CHARACTERIZATION OF FLAME RETARDANTS IN HOME INDOOR DUST FROM CALIFORNIA, USA

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Introduction

California house dust contains some of the highest concentrations of flame retardants (FRs) in the world[1]. Polybrominated diphenyl ethers (PBDEs) levels, in particular, are elevated likely due to a state-wide furniture flammability standard[1]. With a phase out of Penta-BDE in the US starting in 2004, other "novel" FRs have been used as replacements. The goals of this study were to measure levels of a broad spectrum of FR chemicals in California homes and to evaluate potential temporal changes in the light of chemical bans.

Materials and methods

Samples. Dust samples were collected in 16 Northern California homes in 2006 and again in the same homes in 2011. Samples were collected by trained field staff using a Eureka Mighty-Mite vacuum cleaner (9 amp) fitted with a specially designed PTFE Teflon crevice tool attachment modified to collect dust into a cellulose extraction thimble (19x90 mm). Samples were collected by slowly dragging the crevice tool for approximately 30 minutes over surfaces in the most frequently used rooms in the home. Samples were sieved to <150 µm prior to long-term storage (at 4°C) and extraction.

Materials and reagents. Standards of BDE 28, 47, 66, 85, 99, 100, 153, 154, 183, 196, 197, 203 and 209, α-HBCD, β-HBCD, γ-HBCD, BTBPE, DBDPE, HCDBCO, TBB, TBPH, HBB, TBBPA-dbpe, TBBPA, TBECH isomers, ATE, BATE, DPTE, TBCO isomers, OBIND, DP isomers, and labeled internal standards (IS) ^{13}C-BDE 209, ^{13}C-α-HBCD, ^{13}C-β-HBCD, ^{13}C-γ-HBCD, and ^{13}C-TBBPA were purchased from Wellington Laboratories. Standards of PCBs, PBBs and OCPs were purchased from Dr. Ehrenstorfer. BDE 77 and 128 (IS) were obtained from AccuStandard. Standards of T*i*BP, T*n*BP, TPhP, TCEP, TEHP, EHDPP, TCP (mixture of 4 isomers), TDBPP (or brominated Tris) and TDCPP (or chlorinated Tris, mixture of 2 isomers) were purchased from Chiron. Triamyl phosphate (TAP; IS) was purchased from TCI Europe. Labeled TPhP-d15 (IS) and TBEP were purchased from Sigma Aldrich. TCPP (mixture of 3 isomers) was purchased from Pfaltz & Bauer. Purity of analytical standards was >98%, except for TBEP (>94%). See Table 1 for abbreviations and acronyms. Standard stock solutions were prepared in *iso*-octane, except for NBFRs which were prepared in a mixture of *iso*-octane:toluene (8:2, *v/v*).

Indoor dust (SRM 2585) was from the US National Institute of Standards and Technology (NIST, USA), silica SPE cartridges (500 mg/3 mL, Bond Elut) from Agilent, while empty polypropylene filtration tubes (3 mL) SPE cartridges and 500 mg/3 mL Supelclean ENVI- Florisil cartridges from Supelco. Silica gel, anhydrous sodium sulfate (Na_2SO_4), and concentrated sulfuric acid (H_2SO_4, 98%) were purchased from Merck. Glass test tubes were cleaned by soaking for at least 12 h in an alkali solution (diluted RBS 35, pH 11–12). After washing, the tubes were rinsed with water, dried at 400 °C for at least 12 h and rinsed with *n*-hexane (Hex) before use.

Sample preparation: Due to the comprehensive list of targeted FRs and the large differences in their physico-chemical properties, we have used two different sample preparation methods which have led to four extracts per sample (two fractions per method). These extracts were injected in various instruments, according to the expected presence of the FR groups.

Method I (Florisil). The fractionation on Florisil was employed to measure the bulk of BFRs and organochlorines (OCs which elute in the first fraction (Fraction 1 – F1) and OPFRs which elute in the 2nd fraction (Fraction 2 – F2). The method is largely based on the recent method described by Van den Eede et al.[2]. In detail, a sample aliquot (around 50 mg) was accurately weighed and spiked with IS (^{13}C-BDE 209, BDE 77, BDE 128, CB 143, TCEP-d12, TBEP-d6, TDCPP-d15, TAP, and TPhP-d15). Samples were extracted using 2 mL Hex/Ac (3:1, *v/v*) by a combination of vortexing and ultrasonic extraction (2 × 1 min vortex and 5 min ultrasonic extraction) which was repeated three times. After each extraction cycle, dust extracts were centrifuged

at 3500 rpm for 2 min, supernatants were collected and transferred into clean glass tubes. The pooled supernatants were evaporated until dryness under a gentle nitrogen flow and redissolved in 1 mL Hex.

The extract was quantitatively transferred to a Florisil cartridge and fractionation was achieved by elution with 8 mL of Hex (F1) and 10 mL of EA (F2). The 1st fraction (F1) was evaporated until 1 mL and quantitatively transferred onto acidified silica 44% cartridges for a second clean-up. The target analytes were eluted with 10 mL of Hex/DCM (1:1, *v/v*), and afterwards evaporated until dryness under gentle nitrogen flow and reconstituted in 100 µL of *iso*-octane. In the 2nd fraction (F2), IS BDE 128 was added for the quantification of TBPH and TDBPP, followed by evaporation until dryness and resolubilized in 100 µL of *iso*-octane. Fraction F1, containing PBDEs, most NBFRs, OCs and PBBs, was subjected to analysis by GC-ECNI/MS (different acquisition methods) and GC-EI/MS (confirmation of OCs and PBBs). The 2nd fraction (F2), containing OPFRs and TBPH, was subjected to analysis by GC-EI/MS (for OPFRs) and GC-ECNI/MS (for TBPH and TDBPP).

Method II (Silica). The fractionation on silica was employed to measure HBCDs and TBBPA, which eluted in the 2nd fraction (Fraction B – FB) and to confirm PBDEs which eluted in the first fraction (Fraction A – FA). The extraction was similar to that described above, while the fractionation on silica was similar to the procedure described by Roosens et al.[3]. In detail, a sample aliquot (typically 50 mg) was accurately weighed and spiked with a mixture containing IS (^{13}C-α-, β-, γ-HBCD, ^{13}C-TBBPA, ^{13}C-BDE 209, BDE 77, and BDE 128). Samples were extracted as described above (Florisil fractionation). Prior to fractionation, silica cartridges were topped with 100 mg acid silica (44%) and prewashed with 6 mL of Hex. The extracts were quantitatively transferred and fractionation was achieved by eluting with 8 mL of Hex (Fraction A – FA) and 10 mL of DCM (Fraction B – FB). Both fractions were afterwards evaporated until dryness under gentle nitrogen flow. Fraction FA, containing PBDEs, was reconstituted in 100 µL of *iso*-octane and was subjected to GC-ECNI/MS. The 2nd fraction (FB), containing HBCDs and TBBPA, was resolubilized in 100 µL of methanol and further subjected to LC-MS/MS analysis.

Analysis

Analysis of dust samples collected in 2006 and 2011 took place in January 2012.

GC-ECNI/MS analysis. The analysis of F1, containing PBDEs, most NBFRs, and OCs, and the analysis of F2, containing TBPH, was performed by GC-ECNI/MS. Two µL extract were injected on a DB-5 column (15 m × 0.25 mm × 0.10 µm) using solvent vent injection and ramped flow of the carrier gas. The mass spectrometer was employed in selected ion monitoring (SIM) mode, with ions *m/z* 79 and 81 monitored the whole run time. For BDE 209, ions *m/z* 487 and 485 were used, while ^{13}C-BDE 209 was monitored using ions *m/z* 495 and 497. Dwell times were set on 35 ms. The ion source, quadrupole and interface temperatures were set at 250, 150 and 300 °C, respectively and the electron multiplier voltage was at 2200 V. Methane was used as moderating gas.

GC-EI/MS. Analysis of OPFRs in F2 was performed by GC-EI/MS. One µL extract was injected on a HT-8 column (25 m × 0.22 mm × 0.25 µm) using cold pulsed splitless injection and constant flow of the carrier gas (1.0 mL/min). The mass spectrometer was run in SIM mode. Dwell times ranged between 20 and 30 ms in different acquisition windows. The ion source, quadrupole and interface temperatures were set at 230, 150 and 300 °C, respectively and the electron multiplier voltage was at 2200 V.

LC-MS/MS. The determination of individual HBCD isomers and TBBPA in the Fraction B (silica) was achieved by LS-MS/MS using a Luna C18(2) reversed phase analytical column (150 mm × 2 mm × 3 µm, Phenomenex). A mobile phase of (A) ammonium acetate 2mM in water/methanol (1:1, *v/v*) and (B) methanol at a flow rate of 0.25 mL/min was applied; starting at 75% (B) held for 2 min, then increased linearly to 100% (b) until 9 min; held until 12 min followed by a linear decrease to 70% (B) over 0.5 min and held for 7.5 min. The triple quadrupole MS system was operated in the electrospray negative ionization mode and the MS/MS detection operated in the MRM mode was used for quantitative determination of the HBCD isomers based on *m/z* 640.6 to 81 and *m/z* 652.6 to 81 for the native and ^{13}C-labeled diastereomers, respectively. Fragmentor voltage and collision energy were set as 80 and 15 V, respectively. For quantitative determination of TBBPA, the following MRMs were used: *m/z* 552.5 to 79 and *m/z* 540.5 to 79 for the native and ^{13}C-labeled TBBPA, respectively.

***Quality Control*:** Six procedural blanks were analysed in the same batches as the samples and concentrations are blank corrected. This implies subtraction of mean blank values (in pg) from the raw FR values (in pg) in the samples. Method limits of quantification (LOQ) were calculated as on 3 × SD of blank values and divided by the amount of dust used for analysis (typically 50 mg). For compounds not detected in the blanks, the LOQ was calculated based on the signal to noise ratio 10/1. Since LOQs are compound-specific variables, they spanned a

large range of concentrations (Table 1). The method has been recently validated as described by Van den Eede et al.[2]. Certified material SRM 2585 (Organics in indoor dust) has been used to test the accuracy.

Results and discussion

The dust samples from California were analyzed for 62 FRs and OCs, including 13 PBDEs, 12 OPFRs, 19 NBFRs, dechlorane plus, HBCDs and TBBPA (Table 1). Overall, 55 compounds were detected in at least one sample and 41 in at least 50% of samples. Eighteen of 19 OPFRs were detected in both sampling rounds and the HBCD isomers were detected in all samples.

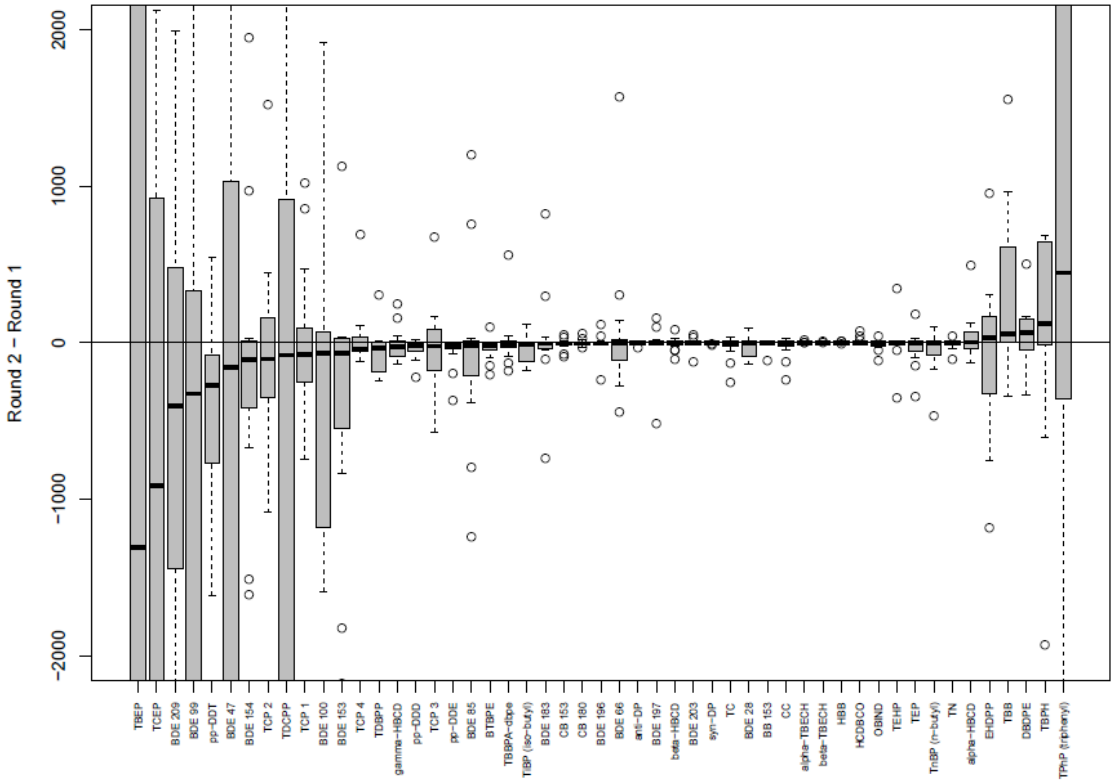
Table 1. Summary statistics for FRs and OCs in California house dust (concentrations given in ng/g dust).

			Dust samples from 2006				Dust samples from 2011			
Chemical Name	**Abbrev.**	**Detection Limit**	**Det. Frequency (%)**	**Min.**	**Median**	**Max.**	**Det. Frequency (%)**	**Min.**	**Median**	**Max.**
2,2',4,4',5,5'-Hexachlorobiphenyl	CB 153	5	100	6	18	200	81	--	9,5	130
1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane	pp-DDT	10	100	44	530	4100	100	50	160	1500
2,2',4,4',5,5'-Hexabromo biphenyl	BB 153	3	56	--	4,5	160	44	--	--	47
2,4,4'-Tribromodiphenyl ether	BDE 28	2	100	5	26	270	100	3	14	310
2,2',4,4'-Tetrabromodiphenyl ether	BDE 47	2	100	270	2300	23000	100	140	1000	17000
2,3',4,4'-Tetrabromodiphenyl ether	BDE 66	2	100	8	64	520	100	4	23	1800
2,2',3,4,4'-Pentabromodiphenyl ether	BDE 85	3	100	13	110	1300	100	9	66	6000
2,2',4,4',5-Pentabromodiphenyl ether	BDE 99	2	100	280	2200	24000	100	190	1100	25000
2,2',4,4',6-Pentabromodiphenyl ether	BDE 100	2	100	56	520	4900	100	37	240	11000
2,2',4,4',5,5'-Hexabromodiphenyl ether	BDE 153	3	100	2	250	2400	100	21	150	7800
2,2',4,4',5,6'-Hexabromodiphenyl ether	BDE 154	3	100	22	240	1800	100	17	110	6700
2,2',3,4,4',5',6-Heptabromodiphenyl ether	BDE 183	4	100	9	28	770	100	3	18	920
2,2',3,3',4,4',5,6'-Octabromodiphenyl ether	BDE 196	4	88	--	7,5	240	56	--	4	180
2,2',3,3',4,4',6,6'-Octabromodiphenyl ether	BDE 197	4	81	--	9	530	56	--	4	230
2,2',3,4,4',5,5',6-Octabromodiphenyl ether	BDE 203	4	81	--	5	130	50	--	2	110
Decabromodiphenyl ether	BDE 209	10	100	580	1400	15000	100	110	1200	8500
Hexabromobenzene	HBB	2	50	--	1	8	31	--	--	13
1,2-bis(2,4,6-tribromophenoxy)ethane	BTBPE	2	100	7	30	220	100	3	12	130
Decabromodiphenylethane	DBDPE	10	94	--	51	430	100	18	140	2800
Tetrabromobisphenol A - bis(2,3-dibromopropylether)	TBBPA-dbpe	10	75	--	22	180	50	--	7	560
Tris(2,3-dibromopropyl) phosphate	TDBPP	20	62	--	35	8900	38	--	--	310
2-ethylhexyl-2,3,4,5-tetrabromobenzoate	TBB	2	100	4	48	740	100	45	100	5900
bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate	TBPH	2	100	36	140	1900	94	--	260	3800
Tri-phenyl phophate	TPhP	20	100	580	3000	14000	100	790	2800	36000
Tri-iso-butyl-phosphate	TiBP	80	56	--	84	180	19	--	--	120
Tri-n-butyl-phosphate	TnBP	80	50	--	32	1800	38	--	--	1800
Tris-(2-chloroethyl)-phosphate	TCEP	20	100	610	5100	160000	100	330	2700	110000
Tris-(2,3-dichloropropyl)-phosphate	TDCPP	20	100	730	2800	24000	100	920	2100	44000
Tri-(2-butoxyethyl)-phosphate	TBEP	300	100	2300	12000	68000	100	790	11000	170000
Ethylhexyl Diphenyl phosphate	EHDPP	100	100	180	610	3000	100	140	560	1500
Tri-cresyl phosphate 1	TCP 1	20	100	100	270	1300	100	54	180	1600
Tri-cresyl phosphate 2	TCP 2	20	100	140	440	1900	100	82	310	4200
Tri-cresyl phosphate 3	TCP 3	20	100	86	260	1000	100	45	150	3400
Tri-cresyl phosphate 4	TCP 4	20	88	--	48	200	75	--	34	880
syn-dechlorane plus	syn-DP	2	81	--	3	22	44	--	--	7
anti-dechlorane plus	anti-DP	2	100	3	7,5	35	75	--	3	8
alpha-hexabromocyclododecane	α-HBCD	5	100	31	62	710	100	17	62	910
beta-hexabromocyclododecane	β-HBCD	5	100	8	18	330	100	7	16	230
gamma-hexabromocyclododecane	γ-HBCD	5	100	29	94	6700	100	13	73	790

The major Penta- and Deca-BDE constituents were detected in 100% of homes in both sampling rounds. The highest concentrations, greater than 0.1 mg/g, were for three OPFRs, including one listed as a carcinogen under California's Proposition 65 (TCEP). Median concentrations of BDE-47 and BDE-99, predominant components of the Penta-BDE mixture, went down from 2006 to 2011, possibly reflecting reduced use. Components of Firemaster 550 (TBPH, TBB, and TPhP), suspected as the major penta-BDE replacement, were detected in nearly all samples and with 90th percentiles in 2011 up to a order of magnitude higher than in 2006 (Figure 1). Preliminary cluster analysis shows that manufacturing and use patterns are reflected in house dust. Comparisons of dust levels, furniture foam samples, and household survey data suggest potential sources.

These data, which include first US measures for many FRs, illustrate changing exposure patterns as manufacturers substitute chemicals to meet regulatory and consumer requirements.

Figure 1. Plot indicating differences in the concentrations (ng/g) of FRs between Round 2 (2011) and Round 1 (2006) measured in California houses. Compounds on the left hand side indicate a decrease from 2006 to 2011 (e.g. PBDEs, TBEP, and TCEP), while compounds on the right hand side of the graph indicate an increase in concentration from 2006 to 2011 (e.g. TPhP, TBPH, TBB, and DBDPE). Non-detects set to zero for difference calculations. Compounds not detected in either round are excluded. Y-axis limited to -2000 to 2000, which truncates some boxplots.



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