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Particle size distribution of brominated flame retardants in house dust from Japan

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This article is dedicated to the memory of my respected supervisor, Dr. Hidetaka Takigami, who sadly passed away after completion of this study. I would like to express my sincere gratitude for all of his support in the past.

Keywords:
Brominated flame retardant
PBDEs
HBCDs
House dust
Particle size

ABSTRACT

The present study was conducted to examine the concentrations, profiles, and mass distributions of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), and polybrominated dibenzo-*p*-dioxins/furans (PBDD/Fs) based on the particle sizes of house dust samples from five homes in Japan. After removal of impurities from house dust from vacuum cleaner bags, selected indoor dust samples were size fractionated (>2 mm, 1–2 mm, 0.5–1 mm, 250–500 μm, 106–250 μm, 53–106 μm, and <53 μm). Fluffy dust was collected separately for particle size analysis. PBDEs, HBCDs, and PBDFs were detected in all the samples analyzed. In general, PBDE levels of particulate and fluffy dust were comparable and the highest concentrations were found in 106–250 μm or 53–106 μm fractions. HBCD concentrations in fluffy dust were higher than those in particulate dust, and their levels were the highest in 106–250 μm and 250–500 μm factions, respectively. The highest concentrations of all three compound groups were not found in particles <53 μm in size, suggesting that the distribution of brominated flame retardants does not depend solely on the surface area-to-volume ratios of dust particles. The concentrations of PBDEs and PBDD/Fs depended principally on the concentrations in particles <53 μm in size because the predominant mass of particulate dust were found in this fraction. The mesh size used for sample preparation will thus have little effect on the concentrations as long as particles <53 μm are included. In contrast, HBCD concentrations increased by as much as 80% when particles >250 μm in size and fluffy dust were included. The conclusion is that particulate dust <250 μm in size without fluffy dust should be used to analyze dust for brominated flame retardants.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) are among the brominated flame retardants (BFRs) that are widely used as synthetic additives to reduce the flammability of plastics, textile coatings, and electronic appliances. However, despite the benefits of BFRs, their use problematic because of their persistence, tendency to bioaccumulate, and possible adverse effects on wildlife and humans, even in remote areas. The use of PBDEs and HBCDs has been phased out because of international regulations such as the Restriction of Hazardous Substances (RoHS) Directive (Directive 2002/95/EC) of the European Commission [1] and the Stockholm Convention on Persistent Organic Pollutants (POPs) [2]. However, even though the use of the BFRs of concern has been phased out, special attention should be paid to the potential for their emission from treated products to indoor and outdoor environments, which will continue for a long time. Another environmental and health concern is that PBDEs have the potential to form polybrominated dibenzo-*p*-dioxins and furans (PBDD/Fs) in combustion processes and under thermal stress during extrusion, molding, or shredding [3] as well as via photolysis in various matrices such as solvents, sediment, soil, house dust, and treated-articles [4–8]. The toxicity of these resultant compounds is estimated to be similar to that of

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chlorinated dioxins [9]. In addition, PBDD/Fs have been found as impurities in commercial PBDE mixtures [10]. Recently, PBDD/Fs were identified for possible future inclusion in the list of toxic equivalency factors (TEFs) and for consideration in the toxic equivalency (TEQ) concept proposed by World Health Organization [11].

Humans are exposed to various chemicals, including BFRs, in daily life through multiple media, including food, water, and air. House dust is also a significant source of exposure to BFRs for humans, and especially for young children, who frequently touch their hands to their mouths. House dust is a complex heterogeneous mixture of biologically derived, particle-bound matter; indoor aerosols; and soil particles with a composition strongly dependent on seasonal, environmental, and personal factors [12,13]. It has been reported that BFR concentrations in human blood and breast milk are significantly correlated with those in indoor dust [14], the suggestion being that indoor dust reflects the lifestyles and activities of the people who reside there. Dust has therefore been used as an indicator of indoor contamination over the past decade [15]. However, it is usually not easy to obtain a representative dust sample from a home for chemical analysis because the composition of house dust is inhomogeneous throughout a home as well as between homes [16]. The concentrations of contaminants in dust are influenced by many factors, including sampling season [17], building structure, the room in the home, furnishing materials, heating and ventilation, how well and how often the area is cleaned, and the experimental design of the sampling. Since there is no universally accepted standard method for the collection and pretreatment of dust samples, many studies of indoor environmental contaminants have employed their own unique sampling strategies which sometime lead to difficulties in the interpretation of contaminant levels. The result of a dust analysis might depend strongly on the particle size distribution used for the chemical analysis [16–21], however, research in this area is limited and more research is needed to generalize the fact. Moreover, whether it is appropriate to include fluffy dust (lint) in the sample to be analyzed is always problematic for the chemical analyst.

At the moment there are three hypothesized pathways of BFR transfer from products to dust: (1) volatilization of BFRs from the treated product, with subsequent partitioning to dust; (2) transfer via direct contact between the treated product and dust [22,23]; and (3) abrasion via physical wear and tear of the treated product, resulting in the transfer of particles or fibers of the treated product directly to dust [24,25]. Pathways 1 and 2 are thought to depend basically on the surface area of the dust. Because chemical contaminants are usually adsorbed onto the surface of particles, finer particles with larger surface area-to-volume ratios have more capacity to retain chemical contaminants, the result being higher contaminant concentrations in finer particles [26,27]. So far, no studies have focused on which pathways account for most of the transfer of BFRs from products to indoor dust.

Based on this background, the aims of this study were to (1) elucidate the particle size dependence of the levels of BFRs and related substances in Japanese house dust; (2) obtain clues as to the characteristics of the sources of BFRs in the dust; and (3) propose a range of particle sizes best suited for BFR chemical analysis. To the authors' knowledge, this study is the first to include an analysis of the particle size distribution of PBDD/Fs in dust, and the first to compare the distribution of BFRs in particulate and fluffy dust separately.

2. Material and methods

2.1. Samples

House dust samples were collected in 2009 from vacuum cleaner bags of vacuum cleaners that were routinely used at five homes in the Kanto region of Japan (designated HD-01, -02, -03, -04, and −05). After manual removal of debris, hair, and small pebbles with tweezers from the dust of individual bags, the dust was sequentially sieved into seven fractions based on particle sizes (>2 mm, 1–2 mm, 0.5–1.0 mm, 250–500 μm, 106–250 μm, 53–106 μm, and <53 μm) with a vibratory sieve shaker (Model PRO, FRITSCH, Yokohama, Japan). To enhance the sieving efficiency, 10 zirconium oxide grinding balls (10 mm in diameter) were placed on the top sieve, which had the largest mesh size (2 mm). Sieving was continued until the weight of dust on the top sieve stopped decreasing and became constant. Fluffy dust was also separately allocated to each of the particle fractions (Fig. 1). It may be inappropriate to classify fluffy dust on the basis of 'particle' size, because fluffy dust is fibrous. To the extent possible, however, particulate and fluffy dust were included in each size fraction, and the size fractions were separated for purposes of chemical analysis. Prior to extraction, samples were weighed and then stored in a cold, dark place.

2.2. Chemical analysis

PBDEs, HBCDs, and PBDD/Fs in the size-fractionated dust samples were extracted by using a rapid solvent extractor (SE-100, Mitsubishi Chemical Analytech Co., Ltd., Japan). First, approximately 0.5 g–2 g of each sample was mixed with 10 g of anhydrous sodium sulfate (for PCB analysis, Kanto Chemical Co., Inc., Japan). The mixture was transferred to an extraction column, and the column was then filled with acetone/hexane (1:1). For the next 40 min the solvent was gradually replaced with toluene at a flow rate of 2 mL min^{-1}. The temperature of the extraction column was then increased to 80 °C and held for 10 min. The extraction with toluene continued for another 30 min at a flow rate of 2 mL min^{-1}. After the addition of $^{13}C_{12}$-labeled PBDE (MBDE-MXE, Wellington Laboratories, Inc., Canada), PBDD/Fs, and HBCD mixtures (MaHBCD, MbHBCD, and MgHBCD, Wellington Laboratories) as internal standards, a portion of the crude extract was quantitatively transferred onto a multilayer column that consisted of Wakogel DX (Wako Pure Chemical Industries, Ltd., Japan), 22% sulfuric acid–impregnated silica gel (6 g, Wako Pure Chemical Industries, Ltd.), 44% sulfuric acid–impregnated silica gel (4.5 g, Wako Pure Chemical Industries, Ltd.), and 2% potassium hydroxide–impregnated silica gel (3 g, Wako Pure Chemical Industries, Ltd.) that had been pre-washed and conditioned with 50 mL of 5% dichloromethane/hexane. PBDE and PBDD/F homologs were eluted in the first fraction with 70 mL of 5% dichloromethane/hexane; HBCD diastereomers were eluted in the second fraction with 60 mL of 50% dichloromethane/hexane. The PBDE and PBDD/F fraction was evaporated and loaded onto a sulfoxide silica gel column (3 g, Supelclean Sulfoxide, Sigma-Aldrich Co., LLC) for further clean up. The first fraction of sulfoxide silica gel clean-up was eluted with 9 mL of hexane and discarded. The second fraction of sulfoxide silica gel clean-up was eluted with 50 mL of 10% acetone/hexane and was collected. This fraction was evaporated to incipient dryness and further loaded onto an active carbon-dispersed silica gel reversible column (Kanto Chemical Co., Inc., Japan), where it remained for 30 min. After PBDE homologs were eluted with 80 mL of 25% dichloromethane/hexane, the column was turned upside down, and then PBDD/F homologs were eluted with 60 mL of toluene. After evaporation to incipient dryness, each fraction for

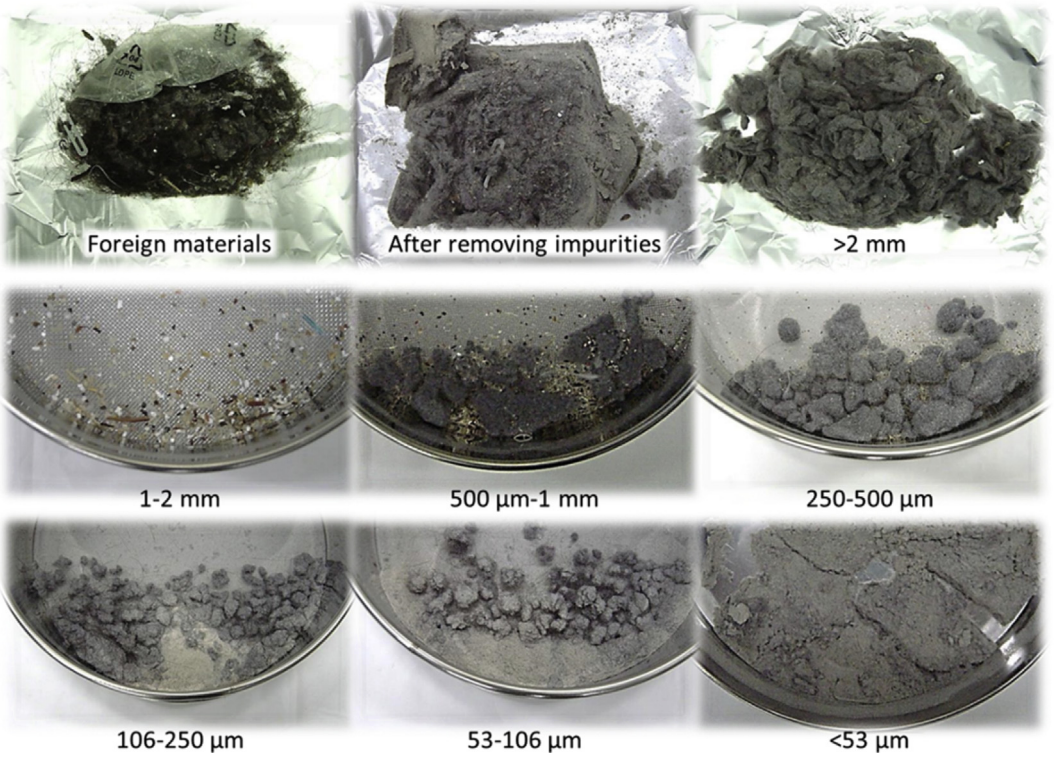

Fig. 1. Appearance of dust in each fraction after sequential sieving.

PBDE and PBDD/F analysis was re-dissolved in decane; the HBCD fraction was re-dissolved in methanol.

PBDE and PBDD/F homologs were analyzed by high-resolution gas chromatography (Agilent 6890N, CA, USA) coupled with high-resolution mass spectrometry (AutoSpec Premier, Waters, USA) in the selected ion-monitoring (SIM) mode after addition of $^{13}C_{12}$-labeled BDE 138 or 1,2,3,7,8-penta-BDF as a recovery standard. Twenty-five congeners of PBDEs (BDE 7, 15, 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 183, 184, 191, 196, 197, 206, 207, and 209), five congeners of PBDDs (2,3,7-tri-BDD, 2,3,7,8-tetra-BDD, 1,2,3,7,8-penta-BDD, 1,2,3,4,7,8-hexa-BDD, and octa-BDD), and seven congeners of PBDFs (2,8-di-BDF, 2,4,8-tri-BDF, 2,3,7,8-tetra-BDF, 2,3,4,7,8-penta-BDF, 1,2,3,4,7,8-hexa-BDF, 1,2,3,4,6,7,8-hepta-BDF, and octa-BDF) were identified and quantified by the isotope dilution method using the corresponding ^{13}C-labeled congeners. Recoveries of ^{13}C-labeled congeners added as recovery surrogates prior to sample cleanup were in the range 60–120%. Unknown peaks that matched the isotopic ratios of the primary and secondary ions of these compounds in authentic standards were quantified by using the response factor for the same homolog group. Total concentrations of each homolog group of PBDEs and PBDD/Fs were determined on the basis of the total area of all standard-assigned and potential peaks of the same homolog groups.

Identification and quantification of HBCD diastereomers were carried out by using an Alliance 2695 liquid chromatograph equipped with a Quattro Ultima triple quadrupole mass spectrometer (Waters, Tokyo, Japan) after the addition of d_8-α-, β-, and γ-labeled HBCDs as recovery standards. Separation of α-, β-, γ-, δ-, and ε-HBCDs was achieved by using a 100 mm × 2.1 mm i.d., 2.7 μm Ascentis Express C_{18} column (Sigma-Aldrich Co., LLC.) at a column temperature of 40 °C. The quantities of the five HBCD diastereoisomers were determined by electrospray ionization mass spectrometry in negative ion mode by using a multiple reaction monitoring mode based on m/z 640.6→ m/z 79, m/z 652.6→ m/z 79, and m/z 657.6→ m/z 79 for the native, $^{13}C_{12}$-, and d_8-labeled diastereomers, respectively.

All glassware was ultrasonically cleaned, heated to 400 °C overnight, and sequentially rinsed with acetone, toluene, and hexane just before use. The extracts were at all times shielded from UV light and from the deposition of dust or other particles in the laboratory air. The samples were quantified with calibration standard solutions at a series of five different concentrations, which were analyzed every 20 to 25 samples. Procedural blanks were run in parallel with every batch of five samples to check for interference or contamination from solvents and glassware. BFRs in certified dust sample (SRM 2585, NIST, Gaithersburg, MD) were analyzed in triplicate and the results indicated both good repeatability (relative standard deviation for individual congeners, between 0.68 and 16%) and accuracy (mean SRM value/certified SRM value, between 76 and 155%) through good agreement with the certified values.

Table 1
Weight distribution according to the particle size of house dust.

	Particulate dust (wt%)				Fluffy dust (wt%)			
	Median	Average	Min	Max	Median	Average	Min	Max
>2 mm	nd	0.95	nd	4.7	73	69	47	86
1–2 mm	5.7	7.9	3.0	18	0.25	0.66	nd	2.4
0.5–1 mm	6.4	6.7	2.3	12	4.7	7.2	1.7	19
250–500 μm	6.8	8.8	3.2	21	5.4	6.5	3.1	11
106–250 μm	10	10	7.7	14	5.0	7.7	3.0	19
53–106 μm	12	11	8.0	14	6.2	8.1	4.0	18
<53 μm	56	54	30	67	0.34	1.1	nd	4.1

nd: not detected.

3. Results and discussion

3.1. Particle size distribution of house dust

Table 1 and Fig. 2 show the weight distribution of the house dust based on the particle size of particulate and fluffy dust investigated in this study. After removal of impurities, the total weights of the five house dust samples ranged from 78 to 194 g. Among the samples, particulate dust accounted for 41–68 wt%. Particulate dust consisted mainly of fine particles <53 μm; coarse particles >2 mm were scarce. In contrast, most fluffy dust was in the >2 mm fraction, the median contribution of which was more than 70 wt% of the total. Fluffy dust was also found in the <1 mm mesh size fraction and formed clumps about 5–10 mm in diameter. However, there was little fluffy dust in the <53 μm fraction. The 1–2 mm and 0.5–1.0 mm coarse fractions were composites of mixed materials, including tiny pebbles, pieces of plants, and rice grains (Fig. 1). A uniform representative sample could not be collected from these fractions, and thus they were excluded from our chemical analyses.

3.2. Distributions of BFRs and PBDD/Fs in dust with respect to particle size

PBDEs, HBCDs, and PBDFs were detected in all the samples analyzed (Table 2). Tables S1–3 provides detailed information on isomer concentrations in individual samples. In general, the particle size distributions of PBDEs and PBDD/Fs were similar to each other, but the profiles of HBCDs particle sizes were different.

3.2.1. PBDEs

Fig. 3 and Table 2 show PBDE distributions in particulate and fluffy dust as a function of particle size. PBDE concentrations in particulate and fluffy dust were roughly comparable. In particulate dust with particle sizes of <53 μm–500 μm, PBDE concentrations were lowest in the 250–500 μm size fraction and highest in the 106–250 μm and 53–106 μm size fractions (Fig. 3a). Concentrations of PBDEs in particulate dust tended to increase with decreasing particle size, but PBDE concentrations in particles <53 μm in size, the finest fraction, were not the highest, the indication being that the distribution of PBDEs in house dust does not depend mainly on the specific surface area of dust particles. The implication is that PBDEs become incorporated into house dust via multiple pathways, and the inclusion of abraded particles from BFR-treated products may not be negligible. For fluffy dust, PBDE concentrations in fractions ≤2 mm in size were comparable (Fig. 3b), the suggestion being that they originated from the same fibrous material.

Comparison of the PBDE homolog profiles (Fig. 4) revealed that BDE 209 (deca-BDE) contributed the most to the total PBDE concentrations in both particulate and fluffy dust (63–94% and 77–94%, respectively). Note that, except for the HD-01 sample, the proportions of di-to nona-BDEs of particulate dust were larger in the 250–500 μm size fraction than in the three smaller particle size fractions. This observation implies that the 250–500 μm particles contained PBDE from sources different from the sources of PBDEs in the other particles and that they contained relatively high amounts of PBDEs volatilized from treated products. In contrast, profiles of PBDE homologs in the fluffy dust that was passed through different screen sizes were very similar throughout all the samples. Combined with the concentrations of PBDEs in the fluffy dust shown in Fig. 3b, these results confirm that the PBDEs in the fluffy dust originated from the same fibrous material. During sieving, fluffy dust initially placed on the 2-mm screen may have been disaggregated and diminished in size; consequently it may have passed through screens with nominal mesh sizes smaller than its original size.

3.2.2. PBDD/Fs

Table 2 summarizes PBDD/F concentrations detected in house dust samples. The concentrations were one to three orders of magnitude lower than those of PBDEs and HBCDs. PBDFs contributed the most, and only tetra-brominated congeners were detected among PBDD homologs (supplementary information, Table S1). PBDD/F concentrations in particulate dust ranged from 0.33 to 12 ng g^{-1} and were lowest in the 250–500 μm size fraction, as was the case with PBDEs. Because most of the PBDFs were derived from impurities in technical PBDEs mixtures [10] or were products of PBDF photodegradation during the use of treated articles [7,8], it is reasonable that the accumulation profile of PBDD/Fs was linked

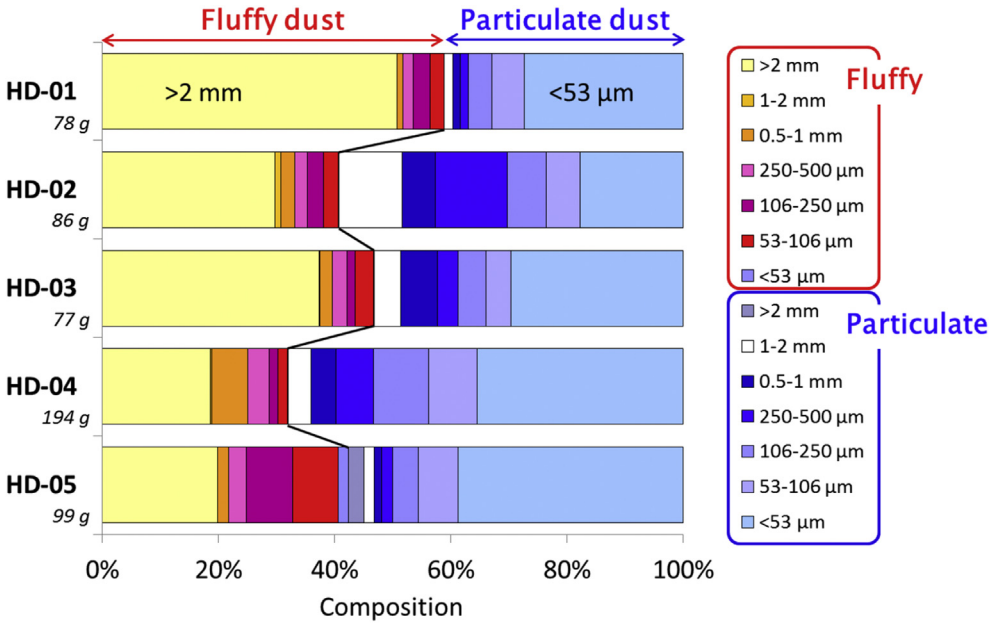

Fig. 2. Weight distribution of house dust as a function of particle size in samples from five houses.

Table 2
Concentrations (ng g^{-1} wet wt) of BFRs and PBDD/Fs in each fraction after sequential sieving.

	Particulate dust				Fluffy dust			
	250–500 μm	106–250 μm	53–106 μm	<53 μm	>2 mm	250–500 μm	106–250 μm	53–106 μm
PBDEs								
HD-01	300	1400	1100	500	170	1000	1000	1400
HD-02	2100	7500	7100	5800	1500	5400	7900	5900
HD-03	45	730	1500	790	250	400	620	870
HD-04	68	260	1300	580	170	380	290	390
HD-05	85	600	1000	490	230	430	420	450
PBDD/Fs								
HD-01	1.6	6.4	5.5	4.7	1.4	5.4	6.3	7.1
HD-02	3.3	8.4	12	11	5.7	10	12	12
HD-03	0.33	0.96	2.0	2.8	0.84	2.1	2.6	2.8
HD-04	1.5	4.0	7.9	10	4.1	6.2	7.4	5.9
HD-05	1.5	3.9	7.2	5.9	3.4	4.4	5.7	5.2
HBCDs								
HD-01	660	1100	470	270	45	470	390	260
HD-02	18000	32000	10000	1700	8800	99000	53000	7700
HD-03	270	1200	2000	2400	4700	5900	5500	5500
HD-04	29	89	630	420	480	1000	470	790
HD-05	550	300	480	390	330	680	690	830

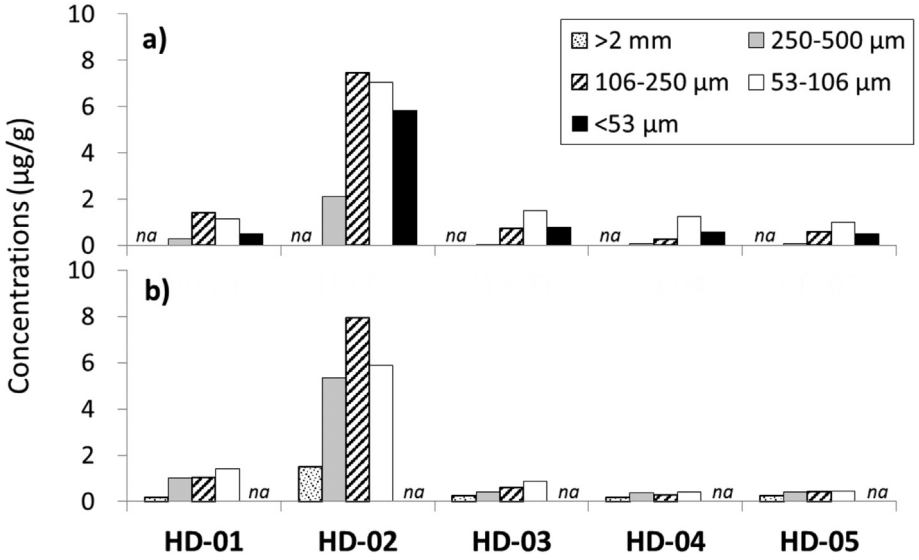

Fig. 3. PBDE distributions in particulate (a) and fluffy dust (b) as a function of particle size.

with the profiles of PBDEs. Because the concentrations were very similar in the three fractions of particulate dust <250 μm, only the data obtained in this study made it impossible to distinguish which pathways (transfer via volatilization, direct contact, or abrasion) contributed the most to the accumulation of PBDD/F in indoor dust. Similar to the patterns found for PBDEs, PBDD/F concentrations in fluffy dust were lowest in the >2 mm size fraction; the concentrations in the other three fractions were comparable to each other. Octa-BDF contributed the most to the total PBDD/F concentrations in both particulate and fluffy dust; the contributions fell in the ranges 30–57% and 41–56%, respectively, except for octa-BDF concentrations in two samples that were below the limit of detection (<0.1 ng/g). The percentage contributions of tetra-BDDs were as high as 14% (detection frequencies of tetra-BDDs: 14/20 and 9/20 in particulate and fluffy dust, respectively) (Table S1). Homolog profiles of PBDD/Fs in particulate and fluffy dust were comparable and independent of particle size.

The PBDD/F concentrations expressed as percentages of the PBDE concentrations in the corresponding particulate and fluffy dust were 0.11–2.2% and 0.15–2.5%, respectively. Hanari et al. [10] have reported that PBDF impurities account for 0.00003% and 0.005%, respectively, of technical PentaBDE and DecaBDE mixtures. The percentage of PBDFs in the house dust in this study was two to three orders of magnitude higher than the percentage of PBDFs in commercial mixtures, the suggestion being that some part of the PBDEs found in dust are photodegraded and converted to PBDFs before and/or after being transferred to dust.

3.2.3. HBCDs

HBCD concentrations in particulate dust varied quite widely among size fractions and did not show an obvious trend with the surface area of dust particles (Table 2). A maximum concentration of 32 mg kg^{-1} was found in the 106–250 μm size fraction of HD-02. The main use of HBCDs, accounting for 80–90% of consumption, is for flame retardation of polystyrene insulation foams for buildings; the rest is used for upholstery textiles; thus, the main source of the HBCDs in indoor dust is certainly upholstery textiles such as flame-retarded curtains, to which 2.2–4.3% by weight of HBCDs are added

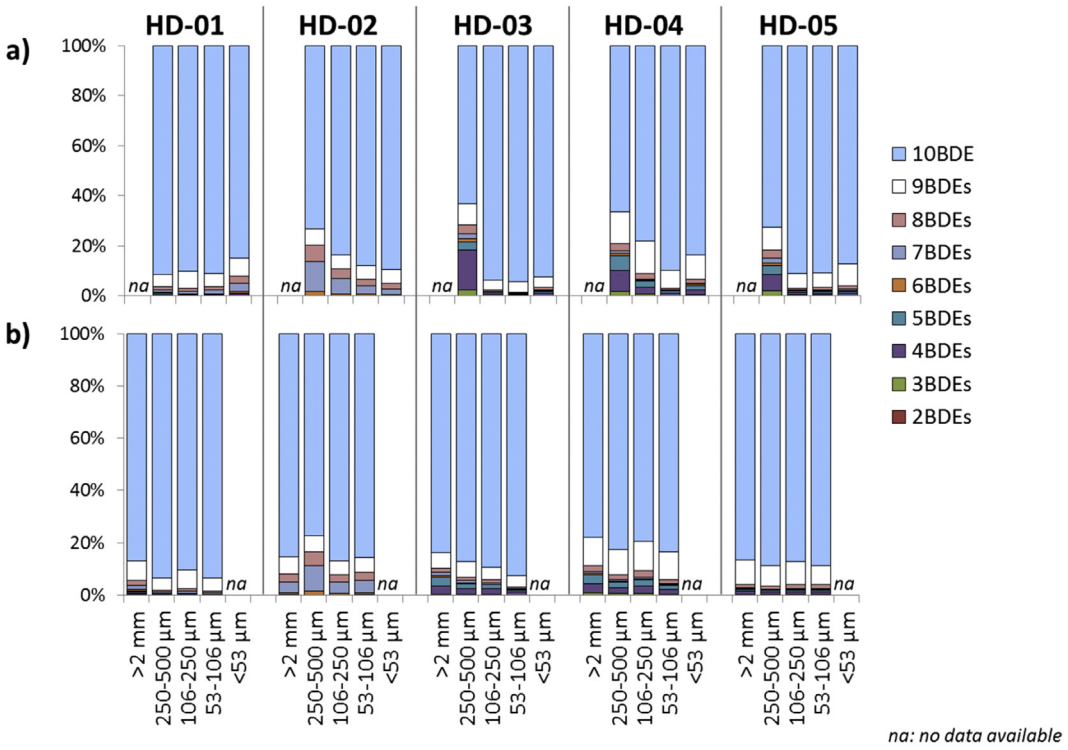

Fig. 4. PBDE homolog profiles in the sieved dust. a) Particulate dust, b) fluffy dust.

[28]. In most cases of this study, HBCD concentrations in fluffy dust (up to 99 mg kg^{-1}) were higher than those in particulate dust in the corresponding size fraction, the suggestion being that there is a direct contribution to dust from flecks of fiber from HBCD-treated textiles. HBCD levels in particulate dust were high when the concentrations in the corresponding fluffy dust were relatively high.

The HBCD diastereomer profiles in particulate and fluffy dust from five homes varied among size fractions and households investigated (Fig. 5), but very similar profiles were found for particulate and fluffy dust samples from the same house. Contributions of α-HBCD were high in HD-01 and HD-02, but γ-HBCD accounted for most HBCDs in HD-03 and HD-04. In these two-sample sets, a certain amount of ε-HBCD was also detected. Although α-, β- and γ-diastereomers accounted for 26–46%, 12–17%, and 38–62%, respectively, of the total HBCDs in the treated textiles [28], γ-HBCD always formed the majority (>75%) of the technical mixtures, with smaller amount of the other two diastereomers being present [29]. Interestingly, the contributions of α-HBCD were higher in three out of five house dust samples in this study than in treated-textiles (Fig. 5), the suggestion being that photolytic isomerization had changed the distribution of isomers in the dust samples. Chemical transformations of HBCDs have not yet been observed in treated-textiles exposed to natural sunlight [8], but a rapid photolytically mediated conversion of γ-HBCD to α-HBCD has been found in indoor dust and standard solutions [30]. These observations suggest that HBCDs incorporated into treated products are not susceptible to photolytic alteration but undergo isomerization quite easily once they are released into the air and indoor dust.

3.2.4. Total burden of BFRs in dust

The absolute amounts of BFRs and PBDD/Fs in each size fraction of fluffy and particulate dust were obtained by multiplying the concentrations by the weights of dust in each size fraction. It is apparent that over half of the total amount of PBDEs (Fig. 6a) and PBDD/Fs (Fig. 6b) were present in the particulate dust in all five of the houses; the particulate dust contributed 61–86% and 59–80% of the total, respectively. Furthermore, the percentage contributions to the total abundances of PBDEs and PBDD/Fs were highest in the <53 μm particulate size fraction (32–52% and 8.2–20%, respectively) and >2 mm fluffy dust size fraction (32–61% and 13–27%, respectively). The distributions of HBCDs in dust with respect to particle size were not uniform among the dust samples collected from the different homes (Fig. 6c). In particular, HBCDs in the HD-01 sample were predominantly distributed in particulate dust (76%), whereas fluffy dust contributed more than 70% of the total HBCDs in the HD-03 dust.

3.3. Size-selection strategy for dust analysis

To determine a size-selection strategy for dust analysis, BFR and PBDD/F concentrations in specific ranges of dust size fractions were estimated by using the BFR and PBDD/F concentrations and dust weight data in each size fraction as follows:

$$C = \sum C_f W_f \Big/ \sum W_f \qquad (1)$$

where C is the estimated concentration of BFR or PBDD/F in a specific size fraction (ng g^{-1}), ??$_{??}$ is the corresponding concentration in each size fraction (ng g^{-1}), and ??$_{??}$ is the weight of dust in each fraction (g). We focused on the concentrations in two cases, A and B, which are common size fractions employed for chemical analysis. Case A corresponds to particulate dust sieved through a 250-μm screen (without fluffy dust). Case B corresponds to a composite of dust sieved through a 500-μm screen (the sum of particulate and fluffy dust). With Case A as a benchmark, the percentage difference of concentrations between Case A and B was then calculated with a simple equation as follows:

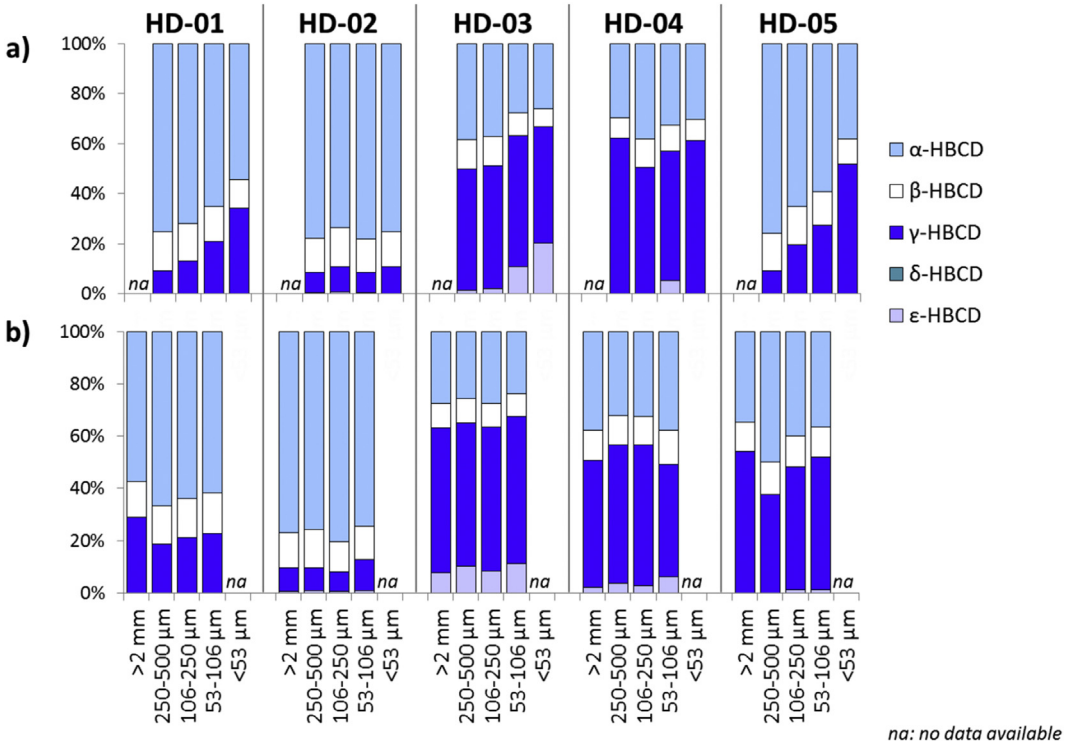

Fig. 5. HBCD isomer profiles in the sieved dust. a) Particulate dust, b) fluffy dust.

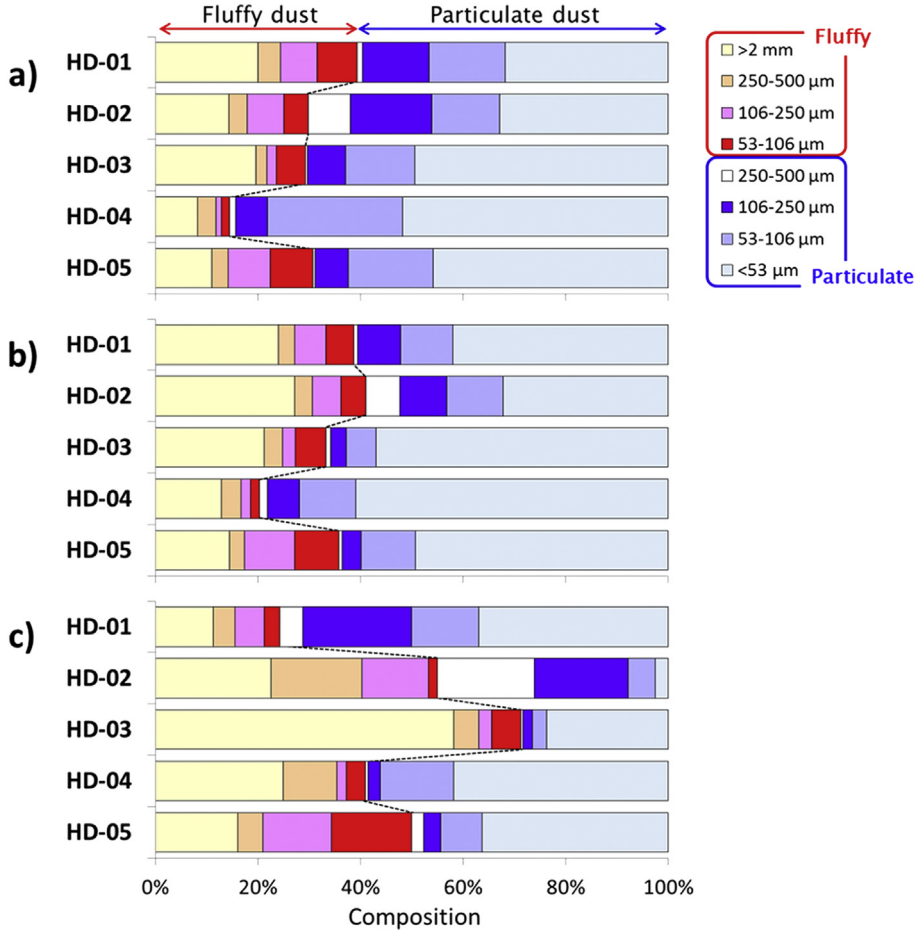

Fig. 6. Distribution of total burdens of PBDEs (a), PBDD/Fs (b), and HBCDs (c) in the sieved dust.

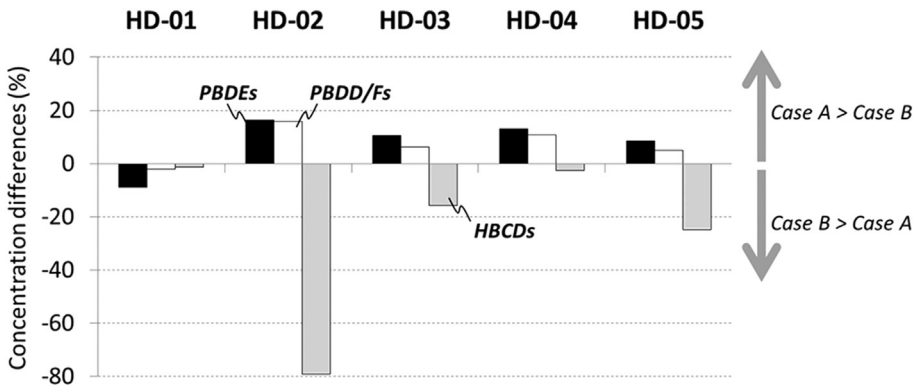

Fig. 7. Concentration differences (%) between cases A (concentrations in <250 μm particulate dust) and B (concentrations in <500 μm whole composite dust). Positive values indicate that Case A was higher than Case B, whereas negative values indicate that Case B exceeded Case A.

$$\text{Concentration differences (\%)} = 100 \times (C_{\text{Case A}} - C_{\text{Case B}})/C_{\text{Case A}} \quad (2)$$

The concentrations of PBDEs and PBDD/Fs were 10–20% higher in the <250 μm particle dust (Case A) than in the <500 μm composite dust (Case B) (Fig. 7). This result indicates PBDE and PBDD/F concentrations would be underestimated by inclusion of >250 μm particles and fluffy dust. The differences attributable to the particle size fraction used for the chemical analysis, however, were much smaller than originally expected. These small differences can be explained by the weight distribution of particulate dust, which was dominated by particles <53 μm in size (Table 1, Fig. 2), and by the fact that the concentrations of PBDEs and PBDD/Fs in particles 250–500 μm in size were the lowest (Table 2, Fig. 3). Consequently, the greatest amounts of PBDEs and PBDD/Fs were in particles <53 μm in size, and very small amounts of PBDEs and PBDD/Fs were present in particles 250–500 μm in size (Fig. 6a and b). In other words, the concentrations of PBDEs and PBDD/Fs depend principally on the concentration of particles <53 μm in size, and thus the mesh size used for sample preparation will have little effect on the concentrations of PBDEs and PBDD/Fs as long as particles <53 μm are included. In contrast, the HBCD concentrations increased by as much as 80% when particles >250 μm in size and fluffy dust were included (Fig. 7). When flame-retarded textiles are abraded and the products of abrasion appear in the fluffy dust, the abrasion products seem to have a non-negligible influence on HBCD concentrations in dust. The implication of this study is that the particle size distribution of the polymer additives of concern in indoor dust may vary as a function of the properties of the treated materials (rigid or non-rigid plastic, fibrous material, *etc.*) as well as on the frequency of contact and abrasion associated with age and use.

Yamamoto et al. [31] have conducted an analysis of the actual size distribution of soil particles adhering to children's hands after the children engaged in outdoor activities in the field or playground. The authors found that most of the soil particles that adhered were <200–300 μm in size, with a mode diameter of 39 ± 26 μm. In the present study, the highest concentrations of target compounds were detected in either the 106–250 μm or 53–106 μm size fractions, the indication being that the dust particles that tended to adhere most efficiently to human hands and that accounted for the highest exposure to contaminants were comparatively small in size. It is therefore essential to know the concentrations in dust particles <250 μm in size to estimate the risk of unintentional exposure to BFRs through hand-to-mouth activity. This knowledge, combined with the fact that PBDE homolog profiles of particles 250–500 μm in size differed from the profiles of other particle sizes (Fig. 4a), suggest that it would be suitable to use particulate dust <250 μm in size without fluffy dust for chemical analysis of BFRs in indoor dust.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.emcon.2016.03.005.

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