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CONCENTRATIONS OF "LEGACY" AND NOVEL BROMINATED FLAME RETARDANTS IN MATCHED SAMPLES OF UK KITCHEN AND LIVING ROOM/BEDROOM DUST

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1. Introduction

Brominated flame retardants (BFRs) have raised great concern due to their ubiquitous occurrence, persistence and toxicity. Current understanding of human exposure to BFRs is that it occurs via a number of pathways including diet, indoor dust ingestion, dermal exposure, and inhalation of (largely indoor) air (Abdallah et al., 2008). Of these pathways, indoor dust ingestion plays an important role. With respect to the contamination of indoor dust with BFRs, most attention has been paid to house dust, with offices, cars and schools also featuring in some studies (Harrad et al., 2010). Within homes, the majority of studies have examined living room dust, with a smaller proportion studying bedrooms. To our knowledge however, no data exist about concentrations of BFRs in dust from domestic kitchens. This is a surprising omission, given that people may spend a substantial proportion of time in this microenvironment, and that kitchens contain a substantial number of goods such as microwave ovens, food processors and fridges etc. that because their plastic components represent a fuel source in the event of fire, are likely to be flame-retarded.

Given this background, the objectives of this study are: 1. to report for the first time the concentrations of selected BFRs in kitchen dust; 2. to test the hypothesis that concentrations of BFRs in domestic kitchen dust exceed those in dust sampled simultaneously from other areas (living rooms/bedrooms) in the same houses, and 3. to test the hypothesis that restrictions on polybrominated diphenyl ethers (PBDEs) in the EU, have led to reductions in concentrations of PBDEs in dust from UK living rooms, accompanied by concomitant increases in concentrations of "novel" BFRs (NBFRs).

To achieve these objectives, we determined concentrations of 8 PBDEs (BDEs-28, 47, 99, 100, 153, 154, 183 and 209), 5 NBFRs (pentabromoethylbenzene (PBEB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP) and decabromodiphenyl ethane (DBDPE)) and α-, β-, γ- hexabromocyclododecanes (HBCDDs) in paired UK kitchen and living room (or bedroom) dust samples taken from 30 homes in the UK West Midlands conurbation in 2015. Data from kitchens are compared with those from living rooms and bedrooms; with those from living rooms/ bedrooms in this study compared with those recorded in an earlier study conducted by our research group of dust from living rooms sampled in the UK West Midlands conurbation in 2006-07 (Harrad et al., 2008).

2. Material and methods

2.1 Sampling

In total, 30 homes from the West Midlands conurbation in the UK were sampled in 2015. For each home, a dust sample from the kitchen floor was collected with a floor dust sample collected from the living room in the same house for comparison. For the 11 homes in which the living room and kitchen were in the same room, dust in the bedroom was collected instead. For carpeted floor, dust was collected by vacuuming a 1 m2 area for 2 min; while for bare floors, the vacuuming area and time were 4 m2 and 4 min, respectively. More details about dust collection and storage protocols have been described in our previous studies (Harrad et al., 2008). An aliquot of 2-3 g pre-baked sodium sulfate vacuumed from a clean Al foil surface served as a field blank.

2.2 Chemicals

Native BDEs 77 and 128, 13C-BTBPE, 13C-BEH-TEBP, 13C-BDE-209 and 13C- α-, β-, γ-HBCDDs were used as internal standards. All standards above were purchased from Wellington Laboratories Inc. All solvents used (acetone, hexane, iso-octane and methanol) were HPLC grade.

2.3 Analysis

The detailed method may be found elsewhere (Kuang et al., 2016). Briefly, the internal standard spiked dust was extracted by hexane : acetone (3:1) for 3 times via sonication. The combined supernatants were reduced in volume to ~ 2 mL and then washed with 3-4 mL 98 % sulfuric acid. After vortex and centrifugation, the supernatant was collected and reduced to incipient dryness. The final concentrate was re-dissolved in 200 μL iso-octane prior to analysis of PBDEs and NBFRs by GC-MS. Following GC-MS analysis, solvent exchange from iso-octane to methanol was conducted to facilitate determination of HBCDDs on LC-MS-MS. Details of GC-MS and LC-MS-MS conditions are reported elsewhere (Kuang et al., 2016). One aliquot of SRM2585 (organics in house dust, NIST) was analysed for every 20 samples and one field blank was analysed every 10 samples for QA/QC purpose.

3. Results and discussion

3.1 Concentrations of BFRs

Table 1 lists minimum, maximum, and median concentrations of target BFRs in both kitchen and living room/bedroom dust in this study. The concentration ranges and profiles obtained in this study are broadly consistent with previous studies. A more detailed comparison with previous data (Kuang et al., 2016) shows that for most compounds, concentrations in this study are lower than previously reported, especially for BDEs-47, -154 and -153. This finding is not inconsistent with a reduction in the use of the Penta-BDE formulation since the early-mid-2000s. In contrast, concentrations of NBFRs, HBCDDs and BDE-209 recorded in this study are similar or even slightly higher than previously reported, which is consistent with the later introduction (or absence to date) of restrictions on use of these BFRs.

3.2 Is there evidence of temporal changes in BFR concentrations in living room/bedroom dust following restrictions on PBDE use?

We compared BFR concentrations in living room dust from 2006-07 (Harrad et al., 2008) with our combined data for living room and bedroom dust via a t test comparison of log-transformed concentrations in the two temporally-distinct sample groups. This revealed concentrations of most target BFRs to be statistically indistinguishable ($p>0.05$) between the two time periods. However, concentrations of BDE-209 and BDE-154 are significantly lower ($p<0.05$) and those of DBDPE and BDE-28 significantly higher ($p<0.05$) in this (later) study. While it is hard to rationalise the opposite trends in BDEs-28 and -154, and acknowledging the small sample numbers involved; the apparent decrease in concentrations of BDE-209, coupled with the corresponding increase of DBDPE, is consistent with the 2008 introduction of restrictions on use of Deca-BDE in the EU, and that DBDPE is the main alternative to Deca-BDE.

3.3 Are concentrations of BFRs higher in kitchen than living room/bedroom dust?

To test our hypothesis that concentrations of BFRs in kitchen dust will exceed significantly those in living area and bedroom dust from the same homes, we conducted a paired t test comparison between concentrations of individual BFRs in kitchen dust and those in living room/bedroom dust. This revealed concentrations for all but BDE-28, PBEB, and DBDPE to be significantly higher ($p<0.05$) in living room/bedroom dust compared to that from kitchens. To investigate the reasons driving this difference, we compared the BFR profile in these two microenvironment categories. Figure 1 is drawn based on the median value of each compound from which it can be found that the composition profiles of kitchen and living room/bedroom dust are similar. A Wilcoxon test comparing the mass percentage of each compound in living room/bedroom and kitchen dust further confirmed this. The proportion difference between kitchen and living room/bed room is insignificant ($p>0.05$) for all compounds, except BDE-28 (higher in kitchen), BTBPE and α-HBCDD (higher in living room/bedroom). Notwithstanding these differences in the relative abundances of a small number of our target BFRs, there appears no clear evidence of major differences between the BFR profiles in kitchens and living rooms/bedrooms, which suggests that there are no major differences in source types between these two microenvironment categories.

As no specific source was identified as responsible for the higher BFR concentrations in dust from living rooms/bedrooms compared to those in kitchen dust, we propose instead that the cause is a generally higher BFR emission rate in living rooms/bedrooms. Although kitchens contain more putative sources, the rate at which BFRs may be emitted from these are influenced by factors such as material, volume and BFR content of sources, which can combine to obscure clear relationships between BFR contamination of dust and putative source counts. Moreover, our study only monitors a selection of BFRs, so it is

possible that some FRs not targeted in our study are used in kitchen appliances. Further studies will be carried out to test this hypothesis.

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Table 1 Maximum (max), minimum (min) and median values of kitchen dust BFR concentration (K, ng/g), living room/bedroom dust BFR concentration (L, ng/g) and matched kitchen-living room/bedroom dust BFR concentration ratio (K/L)

	K			L			K/L		
	max	min	median	max	min	median	max	min	median
BDE-28	150	<0.2	1.2	55	<0.2	1.0	9.55	0.10	1.00
BDE-47	940	0.4	7.6	590	2.4	13	10.30	0.05	0.54
BDE-99	1400	2.6	17	930	4.0	33	15.37	0.06	0.46
BDE-100	320	<0.2	1.7	140	0.7	3.2	7.23	0.03	0.40
BDE-153	410	0.1	1.7	170	<0.4	1.9	10.02	0.01	0.58
BDE-154	180	<0.4	0.4	60	<0.4	0.7	8.64	0.03	0.52
BDE-183	29	<1.0	1.9	120	0.6	4.2	4.57	0.02	0.46
BDE-209	32000	22	590	170000	170	1500	3.92	0.03	0.33
PBEB	25	<0.2	0.3	15	<0.2	0.4	4.45	0.06	0.84
EH-TBB	290	<0.2	4.1	450	<0.2	12	2.85	0.01	0.37
BTBPE	10	<1.0	1.2	97	<1.0	4.5	5.29	0.02	0.44
BEH-TEBP	420	2.7	36	630	7.8	75	2.35	0.05	0.36
DBDPE	450	<9.2	74	680	21	120	12.09	0.03	0.72
α-HBCDD	3800	5.2	110	4900	75	280	2.88	0.05	0.37
β-HBCDD	1100	2.3	29	1600	6.4	67	1.86	0.08	0.41
γ-HBCDD	13000	1.7	35	21000	14	110	34.85	0.003	0.37

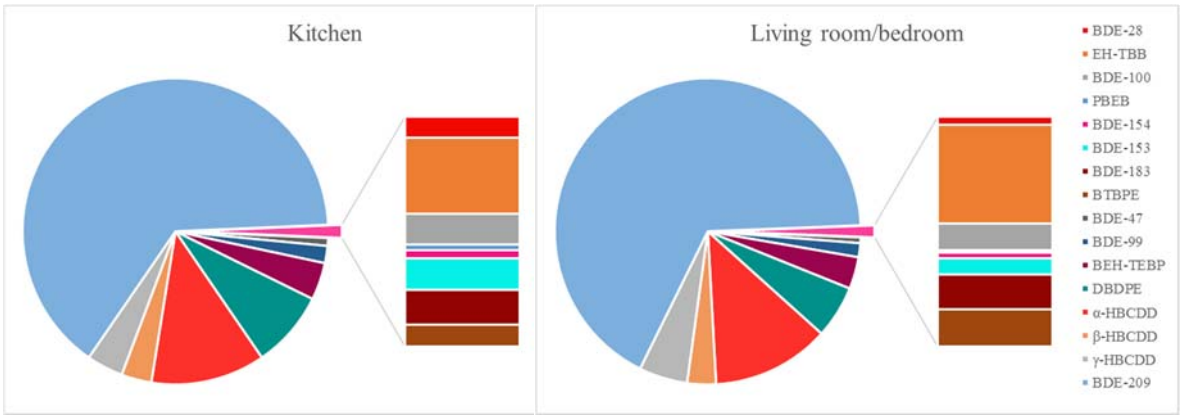

Figure 1 Median BFR compositions in dust from kitchens and living rooms/bedrooms