Title

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Journal

Indoor air, 25(2)

ISSN

0905-6947

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Publication Date

2015-04-01

DOI

10.1111/ina.12130

Peer reviewed

HHS Public Access

Author manuscript

Indoor Air. Author manuscript; available in PMC 2016 December 05.

Published in final edited form as:

Indoor Air. 2015 April ; 25(2): 220–229. doi:10.1111/ina.12130.

Polybrominated diphenyl ether (PBDE) concentrations and resulting exposure in homes in California: relationships among passive air, surface wipe and dust concentrations, and temporal variability

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Abstract

Polybrominated diphenyl ethers (PBDEs) are used as flame retardants in furniture foam, electronics, and other home furnishings. A field study was conducted that enrolled 139 households from California, which has had more stringent flame retardant requirements than other countries and areas. The study collected passive air, floor and indoor window surface wipes, and dust samples (investigator collected using an HVS3 and vacuum cleaner) in each home. PentaBDE and BDE209 were detected in the majority of the dust samples and many floor wipe samples, but the detection in air and window wipe samples was relatively low. Concentrations of each PBDE congener in different indoor environmental media were moderately correlated, with correlation coefficients ranging between 0.42 and 0.68. Correlation coefficients with blood levels were up to 0.65 and varied between environmental media and age group. Both investigator-collected dust and floor wipes were correlated with serum levels for a wide range of congeners. These two sample types also had a relatively high fraction of samples with adequate mass for reliable quantification. In 42 homes, PBDE levels measured in the same environmental media in the same home 1 year apart were statistically correlated (correlation coefficients: 0.57–0.90), with the exception of BDE209 which was not well correlated longitudinally.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Table S1. QA/QC information for air and wipe BDE samples.

Table S2. Limit of Detection (LOD) of BDE congeners in serum samples.

Table S3. Demographics of study population.

Table S4. Correlations among BDE congener concentrations within each environmental media.

Keywords

Polybrominated diphenyl ethers; Residential environment; Air concentration; Wipe; Dust; Temporal variability

Introduction

Polybrominated diphenyl ethers (PBDEs) are used as flame retardants in many household items, including furniture, electronics, fabrics, and carpeting. PBDEs are of concern because they disrupt thyroid hormones, have neurodevelopmental consequences (Alva-Sánchez et al., 2004; Costa and Giordano, 2007; Herbstman et al., 2010; Roze et al., 2009) and are endocrine disrupting compounds in humans and other animals (Birnbaum and Staskal, 2004; Legler, 2008). Furniture sold in California prior to 2014 potentially contains more PBDEs or other flame retardants in the foam than furniture found in other states because it must meet Technical Bulletin 117 (TB117), the state's 1975 performance-based furniture flammability standard (State of California, 2000, 2013). Because of these ubiquitous indoor sources indoor air, and dust are thought to contribute to human exposure (Harrad et al., 2010; Jones-Otazo et al., 2005; Lorber, 2007; Watkins et al., 2012; Wu et al., 2007; Zota et al., 2008).

The commercial formulation pentaBDE (DE-71) is predominantly comprised of BDE47 and 99, with smaller contributions from BDE100, 153, and 154 (La Guardia et al., 2006); it was traditionally used in polyurethane foam. Commercial octaBDE is primarily made up of BDE183 and used primarily in electronics and other plastic products. Penta and Octa formulations have been banned in Europe and were voluntarily removed from products by U.S. manufacturers at the end of 2004 but may still be present in older household items and continue to persist in the household environment. The decaBDE formulation, consisting of mostly BDE209, is used primarily in electronics (USEPA, 2006), and is being phased out by the end of 2013 by the manufacturers/importers in the United States and Europe. A portion of the PBDE congeners present in the environment are debromination products of BDE209 due to environmental degradation pathways (Davis and Stapleton, 2009).

Dust and air are the two most commonly collected environmental media for measuring indoor levels of PBDEs. However, collection of dust is time-consuming and often does not yield enough dust for chemical analysis. Collection of either passive or active air samples often requires multiple field technician visits to the home. Less burdensome approaches to consider may include vacuum cleaner dust collection and wipe samples. Information on concentration variability over time is also needed to evaluate the effectiveness of a single concentration measure in epidemiology studies where long-term exposure may be important, as there is little relevant data (Allen et al., 2008; Quirós-Alcalá et al., 2011).

To address these research needs, a field study was conducted that enrolled 139 households from northern California and the southern portion of California's Central Valley. In each home, we collected air, surface wipes from interior floors and windows, and two types of dust samples. One dust sample was collected from household vacuum cleaner bags, the other by study staff using a High Volume Surface Sampler (HVS3). These samples allowed for comparisons across multiple environmental media. Environmental levels were also

compared against blood serum levels, a marker of exposure. For a subset of homes, two visits were conducted 1 year apart to evaluate whether a one-time measurement is sufficient to represent the PBDE levels in the home over a longer time period.

Methods

Study population

This study was conducted as part of the Study of Use of Products and Exposure-Related Behaviors (SUPERB), which gathered information on exposure-related behavior through telephone interviews, web-based interviews, and home visits. Methods of data collection were intended to be low burden to participants. Participant selection and demographic information for the SUPERB study is described (Hertz-Picciotto et al. 2010). Briefly, the SUPERB study enrolled California residents from homes with young children (97% had a child 5 years or younger at enrollment) and older adults (generally aged 55 years and above). Homes with young children were identified through birth certificate records for children born from an 18-county region in northern California between 2000 and 2005. The older-adult households were a population-based sample randomly selected from housing units in the southern portion of California's Central Valley.

Participants were recruited into this home visit component of the SUPERB study by calling households enrolled in the main SUPERB study. A total of 139 households participated, comprising 90 households with both a parent and a young child (97% under the age of 8 years at the first home visit, with 62% under the age of 6) and 49 households with an older adult (96% greater than 55 years).

All recruitment and data collection protocols were approved by the Institutional Review Board at the University of California, Davis, and informed consent for participation was obtained upon enrollment into the study. A technical assistance agreement was established between the Division of Laboratory Sciences at the National Center for Environmental Health, Centers for Disease Control and Prevention (CDC), and the University of California.

Sample collection and analysis

Sample collection was conducted between 2008 and 2009. One hundred and thirty-nine households had an initial visit, which included collection of multiple indoor samples: investigator-collected dust using an HVS3, dust from the participant's vacuum cleaner, floor and window wipes, and a passive air sample. Blood samples were also collected from one adult and one child participant in northern California homes with children, and from one or two adults in central California homes with older adults by a trained phlebotomist during the visit. Forty-two households with a parent/child pair participated in a second study visit approximately 1 year after their first study visit (average = 341 days between visits, range: 225–505 days). All sampling was conducted with the same equipment, using the same methods, by a consistent field staff team.

Dust samples collected by the study staff were vacuumed from approximately 2.3 m^2 (60 × 60 $inch^2$) of carpet or area rug in the main living area of the home using an HVS3 (CS3 Industries, OR) following a standard protocol (ASTM, 1994). Dust samples were also

obtained from a participant's vacuum cleaner (vacuum dust), by collecting either the entire bag, partial contents from a bag, or the contents from a bag-less vacuum or central repository.

Surface wipe samples were collected from the floor in the kitchen (approximately 1.5 m^2 section) and a window in the main living area (approximately 1 m^2) using cotton Twillwipes (M.G. Chemicals, P/N 829-50) dampened with 4.0 ml of isopropanol (pesticide residue analysis grade). Twillwipes were pre-cleaned by soxhlet extraction for 24 h with isopropanol followed by an additional 24-h extraction with hexane. Details of the pre-cleaning method have been reported previously (Clifton et al., 2013). Not all homes had sufficient window area for a sample of this size, so the exact sample area was recorded. Wipe samples were stored in a cleaned, sealed glass jar (I-Chem 300 Series) for subsequent extraction and analysis by GC/MS (Clifton et al., 2013).

Passive air samplers were placed on a shelf or table out of direct sunlight and reach of children and pets in the main living area of each home for an average of 31 days (range: 26–42). The passive air sampling method has been used in previous studies (Bohlin et al., 2008). In short, a polyurethane foam (PUF; Tisch Environmental, TE-1014, Cleves, OH, USA) disk was placed on a rack in a covered open housing unit (Tisch, TE-300-PAS). Prior to field deployment, the PUF disks were cleaned with water, acetone, and hexane. This series of solvents was chosen to remove a broader range of chemicals from the foam media than would be removed using only hexane. At the end of the sampling period, study staff returned to the participant's home to retrieve the sampler; the PUF was placed in a pre-cleaned glass jar; the jar was wrapped in foil and was transported on ice prior to extraction and analysis.

Field blank, laboratory blank, and duplicate samples were collected for both air and wipe sampling methods (more information on QA/QC can be found in the Supporting Information (SI) and Clifton et al. (2013)).

Detailed explanations of the extraction, cleanup, and analysis procedures for PBDE analysis are published elsewhere (Clifton et al., 2013; Shin et al., 2013). Briefly, dust samples were sieved to ≤150 μm and extracted using accelerated solvent extraction. Sample cleanup was accomplished using two silica solid-phase extraction (SPE) tubes (Bond Elut NH2 1 g, 6 ml, Agilent Technologies, Palo Alto, CA, USA) in tandem. Wipe samples were solvent extracted inside their collection jars with acetone and hexane (50/50) using an ultrasonic cleaner. Cleanup was accomplished by base partitioning with 0.1 N NaOH solution followed by NH_2 SPE. Air samples had PBDEs extracted from the PUF discs using a Soxhlet apparatus with hexane; extracts were concentrated and transferred to autosampler vials for gas chromatography/mass spectrometry (GC/MS) analysis. Samples from all media were analyzed for five major pentaBDE congeners, including BDE47, 99, 100, 153, and 154 as well as BDE209, by GC/MS in negative chemical ionization mode.

Concentrations are available for 83 households for HVS3 dust samples (17 with two time points), 105 households for vacuum dust samples (24 with two time points), 123 households for floor wipes (34 with two time points), 135 households for window wipes (36 with two time points), and 136 households for air samples (38 with two time points).

Blood samples were drawn by a trained phlebotomist into 10-ml red top Vacutainer™ tubes (Becton-Dickinson, Rutherford, NJ, USA) with no anticoagulant and then transported to the UC Davis lab on ice. Blood samples were allowed to clot for at least 2 h and were then centrifuged for 15 min at 3300 rpm and a g factor of 1327. Some samples were centrifuged a second time for 10 min, to obtain maximum serum yield. A 4–6 ml aliquot of the serum was transferred into a pre-cleaned 10-ml brown glass bottle. Aliquots were stored at −80°C until shipped on dry ice to CDC (Atlanta, GA) for analysis. The sample extraction procedure has been published (Jones et al., 2012). Briefly, serum samples were extracted using an automated liquid/liquid extraction followed by lipid removal using a two-layered silica/silica/sulfuric acid column. Identification and quantification of five major pentaBDE congeners, including BDE47, 99, 100, 153, and 154 as well as BDE209 were performed by isotope dilution gas chromatography high-resolution mass spectrometry.

Data analysis

All air samples were blank corrected by subtracting the mean value of field blanks from the measured value. An estimated air concentration was then calculated using an average sampling rate of 2.5 m^3 per day for the indoor housing unit (Wilford et al., 2004). The mass of compound in the wipe samples was converted to an area concentration by dividing by the area sampled in each home. Blood serum samples were converted to per gram lipid for analysis.

Summary statistics are presented for the two populations from northern California and Central Valley, respectively, and comparisons were made between the two populations using the Wilcoxon–Mann–Whitney test. Many of the reported values for environmental samples were below the estimated limit of quantification (ELOQ) and are thus subject to greater uncertainty, but they are included in the statistical analyses to fully utilize all information and have as large a dataset as possible. The ELOQ is determined based on the lowest level that can be accurately quantified by the instrumentation in the EPA laboratory. Detectable but below ELOQ environmental samples were reported and used in data analysis as is. By not reporting all values below ELOQ as a single value, we better fit the distribution at the lower end of the curve. Nondetect environmental concentration (or concentrations below the average value of the field blanks for air samples) was replaced by half of the lowest nonzero concentration observed for each congener in each media after samples were blank corrected. We note that the geometric means and geometric standard deviation are subject to uncertainty due to the choice of values we used to replace the nondetect levels. The limit of detection (LOD) for blood samples varies by the available sample volume for each sample, with ranges given in the Supporting Information. Serum concentrations below LODs were replaced by LODs divided by the square root of 2.

The relationships between congener concentrations within a sample type and between samples collected from different media were quantified by Spearman correlation coefficients. The magnitude of concentrations in window wipe versus floor wipe and vacuum dust versus HVS3 dust were compared using a paired t-test on log-transformed data. Spearman correlation coefficients between serum and each environmental media

concentration for each age group were also examined, including only homes that had HVS3 dust samples for major congeners including BDE47, 99, 100, and 153.

The changes between the two visits 1 year apart were examined both in terms of correlation by calculating Spearman correlation coefficients and for changes over time by calculating the percent change between concentrations measured in the same home at two different time points over the average concentration of the two measurements. In addition, as the time intervals between the two visits varied between homes, we conducted a generalized linear regression analysis to examine whether the percent change in PBDE concentrations increased as the length of the time period between visits increased. All statistical analyses were conducted using SAS 9.2 for Windows® (SAS Institute Inc., Cary, NC, USA). Statistical significance was set as $\alpha = 0.05$ (two sided).

Results and discussion

Demographics

The adult participants in northern California had an average age of 39 years, and 67% of them were Caucasian. The average age of the central California population was 67 years, and 76% of them were Caucasian. Participants of both groups were above average in education, with 90% having at least some college. Northern California parents of young children were almost equally employed (42%) or stay-at-home parents (48%), while only 37% of older adult participants in central California were employed. Full demographic information is presented in the Supporting Information.

Summary statistics

Summary statistics of PBDE concentrations in multiple media are presented for the two age groups in Table 1. The number of nondetects and the number of values below ELOQ is compared with the sum of the two N values for households with young children and households with older adults. Summary statistics for the combined age groups were reported previously (Clifton et al., 2013). While the vast majority of samples of various types had detectable levels for most congeners, 35–95% of the air samples and 31–89% of the window wipe samples were below the ELOQ for a given congener, indicating that these values are uncertain, especially for BDEs 100–154 in air, which had a high percentage of sample values below the ELOQ. Floor wipe and dust samples had a greater fraction of data above the ELOQ, potentially because PBDEs have relatively low vapor pressures and are thus more likely to be detected in dust and floor wipes. Pairwise comparison suggests that, for all congeners, floor wipe concentrations were statistically significantly higher than window wipe concentrations in the same household measured at the same time, as expected because these compounds are heavily dust bound and thus may not sufficiently partition to air, limiting their ability to transfer to window film. Geometric mean concentrations for the floor wipes for all congeners except BDE154 were at least a factor of two higher than those for the window wipes. The increased chemical mass in the floor wipes increases the fraction of samples above the ELOQ, improving the reliability. The median relative percent of difference (RPD), a measure of precision, for most congeners in duplicate floor and window wipes ranged from 15 to 30%, with BDE209 at 49%. The RPD values between duplicate

samples were greater for the air samples, with median RPD values of most congeners ranging from 29 to 54% and the RPD value of BDE100 at 92% indicating lower precision. Details are available in the Supporting Information (SI) for quality control (blanks and duplicates) samples by media type.

Comparison between the two age groups suggested statistically significantly higher concentrations of BDE209 in households with young children than households with older adults in samples from all measured media (BDE209 was not measured in air) (Table 1). BDE209 is the major congener in decaBDE and was largely in use while the study was conducted. Our finding suggests that younger families were potentially exposed to higher levels of BDE209 possibly because their homes had more recently manufactured electronics, that is, ones most likely containing BDE209. As a result, young children are at higher risk of exposure to BDE209. Besides the difference in BDE209, younger families also had lower air concentrations of BDE47 than households with older adults.

One previous study collected a limited number of window wipe samples using a similar collection method in Canada in 2001, reporting a range of 1.9–7.6 pg/cm^2 for total summed PBDE concentrations of 14 congeners, including the 6 congeners we reported (Butt et al., 2004). Those values were much lower than the summed concentrations measured in these California samples (summed PBDE median concentration of 6 congeners = 6.8 pg/cm^2, range 0.23–110 pg/cm^2). This is expected given the greater prevalence of PBDEs in California furniture (Zota et al., 2008). We are not aware of any floor wipe data available for comparison.

The measured BDE47 and 99 air concentrations in California were substantially higher than the level measured in Japan, Kuwait, and Sweden (Gevao et al., 2006; Takigami et al., 2009; Thuresson et al., 2012) (Figure 1). Data obtained in Denmark, Australia, Canada, and other US areas such as Boston and Wisconsin were at the lower range of our levels (Allen et al., 2007; Imm et al., 2009; Toms et al., 2009; Vorkamp et al., 2011; Wilford et al., 2004). Only data observed in Albany, New York, USA are comparable with the level we obtained (Johnson-Restrepo and Kannan, 2009). Those samples with lower values than ours were all collected earlier than our samples, and thus either while pentaBDE was being used or closer to the time pentaBDE was voluntarily phased out in 2004. The levels similar to ours from Albany, NY, were collected 1 year prior to ours but with active sampling. The various studies used either passive or active sampling, but these methods have been shown to result in compatible values (Gouin et al., 2005; Wilford et al., 2004).

We calculated the correlation coefficients between individual congeners within each environmental media (Table S4). Among congeners present in the commercial pentaBDE mix (BDE47, 99, 100, 153, and 154), correlations were strong. Both types of dust samples showed the strongest correlations across the pentaBDE congeners: Spearman correlation coefficients ranged between 0.89 and 0.99. In the wipe samples, BDE47, 99, 100, and 154 were well correlated, with correlation coefficients between 0.74 and 0.95. In the wipe and air samples, BDE153 was not well correlated with the other congeners, most likely due to uncertainty in the measurements, or possibly because this congener is also found in the octaBDE commercial formulation. The high correlations between the congeners of penta-

BDE also indicated they come from the same source, that is, goods containing the pentaBDE product. BDE209 was moderately correlated with pentaBDE congeners in HVS3 dust samples, and the correlations were weaker in vacuum cleaner dust samples. Similar patterns of correlation have been found in other studies (Allen et al., 2008; Björklund et al., 2012; Zhang et al., 2011).

Correlation between environmental media and with blood

We calculated the correlation across the different environmental media for each specific congener to determine whether all environmental media give an equivalent relative measure of potential loading of the chemical in the home and thus potential for environmental exposure. If all environmental media result in equivalent ranking of congeners with respect to indoor loading and thus potential exposure, the method used in a study can be selected based on what is most convenient for the study design.

Correlations between media were highest between the two dust collection methods, with correlation coefficients for all congeners exceeding 0.5 (Table 2). It is not surprising that levels are more highly correlated among the two dust samples as these compounds have relatively low vapor pressure values and relatively high K_{oa} values, resulting in the dust being a significant reservoir for these compounds. Concentrations of BDE47 and 99, the two compounds with the highest vapor pressure, were moderately correlated across most media (R values between 0.37 and 0.66), with the highest values resulting from comparisons of air versus another media and between the two dust types. Correlations were also moderate for the window and floor wipes and other media (R values primarily between 0.35 and 0.52). For BDE209, the strongest correlations were between vacuum cleaner and HVS3 dust, and there was also moderate correlation between the two wipe samples, and between both wipe samples and dust samples.

While the overall correlation between the two dust samples was higher than for the floor or window wipe versus any other environmental media, the correlations for the two types of wipe samples are high enough that either appears to be an adequate indicator of overall indoor environmental levels for many of the congeners.

Ultimately, environmental concentrations should be evaluated against a measure of exposure, in this case, blood serum. BDE47, 99, and 100 environmental concentrations and serum were correlated, with a higher level of correlation for young children than parents of young children and older adult groups (Table 3). Floor wipe and HVS3 dust concentrations strongly correlated with young children's serum concentrations for BDE47, 99, and 100 (R = 0.47–0.65); air and window wipe concentrations were strongly correlated for BDE47 and 99 (R = 0.50–0.62). The lack of correlation for BDE100 may result from this compound being less volatile. For parents, the correlations of BDE47 and 99 in serum with air concentrations were stronger than for other environmental media, but BDE100 correlations were stronger with wipes. Older adults' BDE47 and 99 serum concentrations were correlated with air and HVS3 dust concentrations with little correlation for floor wipe and vacuum dust concentrations.

Overall, based on the correlation with serum levels across all congeners, HVS3 dust and floor wipe appeared to be the most optimistic measurement approaches. Air and window wipe concentrations had good correlations with serum concentrations of BDE47 and 99; however, due to the low detection level of PBDEs in air and window wipe samples, it is less reliable especially for congeners with higher molecular weight. Vacuum dust concentrations were less correlated with serum concentrations of PBDEs, and thus, we do not recommend this method. Additionally, vacuum bags can be problematic to collect. There are a number of homes where participants may be unwilling to give researchers their vacuum bag, and not everyone has a vacuum cleaner with a bag, as bagless vacuum cleaners are becoming more popular. With bagless vacuum cleaners, there is often either no dust or an inadequate amount of dust for analysis as participants empty them frequently. Consideration must also be given to ease of collection, especially in a large study. Though reliable, HVS3 is heavy and not convenient to transport to the field. Considering all these points, the floor wipe is a comparably easy and reliable method to measure residential indoor PBDEs levels. The advantage of a wipe sample is that it is significantly easier to collect than a dust sample collected using HVS3 and thus more cost-effective when conducting field studies. However, we note that, compared with dust samples, some congeners in the floor wipe samples had a greater proportion of the samples below the ELOQ (1–90% varied by congener), which is a disadvantage of this method.

Temporal variation

PBDE levels measured in the same household at the two visits approximately 1 year apart were statistically correlated for most congeners in most sample media indicating that the homes ranked high in the first year had high ranks the second year (Table 4). One exception was the more highly brominated BDEs found in the air samples, which may not have been well correlated partly due to low volatility resulting in a lack of precision in the measurements. The correlations between the two measurements 1 year apart tend to be strongest for the HVS3 dust samples, with the two wipe samples slightly less correlated. Air concentrations may be more variable throughout the year as they may be influenced by the air exchange rate of the home. BDE209 was less correlated between two measurements in all media as compared to the pentaBDE congeners. Multiple reasons may contribute to the low correlation for BDE209. BDE209 is still used as a flame retardant in electronics, which are more frequently acquired and disposed of than foam filled furniture. A study conducted by Webster et al. (2009) suggested that BDE209 does not partition evenly throughout the surface dust, but also exists as discrete fragments of plastic polymer that contained BDE209. Also, BDE209 measurements are somewhat uncertain as this compound debrominates in the environment (Allen et al., 2008) and during the analytical process (Stapleton and Dodder, 2008). Therefore, more variation in concentration is expected throughout the dust, which may explain the low correlation over a span of 1 year.

Similar to our findings, Allen et al. (2008) showed that penta and decaBDE concentrations in house dust did not significantly change over an 8-month period because home furnishings change very little in such a short period of time. Quirós-Alcalá et al. (2011) collected two dust samples only a few days apart in California homes and reported that the concentrations were statistically significantly correlated between collection rounds, as would be expected

for this very narrow time period. Ideally, additional studies should be conducted that measure concentrations repeatedly at different intervals, but extended for at least a year.

We also determined if levels went up or down between the two visits. In general, PBDE concentrations in air and HVS3 samples stayed the same or were lower at the second time point compared with the first measurement in the majority of the homes (Figure 2). Concentrations in floor wipes, HVS3 dust, and vacuum cleaner dust were higher 1 year later in ~20–40% of the households for many of the congeners. The change in PBDE concentrations varied by congener. As penta-BDE has been phased out in the United States, the concentrations of most pentaBDEs were trending downward. DecaBDE is still widely used in electronics, suggesting that BDE209 levels were less likely to decrease and actually showed an increase in both window and floor wipes as well as HVS3 dust samples, with higher concentration at the second time point in more than half of the households. On average, BDE209 levels were 9% higher in window and 12% higher in floor wipe samples.

The regression analysis with the length of the time period between visits suggests a significant positive association with time for all pentaBDE congeners in HVS3 dust samples as well as for BDE100 and 154 in floor wipes, while no association was observed for air, window wipe and vacuum dust samples.

The strength of this study is the ability to compare different types of environmental samples to quantify residential exposure to PBDEs. A limitation is that given that the main SUPERB study focused on the exposure of young children and older adults, the participating households of this study may not be representative of the California or U.S. population. The population was also more educated than the general population. Characteristics of the study population need to be considered when comparing our observed PBDE concentrations with other studies.

Conclusions

Our goal was to evaluate various methods for estimating exposures to support epidemiology studies. For estimating indoor exposures, floor wipes may be a useful method. Results from this study found that they were correlated with other indoor measurements, and with blood serum levels, and had a relatively high fraction of samples with adequate mass for reliable quantification. Collection of wipe samples is considerably less time-consuming in the field when compared with collecting other media, minimizing both field technician and participant burden, making them a suitable sampling method for large epidemiology studies where an exposure component is included.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The United States Environmental Protection Agency through its Office of Research and Development partially funded and collaborated in the research described here under STAR Grant # RD-83154001-0 to Irva Hertz-Picciotto. It has been subjected to Agency review and approved for publication. Environmental sample analysis was

conducted by the USEPA's Office of Research and Development's National Exposure Research Laboratory. Blood sample analysis was conducted by the Centers for Disease Control and Prevention Laboratory. The findings and conclusions in this report are those of the authors and do not necessarily represent the official position of the Centers for Disease Control and Prevention. Data analysis was supported by the International Society of Exposure Analysis Young Investigator Award. We thank all our study participants and field staff (Colleen Phillips, Esther Rivera, Amanda Eberle, Robin Joseph, Candice Teague, Elizabeth Marder and Ashley Ratcliffe).

References

Allen JG, McClean MD, Stapleton HM, Nelson JW, Webster TF. Personal exposure to polybrominated diphenyl ethers (PBDEs) in residential indoor air. Environ. Sci. Technol. 2007; 41:4574–4579. [PubMed: 17695899]

Allen JG, McClean MD, Stapleton HM, Webster TF. Critical factors in assessing exposure to PBDEs via house dust. Environ. Int. 2008; 34:1085–1091. [PubMed: 18456330]

Alva-Sánchez C, Ortiz-Butrón RO, Pacheco-Rosado J. Kainic acid does not affect CA3 hippocampal region pyramidal cells in hypothyroid rats. Brain Res. Bull. 2004; 63:167–171. [PubMed: 15130707]

ASTM. Annual Book of ASTM Standards. Philadelphia, PA: American Society for Testing and Materials; 1994.

Birnbaum LS, Staskal DF. Brominated flame retardants: cause for concern? Environ. Health Perspect. 2004; 112:9–17. [PubMed: 14698924]

Björklund JA, Sellström 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]

Bohlin P, Jones KC, Tovalin H, Strandberg B. Observations on persistent organic pollutants in indoor and outdoor air using passive polyurethane foam samplers. Atmos. Environ. 2008; 42:7234–7241.

Butt CM, Miriam L, Truong J, Ikonomou MG, Ter Schure AFH. Spatial distribution of polybrominated diphenyl ethers in southern Ontario as measured in indoor and outdoor window organic films. Environ. Sci. Technol. 2004; 38:724–731. [PubMed: 14968856]

Clifton MS, Wargo JP, Weathers WS, Colon M, Bennett DH, Tulve NS. Quantitative analysis of organophosphate and pyrethroid insecticides, pyrethroid transformation products, polybrominated diphenyl ethers and bisphenol-A in residential surface wipe samples. J. Chromatogr. A. 2013; 1273:1–11. [PubMed: 23265991]

Costa LG, Giordano G. Developmental neurotoxicity of polybrominated diphenyl ether (PBDE) flame retardants. Neurotoxicology. 2007; 28:1047–1067. [PubMed: 17904639]

Davis EF, Stapleton HM. Photodegradation pathways of nonabrominated diphenyl ethers, 2-ethylhexyltetrabromobenzoate and di (2-ethylhexyl) tetrabromophthalate: identifying potential markers of photodegradation. Environ. Sci. Technol. 2009; 43:5739–5746. [PubMed: 19731671]

Gevao B, Al-Bahloul M, Al-Ghadban AN, Ali L, Al-Omair A, Helaleh M, Al-Matrouk K, Zafar J. Polybrominated diphenyl ethers in indoor air in Kuwait: implications for human exposure. Atmos. Environ. 2006; 40:1419–1426.

Gouin T, Harner T, Blanchard P, Mackay D. Passive and active air samplers as complementary methods for investigating persistent organic pollutants in the Great Lakes Basin. Environ. Sci. Technol. 2005; 39:9115–9122. [PubMed: 16382932]

Harrad S, de Wit CA, Abdallah MAE, Bergh C, Björklund JA, Covaci A, Darnerud PO, de Boer J, Diamond M, Huber S, Leonards P, Mandalakis M, Östman C, Haug LS, Thomsen C, Webster TF. Indoor contamination with hexabromocyclododecanes, polybrominated diphenyl ethers, and perfluoroalkyl compounds: an important exposure pathway for people. Environ. Sci. Technol. 2010; 44:3221–3231. [PubMed: 20387882]

Herbstman JB, Sjödin A, Kurzon M, Lederman SA, Jones RS, Rauh V, Needham LL, Tang D, Niedzwiecki M, Wang RY, Perera F. Prenatal exposure to PBDEs and neurodevelopment. Environ. Health Perspect. 2010; 118:712–719. [PubMed: 20056561]

Hertz-Picciotto I, Cassady D, Lee K, Bennett DH, Ritz B, Vogt R. Study of Use of Products and Exposure-Related Behaviors (SUPERB): study design, methods, and demographic characteristics of cohorts. Environ. Health. 2010; 9:54. [PubMed: 20799988]

Imm P, Knobeloch L, Buelow C, Anderson HA. Household exposures to polybrominated diphenyl ethers (PBDEs) in a Wisconsin cohort. Environ. Health Perspect. 2009; 117:1890. [PubMed: 20049208]

Johnson-Restrepo B, Kannan K. An assessment of sources and pathways of human exposure to polybrominated diphenyl ethers in the United States. Chemosphere. 2009; 76:542–548. [PubMed: 19349061]

Jones R, Edenfield E, Anderson S, Zhang Y, Sjödin A. Semi-automated extraction and cleanup method for measuring persistent organic pollutants in human serum. Organohalogen Compd. A. 2012; 3:104.

Jones-Otazo HA, Clarke JP, Diamond ML, Archbold JA, Ferguson G, Harner T, Richardson GM, Ryan JJ, Wilford B. Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to PBDEs. Environ. Sci. Technol. 2005; 39:5121–5130. [PubMed: 16082939]

La Guardia MJ, Hale RC, Harvey E. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. Environ. Sci. Technol. 2006; 40:6247–6254. [PubMed: 17120549]

Legler J. New insights into the endocrine disrupting effects of brominated flame retardants. Chemosphere. 2008; 73:216–222. [PubMed: 18667224]

Lorber M. Exposure of Americans to polybrominated diphenyl ethers. J. Expo. Sci. Environ. Epidemiol. 2007; 18:2–19. [PubMed: 17426733]

Quirós-Alcalá L, Bradman A, Nishioka M, Harnly ME, Hubbard A, McKone TE, Eskenazi B. Concentrations and loadings of polybrominated diphenyl ethers in dust from low-income households in California. Environ. Int. 2011; 37:592–596. [PubMed: 21239062]

Roze E, Meijer L, Bakker A, Van Braeckel KN, Sauer PJ, Bos AF. Prenatal exposure to organohalogens, including brominated flame retardants, influences motor, cognitive, and behavioral performance at school age. Environ. Health Perspect. 2009; 117:1953. [PubMed: 20049217]

Shin HM, McKone TE, Tulve NS, Clifton MS, Bennett DH. Indoor residence times of semivolatile organic compounds: model estimation and field evaluation. Environ. Sci. Technol. 2013; 47:859–867. [PubMed: 23244175]

Stapleton HM, Dodder NG. Photodegradation of decabromodiphenyl ether in house dust by natural sunlight. Environ. Toxicol. Chem. 2008; 27:306–312. [PubMed: 18348638]

State of California. TECHNICAL BULLETIN 117: Requirements, Test Procedure, and Apparatus for Testing the Flame Retardance of Resilient Filling Materials Used in Upholstered Furniture. North Highlands, CA: Department of Consumer Affairs, Department of Consumer Affairs, Bureau of Home Furnishings and Thermal Insulation; 2000.

State of California. TECHNICAL BULLETIN 117-2013: Requirements, Test Procedure, and Apparatus for Testing the Flame Retardance of Resilient Filling Materials Used in Upholstered Furniture. Sacramento, CA: Department of Consumer Affairs, Department of Consumer Affairs, Bureau of Electronic & Appliance Repair, Home Furnishings and Thermal Insulation; 2013.

Takigami H, Suzuki G, Hirai Y, Sakai S-I. Brominated flame retardants and other polyhalogenated compounds in indoor air and dust from two houses in Japan. Chemosphere. 2009; 76:270–277. [PubMed: 19361833]

Thuresson K, Björklund JA, De Wit CA. Tri-decabrominated diphenyl ethers and hexabromocyclododecane in indoor air and dust from Stockholm microenvironments 1: levels and profiles. Sci. Total Environ. 2012; 414:713–721. [PubMed: 22137481]

Toms LM, Bartkow ME, Symons R, Paepke O, Mueller JF. Assessment of polybrominated diphenyl ethers (PBDEs) in samples collected from indoor environments in South East Queensland, Australia. Chemosphere. 2009; 76:173–178. [PubMed: 19394067]

USEPA. [accessed March 2006] Polybrominated diphenyl ethers (PBDEs) project plan office of prevention, pesticides, and toxic substances. http://wwwepagov/op-pts/pbde/

Vorkamp K, Thomsen M, Frederiksen M, Pedersen M, Knudsen LE. Polybrominated diphenyl ethers (PBDEs) in the indoor environment and associations with prenatal exposure. Environ. Int. 2011; 37:1–10. [PubMed: 20609475]

Watkins DJ, McClean MD, Fraser AJ, Weinberg J, Stapleton HM, Sjödin A, Webster TF. Impact of dust from multiple microenvironments and diet on pentaBDE body burden. Environ. Sci. Technol. 2012; 46:1192–1200. [PubMed: 22142368]

Webster TF, Harrad S, Millette JR, Holbrook RD, Davis JM, Stapleton HM, Allen JG, McClean MD, Ibarra C, Abdallah MA. Identifying transfer mechanisms and sources of decabromodiphenyl ether (BDE 209) in indoor environments using environmental forensic microscopy. Environ. Sci. Technol. 2009; 43:3067–3072. [PubMed: 19534115]

Wilford BH, Harner T, Zhu J, Shoeib M, Jones KC. Passive sampling survey of polybrominated diphenyl ether flame retardants in indoor and outdoor air in Ottawa, Canada: implications for sources and exposure. Environ. Sci. Technol. 2004; 38:5312–5318. [PubMed: 15543731]

Wu N, Herrmann T, Paepke O, Tickner J, Hale R, Harvey E, La Guardia M, McClean MD, Webster TF. Human exposure to PBDEs: associations of PBDE body burdens with food consumption and house dust concentrations. Environ. Sci. Technol. 2007; 41:1584–1589. [PubMed: 17396645]

Zhang X, Diamond ML, Robson M, Harrad S. Sources, emissions, and fate of polybrominated diphenyl ethers and polychlorinated biphenyls indoors in Toronto, Canada. Environ. Sci. Technol. 2011; 45:3268–3274. [PubMed: 21413794]

Zota AR, Rudel RA, Morello-Frosch RA, Brody JG. Elevated house dust and serum concentrations of PBDEs in California: unintended consequences of furniture flammability standards? Environ. Sci. Technol. 2008; 42:8158–8164. [PubMed: 19031918]

Practical Implications

The frequency of detection of pentaBDEs was high in dust and floor wipes, but low in air and window wipes. By comparing concentrations of each PBDE congener in different media and with blood serum levels and considering the burden of sample collection, we suggest that collecting floor wipes is a good method for measuring PBDEs in large epidemiology studies. PentaBDE levels measured in the same home 1 year apart were longitudinally consistent, but BDE209 was not longitudinally consistent, indicating that a single sample is representative of a longer exposure window for pentaBDE, but not BDE209 levels.

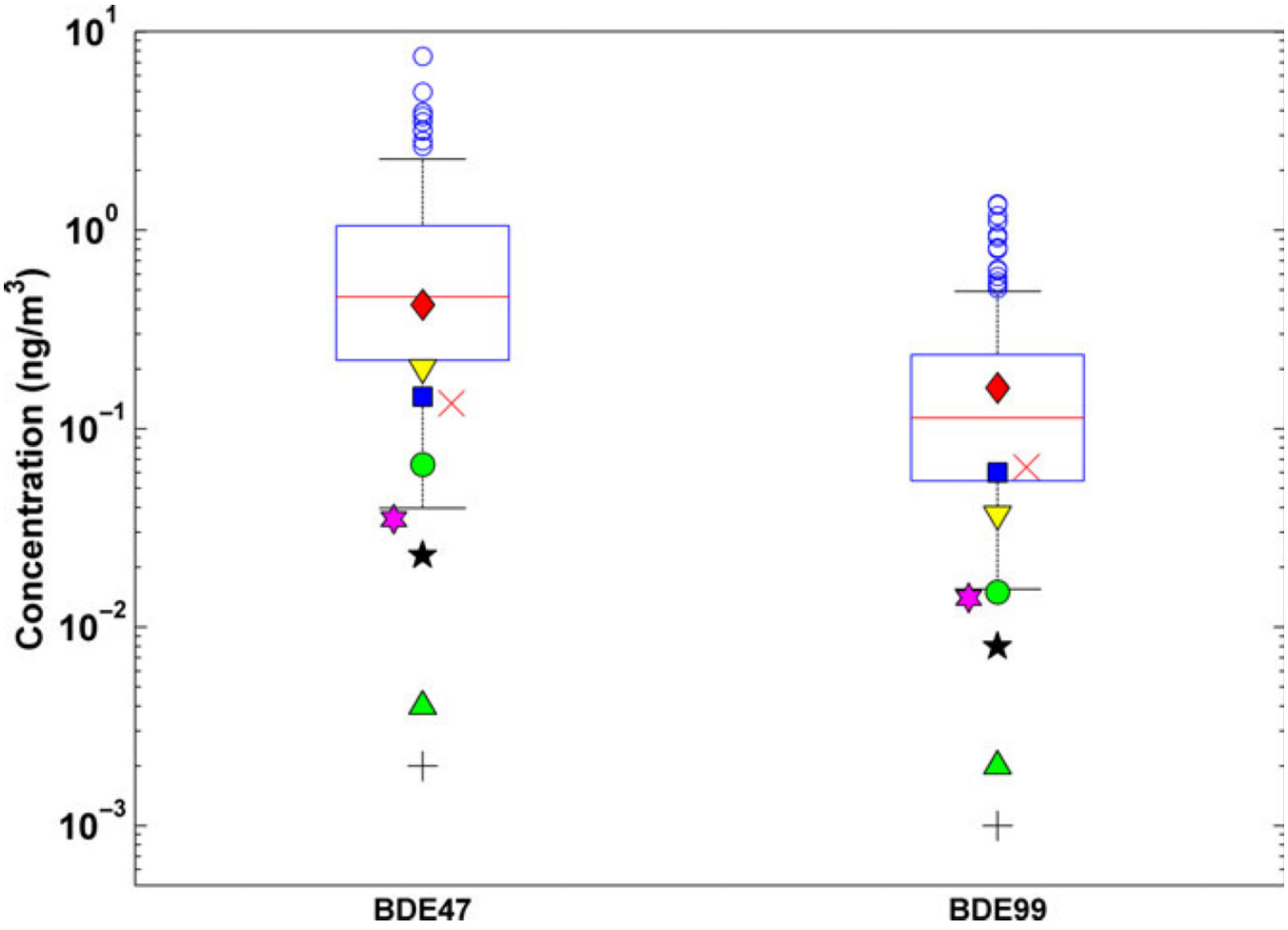

Fig. 1.

Air concentrations (ng/m^3) measured in our study and compared with BDE air concentrations from the literature. Diamond: Albany, New York, USA, active sampling, samples collected in 2007 (Johnson-Restrepo and Kannan, 2009) (median). Upside down triangle: Wisconsin, USA, passive sampling, samples collected in 2008 (Imm et al., 2009) [GM reported as ng/PUF, converted to ng/m^3 by dividing by (2.5 m^3/day *30 days)]. Multiplication sign: Denmark, active sampling, samples collected in 2007 (Vorkamp et al., 2011) (median). Square: Boston, MA USA, active sampling, samples collected in 2006 (Allen et al., 2007) (GM ng/m^3). Circle: Ottawa, Canada, passive sampling, samples collected in 2002–2003 (Wilford et al., 2004) (median). Six-pointed star: Queensland, Australia, passive sampling, samples collected in 2007–2008 (Toms et al., 2009) (median). Star: Stockholm, Sweden, active sampling, samples collected in 2006 (Thuresson et al., 2012) (median). Triangle: Kuwait, passive sampling, samples collected in 2004 (Gevao et al., 2006) (median). Plus sign: Hokkaido, Japan, active sampling, samples collected in 2006 (Takigami et al., 2009) (median)

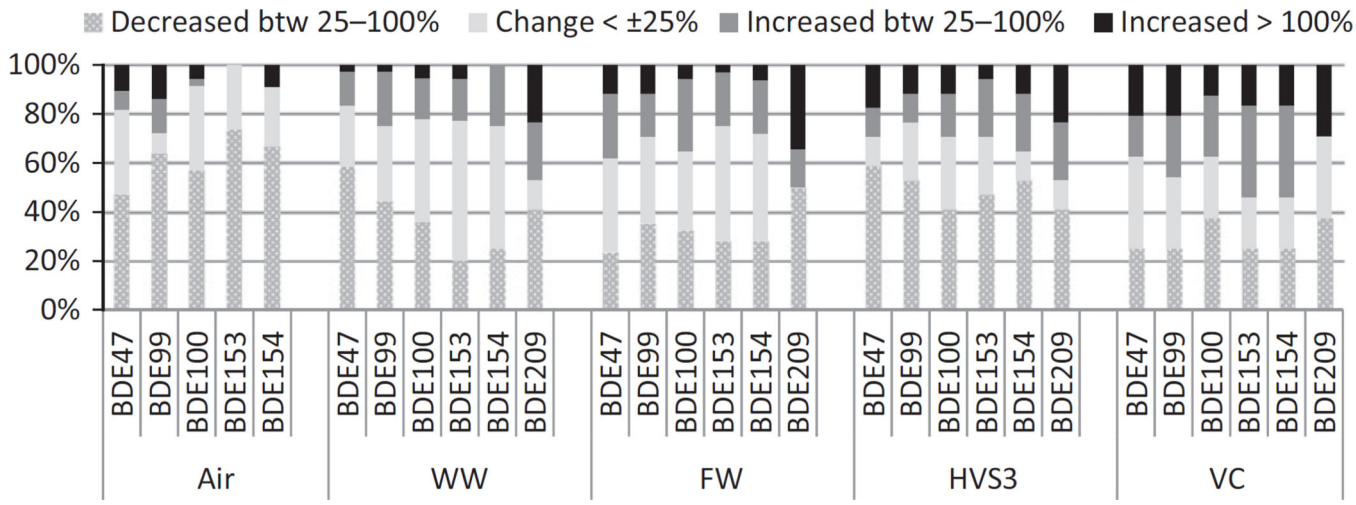

Fig. 2.

Concentration changes in various environmental media within a home collected approximately 1 year apart. (Air, air PUF; WW, window wipes; FW, floor wipes; HVS3, HVS3 dust; VC, vacuum cleaner dust)

Table 1

Summary statistics for all media[a]

				Households with young children				Households with older adults				
PBDE	***N* ND[b]**	***N* < ELOQ[c]**	**Nominal ELOQ[d]**	**GM**	**GSD**	**Med**	**p95**	**GM**	**GSD**	**Med**	**p95**	**Comp btw 2 groups Pr > |Z|[e]**
Air (ng/m^3)[f]				*N* = 88				*N* = 48				
BDE47	0	47	0.33	0.38	2.7	0.37	1.8	0.73	3.4	0.77	5.0	**<0.01**
BDE99	0	109	0.33	0.10	3.1	0.10	0.55	0.12	3.9	0.12	1.1	0.47
BDE100	6	126	0.33	0.02	5.3	0.04	0.18	0.02	8.1	0.04	0.26	0.84
BDE153	6	130	0.33	0.01	4.6	0.02	0.11	0.005	3.3	0	0.07	**<0.01**
BDE154	19	115	0.33	0.02	3.7	0.04	0.09	0.03	2.7	0.03	0.08	0.53
Window wipe (pg/cm^2)				*N* = 87				*N* = 48				
BDE47	1	42	1.0	2.0	3.2	1.70	18	2.1	3.0	1.94	19	0.83
BDE99	1	93	2.5	1.7	3.3	1.59	11	1.9	3.2	1.60	19	0.63
BDE100	2	107	1.0	0.44	3.3	0.47	2.7	0.47	2.8	0.48	3.3	0.79
BDE153	36	96	2.5	0.13	6.2	0.25	1.6	0.35	3.3	0.32	2.0	**0.01**
BDE154	4	120	1.0	0.22	4.0	0.24	1.5	0.30	3.1	0.25	1.8	0.44
BDE209	32	86	5.0	1.0	8.3	1.26	20	0.14	21	0.25	10	**<0.01**
Floor wipe (pg/cm^2)				*N* = 84				*N* = 39				
BDE47	0	1	0.67	5.6	2.8	5.7	39	4.2	2.8	4.7	39	0.16
BDE99	2	25	1.7	4.7	3.0	5.4	26	3.6	3.2	3.3	32	0.16
BDE100	0	38	0.7	1.1	3.1	1.2	6.2	0.81	3.1	0.7	8.1	**0.05**
BDE153	10	90	1.7	0.26	18	0.63	3.4	0.65	3.8	0.47	4.5	0.89
BDE154	5	80	0.67	0.49	3.3	0.54	2.6	0.39	2.8	0.32	3.1	0.15
BDE209	13	42	3.3	4.2	4.7	4.5	30	0.47	15	0.97	14	**<0.01**
HVS3 dust (ng/g)				*N* = 57				*N* = 26				
BDE47	0	1	59	870	3.7	740	12000	630	4.6	440	6100	0.44
BDE99	0	0	96	1200	3.9	960	19000	780	4.6	550	6100	0.35
BDE100	0	19	20	190	3.8	170	4500	120	5.4	99	880	0.40
BDE153	0	4	19	130	3.7	120	3600	73	5.7	55	590	0.20
BDE154	1	3	17	110	3.9	97	2800	67	6.0	76	440	0.45

				Households with young children				Households with older adults				
PBDE	***N* ND[b]**	***N* < ELOQ[c]**	**Nominal ELOQ[d]**	**GM**	**GSD**	**Med**	**p95**	**GM**	**GSD**	**Med**	**p95**	**Comp btw 2 groups Pr > |Z|[e]**
BDE209	0	25	78	2000	2.6	1900	13000	740	4.0	780	3100	**<0.01**
Vacuum cleaner dust (ng/g)				*N* = 66				*N* = 39				
BDE47	0	1	59	980	3.7	1300	4900	900	3.4	840	7700	0.55
BDE99	0	1	96	1300	3.8	1400	5500	1100	3.9	960	11000	0.41
BDE100	0	19	20	240	3.3	280	1100	200	3.7	190	2100	0.30
BDE153	0	0	19	140	3.1	150	720	130	3.6	120	1400	0.45
BDE154	0	2	17	130	3.5	160	830	93	4.0	79	1200	0.15
BDE209	0	44	78	2300	2.5	2400	10000	1400	4.0	1100	19000	**<0.01**

[a] Samples included in baseline dataset are mostly Year 1 samples. Some Year 2 samples were used if no Year 1 data was available. GM, geometric mean; GSD, geometric standard deviation; med, median, p95, 95th percentile.

[b] *N* ND is Number of sample with non-detectable BDE level. The total sample size is the sum of the Ns for households with young children and households with older adults, reported to the right.

[c] *N* < ELOQ is the number of samples that had a reported value that was less than the ELOQ.

[d] The nominal ELOQ values were based on the nominal value of air collected (2.5 m^3/day for 30 days) and the nominal surface area of the wipe (1 m^2 for window wipe and 1.5 m^2 for floor wipe). The air concentrations were corrected by field blank, and thus are not directly comparable to nominal ELOQ.

[e] Comparison between two groups was tested using Wilcoxon-Mann–Whitney test.

[f] BDE209 concentrations are not available in the air samples.

Values below 0.05 are in bold.

Table 2

Spearman correlations between media

PBDEs	Air vs. WW (*N* = 132)	Air vs. FW (*N* = 120)	Air vs. HVS3 (*N* = 83)	Air vs. VC (*N* = 104)	WW vs. FW (*N* = 119)	WW vs. HVS3 (*N* = 83)	WW vs. VC (*N* = 104)	FW vs. HVS3 (*N* = 73)	FW vs. VC (*N* = 96)	HVS3 vs. VC (*N* = 67)
BDE47	**0.53*****	0.47***	**0.57*****	**0.56*****	0.47***	0.37***	0.29**	0.41***	0.42***	**0.66*****
BDE99	**0.51*****	0.45***	**0.60*****	**0.55*****	0.44***	0.40***	0.31**	0.40***	0.41***	**0.63*****
BDE100	0.16^{+}	0.31**	0.44***	0.41***	0.41***	0.31**	0.13	0.43***	0.44***	**0.63*****
BDE153	0.04	0.15*	0.36***	0.25**	**0.51*****	0.21^{+}	0.07	0.39***	0.32**	**0.56*****
BDE154	0.06	0.24***	0.28**	0.33***	**0.52*****	0.33**	0.11	**0.53*****	0.37***	**0.61*****
BDE209	–	–	–	–	0.41***	0.42***	0.36***	0.35**	0.28**	**0.64*****

Air, air PUF; WW, window wipes; FW, floor wipes; HVS3, HVS3 dust; VC, vacuum cleaner dust.

*** $P < 0.001$;

** $P < 0.01$;

* $P < 0.05$;

$^{+}$ $P < 0.1$.

Values above 0.50 are in bold.

Table 3

Spearman correlation coefficients between serum and environmental concentrations

	Serum vs. air	Serum vs. window wipe	Serum vs. floor wipe	Serum vs. HVS3 dust	Serum vs. vacuum cleaner dust
Children					
N	38	37	38	38	28
BDE47	0.52**	0.50**	0.57**	0.62**	0.37
BDE99	0.62**	0.54**	0.63**	0.65**	0.43*
BDE100	0.17	0.40*	0.63**	0.47**	0.43*
BDE153	0.20	0.10	0.33*	0.20	0.29
Parents of young children					
N	50	49	47	50	37
BDE47	0.51**	0.40**	0.43**	0.35*	0.27
BDE99	0.50**	0.37**	0.42**	0.40**	0.37*
BDE100	0.35*	0.44**	0.42**	0.29*	0.34*
BDE153	0.18	0.29*	0.29*	0.06	0.21
Older adults					
N	33	33	25	33	28
BDE47	0.49**	0.33	0.33	0.52**	0.35
BDE99	0.53**	0.42*	0.34	0.48**	0.32
BDE100	0.27	0.30	0.34	0.37*	0.14
BDE153	0.07	0.04	−0.16	0.19	0.18

*$P < 0.05$;

**$P < 0.01$.

Table 4

Year-to-year correlations

PBDEs	Air (*N* = 38)	WW (*N* = 36)	FW (*N* = 34)	HVS3 (*N* = 17)	VC (*N* = 24)
BDE47	0.64***	0.69***	**0.83*****	**0.89*****	0.70***
BDE99	0.56***	0.71***	0.74***	**0.90*****	0.60**
BDE100	0.09	0.71***	0.60***	**0.87*****	0.45*
BDE153	−0.04	**0.85*****	0.78***	**0.88*****	0.58**
BDE154	0.11	**0.82*****	**0.81*****	**0.85*****	0.57**
BDE209	–	0.38*	0.40*	0.45	0.34

Air, air PUF; WW, window wipes; FW, floor wipes; HVS3, HVS3 dust; VC, vacuum cleaner dust.

*** $P < 0.001$;

** $P < 0.01$;

* $P < 0.05$.

Values above 0.80 are in bold.