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POLYURETHANE FOAM AS A SOURCE OF PBDEs TO THE ENVIRONMENT

Wilford, B.H.[1]; Thomas, G.O.[1]; Alcock, R.E.[1,2]; Jones, K.C.[1]; Anderson, D.R.[3]

[1]Department of Environmental Science, IENS, Lancaster University, Lancaster, LA1 4YQ, UK.
[2]Present address: Environmental Research Solutions, Ghyll Cottage, Mill Side, Witherslack, Grange-over-Sands, Cumbria, LA11 6SG, UK.
[3]Corus RD & T, Environment Department, Swinden Technology Centre, Moorgate, Rotherham, S60 3AR, UK.

Introduction

Polybrominated diphenyl ethers are used as flame retardants in a variety of polymers, with numerous end uses including printed circuit boards and other electronic components, polyurethane foam cushioning, electrical appliance casings, and coatings for textiles. They are marketed as 3 commercial mixtures and are increasingly causing concern due to their increasing levels in the environment[1], and in humans[2], although their toxicology remains unclear. Concentrations of PBDEs found in some environmental samples are now higher than those of PCBs[3]. Flame retarded polyurethane foam (PUF) used for car seating, home furnishing and insulation etc. is the principal use of the commercial pentabromodiphenyl ether (penta-BDE) mix which contains mainly tetra and penta-BDEs, particularly BDE-47 and BDE-99. PBDEs make up 5-30% by mass of a flame retarded plastic[4]. This therefore represents a significant reservoir of PBDEs. This usage pattern results in PBDE distribution throughout the indoor environment, and PBDEs released by volatilisation from products in service[5], may represent an important pathway of human exposure[6].

A foam survey was carried out to estimate the size of this PBDE pool within PUF "products in use" in the UK, with some comparison to North American-origin foams. The potential for release of this flame retardant from PUF to air was also investigated using chamber studies to assess whether a significant proportion of the flame retardant would be lost over the normal "useful" life of the material: to determine whether detectable levels of PBDEs do volatilise to the air, and if so, the rate at which they are released.

Sampling and methods

Foam survey: 94 samples of foam were collected between winter 2001 and spring 2002 from vehicle scrap yards, sofas and chairs sent for waste disposal, and donated samples from sofas and cars. Exact details of the age and origin of the foam were not always known, most were probably over 6 years' old. Samples were extracted using a Soxhlet system for 8hrs in DCM. The resulting samples were weighed, and an aliquot was diluted 2500 times and analysed by GC-NCI (HP MD800) to screen for high level (>0.1% by weight) samples. The % PBDE of the foam by weight was calculated for each sample.

Chamber study: A standard hi-vol air sampling module was adapted to contain 3 PUF plugs: A pre-extracted PUF to pre-clean the air passing through the module, followed by a penta-BDE treated PUF plug, and finally another pre-extracted PUF plug to measure PBDEs released. A glass fibre filter was placed in the front of the sampler, and between the treated and sampling plugs to prevent access and migration of dust and/or foam particles through the chamber. Treated PUF plugs were analysed and found to contain approx. 12% ΣPBDE (w/w). Two such samplers were run simultaneously in an indoor environment at high, medium and low settings. The average temperature range during sampling was 30-34°C. The sampling plug and filter paper were changed approx. every 12 hours, giving an average of 106 m^3, 76 m^3 and 56 m^3 air-flow for each sample respectively. The pre-cleaning plug and filter paper were also changed every time a sample was taken. The high-speed chambers were run for 4 days (8 x 12 hr samples), while the medium and low speed studies were run for 1.5 days (3 x 12 hr samples) each. The treated PUF plugs were also retained for analysis at the end of each study. Samples were extracted in DCM using a Soxhlet system for 8 hrs, an aliquot of DCM extract was taken quantitatively, diluted 4 times and analysed for PBDEs using GC-MS (NCI) to quantify for high concentration congeners such as BDE-47, -99, and -100. Congeners present at lower concentrations were quantified by re-analysing samples concentrated 40 times. Treated PUF plug extracts were diluted appropriately so as not to overload the GC-MS. Blank and exposed pre-cleaning plugs were analysed to ensure that the pre-extraction method was effective. A blank run was also conducted (set up as previously described but no penta-BDE treated PUF plug was present) to test for PBDE sources from the room and the effectiveness of the pre-cleaning method. Tests for variability in the original foam and analytical method were also carried out.

For all samples PBDEs 17, 28, 32, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 166, 181 and 190 were monitored. $^{13}C_{12}$ labelled PCBs 141 and 208 were added as internal standards.

Results and Discussion

Foam Survey:

Table 1 provides a summary of results from the foam survey. Typical detection limits were 0.001% (w/w) of ΣPBDE. This indicates that, surprisingly, given that that these compounds have only recently been phased out in Britain, only low levels or non-detected levels of PBDEs were present. Two of the sofa samples containing PBDEs were in fact different foams from the same sofa, therefore it is possible that only one type of foam was treated and the other has become PBDE contaminated during the life of the sofa. The car foam containing PBDE was from a builders' van and the foam was very dirty. It is therefore impossible to tell whether the PBDE found resulted from the foam itself being treated, or whether the dust within the foam was the source. The North American foam samples, which comprised both new and in-use material, in contrast to those sampled in the UK, contain approximately 5% PBDE by weight.

Table 1. Percentage ΣPBDE (w/w) in foam analysed from the UK and North America
Results for the individual PBDE-containing samples are listed in the right-hand columns.

Foam type	**n**	**no. containing PBDE**	**Total PBDE % (w/w)** for individual PBDE containing samples		
New UK Foam	3	0			
Office chair foams	12	0			
Sofa foams	28	3	0.0043	0.012	0.0095
Child seat	1	0			
Car seat foams	17	1	0.0022		
North American foam	3	3	4.8	5.3	5.5

Chamber Study:

Figure 1 shows the release rate of the principal 3 congeners detected in air. This corresponds to a loss rate of 360 ng/m^3/g foam, 85 ng/m^3/g foam and 30 ng/m^3/g foam for BDE-47, 99 and 100 respectively.

Figure 1. Release of the principal PBDE congeners from penta-treated PUF foam.

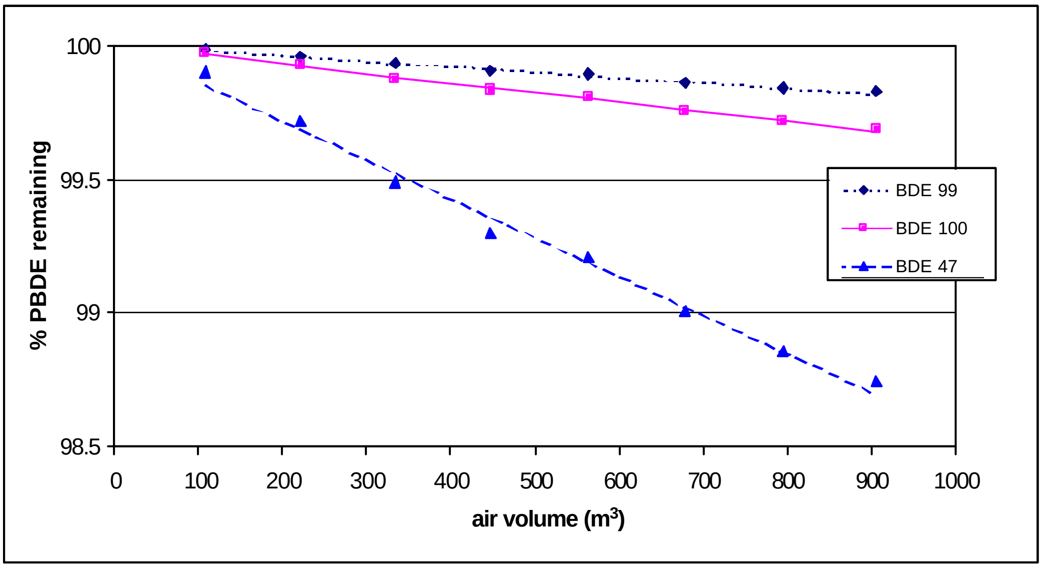
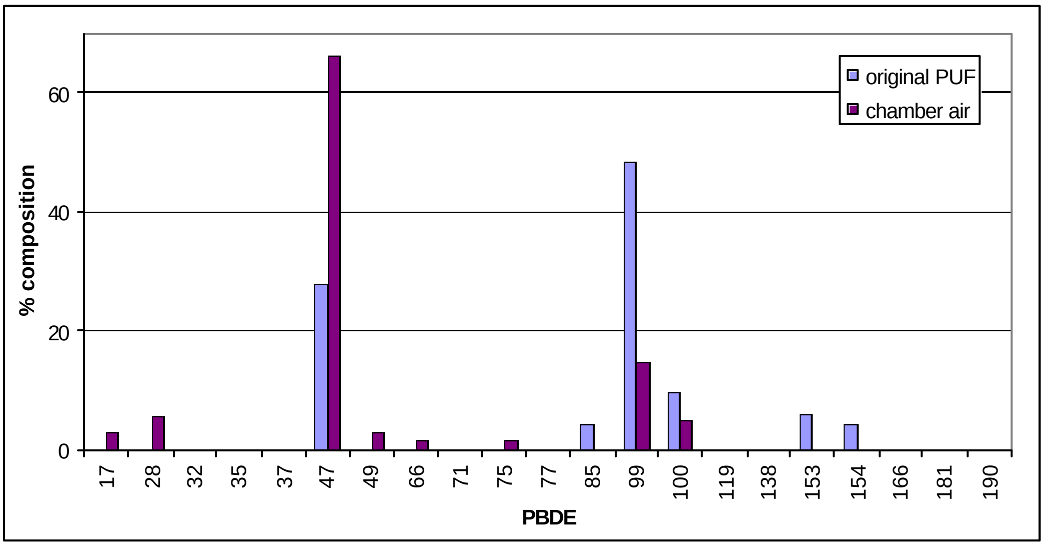


Figure 2. PBDE congener profiles of penta-treated PUF, and in air passed through it.



PBDEs do volatilise from PUF at significant levels in our experiments – average ΣPBDE levels of 500ng/m^3/g foam were released from the chamber, whereas average rural air levels for ΣPBDE in the UK[7] are 3-12 pg/m^3 and 5.5-15 pg/m^3 for the Great Lakes region of USA/Canada, with 52 pg/m^3 found in Chicago, USA[8]. Figure 1 shows that the PBDE congeners are released at different rates, determined by their physical properties: the log K_{OA} values for BDE-47, 99 and 100 are 10.53, 11.31 and 11.13 respectively[9]. Figure 2 highlights this preferential loss of the lighter congeners, and points to volatilisation, as opposed to crumbling of the foam, as the means of transfer through the chamber.

Significance for human exposure/ environmental fate:

Indoor environments typically have low air circulation. Passive samplers with a planar surface area of 365 cm^2 sample a few m^3/day in an indoor environment[10]. Therefore for e.g. a standard office chair seat cushion, we calculate passive air exchange of approx. 20 m^3/day. If the chamber release rates mentioned above apply, and depending on the foam density, this would result in the release of hundreds of μg ΣPBDE per day. It is possible that dust from the foam could also contribute to overall releases. However, analysis of the filter papers from this study does not indicate that dust is the principal emission pathway from new foam, in contrast to Hale et al.'s theory of crumbling of foam from products in use[11]. Clearly the rate of release of PBDEs from PUF will be highly variable, affected by temperature, UV light/ageing, humidity, as well as "active ventilation" by people sitting down on the furniture. The small percentage PBDE loss over the short period of this study would have a negligible effect on flame retardancy, however over the long term this may indicate potential loss of flame retarding properties. We conclude that volatilisation of PBDEs from treated PUF is a significant source to indoor air, and hence to the outdoor environment. This would explain why indoor PBDE air levels are on average 20 times higher than those outdoors[12] and why PBDEs are observed at elevated levels in urban areas[8] where there is a higher concentration of treated PUF and other treated consumer goods. Further work is in progress to investigate the kinetics of PBDE loss from PUF over the longer term.

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