

OCCURRENCE OF SELECTED NON-BDE HALOGENATED FLAME RETARDANTS IN THE CANADIAN HOUSE DUST STUDY

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Introduction

The market for flame retardants is growing rapidly due to product specific and tough fire safety regulations. Many commercial products have been treated with brominated flame retardants (BFRs) in order to reduce their flammability and meet national or international regulations. The most commonly used BFRs include polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA), and hexabromocyclododecane (HBCD). Potential human health effects associated with the most produced BFRs have been reviewed elsewhere¹. Two major PBDE commercial mixtures (i.e., PentaBDE and OctaBDE) were banned by the European Union and phased out in the United States by 2004². PentaBDE and OctaBDE were also added to the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2009, which restricts or prohibits the production of persistent organic pollutants³. In Canada, the manufacturing of these previously assessed PBDEs has been banned and the use and importation of some PBDEs have been prohibited as well. Therefore, various halogenated flame retardants have been developed as alternatives to PBDEs and are currently used in many applications. House dust is known to be a sink for semi-volatile organic compounds and particle-bound organic matter and thus may be a significant route of human exposure to environmental pollutants, including the so-called “novel” flame retardants. The objective of this study was to generate exposure data for 18 non-BDE halogenated flame retardants from house dust samples collected under the Canadian House Dust Study (CHDS).

Materials and methods

Chemicals

Target non-PBDE halogenated flame retardants included allyl 2,4,6-tribromophenyl ether (ATE), 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (α -, β -, γ -, and δ -TBECH), 2,3,5,6-tetrabromo-p-xylene TBpX), 2-bromoallyl 2,4,6-tribromophenyl ether (BATE), 1,2,3,4,5-pentabromobenzene (PBB), tetrabromo-o-chlorotoluene (TBCT), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), 2,3-dibromopropyl 2,4,6-tribromophenyl ether (DPTE), hexabromobenzene (HBB), pentabromobenzyl bromide (PBBB), pentabromobenzyl acrylate (PBBA), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), *syn*-dechlorane Plus (*syn*-DP), and *anti*-dechlorane Plus (*anti*-DP). Individual non-PBDE FRs standards were purchased from Wellington Laboratories (Guelph, ON, Canada). Individual stock solutions were prepared in toluene and working standard solutions were prepared by mixing individual standard solutions and diluting in toluene. Solvents (hexane, acetone, and toluene, all GC-grade) were purchased from EMD Chemicals Inc. (Gibbstown, NJ, USA).

Sample collection

Two types of vacuum samples were collected from randomly selected urban Canadian single family dwellings under Health Canada's Canadian House Dust Study as previously described^{4,5} and briefly summarized here. Household vacuum dust (HD) samples were obtained from the vacuum systems used by the study participants as part of their regular house cleaning routine. Fresh dust (FD) sampling was conducted by trained technicians following protocols developed for the CHDS⁴. FD samples were collected in living areas (bedrooms, living rooms, hallways, offices) using a Pullman Holt (model 102 ASB-12PD) vacuum sampler, in which dust particles followed a direct pathway from the floor to the vacuum bag, without contacting the internal mechanical parts, thus avoiding potential contamination. The areas sampled to collect the FD samples consisted of “active” dust and minimized the inclusion of old house dust found in joints and cracks in flooring or in areas where the householder did not vacuum on a regular basis. Wet areas in the home (kitchens, bathrooms, laundry rooms) were avoided to protect the integrity of the FD sample. The home owner was asked not to vacuum the sampling areas for a period of one week before the scheduled FD sampling. The samples were collected in the winter season. The dust was fractionated using stainless steel sieves, and the <80 μ m particle size fraction was retained

for chemical analysis. Sieved dust samples were kept frozen in gas tight amber glass jars to prevent potential photolysis.

Sonication extraction and sample cleanup

Dust samples were accurately weighed ($0.1 \text{ g} \pm 0.003 \text{ g}$) and transferred to a 10-mL glass centrifuge tube. 25 μL of the internal standard mixture solution, which contained 6-fluoro-2,2',4,4'-tetrabromodiphenylether (F1BDE-47, 0.2 ng/ μL), BDE-105 (0.2 ng/ μL), ^{13}C -syn-DP (1.0 ng/ μL), and ^{13}C -anti-DP (1.0 ng/ μL), was spiked into the sample. The tube was then vortexed. Hexane/acetone (1.5 mL, 1:1, v/v) was added into the tube. The tube was vortexed and then sonicated for 5 min and vortexed again to re-suspend the dust pellets. This process was repeated twice and then the tube was centrifuged for 5 min at 1500 rpm. The clear supernatant was transferred to a 4-mL amber vial. The extraction cycle was repeated two more times and the supernatant combined. The combined extract was concentrated by a gentle stream of nitrogen at room temperature and solvent exchanged to hexane. The concentrated extract (0.5 mL in hexane) was then subjected to sample cleanup on a Florisil SPE cartridge (500mg/6cc, UCT, Bristol, PA). The cartridge was preconditioned with 2 x 5 mL of hexane. The concentrated extract was loaded onto the cartridge. The vial was rinsed with hexane (2 x 0.5 mL) and the rinse was also added to the cartridge. The cartridge was eluted with 2 x 5 mL of hexane. The eluent was evaporated at room temperature under a gentle stream of nitrogen to just dryness. The residue was reconstituted in 175 μL of toluene. After 25 μL of recovery standard BDE-77 (0.2 ng/ μL) was added, the final solution was subjected to GC/MS analysis operated in electron capture negative ionization (ECNI) mode.

Table 1. Target FRs, molecular weights (MW), SIM ions (bold ion for quantitation, another ion for confirmation), method detection limit (MDL), limit of quantitation (LOQ), and average recovery (Ave. Rec., %).

CASRN#	Compound	MW	SIM Ions	MDL (ng/g)	LOQ (ng/g)	Av. Rec. (% \pm RSD)
3278-89-5	ATE	370.9	81/79	0.5	1.7	100 \pm 6
3322-93-8	α -TBECH	427.8	81/79	0.9	3.0	92 \pm 5
3322-93-8	β -TBECH	427.8	81/79	0.6	2.1	112 \pm 6
23488-38-2	TBpX	421.8	81/79	0.6	1.9	100 \pm 4
99717-56-3	BATE	450.0	81/79	0.5	1.6	107 \pm 4
608-90-2	PBB	472.6	81/79	0.8	2.7	107 \pm 4
3322-93-8	(γ + δ)-TBECH*	427.8	81/79	0.6	2.0	72 \pm 4
39569-21-6	TBCT	442.2	81/79	0.9	3.1	79 \pm 3
87-83-2	PBT	486.6	81/79	0.6	1.9	78 \pm 3
85-22-3	PBEB	500.7	81/79	0.6	1.9	72 \pm 3
35109-60-5	DPTE	530.7	81/79	0.5	1.7	94 \pm 5
87-82-1	HBB	551.5	81/79	0.5	1.8	81 \pm 4
38521-51-6	PBBB	565.5	81/79	1.0	3.3	61 \pm 14
59447-55-1	PBBA	556.7	81/79	1.6	5.5	68 \pm 13
183658-27-7	EHTBB	549.9	81/79	1.5	4.9	84 \pm 12
37853-59-1	BTBPE	687.6	81/79	1.7	5.5	80 \pm 16
135821-74-8	syn-DP	653.7	654/652	1.2	3.9	105 \pm 6
135821-03-3	anti-DP	653.7	654/652	1.9	6.3	107 \pm 8

(*): γ -TBECH and δ -TBECH could not be well separated and thus quantitated as the sum of these two isomers.

GC/MS analysis

Sample extracts were analyzed using an Agilent 6980 gas chromatograph coupled with a Waters Quattro micro triple quadrupole mass spectrometer (Waters Corp., Milford, MA, USA) operated in ECNI mode. Methane was used as reagent gas. The ion source and GC interface temperatures were set at 130 °C and 260 °C, respectively. The GC column was a Zebron ZB-5HT (15 m x 0.25 mm, 0.10 µm of film thickness) from Phenomenex (Torrance, CA, USA). The carrier gas was helium with a constant flow of 1 mL/min. The oven temperature was initially held at 80 °C for 2 min; ramped to 200 °C at 4 °C/min; held at 200 °C for 1 min; ramped to 300 °C at 25 °C/min; held at 300 °C for 2 min; ramped up to 330 °C at 35 °C/min, and finally held at 330 °C for 5 min. The GC injector was equipped with a programmable-temperature vaporizer inlet (PTV) which was run in solvent vent mode. The initial inlet temperature was held at 90 °C for 0.20 min; ramped to 295 °C at 700 °C/min; held at 295 °C for 20 min. Vent pressure was set at 30 kPa with vent flow of 200 ml/min ending at 0.10 min. Purge flow was 50 ml/min after 2 min. The injection volume was 2 µL. Selected ion monitoring (SIM) mode was employed to monitor two ions for each individual compound, one for quantitation and another for confirmation.

Results and discussion

The method detection limit (MDL) and limit of quantitation (LOQ), calculated using the procedure outlined in the US EPA Regulation 40 CFR part 136⁶, ranged from 0.5 ng/g to 1.9 ng/g (Table 1). The method demonstrated good recoveries, ranging from 61% to 112% (Table 1).

Table 2. Concentrations (ng/g) of non-BDE halogenated flame retardants in a sub-sample (n=168) of Canadian House Dust Study samples

Analyte	MDL	5th PCTL*	Median	99th PCTL	Max	Detection (%)
ATE	0.5	< 0.5	1	144	391	64
α-TBECH	0.9	< 0.9	1	131	245	55
β-TBECH	0.6	< 0.6	1	109	288	70
TBpX	0.6	< 0.6	< 0.6	2	20	10
BATE	0.5	< 0.5	< 0.5	23	47	35
PBB	0.8	< 0.8	1	24	111	59
(γ+δ)-TBECH	0.6	ND**	ND	ND	ND	0
TBCT	0.9	< 0.9	4	79	104	89
PBT	0.6	< 0.6	< 0.6	4	6	21
PBEB	0.6	ND	ND	ND	ND	0
DPTE	0.5	ND	ND	ND	ND	0
HBB	0.5	< 0.5	10	237	327	90
PBBB	1	ND	ND	ND	ND	0
PBBA	1.6	ND	ND	ND	ND	0
EHTBB	1.5	< 1.5	64	2768	12968	87
BTBPE	1.7	< 1.7	8	882	2389	80
syn-DP	1.2	< 1.2	< 1.2	58	80	86
anti-DP	1.9	< 1.9	< 1.9	89	121	86

(*) PCTL = Percentile; (**): ND = Non-detectable

Concentrations of selected non-BDE halogenated flame retardants are reported here for a subset of 168 house dust samples collected in Canadian homes (Table 2). In this study, a detection frequency (>MDL) between 55% and 90% was observed for ten out of the 18 non-BDE halogenated flame retardants analyzed including: ATE, α-TBECH, β-TBECH, PBB, TBCT, HBB, EHTBB, BTBPE, syn-DP and anti-DP. These data are not normally distributed. The median concentrations were low for most analytes, with the exception of EHTBB (64 ng/g). Higher concentrations were observed (range in parentheses) for ATE (<0.5 - 391), α-TBECH (<0.9 - 245), β-

TBECH (<0.6 - 288), BATE (<0.5 - 47), PBB (<0.8 - 111), TBCT (<0.9 - 104), HBB (<0.5 - 327), EHTBB (<1.5 - 12968), BTBPE (<1.7 - 2389), syn-DP (<1.2 - 80), and anti-DP (<MDL - 121, 86). Similar concentrations of the above flame retardants were reported in other studies summarized elsewhere^{7,8}. TBpX, BATE, and PBT were detected at frequencies of 10%, 35% and 21%, respectively, at lower concentrations. γ - and δ -TBECH, PBEB, DPTE, PBBB and PBBA were not detected in any of the samples analyzed. The present study showed widely scattered concentration levels for those FRs detected in house dust, suggesting a wide variability in their use and potential for human exposure in Canadian indoor environments. The full set of house dust samples from the CHDS is currently being analyzed in order to generate statistically robust national baseline values for the selected non-BDE flame retardants. Finally, the data from this study will contribute to the risk assessment and/or risk management of these non-BDE halogenated flame retardants.

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