

PBDEs AND PBDD/Fs IN HOUSE AND OFFICE DUST FROM JAPAN

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Introduction

In order to reduce the accidental fire, brominated flame retardants (BFRs) such as PBDEs are added to plastics, polyurethane foams, and textiles for household materials. The rapid decrease in PBDE consumption after 1990 could be due to the industry's voluntary phasing out of PBDEs in Japan because of global concern regarding their potential adverse environmental and health effects and their thermal-breakdown products.¹ However, lots of products such as TV and computer have contained PBDEs used in the past, which may be sources of them in the indoor air.² Previous studies have indicated that PBDEs accumulate through food chain and are potential toxic compounds for human, suggesting that the control strategy for them contained in products is very important. Recently, the analysis of PBDEs in house dust has been conducted all over the world, indicating that PBDE concentrations of house dust are relatively higher than other media such as sediment.³⁻⁶ Many researchers also demonstrated the importance of house dust as the routes of human exposure to PBDEs. On the other hand, there is no systematic monitoring investigation for grasping PBDEs level of dust in Japan.

In this study, we investigated the PBDE concentrations in dust derived from household and office in Japan. PBDD/Fs, the thermal-breakdown products of PBDEs, were also investigated. First, in order to evaluate the PBDE and PBDD/F level of collected dust in Japan, we compared the obtained data with those reported in previous studies. Then we tried to identify an indoor source of them in dust by evaluating the relevance of the concentration in dusts and the investigated indoor information.

Materials and Methods

The sampling procedure has been described elsewhere⁷. House dust (HD) and office dust (OD) samples were collected from 19 households (n=19) and 3 institutions (n=14) in Japan in May to December, 2005. HDs were collected by vacuum cleaners. While OD 6, 7, 9, 10, 11, 12, 13, and 14 were also collected from vacuum cleaner bags used in the office and laboratory, OD 1, 2, 3, 4, 5 and 8 were collected with a broom from the floor of office and laboratory manually. Dust was transferred to an all stainless steel sieve (< 1.0 mm), covered with the steel lid, and shaken automatically using Sieve Shaker AS300 (Retsch Co., Ltd.). Sieved dust was collected in a glass bottle covered with aluminum foil. Samples were stored at room temperature until analysis.

A questionnaire survey was performed for households and institutions where dusts were collected. To identify factors affecting chemical concentrations, data investigated was included cleaning frequency, area, year of construction, floor type, ventilation condition, the number and use time of electric appliance such as TVs and computer, etc.

Approximately 5.0 g of each sample was extracted using Soxhlet apparatus with toluene. Toluene fraction

was concentrated and transferred to *n*-hexane by rotary evaporation. After removing elemental sulfur with activated copper, *n*-hexane fraction was subjected to sulfuric acid treatment. The *n*-hexane fraction was washed with water and dehydrated. After spiking isotope labeled compounds, a portion of the fraction was separated into two fractions for PBDEs and PBDD/Fs, respectively by a tandem column, which was composed of a multilayer silica gel/Florisisil® column and an activated carbon dispersed silica gel column^{8,9}. Evaluation of the accuracy and reliability of this method has previously been performed as an intercalibration study between 13 laboratories in Japan¹⁰. Each fraction was concentrated to 100 µl and analyzed by HRGC-HRMS.

Results and Discussion

PBDEs in house and office dusts: PBDEs were detected in all dust extracts, and Table 1 summarizes the levels found in the house and office dusts. Total PBDEs in house dusts ranged from 140 to 3,000 ng/g (median 700 ng/g) while a concentration range of 260 to 20,000 ng/g (median 1,800 ng/g) was found in office dusts. The difference of concentration was one order of magnitude at the maximum among house dusts, and one order of magnitude at the maximum among office dusts except for OD4 which indicated the highest concentration. Proportional

Table 1. PBDE levels detected in house and office dusts

[pg/g]		House dust (n=19)				Office dust (n=14)			
Congener	Isomer	median	average	minimum	maximum	median	average	minimum	maximum
1BDE	BDE 3	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5	32	< 2.5	250
2BDE	BDE 7	2.5	4.0	< 1.0	18	14	31	< 1.0	98
	BDE 15	91	140	37	480	125	730	42	6,300
3BDE	BDE 17	110	190	48	760	365	880	77	4,100
	BDE 28	620	1,300	240	7,600	1,140	7,100	490	67,000
4BDE	BDE 49	740	1,300	340	7,600	2,700	11,000	550	92,000
	BDE 71	< 1.0	30	< 1.0	340	16	340	< 1.0	3,400
	BDE 47	5,400	7,300	1,100	22,000	30,500	110,000	4,300	580,000
	BDE 66	480	1,200	270	8,500	1,600	7,800	320	64,000
5BDE	BDE 77	< 1.0	83	< 1.0	700	11	440	< 1.0	4,000
	BDE 100	1,100	1,400	160	5,700	6,850	30,000	700	130,000
6BDE	BDE 119	110	140	< 2.5	520	215	1,100	< 2.5	6,000
	BDE 99	5,100	8,400	180	39,000	38,000	170,000	3,100	810,000
	BDE 85	340	560	88	3,100	2,100	8,700	< 2.5	43,000
	BDE 126	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5
7BDE	BDE 126	900	1,400	370	5,700	5,150	16,000	960	68,000
	BDE 154	2,500	3,800	660	11,000	15,500	34,000	3,300	100,000
8BDE	BDE 184	< 5.0	49	< 5.0	940	< 5.0	530	< 5.0	3,600
	BDE 183	7,500	12,000	1,500	50,000	20,000	81,000	5,000	280,000
	BDE 191	< 5.0	120	< 5.0	2,300	< 5.0	1,200	< 5.0	5,300
9BDE	BDE 196	6,300	9,200	1,900	24,000	25,000	30,000	6,000	100,000
	BDE 197	6,100	7,700	1,200	24,000	20,000	39,000	4,800	180,000
10BDE	BDE 207	50,000	60,000	8,000	160,000	100,500	140,000	21,000	690,000
	BDE 206	67,000	98,000	11,000	250,000	123,500	220,000	15,000	1,300,000
Total PBDEs	BDE 209	550,000	820,000	100,000	2,600,000	1,100,000	2,400,000	150,000	17,000,000
		700,000	1,000,000	140,000	3,000,000	1,800,000	3,300,000	260,000	20,000,000

contribution of each BDE-congener (including concentrations calculated from potential peak area of each congener) for dust samples in this study was shown in Fig. 1. DecaBDE was the most abundant congener in most samples, dominating more than 50% of total PBDEs. However, in a few of dust samples, TetraBDEs or PentaBDEs were detected as the major congeners. It was estimated that these gaps were depending on the difference of indoor source. As compared with previously reported values, the level detected in this study was between those in the North America^{3,5,11} and those in EU^{11,12} (Fig. 2). However, DecaBDE level in dusts from Japan is comparable to those sampled in Canada (median 630 ng/g)⁵ and U.S.A (median 2,000 and 1,350 ng/g)^{3,11}, suggesting that indoor pollution level derived from DecaBDE use in this study is relatively higher.

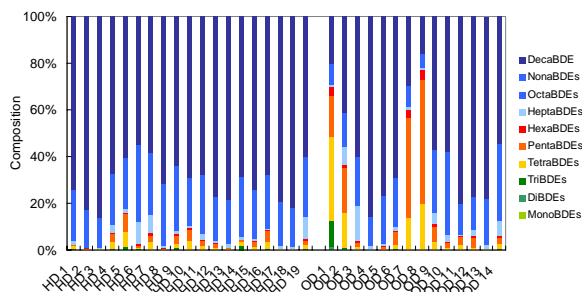


Fig. 1. Composition of BDE-congener in dust samples
Abbreviations: HD, house dust; OD, office dust.

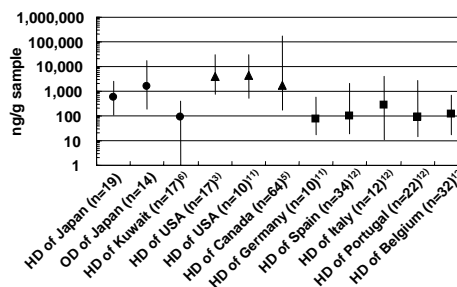


Fig. 2. Comparison of PBDE levels to the previous studies
This study, Ref. 3 and Ref. 6: Sum of 9 isomers: BDE-28, -47, -100, -99, -85, -154, -153, -183, and -209. Ref. 11: Sum of 7 isomers: BDE-47, -100, -99, -154, -153, -183, and -209. Ref. 5: Sum of 13 isomers: BDE-17, -28, -47, -66, -100, -99, -85, -154, -153, -138, -183, -190, and -209. Ref. 12: Sum of 22 isomers: BDE-3, -7, -15, -17, -28, -49, -71, -47, -66, -77, -100, -119, -99, -85, -126, -154, -153, -138, -184, -183, -191, and -209. Abbreviations: HD, house dust; OD, office dust.

PBDD/Fs in house and office dust: PBDD/Fs were detected in all dust samples, and Table 2 summarizes the levels in the house and office dusts. Total PBDD/Fs in house dusts ranged from 610 to 7,700 pg/g (median 1,800 pg/g) while a concentration range of 1,000 to 8,800 pg/g (median 2,500 pg/g) was found in office dusts. The difference of concentration was one order of magnitude at the maximum among house or office dusts. The 2,3,7,8-substituted PBDDs were not detected in all dust samples. Proportional contribution of each BDD/F-congener (including concentrations calculated from potential peak area of each congener) for dust samples in this study was shown in Fig. 3. Although TetraBDD was detected in most dust samples, PBDFs dominated more than 90% of total PBDD/Fs in all dusts, and HexaBDFs or HeptaBDFs was detected as the major congeners. Recent study conducted by Ministry of the Environment of Japan also detected high concentration of PBDD/Fs, mainly PBDFs, in house and office dusts¹³, supporting our results. The values in dust samples are relatively higher as compared to those in coastal sediments of a large city obtained from Osaka bay, Japan¹⁴, which suggest that dust is an environmental media containing high concentration of PBDD/Fs.

Search for Indoor source of PBDEs and PBDD/Fs: We tried to identify the indoor source of PBDEs and PBDD/Fs by evaluating the relevance of chemical concentrations in dusts and the investigated indoor environment information. As a result of spearman rank-order correlation test, the concentration of TriBDEs ($r=0.51$, $P=0.027$), TetraBDEs ($r=0.73$, $P=0.0014$), PentaBDEs ($r=0.75$, $P=0.0027$), HexaBDEs ($r=0.80$, $P=0.00049$), and HeptaBDEs ($r=0.60$, $P=0.0088$) in dust correlated closely with the investigated total use time of electrical appliances such as TV and computer in a questionnaire survey. Significant correlations were also observed between TetraBDFs in dusts and the use time of computer but not the total use time of electrical appliances. Previous studies pointed out that PBDEs contained in products may be a source of them, especially lower BDE, in the indoor air^{15,16}. These results suggest that lower BDEs and TetraBDFs are derived from them in indoor air.

However, there was little correlation between the investigated indoor information and concentrations of the higher BDEs or most

Table 2. PBDD/F levels detected in house and office dusts

Congener	Isomer	House dust (n=19)					Office dust (n=14)				
		median	average	minimum	maximum	median	average	minimum	maximum		
4BDD	2,3,7,8	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5	< 2.5		
5BDD	1,2,3,7,8	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10		
6BDD	1,2,3,4,7,8	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25		
7BDD	1,2,3,4,6,7,8	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50		
8BDD	1,2,3,4,6,7,8,9	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50		
T4BDF	2,3,7,8	37	37	< 10	85	56	59	20	110		
P5BDF	2,3,4,7,8	< 10	2	< 10	31	11	27	< 10	79		
H6BDF	1,2,3,4,7,8	< 25	< 25	< 25	< 25	205	230	< 25	660		
H7BDF	1,2,3,4,6,7,8	1,700	2,100	590	7,700	2,300	3,500	1,000	8,100		
Total PBDD/Fs		1,800	2,100	610	7,700	2,500	3,800	1,000	8,800		

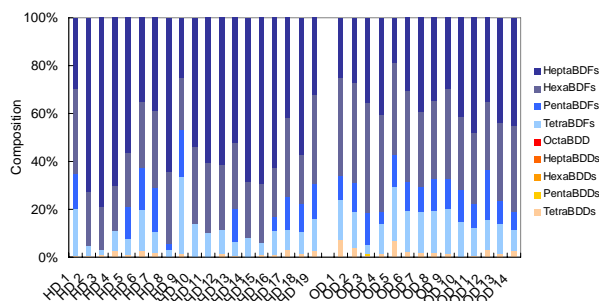


Fig. 3. Composition of BDD/F-congener in dust samples

Abbreviations: HD, house dust; OD, office dust.

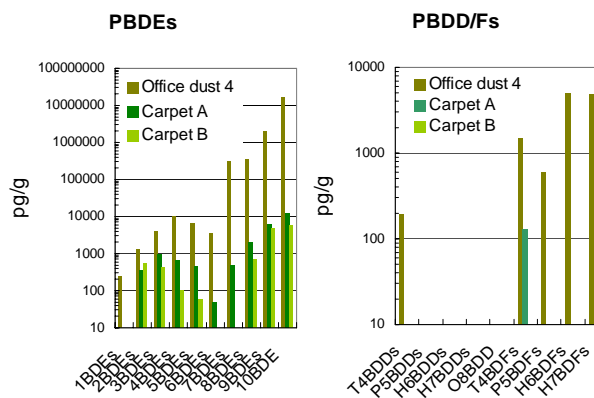


Fig. 4. PBDE and PBDD/F congener profile of office dust 4 and carpet materials (Carpet A, surface; Carpet B, inside)

PBDD/Fs in dusts. Further investigation for indoor source was conducted for OD4 which contained high concentration of DecaBDE (17,000 ng/g). The indoor carpet was obtained from the office which OD4 was collected because dust matrix of OD4 may be mainly derived from a carpet material. The PBDE and PBDD/F congener profile of OD4 and carpet materials were shown in Fig. 4. For PBDEs, there was a big difference between PBDE concentrations in carpet materials and dust, especially in terms with higher BDEs. Furthermore, most PBDD/Fs were not detected in carpet materials. These results suggested that carpet materials were not the main indoor source of the higher BDEs and most PBDD/Fs. The inner dust of electric appliance¹⁷ or the dust derived from lint of upholstery³ containing high concentration of them may be the potential indoor source.

Now, we are trying to identify the indoor source of them contained in house and office dusts. Furthermore, we are also evaluating the potential risk of house dust containing high concentration of BFRs using *in vitro* bioassays^{7,18}.

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