DETERMINATION OF THE EMISSION AMOUNT OF ORGANIC POLLUTANTS FROM HOUSEHOLD PRODUCTS USING A MODEL ROOM

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Introduction

To improve physical/chemical properties of polymer materials, some organic additives are used for products. Especially for fire safety, brominated and/or phosphorous organic compounds are widely used as flame retardants for polymer materials in various products, such as buildings, interiors, textile products, and home electronic products. A survey of indoor air in houses and laboratories showed that the concentrations of polybrominated diphenyl ethers (PBDEs) in indoor air were significantly higher than those in outdoor air.[1] Additionally, some phosphorous flame retardants (PFRs) were also reported to be detected in air samples from schools, offices, electronics and furniture stores.[2,3]

Emission behavior of persistent organic pollutants including brominated flame retardants (BFRs) in the indoor environment has been studied using a stainless chamber[4] and actual houses[5] so far. An emission test using an inert stainless chamber can estimate a mass balance of the pollutants including the adsorbed and deposited amounts, however, chemical characteristics of its floor and wall surface are far from those in actual houses. Contrarily, it is also difficult to identify the source of pollutants in houses furnished and equipped with various products due to the existence of enormous unknown pollution sources.

In this study, a blank room in the model house was used as an experimental chamber. Several selected household products containing flame retardants were placed in the chamber to determine the origin and emission behavior of organic pollutants including BFRs and PFRs.

Materials and Methods

Chamber test procedure

A flooring type room (floor area: 11.3 m^2, room space: 23 m^3) in a general model house was used as a test chamber. The room adopted the type III ventilation (mechanical exhaustion and natural aspiration of the air). Ventilation rate of the chamber was 4.3 times/h. Three television sets (TV sets), two personal computers and a copying machine containing brominated compounds such as BFRs were selected as electronic products. Three curtains containing BFRs, a blanket and a mattress were also selected as textile products. Chamber test was carried out from August to November 2007. Three product-loaded tests were conducted, which were the blank test without placing any household products (blank test), the test loaded with home electronic products (test A) and that with both home electronic and textile products (test B) The layout drawing of the chamber room and products installed is shown in Figure 1. Detail information of household products is shown in Table 1.

Sample collection and analytical procedure

Bromine and phosphorous contents in household products were analyzed with a handheld X-ray fluorescence spectrometer (Innov-X α6500, Innov-X Systems Inc.) by the RoHS/WEEE and soil mode, respectively. Outdoor and indoor air samples were collected by high volume air sampler for the measurement of PBDEs, hexabromocyclododecanes (HBCDs), tetrabromobisphenol A (TBBPA), tribromophenols (TrBPhs), polybrominated dibenzo-p-dioxins and furans (PBDD/Fs) and polychlorinated biphenyls (PCBs). These compounds were analyzed by HRGC (Agilent 6890, Agilent) with HRMS (Autospec Ultima, micromass). PFRs in indoor air samples were collected by a low volume air sampler and analyzed by GC/QMS (Agilent 5973A, Agilent). In addition, as shown in Figure 2, emission samplers were attached directly to the surface of household products during the chamber tests to determine emission fluxes of PBDEs and HBCDs from them.

Table 1 Detail information on the loaded household products

Household products	Products category	Products detail	Year of manufacture	Surface area (cm^2)	Element content		P
					Br		
TV1	home electorics products	29inch television	1996	11000	front 64 ppm	rear 14%	N.A.
TV2		21inch television	1998	11000	front 15%	rear 15%	N.A.
TV3		20inch television	1994	8400	front 11%	rear 13%	N.A.
PC1		desktop PC	2003	3800	N.A.		N.A.
		17inch CRT	1996	7400	N.A.		N.A.
PC2		desktop PC	2002	3000	N.A.		N.A.
		19inch CRT	1998	10000	N.A.		N.A.
copying machine		copying machine	1998	25000	8.4%		N.A.
mattress	textile products	spring mattress	unknown	19000	N.D.		N.A.
blanket		chemical textile blanket	2007	28000	N.D.		N.D.
curtain 1		black curtain	2007	50000	3.5%		N.D.
curtain 2		flesh color curtain	2007	36000	front 8.8%	rear 9.4%	N.D.
curtain 3		green curtain	2007	36000	front 1.7%	rear 1.7%	N.D.

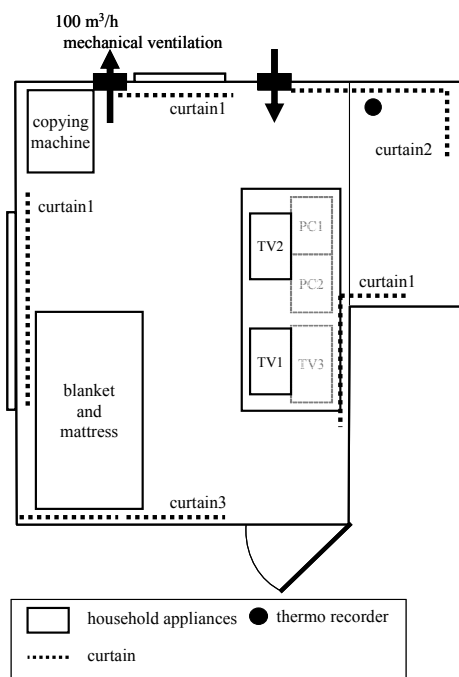N.D. : not detected

N.A. : not analyzed

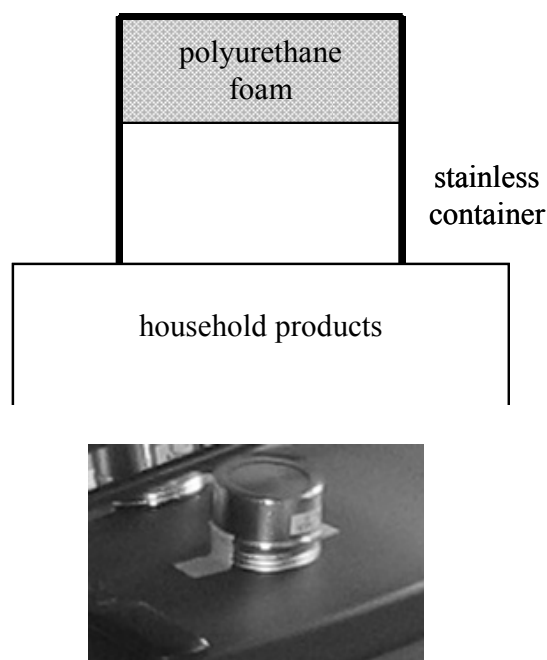**Figure 1 Layout of household products in a chamber room**

Figure 2 Schematic diagram and picture of an emission sampler

Results and Discussion

Contaminant source of organic pollutants

Figure 3 shows a change in concentrations of the investigated organic pollutants in the indoor and outdoor air samples during a series of chamber tests. Concentrations of HBCDs, TBBPA, TrBPhs and PCBs in indoor air

were higher than those in outdoor air in the blank test. These compounds probably have their pollution sources in the chamber room itself. On the contrary, concentrations of PBDEs and PBDD/Fs in outdoor air in the blank test were higher than those in indoor air, which means PBDE and PBDD/F concentrations were not influenced by the housing materials.

Concentrations of PBDEs, TBBPA, TrBPhs, PCBs and PBDD/Fs in the indoor air showed a significant increase when home electronic products were placed in the room (Figure 3). Therefore, these compounds probably have their emission sources in home electronic products. On the other hand, concentration of HBCDs increased with the load of textile products, suggesting that HBCDs were derived from the textile products. Concentration of PFRs in indoor air did not increase with the installation of any household products. However, these concentrations were almost the same as those in offices, electronics and furniture stores (n=8, median value: 49 ng/m^3) reported to possess sources of PFRs by Hartmann et al.[3] Therefore, the installed products were not the sources of PFRs, and may have their contaminant source in the chamber room itself.

Concentrations of PBDEs, TBBPA, TrBPhs, PCBs and PBDD/Fs in the indoor air during test B were slightly lower than those for test A. Average room temperature in the chamber on October 2 (at the end of test A) and November 1 (at the end of test B) were 25.2°C and 21.6°C, respectively. Therefore, decreases in concentrations of these compounds in indoor air could be due to a decline of room temperature.
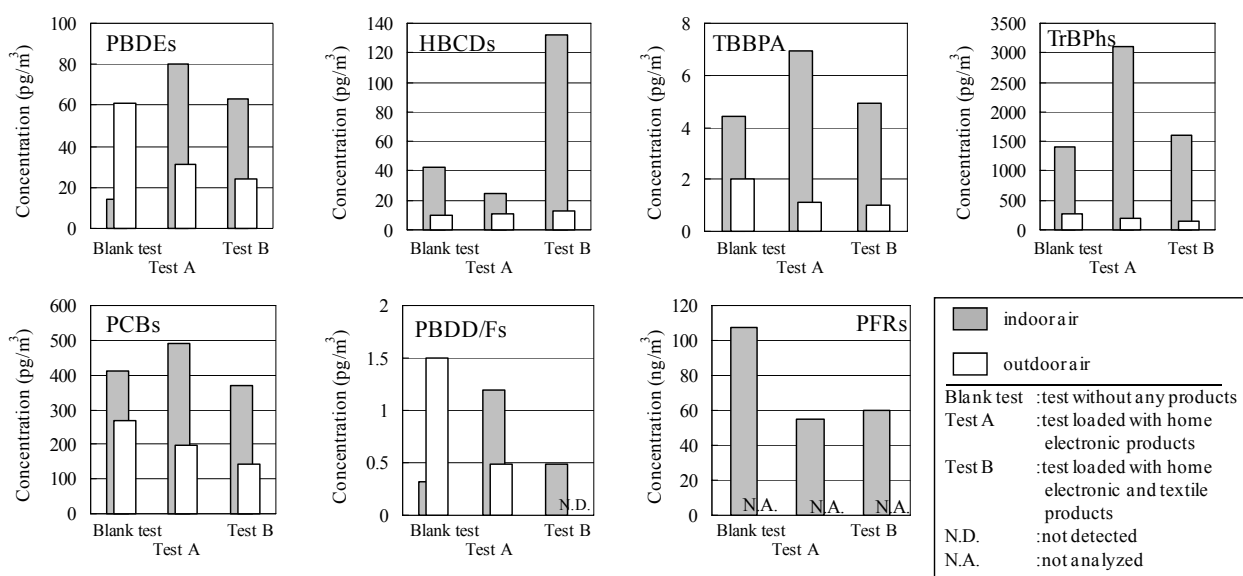

Figure 3 Change in the concentrations of the investigated organic pollutants in indoor and outdoor air during the chamber tests

Emission factors of PBDEs and HBCDs
Area specific emission rate EF_a was denoted as equation (1).

$$EF_a = (C_{load} - C_{blank})\frac{nV}{A} \tag{1}$$

where, C_{load} and C_{blank} (pg/m^3) are concentrations of the target compound in indoor air with and without the loaded product, respectively, n (times/h) is a ventilation rate, V (m^3) is volume of chamber and A (m^2) is surface area of the loaded product.

EF_a for PBDEs and HBCDs estimated was summarized in Table 2, based on the hypothesis that PBDEs and HBCDs were emitted only from TV sets and curtains, respectively. Annual emission factors, EF (/year) of PBDEs from TV sets and HBCDs from curtains were estimated by equation (2)

$$EF = \frac{EF_a A_n}{M_n C_{BFR}}$$
<div align="right">(2)</div>

where, A_n (m^2) is surface area of the product, M_n (pg) is weight of flame-retarded materials in product and C_{BFR} (-) is a concentration of BFRs in materials. Average values of EF TV sets and curtains were summarized in Table 2. For this estimation, it was assumed that the weight of the cabinet of TV and curtain were 2 kg and 1.2 kg, respectively. Hirai et al.[4] reported that EF for PBDEs from each of three TV sets was in the range of 7.1×10^{-7} – 4.8×10^{-6} /year. These values were slightly higher than that obtained in this study as shown in Table 2. Hirai et al. [4] also reported that almost all the emitted PBDEs were adsorbed or deposited on the surface of chamber, especially for high (five or larger) brominated congeners. EF shown in Table 2 was estimated from concentration of PBDEs only in indoor air and could not reflect adsorbed or deposited fraction. On the other hand, emission fluxes of PBDEs determined by emission sampler from TV sets were ranged from 6,000 to 21,000 pg/m$^2\cdot$h. These values were three to ten times larger compared to EF_a shown in Table 2. This result suggests that most of emitted PBDEs were adsorbed or deposited on the surface of the chamber. Average value of EF for HBCDs estimated from indoor air concentration was 6.1×10^{-7}. The emission fluxes of HBCDs determined by emission sampler from curtains were ranged from 13,000 to 140,000 pg/m$^2\cdot$h. This values were 15 to 160 times larger compared to EF_a shown in Table 2. Therefore, emitted HBCDs also adsorbed or deposited on the surface of chamber and adsorption or deposition of HBCDs may be more significant compared to PBDEs.

Table 2 Emission rates of PBDEs from TV sets and HBCDs from curtains.

		C_{blank} pg/m^3	C_{load} pg/m^3	EF_a pg/m$^2\cdot$h	EF /year
PBDEs	TV sets	14	80	2000	6.7×10^{-8}
HBCDs	curtains	25	130	850	6.1×10^{-7}

In conclusion, the concentrations of PBDEs, TBBPA, TrBPhs, PCBs and PBDD/Fs in the indoor air showed a significant increase when home electronic products such as TV sets and computers were placed in the room, while HBCD concentrations increased with the load of curtains. Gas-phase EF of PBDEs from a TV set and that of HBCDs from a curtain to indoor air were estimated at the orders of 10^{-8} /year and 10^{-7} /year, respectively.

References
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