

POLYBROMINATED DIPHENYL ETHERS (PBDEs) AND POLYCHLORINATED BIPHENYLS (PCBs) IN HOUSEHOLD DUST IN BIRMINGHAM, UK.

Ibarra C, Hazrati S and Harrad S

Division of Environmental Health and Risk Management, University of Birmingham, Birmingham, B15 2TT, United Kingdom.

Introduction

Polychlorinated biphenyls (PCBs) are persistent organic pollutants that were used primarily as insulating fluids in electrical equipment and were banned in the 1970s, even so they are still being found in humans. Polybrominated diphenyl ethers (PBDEs) are nowadays widely used as flame retardants in electronic components, plastics, textiles and building materials.¹ The characteristics of PBDEs and PCBs are very similar, being persistent, bioaccumulative and ubiquitous. Levels of PBDEs have been determined in human tissues and concentrations found in the USA are more than ten fold higher than in Europe.² This presence in humans means that it is important to identify routes of exposure to the general population and the fact that North American and European dietary exposures are similar, suggests that sources in addition to diet are important.^{3,4} In particular, inhalation and ingestion of indoor air and dust could account for a significant proportion of the human body burden of Σ PBDE. In this study we analysed vacuum cleaner dust collected from different households and offices in Birmingham where the air was previously analysed using a passive air sampler. We report PCB and PBDE concentrations and determine the proportion of human exposure to PBDEs that can be attributed to household dust.

Methods and Materials

Dust samples were collected from 11 homes and 5 offices. The volunteers were asked to empty the contents of their vacuum bags into a plastic bag or, if the vacuum had disposable bags these were provided instead. For the offices, a Black and Decker Dustbuster Minivac (Mod. VH780) with washable filters was used to collect the samples. Each sample was sieved using a 500 μ m mesh, then transferred to a preweighed clean glass container; after the weight was recorded the jar was placed in the freezer (-20°C) until analysis. Dust was mixed thoroughly before 1 g of each sample was weighed and transferred to an accelerated solvent extraction (ASE) cell (66 ml) and treated with ¹³C-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: 150°C; Pressure: 1500 psi; Heating time: 7 min; Static time: 5 min; Flush Volume: 50%; Purge time: 100 secs; Static Cycles: 1

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/Na₂SO₄ 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/Na₂SO₄ column, eluted with hexane, and the eluate was concentrated under nitrogen, then 10 μ l of recovery determination standard were added 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 μ m film thickness) and helium as carrier gas. As a QA/QC measure, every 5 samples, sodium sulfate was analysed as a blank matrix.

Results and Discussion

The concentrations of PBDEs found in household dusts in this study are shown in Table 1. Σ PBDE concentrations ranged from 16 to 626 ng g⁻¹ dust (median=91 ng g⁻¹, mean=179 ng g⁻¹, σ_{n-1} = 213). BDE 99 was the major congener detected in all samples (on average contributing 50% of the total PBDE burden) followed by BDE 47 (23%).

Brominated compounds - Human exposure

House No.	Congeners										Σ PBDE (ng g ⁻¹)
	17	28	49	47	66	100	99	85	154	153	
1	0.11	0.37	0.37	5.2	0.25	1.1	7.4	0.00	0.48	1.0	16
2	0.58	0.90	1.6	5.8	0.69	2.0	13	0.35	3.2	6.9	35
3	0.00	0.00	0.67	6.2	0.00	2.1	17	0.00	2.0	8.3	36
4	0.06	0.45	0.67	16	0.48	3.9	20	0.51	1.9	3.8	48
5	0.00	0.29	0.61	13	0.47	4.5	25	0.56	2.7	19	66
6	0.47	1.2	1.8	18	1.3	7.5	45	1.4	5.8	9.3	91
7	0.20	0.98	1.5	25	0.96	7.3	43	1.2	4.5	9.7	95
8	0.29	1.5	4.6	25	3.2	7.9	49	0.97	4.9	11	109
9	0.35	1.4	2.5	95	1.8	31	167	6.0	15	15	335
10	1.8	2.2	13.3	89	2.2	20	263	6.3	26	94	517
11	0.46	2.3	6.2	163	5.0	50	317	11	31	39	626
Mean	0.39	1.0	3.1	42	1.5	12	88	2.6	8.9	20	179
Median	0.29	0.98	1.6	18	0.96	7.3	43	0.97	4.5	9.7	91
% of ΣPBDE	0.2	0.6	1.7	23.4	0.8	6.9	48.9	1.4	4.9	11.0	

Table 1. Summary of PBDE concentrations found in house dust in ng g⁻¹ dry weight.

The concentrations reported in this study are higher when compared to average concentrations found in other European countries^{5, 6}, (Figure 1) but they were very low compared to concentrations reported in North America which were on average 20 times higher.^{7, 8}

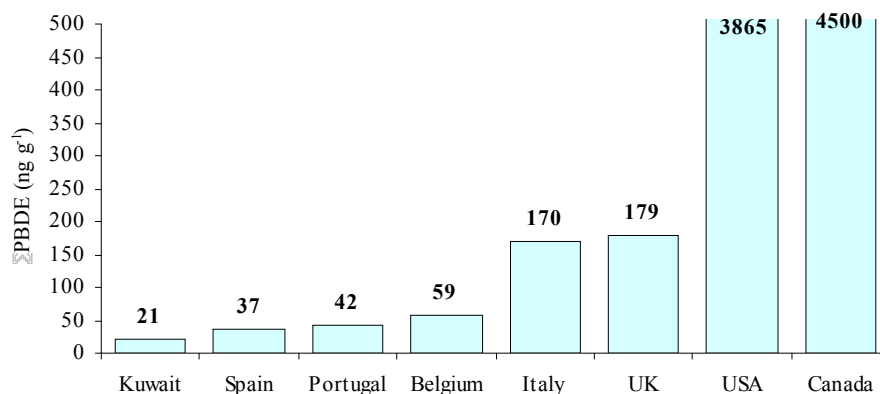


Figure 1. Comparison of indoor dust PBDE concentrations in ng g⁻¹ to other

When concentrations of BDEs in household and office dust were regressed against concentrations in air from the same indoor locations⁹, they were significantly correlated at the 99% confidence level ($r = 0.91$, $p < 0.01$) suggesting a common source for both burdens.

On average, concentrations of Σ PBDE in office dust (Table 2) were slightly higher than those in house dusts. However, one office dust sample was highly contaminated, being about 10 times higher than the rest (office 5). The congener profiles reported in this study are similar to those reported for other countries and the profile found in the commercial penta-BDE mixture Bromkal 70-5DE.¹⁰ This resemblance between relative compositions indicates that the penta-BDE mixture is responsible for the BDE concentrations found in the collected dust. We have observed that typically in our samples concentrations of BDE-47 are lower than those of BDE-99, and that the median ratio of 47:99 in dust is lower than that found in air, which suggests that BDE-99 after volatilisation, undergoes preferential sorption to dust.

Brominated compounds - Human exposure

Office No.	Congeners										ΣPBDE (ng g ⁻¹)
	17	28	49	47	66	100	99	85	154	153	
1	0.27	1.2	2.5	45	0.04	15	75	2.0	4.8	4.4	150
2	1.4	2.2	5.4	50	4.3	18	126	5.4	11.5	16	240
3	0.32	0.97	4.6	120	4.7	80	432	14	27.5	19	703
4	0.50	2.1	7.5	146	7.0	76	463	15	52.2	59	829
5	8.6	38	82	2960	74	585	2862	117	350.2	385	7463
Mean	2.2	8.8	20.43	664	18	155	792	31	89.2	97	1877
Median	0.50	2.1	5.36	120	4.7	76	432	14	27.5	19	703
% of ΣPBDE	0.1	0.5	1.1	35.4	1.0	8.2	42.2	1.6	4.8	5.2	

Table 2. Summary of PBDE concentrations found in office dust in ng g⁻¹ dry weight

Estimated daily exposures of adults and toddlers to PBDEs through air, food and dust ingestion are shown in Table 3. These estimates 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 55 mg day⁻¹ and that high dust intakes are 100 mg day⁻¹ and 200 mg day⁻¹ for adults and toddlers respectively.⁷ UK adult dietary exposure is assumed to be 90.5 ng ΣBDE day⁻¹ with that of toddlers to be 57% of that of adults.^{4,7} Adult dust intakes were calculated using the following algorithm:

$$\Sigma \text{Exposure} = [(C_w F_w) + (C_h F_h)] \times \text{DIR}$$

Where C_w and C_h are the ΣPBDE concentrations (ng g⁻¹) at workplace and at home respectively, F is the fraction of day spent at workplace or home and DIR is the dust intake rate (g d⁻¹) mentioned above. In this estimate we assume that an adult would spend 40 hours at the workplace ($F_w=0.238$) and the rest of the time at home. Toddlers were assumed to spend all their time at home.

Intake (ng d ⁻¹)	Adult				Toddler (6 - 24 months)			
	5th percentile	Median	Average	95th percentile	5th percentile	Median	Average	95th percentile
Air	0.18	0.82	2.1	8.8	0.03	0.16	0.4	1.7
Food	90.5	90.5	90.5	90.5	51.6	51.6	51.6	51.6
Dust (mean)	0.2	0.4	1.5	7.9	1.4	2.3	12.2	31.4
Dust (high)	6.0	8.9	36.6	189.7	5.1	8.4	44.4	114.2
Σ intake (mean dust)	90.9	91.7	94.1	107.2	53.0	54.1	64.2	84.7
Σ intake (high dust)	96.6	100.2	129.2	289.0	56.7	60.2	96.3	167.5
% contribution								
Mean dust intake scenario								
Air	0.2	0.9	2.2	8.2	0.1	0.3	0.6	2.0
Food	99.5	98.7	96.1	84.4	97.3	95.4	80.4	60.9
Dust	0.3	0.4	1.6	7.4	2.7	4.3	19.0	37.1
% contribution								
High dust intake scenario								
Air	0.2	0.8	1.6	3.0	0.1	0.3	0.4	1.0
Food	93.7	90.3	70.0	31.3	90.9	85.8	53.5	30.8
Dust	6.2	8.9	28.3	65.6	9.0	14.0	46.0	68.2

Table 3. Estimates of exposure of UK adults and toddlers (ng day⁻¹) to PBDEs via dust ingestion, inhalation, and diet, and relative significance (%) of each pathway, calculated for mean and high dust intake scenarios.

We can conclude from this table that while in most cases diet is the main contributor to the PBDE exposure of UK adults, dust ingestion is also an important factor. When dust is ingested in a highly contaminated environment (e.g. Office No. 5) it could help explain the unusual high BDE body burdens displayed by some individuals, because dust becomes the major contributor to the BDE daily intake (up to 66% for adults).

Brominated compounds - Human exposure

Concentrations of Σ PCB in household dust and in office dust were very similar in magnitude to those of Σ PBDE (Table 4). As a result, human exposure to Σ PCB via dust ingestion will be of similar magnitude to that for Σ BDE. Given that average UK adult exposure to Σ PCB via inhalation is - at 150 ng d^{-1} - much higher than that for Σ BDE¹¹, the contribution made by dust ingestion to overall UK adult exposure to Σ PCB is comparatively low.

	Homes		Offices	
	Σ PCB	Σ PBDE	Σ PCB	Σ PBDE
Min	15	16	59	150
Percentile 5	18	26	62	168
Percentile 25	51	42	74	240
Average	123	179	158	1878
Percentile 50	64	91	117	705
Std Deviation	108	213	112	3137
Percentile 75	212	222	212	829
Percentile 95	292	571	304	6138
Max	305	626	327	7466

Table 4. Summary of Σ PCB and Σ PBDE concentrations in ng g^{-1} dry weight in homes and offices.

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References:

1. Bromine Science and Environmental Forum, BSEF-Our Industry. November 1, 2005, <http://www.bsef.com/>.
2. Schecter, A.; Pavuk, M.; Papke, O.; Ryan, J. J.; Birnbaum, L.; Rosen, R. *Environ. Health Perspect.* 2003; 111: 1723.
3. Jones-Otazo, H. A.; Clarke, J. P.; Diamond, M. L.; Archbold, J. A.; Ferguson, G.; Harner, T.; Richardson, G. M.; Ryan, J. J.; Wilford, B. *Environ. Sci. Technol.* 2005; 39: 5121.
4. Harrad, S.; Wijesekera, R.; Hunter, S.; Halliwell, C.; Baker, R. *Environ. Sci. Technol.* 2004; 38: 2345.
5. Fabrellas, B.; Martinez, M. A.; Ramos, B.; Ruiz, M. L.; Navarro, I.; de la Torre, A. Poster presented at the 25th International Symposium on Halogenated Persistent Organic Pollutants (Dioxin 2005), Toronto, Canada, 21-26 August 2005.
6. Gevao, B.; Al-Bahloul, M.; Al-Ghadban, A. N.; Al-Omair, A.; Ali, L.; Zafar, J.; Helaleh, M. *Chemosphere* 2006; [Epub ahead of print].
7. Wilford, B. H.; Shoeib, M.; Harner, T.; Zhu, J.; Jones, K. C. *Environ. Sci. Technol.* 2005; 39: 7027.
8. Stapleton, H. M.; Dodder, N. G.; Offenber, J. H.; Schantz, M. M.; Wise, S. A. *Environ. Sci. Technol.* 2005; 39: 925.
9. Hazrati, S.; Harrad, S. Paper submitted to the 26th International Symposium on Halogenated Persistent Organic Pollutants (Dioxin 2006), Oslo, Norway, 21-25 August 2006.
10. Sjodin, A.; Jakobson, E.; Kierkegaard, A.; Marsh, G.; Sellstrom, U. *J. Chromatogr. A.* 1998; 822:83.
11. Harrad, S.; Hazrati, S.; Ibarra, C. "Concentrations of Polybrominated Diphenyl Ethers in Indoor Air and Dust and Polychlorinated Biphenyls in Indoor Air in Birmingham, United Kingdom: Implications for Human Exposure", *Environ. Sci. Technol.* (in press).