Concentration of Polybrominated Diphenyl Ethers (PBDEs) in Household Dust from Various Countries – Is Dust a Major Source of Human Exposure?

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Introduction

Polybrominated diphenyl ethers (PBDEs) have been used extensively in consumer products for improving fire resistance (1,2). Commercial PBDE preparations are commonly categorized according to the average bromine content as pentaBDE, octaBDE, and decaBDE. The pentaBDE preparation is primarily used in polyurethane for applications such as carpet padding and furniture upholstery (1), and octaBDE and decaBDE preparations are used, for example in hard plastics that house electrical appliances such as TV sets and computers (1). Use of PBDEs has improved fire safety in modern indoor environments where potentially flammable polymeric materials are found. However, in recent years the bioaccumulation of PBDEs has been given serious consideration because of increasing levels in Swedish human milk (3), in North American blood donors (4), and in wildlife species in North America (5) and Europe (6).

That levels of PBDEs are much higher in North America than in Europe has been clear for some time as illustrated by the finding of approximately 2 ng BDE-47 per gram lipid in human milk from Sweden (3) and much higher concentrations (2.9-270 ng/g lipid) reported in the United States (7). The higher U.S. concentration probably reflects a much higher usage of the pentaBDE preparation in North America than in Europe (8). According to an industry report published in 2000, 98% of the 8,500 metric tones of pentaBDE produced were used in North America (8). However, the route by which people in North America are exposed to these kinds of chemicals is not known. Exposure to traditional persistent organic pollutants such as polychlorinated biphenyls (PCBs) is primarily through the diet (9). The association between body burdens of organohalogen compounds and consumption of fish has been studied previously (9,10). Also, an association between fish consumption and body burdens of 2,2',4,4'-tetraBDE has been found in Swedish fishermen (9). However, the prevalence and high levels of PBDEs present in the pentaBDE technical product in North America indicate that exposure routes may be different here given the relatively low concentration of PBDEs found in a North American food basket survey (11). In this survey, the highest levels were found in fish (salmon, catfish, and rainbow trout), at a concentration range of 0.3 – 2.1 ng/g fresh weight. This level is comparable to or lower than the levels found in wild salmon (1 – 6 ng/g fresh weight) from Sweden (12). Swedish fishermen in the high consumption group were known to consume fish very frequently (12-32 times per month) (9). Hence, in North America an exposure route other than the diet must be of greater quantitative importance. This is further shown by the median serum level of BDE-47 in the United States being reported at 18 ng/g lipid vs. 2.2 ng/g lipid for the group eating the most Baltic wild salmon in Sweden (7,9). Other exposure routes of importance could include inhalation and ingestion of indoor dust as indicated by a recent computer model (13). These assumptions are further supported by the absence of a substantial association between PBDE body burdens and the consumption of sport-caught fish from the Great Lakes (14).

A corollary from this is that indoor exposure to PBDEs could be of quantitative importance in the overall exposure to PBDEs in North America. This study reports the concentration of PBDEs in indoor dust in four different countries, including the United States. The levels in dust from the investigated countries are further contrasted to literature data on human body burdens in each country.

Experimental Section
Sample Collection. Forty dust samples from Australia (Brisbane, Queensland n=10), Germany (Hamburg n=4, Harburg n=1, Konstanz n=2, Muenster n=1, Berlin n=1, and Freiburg n=1), Great Britain (Newcastle upon Tyne n=10), and the United States (Atlanta, GA n=10) were collected from disposable vacuum cleaner bags from private households.

All samples were shipped in unopened vacuum-cleaner bags from the respective countries to the Centers for Disease Control and Prevention (CDC) in Atlanta, GA, USA. Each bag was then opened and the content was transferred to a household sieve (~2 mm filter size). Most bags contained in excess of 1kg of material. The samples were then sifted by shaking the filtrate onto aluminum foil. After a sufficiently large sample of particulate matter had been collected on the foil, each sample was transferred to a Ziploc® bag and stored at room temperature until analysis. After each sample, the sieve was cleaned and the aluminum foil was replaced. The collected material contained fine particulate matter and to a variable extent sandy material. No attempts were made to collect a field blank during sample collection since contamination from the vacuum cleaner and subsequent sifting of the dust were deemed to be negligible due to the inherent high concentration of PBDEs in residential dust.

During the subsequent analytic procedure when handling diluted sample extracts, method blanks were introduced to control for any contamination from the lab environment.

Method of Analysis. Pressurized liquid extraction (PLE) was chosen as the sample extraction method for dust samples. We also decided to fortify aliquots of the extracted samples with internal standards after extraction and after verifying complete extraction, as described below. This was done to reduce the quantity of labeled internal standards required for the analyses and thus decrease the cost of the study.

Each PLE cell (11 mL) (Dionex Corp.; Sunnyvale, CA) was filled with diatomaceous earth (inert material to reduce void volume of cell). The extraction cell was pre-extracted using an ASE200 (Dionex Corp.) to eliminate any contaminants in the cell. Pre-cleaning of the empty cell and final extraction were performed with the same instrumental settings: oven temperature at 100 °C, 1500 psi cell pressure, static time of 5 min, 30% purge volume, 60 seconds nitrogen purge, and three repeated extraction cycles using n-hexane as the extraction solvent. The collected particulate matter (200-800 mg) was weighed directly into the pre-cleaned cell using an analytic balance AX105 Delta Range (Mettler Toledo; Columbus, OH). Four blank samples were included in each run of 20 samples to track any potential laboratory background during sample preparation. Then samples were extracted on the automated PLE instrument in two batches of 20 samples and 4 blanks each. The hexane extract was collected in 60 mL collection vials (Dionex Corp.). Three samples from the United States and three samples from Germany were extracted a second time to verify complete extraction of the samples. The collection vials were weighed before and after the extraction to calculate the amount of solvent collected (25-30 mL). Sulfuric acid (5 mL) was added to the collection vial, and the samples were gently inverted for 5 minutes. After centrifugation, aliquots (100μl) were added to GC-vials and fortified with ^{13}C-labeled internal standards (750 pg/congener), nonane (10μl), and dodecane (2μl). The samples were evaporated using a Rapid Vap® (Labconco Corp., Kansas City, MO), with vortex action and reduced pressure to aid the evaporation. Once evaporated to a final volume of 10μl, the samples were analyzed by gas chromatography/isotope dilution high-resolution mass spectrometry (GC/IDHRMS). IDHRMS analysis was performed on a MAT95XP (ThermoFinnigan MAT, Bremen, Germany) instrument. The chromatographic separations were carried out on a 6890N gas chromatograph (GC) (Agilent Technologies; Atlanta, GA) fitted with a DB5-HT [(15 m, 0.25 mm I.D., and 0.10 μm film thickness), Agilent Technologies] capillary GC column. Split-less injection was carried out with an injector temperature of 280°C, the oven was programmed from 140°C (1 min) to 320°C (0 min) with a ramp rate of 10°C/min. The source temperature was 280°C and operated in the electron-impact mode using a filament bias of 40eV.

Results

Seven PBDE congeners were measured in the particulate fraction (<2mm) of household dust samples (n=40) (Figure 1). Dust samples from Germany contained the lowest concentrations of total PBDEs with a median level of 74 ng/g dust and a range of 17 – 550 ng/g dust. Australian dust contained the second lowest concentration with a median level of 1,200 ng/g dust and a range of 500-13,000 ng/g of dust. The dust from the United States (median concentration: 4,200 ng/g dust [range 520-29,000 ng/g]) and Great Britain (median: 10,000 ng/g dust [range 950-54,000 ng/g]) contained the highest measured amounts of total PBDEs. The concentrations observed in German dust were significantly lower than those observed in the dust of other countries investigated, with the exception of BDE-100, BDE-153, and BDE-154 in the UK, which were not significantly different from the German levels (U-test). The congener pattern observed in the dust samples was similar to that found in technical pentaBDE; i.e., BDE-99 was similar in concentration to that of BDE-47 (Figure 1).

In the six samples that were extracted twice, PBDEs in the second extract were found at levels below the quantification limit, defined as 3 times the standard deviation of blank samples, or at levels below the instrumental quantification limit.

Discussion

Seven tetra- through deca-brominated diphenyl ethers were measured in household dust samples obtained from four countries (n=10/country): Australia, Germany, Great Britain, and the United States. Completeness of the PLE of the dust was verified by extracting selected samples twice. No detectable levels of PBDEs were observed in the second extracts; hence, the extractions were considered to be complete after one extraction.
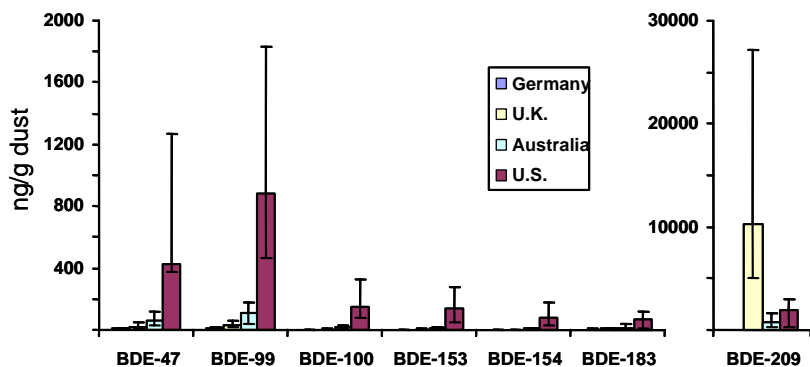
Figure 1. Median concentration (ng/g dust) of polybrominated diphenyl ethers (PBDEs) in dust samples from 4 countries (n=10/country) with quartile ranges indicated.

BDE-209 was found to be the dominating PBDE congener recovered in the dust samples (Figure 1). The median concentrations of BDE-209 are: in Australia (730 ng/g dust [61% of total PBDE]), Germany (63 ng/g dust [85% of total PBDE]), Great Britain (10,000 ng/g dust [100% of total PBDE]) and the United States (2,000 ng/g dust [48% of total PBDE]). The much higher concentration of BDE-209 in Great Britain (median 10,000 ng/g dust) as compared to other countries (Figure 1) and especially the other European country included in the current study is surprising, i.e., compared to Germany (median 63 ng/g dust). Although, the reason for the higher concentration in Great Britain is most likely a much higher use of this flame retardant in this country. It has been reported that 95% of all upholstery materials in Great Britain are flame retarded to comply with fire safety regulations and that approximately 1,000-1,200 tones/year of BDE-209 is used in textile applications in Great Britain (15). It has further been reported that Great Britain is the only country within the European Union that have regulation specifying the level of flame retardancy for domestic upholstery (15). The finding of relatively high levels of BDE-209 compared with other PBDEs in the dust shows that this product is an important indoor contaminant that must be considered in human exposure assessments. However, BDE-209 has a short half-life in the human body making this compound unlikely to accumulate to very high concentrations in humans. (16,17). Nevertheless, potential de-bromination products of BDE-209 with longer half-lives may be formed as has been indicated in carp (18); this possibility should be studied and considered in the total risk assessment of BDE-209.

Compounds with longer half-lives, such as the tetra- though hexa-BDEs (16), may be of greater concern from a toxicologic point of view despite the fact that overall these compounds are found at lower levels in the dust. The fact that these compounds are more likely to accumulate to higher concentrations in humans over time because of their longer half-lives, has been observed in numerous studies measuring human body burdens of PBDEs in the United States (4,7,19,20). In fact, the higher concentrations of the tetra- through hexa-BDEs observed in U.S. dust is consistent with higher concentrations of these compounds observed in the U.S. general population compared with Europe, as shown in human serum (4,9,21) and milk (3,7,19). Australian dust also contained higher levels of lower-brominated PBDEs than did European dust but still much lower than the U.S. samples (Figure 1).

Dietary intake is commonly accepted to be the main exposure route for many lipophilic and persistent organohalogen compounds, such as PCBs and persistent pesticides (9). However, in the case of PBDEs, evidence suggests that food is not the only major pathway and that indoor exposure through inhalation and skin contact may be important. Available data on dust ingestion rates are limited and are subject to uncertainties. However, according to an Environmental Protection Agency document (22), the magnitude of exposure is highly dependant on daily activities. For example, the daily intake for an adult has been estimated to range from 0.56 mg/day up to 110 mg/day for work in attics (23). For children of age 2.5 years, the intake of indoor dust has been estimated to be in the range of 50-100 mg/day/person, and for older children (6 years), the intake of indoor dust has been estimated to be 3 mg/day/person (23). These dust-intake rates may be used to estimate the extent of exposure to PBDEs originating from the indoor environment.
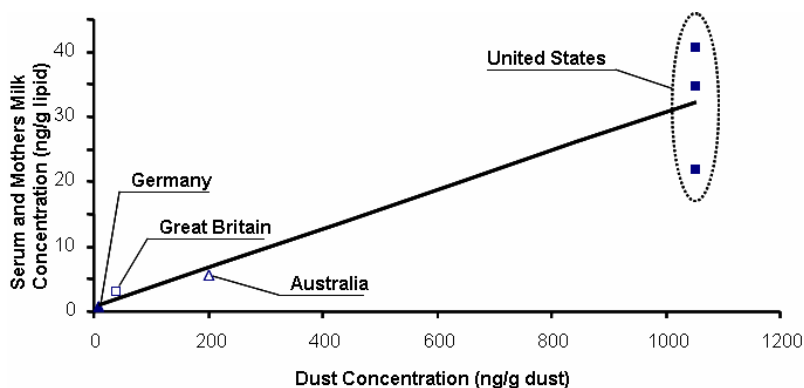

Figure 2. Correlation of the median dust levels of 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) for the investigated countries as measured in this study and published literature data on BDE-47 in human matrixes (serum and breast milk) for the four countries included in the study. Human BDE-47 levels are given in the references (7,28-31).

The calculated daily intake rates of the sum of PBDEs are <1-45 ng/day/person for an adult living in Germany and <1-2,300 ng/day/person for adults in the United States . These levels can be contrasted with the estimates of the sum of PBDE intake for a 2.5-year-old child, which are 6-2,100 ng/day/person for the U.S. child and <1-41 ng/day/person for the German child. These daily intake rates originating from dust may be compared with estimates of the daily dietary intake as reported by Ryan et al. (24) and Bocio et al. (25) to be in the range of 50-100 ng/day. Thus, intake through the indoor environment may contribute substantially to the overall exposure to PBDEs although the absolute magnitude of the exposure is highly dependent on the specific activities of the individual. The high estimate of dust exposure of 110 mg/day for the adult assumes dusty work such as cleaning an attic. Hence, certain subgroups within the general population may be hypothesized to be at increased risk of PBDE exposure. These groups may include persons who clean and dust at some facilities. The magnitude of such exposures should be studied in the future.

The importance of dust as an exposure route of PBDEs for humans has been illustrated at an electronics recycling plant in Sweden (21,26). At this facility, higher concentrations of all measured PBDE congeners were observed in the group of workers recycling electronics compared with a control group. In addition, the largest difference was observed for the highly brominated PBDE congeners, for example the hepta- to deca-BDEs that are known to be found in the materials processed at this recycling plant. This study, conducted in Europe, concluded that PBDE exposure through food was most likely the dominat exposure route for congeners of low bromination degree (penta- to hexa-BDEs) present in commercial penta-BDE preparations. Occupational exposure was the dominat pathway for the hepta- through deca-BDE congeners (21). People working in the field of computer repair and maintenance have also been shown to have increased exposures to the hepta- through deca-BDEs (27). Future studies are needed to assess whether the observed higher concentrations of the tetra- through hexa-BDEs in the North American population compared with Europe are due to exposure to dust in North America that has much higher levels of these compounds than does dust in Europe. Interestingly, the dust levels observed in this study correlate well with human body burdens measured in serum and breast milk from the investigated countries (7,14,28-31) (Figure 2). This correlation may indicate that dust is important in the overall exposure to PBDEs or, alternatively, that dust is an indicator of another exposure pathway. Further studies are needed to elucidate the exact mechanism of exposure to PBDEs.

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