

# ALTERNATE AND NEW BROMINATED FLAME RETARDANTS DETECTED IN U.S. HOUSE DUST

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## Introduction

Due to the phase-out of PentaBDE, OctaBDE, and recently DecaBDE (in some regions), it is to be expected that an increasing number of alternate flame retardant chemicals will be introduced to comply with consumer product fire safety standards. Potential replacements include tetrabromobisphenol-A (TBBPA), hexabromocyclododecane (HBCD), bistris(bromophenoxy) ethane (BTBPE), decabromodiphenyl ethane (DBDPE) and several phosphate based compounds, such as triphenyl phosphate. Given that these alternate flame retardants often share similar properties to the PBDE mixtures (e.g. aromatic moieties, high bromination, low aqueous solubility, etc.) and that most are used as additive, as opposed to reactive (e.g. covalently bound) flame retardants, environmental fates, similar to PentaBDE, may be expected. HBCD for example has been detected in several environments and species (1). In addition, temporal increases in the concentrations of HBCD have been observed in California sea lions (2), and harbor porpoises (3), similar to trends previously reported for PBDEs (4), and perhaps a result of their use as PBDE replacements. In addition, BTBPE has recently been identified in air collected near the Great Lakes (5). Thus these new flame retardants are leaching into the environment; however, little is known about their potential bioaccumulation and toxicity.

We recently reported on PBDEs levels in air and dust with considerations of temporal and spatial trends, and linking household products (eg. televisions, furniture) to PBDE dust concentrations using XRF technology (6-8). Here we are reporting on measurements of alternate and new brominated flame retardants determined in the same dust samples. Our objectives were to determine the distribution, range and median levels of BTBPE, HBCD and DBDPE in these dust samples. During this investigation we also discovered the presence of two previously unidentified flame retardants in dust, 2-ethylhexyltetrabromobenzoate (TBB) and bis(2-ethylhexyl) tetrabromophthalate (TBPH). TBB and TBPH are the brominated components of Firemaster 550®, a commercial mixture which is now known to be a replacement product for PentaBDE.

## Materials and Methods

Information on the collection of dust samples is detailed in Allen et al. (7). Briefly, researcher-collected dust samples were obtained from the bedroom and living room from 20 homes during the fall of 2006. Dust samples were collected using a Eureka Mighty-Mite vacuum cleaner (Model 3670) and crevice tool attachment. The dust was collected in a cellulose extraction thimble (Whatman International) inserted between the crevice tool and the vacuum tube extender and secured using a rubber o-ring. The equivalent of the entire floor-surface area for each room was vacuumed by gently drawing the crevice tool across the top of all surfaces. Dust was also collected from the participant's home vacuum cleaner as a comparison. Field blanks were prepared using sodium sulfate powder as a surrogate for dust and collected using the Mighty-Mite vacuum.

Analysis of BTBPE in dust samples was conducted using the same extraction method previously published for the analysis of PBDEs in dust (7). Therefore, dust extracts analyzed for PBDEs and previously published were re-analyzed to determine the concentrations of BTBPE using 4-fluoro-2,3',4,4',6-pentabromodiphenyl ether (F-BDE 160) as a quantification standard that were previously added to the extracts for the analysis of PBDEs. However, analysis of dust samples for total HBCD, DBDPE, TBB, and TBPH required a separate extraction and clean-up method. For these analyses approximately 0.3 grams of dust was extracted three times with 100% dichloromethane at a temperature of 100°C and at 1500 psi using pressurized liquid extraction. The final extract was reduced in volume to approximately 1.0 mL using an automated nitrogen evaporation system (Turbo Vap II, Zymark Inc.). Extracts were then purified by elution through a column containing 8.0 g of 2.5% deactivated Florisil. HBCD, TBB and TBPH were eluted with 50 mL of a 50:50 mixture of hexane:dichloromethane. The final extract was again reduced in volume to 0.5 mL and then spiked with 50 ng of the quantification standards, F-BDE-160 and <sup>13</sup>C-labeled BDE-209. All samples were analyzed using gas chromatography mass spectrometry operated in electron capture negative ionization mode (GC/ECNI-MS), similar to our previous analysis of dust samples. PBDEs, BTBPE, HBCD and DBDPE were quantified by monitoring bromide ions (*m/z* 79/81). TBB was quantified using ion fragments (*m/z*) 357 (Quantitative) and 471 (Qualitative) while TBPH was quantified using ion fragments (*m/z*) 463 (Quant) and 515 (Qual).

## Results and Discussion

In our previous study we determined the concentrations of PBDEs in dust samples collected from 19 different homes in the Boston, MA area (7). During this analysis we identified several additional peaks in the GC/ECNI-MS chromatograms which contained a strong 1:1 ratio of 79/81, indicative of the presence of bromine. Some of these peaks were identified as HBCD, BTBPE and DBDPE based on comparisons with authentic standards. However, during these comparisons there was one remaining and significant peak present in several of the chromatograms which was not identified. A full ECNI-MS scan of this compound revealed that the molecular weight of the compound was approximately 706 amu and the ion clusters suggested the presence of four bromine atoms. A recent publication characterizing different flame retardants reported on the use a brominated phthalate as an additive flame retardant in polyvinylchloride and neoprene rubber (9). This brominated phthalate, known as bis(2-ethylhexyl)tetrabromophthalate (TBPH), has a molecular weight of 706 amu, suggesting that it might be the compound we were observing in the dust samples.

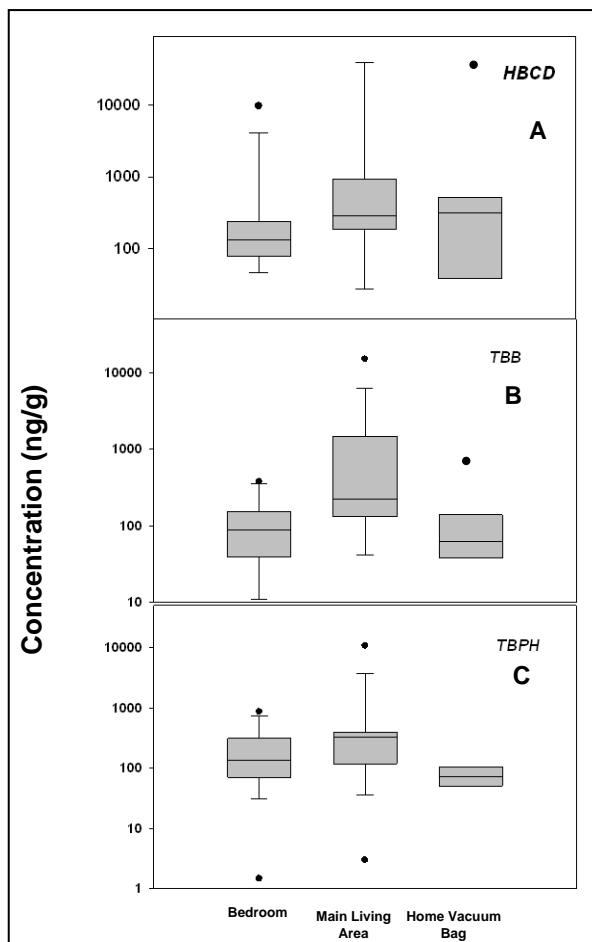
Using a pure TBPH standard we compared the mass spectrum and retention times to confirm the identity of TBPH in the dust. Due to the prevalence of the compound among the dust samples it seemed plausible that this brominated compound may be one of the replacements for the withdrawn PentaBDE and OctaBDE commercial mixtures. To investigate potential sources and applications of TBPH we tested a sample of Great Lakes Chemical's primary PentaBDE replacement mixture, known as Firemaster 550® (FM 550), to determine if it contained TBPH. The comparison confirmed that TBPH was present in FM 550, in addition to another brominated compound. Due to the structure and molecular weight (550 amu) of this second brominated compound present in FM 550, it was hypothesized to be a decarboxylated form of TBPH. Using a pure standard we confirmed the identity of 2(ethylhexyl)tetrabromobenzoate (TBB) as the second, and dominant, brominated compound present in FM 550. The structure of the major brominated component in FM 550 was elucidated from GC/EI-MS, GC/NCI-MS, <sup>1</sup>H NMR spectroscopy along with <sup>13</sup>C two-dimensional homonuclear <sup>13</sup>C-<sup>13</sup>C Incredible Natural Abundance Double Quantum Transfer Spectroscopy (INADEQUATE) to be 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB).

**Table 1** presents the % detect, geometric mean (GM), geometric standard deviation (GSD) and range of the concentrations of the brominated flame retardants that were measured in the dust samples. Dust concentrations for all compounds failed normality assumptions (Shapiro-Wilk, *p*<0.05) and demonstrated log-normal distributions. The detection frequency of all compounds was high, particularly TBB and TBPH which had 95% and 100% detection frequencies, respectively. This suggests they have a ubiquitous presence in indoor environments in the U.S., which may be a reflection of their use as a PentaBDE replacement in polyurethane foam. The largest range in

concentration was observed for HBCD, with a maximum concentration of 130,220 ng/g. This is more than 500 times the median HBCD level measured among the dust samples, and is consistent with the log-normal distribution observed for many flame retardants. Levels of BTBPE were an order of magnitude lower than the other flame retardants measured in this study. The geometric mean ranged from 18 to 48 ng/g (depending on the room from which the dust was collected), with a maximum value of 789 ng/g. DBDPE levels ranged from less than detection (<10 ng/g) to a maximum of 11,067 ng/g and were higher than BTBPE levels. The geometric mean levels were generally an order of magnitude higher than BTBPE, except in the vacuum cleaner bags where DBDPE was 2X higher than BTBPE. The levels of TBB and TBPH measured in the house dust samples were comparable to HBCD. Of particular interest to note was the ratio of TBB:TBPH. In the FM 550 mixture the ratio is approximately 4; however, among all the dust samples analyzed this ratio ranged from 0.05 to 50, with a mean value of 4.4. This wide range in ratios suggests different sources of these compounds with different relative compositions, and/or differential fate and migration from source products. A previous screening study reported use of TBPH as an additive flame retardant in neoprene and polyvinylchloride (PVC), suggesting sources of TBPH other than FM 550 are likely (9). We also compared the levels of these flame retardants with our previously measured levels of PBDEs in these samples and no consistent associations were found except for a moderate correlation between decaBDE and DBDPE (Spearman  $r=0.46 - 0.64$ ,  $p<0.05$ ).

The dust samples analyzed in this study were collected from different rooms (i.e. main living room areas and bedrooms) in 19 different homes of the Boston, MA area. Previously we had reported on the differences in PBDE levels measured in dust collected by investigators from main living areas and bedrooms, and their comparison to the occupant's home vacuum cleaner bags. Here we were also able to investigate any spatial differences in BFR levels among rooms in the same home. As seen in

**Figure 1**, the range and median concentrations of all three compounds were significantly higher in the main living area dust samples compared to the bedroom (linear mixed effects model,  $p<0.05$ ). This was particularly evident for TBB, and may be a reflection of its use in polyurethane foam commonly found in main living area furniture (e.g. couches, chairs, etc.).



Little information is available regarding the exposure and potential toxicity of these compounds, which may be warranted given their presence and log-normal distribution in indoor dust. Children are particularly prone to exposure from compounds in indoor dust due to their crawling and mouthing behaviors, and children living in homes where the dust levels of these BFRs are >90<sup>th</sup> percentile may be receiving significant exposures. Also of interest to note are the increasing numbers and different types of BFRs now detected in house dust. Recent screening efforts have documented more than 40 different types of brominated flame retardants that are available for commercial use

(9). Thus the number of halogenated flame retardants available is quite extensive and consideration should be given to potential health effects from exposure to these mixtures present in indoor environments.

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Table 1. Summary Statistics for DBDPE, BTBPE, HBCD, TBB, TBPB concentrations (ng/g) in dust by sample type

BFR	Main Living Area				Bedroom				Home Vacuum Bag			
	% detect	n	GM (GSD)	Range	% detect	n	GM (GSD)	Range	% detect	n	GM (GSD)	Range
DBDPE	81%	16	138.1 (5.4)	<10 - 11,067	86%	14	153.2 (4.2)	<10 - 3,415	71%	7	39.4 (6.7)	<10 - 261.7
BTBPE	100%	19	48.1 (4.6)	4.7 - 653.7	100%	19	47.8 (5.1)	1.6 - 788.9	100%	10	17.7 (3.6)	2.5 - 219.1
HBCD	94%	16	354.4 (8.6)	<4.5 - 130,224	93%	14	144.1 (5.1)	<4.5 - 9,707	100%	7	281.7 (11.6)	21.0 - 35,060
TBB	94%	16	321.9 (5.9)	<6.6 - 15,034.0	86%	14	90.4 (2.8)	<10.6 - 378.4	100%	7	91.1 (2.6)	35.7 - 669.4
TBPB	100%	16	237.9 (5.3)	3.0 - 10,626.7	100%	14	104.5 (4.3)	1.5 - 763.1	100%	7	65.8 (1.7)	24.3 - 110.7