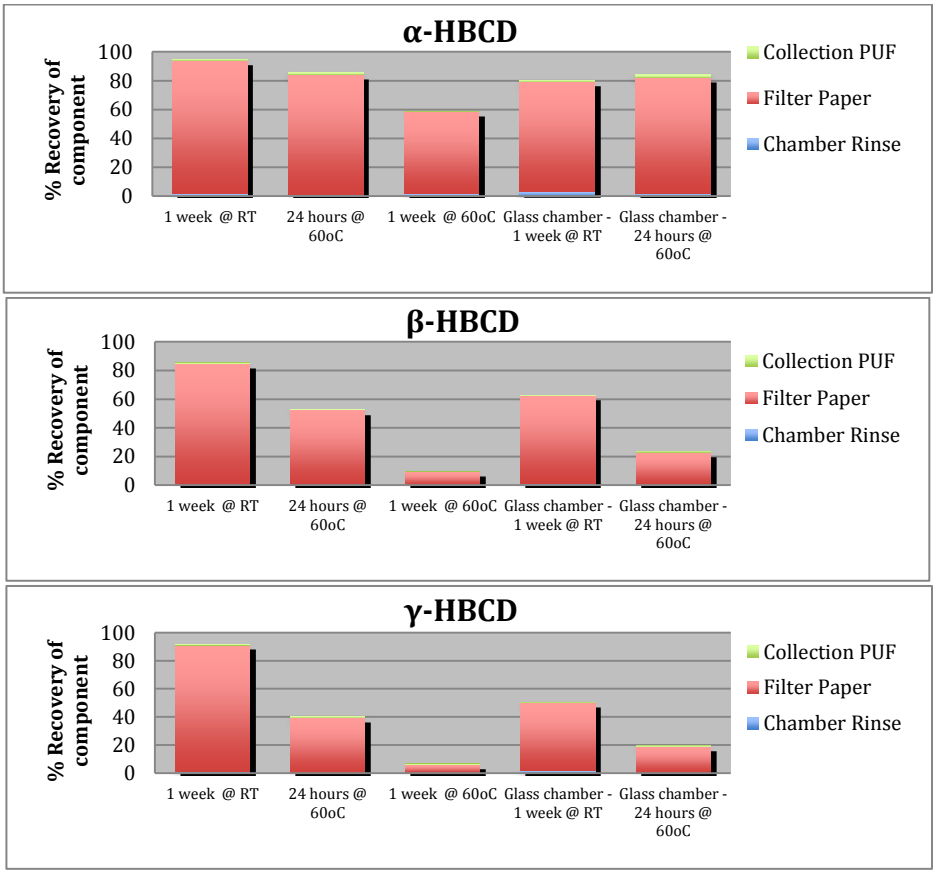

Figure 3: Dependence of HBCD diastereomer recovery on chamber temperature and experimental duration

Acknowledgements

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