



Hexabromocyclododecanes in the indoor environment of two cities in South China: their occurrence and implications of human inhalation exposure

Jianwen Hong^{1,2,3}, Shutao Gao¹, Laiguo Chen⁴,
Qian Han^{1,2}, Zhiqiang Yu¹, Pingan Peng¹ and Jiamo Fu¹

Abstract

Indoor and outdoor air samples were collected from two industrialized cities (Guangzhou and Foshan) in Southern China to determine the concentrations and diastereoisomer profiles of hexabromocyclododecanes (HBCDs) in built environments. The mean concentrations of total HBCDs in air were 5.43 pg m⁻³ in homes, 8.21 pg m⁻³ in offices, 48.2 pg m⁻³ in other workplaces and 33.3 pg m⁻³ in the air outdoors. These HBCD levels are slightly higher than or comparable with those at the remote or urban sites in the United States, but are significantly lower than those in the European atmosphere. Diastereoisomer profiles of the samples indicated that α -HBCD was the dominant isomer, with a relative abundance ranging from 53.2% to 83.0%, which is notably different from its fractions in the air samples from the UK and the domestic technical-grade mixtures. Analysis of the gas-particle distribution showed that HBCDs were present predominantly (87.6–99.9%) in the particle phase. The estimated average daily human exposure to HBCDs via inhalation was 0.39 ng day⁻¹ for adults, which is one order of magnitude lower than the values (5.0 and 5.47 ng day⁻¹) for the UK adults reported in two other studies. Further air and dust sampling and continued monitoring are needed to improve our understanding of human exposure to HBCDs.

Keywords

Diastereoisomer profiles, Hexabromocyclododecane, Human exposure, Indoor air, Partition

Accepted: 5 July 2013

Introduction

As an additive flame retardant, hexabromocyclododecanes (HBCDs) are considered to be an alternative to the banned polybrominated diphenyl ether (PBDE) formulations, and are used primarily in extruded (XPS) and expanded polystyrene (EPS) for thermal insulation of buildings, in upholstery textiles, and, to a minor extent, in electrical household equipment.¹ Like PBDEs, HBCDs are not chemically bound to the flame-retarded materials, and thus can enter the environment during the manufacturing process of HBCD-containing products, during their use and service life, and after they have been disposed of as waste.² These migration routes combined with the widespread use of

¹State Key Laboratory of Organic Geochemistry, Guangdong Key Laboratory of Environment and Resources, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China

²University of Chinese Academy of Sciences, Beijing, China

³Guangdong Institute for Drug Control, Guangzhou, China

⁴Center for Research on Urban Environment, South China Institute of Environmental Sciences, SEPA, Guangzhou, China

Corresponding author:

Zhiqiang Yu, State Key Laboratory of Organic Geochemistry, Guangdong Key Laboratory of Environment and Resources, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China.
Email: zhiqiang@gig.ac.cn

and increasing demand for HBCDs make these chemicals ubiquitous in the environment. As a result, HBCDs are frequently detected in various environmental matrices and biota samples, such as air/dust, soil, sediment, fish, marine mammals and human tissues.^{1,3-4} At present, HBCDs are under the European chemicals management regulations (REACH) as substances of very high concern, and are currently under assessment for inclusion in the Stockholm Convention and in the United Nations Economic Commission for Europe Protocol on Persistent Organic Pollutants owing to their adverse health impacts in aquatic/terrestrial organisms and in humans.^{2,5}

Recent studies have indicated that release to the air is an important pathway by which HBCDs can enter the environment.^{6,7} However, to date, relatively few studies have been conducted on HBCDs in indoor air. The majority of previous studies have mainly focused on outdoor air from background locations in northern European countries⁸ and the United States,⁹ urban locations in European countries^{8,10} and China¹¹ and industrial locations.¹² The only available data for indoor environment were reported from UK¹⁰ and Japan.¹³

In 2010, the US Environmental Protection Agency initiated an exposure assessment of PBDEs and suggested that contact with house dust accounts for between 80% and 90% of total exposures, with the remainder due primarily to food ingestion.¹⁴ Because HBCDs and higher brominated diphenyl ethers have similar physicochemical properties, inhalation and ingestion might be critical routes for human exposure to indoor HBCDs.¹⁵ Roosens et al.¹⁶ also reported that positive correlations were found between HBCD concentrations in serum and indoor dust, whereas no correlation was observed with dietary exposure. Furthermore, some recent studies indicated that the role of dermal exposure via airborne (both gaseous and particle-bound) semi-volatile organic compounds (SVOCs) might have been previously underestimated.^{17,18}

In China, there is little information about the distribution and levels of HBCDs in the environmental matrices, in spite of the huge production capacity of HBCDs – an estimated 7500 tonnes in 2007.¹⁹ To date, only a few studies have reported concentration levels of HBCDs: in outdoor air,¹¹ sediment^{20,21} and soil.^{22,23} To our knowledge, no data have been published for the occurrence of HBCDs in the indoor environment, where most inhalation exposure takes place. The aim of this study was to investigate the concentrations and diastereoisomer profiles of HBCDs in indoor and outdoor air samples collected from a number of locations in two industrialized cities (Guangzhou and Foshan) in Southern China. Furthermore, the inhalation exposure to HBCDs was also preliminarily estimated.

Both cities are densely populated and have been undergoing rapid economic growths. Guangzhou is well known for the manufacture of electronics, automobiles and petrochemicals, while Foshan is well-known for its plastics industry, electronic and electrical equipment and indoor decorating and refurnishing materials.

Materials and methods

Sample collection

A total of 37 air samples (including gas and particle) were collected from Guangzhou and Foshan cities between October 2004 and April 2005. Detailed information about the sampling sites was described in our previous study.²⁴ To minimize the dilution effect caused by air sampling, the air sampling duration was controlled such that the sampling volume is equivalent to one home volume. The home was then allowed to re-equilibrate before another sample was taken. In brief, 12 homes (H1-H12), 16 workplaces (including 6 offices (O1-O6) and 10 other indoor workplaces (IN1-IN10)) and 9 outdoor sites were included for comparison in this study. Gas-phase HBCDs were sampled by using a high-volume sampler (Tianhong Intelligent Instrument Plant of Wuhan, China) with a 20.3 cm × 25.4 cm glass fibre filters (GFF; Whatman, EPM2000); particle-phase samples were collected with a 6.5 cm diameter × 7.5 cm thickness (with a density of 0.030 g cm⁻³) polyurethane foam (PUF) plugs. Indoor air samples were drawn at the floor level with total air volumes of ca. 175–385 m³ at a flow rate of 0.4–0.7 m³ min⁻¹ for 8–10 h. Outdoor air samples were drawn at 1.5 m height above ground for about 20 h with total air sample volumes of ca. 300–840 m³. At least one set of duplicate samples were collected for each home and analysed together with other field samples.

Materials

Non-labelled and ¹³C-labelled α -, β - and γ -HBCD were purchased from Cambridge Isotope Laboratories (Andover, MA). Commercial HBCDs were purchased from the marketplace in China. HPLC-grade methanol and acetonitrile were obtained from Merck (Darmstadt, Germany). Ammonium acetate was obtained from J.T. Baker (Phillipsburg, NJ). All of the solvents used for the extraction and cleanup were of analytical grade and were redistilled using a glass system. Prior to use, neutral silica gel (80–100 mesh) and alumina (100–200 mesh) were Soxhlet extracted with methanol and methylene chloride for

48 h, respectively. Sodium sulphate was baked at 450°C and stored in sealed containers.

Sample preparation and cleanup

Prior to use, the GFFs were baked at 450°C for 12 h to remove any organic contaminants, and PUF plugs were Soxhlet extracted for 48 h with methanol and a mixture of acetone/hexane (1:1, v:v). The procedures used for sample extraction and cleanup have been described in detail in our previous study.²⁵ In brief, the GFF filters and PUF plugs were spiked with PCB-209 and ¹³C-PCB-141 and then Soxhlet extracted for 72 h with a mixture of acetone:*n*-hexane mixture (1:1, v:v). Activated copper was added to remove elemental sulphur. Concentrated extracts were cleaned on multilayer silica/alumina columns (1-cm internal diameter) that had been wet-loaded sequentially with 6 cm of aluminium, 2 cm of silica gel, 5 cm of basic silica gel (3:1 silica gel:1 M NaOH, w/w), 2 cm of silica gel, 8 cm of acid silica gel (1:1 silica gel:sulphuric acid, w/w) and 2 cm of anhydrous Na₂SO₄ from the bottom to the top. Seventy millilitres of methylene chloride:*n*-hexane (1:1) was used as the eluent. The eluent was then concentrated to near dryness under a gentle nitrogen stream and redissolved in 200 μL of methanol. Ten millilitres of 500 μg L⁻¹ ¹³C-labelled α-, β- and γ-HBCD were added as an internal standard prior to diastereoisomer determination by liquid chromatography-tandem mass spectrometry (LC-MS/MS).

Instrumental analysis

Sample analysis was performed with an Agilent 1100 series liquid chromatograph (Agilent Technologies, Palo Alto, CA) coupled with an Applied Biosystems/Sciex API 4000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA) in electrospray ionization negative ion mode with multiple reaction monitoring. The injection volume was set at 10 μL and the flow rate at 0.5 mL min⁻¹. The [M-H]⁻ → Br⁻ transitions at *m/z* 640.8 → 79 and 652.8 → 79 were monitored for the three native and ¹³C-labelled HBCD isomers, respectively. MS/MS-optimized parameters for the three HBCD isomers have been described previously.²⁶

HBCD diastereoisomers were separated using a Zorbax SB-C18 reversed-phase column (4.6 × 250 mm, 5 μm, Agilent). The gradient mobile phase consisted of methanol (A)/acetonitrile (B)/water with 10 mM ammonium acetate in water (C). The flow rate was set at 0.5 mL min⁻¹. The gradient program started at an initial composition of 80:10:10 A/B/C (v/v) and was ramped to 50:40:10 A/B/C in 18 min, followed by 30:70 A/B at 23 min, held for 7 min, and then returned

to 80:10:10 A/B/C in 8 min. The column was equilibrated for a further 6 min.

Quality assurance/quality control

Field blanks were prepared by loading a PUF plug and a GFF filter to the sampler for 24 h during the sampling period with no air drawing through. The procedure blanks were also analysed sequentially with the samples. No analyte was detected in either the field blanks or the procedure blanks. Recovery experiments were performed at three concentration levels of 1, 4 and 10 ng by spiking nine clean GFF filters and nine PUF plugs with three ¹³C-labelled diastereoisomers. The recoveries were 75.0 ± 6.1%, 73.5 ± 5.3% and 75.6 ± 4.8% for α-, β- and γ-HBCD, respectively. All the samples were analysed in triplicate by LC-MS/MS. Concentrations were calculated using a six-point calibration standard curve with a concentration range of 2–100 μg L⁻¹. One 25 μg L⁻¹ HBCD standard mixture was injected to control instrumental sensitivity for each batch of 10 sample injections. Reported concentrations were not surrogate recovery corrected.

The differences in the diastereoisomer profiles of HBCDs between indoor and outdoor air samples were determined using one-way analysis of variance and least significant difference post hoc tests by SPSS 13.0 software, and statistical significance was defined as *p* < 0.05.

Results and discussion

Concentrations of HBCDs in indoor and outdoor air

The gas- and particle-phase concentrations of α-, β- and γ-HBCDs in indoor and outdoor air samples were all determined by LC-MS/MS, in this study. Table 1 summarizes the concentrations of α-, β- and γ-HBCD and total HBCDs (ΣHBCDs, including gas- and particle-phase) in indoor (including homes, offices and other workplaces) and outdoor air samples. As shown in Table 1, for indoor air, the ΣHBCDs mean concentrations were 5.43 and 8.21 pg m⁻³ for homes and offices, respectively, which are significantly lower than those in other workplaces with a mean value of 48.2 pg m⁻³. The highest concentration (246 pg m⁻³) of ΣHBCDs was detected in an office (O2) located in a large electrical appliances shop. This was probably due to the strong emissions from unknown sources of HBCDs in the office. Abdallah et al.¹⁰ and Takigami et al.¹³ have reported significantly higher levels of HBCDs in indoor air than in outdoor air. However, the opposite result was obtained in this study, whereby the mean concentration of ΣHBCDs in outdoor air was

Table 1. HBCD concentrations in indoor and outdoor air samples in this study.

Sampling type		Concentration (pg m^{-3})			
		α -HBCD	β -HBCD	γ -HBCD	Σ HBCDs
Homes, $n = 12$	Mean	3.89	0.58	0.96	5.43
	Standard deviation	1.86	0.30	0.78	2.73
	Median	4.78	0.73	0.92	6.65
	Minimum	0.72	0.07	0.10	0.89
	Maximum	6.03	0.87	2.83	8.47
Offices ^a , $n = 5$	Mean	5.45	1.05	1.72	8.21
	Standard deviation	2.22	0.85	1.92	4.64
	Median	4.31	0.63	0.97	6.43
	Minimum	3.15	0.44	0.45	4.05
	Maximum	8.39	2.52	5.05	16.0
Other workplaces, $n = 10$	Mean	35.0	5.62	7.57	48.2
	Standard deviation	24.8	4.74	5.99	34.8
	Median	29.4	4.75	5.72	39.6
	Minimum	7.73	1.13	1.15	10.0
	Maximum	87.5	17.4	19.9	125
Outdoor, $n = 9$	Mean	20.6	4.23	8.40	33.3
	Standard deviation	16.7	3.74	8.24	28.1
	Median	16.1	2.90	5.21	24.2
	Minimum	4.84	1.06	2.79	8.69
	Maximum	54.4	11.5	25.7	85.3

HBCD: hexabromocyclododecane.

^aThe highest concentration (up to 246 pg m^{-3}) of Σ HBCDs was not included.

33.3 pg m^{-3} , slightly lower than that in other workplaces, but significantly higher than those in homes and offices.

To date, information on the levels of HBCDs in indoor and outdoor air is scarce. In this study, the concentrations of Σ HBCDs in indoor air in homes and offices were significantly lower than those reported in homes ($67\text{--}1300 \text{ pg m}^{-3}$) and offices ($70\text{--}460 \text{ pg m}^{-3}$) in Birmingham, UK,¹⁰ but comparable with those from two homes ($6.7\text{--}280 \text{ pg m}^{-3}$) in Japan.¹³ The concentration levels of Σ HBCDs in other workplaces (mean value 48.2 pg m^{-3}) in this study were also one order of magnitude lower than those in the public microenvironments (mean value 900 pg m^{-3}) in Birmingham, UK.¹⁰ In the outdoor air, the mean concentration of Σ HBCDs in this study was 33.3 pg m^{-3} , comparable with those from Birmingham, UK (37 pg m^{-3}).¹⁰ Remberger et al. reported atmospheric HBCDs concentrations ranging from 2 to 280 pg m^{-3} at remote sites in northern Sweden and Finland, and 76 to 610 pg m^{-3} in urban air in Stockholm, Sweden.⁸ In addition, HBCDs concentrations of up to $150,000,000 \text{ pg m}^{-3}$ were detected in plants manufacturing XPS foam in Norway.¹² In summary, the concentration levels of HBCDs in indoor and outdoor air in this study were

noticeably lower than those in the European atmosphere. This may be due to the fact that HBCDs were used to replace the penta- and octa-BDE flame retardant products in Europe much earlier than in other countries elsewhere in the world, and also because the HBCD consumption in Europe accounted for more than half of the world market demand, according to a technical report.²⁷

Diastereoisomer profiles

Table 2 summarizes the diastereoisomer profiles of HBCDs in indoor and outdoor air samples in this study. As shown in Table 2, there are noticeable differences in the diastereoisomer profiles of HBCDs observed in indoor and outdoor air samples. To examine whether this difference was statistically significant, the relative abundances (%) of α -, β - and γ -HBCD as fractions of Σ HBCDs were compared. The results showed that α -HBCD was the dominant isomer in indoor air samples, with a relative abundance ranging from 56.3% to 83.0% (mean value 73.6%), much higher than its abundance (53.2–70.4%, mean value 62.3%) in outdoor air samples ($p < 0.01$). However, the reverse trend was exhibited for γ -HBCD, which

Table 2. Diastereoisomer profiles of HBCD in indoor and outdoor air samples in this study.

Sampling type		Relative abundance (%)		
		α -HBCD	β -HBCD	γ -HBCD
Homes, $n = 12$	Mean	73.8	10.4	15.3
	Standard deviation	7.1	1.4	6.9
	Median	73.5	10.6	14.3
	Minimum	56.3	8.2	7.2
	Maximum	83.0	12.7	33.4
Offices, $n = 6$	Mean	73.7	11.6	14.7
	Standard deviation	10.6	1.3	10.1
	Median	79.5	11.4	9.8
	Minimum	56.6	10.1	6.4
	Maximum	81.3	13.8	29.6
Other workplaces, $n = 10$	Mean	73.2	11.5	15.4
	Standard deviation	6.8	2.3	5.4
	Median	74.2	11.9	14.0
	Minimum	56.5	7.5	9.1
	Maximum	79.8	14.4	29.1
Outdoor, $n = 9$	Mean	62.3	12.6	25.2
	Standard deviation	6.0	1.8	5.9
	Median	63.7	12.6	22.8
	Minimum	53.2	9.0	18.5
	Maximum	70.4	14.7	34.2

HBCD: hexabromocyclododecane.

had a mean relative abundance of 15.2% (ranging from 6.4% to 33.4%) in indoor air samples, as compared with the mean value 25.2% (ranging from 18.5% to 34.2%) in outdoor air samples. The difference is statistically significant ($p < 0.01$). For β -HBCD, similar relative abundances were observed in both indoor and outdoor air samples.

HBCDs diastereoisomer profiles, in this study, were also compared with those in commercial products in China and reported data in the literature.^{9–11} As shown in Figure 1, the HBCDs diastereoisomer profiles were dominated by α -HBCD in both indoor and outdoor air samples. This was noticeably different from the profiles of domestic commercial products, in which γ -HBCD was the dominant isomer with a relative abundance ranging from 77% to 80%. We have previously reported higher percentages of α -HBCD (59–68%) in urban air samples from Guangzhou, China,¹¹ and this same result was found again in outdoor air in this study. Contrary to our results, Thomsen et al. reported that γ -HBCD dominated the diastereoisomer profiles in the working environment in the plant manufacturing XPS foam.¹² In indoor air samples from Birmingham, UK, Abdallah et al. found elevated relative abundances of α -HBCD relative to those in the technical neat products, even though γ -HBCD was

still the predominant isomer.¹⁰ In US outdoor air samples, variable HBCDs diastereoisomer profiles were found, with three of the seven samples dominated by γ -HBCD, one with a comparable proportion of α -HBCD and the other three dominated by α -HBCD.⁹

In general, the occurrence of HBCDs in air seems to be the consequence of volatilization from HBCD-containing products, and thus the profile in air would likely reflect that present in HBCD-containing goods.¹⁰ As previous studies indicated, thermal isomeric interconversion of HBCDs (dominated by transformation of γ -HBCD to α -HBCD) can occur and may result in the enrichment of α -HBCD when exposed to elevated temperatures (140–160°C) during the manufacturing process of HBCD-containing products such as EPS and XPS.²⁸ Similarly, a rapid photolytically mediated shift from γ -HBCD to α -HBCD has been illustrated in light-exposed indoor dust by Harrad et al.²⁹ Furthermore, Davis et al. reported that the degradation rate of γ -HBCD was much faster than that of α -HBCD.^{30,31} In addition, vapour pressures of individual HBCDs might be another important factor to affect the diastereoisomer profiles. Kuramochi and Sakai reported vapour pressures of HBCD diastereoisomers have significant difference, with 1.05×10^{-8} , 5.82×10^{-9} , 8.39×10^{-11} for α -, β - and γ -HBCD, respectively.³²

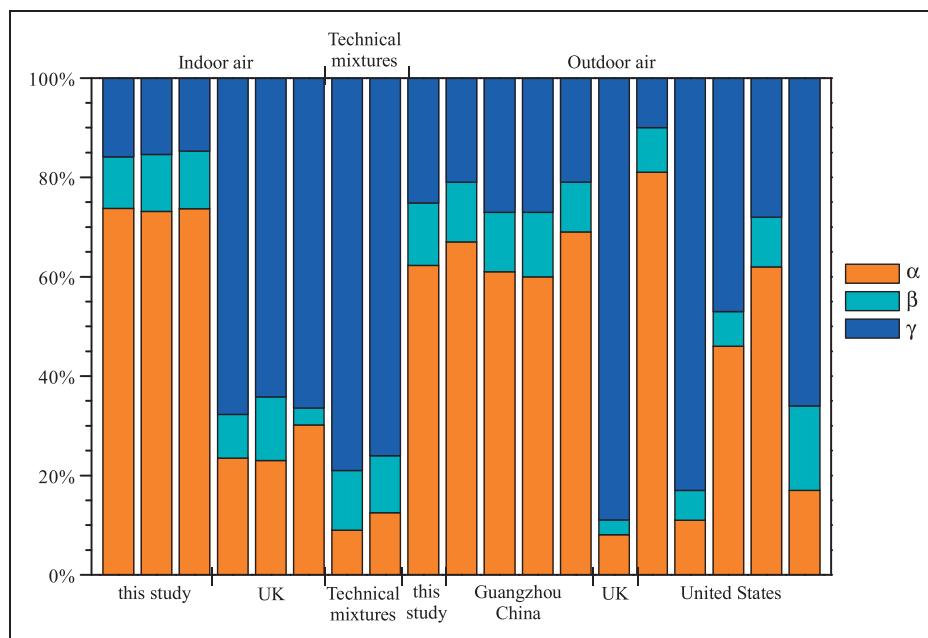


Figure 1. The legend of Figure 1 was not showed correctly; it should be α , β , and γ from top to bottom.

Because many factors mentioned above could affect HBCD diastereoisomer profiles, it remains unclear what mechanism might be responsible for the variable diastereoisomer profiles in this study.

Gas-particle distribution

Like other persistent organic pollutants, the partitioning behaviour between the gas and particle phases greatly affects the deposition, degradation, transport and subsequent fate of HBCDs. Figure 2 shows the relative distribution of total HBCDs in the gas and particle phases in this study. As shown in Figure 2, airborne HBCDs were predominantly present in the particulate phase. In outdoor air samples, the HBCDs were almost exclusively present in the particle phase (98.7–99.6%), except for samples OU1 and OU8 (94.4% and 96.3% particle phase, respectively). This may suggest that the distribution of HBCDs between the gas- and particle-phases at these sampling sites is closer to equilibrium than at other sites. These results were also similar to the partitioning of HBCDs/PBDEs between the gas and particle phases in our previous studies^{11,25} of an urban sampling site (U-1) in Guangzhou, China. In the indoor air samples, the relative abundance of HBCDs present in the particle phase ranged from 87.6% to 99.9%. It was obvious that the variation in HBCDs distribution in the gas and particle phases was greater in indoor air samples than in outdoor air samples. This may imply that fresh HBCDs were being continuously emitted into the indoor air, so

that an equilibrium state could not be established. Another possible explanation for the differences in HBCDs distributions in the gas and particle phases in indoor and outdoor air is that the outdoor air samples were all (except for OU8) collected from highly populated areas with heavy traffic flows in Guangzhou and Foshan, China; the total suspended particulate contents in these sampling sites should be enriched with soot-type particulates, which have a strong sorption capacity for SVOCs including HBCDs. Obviously, it is necessary to further explore the effects of soot carbon or other types organic carbon on the HBCDs distribution between the gas and particle phases.

Human inhalation exposure to HBCDs

The concentration values determined in this study were used to estimate the inhalation exposure of HBCDs by adults (assuming 100% absorption of intake, and no selective absorption of HBCD diastereoisomers). The inhalation exposure of HBCDs was estimated using equation (1) of the following algorithm²⁴:

$$\Sigma \text{exposure} = [(C_w F_w) + (C_h F_h) + (C_o F_o)] R_R \quad (1)$$

where $\Sigma \text{exposure}$ is the daily human exposure via inhalation (ng day^{-1}), $C_{w/h/o}$ are the HBCDs concentrations in the workplace/house/outdoor air (ng m^{-3}), R_R is the adult respiration rate ($20 \text{ m}^3 \text{ day}^{-1}$),³³ and $F_{w/h/o}$ is the fraction of the day spent in the workplace/house/outdoors. Due to the absence of data to describe the

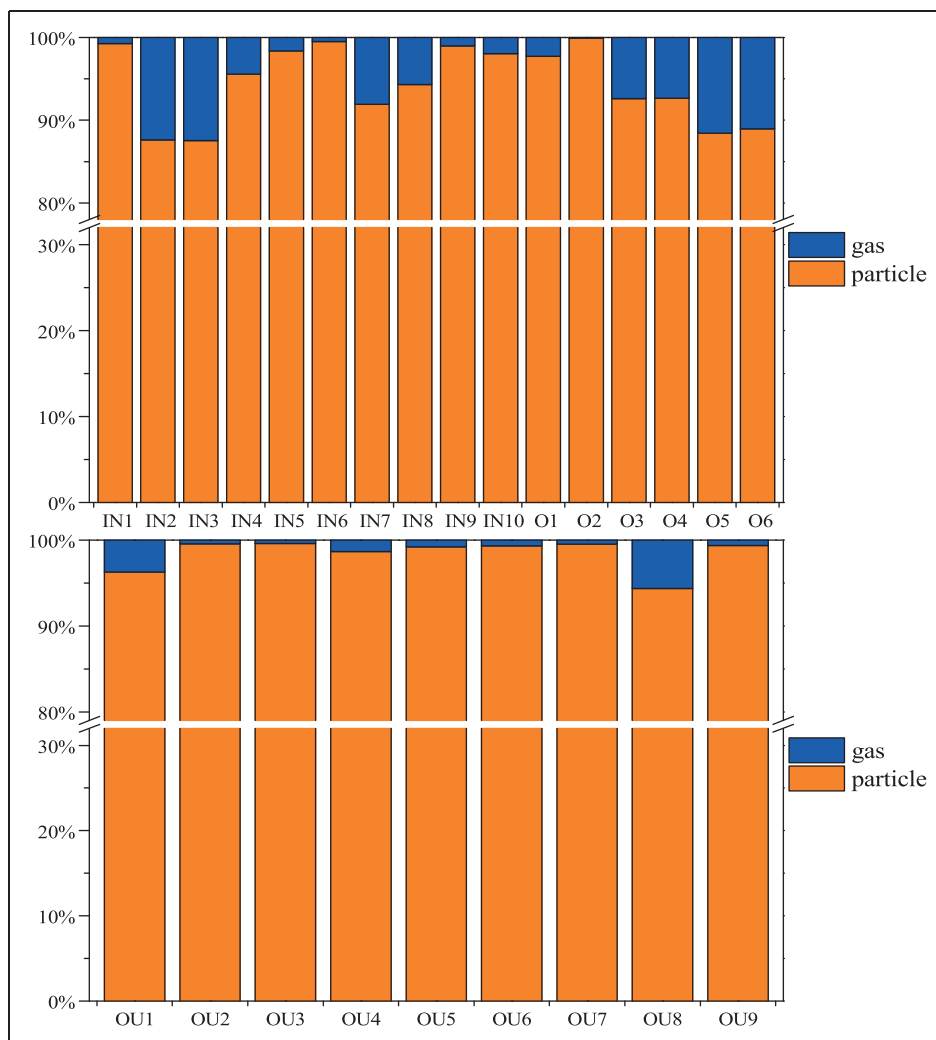


Figure 2. Relative distribution of HBCDs between gas- and particle-phase in indoor and outdoor air samples. O1 to O6: office samples; IN1 to IN10: samples from other indoor workplaces; OU1 to OU9: outdoor samples. HBCD: hexabromocyclododecane.

time-activity patterns of the Chinese population, we estimated that average adults would spend 63.8% of their time at home, 27.4% at the workplace and the remainder outdoors.³⁴ Under these conditions, the estimated average daily human exposure to HBCDs via inhalation was 0.39 ng day^{-1} for adults. Table 3 summarizes the estimates of average, median, 5th percentile and 95th percentile values. According to Harrad's research group, the estimated average daily inhalation exposure to HBCDs was $5.0\text{--}5.47 \text{ ng day}^{-1}$ for adults in the UK.^{10,35} In another study of two Japanese houses, the corresponding value was 0.73 ng day^{-1} .¹³ The average value (0.39 ng day^{-1}) of human inhalation exposure in this study was therefore one order of magnitude lower than that of UK adults,^{10,35} but comparable to that of Japanese adults.¹³ This geographic difference in human exposure to HBCDs is consistent with the available data on world market demand for HBCDs.²⁷ In an

earlier study by our group, we estimated human exposure to PBDEs and found that the mean value of exposure via inhalation was 77.1 ng day^{-1} .²⁴ This is approximately 200 times larger than that of the total HBCDs inhalation estimated in the present study. The new data also support our earlier suggestion that HBCDs might not be the main BFR contaminants in the Pearl River Delta regions.²³

A previous study indicated that inhalation exposure accounted only for 0.9% of total daily exposure of HBCDs for adults while dietary and indoor dust ingestion contributed 75% and 24% of the total exposure, respectively.¹⁰ However, the contribution of inhalation exposure (0.9%) appears too small, when considering ventilation between outdoor and indoor air. Unfortunately, we cannot further discuss the relative contribution of indoor air and dust to total human exposure because we were unable to collect indoor

Table 3. Estimated human inhalation exposure of HBCDs by adults (ng day⁻¹) in this study and other reported data.

		α -HBCD	β -HBCD	γ -HBCD	Σ HBCDs
This study ^a	Average	0.29	0.05	0.05	0.39
	Median	0.14	0.02	0.03	0.20
	Fifth percentile	0.04	0.01	0.01	0.05
	95th percentile	1.15	0.18	0.18	1.48
Abdallah's study ^a [Ref. 10]	Average	1.2	0.6	3.2	5.0
	Median	0.8	0.4	2.6	3.9
	Fifth percentile	0.5	0.2	1.3	2.3
	95th percentile	2.7	1.1	7.1	10.4
Abdallah's study ^a (Ref. 34)	Average	1.24	0.62	3.29	5.47
Takigami's study ^b (Ref. 13)	Average				0.73
	High level				1.30

HBCD: hexabromocyclododecane.

^aBased on average air inhalation rate of 20 m³ day⁻¹ (Wilford et al.³³).

^bBased on average air inhalation rate of 13.7 m³ day⁻¹ (Takigami et al.¹³).

dust samples during the sampling campaign. Further air and dust sampling and continued monitoring will be helpful in gaining a better understanding of human exposure to HBCDs.

Conclusions

Inhalation and ingestion are potentially important exposure routes for human exposure to HBCDs in the indoor environment. In this study, the concentration levels of HBCDs in indoor and outdoor air from two cities were lower than those in the European atmosphere. The average daily human exposure to HBCDs via inhalation was estimated to be 0.39 ng day⁻¹ for adults, which is one order of magnitude lower than that the values (5.0 and 5.47 ng day⁻¹) for UK adults reported in previous studies. However, the patterns of the diastereoisomer profiles and the gas-particle distribution in both indoor and outdoor samples from this study are significantly different from those in the reported UK samples. Our study showed that α -HBCD was the dominant isomer (53.2–83.0%), and that 87.6–99.9% of the total HBCDs were adsorbed onto airborne particles. Although these might be explained by the abiotic transformation (such as thermolysis and photolysis) and higher PM_{2.5} in the air, more air sampling, laboratory experiments and mathematical modelling are still needed in further investigations.

Funding

This study was supported by National Natural Science Funds for Distinguished Young Scholar (grant no. 41225013) and National Natural Scientific

Foundation of China (grant no. 21107110). Partial funding was also provided by China Postdoctoral Science Foundation funded project (grant no. 2011M501344). This is contribution No. IS-1700 from GIGCAS.

Conflict of interest

None.

References

- Covaci A, Gerecke AC, Law RJ, Voorspoels S, Kohler M, Heeb NV, Leslie H, Allchin CR and de Boer J. Hexabromocyclododecanes (HBCDs) in the environment and humans: a review. *Environ Sci Technol* 2006; 40: 3679–3688.
- POPs Review Committee (POPRC). Draft risk profile on hexabromocyclododecane. <http://chm.pops.int/Convention/POPsReviewCommittee/hrPOPRCMeetings/POPRC5/POPRC5Followupcommunications/HBCDInvitationforcommentsondraftRP/tabid/742/language/en-US/Default.aspx>. (2010, accessed 4 July 2013).
- Law RJ, Herzke D, Harrad S, Morris S, Bersuder P and Allchin CR. Levels and trends of HBCD and BDEs in the European and Asian environments, with some information for other BFRs. *Chemosphere* 2008; 73: 223–241.
- Tanabe S. Temporal trends of brominated flame retardants in coastal waters of Japan and South China: retrospective monitoring study using archived samples from es-Bank, Ehime University, Japan. *Mar Poll Bull* 2008; 57: 267–274.
- European Commission. Risk assessment report on hexabromocyclododecane; CAS-No.: 25637-99-4. EINECS No.: 247-148-4, Final Report. The Scientific Committee on Health and Environmental Risks (SCHER), European Commission, Brussels, January 2008.
- Morf L, Buser A, Taverna R, Bader HP and Scheidegger R. Dynamic substance flow analysis as a valuable tool – a case study for brominated flame retardants as an example of potential endocrine disruptors. *Chimia* 2008; 62: 42–431.

7. Managaki S, Miyake Y, Yokoyama Y, Hondo H, Masunaga S, Nakai S, Kobayashi T, Kameya T, Kimura A, Nakarai T, Oka Y, Otani H and Miyake A. Emission load of hexabromocyclododecane in Japan based on the substance flow analysis. *Organohalogen Compd* 2009; 71: 2471–2476.
8. Remberger M, Sternbeck J, Palm A, Kaj L, Strömberg K and Brorström-Lundén E. The environmental occurrence of hexabromocyclododecane in Sweden. *Chemosphere* 2004; 54: 9–21.
9. Hoh E and Hites R. Brominated flame retardants in the atmosphere of the East-Central United States. *Environ Sci Technol* 2005; 39: 7794–7802.
10. Abdallah MA, Harrad S and Covaci A. Hexabromocyclododecanes and tetrabromobisphenol-A in indoor air and dust in Birmingham, UK: Implications for human exposure. *Environ Sci Technol* 2008; 42: 6855–6861.
11. Yu Z, Chen L, Mai B, Wu M, Sheng G, Fu J and Peng P. Diastereoisomer- and enantiomer-specific profiles of hexabromocyclododecane in the atmosphere of an urban city in South China. *Environ Sci Technol* 2008; 42: 3996–4001.
12. Thomsen C, Molander P, Daae HL, Janák K, Froshaug M, Liane VH, Thorud S, Becher G and Dybing E. Occupational exposure to hexabromocyclododecane at an industrial plant. *Environ Sci Technol* 2007; 41: 5210–5216.
13. Takigami H, Suzuki G, Hirai Y and Sakai S. Brominated flame retardants and other polyhalogenated compounds in indoor air and dust from two houses in Japan. *Chemosphere* 2009; 76: 270–277.
14. U.S. Environmental Protection Agency (EPA). An exposure assessment of polybrominated diphenyl ethers. EPA/600/R-08/086 F. <http://cfpub.epa.gov/ncea/cfm/recorddisplay.cfm?deid=210404> (2010, accessed 3 July 2013).
15. Harrad S, de Wit C, Abdallah MA, Bergh C, Björklund J, Covaci A, Darnerud P, de Boer J, Diamond M, Huber S, Leonards P, Mandalakis M, Ostman C, Haug L, Thomsen C and Webster T. Indoor contamination with hexabromocyclododecanes, polybrominated diphenyl ethers, and perfluoroalkyl compounds: an important exposure pathway for people. *Environ Sci Technol* 2010; 44: 3221–3231.
16. Roosens L, Abdallah MA, Harrad S, Neels H and Covaci A. Exposure to hexabromocyclododecanes (HBCDs) via dust ingestion, but not diet, correlates with concentrations in human serum: preliminary results. *Environ Health Perspect* 2009; 117: 1707–1712.
17. Weschler C and Nazaroff W. Semivolatile organic compounds in indoor environments. *Atmos Environ* 2008; 42: 9018–9040.
18. Weschler C and Nazaroff W. SVOC exposure indoors: fresh look at dermal pathways. *Indoor Air* 2012; 22: 356–377.
19. Shi Z, Wu Y, Li J, Zhao Y and Feng J. Dietary exposure assessment of Chinese adults and nursing infants to tetrabromobisphenol-A and hexabromocyclododecanes: occurrence measurements in foods and human milk. *Environ Sci Technol* 2009; 43: 4314–4319.
20. Zhang X, Yang F, Luo C, Wen S, Zhang X and Xu Y. Bioaccumulative characteristics of hexabromocyclododecanes in freshwater species from an electronic waste recycling area in China. *Chemosphere* 2009; 76: 1572–1578.
21. Wu J, Guan Y, Zhang Y, Luo X, Zhi H, Chen S and Mai B. Trophodynamics of hexabromocyclododecanes and several other non-PBDE brominated Flame retardants in a freshwater food web. *Environ Sci Technol* 2010; 44: 5490–5495.
22. Meng X, Duan Y, Yang C, Pan Z, Wen Z and Chen L. Occurrence, sources, and inventory of hexabromocyclododecanes (HBCDs) in soils from Chongming Island, the Yangtze River Delta (YRD). *Chemosphere* 2011; 82: 725–731.
23. Gao S, Wang J, Yu Z, Guo Q, Sheng G and Fu J. Hexabromocyclododecanes in surface soils from e-waste recycling areas and industrial areas in South China: concentrations, diastereoisomer- and enantiomer-specific profiles, and inventory. *Environ Sci Technol* 2011; 45: 2093–2099.
24. Chen L, Mai B, Xu Z, Peng X, Han J, Ran Y, Sheng G and Fu J. In- and outdoor sources of polybrominated diphenyl ethers and their human inhalation exposure in Guangzhou, China. *Atmos Environ* 2008; 42: 78–86.
25. Chen L, Mai B, Bi X, Chen S, Wang X, Ran Y, Luo X, Sheng G, Fu J and Zeng EY. Concentration levels, compositional profiles, and gas-particle partitioning of polybrominated diphenyl ethers in the atmosphere of an urban city in South China. *Environ Sci Technol* 2006; 40: 1190–1196.
26. Yu Z, Peng P, Sheng G and Fu J. Determination of hexabromocyclododecane diastereoisomers in air and soil by liquid chromatography- electrospray tandem mass spectrometry. *J Chromatogr A* 2008; 1190: 74–79.
27. Bromine Science and Environmental Forum (BSEF). Major brominated flame retardants volume estimate. Total market demand by region in 2001. <http://www.bsef.com/> (2003, accessed 15 October 2012).
28. Heeb NV, Graf H, Schweizer WB and Lienemann P. Thermally-induced transformation of hexabromocyclododecanes and isobutoxypenta bromocyclododecanes in flame-proofed polystyrene materials. *Chemosphere* 2010; 80: 701–708.
29. Harrad S, Abdallah MA and Covaci A. Causes of variability in concentrations and diastereomer patterns of hexabromocyclododecanes in indoor dust. *Environ Int* 2009; 35: 573–579.
30. Davis JW, Gonsior S, Marty G and Ariano J. The transformation of hexabromocyclododecane in aerobic and anaerobic soils and aquatic sediments. *Water Res* 2005; 39: 1075–1084.
31. Davis JW, Gonsior S, Markham D, Friederich U, Hunziker R and Ariano J. Biodegradation and product identification of [¹⁴C] hexabromocyclododecane in wastewater sludge and freshwater aquatic sediment. *Environ Sci Technol* 2006; 40: 5395–5401.
32. Kuramochi H and Sakai S. Measurement of vapor pressures of some PBDEs and HBCD diastereoisomers. In: *Fifth international symposium on brominated flame retardants*, Tokyo, Japan, 7–9 April 2010; paper no. 90071. <http://www.bfr2010.com/abstract-download/2010/90071.pdf> (2010, accessed 4 July 2013).
33. Wilford B, Shoeib M, Harner T, Zhu J and Jones C. Polybrominated diphenyl ethers in indoor dust in Ottawa, Canada: Implications for sources and exposure. *Environ Sci Technol* 2005; 39: 7027–7035.
34. Klepeis N, Nelson W, Ott W, Robinson J, Tsang A, Switzer P, Behar J and Engelmann W. The National Human Activity Pattern Survey (NHAPS): a resource for assessing exposure to environmental pollutants. *J Exposure Anal Environ Epidemiol* 2001; 11: 231–252.
35. Abdallah MA and Harrad S. Tetrabromobisphenol-A, hexabromocyclododecane and its degradation products in UK human milk: relationship to external exposure. *Environ Int* 2011; 37: 443–448.