Polybrominated Diphenyl Ethers (PBDEs) in Household Dust from Wellington, New Zealand and Birmingham, United Kingdom.

Catalina Ibarra[1], Jeroen Douwes[2], Neil Pearce[2], Stuart Harrad[1]

[1] Division of Environmental Health and Risk Management, University of Birmingham, Birmingham, B15 2TT, United Kingdom.
[2] Centre for Public Health Research, Massey University, Wellington, New Zealand.

Introduction

Polybrominated diphenyl ethers (PBDEs) have found wide use as flame retardants. Their uses are myriad: the penta-BDE formulation was employed principally to flame retard polyurethane foams in carpet underlay, vehicle interiors, furniture and bedding; the octa-formulation was used to flame retard thermoplastics such as high impact polystyrene, and the deca-product is used principally in plastic housings for electrical goods like TVs and computers, as well as textiles (Alcock et al. 2003). As a result of concerns surrounding these contaminants owing to their presence in the diet and indoor air and dust (Harrad et al. 2004) (Jones-Otazo et al. 2005) (Stapleton et al. 2005), and human tissues (Hites 2004), coupled with evidence relating to their potential adverse effects on human health (Darnerud et al. 2001) (McDonald 2002), several jurisdictions have banned the marketing and use of penta- and octa-BDEs. Furthermore, the main U.S. producer, together with the U.S. EPA, have reached a voluntary agreement to discontinue production of the penta- and octa-BDE mixtures. Despite this, there remain strong concerns that the existing (largely indoor) reservoir of PBDEs (and PCBs) associated with treated goods represents a substantial source of current and future exposure to these compounds, both via direct inhalation and ingestion of contaminated indoor air and dust, and in time via dietary exposure following their emission, transport and incorporation into the diet (Harrad & Diamond 2006). Recently, there has been considerable interest in the role of indoor dust ingestion as an exposure pathway; which has been suggested may be the overriding source of exposure to Canadian toddlers (Jones-Otazo et al. 2005), and may explain the order of magnitude difference between PBDE body burdens of Europeans and North Americans (Harrad et al. 2006). One of us reported recently on the presence of PBDEs in New Zealand human blood serum (Harrad & Porter, in press). Interestingly, the concentrations detected were at the high end of the range reported previously for Europe, despite the fact that PBDEs had not been manufactured in New Zealand. This study (which will include samples from North America at a later date) compares concentrations found in household dust samples from New Zealand and the UK. The data are used to estimate the magnitude of human exposure to PBDEs that can be attributed to the ingestion of household dust.

Materials and Methods

Dust samples were collected using identical sampling protocols from 20 homes in New Zealand using a Nilfisk Sprint Plus 1600 W vacuum cleaner, and 20 UK homes with an equivalent Nilfisk compact c220 1600 W vacuum cleaner. Sampling was conducted in January-March 2006 (New Zealand), and July-August 2006 (UK); the houses selected for the New Zealand study comprised a convenience sample of university staff. 1m^2 of carpet was vacuumed for 2 min in each location and in case of bare floors 4 m^2 for 4 min (Schram et al., 2006). Samples were collected using nylon sample socks that were mounted in the tube of the vacuum cleaner. After sampling, socks with dust were closed with a twist tie, kept in a plastic bag and stored at -20°C. Each sample was sieved using a 500µm mesh, then weighed and transferred to an accelerated solvent extraction (ASE) cell (66 ml) and treated with ^{13}C-BDE standards. The cell was filled with 1.5 g Florisil, and Hydromatrix (Varian Inc) was used to fully

pack the cell. The samples were extracted using a Dionex 300 ASE system with the following extraction conditions:
Solvent: Hexane; Temperature: 100˚C; Pressure: 1500 psi; Heating time: 5 min; Static time: 4 min; Flush Volume: 60%; Purge time: 60 secs; Static Cycles: 3

The resulting extract was concentrated to 0.5 ml using a Zymark Turbovap II and washed with concentrated sulfuric acid. The resulting hexane layer was loaded onto a Florisil/Na_2SO_4 column and eluted with hexane. The eluate was extracted with DMSO followed by hexane back-extraction. The extract was concentrated and loaded onto a second Florisil/Na_2SO_4 column, eluted with hexane, and the eluate was concentrated under nitrogen, before addition of 10 µl of recovery determination standard prior to GC/MS analysis. GC/MS analysis was carried out on a Fisons MD-800 instrument fitted with a HP-5 trace analysis column (60m x 0.25 mm i.d, 0.25 µm film thickness) and helium as carrier gas. The MS was operated in EI mode, and target congeners were BDEs: 17, 28, 49, 66, 85, 99, 100, 153, and 154. As a QA/QC measure, every 5 samples, 1g of sodium sulfate was analysed as a blank matrix. Concentrations in blanks were less than 5% of those in samples, and samples are therefore not corrected for concentrations in blanks.

Results and Discussion

PBDEs were detected in all samples. A summary of ΣPBDE concentrations found is presented in Table 1, and Figure 1 places them in context with concentrations reported previously from studies elsewhere in the world. In the UK homes, sample concentrations varied from 5.8 to 173 ng g^{-1} with a geometric mean of 40.3 ng g^{-1}. These concentrations are lower than those previously reported by us for a small set (n=8) of UK domestic dust samples taken from vacuum cleaner contents provided by household owners. However, comparison via t-test of log-normalised concentrations from both these UK studies shows the difference in concentrations is not significant ($p>0.1$). This may indicate that the sample collection method does not appear to significantly influence concentrations detected, but more detailed study is required to confirm this. In samples from New Zealand, the concentrations ranged from 12.9 to 683.2 ng g^{-1} with a geometric mean of 93.6 ng g^{-1}. A t-test comparison performed on log-normalised data reveals that concentrations in the New Zealand samples exceed significantly those in the UK samples ($p<0.05$).

Table 1. Summary of ΣPBDE concentrations in ng g^{-1} dry weight in homes sampled in New Zealand and the UK.

	ΣPBDE	
	NZ	**UK**
Min	12.9	5.8
Percentile 5	14.9	8.4
Percentile 25	37.9	17.6
Average	164.0	63.1
Percentile 50	97.5	50.0
Std Deviation	182.6	55.0
Percentile 75	191.3	94.4
Percentile 95	541.6	162.9
Max	683.2	173.0

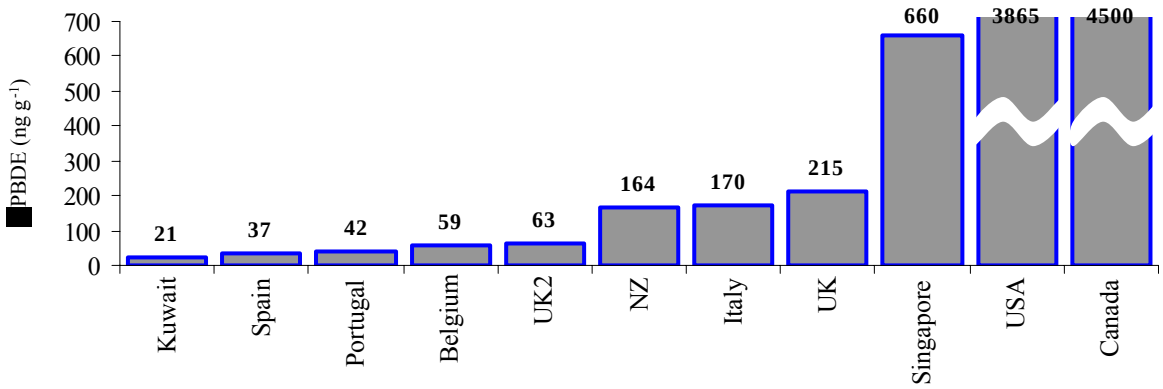
The mean and median values and the percentage contribution of each analysed PBDE congener to the total are shown in Table 2. The most abundant PBDE congener in dust samples from both countries

was BDE 99 followed by BDE 47. The median ratio of 47:99 was 0.45 for the UK and 0.49 for New Zealand. This compares very closely with the median value of 0.51 reported previously for UK domestic samples (Harrad et al. 2006). The agreement between these ratios for the two sample sets, suggests a common source to dusts in both countries. As discussed previously (Harrad et al. 2006), while these ratios are lower than those detected in two of the most widely used penta-BDE formulations, we believe that following volatilization from treated products (which will favour the less brominated congener 47 and results in median 47:99 ratios in indoor air of 1.2 that exceed those in the commercial formulations), the higher brominated congener 99 undergoes preferential sorption to dust.

Table 2. Concentrations in ng g^{-1} of PBDE congeners in house dust from New Zealand and the UK.

	17	**28**	**49**	**47**	**66**	**100**	**99**	**85**	**154**	**153**	**ΣPBDEs**
UK Average	0.14	0.61	0.82	11.8	0.58	4.99	28.9	1.03	3.63	10.6	**63.1**
UK Median	0.10	0.50	0.62	8.64	0.41	3.00	16.5	0.51	2.67	4.41	**50.0**
% ΣPBDEs	0.2	1.0	1.3	18.7	0.9	7.9	45.8	1.6	5.8	16.8	
NZ Average	0.14	0.85	1.78	36.0	1.20	15.9	87.1	2.43	8.68	9.82	**164.0**
NZ Median	0.11	0.67	1.42	24.0	0.89	8.92	50.2	1.47	5.05	5.34	**97.5**
% ΣPBDEs	0.1	0.5	1.1	22.0	0.7	9.7	53.1	1.5	5.3	6.0	

Figure 1. Comparison of average ΣPBDE concentrations in ng g^{-1} in house dust from different countries, where UK is that found in a previous study (Harrad et al. 2006) and UK2 are this study.



Using the PBDE concentrations reported in this study it is possible to estimate the contribution of dust to human exposure. These estimates (Tables 3 and 4) assume 100% absorption of dust and that the average dust intake rate for an adult person is 4.16 mg day^{-1} while that of toddlers is 100 mg day^{-1} and that high dust intakes are 55 mg day^{-1} and 200 mg day^{-1} for adults and toddlers respectively.

Table 3. Estimates of exposure for UK and NZ adults (ng day^{-1}) to PBDEs via dust ingestion

Intake (ng d^{-1})	**UK Adult**				**NZ Adult**			
	5th percentile	**Median**	**Average**	**95th percentile**	**5th percentile**	**Median**	**Average**	**95th percentile**
Dust (mean)	0.03	0.2	0.3	0.7	0.06	0.4	0.7	2.3
Dust (high)	0.46	2.8	3.5	9.0	0.82	5.4	9.0	29.8

Table 4. Estimates of exposure for UK and NZ in toddlers (ng day^{-1}) to PBDEs via dust ingestion

Intake (ng d^{-1})	UK Toddler (6 - 24 months)				NZ Toddler (6 - 24 months)			
	5th percentile	Median	Average	95th percentile	5th percentile	Median	Average	95th percentile
Dust (mean)	0.84	5.0	6.3	16.3	1.49	9.8	16.4	54.2
Dust (high)	1.67	10.0	12.6	32.6	2.98	19.5	32.8	108.3

There are no data relating to exposure to PBDEs via the diet or inhalation for New Zealanders, against which these estimates of exposures via dust ingestion may be placed in context. However, given concentrations in New Zealand dust exceed those found in the UK, it is reasonable to assume the contribution of dust ingestion to the exposure of New Zealanders will be similar or even slightly exceed that reported previously for the UK – i.e. up to 37% for adults, and 69% for toddlers.

Conclusion

Despite never having produced PBDEs, this preliminary study provides evidence that appreciable exposure of New Zealanders to PBDEs may be occurring via ingestion of indoor dust, at levels that – while substantially lower than those reported for North Americans (Jones-Otazo et al. 2005) (Stapleton et al. 2005) - may exceed those in the UK and other European countries. Further studies are needed to elucidate the importance of this exposure pathway for New Zealanders relative to others such as diet.

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