Alternate and New Brominated Flame Retardants Detected in U.S. House Dust

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Due to the voluntary withdrawals and/or bans on the use of two polybrominated diphenyl ether (PBDE) commercial mixtures, an increasing number of alternate flame retardant chemicals are being introduced in commercial applications. To determine if these alternate BFRs are present in indoor environments, we analyzed dust samples collected from 19 homes in the greater Boston, MA area during 2006. Using pure and commercial standards we quantified the following brominated flame retardant chemicals using GC/ECNI-MS methods: hexabromocyclododecane (ΣHBCD), bis(2,4,6,-tribromphenoxy)ethane (BTBPE), decabromodiphenyl ethane (DBDPE), and the brominated components found in Firemaster 550 (FM 550): 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB) and (2-ethylhexyl) tetrabromophthalate (TBPH), the latter compound being a brominated analogue of di(2-ethylhexyl)phthalate (DEHP). The concentrations of all compounds were log-normally distributed and the largest range in concentrations was observed for HBCD (sum of all isomers), with concentrations ranging from <4.5 ng/g to a maximum of 130,200 ng/g with a median value of 230 ng/g. BTBPE ranged from 1.6 to 789 ng/g with a median value of 30 ng/g and DBDPE ranged from <10.0 to 11,070 ng/g with a median value of 201 ng/g. Of the FM 550 components, TBB ranged from <6.6 to 15,030 ng/g with a median value of 133 ng/g; whereas TBPH ranged from 1.5 to 10,630 ng/g with a median value of 142 ng/g. Furthermore, the ratio of TBB/TBPH present in the dust samples ranged from 0.05 to 50 (average 4.4), varying considerably from the ratio observed in the FM 550 commercial mixture (4:1 by mass), suggesting different sources with different chemical compositions, and/or differential fate and

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transport within the home. Analysis of paired dust samples collected from different rooms in the same home suggests HBCD, TBB, and TBPH are higher in dust from the main living area compared to dust collected in bedrooms; however, BTBPE and DBDPE levels were comparable between rooms. This study highlights the fact that numerous types of brominated flame retardants are present in indoor environments, raising questions about exposure to mixtures of these contaminants.

Introduction

Over the past decade there has been a large focus on the prevalence and fate of the brominated flame retardant chemicals known collectively as polybrominated diphenyl ethers (PBDEs). Historically these chemicals have been used in high volumes to reduce the flammability of numerous types of polymers and resins commonly found in furniture and electronic components. However, many studies have now reported on their ubiquitous presence in the environment (*1–3*), their accumulation in human tissues (*4–6*), and their potential toxicity (*7–9*). For these reasons, two of the three commercial PBDE mixtures, PentaBDE and OctaBDE, have been voluntary withdrawn or banned from use in some parts of the world. The third and last commercial mixture, DecaBDE, continues to be used in high volumes with production reported as high as 56,000 t (*10*). Despite its common use, much controversy has arisen over the use of DecaBDE, particularly in electronic enclosures such as those found in TVs, and several U.S. state legislatures are currently considering bans or phase-outs of DecaBDE.

Due to phase-outs of PentaBDE and OctaBDE, it is 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), bis(2,4,6,-tribromphenoxy)ethane (BTBPE), and several phosphate based compounds, such as triphenyl phosphate (*11–13*). Given that these alternate flame retardants share properties similar to those of 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 (*14–16*), suggesting disperse exposure. In addition, temporal increases in the concentrations of HBCD have been observed in California sea lions (*17*), harbor porpoises (*18*), and guillemot eggs (*19*), similar to trends previously reported for PBDEs (*20, 21*), and perhaps a result of their use as PBDE replacements. In addition, BTBPE has recently been identified in air collected near the Great Lakes (*22*) and tree bark (*23*), while DBDPE has been detected in air, soils, and sewage sludge samples from Sweden and the United States (*24, 25*). Thus these new flame retardants are leaching into the environment; however, little is known about their potential bioaccumulation and toxicity.

In our previous studies we reported on PBDEs levels in air and dust with considerations of temporal and spatial trends, and linking household products (e.g., televisions, furniture) to PBDE dust concentrations using XRF technology (*26–28*). 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
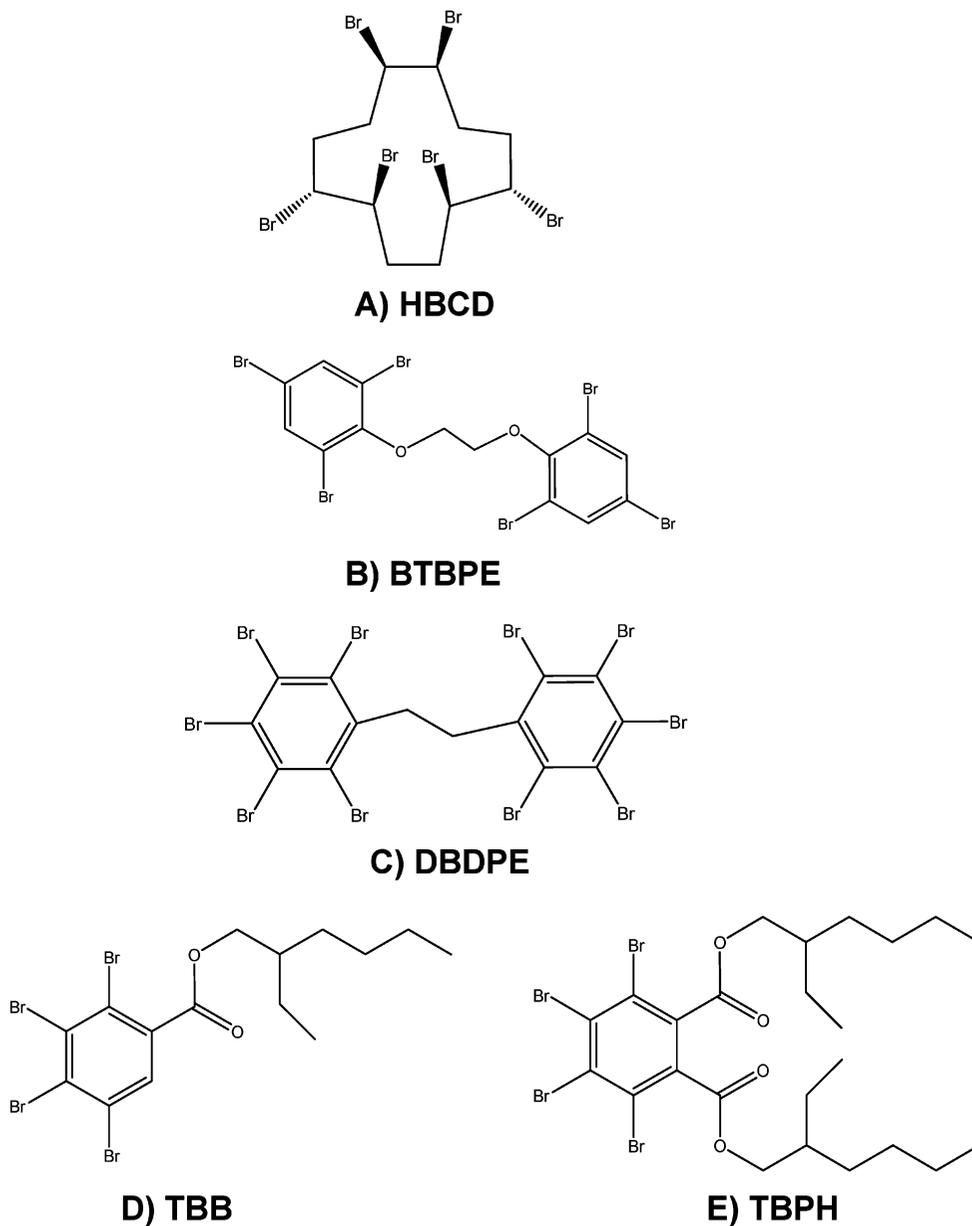
FIGURE 1. Structures of (A) HBCD, (B) BTBPE, (C) DBDPE, (D) TBB, and (E) TBPH.

flame retardants in dust: 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB) and bis-(2-ethylhexyl)-tetrabromophthalate (TBPH) (see Figure 1 for structures). TBB and TBPH are the brominated components of Firemaster 550, a commercial mixture which is a replacement product for PentaBDE (29).

Materials and Methods

Materials. Internal and surrogate standards used in this study were purchased from Chiron (Trondheim, Norway) and Wellington Laboratories (Guelph, Ontario). PBDE quantification standards were purchased from Accustandard (New Haven, CT), and bis(2,4,6,-tribromphenoxy)ethane (BTBPE) and decabromodiphenyl ethane (DBDPE) were purchased from Wellington Laboratories. A sample of Firemaster 550 was donated by Great Lakes Chemical (West Lafayette, IN). 2-Ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB) and (2-ethylhexyl) tetrabromophthalate (TBPH) were provided by Wellington Laboratories. All solvents used throughout this study were HPLC grade.

Sample Collection. Information on the collection of dust samples is detailed in Allen et al. (27). 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 (30, 31). 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.

Sample Extraction. Analysis of BTBPE in dust samples was conducted using the same extraction method previously published for the analysis of PBDEs in dust (27). Therefore, dust extracts analyzed for PBDEs (previously published (27)) were reanalyzed to determine the concentrations of BTBPE using 4-fluoro-2,3′,4,4′,6-pentabromodiphenyl ether (F-BDE 160) as a quantification standard that was previously added to the extracts for the analysis of PBDEs. However, analysis of dust samples for ΣHBCD (sum of all isomers), DBDPE,

TBB, and TBPH required a separate extraction and cleanup method. From the total number of dust samples collected from the initial study, 37 dust samples had sufficient mass remaining for reanalysis of these alternate flame retardants. For this method approximately 0.3 g of dust was extracted using pressurized fluid extraction (ASE 300, Dionex Inc.). Dust samples were extracted three times with 100% dichloromethane at a temperature of 100 °C and at 1500 psi. 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, 4′-fluoro-2,3′,4,6-tetrabromodiphenyl ether (F-BDE-69) and ^{13}C-labeled BDE-209.

Sample Analysis. 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 (*27*). A 0.25 mm (I.D.) × 15 m fused silica capillary column coated with 5% phenyl methylpolysiloxane (0.25 μm film thickness) was used for the separation of BDE congeners. Pressurized temperature vaporization (PTV) injection was employed in the GC. The inlet was set to a temperature of 50 °C for 0.3 min and then a 600 °C/min ramp to 275 °C was employed to efficiently transfer the samples to the head of the GC column. The oven temperature program was held at 40 °C for 1 min followed by a temperature ramp of 18 °C/min to 250 °C, followed by a temperature ramp of 1.5 °C/min to a temperature of 260 °C, followed by a final temperature ramp of 25 °C/min to 300 °C which was held for an additional 20 min. The transfer line temperature was maintained at 300 °C and the ion source was held at 200 °C. BTBPE, HBCD, and DBDPE were quantified by monitoring bromide ions (m/z 79 and 81). ^{13}C BDE-209 was monitored through m/z 494.6 and 496.6. 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).

Quality Assurance. As part of our quality assurance criteria we examined levels of these specific BFR analytes in field and laboratory blanks ($n = 3$), replicate samples ($n = 3$), a dust Standard Reference Material (SRM 2585, National Institute of Standards & Technology, Gaithersburg, MD; $n = 3$), and a matrix spike ($n = 3$). TBB was detected in field/laboratory blanks (11.5 ± 1.3 ng), and is likely a reflection of contamination in the laboratory from the presence and analysis of the highly concentrated commercial mixture. Minor levels of TBPH, BTBPE, and HBCD (0.06 ± 0.07, 0.44 ± 0.11, and 0.58 ± 0.42 ng, respectively) were also detected in field and laboratory blanks. DBDPE was below detection limits in all the blank samples. All sample measurements were blank corrected by subtracting the average level measured in the field/laboratory blanks. Method detection limits were calculated by taking three times the standard deviation of the blank levels. Matrix spikes were prepared by adding approximately 100 ng of BTBPE, DBDPE, α-HBCD, TBB, and TBPH to cells filled with sodium sulfate powder. Matrix spikes were extracted alongside the dust samples and examined for percent recovery of the target compounds. As a further quality control procedure, SRM 2585 was also analyzed for these BFR compounds. Our measurement of total HBCD in SRM 2585 is very comparable to measurements reported by NIST (*32*) and by other researchers (*33*). Table 1 presents the recovery of each BFR analyte observed in the matrix spikes in addition to the levels of BFRs measured in SRM 2585. Recovery of TBPH was less than 50%; therefore, our dust estimates are likely underestimated.

TABLE 1. Recovery of Flame Retardants in Matrix Spikes ($n = 3$) and Concentrations Measured in Standard Reference Material 2585 ($n = 3$)

| | matrix spike | SRM 2585 | |
compound	percent recovered	concentration (ng/g)	reference value
BTBPE	93 ± 5	<0.8	NA[a]
DBDPE	94 ± 4	<10	NA
HBCD	94 ± 13	137 ± 7.8	143 ± 26.8[b], 148 ± 22.0[c]
TBB	103 ± 3	<30	NA
TBPH	46 ± 10	145 ± 16.7	NA

[a] NA indicates not available. [b] Keller et al., 2007 (*32*). [c] Abdallah et al., 2008 (*33*).

Data Analysis. Because dust was collected for several locations in each home, we used a linear mixed effects model to examine differences within and between homes while appropriately handling correlated data (*27*).

Results and Discussion

Identification of Flame Retardants in Dust. In our previous study (*27*) we determined the concentrations of PBDEs in dust samples collected from 20 different homes in the Boston, MA area. 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. The geometric mean (GM), geometric standard deviation (GSD), and range of these three brominated flame retardants measured in the dust samples are reported in Table 2. 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. Based on this evidence we hypothesized that this compound was an alternate BFR compound and conducted an extensive search of the scientific literature in order to identify this compound. A modeling study conducted by Howard et al. (*34*) revealed that a tetra-brominated analogue of di-(2-ethylhexl)phthalate (DEHP) was being used as a flame retardant. In addition, a recent publication characterizing different flame retardants reported on the use of this same brominated phthalate as an additive flame retardant in polyvinylchloride and neoprene rubber (*35*). 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 spectra 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 Firemaster 550 (FM 550), which is marketed as a replacement for PentaBDE (*29*), to determine if it contained TBPH. The comparison confirmed that TBPH was present in FM 550, in addition to another brominated compound found in greater abundance. 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. The structure of the major brominated component in FM 550 was

TABLE 2. Summary Statistics for DBDPE, BTBPE, HBCD, TBB, and TBPH Concentrations (ng/g) in Dust by Sample Type

	main living area				bedroom				home vacuum bag			
BFR	% detect	n	GM (GSD)	range	% detect	n	GM (GSD)	range	% detect	n	GM (GSD)	range
DBDPE	81%	16	138(5.4)	<10−11,070	86%	14	153(4.2)	<10−3,420	71%	7	39.4(6.7)	<10−262
BTBPE	100%	19	48.1(4.6)	4.7−654	100%	19	47.8(5.1)	1.6−789	100%	10	17.7(3.6)	2.5−219
HBCD	94%	16	354(8.6)	<4.5−130,200	93%	14	144(5.1)	<4.5−9,710	100%	7	282(11.6)	21.0−35,100
TBB	94%	16	322(5.9)	<6.6−15,030	86%	14	90.4(2.8)	<10.6−378	100%	7	91.1(2.6)	35.7−669
TBPH	100%	16	234(5.3)	3.0−10,630	100%	14	105(4.3)	1.5−763	100%	7	65.8(1.7)	24.3−111

elucidated from GC/EI-MS, GC/NCI-MS, and ^{1}H NMR spectroscopy along with ^{13}C two-dimensional homonuclear ^{13}C—^{13}C Incredible Natural Abundance Double Quantum Transfer Spectroscopy (INADEQUATE) to be 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB). Using a pure, synthesized standard we then reconfirmed the identity of TBB as the second, and dominant, brominated compound present in FM 550. It should be noted that during GC/MS analysis no molecular ion is observed for both TBPH and TBB under EI conditions, and only small molecular ion peaks are seen under NCI conditions. The approximate ratio of TBB/TBPH in FM 550 is 4:1 (by mass), and according to the MSDS for FM 550, the brominated compounds contribute approximately 50% of the mixture whereas the remaining 50% comprises an isopropylated triaryl phosphate and triphenylphosphate.

During our analysis of TBB we observed significant coelution with BDE-99 on a 15 m DB5-MS column. Extraction methods that will routinely extract both PBDEs and TBB may thus report confounded measurements of BDE-99 when using short columns. Here we were not able to determine the resolution of BDE-99 and TBB with longer capillary columns; however, methods that employ a 30 or 60 m column may improve the chromatographic resolution. In our initial analysis of PBDEs from these dust samples we employed an alumina purification step on our dust extracts which recovers PBDEs, but does not recover TBB well. Therefore, extract purification and/or cleanup steps can be used to separate the two compounds. In addition, TBB produces several strong signals for molecular fragments (e.g., M-C_8H_{17}Br- and M-Br-), which will help distinguish the two compounds. Figure 2 presents the retention times of these compounds relative to several primary BDE congeners. Figure 3 presents the EI and ECNI mass spectrum of TBB and TBPH obtained by a full scan analysis of pure standards. Of particular interest to note is the low response of the molecular ions and the stronger response for the dealkylated fragments.
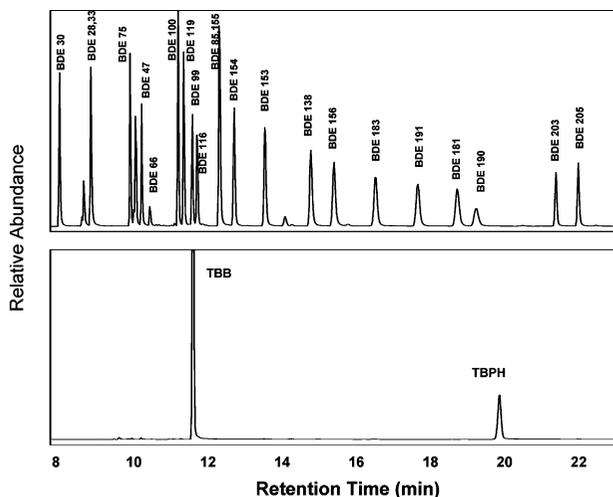

FIGURE 2. GC/ECNI-MS chromatograms revealing the relative retention times of the primary BDE congeners, TBB and TBPH on a 15 m DB5-MS column.

Concentrations Measured in Dust. Table 2 presents the geometric mean (GM), geometric standard deviation (GSD), and range of the brominated flame retardants that were measured in the dust samples categorized by dust location. Dust concentration data 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, 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 geometric mean of HBCD measured in the dust samples, and is consistent with the log-normal distribution observed for many flame retardants. In a previous study, Abdallah et al. (33) determined the HBCD levels in indoor dust collected from home and office dust in the United Kingdom, and in 13 house dust samples collected from Amarillo, TX. The maximum concentration of HBCD detected in U.K. indoor dust was 110,000 ng/g, similar to our findings here for U.S. house dust.

Levels of BTBPE were an order of magnitude lower than the other flame retardants measured in this study. The geometric median ranged from 18 to 48 ng/g (depending on the room from which the dust was collected), with a maximum concentration of 789 ng/g. These values are significantly lower than the PBDE concentrations previously measured (27), where the geometric mean values for individual congeners such as BDE 47 ranged from 330 to 1870 ng/g among the dust samples collected from various rooms.

DBDPE levels ranged from less than detection (<10 ng/g) to a maximum of 10,240 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 were DBDPE was two times higher than BTBPE. To the authors' knowledge, the only other study to measure DBDPE in house dust was conducted by a group in Sweden that measured the levels in five homes (36). Compared to the reported levels of DBDPE in Swedish dust, the U.S. house dust concentrations from the main living area and bedroom are an order of magnitude higher, on average; however, levels of DBDPE measured in the seven vacuum cleaner bags in this study were of the same range as those reported by the Swedish group. Thus method of sampling may have been playing a role in the relative measurements.

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 4:1; however, among 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 which contain 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 polyvinyl-
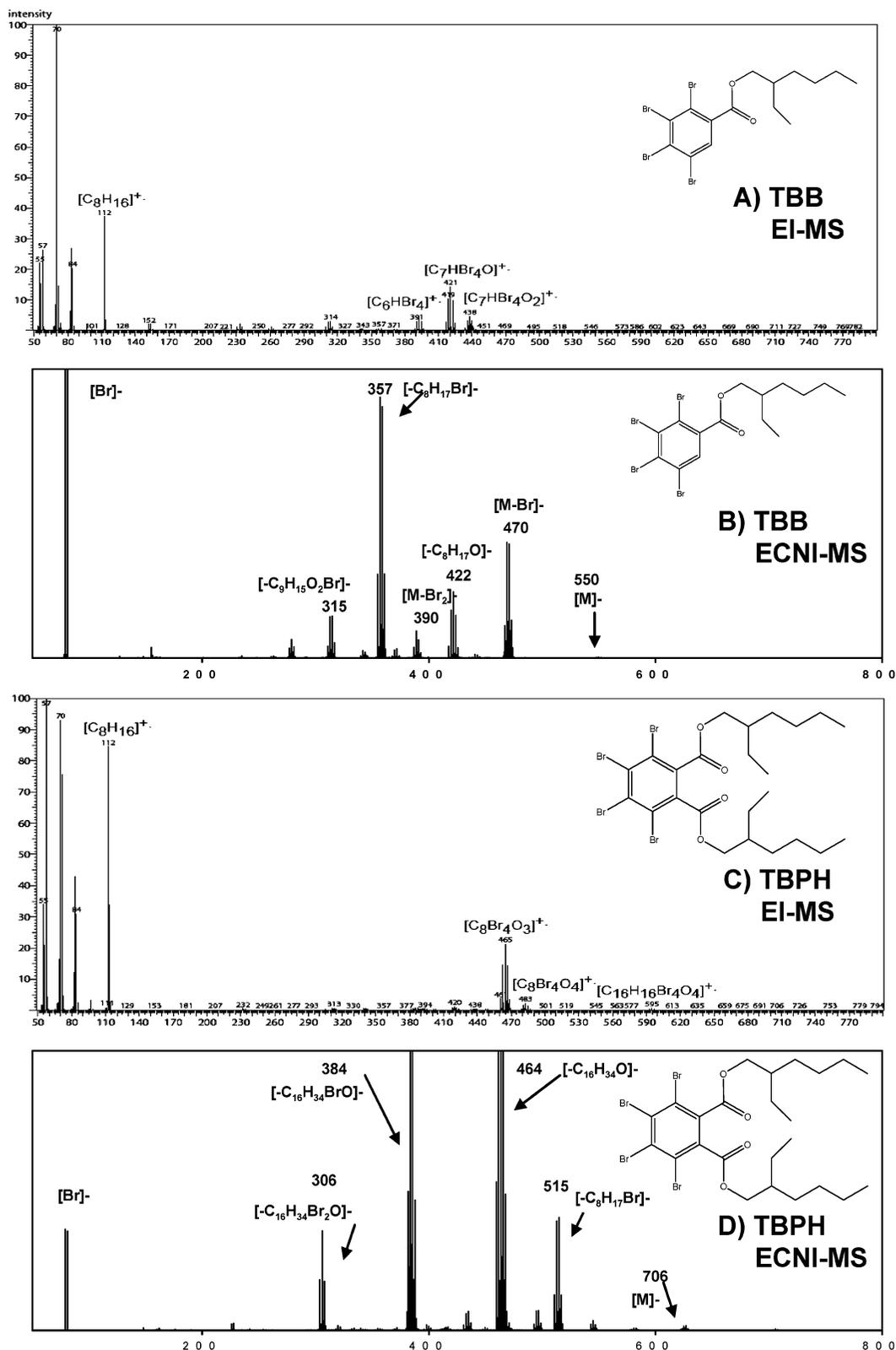
FIGURE 3. Mass spectra for TBB in EI-MS (A) and ECNI-MS (B) and for TBPH in EI-MS (C) and ECNI-MS (D) recorded from purified standards.

chloride (PVC), suggesting that sources of TBPH other than FM 550 are likely (35). But it is interesting to note that TBB and TBPH were significantly correlated among all dust samples with a Spearman correlation coefficient of 0.519 ($p < 0.01$). This observation suggests that TBB and TBPH may have a similar source. We also compared the levels of all 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 $r = 0.46$, $p < 0.05$).

As part of our quality control we investigated the levels of these BFR chemicals in a dust Standard Reference Material (SRM 2585) available from NIST (Gaithersburg, MD). Previous studies have reported on the levels of total HBCD in this material and our reported values were in good agreement with NIST reference values (Table 1) and those of a U.K.
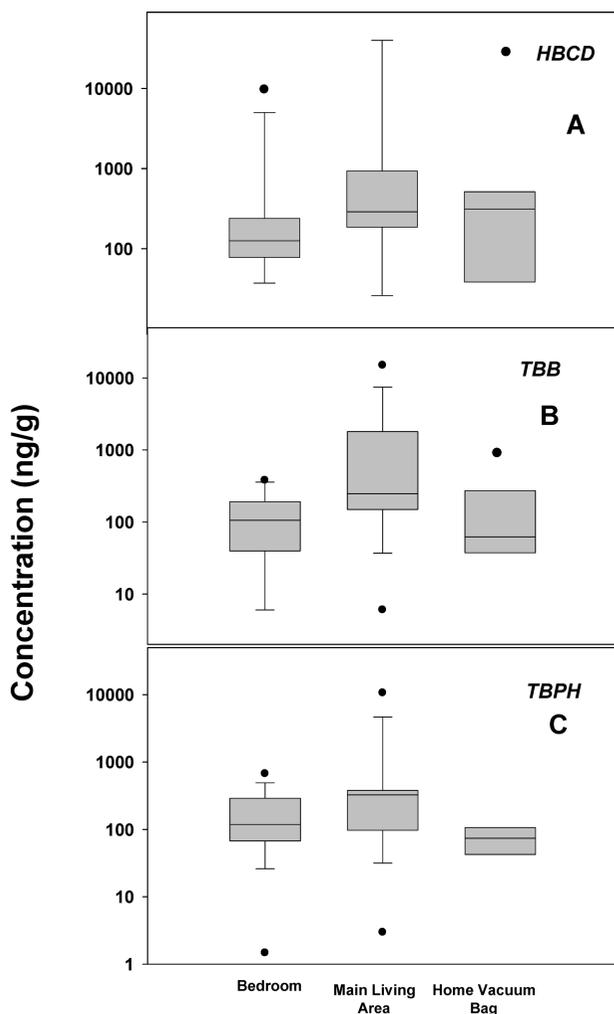
FIGURE 4. Box plots representing the distribution of (A) HBCD, (B) TBB, and (C) TBPH in dust collected from bedrooms (n = 14), main living areas (n = 16), and participants home vacuum cleaner bags (n = 7). The lower, middle, and upper lines of the box represent the 25th, 50th, and 75th percentile values, whereas the lower and upper bars represent the 10th and 90th percentile, respectively.

research group (*33*). It is interesting to note that we also detected levels of TBPH in SRM 2585, but no other BFRs. This may be due to previous use of TBPH as a flame retardant in neoprene rubber and PVC. This SRM was prepared from dust collected in the mid- to late 1990s (*37*), which may explain the absence of TBB in the dust, since FM 550 was only introduced as a flame retardant in 2003.

Inter-Room Variability. 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 occupants' home vacuum cleaner bags (*27*). Here we were also able to investigate spatial differences in BFR levels among rooms in the same home. Figure 4 illustrates the range and median levels of HBCD, TBB, and TBPH measured in dust from the different rooms and the comparison to the occupants' home vacuum bag. The distribution of BTBPE and DBDPE are not presented as there were no significant differences in concentrations between the two rooms. Concentrations of DBDPE were significantly higher in the two rooms compared to the home vacuum bag, however. As seen in Figure 4, the concentrations of all three compounds were significantly higher in the main living area

dust samples compared to the bedroom ($p < 0.05$). 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., sofas, chairs, etc.).

In summary, we have reported the levels and distributions of non-PBDE brominated flame retardants in U.S. indoor dust. Of particular interest is the identification of two brominated components of FM 550 in dust. While our findings suggest FM 550 as a source, we cannot rule out contributions from other uses of TBB and/or TBPH. Our findings suggest that the distribution of these flame retardants is highly skewed, similar to PBDEs, albeit at an order of magnitude lower in concentration. However, given the phase-out of the PentaBDE and OctaBDE commercial mixtures, and the possibility of a phase-out for the DecaBDE mixture, increasing use of these alternate flame retardants is likely in order to comply with fire safety standards. Little information is available regarding the exposure and potential toxicity of these compounds to humans and wildlife; such data are needed given their presence and log-normal distribution in indoor dust. Children are particularly prone to exposure from chemicals in indoor dust due to their crawling and mouthing behaviors, and children living in homes where the dust levels of these BFRs are >90th 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 (*35*). Previous studies have also reported on the levels of several chlorinated flame retardants in indoor dust and environmental samples (*23, 38*). 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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