EMISSION RATE OF HEXABROMOCYCLODODECANE (HBCD) FROM THE SURFACE OF A FLAME RETARDED CURTAIN IN JAPAN

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Abstract
Emission rates of hexabromocyclododecane (HBCD) at ordinary temperature (10–40ºC) from a flame-retarded curtain with HBCD were estimated by the Arrhenius plot. A preliminary health risk assessment for HBCD emitted from the surface of curtain was carried out with exposure calculation tools such as MCCEM and E-FAST. A margin of exposure (MOE) of 5.4×10^8 may indicate no concern for consumers when using HBCD-containing curtain due to the sufficiently greater MOE than an uncertainty factor (UF) of 100.

Introduction
Hexabromocyclododecane (HBCD) is a group of additive brominated flame retardants (BFRs) that are widely used in expandable polystyrene (EPS), extruded polystyrene (XPS), high impact polystyrene (HIPS), and polymer dispersion for textiles[1]. The major commercial preparations of HBCD are composed of the three diastereomers, termed α- β- and γ-HBCD[2]. Approximately 3,200 metric tons of HBCD technical preparations were used in Japan in 2007[3]. The main use of HBCD (80%) is in polystyrene (EPS and XPS), and approximately 20% of the total use of HBCD is in textiles in Japan[3]. Toxicological studies have demonstrated that adverse health effects such as increase of thyroid and liver weight (NOAEL: no observed adverse effect = 10.2 and 22.6 mg/kg bw/day)[4,5] and decrease of trabecular bone mineral density of the tibia (BMDL: benchmark dose lower confidence bound = 0.056 mg/kg bw/day)[6] occurred in rats after HBCD exposure. Furthermore, the widespread application, environmental persistence and bioaccumulative potential of HBCD resulted in the global occurrences of HBCD in biota[7,8] and environmental media[9,10].
In the present study, we determined the concentrations of HBCD isomers in a flame-retarded curtain and emission rate of HBCD from the surface of curtain. In addition, a preliminary health risk assessment for HBCD emitted from the surface of curtain was carried out with the observed emission rate and exposure calculation tools such as E-FAST (Exposure and Fate Assessment Screening Tool) and MCCEM (Multi-Chamber Concentration and Exposure Model).

Materials and Methods
Curtain sample and HBCD content. A flame-retarded curtain with HBCD that have been used for over a decade was used in this study. The curtain was flame retarded and manufactured in Japan. The curtain size and weight are 2.00 m × 3.40 m and 2075 g, respectively. The determination of HBCD content in the curtain was performed according to an established in-house method. Briefly, the sample cut into pieces was completely-dissolved with 20 mL hexafluoroisopropanol. One mL of the solution was diluted 50 times in dichloromethane, and then spiked with $^{13}C_{12}$-γ-HBCD as internal standard. The resin of curtain in the diluted solution was precipitated by adding 9 mL methanol. After centrifugation, the supernatant was mixed and shaken with 200mL 10% sodium chloride aqueous solution and 50 mL n-hexane. The hexane layer was concentrated and passed through pre-conditioned florisil cartridge. The target analyte was eluted by 10% diethyl ether/hexane, and then concentrated under high-purity nitrogen after adding 80% methanol aqueous.
Sampling method for determination of HBCD emission rate from curtain. A typical procedure to measure the HBCD emission rate from curtain was carried out as follows. Samples were cut into 0.5 g of pieces and put into headspace vials. After sealing, the vials were placed into a temperature-controlled chamber (50–150ºC). High-purity nitrogen (200mL/min, 3h) was passed through the vials, and thermally-emitted HBCD in the headspace of vials was then trapped in a solid-phase extraction (SPE) cartridge (ABS Elut NEXUS, 200 mg / 6 mL, Varian). The target analyte was eluted by acetone after adding $^{13}C_{12}$-γ-HBCD as internal standard.

Schematic illustration of experimental apparatus for determining HBCD emission rate from curtain is shown in Figure 1.

Analytical procedures for HBCD. HBCD including α-HBCD, β-HBCD, and γ-HBCD were determined by HPLC-MS/MS quantification. Briefly, a liquid chromatograph (Shimazu Prominence, Shimazu Co., Kyoto, Japan) interfaced with a mass spectrometer (API4000, Applied Biosystems, Foster City, CA) was used in the negative atmospheric pressure chemical ionization mode (APCI). A 10 μL aliquot of the sample extract was injected onto a L-column2 ODS (2.1mm i.d.×150mm length, 3 μm; Chemicals Evaluation and Research Institute, Tokyo, Japan) with 5mM ammonium acetate aqueous solution (solvent A) and acetonitrile (solvent B) as mobile phases, starting at 80% acetonitrile. At a flow rate of 200 μL/min, the gradient was increased to 100% acetonitrile at 10 min, and was kept at that level until 15 min before reversion to original conditions, at the 20-min time point. Column temperature was kept at 40ºC. MS/MS was operated under multiple reaction monitoring (MRM) mode.

Quality assurance and quality control (QA/QC). QA/QC protocols included the analysis of matrix spikes and procedural blanks. Peaks were identified by comparison of the retention times of samples to standards if the signal-to-noise (S/N) ratio was >3, and were quantified if target/qualifier ion ratios were within 15% of the theoretical values. Recoveries of the internal standard ($^{13}C_{12}$-γ-HBCD) in this study were 87.8–105%.

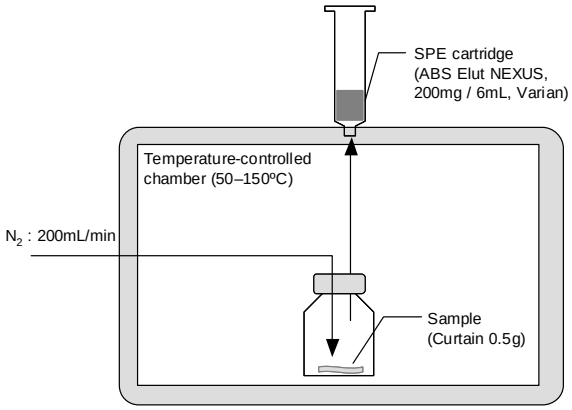

Figure 1 Schematic illustration of experimental apparatus for determining HBCD emission rate from curtain

Results and Discussion

HBCD content in curtain. Concentrations and distribution of α-HBCD, β-HBCD, γ-HBCD, and ΣHBCDs in the curtain are given in Table 1. The concentrations of α-HBCD, β-HBCD, γ-HBCD, and ΣHBCDs in the curtain were 340, 150, 1000, and 1500 μg HBCD/g curtain, respectively. The distribution of α-HBCD, β-HBCD, and γ-HBCD in the curtain were 23, 10, and 67%, respectively. Peled *et al.* have reported that distributions of α-HBCD, β-HBCD, and γ-HBCD in commercial preparations ranged from 11.3 to 13.3%, 9.5 to 11.7%, and 72.3 to 77.0%, respectively[11]. Therefore, the distribution of HBCD isomers in the curtain used in this study was similar to those in commercial preparations.

Table 1 Concentrations and distributions of HBCD isomers in the curtain

	α-HBCD	β-HBCD	γ-HBCD	ΣHBCDs
HBCD concentration (μg HBCD/g curtain)	340	150	1000	1500
Distribution of isomers (%)	23	10	67	100

Determination of HBCD emission rate from curtain. Emission rates of α-HBCD, β-HBCD, γ-HBCD, and ΣHBCDs from curtain at 50–150ºC are given in Table 2. The emission rates of HBCDs at 50–80ºC were not determined because HBCDs in the samples were all below the detection limit in the above method, whereas those over 90ºC were exponentially increased with increasing temperature. Arrhenius plot shown in Figure 2 was made for estimating the emission rates of HBCD at ordinary temperature (10–40ºC):

$$k = Ae^{\frac{-E}{RT}} \quad \text{.....} (1)$$

where k (ng/h/cm^2) is the emission rate of HBCD, A (ng/h/cm^2) is the pre-exponential factor, E (kJ/mol) is the apparent activation energy, R (kJ/mol/K) is the gas constant, and T (K) is the absolute temperature. The Arrhenius plot exhibited good linearity (R^2 = 0.996), and the apparent activation energy E and the pre-exponential factor A calculated from the intercept and slope of Arrhenius plot was 160 kJ/mol and 6.45×10^{21} ng/h/cm^2, respectively. Emission rates of HBCD at 10–40ºC estimated by the Arrhenius plot are given in Table 3.

Table 2 Observed emission rates of HBCD at 50–150ºC

Temperature (ºC)	α-HBCD (ng/h/cm^2)	β-HBCD (ng/h/cm^2)	γ-HBCD (ng/h/cm^2)	ΣHBCDs (ng/h/cm^2)
50	<0.01	<0.01	<0.01	<0.01
60	<0.01	<0.01	<0.01	<0.01
70	<0.01	<0.01	<0.01	<0.01
80	<0.01	<0.01	<0.01	<0.01
90	0.02	<0.01	0.05	0.07
90	0.02	<0.01	0.04	0.07
110	0.23	0.09	0.62	0.94
130	5.7	1.7	9.2	17
150	53	13	27	93
150	89	20	39	150

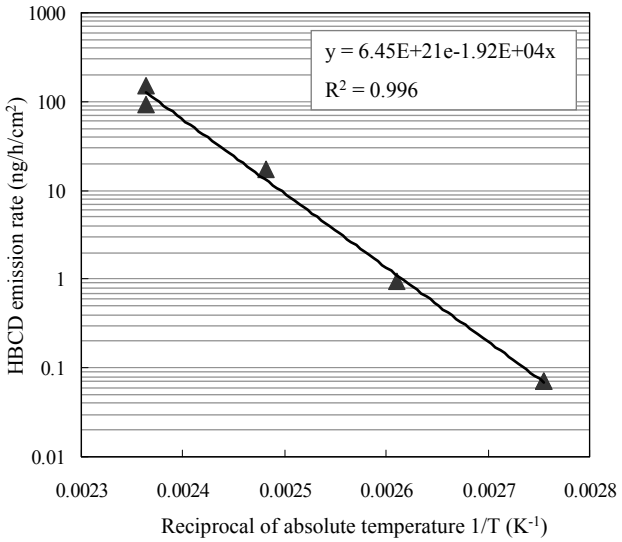

Figure 2 Relationships between reciprocal of absolute temperatures (T^{-1}) and HBCD emission rates.

Table 3 Emission rate of HBCD at 10–40ºC estimated by Arrhenius equation (Figure2)

Temperature (ºC)	Emission rate* (ng/h/cm^2)	(mg/h)
10	2.21E-08	1.51E-09
20	2.24E-07	1.51E-08
30	1.95E-06	1.33E-07
40	1.48E-05	1.00E-06

* The emission rate of HBCD was calculated from the observed emission rate at 90–150ºC described in this study.

Thermal rearrangement of HBCD. Distributions of HBCD isomers before and after thermal processing are shown in Figure 3. Due to increasing temperature, the respective distributions of α-HBCD and γ-HBCD changed from 23 to 60% and 67 to 26%, whereas no significant differences in β-HBCD distributions that were 10–14% were observed. In addition, the distributions of HBCD isomers with increasing temperature gradually approached to those in thermal equilibrium that were 78% for α-HBCD, 13% for β-HBCD, and 9% for γ-HBCD[11]. These results indicated the principal mechanism on thermal rearrangement of HBCD with easy conversion from γ-HBCD to α-HBCD.

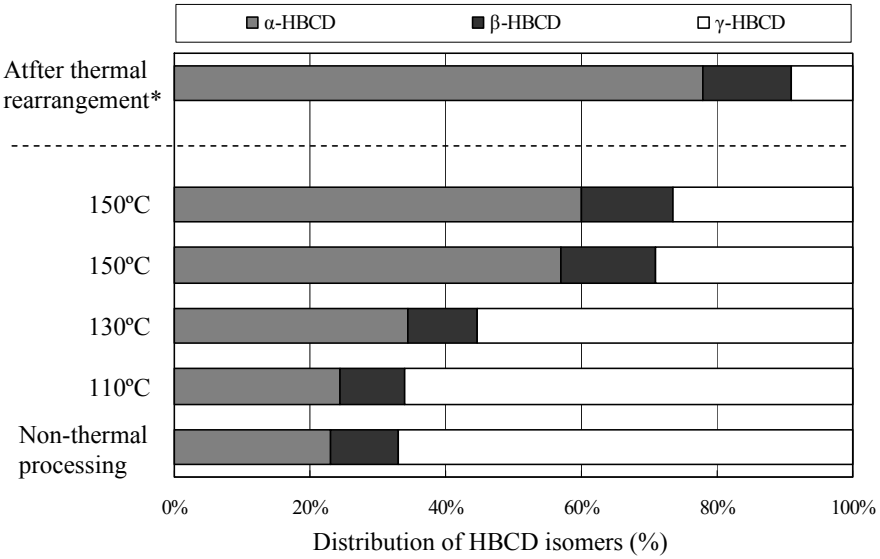

Figure 3 Distribution of HBCD isomers before and after thermal processing
***** Peled *et al.* have reported distribution of HBCD isomers after thermal rearrangement.

Exposure and health risk assessment of HBCD in a room. A preliminary health risk assessment for HBCD emitted from the surface of curtain was carried out with exposure calculation tools such as MCCEM and E-FAST authorized by the US Environmental Protection Agency (U.S.EPA). Lifetime average daily dose (LADD) in MCCEM was calculated from the emission rate observed in this study, whereas that in E-FAST was calculated from the molecular weight and vapor pressure of HBCD[12,13]. Input parameters for the calculations are given in Table 4, and room size, room volume, and air exchange rate were set to be 5.25 m × 3.80 m × H 2.70 m, 53.9 m^3, and 0.45 h^{-1}, respectively.

Completely different LADDs of HBCD that were 1.04×10^{-10} mg/kg bw/day for MCCEM and 5.86×10^{-4} mg/kg bw/day for E-FAST were observed for calculations with MCCEM and E-FAST. In E-FAST, HBCD having lower vapor pressure than 6.68×10^{-5} Pa was out of target for accurate calculation because general target was a solid air freshener has a greater volatility than that of HBCD. Therefore, the LADD obtained with E-FAST was extrapolated from the data calculated with higher vapor pressure than 6.68×10^{-5} Pa. In contrast, the LADD obtained with MCCEM would be relatively accurate due to the usage of observed emission rate.

The lowest reported NOAEL or BMDL for HBCD was 0.056 mg/kg bw/day[6]. A margin of exposure (MOE) was calculated by dividing the BMDL for HBCD by the LADD obtained with MCCEM. A MOE of 5.4×10^{8} may indicate no concern for consumers when using HBCD-containing curtain due to the sufficiently greater MOE than an uncertainty factor (UF) of 100, accounting for a ten-fold uncertainty factor of interspecies extrapolation and a ten-fold uncertainty factor for interindividual susceptibility in humans. In a calculation, deriving lower MOE than UF of 100 was required to be over 111ºC for room temperature.

Although the MOE regarding a limited exposure scenario obtained in this study was sufficiently greater than an uncertainty factor, registering HBCD as substances of very high concern from its candidate list established by The European Chemicals Agency has been prioritized based on its hazardous properties, the volumes used, and the likelihood of exposure to humans or the environment[14]. Furthermore, Takigami *et al.* have reported the very persistent and very accumulative of HBCD in house dust[15] that was not considered in our study. Therefore, further studies are needed to evaluate the human health and environmental risks for exposures to HBCD.

Table 4 Input parameters for calculating lifetime average daily dose (LADD, mg/kg bw/day) using MCCEM and E-FAST

MCCEM			**CEM in E-FAST**		
Emission model		Constant	**Emission senario**		Product placed in room environment
Constant emission rate*	mg/h	1.51E-08	**HBCD molecular weight**	g/mol	641.7
			HBCD vapor pressure**	Pa	6.27E-05
			Mass of product	g	2075
Duration of event	h/event	24	**Duration of event**	h/event	24
Inhalation rate	m^3/day	15	**Inhalation rate**	m^3/day	15
Frequency of event	event/year	365	**Frequency of event**	event/year	365
Exposure duration	year	60	**Exposure duration**	year	60
Body weight	kg	71.8	**Body weight**	kg	71.8
Length of life	year	75	**Length of life**	year	75

* The constant emission rate of HBCD at 20ºC was calculated from the observed emission rate at 90–150ºC described in this study

** HBCD vapor pressure is that at 21 ºC reported by Stenzel and Nixon, 1997.

Acknowledgments
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