

PARTICLE SIZE DISTRIBUTION OF BROMINATED FLAME RETARDANTS AND RELATED SUBSTANCES IN INDOOR DUST

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Introduction

Indoor dust is a significant source of exposure to chemicals including brominated flame retardants (BFRs) to humans, especially for young children because of frequent hand-to-mouth contact. 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, across seasons, and among locations within a given country. The concentrations of contaminants in dust are influenced by factors such as sampling season, building structure, the room in the home, furnishing materials, heating and ventilation, how well and often the area is cleaned, and also sampling strategies. Although it is a common view of the researchers that pollutants in house dust as indicators of indoor contamination, so far there is no standard method of collection and pretreatment for dust sample and many studies on indoor environmental contaminants employ different sample preparation (e.g., sampling devices, sampling area, dust storage period in a vacuum cleaner bag, screen mesh size, particle size fraction) which sometime lead difficulty in the interpretation of contaminant levels.

This study attempts to determine the particle size-dependent variation in levels of BFRs and related substances including polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), and polybrominated dibenzo-*p*-dioxins/furans (PBDD/Fs) in house dust from Japan.

Materials and methods

House dust samples were collected in 2009 from vacuum cleaner bags of respective cleaners which are usually used at 5 homes in Kanto region, Japan (HD-01, -02, -03, -04, -05). After manual removal of debris, hair, and small pebbles from individual vacuum house dust with tweezers, they were individually fractionated into 7 fractions based on particle size (>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). To enhance the sieving efficiency, 10 zirconium oxide grinding balls (10 mm in diameter) were put on the top sieve in 2 mm mesh size. Sieving was continued until the point when the weight of dust on the top sieve stopped decreasing and became constant. Fluffy dust also got separately distributed into each of the particle fraction (Figure 1). It may not be suitable to classify fluffy dust by 'particle' size because of the fibrous form, but as far as possible, particulate and fluffy dust included in each fraction were separated and collected for chemical analysis. Prior to extraction, samples were weighed and stored in a cold dark place.

BFRs and PBDD/Fs in dust samples after classification (approximately 0.5 g) were extracted by using a rapid solvent extractor (SE-100, Mitsubishi Chemical Analytech Co., Ltd., Japan) sequentially with acetone/hexane and toluene. After the addition of $^{13}\text{C}_{12}$ -PBDE, PBDD/Fs, and HBCD mixtures as internal standards, a portion of the crude extract was cleaned up and fractionated by a multilayer column of silica gel, a sulfoxide silica gel column (Supelclean Sulfoxide, Sigma-Aldrich Co. LLC), and an activated-carbon-dispersed silica gel column. Identification and quantification of PBDEs and PBDD/Fs were performed by a HRGC-HRMS whereas HBCD diastereomers were analyzed by using a LC-MS/MS.

Results and discussion

Particle size distribution of house dust

Total weight of vacuum house dust after removing impurities ranged from 78 to 194 g. Among them, particulate dust accounted for 41–68 wt%. Table 1 shows weight distribution according to the particle size of particulate

and fluffy dust investigated in this study. Among particulate dust, coarse particles >2 mm were scarce and it was mainly dominated by the particles <53 μm . On the other hand, fluffy dust was predominantly distributed to >2 mm fraction, accounting for more than 70 wt% of the total (median). Fluffy dust was found in the fraction less than 1 mm mesh size and formed clumps of around 5–10mm in diameter, however, they were few in <53 μm fraction.

The fractions of 1–2 mm and 0.5–1.0 mm were a composite of mixed material including tiny pebbles, pieces of plants, and rice grains (Figure 1). A uniform representative sample could not be collected and thus were excluded from the target of chemical analysis.

PBDEs, HBCDs, and PBDD/Fs distribution in dust with respect to particle size

PBDEs, HBCDs and PBDFs were detected in all the samples analyzed. PBDD/F concentrations were one to two orders of magnitude lower than those of PBDEs and HBCDs. Particle size distributions of PBDEs and PBDD/Fs were similar to each other, but HBCD showed different profiles.

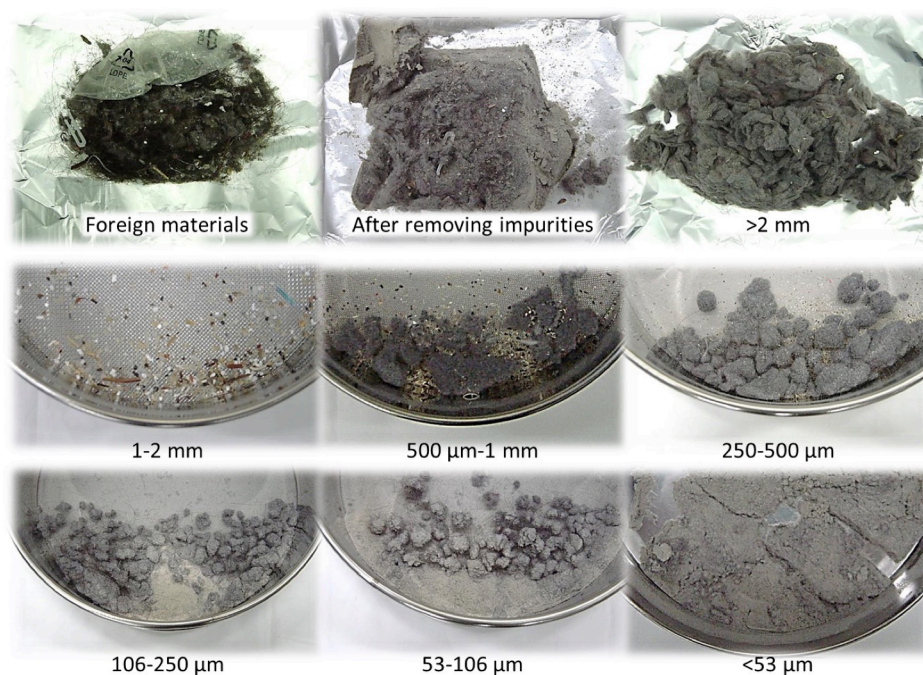


Figure 1. Particle size distribution of house dust

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	0	0.95	0	4.7	73	69	47	86
1-2 mm	5.7	7.9	3.0	18	0.25	0.66	0	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	0	4.1

Figure 2a shows PBDE distribution in particulate dust with particle size from $<53\ \mu\text{m}$ to $500\ \mu\text{m}$. Concentrations of PBDEs basically tended to increase with the decreasing particle size, but PBDEs in the particles $<53\ \mu\text{m}$, the smallest fraction, did not show the maximum concentrations. In general, levels of contaminants absorbed to a particle surface are known to increase with the decreasing particle size. This is because the specific surface area increases with the decreasing particle size. In this study, PBDEs in the particles $<53\ \mu\text{m}$ did not show the maximum concentrations, indicating that PBDE distribution in house dust does not depend solely on specific surface area of dust particles. Currently hypothesized pathways of BFR transfer from products to dust include: (1) volatilization of BFRs from the treated product with subsequent partitioning to dust; (2) abrasion via physical wear and tear of the treated product, resulting in the transfer of particles or fibres of the treated product directly to dust¹⁻³; and (3) transfer via direct contact between the treated product and dust⁴⁻⁵. The pathways (1) and (3) are thought to depend mostly on the surface area. The results of this study suggest that the source of PBDEs in house dust are from multiple pathways and among them abraded particles from BFR-treated products in house dust might be a significant source of PBDEs

For fluffy dust, concentrations and profiles of PBDE congeners found in the fractions other than $>2\ \text{mm}$ were almost similar (Figure 2b), suggesting that they originated from the same fibrous material. During sieving, fluffy dust initially put on the $2\ \text{mm}$ screen might have loosened and diminished in size and may pass through one screen to another.

When we see the PBDE homolog profiles, BDE 209 contributed the most to the total PBDE concentrations in both particulate and fluffy dust (63–94% and 77–94%, respectively). The proportions of di- to nona-BDEs in the fraction $250\text{--}500\ \mu\text{m}$ of particulate dust were apparently larger than other three fractions with smaller particle size. This observation implies that the component of PBDE sources in the $250\text{--}500\ \mu\text{m}$ particles may differ from the others and they contain relatively higher amount of PBDEs volatilized from the treated product.

As for HBCDs, concentrations in particulate dust varied quite widely among fractions and did not show a pronounced trend to surface area. Maximum concentration of $32\ \text{mg/kg}$ was found in the fraction $106\text{--}250\ \mu\text{m}$ of HD-02. HBCD concentrations in fluffy dust (up to $99\ \text{mg/kg}$) were higher than those in particulate dust, suggesting a direct contribution of flecks of fiber from HBCD-treated textile to dust.

To evaluate size-selection strategy for dust analysis, we estimated BFR and PBDD/F concentration in dust when they are sieved through a $500\ \mu\text{m}$ or $250\ \mu\text{m}$ mesh by using their concentration and dust weight in each fraction. In our calculation, we used $<250\ \mu\text{m}$ particulate dust as a benchmark. As a result, the estimated concentrations of PBDEs and PBDD/Fs in $<250\ \mu\text{m}$ dust (without fluffy dust) were 10 to 20% higher than those in $<500\ \mu\text{m}$ dust (the sum of particulate and fluffy dust), indicating underestimation by inclusion of fluffy dust and $>250\ \mu\text{m}$ particles. By contrast, HBCD concentrations showed up to 80% increase when fluffy dust was included.

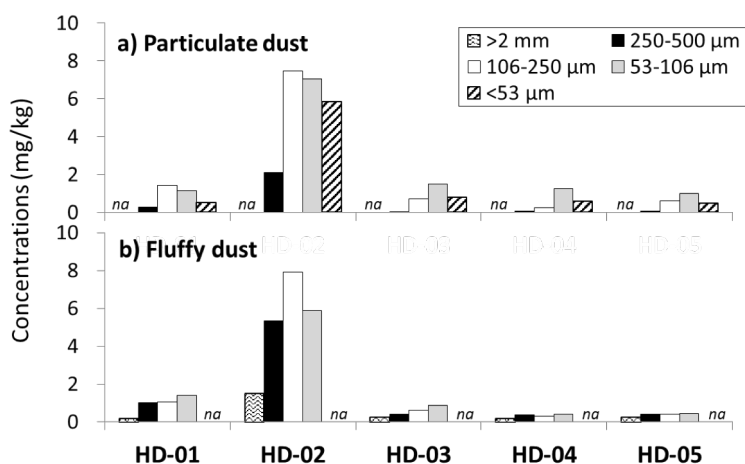


Figure 2. PBDE distributions in dust with particle size

Acknowledgements:

We gratefully acknowledge the technical assistance of A. Hasegawa of the National Institute for Environmental Studies, Japan.

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