Behavior analysis and control of brominated flame retardants from household products using model rooms

Tomohiro KOSE[1], Hidetaka TAKIGAMI[1] and Shin-ichi SAKAI[2]

[1]National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba-City, Ibaraki, 305-8506 Japan
[2]Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto-City, Kyoto, 606-8501 Japan

Abstract
Many household products are treated with flame retardants for the purpose of prevention of fire. Home electronics appliances such as television sets or textile such as curtains contain brominated flame retardants (BFRs) at high concentrations. In this study, behavior of BFRs such as PBDEs and HBCDs emitted from flame retarded household products was investigated using actual room in the model house. The objectives of this study are (1) to determine the concentration of BFRs in indoor air, (2) to evaluate the partition behavior of BFRs among indoor air, house dust and adsorption to room floor and wall, (3) to evaluate efficiency of control methods to remove BFRs in indoor air. Two countermeasures for BFR control, recirculating ventilation through charcoal (to remove BFRs by adsorption) and air cleaner (to remove airborne dust in indoor air) were evaluated. Indoor air concentrations of PBDEs, PBDD/DFs, HBCDs and TBBPA were increased by placing household products in the chamber. Surface loading (i.e., deposition in the room and transfer to house dust) is important when considering indoor behavior of emitted PBDEs and HBCDs from products. Both recirculating ventilation through charcoal and air cleaner were effective methods to control PBDEs and HBCDs emitted from the products.

Introduction
Many household products are treated with flame retardants for the purpose of prevention of fire. Home electronics appliances such as television sets or textile such as curtains contain brominated flame retardants (BFRs) at high concentrations. This can engender high BFR concentrations in indoor air and dust, which are potential exposure media for humans[1,2]. Ingestion of indoor dust has been implicated by many studies[3-5] as an important exposure pathway of polybrominated diphenylethers (PBDEs). In the case of Japanese modern house, concentration of hexabromocyclododecanes (HBCDs) in house dust is two orders of magnitude higher than that of PBDEs[6]. Therefore, indoor behavior of these BFRs emitted from household products is of important concern to evaluate human exposure of BFRs. In a recent study, we clarified emission sources and emission factors of PBDEs and HBCDs[7]. However, subsequent indoor behavior and fate of emitted BFRs, especially partition between indoor air and dust still remains unclear.

In this study, behavior of BFRs such as PBDEs and HBCDs emitted from household products was investigated using actual room in the model house. The objectives of this study are (1) to determine the concentration of BFRs in indoor air, (2) to evaluate the partition behavior of BFRs among indoor air, house dust and adsorption to room floor and wall, and (3) to evaluate efficiency of control methods to remove BFRs in indoor air. Two countermeasures for BFR control, recirculating ventilation through charcoal to remove BFRs by adsorption and air cleaner to remove house dust in indoor air were evaluated.

Materials and methods
Two flooring-type rooms (room 1: 11.3 m^2, 22.4 m^3, room 2: 11.3 m^2, 21 m^3) in a general model house were used as test cambers. The type II ventilation (mechanical air supply with natural exhaustion of room air) was adopted for the two rooms. Approximately 1,000 kg of charcoal made from bamboo was placed in air supply pathway to each room to supply clean air. Ventilation rate in the both chambers was 0.5 h^{-1}. Three tests, 'blank test', 'recirculating ventilation test' and 'air cleaner test' were carried out in this study. Experimental period of the three tests was 6, 12 and 12 days, respectively.

No products were placed in both rooms to determine back ground concentrations of BFRs in a blank test. Air supply was stopped and its openings were sealed to prevent the influence of recirculating ventilation.
During 'recirculating ventilation test' and 'air cleaner test', 40% of the exhaust was recirculated through air

supply pathway. In this recirculating pathway, intaked outdoor air and recirculated indoor air were mixed and passed through in an air supply pathway through charcoal.

Several products were placed in one room (room 1) as BFR sources. Four television (TV) sets, three personal computers (PCs) and three curtains were selected as flame retarded household products. Layout of the products in the rooms was shown in Figure 1. Bromine content of household products analyzed by a handheld X-ray fluorescence spectrometer (Innov-X α6500, Innov-X Systems Inc.) and detailed information on products were shown in Table 1. These products were placed in room 1 during 'recirculating ventilation test' and 'air cleaner test'. TV sets and PCs were actually operated for 8 hours per day. Non-flame-retarded carpet was placed in both rooms as a dust source. Fan-type air cleaner (Ryoushitsu Kukan, Duskin, Japan) equipped with HEPA filter and activated carbon filter was also placed in the both rooms. The cleaner was operated during 'air cleaner test' to evaluate the BFR removal efficiency of air cleaner.

During each test period, approximately 2,000 m^3 of outdoor and indoor air samples were collected by high volume air sampler equipped with quartz filter and polyurethane foam in each test. Strips of wall paper (100 cm x 100 cm, two pieces) and floor board (30cm x 180 cm, two pieces) were placed in both rooms during two tests. To evaluate floor and wall surface loadings of BFRs including deposition of house dust and sorption onto the surface of floor/wall, house dust and wiped samples were collected in rooms 1 and 2. House dust samples were collected by a vacuum cleaner equipped with poly flon filter at the end of 'air cleaner test'. Wiped samples were collected from the strips of housing materials by cotton prewashed by acetone and toluene. Collected samples were extracted to analyze polyhalogenated compounds (PHCs), such as PBDEs, hexabromocyclododecanes (HBCDs), tetrabromobisphenol A (TBBPA), chloro- and bromophenols (CPhs and BPhs), polybrominated dibenzo-*p*-dioxins/dibenzo furans (PBDD/DFs). For house dust and wiped samples, only PBDEs and HBCDs were analyzed, because of the limitation of available sample amount. These compounds except for HBCDs were analyzed by GC (GC6890, Agilent) with HRMS (Autospec Ultima, micromass). HBCDs were analyzed by LC (LC-20A, Shimadzu)/MS (API 3200, Applied Biosystems).

Table 1 Detailed information and Br content of products

product name	manufacturing year	manufacturer	product type	handheld XRF	
				measurement part	Br(%)
TV1	1988	HITACHI	21inch CRT	front side of cabinet	9.3
				rear side of cabinet	12
TV2	1996	FUNAI	19inch CRT	front side of cabinet	<0.0005
				rear side of cabinet	7.8
TV3	1998	TOSHIBA	25inch CRT	front side of cabinet	16
				rear side of cabinet	16
TV4	2008	SHARP	25inch LCD	front side of cabinet	<0.0005
				rear side of cabinet	<0.0005
PC1	2002	NEC	LPX desktop PC with LCD	cabinet	<0.0005
				front side of LCD cabine	12
				rear side of LCD cabinet	13
PC2	2003	emachine	MATX desktop PC with LCD	cabinet	6.4
				front side of LCD cabine	<0.0005
				rear side of LCD cabinet	<0.0005
PC3	2008	TOSHIBA	notebook PC	keyboard side	<0.0005
				bottom side	<0.0005
				top side of LCD	<0.0005
curtain1	2008	Kawashima orimono	1800 mm×2100 mm	inside	<0.0005
curtain2	2008	unknown	1800 mm×2100 mm, two	inside	3.5
carpet	2008	unknown	1800 mm×1800 mm	surface	<0.0005
air cleaner	2008	Duskin		cabinet	<0.0005

< value: not detected. Values denote LOD.

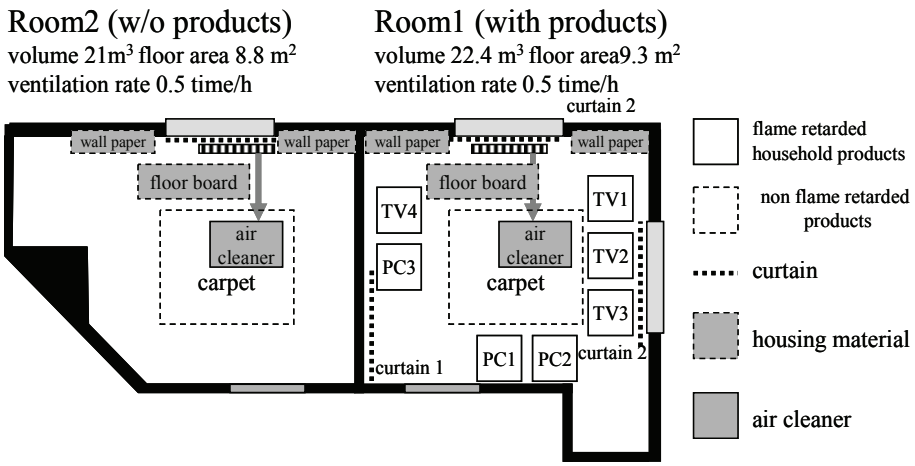

Figure 1 Layout of household products in the rooms

Results and discussion

Figure 2 shows a change in the concentrations of PHCs in room 1 during a series of tests. Concentrations of individual PBDE congeners and HBCD isomers in air samples were shown in Table 2. Indoor air concentrations of PBDEs, PBDD/DFs, HBCDs and TBBPA in blank test were the same level as those in outdoor air and the room has no apparent emission sources of these compounds. On the other hand, indoor air concentrations of BPhs and CPhs in blank test were significantly higher than those in outdoor air. Therefore, these compounds could be derived from unknown emission sources in the room (house).

Indoor air concentration of PBDEs in 'recirculating ventilation test' (2,400 pg/m^3) is three orders of magnitude higher than that in outdoor air. This value is higher than the values in house or office environment reported by Shoeib et al.[8] and our result seems to be a worst case. According to our recent study, TV sets and PCs are major emission sources of PBDEs[7]. Therefore, high indoor air concentration of PBDEs could be due to the TV sets and PCs in the room. Indoor air concentration of HBCDs in 'recirculating ventilation test' (900 pg/m^3) is two orders of magnitude higher than that in outdoor air, which is also higher than those reported by Shoeib et al.[8] Indoor air concentrations of PBDD/DFs, TBBPA and BPhs also showed a significant increase when products were put in the room. These compounds seem to have their emission sources in products.

Indoor air concentrations of PHCs further decreased in 'air cleaner test'. The decreasing ratio of the concentrations compared to 'recirculating ventilation test' for PBDEs, HBCDs, TBBPA, PBDD/DFs, BPhs and CPhs were 12, 40, 83, 25, 49 and 65%, respectively. The efficiency of the air cleaner regarding removal of those compounds is varying depending on the compounds, however, the cleaner used have worked effectively to a certain extent to control PHCs in indoor air.

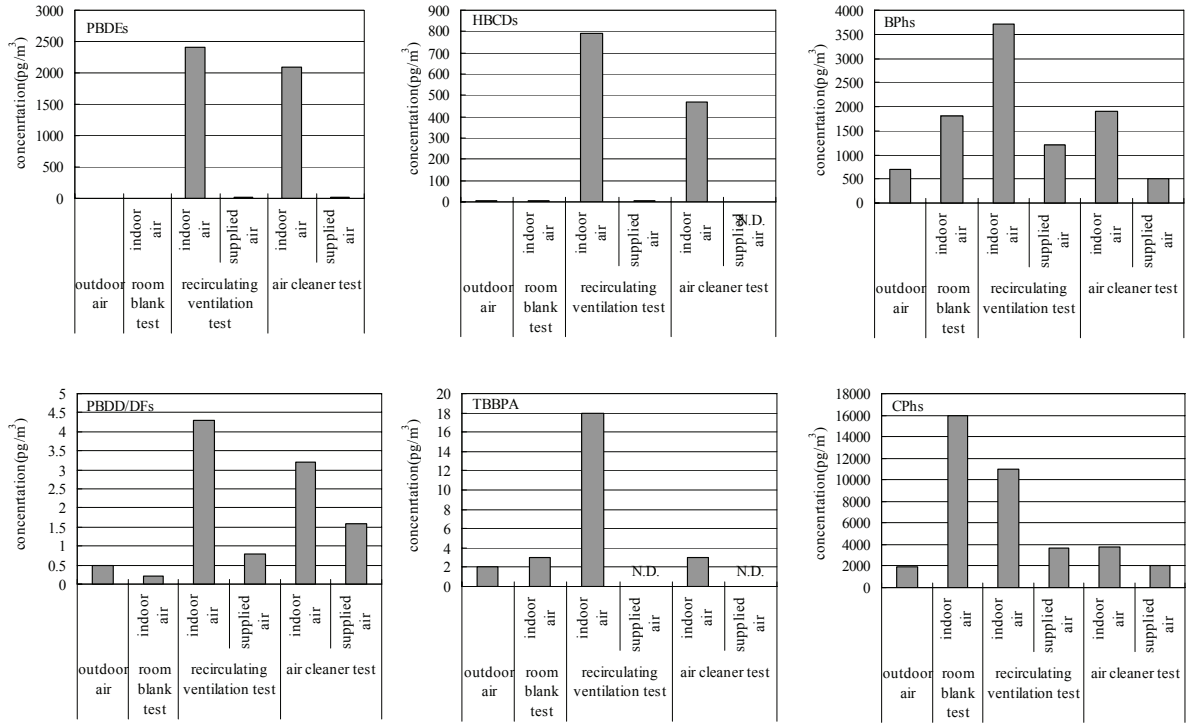

Figure 3 Changes in the concentration of persistent organic pollutants during chamber tests

Table 2 Concentrations of PBDE congeners and HBCD isomers in air, wiped and house dust samples

		recirculating ventilation test		air cleaner test		wiped sample from wall paper		wiped sample from floor board		house dust	
		indoor air	supplied air	indoor air	supplied air						
	outdoor air	room1	room1	room1	room1	room 1	room 2	room 1	room 2	room 1	room 2
	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^2	ng/m^2	ng/m^2	ng/m^2	ng/g	ng/g
PBDEs											
MoBDEs	<0.005	<0.005	<0.005	<0.005	<0.005	<10	<10	<10	<10	<20	<20
DiBDEs	0.0024	0.4	0.0051	0.31	0.0064	1	<1	1	<1	<2	<2
TrBDEs	0.003	0.94	0.0038	0.91	0.0065	2	<1	28	<1	16	<2
TeBDEs	0.0016	0.91	0.0016	0.77	0.0024	3	<1	87	<1	110	4
PeBDEs	<0.0005	0.11	0.0005	0.095	<0.0005	<1	<1	19	<1	46	4
HxBDEs	<0.0005	0.02	<0.0005	0.015	<0.0005	<1	<1	3	<1	15	4
HpBDEs	<0.002	<0.002	<0.002	<0.002	<0.002	<4	<4	<4	<4	13	14
OBDEs	<0.005	<0.005	<0.005	<0.005	<0.005	<10	<10	<10	<10	60	100
NBDEs	<0.02	<0.02	<0.02	<0.02	<0.02	<40	<40	<40	<40	2200	1500
DeBDE	<0.05	<0.05	<0.05	<0.05	<0.05	100	<100	300	100	25000	15000
total-PBDEs	0.007	2.4	0.011	2.1	0.015	110	<100	440	100	27000	17000
HBCDs											
α-HBCD	<0.002	0.081	0.006	0.036	<0.002	<7	14	23	<3	5200	1400
β-HBCD	<0.001	0.004	<0.002	<0.002	<0.002	<6	<7	7	<3	1300	300
γ-HBCD	0.004	0.71	<0.002	0.43	<0.002	<7	<8	18	<3	1800	500
total-HBCDs	0.004	0.79	0.006	0.47	N.D.	<7	14	48	<3	8300	2200

<value :not detected. Value denotes LOD.

Wiped samples from strips of housing material and house dust samples were collected at the end of 'air cleaner test'. Therefore, these samples represent adsorption onto housing material surface and deposition of house dust during two tests and interval period (26 days in total). Concentrations of PBDEs and HBCDs in wiped sample collected from wall paper in both rooms were around or below the limit of detection (LOD) as shown in Table 2. Likewise, no significant surface loading on floor board was observed in room 2. On the other hand, from floor board in room 1, PBDEs and HBCDs were detected at 440 ng/m^2 and 48 ng/m^2, respectively Direct floor surface loading rates (from wipe test results, excluding house dust) of PBDEs and HBCDs could be estimated from

concentrations in wiped samples from floor board. From the analytical results shown in Table 2 and floor area of room 1 (9.3 m^2), direct floor loadings of PBDEs and HBCDs in room 1 were calculated as 3,200 ng (120 ng/day) and 450 ng (17 ng/day), respectively.

House dust collected from room 2 contains PBDEs and HBCDs in spite of no apparent emission source in this room. The reason is not clear, however, two rooms are neighboring and there is a possibility that house dust emitted from room 1 may be transported to room 2 through this pathway. 0.20 g and 0.27 g of house dusts were collected from room 1 and 2, respectively. Overall deposition amount of PBDEs and HBCDs in house dust in room 1 were 5,400 ng and 1,700 ng. Therefore, deposition rate of PBDEs and HBCDs in house dust were estimated to be 210 ng/day and 65 ng/day.

The congener patterns of PBDEs were quite different between indoor air and, wiped and house dust samples. DecaBDE was not detected from indoor air, while it is a predominant congener in wiped and dust samples from the floor. The isomer patterns of HBCDs in wiped and dust samples are slightly different from those in indoor air. α and β-HBCDs are rather dominant in wiped and dust samples.

Overall emission amount of PBDEs and HBCDs from products is a sum of floor surface loading (including wiped and house dust fractions) and emission into indoor air. 930 ng of PBDEs and 250 ng of HBCDs per day were emitted from products placed. Figure 4 shows partition characteristics of emitted PBDEs and HBCDs from products in room 1 through 'recirculating ventilation test' and 'air cleaner test'. Contribution ratio of floor surface loading to totally emitted amount of PBDEs and HBCDs were around 30 %. Therefore, floor surface loading is also an important pathway of the emission of these compounds as well as indoor air.

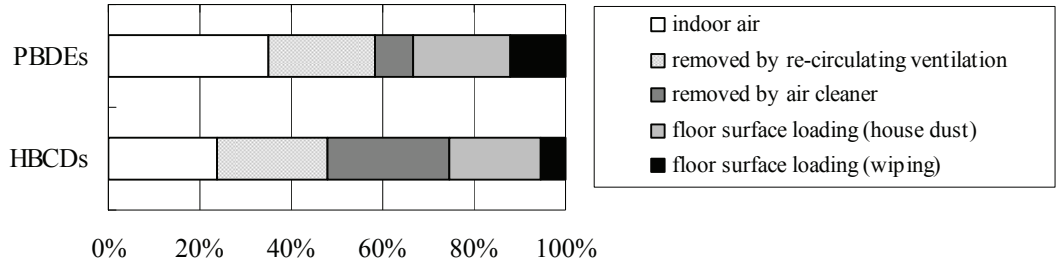

Figure 4 Partition characteristics of PBDEs and HBCDs in room 1

Removal efficiency of PBDEs and HBCDs by recirculating ventilation through charcoal could be estimated from the mass balance in the ventilation pathway expressed by the following equation.

$$S = C_{\sup ply} V_{\sup ply} - \left(\sum C(n)_{room} V(n)_{recycle} + C_{out} V_{\text{int}ake} \right)$$

where, S (pg/h) is a removal efficiency of recirculating ventilation. $C(n)_{room}$ (pg/m^3) is a concentration of a compound in room n. $V(n)_{recycle}$ (m^3/h), V_{supply} (m^3/h) and V_{intake} (m^3/h) are volume of recirculated air from room n, volume of air supply to room n and volume of air intake from outdoor, respectively. C_{out} (pg/m^3) and C_{supply} (pg/m^3) are concentrations of compounds in outdoor air and supplied air, respectively. Estimated removal efficiency of PBDEs and HBCDs by recirculating ventilation was calculated as 230 ng/day and 78 ng/day, respectively.

Difference in indoor air concentrations of the compounds between 're-circulating ventilation test' and 'air cleaner test' could be simply supposed by an additional removal by the air cleaner. Based on this, calculated removal efficiencies of PBDEs and HBCDs by the air cleaner were 81 ng/day and 86 ng/day, respectively.

Figure 4 also shows removal efficiency of recirculating ventilation and air cleaner. Recirculating ventilation remove approximately 24 % of emitted PBDEs and HBCDs. This result showed that recirculating ventilation is effective to the removal of both PBDEs and HBCDs. On the other hand, air cleaner could remove 8 % and 27 % of emitted PBDEs and HBCDs, respectively. This result showed that the applied two countermeasures could

control PBDEs and HBCDs in indoor air...

PBDEs, PBDD/DFs, HBCDs and TBBPA have their emission sources in the loaded products. Floor surface loading was important in terms of exposure of PBDEs and HBCDs emitted from products as well as indoor air. Both recirculating ventilation through charcoal and air cleaner were effective countermeasures to control PBDEs and HBCDs.

Acknowledgement
This study was supported by Japan Ministry of the Environment Grant-in-Aid for Scientific Research (K2062) "3R-Scenario Analysis of Persistent Toxic Chemicals from Household Waste Materials."

References
1. Allen, J.G., McClean, M.D., Stapleton, H.M., Nelson, J.W. and Webster, T.F. *Environ Sci technol* 2007; 41: 4574
2. Allen, J.G., McClean, M.D., Stapleton, H.M., Webster, T.F. *Environ Sci technol* 2008; 42: 4222
3. Jones-Otazo, H.A., Clarke, J.P., Diamond, M.L., Archbold, J.A., Ferguson, G., Harner, T., Richardson, G.M., Ryan, J.J. and Wilford, B. *Environ Sci Technol* 2005; 39: 5121
4. Wilford, B.H., Shoeib, M., Harner, T., Zhu, J. and Jones, K.C. *Environ Sci Technol* 2005; 39: 7027
5. Harrad, S., Hazrati, S. and Ibarra, C. *Environ Sci Technol* 2006; 40: 4633
6. Takigami, H., Suzuki, Go., Hirai Y. and Sakai, S. *Chemosphere* 2009; 76: 270
7. Kose, T., Suzuki, G., Kajiwara, N., Takigami, H. and Sakai, S. *Organohalogen Compounds* 2008; 70: 2035
8. Shoeib M., Harner T., Ikonomou M. and Kannan K. *Environ Sci Technol* 2004; 38: 1313