EXPOSURE TO HEXABROMOCYCLODODECANE (HBCD) EMITTED INTO INDOOR AIR BY DRAWING FLAME RETARDED CURTAIN

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Abstract
Total amount and peak concentrations of hexabromocyclododecane (HBCD) isomers emitted into indoor air by drawing a flame-retarded curtain were observed. A preliminary health risk assessment for HBCD emitted by drawing the curtain was carried out with an exposure calculation tool (MCCEM). A margin of exposure (MOE) of 2.1×10^5 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 observed fibers and dusts attached to the surface of a flame-retarded curtain, and determined the concentrations of HBCD isomers in the fibers and dusts. In addition, exposure estimation to HBCD emitted into indoor air by drawing the curtain was carried out with an exposure calculation tool (MCCEM: Multi-Chamber Concentration and Exposure Model).

Materials and Methods
Curtain sample. A flame-retarded curtain with HBCD that have been used for over a decade was used in this study. The curtain was made of polyester fiber, and flame retarded and manufactured in Japan. The curtain size and weight are 2.00 m × 3.40 m and 2075 g, respectively. We have reported that 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[11].
Procedures for observing fiber shape and HBCD concentration in dust attached to curtain. The observation of fiber shape of dust attached to the curtain and determination of HBCD concentration in the dust were performed according to an established in-house method. Briefly, the surface of curtain (225 mm × 173 mm) was vacuumed by a pump (DOP-40D, ULVAC) connected with PTFE membrane filter (0.2 μm, ADVANTEC). Fiber shapes of dust on the filter were observed under an optical microscope (VH-8000, KEYENCE). Target analyte on the filter was then extracted with 20 mL hexafluoroisopropanol. A part of the extract was spiked with $^{13}C_{12}$-γ-HBCD as internal standard. After dilution with 9 mL methanol, liquid-liquid extraction was performed by adding 200 mL 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 concentration in indoor air after drawing curtain. A procedure to determine HBCD concentrations in indoor air after drawing the curtain was carried out as follows. Before sampling, air in a measurement room shown in Figure 1 was replaced with sufficient volume of cleaned air with hepafilter and activated carbon filter. One of high-volume air samplers was placed at each corner of the measurement room to determine the total amount of HBCD emitted by drawing the curtain. Another high-volume air sampler was placed in the vicinity of curtain to determine peak concentrations of HBCD. Air samples after 5 opening and closing procedures of the curtain were collected with the high-volume air samplers with a glass fiber filter and two polyurethane foams. The sampling flow rate was 700 L/min, and the respective sampling times near the curtain and at each corner were one minute and one hour. After sampling, the glass fiber filter and polyurethane foams were extracted with dichloromethane and acetone, respectively. A mixture of these extracts was spiked with $^{13}C_{12}$-γ-HBCD as internal standard. The solution 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.

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 and recoveries of the internal standard ($^{13}C_{12}$-γ-HBCD) in this study were over 45.0%.

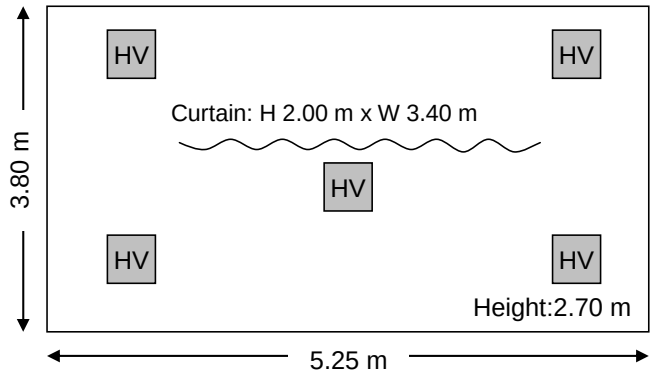

Figure 1 Schematic diagram illustrating the measurement room. HV: high-volume air sampler

Results and Discussion

Fiber shape and HBCD concentration in dust attached to curtain. Micrographs of the surface of the curtain, a grass fiber filter in blank, a polyester fiber derived from the curtain, and other fibers and dusts are shown in Figure 2. No ragged area was observed on the surface of the curtain due to the stability of polyester fiber fabric. Only a few fibers were identified by the color and thickness of polyester fiber as the fiber derived from the curtain. The fiber thickness was approximately 10 μm. In addition, the concentrations of α-HBCD, β-HBCD, γ-HBCD, and ΣHBCDs in the fibers and dusts attached to the curtain were 24, 8.3, 59, and 91 ng/m^2, respectively. Total amount of HBCD isomers on the surface of the curtain (6.8 m^2) was calculated to be 620 ng.

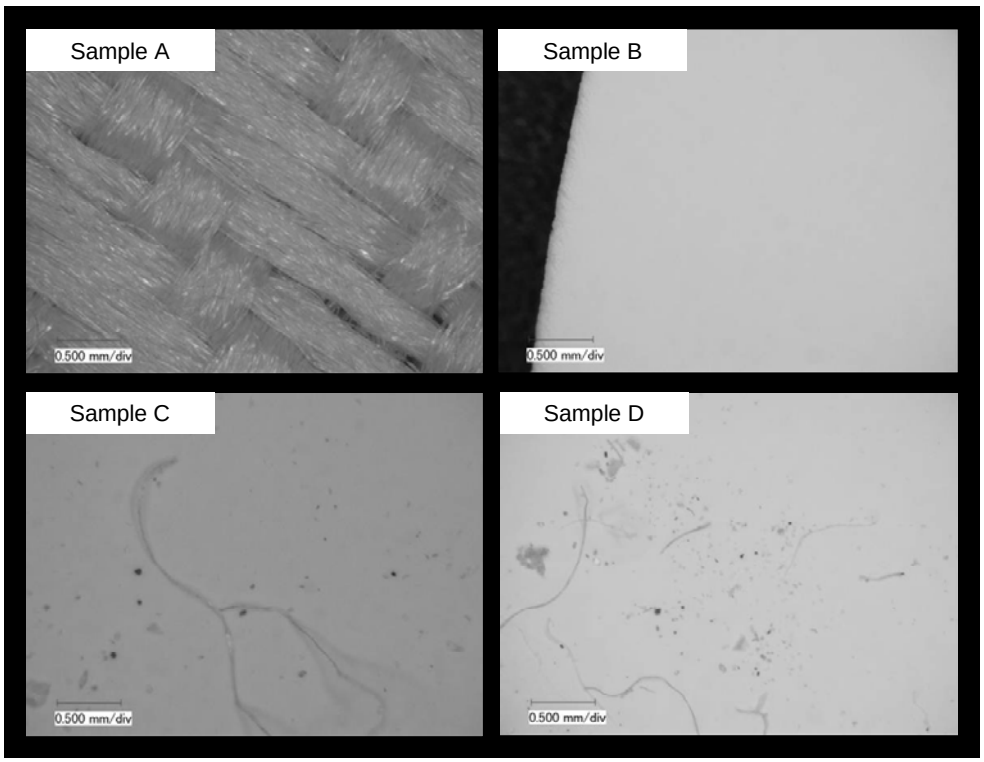

Figure 2 Micrographs of (A) the surface of curtain, (B) grass fiber filter in blank, (C) a polyester fiber derived from the curtain, and (D) other fibers and dusts.

HBCD concentration in indoor air after drawing curtain. Concentrations of HBCD isomers in indoor air obtained from one hour measurement after drawing the curtain ranged from 0.042 to 0.15 ng/m^3 for α-HBCD, 0.012–0.041 ng/m^3 for β-HBCD, 0.052–0.25 ng/m^3 for γ-HBCD, and 0.11–0.45 ng/m^3 for ΣHBCDs (Table 1). The total amount of HBCD isomers were estimated from multiplying the concentrations of ΣHBCDs by the total sampling volume of four air samplers at the corners (168 m^3 = 0.7 m^3/min × 60 min × 4 unit), because the total of sampling volume, was approximately four-fold room volume (53.9 m^3), was sufficiently greater than the room volume. Therefore, the total amount of HBCD emitted by opening and closing procedures of the curtain were calculated at 10^1–10^2 ng order.

Table 1 Concentrations and total amount of HBCD in indoor air obtained from one hour measurement after drawing the curtain

Run	α-HBCD	β-HBCD	γ-HBCD	ΣHBCDs	
	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng)
1	0.15	0.041	0.25	0.45	76
2	0.042	0.012	0.052	0.11	19
3	nq**	nq	nq	nq	–

* Limit of detection (LOD): 0.002 ng/m^3

** na: not quantified due to low recovery of internal standard

Peak concentrations of HBCD isomers obtained from one minute measurement in the vicinity of the curtain ranged from 0.90 to 3.9 ng/m^3 for α-HBCD, 0.30–1.4 ng/m^3 for β-HBCD, 1.4–8.3 ng/m^3 for γ-HBCD, and 2.7–14 ng/m^3 for ΣHBCDs (Table 2). The peak concentrations of HBCD isomers were approximately 30 times higher than the concentrations described in Table 1. In addition, the peak concentrations observed in this study were over ten times higher than those in indoor air of two houses in Japan, which ranged from 0.0067–0.28 ng/m^3 for ΣHBCDs[12], reported by Takigami *et al.* The distributions of HBCD isomers in indoor air after drawing the curtain shown in Figure 3 were similar in all samples.

Table 2 Peak concentrations of HBCD after drawing the curtain.

Run	α-HBCD (ng/m^3)	β-HBCD (ng/m^3)	γ-HBCD (ng/m^3)	ΣHBCDs (ng/m^3)
1	3.9	1.4	8.3	14
2	0.90	0.30	1.4	2.7
3	2.5	0.90	5.7	9.1

* Limit of detection (LOD): 0.3 ng/m^3

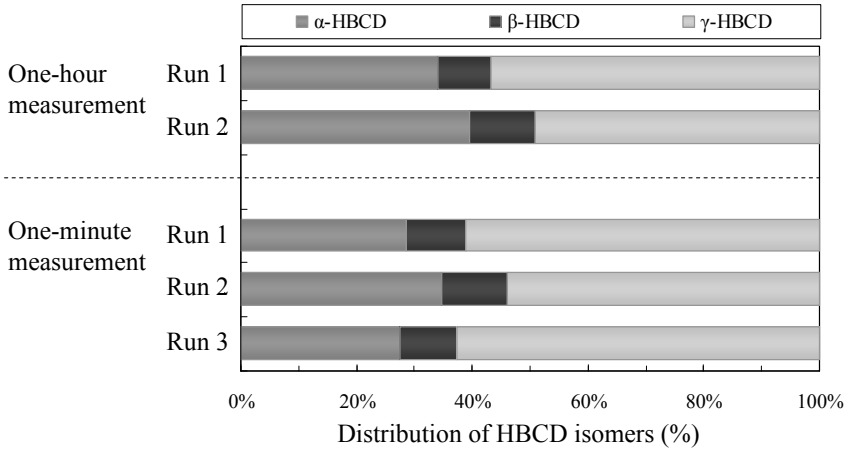

Figure 3 Distributions of HBCD isomers in indoor air after drawing the curtain.

Exposure and health risk assessment of HBCD emitted from the curtain in a room. A preliminary health risk assessment for HBCD emitted into indoor air by drawing the curtain was carried out with an exposure calculation tool (MCCEM) authorized by the US Environmental Protection Agency (U.S.EPA). Lifetime average daily dose (LADD) in MCCEM was calculated using an emission rate estimated from the observed average peak concentration that was 8.6 ng/m^3 for ΣHBCDs. Input parameters for the calculations are given in Table 3, 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.

The LADD of HBCD was calculated to be 2.67×10^{-7} mg/kg bw/day. 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 2.1×10^5 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.

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[13]. Furthermore, Takigami *et al.* reported the very persistent and very accumulative of HBCD in house dust[12] 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 3 Input parameters for calculating lifetime average daily dose (LADD, mg/kg bw/day) using MCCEM

Input parameter		
Emission model		Constant
Constant emission rate*	mg/h	3.05E-02
Duration of event	min/event	1
Inhalation rate	m^3/day	15
Frequency of event	event/day	2
Exposure duration	year	60
Body weight	kg	71.8
Length of life	year	75

* The constant emission rate of HBCD was calculated from the observed peak concentrations after drawing the curtain described in this study.

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