POLYBROMINATED DIPHENYL ETHERS IN DOMESTIC INDOOR DUST FROM CANADA, NEW ZEALAND, UNITED KINGDOM AND UNITED STATES

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Abstract
Polybrominated diphenyl ethers (PBDEs) were measured in domestic indoor dust from: Amarillo/Austin, Texas, US; Birmingham, UK; Toronto, Canada; and Wellington, New Zealand. Concentrations of BDE 209 in two UK samples are – at 520,000 and 100,000 ng g^{-1} - the highest ever recorded in a domestic (or office) indoor dust sample. Median concentrations in ng g^{-1} were: Canada (620 and 560 for Σtri-hexa-BDEs and BDE 209, respectively), New Zealand (96, BDE 209 not measured), UK (59 and 2,800) and US (1,600 and 1,300). With respect to BDE 209, concentrations were in the order: UK ~ US > Canada. For Σtri-hexa-BDEs, the order of concentrations was US ~ Canada >> New Zealand ~ UK. This suggests that while North American dusts are contaminated by both Deca- and Penta-BDE commercial formulations, UK dusts are contaminated predominantly by Deca-BDE. The presence of PBDEs in dusts from New Zealand (where PBDEs were never manufactured or imported as chemicals), suggests international trade in PBDE-containing goods is an important pathway effecting their global distribution.

Introduction
Polybrominated diphenyl ethers (PBDEs) are a group of brominated compounds that are added to a diverse range of products, mostly plastics and textiles, in order to restrict their flammability**.** Previous surveys of the concentrations of PBDEs in indoor air and dust have revealed that while the level of contamination in most samples falls within a relatively small range, some samples are significantly more contaminated than the majority.[1, 2] This could explain why some individuals display significantly higher contamination than the bulk of the population.[3, 4] The plausibility of such a causative link between exposure via ingestion of indoor dust and human body burdens is supported by the recent report of a statistically significant correlation between PBDE concentrations in human milk and those in indoor dust from the homes of US donors.[5] Of further interest is the cause(s) of the observed international differences in the concentrations of PBDEs in human tissues between North America and elsewhere[6]. Because of the international similarities in dietary exposure, it has been suggested that these may be due to international variations in exposure via ingestion of indoor dust.[1, 7] This study has employed similar dust collection and identical analytical procedures to evaluate differences in the concentrations of PBDEs in indoor dust samples taken from 10-28 homes in each of the following cities: Amarillo and Austin, Texas, US; Birmingham, UK; Toronto, Canada; and Wellington, New Zealand.

Materials and Methods
Dust samples were collected from homes in each city using a Nilfisk Sprint Plus 1600 W vacuum cleaner or equivalent. One m^2 of carpet was vacuumed for 2 min in each location and in case of bare floors 4 m^2 for 4 min. Samples were collected using nylon sample socks mounted in the furniture attachment tube of the vacuum cleaner. After sampling, socks were closed with a twist tie, sealed in a plastic bag and stored at -20°C. For some samples, sufficient material remained after determination of tri-hexa-BDEs to permit determination of hepta-deca-BDEs. Determination of concentrations of tri- through hexa-BDEs was conducted at the University of Birmingham, using previously reported methodology.[1, 8] 1 g of each sample was extracted using hexane with an accelerated solvent extraction (ASE) system (ASE 300, Dionex), using a 66 mL cell filled from the bottom with: Florisil (1.5 g), sample, and Hydromatrix (Varian Inc.). The extraction conditions were: temperature: 100˚C, pressure: 1500 psi, heat time: 5 min, static time: 4 min, flush volume: 60%, purge time: 60 s, static cycles: 3. Following extraction, crude extracts were concentrated to approximately 2 mL, treated with 2 mL concentrated sulphuric acid, subjected to liquid:liquid back extraction using dimethyl sulfoxide, prior to elution through a column containing 1 g Florisil topped with 1 g anhydrous sodium sulfate with 20 mL hexane. The eluate was

reduced to incipient dryness, prior to addition of 20 µL of nonane containing 10 ng each of PCBs 29 and 129 as recovery determination standards (RDSs), against which recoveries of internal/surrogate standards may be measured. PBDE analyses were conducted on a Fisons' MD-800 GC/MS system fitted with a 60 m VF5 MS column. The oven temperature program for PBDEs was: 140ºC with 5°C/min ramp to 200°C and 2°C/min to 300°C held for 10 min. The mass spectrometer was operated in EI+ SIM mode; with monitored m/z values as reported previously.[8]

Determination of concentrations of hepta- through deca-BDEs was conducted at the University of Antwerp, based on methods reported previously.[9] Dust samples (typically between 150 and 250 mg) were spiked with internal standard (125 ng ^{13}C-BDE 209) and were then extracted with 100 mL *n*-hexane/acetone (3/1, *v/v*) in hot Soxhlet extraction mode for 2 h. The obtained extract was applied to 8 g acidified silica (40% concentrated sulphuric acid, *w/w*); PBDEs were eluted with 15 mL hexane and 10 mL CH_2Cl_2. The eluate was concentrated to 250 µL prior to determination of PBDEs on an Agilent 6890GC-5973MS equipped with a 15 m x 0.25 mm x 0.10 µm DB-5 capillary column and operated in electron capture negative ionisation (ECNI) mode. The MS was operated in the selected ion monitoring (SIM) mode and the electron multiplier voltage set at 2100 V. One µl of the extract was injected in solvent vent mode (injector temperature at 90°C for 0.06 min, then increased at 700°C min^{-1} to 305°C, vent time 0.04 min, vent flow 75 mL min^{-1}). The splitless time was 1.5 min. The GC temperature program was 90°C for 1.5 min, then 15°C min^{-1} to 295°C for 15 min. Dwell times were 40 ms. Ions *m/z* 79 and 81, together with ions *m/z* = 484.7/486.7 and 494.7/496.7 for BDE 209 and ^{13}C-BDE 209, respectively, were monitored for the entire run.

Statistical analysis of the data was conducted using Excel (Microsoft Office for Mac OS X) to generate descriptive statistics, with other statistical procedures conducted using SPSS version 13.0 for Mac OS X.

Results and Discussion

Table 1 summarises the concentrations of selected PBDE congeners in dust samples taken in this study from each of the four cities studied. Of particular interest is the very wide range of concentrations reported for BDE-209 in the UK samples. Concentrations in two samples are to the authors' knowledge – at 520,000 and 100,000 ng g^{-1}, respectively – the highest concentrations of this contaminant in indoor dust ever reported. However, concentrations of BDE-209 in the rest of the UK samples are grouped much more tightly; this comparatively narrow range is also evident for Canadian and US samples. The data were then statistically evaluated. As a first step, the distribution of concentrations of each congener within each national dataset was evaluated using both Shapiro-Wilks and Kolmogorov-Smirnov tests. The results – combined with visual inspection of frequency diagrams - revealed the data to be log-normally distributed. Hence, we log-transformed all concentrations before performing an ANOVA test on concentrations of individual congeners detected in dusts from each country studied. This analysis revealed the following, with the level of significance (as measured using Scheffe and Bonferroni indicators) being $p<0.05$:

- Concentrations of BDEs 28, 47, 49, 66, 99, 100, 153, and 154 (as individual congeners) in both Canadian and US dusts exceed significantly those in both New Zealand and UK.
- Concentrations of BDEs 28 and 208 in US dusts are significantly higher than those in Canadian dusts.
- Concentrations of BDEs 196 and 209 in UK dusts are significantly higher than those in Canadian dusts.
- No other significant differences were detected.

In short, the data implies that while North American dusts are significantly more contaminated with PBDEs found predominantly in the Penta-BDE formulation than those in either New Zealand or the UK; concentrations of congeners associated with the Deca-BDE product are similar between the UK and the US. These international differences in contamination are consistent with different use patterns of the Penta- and Deca-BDE formulations in North America and elsewhere. Furthermore, the detection of tri-hexa-BDEs in New Zealand dusts at a median concentration that exceeds that for UK dusts, is consistent with the recent report that concentrations of these congeners in blood serum of New Zealanders were at the high end of those detected in Europe.[10] As far as it is possible to ascertain, New Zealand has never manufactured nor directly imported PBDEs; hence their detection in house dust in this location suggests that such contamination is due to their presence in imported goods.

It was suggested recently that ingestion of indoor dust constitutes the principal pathway of exposure to PBDEs in Canada[11] and makes a significant contribution to the exposure of the UK population.[1] Hence, in order to make a preliminary comparative evaluation of the likely magnitude of external exposure via dust ingestion to PBDEs to the inhabitants of the cities in this study, we have assumed (in the absence of experimental data) 100% absorption of intake and similar intake rates for all countries. We have used average adult and toddler dust ingestion figures of 20 and 50 mg day^{-1}, and high dust ingestion figures for adults and toddlers of 50 and 200 mg day^{-1}.[11] These ingestion rates are multiplied by 5th percentile, median, average and 95th percentile dust concentrations to obtain dust intake estimates. It is stressed that the range of exposure estimates via dust ingestion thus derived are only an indication of the likely range within the population. Table 2 summarizes these estimates of the exposure of both adults and toddlers to Σ(tri-hexa)BDEs and (where measured) BDE-209 via dust ingestion in each of the 4 countries studied. These data reinforce previous indications that there is likely to be considerable inter-individual and international variation in human exposure to PBDEs via ingestion of indoor dust. Table 2 also shows our estimates of Canadian, UK, and US exposure via dust ingestion to tri-hexa-BDEs to be in line with those reported previously.[1, 2, 12] The elevated exposures to Σ(tri-hexa)BDEs in North America compared to both New Zealand and UK, together with the fact that estimates of dietary exposure in Canada, UK, and US are similar,[8, 11, 13, 14] support the hypothesis that ingestion of household dust may account for the observed international differences in human body burdens of these congeners. Our measurements in indoor dust suggest that some UK individuals are being exposed to BDE 209 at elevated levels that far exceed the recent estimated UK adult dietary intake of 266 ng d^{-1}.[15] Action is required to establish whether these external exposures to BDE-209 are reflected in human body burdens.

Location		**28**	**47**	**99**	**100**	**153**	**154**	**183**	**207**	**209**	**Σ(tri-hexa) BDE[a]**	**ΣBDE[b]**
Toronto, Canada[c]	Average	6.6	300	510	120	71	69	13	33	670	1100	1500
	Median	4.1	140	330	65	43	39	9.0	29	560	620	970
	Min	1.4	47	80	14	9.4	6.2	7.0	16	290	160	780
	Max	20	720	1800	420	260	280	30	72	1100	3600	3600
Wellington, New Zealand[d]	Average	0.86	36	87	16	9.8	8.7	-	-	-	160	-
	Median	0.65	24	51	8.9	5.4	5.1	-	-	-	96	-
	Min	0.11	3.3	6.4	1.2	0.66	0.56	-	-	-	13	-
	Max	2.1	150	380	70	35	35	-	-	-	680	-
Birmingham United Kingdom[e]	Average	0.75	20	47	7.0	14	5.4	64	210	45000	98	45000
	Median	0.53	13	23	4.2	5.2	3.3	13	57	2800	59	3000
	Min	<dl	1.2	2.8	0.53	0.63	0.31	2.0	6.0	120	5.7	390
	Max	2.3	160	320	50	110	31	550	1300	520000	610	520000
Amarillo & Austin, TX, United States[f]	Average	25	810	1400	240	240	240	28	90	1600	3000	5000
	Median	14	410	820	160	110	89	16	71	1300	1600	4000
	Min	2.1	82	150	33	19	19	4.0	20	530	310	960
	Max	140	3300	6000	840	1800	2200	170	280	3300	14000	17000

Table 1. Summary of concentrations (ng g^{-1}) of selected PBDEs in dust samples from different cities in this study.
[a] sum of PBDEs 28, 47, 49, 66, 99, 100, 153, and 154, [b] sum of PBDEs 28, 47, 49, 66, 99, 100, 153, 154, 183, 196, 197, 203, 206, 207, 208, and 209, [c] ten samples analysed for tri-hexa BDEs; seven samples analysed for tri-deca BDEs, [d] twenty samples analysed for tri-hexa BDEs; hepta-deca BDEs not analysed, [e]twenty eight samples analysed for tri-hexa BDEs; sixteen samples analysed for tri-deca BDEs, [f] twenty samples analysed for tri-hexa BDEs; seventeen samples analysed for tri-deca BDEs.

	Adult				Toddler (6-24 months)			
Intake (ng Σtri-hexa-BDEs day^{-1})	**5th %ile**	**Median**	**Average**	**95th %ile**	**5th %ile**	**Median**	**Average**	**95th %ile**
Canada (mean dust ingestion)	5.2	12	22	60	13	31	55	150
Canada (high dust ingestion)	13	31	55	150	52	120	220	600
New Zealand (mean dust ingestion)	0.30	1.9	3.2	11	0.74	4.8	8.1	26
New Zealand (high dust ingestion)	0.74	4.8	8.1	26	3.0	19	32	110
UK (mean dust ingestion)	0.18	1.2	2.0	7.8	0.46	2.9	4.9	19
UK (high dust ingestion)	0.46	2.9	4.9	19	1.8	12	20	78
US (mean dust ingestion)	11	33	59	200	27	82	150	510
US (high dust ingestion)	27	82	150	510	110	330	590	2000
	Adult				**Toddler (6-24 months)**			
Intake (ng BDE-209 day^{-1})	**5th %ile**	**Median**	**Average**	**95th %ile**	**5th %ile**	**Median**	**Average**	**95th %ile**
Canada (mean dust ingestion)	6.2	11	13	21	16	28	33	53
Canada (high dust ingestion)	16	28	33	53	62	110	130	210
UK (mean dust ingestion)	4.7	56	900	4100	12	140	2200	10000
UK (high dust ingestion)	12	140	2200	10000	47	560	9000	41000
US (mean dust ingestion)	12	26	32	60	29	65	80	150
US (high dust ingestion)	29	65	80	150	120	260	320	600

Table 2. Summary of Estimates of Exposure (ng day^{-1}) of Adults and Toddlers to PBDEs via Dust Ingestion in Canada, New Zealand, UK, and US.

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