COMPARISON OF BROMINATED FLAME RETARDANTS IN INDOOR AIR AND DUST SAMPLES FROM TWO HOMES IN JAPAN

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Abstract
In this study, polyhalogenated compounds such as BFRs were analyzed in indoor air and dust samples from two homes in Japan. Concentrations of PCBs and TBPs in exhaust and indoor air of two houses were detected at 10^2 – 10^3 pg/m^3 orders and were well above those in outdoor air. For dust samples, the detected PBDE and PBDD/F concentrations were in the range of our past study. Interestingly, compared to PBDE concentrations, two orders of magnitude higher concentration (13,000 ng/g) was observed for HBCD in dust sample from one house. Based on the calculation of air/dust partition ratio values (*K*ad), low *K*ad values (i.e., log *K*ad < -1) were obtained for high brominated PBDEs (TeBDEs to DBDE), TBBPA and HBCD, while indoor air contained higher parts of low chlorinated PCBs, low brominated PBDEs and TBPs. Attention should be paid to exposure to TBPs through inhalation of air as well as dust ingestion. By the XRF analysis, high bromine concentrations were found in curtain and roll screen samples possessing high product loading factor.

Introduction
Products treated with brominated flame retardants (BFRs) are reservoirs of BFRs in homes. This could lead to high BFR concentrations in indoor air and dust, which are significant exposure media for humans. [1] In this study, polyhalogenated compounds such as BFRs and polybrominated dioxins were analyzed in indoor air and dust samples from two homes in Japan. The analytical results permitted a comparison of two factors affecting concentrations of investigated chemicals in air and dust at two homes, namely home products and ventilation performance (control measures). In order to obtain information to verify the former factor, handheld X-ray fluorescence (XRF) spectrometry was used to identify bromine element in products in a rapid and undestructive manner. For investigating the latter factor, two homes adopting type II ventilation system (mechanical air supply through charcoal/natural ventilation) and type III system (natural air supply/mechanical ventilation) were surveyed and compared.

Materials and Methods
Field test. Field test was carried out in two family houses in Hokkaido, Japan for a week over October and November, 2006.
House A: newly built in 2006, wooden two-story house with two adult and two children residents, located in a residential area. Building area was 75 m^2 and floor area was 123 m^2. The space in the house was 295 m^3 and the designed ventilation rate was 150 m^3/h adopting type II ventilation system (mechanical air supply through charcoal/natural ventilation).
House B: built in 2004, wooden two-story house with two adult and one child residents, located in a residential neighborhood from busy main road. Building area was 61 m^2 and floor area was 106 m^2. The space in the house was 254 m^3 and the designed ventilation rate was 120 m^3/h adopting type III ventilation system (natural air supply/mechanical ventilation).

Sampling. In each house, the outdoor air, indoor air (taken on the first and second floor, respectively) and exhaust air samples were collected on the quartz filter and PUF filter by high volume air sampler. Sampling rate was approximately 200 m^3/h and total sample volume became approximately 2,000 m^3 for each air sample. Dust samples (contents of vacuum cleaner) were also collected by inhabitants' routine cleaning during the period of air sampling. After dust collection, impurities were removed and all sample amount (4.4 g for house A and 3.7 g for house B) was used for the subsequent analysis.

Analysis. The target substances were extracted from solids (i.e., filters and dust) with toluene in a soxhlet extractor. The combined extracts were cleaned up for the determination of polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs, 4-8 chlorinated), polychlorinated biphenyls (DL-PCBs and total PCBs), polybrominated dibenzo-*p*-dioxins/furans (PBDD/Fs, 4-8 brominated), polybrominated diphenyl ethers (PBDEs, 1-10 brominated), tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD), tribromophenols (TBPs) and pentachlorophenol (PCP) by individual adsorption chromatography with sample derivatization in the case of TBBPA, TBPs and PCP. For analysis of those compounds an HRGC/HRMS system was used.

Handheld XRF screening of bromine. The handheld X-ray fluorescence (XRF) analyzer (Element tester innovxα6500, Innov-X systems) was used for non-destructive analysis of bromine (e.g., brominated flame retardants) in residential settings and home products. Two-minute measurement was conducted for sample analysis and detection limit for bromine in plastics was 5 ppm on this condition.

Results and Discussion

Table 1 summarizes the air and dust concentrations of PCDD/Fs, PBDD/Fs, PCBs, PCP and BFRs in the investigated two houses.

Concentrations of polyhalogenated compounds in air. Concentrations of PCBs, HBCD and TBPs in exhaust and indoor air of house A were detected at $10^2 – 10^3$ pg/m^3 orders and were well above those in outdoor air. The same trend was observed for PCBs and TBPs in house B. When comparing concentrations in indoor air samples (1F and 2F) in the same house, two to three times difference was observed for PCBs and BFRs. There have been frequently reported that indoor air remains contaminated by PCBs used as elastic sealants[2], and also has been possibly influenced by BFRs contained in home products such as electronics and furniture[3], which supports the presented results. There was no significant difference in indoor concentrations of the investigated compounds (except for HBCD and WHO-TEQ) between two houses with different ventilation systems.

Concentrations of polyhalogenated compounds in dust. PBDEs were detected at 730 and 240 ng/g in house A and B, respectively, which was within the range of our previous results for Japanese house dust samples (140 - 3,000 ng/g, median 700 ng/g, n = 19).[4] Likewise, PBDD/F concentrations (1,500 and 680 pg/g) were in the range of the past study (610 - 7,700 pg/g, median 1,800 pg/g, n = 19).[4] Interestingly, compared to PBDE concentrations, two orders of magnitude higher concentration (13,000 ng/g) was observed for HBCD in dust sample from house A.

Air/dust partition of polyhalogenated compounds. Air/dust partition ratio values ("*K*ad") of the polyhalogenated compounds were calculated tentatively by the following equation.

Air/dust partition ratio (*K*ad) = (concentration of the compound in the exhaust gas, pg/m^3)/{(concentration of the compound in the dust, pg/g) x (collected amount of dust, g) / (space in the house, m^3)}

In Fig. 1, log *K*ad values of the compounds were shown for the both case of house A and B. Low *K*ad values (i.e., log *K*ad < -1) were obtained for high brominated PBDEs (TeBDEs to DBDE), TBBPA and HBCD, which means those compounds are preferentially adsorptive to dust. On the other hand, indoor air contained higher parts of low chlorinated PCBs, low brominated PBDEs and TBPs. In this study, most abundant TBP isomer was 2,4,6-tribromophenol, which was reported to be very potent (i.e., thyroid hormone-like) by the human transthyretin (TTR) binding assay with 10 times higher potency than that of thyroxine[5] and was identified as one of responsible compounds for the TTR-binding in Japanese dust samples. [6] Attention should be paid to exposure to TBPs through inhalation of air as well as dust ingestion.

Relevance of home products to BFR concentrations in indoor air and dust. Table 2 shows residential settings and home products which showed high bromine concentrations over 0.01% (100 ppm) by the XRF analysis. The highest bromine concentration was found to be 10% in the casings of television sets in house B. Of our great interest is high bromine content in four curtain and roll screen samples in house A. In house A, 13,000 ng/g of HBCD was detected from dust. HBCD has been frequently used for textile as additive flame retardants. [7] For curtain and roll screen samples, detailed analysis has not been conducted yet. However, if HBCD is contained with high concentrations, emission of HBCD from the textiles should be taken into consideration due to their high product loading factor (product loading factor: ratio of exposed surface area of the product to the room volume).

Conclusive remarks. This study was initiated to clarify the actual conditions on the occurrence of polyhalogenated compounds in Japanese home environment. Difference of controllability of polyhalogenated compounds such as BFRs between two houses (two ventilation systems) has been kept unclear in this study, because the arrangement of the rooms, building materials, home products and settings, and inhabitants' lifestyle were not identical. Further studies using a small chamber or a model room are needed for determination of emission factor of polyhalogenated compounds and development of their control countermeasures.

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Table 1 Air and dust concentrations of the investigated organic halogenated compounds in two houses.

	House A					House B				
	Outdoor air	Exhaust	Indoor air (1F)	Indoor air (2F)	Dust	Outdoor air	Exhaust	Indoor air (1F)	Indoor air (2F)	Dust
	pg/m^3 (at 20 ^oC)				pg/g	pg/m^3 (at 20 ^oC)				pg/g
PCDDs	1.0	0.54	0.49	0.55	450	1.9	0.71	1.2	5.1	150
PCDFs	3	1.6	1.3	1.3	99	4.4	1.6	5.2	37	300
PCDD/DFs	4.1	2.2	1.8	1.8	550	6.2	2.3	6.5	42	450
DL-PCBs	12	4.7	6.2	27	1700	11	48	19	26	1500
Total	16	6.9	8	29	2300	17	50	25	68	2000
WHO-TEQ(1998)										
PCDDs	0.014	0.0098	0.0046	0.0059	0.75	0.022	0.0056	0.023	0.16	0.14
PCDFs	0.051	0.029	0.022	0.023	0.16	0.073	0.029	0.12	0.72	0.46
PCDD/DFs	0.066	0.039	0.027	0.029	0.91	0.096	0.034	0.14	0.88	0.6
DL-PCBs	0.0054	0.0023	0.0028	0.0053	0.28	0.0051	0.009	0.0061	0.016	0.26
Total	0.071	0.041	0.03	0.034	1.2	0.1	0.043	0.15	0.89	0.86
PBDDs	ND	ND	ND	ND	40	ND	ND	0.1	ND	ND
PBDFs	ND	ND	ND	ND	1400	ND	ND	ND	ND	680
PBDD/DFs	ND	ND	ND	ND	1500	ND	ND	0.1	ND	680
	pg/m^3 (at 20 ^oC)				ng/g	pg/m^3 (at 20 ^oC)				ng/g
PCBs	240	410	880	1500	22	730	1500	730	1300	15
PCP	19	19	39	13	47	20	22	19	25	2.7
PBDEs	25	46	17	39	730	19	17	55	33	240
TBBPA	7.1	4.9	8	10	520	9.5	15	20	12	490
HBCD	15	96	280	160	13000	13	11	10	6.7	140
TBPs	73	240	690	220	30	49	670	430	280	15

Table 2 Residential settings and home products which showed high bromine concentrations over 0.01% (100ppm) by the XRF analysis.

	Location	Bromine
House A		
Curtain	1F living room	0.1%
Video casette	1F living room	0.03%
Video tape recorder	1F living room	0.02%
Roll screen	1F living room	2.3%
Roll screen	2F bedroom	2-2.5%
Curtain	2F child's room	1.1-1.5%
House B		
TV casing	1F living room	10%
TV rear casing	2F bedroom	10%
Roll screen	2F landing	0.02%
Stuffed toy	2F child's room	0.3-0.7%
Game machine	2F bedroom	0.1%
Monitor phone	1F living room	6%

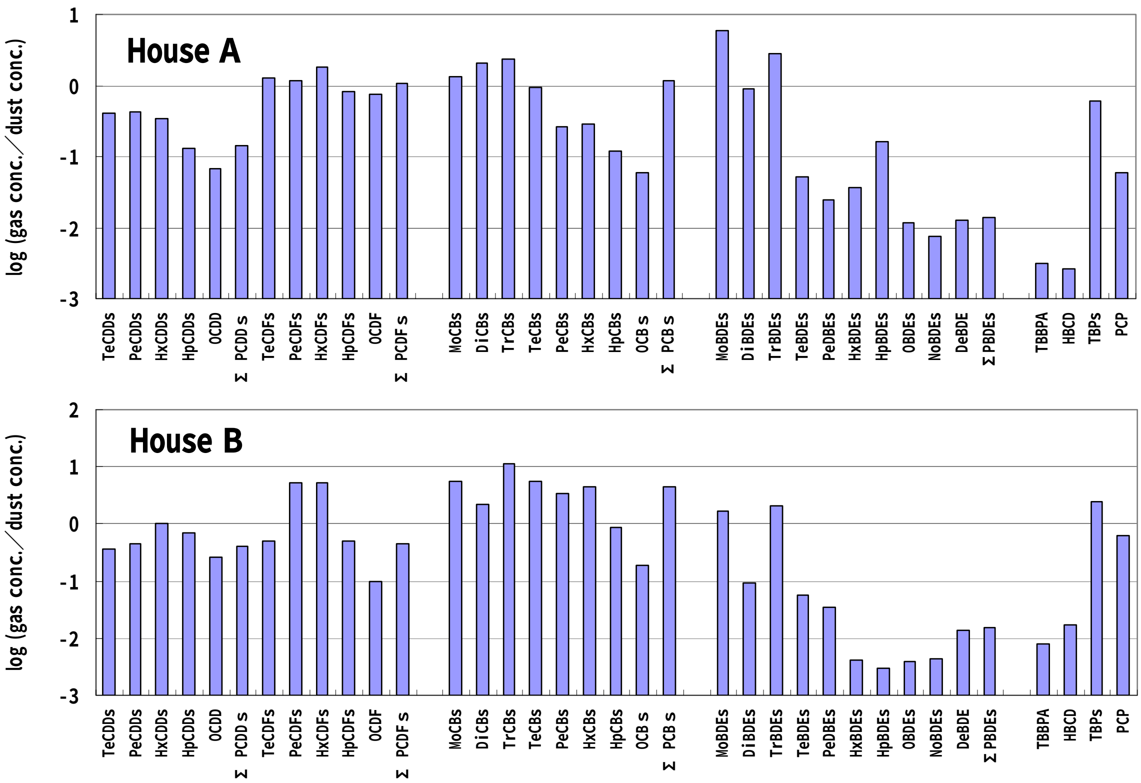

Fig. 1 Air/dust partition ratio values (log *K*ad) for the investigated organic halogenated compounds in two houses.