A COMPARATIVE STUDY OF HUMAN HEALTH RISKS POSED BY A FLAME RETARDED CURTAIN WITH HEXABROMOCYCLODODECANE (HBCD)

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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].

The inhalation exposure scenarios via dust and indoor air have been previously evaluated in our studies[11,12]. In this study, we determined the amount of HBCD isomers on the hand after drawing a flame-retarded curtain. In addition, a preliminary health risk assessment for HBCD in the curtain was carried out.

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].

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 84.7–103%.

Results and Discussion

Main exposure scenarios to HBCD. Schematic outline of main exposure scenarios to HBCD for consumer are shown in Figure 1. The inhalation exposure scenarios via dust and indoor air have been previously evaluated in our studies[11,12]. In this study, lifetime average daily dose (LADD) by dermal exposure via direct contact with the curtain and ingestion exposure via hand-to-mouth contact were calculated based on default values in these exposure scenarios described in the literatures[13,14].

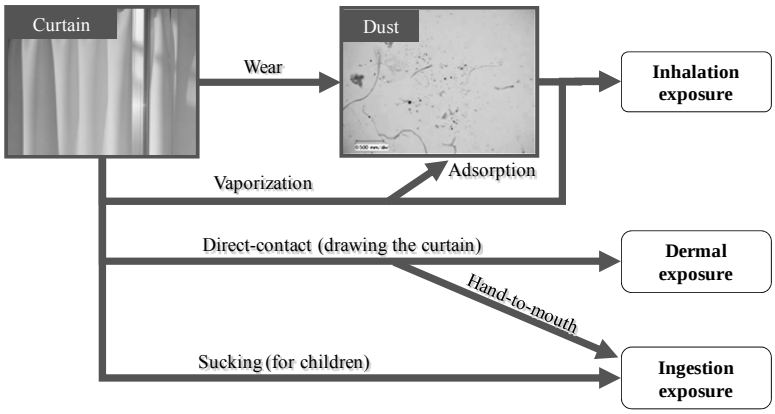

Figure 1 Schematic outline of the main exposure scenarios for consumer

Dermal exposure via direct contact with the curtain. The amounts of HBCD isomers on the hand after drawing the flame-retarded curtain were determined in triplicate. The amounts of ΣHBCD attached on the hand were 0.9±0.6 ng-HBCD (Table 1). The LADD by the dermal exposure via direct contact with the curtain was calculated by assigning default values shown in Table 2 to the equation (1)[13]:

$$LADD_{Dermal} = A_{HBCD} \times EV \times DAF \div BW \quad \ldots\ldots(1)$$

The LADD by the dermal exposure was calculated to be 2.5×10^{-9} mg/kg bw/day.

Table 1 The amounts of ΣHBCD attached on the hand

Run	α-HBCD (ng)	β-HBCD (ng)	γ-HBCD (ng)	ΣHBCDs (ng)
1	0.3	＜0.1	0.4	0.7
2	0.3	0.1	1.3	1.6
3	＜0.1	＜0.1	0.4	0.4

Ingestion exposure via hand-to-mouth contact. The LADD by the ingestion exposure via hand-to-mouth contact in the same sequence, was calculated by assigning default values shown in Table 2 to the equation (2)[13]:

$$LADD_{Hand-to-mouth} = A_{HBCD} \times EV \times HTME \times F_g \times FT \div BW \quad \ldots\ldots(2)$$

The LADD by the ingestion exposure via hand-to-mouth contact was calculated to be 2.3×10^{-9} mg/kg bw/day. The LADDs by the dermal exposure via direct contact and the ingestion exposure via hand-to-mouth contact were comparable. However, these values were 100-fold lower than the LADD by the inhalation exposure of dust (2.7×10^{-7} mg/kg bw/day)[12].

Table 2 Summary of default value used in this study

		Unit	Default value
Amount of HBCD on the hand*	A_{HBCD}	mg	0.9×10^{-6}
Contact Frequency with the surface	EV	day^{-1}	2
Body weight	BW	kg	71.8
Dermal absorption efficiency	DAF	unitless	0.1
Hand-to-mouth events	HTME	unitless	3
Fraction of available dermal area that contacts mouth	F_g	unitless	0.1
Fraction of dust or chemicals transferred from skin to mouth	FT	unitless	0.3

*: This value is the average amount of HBCDs on the hands after drawing a flame-retarded curtain.

Preliminary health risk assessment for HBCD. The lowest reported NOAEL or BMDL for HBCD was 0.056 mg/kg bw/day[6]. Margin of exposure (MOE) calculated by dividing the BMDL for HBCD by the LADDs calculated in this study were 2.2×10^7 for $LADD_{Dermal}$ and 2.5×10^7 for $LADD_{Hand\text{-}to\text{-}mouth}$. The MOEs of 2.2×10^7 and 2.5×10^7 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 (Figure 2).

Although the MOEs regarding a limited exposure scenario obtained in this study were 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. Therefore, further studies are needed to evaluate the human health and environmental risks for exposures to HBCD.

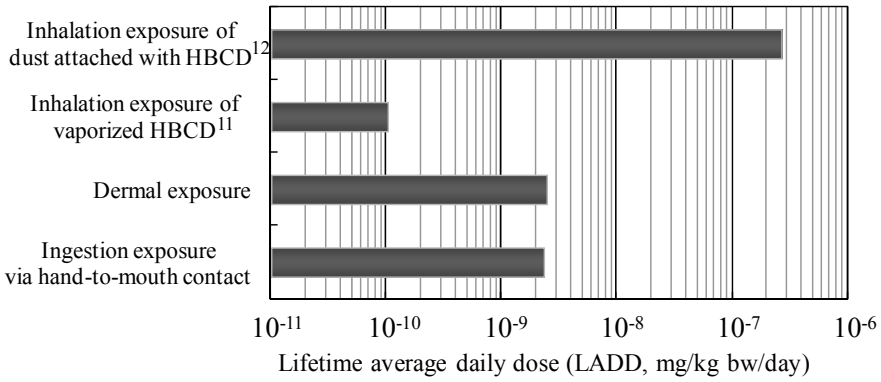

Figure 2 Lifetime average daily dose on the exposure scenarios for consumer

Acknowledgement

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