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Levels of Non-Polybrominated Diphenyl Ether Brominated Flame Retardants in Residential House Dust Samples and Fire Station Dust Samples in California

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Abstract

Eleven novel brominated flame retardants (NBFRs) were analyzed in dust samples from California homes as a part of the Northern California Childhood Leukemia Study (NCCLS) and from the living quarters of California fire stations as a part of the Firefighter Occupational Exposure (FOX) study using high resolution gas chromatography/mass spectrometry. The eleven NBFRs, were: α - and β -1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (α - and β -DBE-DBCH), 2-bromoallyl 2,3,6-tribromophenylether (BATE), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), 2,3-dibromopropyl 2,4,6-tribromophenyl ether (TBP-DBPE), hexabromobenzene (HBB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), 1,2-*bis*(2,4,6-tribromophenoxy) ethane (BTBPE), *bis*(2-ethylhexyl) tetrabromophthalate (BEH-TEBP), and decabromodiphenylethane (DBDPE). Six of the seven NBFRs that are produced in relatively small quantities (i.e., α -, β -DBE-DBCH, BATE, PBEB, PBT, TBP-DBPE) were measured close to or below the limit of quantitation (0.64 ng/g) in both the NCCLS and FOX samples, and the seventh, HBB, was measured at median concentrations of 1.85 ng/g and 9.40 ng/g in the NCCLS and FOX samples, respectively. The remaining four NBFRs, EH-TBB, BEH-TEBP, BTBPE, and DBDPE, are produced in higher quantities, and were detected at median concentrations of 337 ng/g, 186 ng/g, 22.3, ng/g, and 82.8 ng/g, respectively in the NCCLS samples, and at median concentrations of 2687 ng/g, 2076 ng/g, 28.4 ng/g, and 161 ng/g, respectively, in the FOX samples. Concentrations of NBFRs in the NCCLS and FOX dust samples were several times lower than concentrations of PBDEs previously measured in the same samples. Concentrations of NBFRs in the NCCLS and FOX dust samples were generally comparable to concentrations of NBFRs in other studies of house dust from the US and Canada.

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Keywords

Novel brominated flame retardants (NBFRs); Residential house dust; Fire station dust; Human exposure; Environmental exposure

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame retardant that were introduced in the 1970s (Pohl and others 2004) and that came to be used in a wide variety of products (Alaee and others 2003; de Wit 2002; Pohl and others 2004). Because PBDEs are ubiquitous in the environment, biota, and humans (de Wit 2002; de Wit and others 2006; Law and others 2003; Pohl and others 2004; Shaw and Kannan 2009), and potentially toxic (Eskenazi and others 2012; Gascon and others 2012; Kicinski and others 2012; Zota and others 2011), they have been taken out of production in the U.S. and are being replaced by novel brominated flame retardants (NBFRs) (Covaci and others 2011). However, some NBFRs are structurally similar to PBDEs or other toxic compounds (Covaci and others 2011; OEHHA 2008; OEHHA 2009), and presumably have similar physico-chemical properties, so the potential for persistence, toxicity, bioaccumulation, and long range airborne transport is also of concern for these chemicals. Indeed, as NBFRs are used in an ever-growing variety of products, they can now be found in environmental and biological media worldwide (Covaci and others 2011; de Wit and others 2010; Pohl and others 2004).

To estimate the potential for human exposure to NBFRs, it is useful to measure levels of these chemicals in environmental media, including house dust. Various persistent organic pollutants (POPs) are present in house dust (Mercier and others 2011; Shen and others 2012; SRM-2585 2010; Stapleton and others 2012), including NBFRs (Dodson and others 2012; Shoeib and others 2012; Stapleton and others 2008). PBDE levels in paired human serum and milk samples correlate with PBDE concentrations in house dust, suggesting that dermal contact with dust and incidental ingestion of dust are routes of exposure to PBDEs (Johnson and others 2010; Wu and others 2007). Therefore, in this paper, we assess the levels of 11 NBFRs in house dust collected from homes in northern California, and from the living quarters of fire stations in southern California.

The 11 NBFRs included in the analysis were α - and β -1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (α - and β -DBE-DBCH), 2-bromoallyl 2,3,6-tribromophenylether (BATE), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), 2,3-dibromopropyl 2,4,6-tribromophenyl ether (TBP-DBPE), hexabromobenzene (HBB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), 1,2-*bis*(2,4,6-tribromophenoxy) ethane (BTBPE), *bis*(2-ethylhexyl) tetrabromophthalate (BEH-TEBP), and decabromodiphenylethane (DBDPE). Table S1 in the Supplemental Information shows the chemical structure and standardized abbreviation of each analyte. Of the eleven analytes, four are direct substitutes for PBDE formulations: EHTBB and BEH-TEBP are major constituents in FireMaster 550, which replaces Penta-BDE; BTBPE replaces Octa-BDE; and DBDPE replaces Deca-BDE. Although confirmatory data are sparse, we expect that these four NBFRs are produced in the U.S. at higher volumes than the other seven NBFRs analyzed in this study.

2. Methods and Materials

Details regarding materials and equipment used for the analysis can be found in the Supplemental Information Section.

2.1. Dust Sample Sources

Dust samples were obtained from residences and fire stations. Residential dust samples were collected as a part of the Northern California Childhood Leukemia Study (NCCLS), a population-based, matched case-control study conducted in 35 counties in the San Francisco Bay area and the California Central Valley (Bartley and others 2010; Chang and others 2006). From 2001-2007, residential dust samples were collected from study homes as a strategy for identifying possible environmental risk factors for childhood leukemia. In 2010, 203 of the participating homes were resampled and all dust samples have been analyzed for various POPs, including pesticides, polychlorinated biphenyls (PCBs) (Whitehead and others 2014), polycyclic aromatic hydrocarbons (PAHs) (Whitehead and others 2013b), and PBDE (Whitehead and others 2013a). Of the dust samples collected in 2010, a convenience sample of 59 dust samples was also analyzed for NBRs and is discussed here.

Fire station dust samples were collected in 2010-2011 from a subset of fire stations participating in the Firefighter Occupational Exposure (FOX) study, a biomonitoring study of firefighters' occupational exposures (Shen 2012). In the FOX study, 27 dust samples were collected from 20 fire stations in Orange County, California. All 27 dust samples were analyzed for PBDEs, PCBs, PAHs, and NBRs (Shen 2012; Shen and others 2012).

2.2. Dust Collection

For both studies, dust samples were collected from vacuum cleaners (used in the residence or in the living quarters of the fire station). In the NCCLS, participants were instructed to mail their vacuum cleaner bags, or the contents of their vacuum cleaner canisters, to the study center in pre-paid containers. In the FOX study, the interviewer collected the vacuum cleaner bag directly from the fire station. In both studies, dust was collected over unspecified periods of time from unspecified parts of the residence or living quarters. In the laboratory, dust samples were homogenized and sieved on a mechanical shaker through 3 1/2 and 100-mesh sieves to collect the fraction of dust smaller than 150 μm . This material was stored in the dark in amber glass jars at 4 °C until analysis.

2.3. Dust Extraction

Accelerated Solvent Extraction (ASE) cells containing Hydromatrix were washed with 100% dichloromethane at 100 °C and 1500 psi. Subsequently, approximately 0.2 g of dust was mixed with the clean Hydromatrix and ^{13}C -labeled internal standards for PCBs, PBDEs, PAHs, and NBRs were added. The samples were then extracted in five cycles using 95%:5% hexane:dichloromethane at 100 °C and 1500 psi.

2.4. Dust Cleanup

Following extraction, sample extracts were concentrated, loaded onto a glass silica gel column, and eluted with 1:1 dichloromethane:hexane. Anhydrous sodium sulfate was used in

the silica gel column to remove residual moisture. This eluate was reduced to less than 700 μL , transferred to a gel permeation chromatography (GPC) autosampler vial, and passed through the high pressure GPC system. The GPC eluate was concentrated to less than 300 μL , transferred to a 300 μL gas chromatograph autosampler vial, recovery standards added, and concentrated to a final volume of 40 mL using a nitrogen blow down system.

2.5. Sample Analysis

Sample extracts were analyzed using high resolution gas chromatography/mass spectrometry (GC/MS) system. Samples (1 μL) were injected using a programmed temperature vaporizing injector and the following injector temperature program: initial temperature at 175 $^{\circ}\text{C}$; 175 $^{\circ}\text{C}$ to 320 $^{\circ}\text{C}$ at 14.5 $^{\circ}\text{C}/\text{min}$; clean-up step at 360 $^{\circ}\text{C}$ for 33 minutes. The chromatographic column for NBFR analysis was an Agilent/J&W DB5- MS (15m x 0.25 mm id x 0.25 mm film). The GC program was: 2.0 min hold at 130 $^{\circ}\text{C}$; 130 to 200 $^{\circ}\text{C}$ at 15 $^{\circ}\text{C}$; 200 $^{\circ}\text{C}$ to 280 $^{\circ}\text{C}$ at 5.0 $^{\circ}\text{C}/\text{min}$; 280 $^{\circ}\text{C}$ to 320 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$; hold at 320 $^{\circ}\text{C}$ for 8.0 min, with a total run time of 35 min. The transfer line and ion source were kept at 260 $^{\circ}\text{C}$. Helium carrier gas was used in programmed flow mode: initial carrier flow was 1.2 mL/min; at 24.0 minutes, the flow rate was increased at 1.0 mL/min/min to 1.8 mL/min; with a final hold time of 10.5 minutes. The mass spectrometer was operated in multiple ion detection mode (MID) at > 10,000 resolution. Mass spec parameters are shown in Table S2 in the Supplemental Information Section. Elution order and masses to be monitored were determined previously (Guo and others 2013).

2.6. Quality Control

A batch typically numbered 12 samples comprising eight single dust samples, a duplicate sample pair, a QC sample, and a method blank. For the NCCLS, 59 dust samples were analyzed in seven batches. For the FOX study, 27 dust samples were analyzed in three batches. Concentrations in the method blanks are shown in Table 1 and are almost all below LOD.

One of two different samples was used as the QC sample for each batch; either the National Institute of Standards and Technology SRM 2585, or a contemporary house dust sample used as a laboratory control (LC) sample. Descriptive statistics for the analysis of the two QC samples are shown in Table S3.

3. Results

Summary statistics for both the NCCLS and FOX samples are shown in Table 1. The concentrations of NBFRs in the method blanks are all, with two exceptions, < LOQ. For NCCLS dust samples, the exception is BEH-TEBP (0.99 ng/g). For the FOX dust samples, the exception is EH-TBB (0.88 ng/g). For the NCCLS samples, all NBFRs, except for BATE, were detected in at least some of the samples. PBT, PBEB, and TBB-DBPE were detected in fewer than 50% of the samples; α - and β -DBE-DBCH were detected in 54% of the samples; and HBB, EH-TBB, BEH-TEBP, BTBPE, and DBDPE were detected in over 78% of the samples. For the FOX samples, all NBFRs, including BATE, were detected in at least some of the samples. BATE was detected in 4% of the samples; α - and β -DBE-DBCH

were detected in 22% of the samples; and all other NBFrs were detected in over 74% of the samples.

For both the NCCLS and FOX dust samples, the NBFrs found at the highest concentrations were those that are direct substitutes for PBDE formulations: EH-TBB, BEH-TEBP, BTBPE, and DBDPE. For both the NCCLS and FOX dust samples, α - and β -DBE-DBCH, BATE, PBT, PBEB, TBP-DBPE, and HBB were found at lower concentrations than EH-TBB, BEH-TEBP, BTBPE, and DBDPE. For NCCLS samples, the geometric means for α - and β -DBE-DBCH, BATE, PBT, PBEB, TBP-DBPE, and HBB range from < 0.64 to 2.02 ng/g. The geometric means for EH-TBB, BEH-TEBP, BTBPE, and DBDPE range from 21.8 to 310 ng/g. For the FOX samples, the geometric means for α - and β -DBE-DBCH, BATE, PBT, PBEB, TBP-DBPE, and HBB range from 0.66 to 7.78 ng/g. The geometric means for EH-TBB, BEH-TEBP, BTBPE, and DBDPE, range from 31.3 to 1400ng/g.

Descriptive statistics for both the contemporary house dust sample and the SRM 2585 QC samples are shown in Table S3.

4. Discussion

4.1. Comparison of Residential and Fire Station Sample Results

NBFR concentrations were generally higher in the FOX dust samples than in NCCLS dust samples. Concentrations of direct PBDE replacements, EH-TBB, BEH-TEBP, and DBDPE, were significantly higher in the FOX study compared to the NCCLS as were concentrations of less prevalent NBFrs, PBT, PBEB, TBP-DBPE, and HBB. It has been suggested that when materials containing FRs burn in uncontrolled fires, the remaining ashes can be FR sources (de Perio and others 2010). In fact, investigators have measured FR-contaminated ash on firefighter gear, including pant cuffs (Fabarius and others 1990), suggesting that firefighters can carry dust contaminated with FRs back to their fire station living quarters after extinguishing fires. Indeed, we previously reported that the median concentration of BDE-209 in these FOX dust samples was approximately 24 times that measured in NCCLS dust samples (Shen 2012). We suggest that firefighters may track NBFrs back to their fire station living quarters after fire events and hypothesize that this track-back has resulted in higher NBFR concentrations found in fire stations compared to other California residences. In comparison to the dramatic differences observed for BDE-209, we observed a relatively modest 2-fold difference between median concentrations of its replacement, DBDPE, in FOX dust samples and NCCLS dust samples. We hypothesize that the difference between DBDPE concentrations in fire stations and residences may become more substantial as an increasing pool of DBDPE-treated consumer items will increase the likelihood that firefighters will come into contact with DBDPE-contaminated ash at fire events.

In contrast, concentrations of α - and β -DBE-DBCH were significantly higher in NCCLS dust samples than in FOX study dust samples, with a roughly two-fold difference in geometric means between the studies. One possible explanation for the relatively low DBE-DBCH levels in fire station dust is thermal conversion. The technical mixture of DBE-DBCH contains only α - and β -DBE-DBCH diastereoisomers in equal proportion; however, above temperatures of 125° C, the α - and β -DBE-DBCH diastereoisomers begin

to convert to the γ - and δ -DBE-DBCH diastereoisomers, also in equal proportion (Arsenault and others 2008). In a fire, any α - or β -DBE-DBCH present would partially convert to γ - or δ -DBE-DBCH. Thus, any contaminated ash that firefighters bring back to the fire station after a fire event would have less α - and β -DBE-DBCH compared to dust from locations that had not been subjected to high temperatures. We cannot verify this hypothesis, because we did not attempt to measure γ - or δ -DBE-DBCH.

4.2. Comparison of NCCLS Results with Results from Other Studies

We compared our results for the NCCLS samples with the results of three other contemporaneous studies that also measured NBFs in house dust. These studies were of dust collected from: homes in the Boston, Massachusetts (MA) area in 2006 (Stapleton and others 2008); homes in the San Francisco, California (CA) area in 2006 and again in 2011 (Dodson and others 2012); and homes in the Vancouver, British Columbia (BC) area in 2007-2008 (Shoeib and others 2012).

Similar to the median concentrations we measured in the NCCLS samples, in the three comparison studies the median concentrations of most of the lower production volume NBFs (i.e., α -, β -DBE-DBCH, BATE, PBEB, PBT, TBP-DBPE) were less than 2 ng/g, and less than or approaching their limit of quantitation. One exception was HBB, which had a median concentration above LOQ in all studies. It should also be noted that for both HBB and one of the other lower production volume NBFs, TBP-DBPE, the maximum concentrations in the BC samples (130 ng/g and 1,200 ng/g, respectively) were much higher than in the other studies, including the FOX samples (27.4ng/g and 4.68 ng/g for HBB and TBP-DBPE, respectively).

The NCCLS sample results for the higher production volume NBFs (i.e., EH-TBB, BEHTEBP, BDBPE, and DBDPE) are mixed when compared to other studies. For EH-TBB, the median and maximum concentrations (337 and 19198 ng/g, respectively) were higher than the median (or geometric mean) and maximum concentrations for the samples from MA (Stapleton and others 2008), CA (Dodson and others 2012), and BC (Shoeib and others 2012). For BEHTEBP in the NCCLS samples, the median concentrations (186 ng/g) was higher than the geometric mean concentration for the MA samples (65.8 ng/g), the median concentration for the BC samples (99 ng/g), and the median concentration for the CA 2006 samples (140 ng/g), but lower than the median concentration for the CA 2011 samples (260 ng/g). Due to the State of California's unique flammability standards, Penta-BDE was used extensively to treat furniture containing polyurethane foam, and as a result, dust samples from California homes have been reported to have exceptionally high levels of BDE-47 and BDE-99 (Dodson and others 2012; Whitehead and others 2013a). Similarly, we hypothesize that the relatively high concentrations of EH-TBB and BEH-TEBP observed in dust samples collected from California in 2010 (NCCLS) and 2011 (Dodson and others 2012) reflect the recent use of Firemaster 550 as a Penta-BDE replacement. For DBDPE in the NCCLS samples, the median concentration (82.8 ng/g) was higher than the geometric mean concentration for the MA samples (39.4 ng/g) and the median concentration for the 2006 CA samples (51 ng/g), but lower than the median concentration for the 2011 CA samples (140 ng/g). Across all studies, DBDPE concentrations increased by collection year. We

hypothesize that an increasing pool of DBDPE-treated consumer items will continue to cause increasing concentrations of DBDPE in dust. No other relationships between the concentrations of NBFRs and the year of collection across the studies were observed. Other differences between the studies (e.g., sampling method and geographic location) may have been obscured time trends in NBFR dust levels. For BTBPE in the NCCLS samples, the median concentration was similar to the median (or geometric mean) concentrations for the comparison studies.

4.3. Comparison of NBFRs to PBDEs in NCCLS and FOX Studies

Table S4 shows the mean, median, and range of PBDE concentrations in the same NCCLS and FOX samples (Shen and others 2012; Whitehead and others 2013a). The sum of the concentrations of the major PBDE congeners in each formulation (Penta, Octa, Deca) are several times higher than the concentrations of the NBFRs that are replacing them, especially when comparing BDE-209 and DBDPE. The relatively high PBDE concentrations likely reflect the large reservoir of PBDE-treated products that are still in use in California residences and fire stations. In contrast, NBFR-treated products have been produced over a relatively short period of time. We hypothesize that, over time, as PBDE-treated products are taken out of service and NBFR-treated products come into increasing use, concentrations of PBDEs in dust will decrease and concentrations of NBFRs will increase. However, from our current data, we are unable to speculate as to whether the concentrations of NBFRs will ever exceed PBDEs in house dust. Nor, given the lack of toxicity data for NBFRs in humans, can we predict how potential increases in environmental NBFR concentrations might impact human health.

4.4. Use of Vacuum Cleaner Bag as Source of Dust Samples

In both the NCCLS and FOX studies, dust samples were obtained from vacuum cleaners that were used for day-to-day cleaning. The primary advantage of using the contents of the entire vacuum cleaner bag is simplicity. All that is required to obtain the sample is for the participant to send the bag to the researchers, and for the researchers to sieve the contents. The primary limitation of this sampling approach is that from one location to the next, vacuum cleaners may be used in a different combination of rooms and at different proximity to NBFR sources. Differences in vacuum cleaning practices between and within sampling sites as well as differences in the vacuum cleaners used to collect dust (e.g., type, efficiency, flame retardant content) could introduce variability in NBFR levels. Despite these limitations, using the contents of residents' vacuum cleaners is a relatively easy and cost-efficient means of sampling dust from residential and other living spaces to measure NBFRs and other analytes. It also provides useful information for overall contamination with of NBFRs.

Allen et al demonstrated significant differences between concentrations of brominated flame retardants in matched samples of vacuum cleaner-bag dust and researcher-collected dust, with only moderate correlation between the sampling methods (Allen and others 2008). It is not known which dust sample type is more representative of human exposure to brominated flame retardants; however, one study found that vacuum-dust PBDE concentrations were

more highly correlated with breast milk PBDE concentrations than were researcher-collected dust PBDE concentrations (Bjorklund and others 2012).

4.5. Conclusions

Analysis of residential and fire station dust collected from vacuum cleaners showed that EHTBB, TEB-TEBP, BTBPE, and DBDPE, which are direct replacements for various PBDE formulations, were measured at levels well above LOQ. However, despite being measured at higher concentrations than the rest of the NBFRRs of interest, the levels of these four NBFRRs were still several times lower than PBDEs measured in the same samples. As was previously observed for PBDEs, levels of these four PBDE-replacements were higher in fire station dust than in residential dust. The concentrations of NBFRRs measured in residential dust were comparable to those from studies of other residences in North America.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

- Alaee M, Arias P, Sjodin A, Bergman A. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environ Int.* 2003; 29:683–689. [PubMed: 12850087]
- Allen JG, McClean MD, Stapleton HM, Webster TF. Critical factors in assessing exposure to PBDEs via house dust. *Environment International.* 2008; 34:1085–1091. [PubMed: 18456330]
- Arsenault G, Lough A, Marvin C, McAlees A, McCrindle R, MacInnis G, et al. Structure characterization and thermal stabilities of the isomers of the brominated flame retardant 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane. *Chemosphere.* 2008; 72:1163–1170. [PubMed: 18471860]
- Bartley K, Metayer C, Selvin S, Ducore J, Buffler PA. Diagnostic X-Rays and risk of childhood leukaemia. *International Journal of Epidemiology.* 2010; 39:1628–1637. [PubMed: 20889538]
- Bergman A, Ryden A, Law RJ, De Boer J, Covaci A, Alaee M, et al. A Novel Abbreviation Standard for Organobromine, Organochlorine, and Organophosphorus Flame Retardants and Some Characteristics of the Chemicals. *Environ Int.* 2012; 49:57–82. [PubMed: 22982223]
- Bjorklund JA, Sellstrom U, De Wit CA, Aune M, Lignell S, Darnerud PO. Comparisons of polybrominated diphenyl ether and hexabromocyclododecane concentrations in dust collected with two sampling methods and matched breast milk samples. *Indoor Air.* 2012; 22:279–288. [PubMed: 22212125]
- Chang JS, Selvin S, Metayer C, Crouse V, Golembesky A, Buffler PA. Parental smoking and the risk of childhood leukemia. *American Journal of Epidemiology.* 2006; 163:1091–1100. [PubMed: 16597704]

- Covaci A, Harrad S, Abdallah MA-E, Ali N, Law RJ, Herzke D, et al. Novel Brominated Flame Retardants: A Review of Their Analysis, Environmental Fate, and Behavior. *Environ Int.* 2011; 37:532–556. [PubMed: 21168217]
- de Perio MA, Durgam S, Caldwell KL, Eisenberg J. A Health Hazard Evaluation of Antimony Expose in Fire Fighers. *Journal of Occupational and Environmental Medicine.* 2010; 52:81–84. [PubMed: 20042882]
- de Wit CA. An Overview of Brominated Flame retardants in the Environment. *Chemosphere.* 2002; 46:583–624. [PubMed: 11999784]
- de Wit CA, Alae M, Muir DCG. Levels and trends of brominated flame retardants in the Arctic. *Chemosphere.* 2006; 64:209–233. [PubMed: 16458344]
- de Wit CA, Herzke D, Vorkamp K. Brominated flame retardants in the Arctic environment — trends and new candidates. *Sci Total Environ.* 2010; 408:2885–2918. [PubMed: 19815253]
- Dodson RE, Perovich LJ, Covaci A, van den Eede N, Ionas AC, Dirtu AC, et al. After the PBDE Phase-Out: A Broad Suite of Flame Retardants in Repeat House Dust Samples from California. *Environ Sci Technol.* 2012; 46:13056–13066. [PubMed: 23185960]
- Eskenazi B, Chevri er J, Rauch SA, Kogut K, Harley K.g. Johnson C, et al. In Utero and Childhood Polybrominated Diphenyl Ether (PBDE) Exposures and Neurodevelopment in the CHAMACOS Study. *Environ Health Perspect.* 2012
- Fabarius G, Wilken M, Borgas M, Zeschmar-Lahl B. Release of Organic Pollutants During Accidental Fires. *Organohalogen Compounds.* 1990; 3:373–378.
- Gascon M, Fort M, Martinez D, Carsin A-E, Forn J, Grimalt JO, et al. Polybrominated Diphenyl Ethers (PBDEs) in Breast Milk and Neuropsychological Development in Infants. *Environ Health Perspect.* 2012; 120:1760–1765. [PubMed: 23052368]
- Guo T, LaBelle B, Petreas M, Park J-S. Mass Spectrometric Characterization of Halogenated Flame Retardants. *Rapid Communications in Mass Spectrometry.* 2013; 27:1–13. [PubMed: 23239313]
- Johnson PI, Stapleton HM, Sjodin A, Meeker JD. Relationships between Polybrominated Diphenyl Ether Concentrations in House Dust and Serum. *Environmental science & technology.* 2010; 44:5627–5632. [PubMed: 20521814]
- Kicinski M, Viaene MK, Hond ED, Schoeters G, Covaci A, Dirtu AC, et al. Neurobehavioral function and low-level exposure to brominated flame retardants in adolescents: a cross-sectional study. *Environ Health.* 2012; 11
- Law RJ, Alae M, Allchin CR, Boon JP, Lebeuf M, Lepom P, et al. Levels and trends of polybrominated diphenylethers and other brominated flame retardants in wildlife. *Environ Int.* 2003; 29:757–770. [PubMed: 12850094]
- Mercier F, Gloennec P, Thomas O, Le Bot B. Organic Contamination of Settled House Dust, A Review for Exposure Assessment Purposes. *Environ Sci Technol.* 2011; 45:6716–6727. [PubMed: 21667945]
- OEHHA. Brominated and Chlorinated Organic Chemical Compounds used as Flame Retardants. 2008
- OEHHA. Brominated and Chlorinated Organic Chemical Compounds Used as Flame Retardants: Additional Information on Four Flame Retardants. 2009
- Pohl, HR.; Bosch, S.; Amata, RJ.; Eisenmann, CJ. Toxicological Profile for Polybrominated Biphenyls and Polybrominated Diphenyl Ethers. Atlanta, GA: 2004.
- Shaw SD, Kannan K. Polybrominated Diphenyl Ethers in Marine Ecosystems of the American Continent: Foresight from Current Knowledge. *Reviews on Environmental Health.* 2009; 24:157–229. [PubMed: 19891120]
- Shen, B. Occupational Exposures to Brominated Flame Retardants: Methods to Assess Chemical Contamination in California Firehouses. Environmental Health Sciences, School of Public Health; University of California Berkeley; Berkeley, CA: 2012.
- Shen B, Whitehead TP, McNeel S, Brown FR, Das R, Isreal L, et al. Measurement of PAHs, PBDEs, and PCBs in dust from California Firehouses. *Organohalogen Cmpd.* 2012; 74:899–902.
- Shoeib M, Harner T, Webster G, Sverko E, CHeng Y. Legacy and current-use flame retardants in house dust from Vancouver, Canada. *Environmental Pollution.* 2012; 169:175–182. [PubMed: 22402458]
- SRM-2585. Organic Contaminants in House Dust. NIST; Gaithersburg, MD, USA: 2010.

- Stapleton HM, Allen JG, Kelley SM, Konstantinov A, Klosterhaus S, Watkins D, et al. Alternate and New Brominated Flame Retardants Detected in US House Dust. *Environ Sci Technol*. 2008; 42:6910–6916. [PubMed: 18853808]
- Stapleton HM, Eagle S, Sjodin A, Webster TF. Serum PBDEs in a North Carolina Toddler Cohort: Associations with Handwipes, House Dust, and Socioeconomic Variables. *Environmental Health Perspectives*. 2012; 120:1049–1054. [PubMed: 22763040]
- Whitehead TP, Brown FR, Metayer C, Park J-S, Does M, Dhaliwal J, et al. Polychlorinated Biphenyls in Residential Dust: Sources of Variability. *Environm SciTechnol*. 2014; 58:157–164.
- Whitehead TP, Brown FR, Metayer C, Park J-S, Does M, Petreas MX, et al. Polybrominated diphenyl ethers in residential dust: Sources of variability. *Environm Int*. 2013a; 57-58:11–24.
- Whitehead TP, Metayer C, Petreas M, Does M, Buffler PA, Rappaport SM. Polycyclic Aromatic Hydrocarbons in Residential Dust: Sources of Variability. *Environm Health Perspect*. 2013b; 121:543–550.
- Wu N, Herrmann T, Paepke O, Tickner J, Hale R, Harvey E, et al. Human Exposure to PBDES: Associations of PBDE Body Burdens with Food Consumption and House Dust Concentrations *Environ Sci Technol*. 2007; 41:1584–1489.
- Zota AR, Park J-S, Wang Y, Petreas M, Zoeller RT, Woodruff TJ. Polybrominated Diphenyl Ethers, Hydroxylated Polybrominated Diphenyl Ethers, and Measures of Thyroid Function in Second Trimester Pregnant Women in California. *Environ Sci Technol*. 2011; 45:7896–7905. [PubMed: 21830753]

Highlights

- Novel brominated flame retardants (NBFR) found in residential and fire station dust
- NBFR levels were lower than PBDE levels in the same samples
- The NBFRs measured at the highest levels were direct replacements of PBDEs
- NBFR levels in California homes were consistent with other studies from N. America

Table 1

Summary statistics^a for NCCLS and FOX study dust samples^b, compared to results from similar studies. All concentrations in ng/g. GM/GSD = geometric mean/geometric standard deviation

	Northern California Childhood Leukemia Study 2010 (n=59)					Firefighter Occupational Exposure Study Southern California 2010-2011 (n = 27)					Boston, MA Area Homes (Stapleton and others 2008) 2006 (n=7-10)			San Francisco Bay Area, CA Homes(Dodson and others 2012) 2011 (n=16)			San Francisco Bay Area, CA Homes (Dodson and others 2012); 2006 (n=16)			Vancouver, BC, homes (Shoeb and others 2012) 2007-2008 n=116				
	% Detect	Blank ^c (ng, n=7)	GM	GSD	Min ^a	Median	Max	% Detect	Blank ^c (ng, n=3)	GM	GSD	Min	Max	GM	GSD	Min	Max	GM	GSD	Min	Max	Median	Max	
					<0.64																			
β-DBE-DBCH	54.2	<0.64	1.46	3.46	<0.64	0.91	359	21.7	<0.64	0.76	1.47	<0.64	<0.64	<0.64	<2	<2	11	<2	<2	<2	<2	<2	<2	16
α-DBE-DBCH	54.2	<0.64	1.38	3.34	<0.64	0.75	307	21.7	<0.64	0.74	1.42	<0.64	<0.64	<0.64	<2	<2	13	<2	<2	<2	<2	<2	<2	25
BATE	0.0	<0.64	<0.64	1.00	<0.64	<0.64	<0.64	4.3	<0.64	0.66	1.16	<0.64	<0.64	<0.64	-	-	-	-	-	-	-	-	-	-
PBT	28.8	<0.64	0.87	1.92	<0.64	<0.64	7.87	73.9	<0.64	1.30	1.84	<0.64	1.39 ^b	5.28	-	-	-	-	-	-	-	<0.02	0.30	12
PBEB	44.1	<0.64	1.26	2.60	<0.64	<0.64	12.8	82.6	<0.64	1.79	2.53	<0.64	1.89 ^b	21.4	-	-	-	-	-	-	-	<0.07	0.5	4.1
TBP-DBPE	28.8	<0.64	0.79	1.58	<0.64	<0.64	4.21	73.9	<0.64	1.24	1.93	<0.64	1.01 ^b	4.68	<2	<2	2	-	-	-	-	<0.30	1.5	1,200
HBB	81.4	<0.64	2.02	2.53	<0.64	1.85	16.3	91.3	<0.64	7.78	2.84	<0.64	9.40 ^b	27.4	<2	<2	8	<2	<2	<2	<2	<0.02	3.7	130
EH-TBB	93.2	<0.64	310	8.59	<0.64	337	19198	91.3	0.88	1400	17.3	<0.64	2687 ^b	29007	4	48	740	45	100	5900	<0.30	120	18,000	
BEH-TEBP	93.2	0.99	144	5.94	<0.64	186	3483	91.3	<0.64	1096	12.0	<0.64	2076 ^b	11422	36	140	1900	<2	260	3800	10	99	6,400	
BTPE	93.2	<0.64	21.8	4.41	<0.64	22.3	1505	91.3	<0.64	31.3	4.84	<0.64	28.4	626	7	30	220	3	12	130	1.8	30	610	
DBDPE	78.0	<2.60	53.5	6.40	<2.60	82.8	5564	82.6	<2.60	96.5	5.99	<2.60	161 ^b	1650	<10	51	430	18	140	2800	<0.30	120	18,000	

^a Summary statistics calculated using value of LOD for non-detects.

^b Dust-NBFR concentrations differed between the NCCLS and FOX study using the non-parametric Wilcoxon-Mann-Whitney test, $p < 0.05$

^c < X.X – Below lowest calibration standard converted to ng/g