Environ Monit Assess (2022) 194: 371
https://doi.org/10.1007/s10661-022-10049-0

Levels, distribution and risk assessment of hexabromocyclododecane (HBCD) in fish in Xiamen, China

Zhuozhen Qian · Shuifen Tang · Zhiyu Liu · Fangfang Luo · Shaohong Wei

Received: 14 July 2021 / Accepted: 9 April 2022 / Published online: 16 April 2022

Abstract In this study, hexabromocyclododecane (HBCD) was detected in 114 fish samples collected from 6 administrative regions of Xiamen city, China. HBCD amounts ranged between ND (not detected) and 2.216 ng g^{-1} ww (mean, 0.127 ± 0.318 ng g^{-1} ww). Besides, α-HBCD was the main diastereoisomer in these fish specimens, followed by β-HBCD. Meanwhile, γ-HBCD was not detected in any of the samples. Significant differences were recorded among fish species. The results indicated that the levels and detection rates of HBCD were higher in *Trachinotus ovatus* compared with other aquatic organisms. Therefore, *Trachinotus ovatus* could be used as a marine biological indicator of HBCD. Within the regions investigated, Siming was significantly different from Jimei, Haicang, and Xiang'an. The spatial distribution of HBCD concentrations indicated higher mean levels in samples collected from Haicang, Jimei, and Xiang'an, respectively, with the highest detection rates in Jimei and Xiang'an, which might be related to geographical location and intense industrial and urban activities. Estimation of daily HBCD intake was performed according to fish consumption in Xiamen residents. The medium bound HBCD amounts in fish were approximately 0.073 and 0.088 ng kg $bw^{-1}d^{-1}$ for male and female residents of Xiamen, respectively. Exposure doses of HBCD indicated no health concern for Xiamen residents.

Keywords Hexabromocyclododecane (HBCD) · Bioindicator · Regional distribution · Daily intake

Supplementary information The online version contains supplementary material available at https://doi.org/10.1007/s10661-022-10049-0.

Z. Qian (✉) · S. Tang · Z. Liu · F. Luo · S. Wei
Fisheries Research Institute of Fujian, 7 Haishan Road, Xiamen 361013, China
e-mail: qianzhuozhen@126.com

Z. Qian · S. Tang · Z. Liu · F. Luo · S. Wei
Key Laboratory of Cultivation and High-Value Utilization of Marine Organisms in Fujian Province, 7 Haishan Road, Xiamen 361013, China

Introduction

Persistent organic pollutants (POPs) represent an important group of substances with the characteristics of high toxicity, persistence, and bioaccumulation (Cunha et al., 2017; Liu et al., 2016; Tang et al., 2015; Tao et al., 2016; Van der Ven et al., 2008). Hexabromocyclododecane (HBCD) has been extensively used as a brominated flame retardant (BFR) for a long period of time in textiles, electronics, construction materials, thermal insulation materials, etc. γ-HBCD constitutes the main diastereoisomer of industrial HBCD, accounting for 75–89% of the overall weight, while α-HBCD (10–15%) and β-HBCD (1–12%) are two other diastereomers (Covaci et al., 2006). In 2011, about 31,000 tons of HBCD were produced worldwide (POPRC.7, 2011; POPRC.8, 2012). The Chinese HBCD production accounts for more than half of the global production (POPRC.8, 2012). Given the strong persistence, bioaccumulation, liver toxicity, neurotoxicity, and immunotoxicity of HBCD (Marvin et al., 2011; Samuelsen et al., 2001; Tomy et al., 2008; Wang et al., 2016; Zhang et al., 2018; Zhu et al., 2016), it was included in the list of POPs in 2013 (POPRC8.3, 2013). Besides, its production and utilization have been globally recommended to be banned since 2016. However, HBCD is still produced and applied in China, which allows its use in special building materials.

Additionally, HBCD is found in multiple environmental media, e.g., air, riverine water, sediments, sewage sludge, and animal tissues (Ni & Zeng, 2013; Feng et al., 2012; Gorga et al., 2013; Xia et al., 2018), as well as in humans (Kim & Oh, 2014) and biota in pristine regions, including the Antarctic Peninsula. Due to its low water solubility and high lipophilicity, HBCD can easily accumulate in aquatic organisms. Previous studies (Barghi et al., 2016; Shi et al., 2009; Törnkvist et al., 2011) demonstrated that HBCD levels are generally elevated in aquatic foods compared with other food products. Therefore, environmental pollution and human health problems caused by extensive application of HBCD have significantly attracted the attention of the international community.

Xiamen, in the southeast coast of China, currently undergoes rapid urbanization and industrialization; thus, seawater in this area tends to have poor quality. Furthermore, fish accounts for a great proportion of the dietary composition of Xiamen residents. This makes Xiamen residents even more vulnerable to exposure to persistent organic pollutants (POPs) via fish intake than inland inhabitants. Despite the importance of the abovementioned serious health problem in Xiamen, there are limited studies (Qian et al., 2017; Zhang et al., 2012) examining "classic" POPs, including DDT, HCH, and PCB, in aquatic products in Xiamen, China. Hence, to date, data related to permissible levels of environmental exposure and associated risk factors in Xiamen are scarce.

No large-scale study focusing on HBCD quantitation in fish samples has been performed in Xiamen until now. Therefore, this work aimed to assess the contamination status of HBCD in fish collected from Xiamen, as well as species and regional distributions. Additionally, the related health risk for local residents consuming fish was estimated. We, for the first time, determined the estimated daily intake (EDI) of HBCD in Xiamen residents.

Materials and methods

Sample collection

In the present research, as shown in Table S1, 114 fish samples were collected from 6 administrative regions (Siming, Huli, Haicang, Jimei, Xiang'an, and Tong'an) of Xiamen between March 2017 and December 2018 (Fig. 1). Totally, 14 fish species were regularly used by local residents as food. For a meaningful interpretation of data, we collected the same fish species during the same seasons in various regions. Specimens were preserved in a car refrigerator and transported within hours to the laboratory. In the laboratory, dorsal muscles were taken, homogenized, lyophilized, grinded, and stored at −20 ℃ till analysis.

Chemicals and analytical methods

The surrogate standards (α-, β-, and γ-HBCD) were purchased from AccuStandard Inc. (New Haven, CT, USA). $^{13}C_{12}$-β-HBCD standard was purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). The HPLC grade solvents, including hexane, dichloromethane, acetone, acetonitrile, and methanol, were supplied from Tedia Company, Inc. (Fairfield,

Fig. 1 Geographical locations of sampling sites

OH, USA). Sodium sulfate was baked at 500 °C and stored in the sealed containers. Silica solid phase extraction (SPE) column was obtained from Waters Corp. (Milford, MA, USA).

The analytical methods used for HBCD have been described previously (Qian et al., 2021). Approximately 5.0 g of each homogenized sample was spiked with internal standards ($^{13}C_{12}$-β-HBCD). A 30-mL mixture of n-hexane and dichloromethane (1:1, v/v) was added to the sample, which was then homogenized for about 1 min, and ultrasonically extracted for 30 min. Subsequently, the sample was soaked in a mixture of n-hexane and dichloromethane (1:1, v/v) overnight. The extraction process was repeated on the next day with a mixture of 20 mL n-hexane and dichloromethane (1:1, v/v). All of the extracts were placed in an anhydrous sodium sulfate column and eluted with 5 mL of an n-hexane and dichloromethane mixture (1:1, v/v). The eluate was then evaporated to near dryness with a rotary evaporator and re-dissolved in 4 mL hexane, and cleaned up twice with 0.5 mL concentrated sulfuric acid to degrade the remaining lipid. After centrifugation, the supernatant was purified on a silica solid phase extraction (SPE) cartridge (500 mg, 6 mL, Waters) preconditioned with 8 mL of hexane (2 mL·min^{-1}). The cartridge was then rinsed with 12 mL of hexane (2 mL·min^{-1}) and eluted with 8 mL of acetone (2 mL·min^{-1}). The eluate was blown to dryness under nitrogen at 50 °C and reconstituted with water, acetonitrile, and methanol (4:3:3, 500 μL) prior to analysis.

Identification and quantification analyses were executed by high performance liquid chromatography-tandem mass spectrometry (HPLC–MS/MS, TSQ Quantum Ultra, Thermofisher, Waltham, MA, USA) in the electrospray negative ionization (ESI) mode, with selective reactions monitoring (SRM), and fitted with a Hypersil Gold-C_{18} column (100 mm × 2.1 mm id, 5 μm, Thermofisher, Waltham, MA, USA). Mobile phase A was water and mobile phase B consisted of acetonitrile/methanol (1:1, v/v). The linear gradient profile was as follows: 0 min, 40% A and 60% B; 10–11 min, 100% B; 12–17 min, 40% A; and 60% B. The flow rate was 0.25 mL·min^{-1} and the column temperature was 40 °C. The parameters of the mass spectrometer were as follows: spray voltage, 2500 V; capillary temperature, 320 °C; vaporizer temperature, 150 °C; sheath gas (nitrogen), 25 psi; auxiliary gas (nitrogen), 15 L·min^{-1}; Q1/Q3 peak width, 0.7 u; collision gas (argon), 1.5 mTorr. Selected reaction monitoring (SRM) signals for quantification and confirmation for HBCD were from m/z 640.9 to 81.2 and 640.9 to 79.2, respectively. A transition of 652.9 to 81.2 m/z was applied to quantify $^{13}C_{12}$-β-HBCD.

Quality control (QC)

HBCD was identified according to relative retention time and the corresponding selected reaction monitoring (SRM) for various analytes. To prevent potential unexpected matrix effects, isotopically labeled standards were utilized for HBCD isomers. Then, a matrix-matched calibration curve was generated for quantification. A 5-point calibration curve spanning the concentration range of 1–100 ng·mL^{-1} including internal standards was employed ($R^2 \geq 0.990$). The limit of detection (LOD) on the column, defined as a signal-to-noise ratio of 3:1, was 0.05 ng·g^{-1}. Procedural blank specimens were run after a block of 20 samples to rule out contamination. Recovery and precision rates were evaluated by spiking different matrix samples with HBCD at two concentration levels (0.25 ng·g^{-1} and 0.5 ng·g^{-1} ww). Recovery rates were 70–110%. Intra-day reproducibility (0.25 ng·g^{-1}) for HBCD detection ($n = 5$) was 4.3–10.3%. Inter-day reproducibility (0.5 ng·g^{-1}) for HBCD detection ($n = 6$) was 8.2–11.2%. Spiking assay data are given in supplementary materials (Table S2). HBCD concentrations per wet weight (ww) were derived from Eq. (1) (Table 1).

$$C_i = C_j \times (100\% - \omega_{H_2O}) \quad (1)$$

where C_i is HBCD level in ng·g^{-1} (ww) in the wet specimen, C_j represents HBCD amounts (ng·g^{-1}) in the lyophilized specimen, and ω_{H_2O} is the wet specimen's water content (%), derived from Eq. (2).

$$\omega_{H_2O} = \frac{m_w - m}{m_w} \times 100\% \quad (2)$$

where m_w and m represent the weights of the wet and lyophilized samples, respectively (g).

The laboratory's performance was validated through participation in an interlaboratory comparison test for HBCD powered by the State Oceanic Administration People's Republic of China. Data reported by our laboratory were within consensual values.

Table 1 Concentrations and detection rates of HBCD in fish samples obtained from Xiamen (ng g^{-1} ww)

Species	α-HBCD			β-HBCD			γ-HBCD			HBCD			
	Mean ± SD	Median	Range	Mean ± SD	Median	Range	Mean ± SD	Median	Range	Mean ± SD	Median	Range	Detection rates (%)
Psenopsis anomala	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	—
Larimichthys crocea	0.210 ± 0.246	0.161	ND–0.580	ND	ND	ND	ND	ND	ND	0.210 ± 0.246	0.161	ND–0.580	50.0
Scophthalmus maximus	0.513 ± 0.868	0.112	ND–2.216	ND	ND	ND	ND	ND	ND	0.513 ± 0.868	0.112	ND–2.216	66.7
Trichiurus lepturus	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	—
Nibea albiflora	0.165 ± 0.231	0.041	ND–0.530	0.040 ± 0.098	ND	ND–0.239	ND	ND	ND	0.205 ± 0.313	0.041	ND–0.770	50.0
Acanthopagrus latus	0.037 ± 0.074	ND	ND–0.219	ND	ND	ND	ND	ND	ND	0.037 ± 0.074	ND	ND–0.219	25.0
Nemipterus virgatus	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	—
Decapterus maruadsi	0.111 ± 0.146	0.041	ND–0.333	ND	ND	ND	ND	ND	ND	0.111 ± 0.146	0.041	ND–0.333	50.0
Lateolabrax japonicus	0.029 ± 0.072	ND	ND–0.232	ND	ND	ND	ND	ND	ND	0.029 ± 0.072	ND	ND–0.232	16.7
Trachinotus ovatus	0.353 ± 0.427	0.257	ND–0.333	ND	ND	ND	ND	ND	ND	0.353 ± 0.427	0.257	ND–0.333	83.3
Epinephelus awoara	0.045 ± 0.079	ND	ND–0.194	ND	ND	ND	ND	ND	ND	0.045 ± 0.079	ND	ND–0.194	33.3
Hapalogenys nitens	0.239 ± 0.586	ND	ND–1.435	ND	ND	ND	ND	ND	ND	0.239 ± 0.586	ND	ND–1.435	16.7
Pampus argenteus	0.106 ± 0.211	ND	ND–0.527	ND	ND	ND	ND	ND	ND	0.106 ± 0.211	ND	ND–0.527	33.3
Pagrus major	0.070 ± 0.181	ND	ND–0.602	ND	ND	ND	ND	ND	ND	0.070 ± 0.181	ND	ND–0.602	16.7

ND not detected, *SD* standard deviation

Statistical analysis

SPSS 20.0 (SPSS, USA) was utilized for analysis. All concentrations in fish samples were presented on a ww basis. Levels below the LOD were set to half of the LOD. Data were presented as median, mean ± standard deviation (SD) and range, respectively. Data normality and homogeneity of variance were assessed, followed by logarithm transformation. The data were all non-normally distributed. The nonparametric tests were performance with transformed data. The nonparametric Kruskal–Wallis (KW) test was utilized for comparing HBCD concentrations among species and regions. $P<0.05$ indicated statistical significance. Data on fish lipid content, body length, and body weight versus the concentrations of HBCD were linearly regressed to determine whether any significant correlation existed using Spearman's rank test. Here, we conducted the correlation analysis only for *T. ovatus* because of its highest detection rate.

Daily intake calculations

Estimated dietary intake (EDI) of HBCD (ng kg^{-1} d^{-1}) was assessed as follows:

$$EDI = \frac{C \times DR}{B_w} \quad (3)$$

where C represents mean HBCD level (ng g^{-1} ww), DR is the daily consumption rate of fish (g d^{-1}), and B_w is mean human body weight (70.3 and 57.8 kg for adult males and females, respectively), according to the National Physique Monitoring Center of China (2014).

Results and discussion

HBCD amounts in fish and isomer profile

In the present study, HBCD was detected in 30.7% of all studied specimens at amounts between ND to 2.216 ng g^{-1} ww (mean, 0.127 ± 0.318 ng g^{-1} ww). Of note, α-HBCD was the remarkably predominant diastereoisomer, whereas β-HBCD was only detected in one fish sample. Besides, unlike environmental samples and commercial HBCD, γ-HBCD was found in no fish specimen. α-HBCD predominance in fish specimens most likely results from elevated assimilation and reduced elimination rates of α-HBCD in comparison with β- and γ-HBCD (Du et al., 2012; Eljarrat et al., 2014; Law et al., 2006; Zhang et al., 2013). The bio-isomerization of β- and γ-HBCD to α-HBCD was suggested as another potential reason (Luo et al., 2013; Su et al., 2018). In addition, HBCD's bioavailability may influence the diastereoisomer profile of HBCD (Ashizuka et al., 2008). Water solubility levels of α-, β-, and γ-HBCD are 48.8, 14.7, and 2.1 μg·L^{-1}, respectively (Hunziker et al., 2004). This meant α- and β-HBCD are more easily enriched in aquatic organisms via the aquatic environment. Therefore, α-HBCD exhibited higher bioaccumulation than β- and γ-HBCD in aquatic organisms.

HBCD levels (range, ND–2.216 ng g^{-1} ww; mean, 0.127 ± 0.318 ng g^{-1} ww) detected in the present study were approximately 2 times higher than those reported by another work (range, ND–1.1 ng/g ww; median, 0.3 ng/g ww; mean, 0.41 ± 0.41 ng g^{-1} ww) conducted in Beijing (Wang et al., 2014), and also higher than those observed in twelve fish species (range, ND–0.194 ng g^{-1} ww; mean, 0.016 ng g^{-1} ww) collected in 11 Chinese coastal cities (Meng et al., 2012). In addition, reduced HBCD amounts were found in the current fish specimens in comparison with those from fish caught in the Japanese coast (range, ND–77.3 ng g^{-1} ww; Nakagawa et al., 2010) and a Japanese fish market (range, ND–21.9 ng g^{-1} ww; Kakimoto et al., 2012). A great deal of HBCD-based studies have been conducted in European countries, where HBCD is used intensively. HBCD amounts found in this work were slightly elevated than described for seafood products in Belgium (range, ND–0.84 ng g^{-1} ww; Goscinny et al., 2011), Sweden (range, 0.11–0.63 ng/g ww; mean, 0.145 ng g^{-1} ww; Törnkvist et al., 2011), and France (range, 0.01–0.55 ng g^{-1} ww; Munschy et al., 2013). However, HBCD levels in the current work were lower than reported for seafood products in Czech Republic (range, 0.02–11.6 ng g^{-1} ww; median, 0.44 ng g^{-1} ww; Hloušková et al., 2013), the Netherlands (range (marine), ND–7.3 ng g^{-1} ww; range (freshwater eel), ND-230 ng g^{-1} ww; van Leeuwen & de Boer, 2008), and Scotland (range, 0.03–12.1 ng g^{-1} ww; Fernandes et al., 2008). Jointly, fish HBCD levels in this study were in the middle range of those previously reported.

Correlation of HBCD and physiological parameters

The relationships between the HBCD concentrations in *T. ovatus* and certain physiological parameters (including lipid content, body mass, and body length) are displayed in Fig. 2. No significant correlation was found between the HBCD concentrations and fish lipid content ($r^2=0.006$, $p=0.087$; Fig. 2a) or body length ($r^2=0.09$, $p=0.345$; Fig. 2b) or body mass ($r^2=0.129$, $p=0.252$; Fig. 2c).

T. ovatus as a biological indicator of HBCD

The investigated fish species are grouped into three categories, herbivorous (*N. virgatus*), omnivorous (*A. latus* and *P. major*), and carnivorous (the other fish species). The highest detection rates were found in *T. ovatus* (83.3%) and *S. maximus* (66.7%), followed by *L. crocea* (50.0%), *N. albiflora* (50.0%), and *D. maruadsi* (50.0%). The mean value above 0.100 ng g^{-1} ww decreased stepwise in the following order: *S. maximus* (0.513 ± 0.868 ng g^{-1}

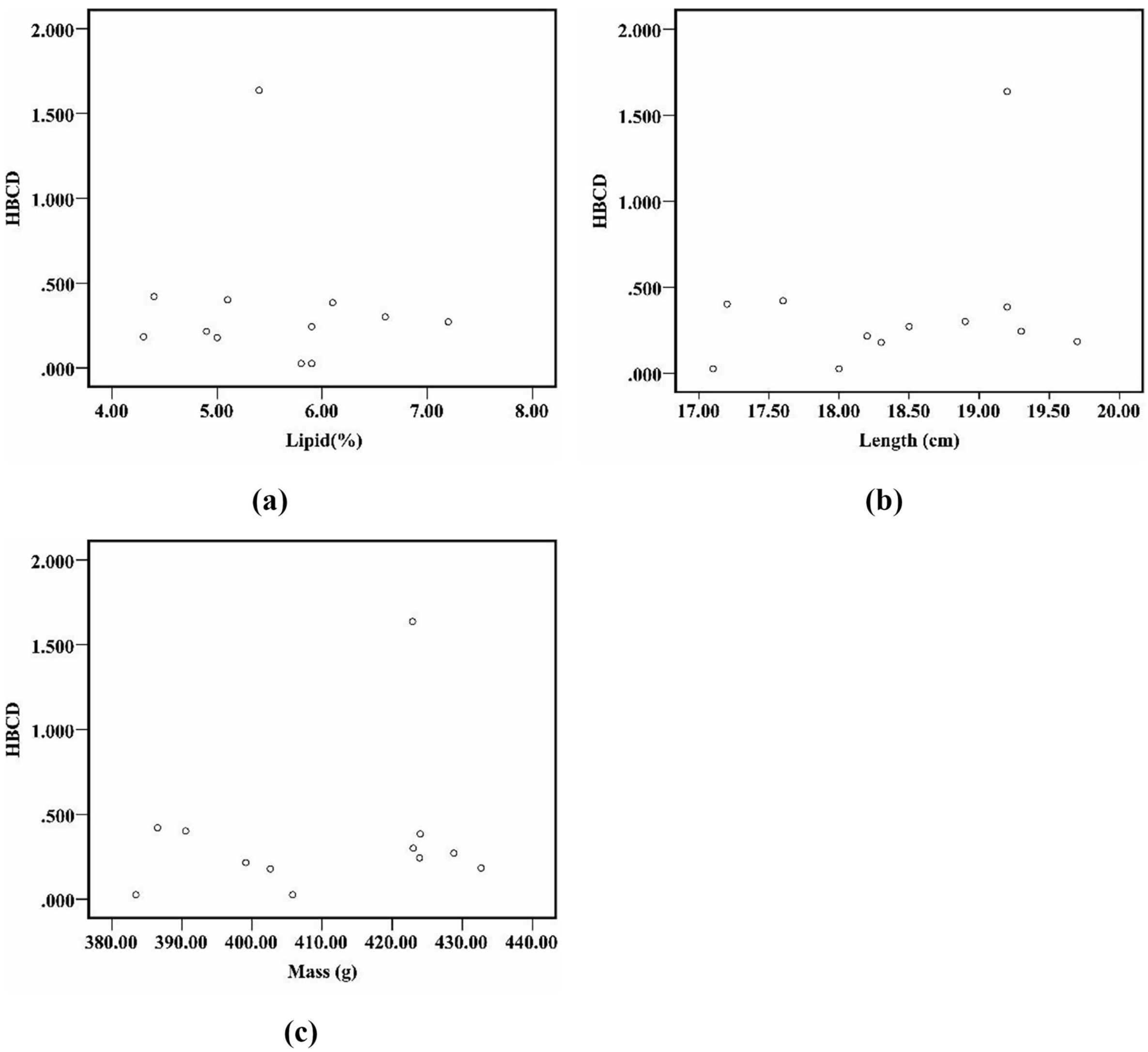

Fig. 2 Correlations between the concentrations of the sum of HBCD and lipid content (**a**), body length (**b**), and body mass (**c**) in *T. ovatus*

ww), *T. ovatus* (0.353 ± 0.427 ng g^{-1} ww), *L. crocea* (0.210 ± 0.246 ng g^{-1} ww), *N. albiflora* (0.205 ± 0.313 ng g^{-1} ww), and *D. maruadsi* (0.111 ± 0.146 ng g^{-1} ww). In the present study, statistical analysis showed *T. ovatus* was markedly different from other fish species (KW test; $p < 0.05$). In addition, the pollution level and detection rate of HBCD in *T. ovatus* in Xiamen were higher than those of other aquatic organisms, as shown in Fig. 3. These results suggested that they were substantially exposed to HBCD. However, no obvious point source discharges were identified in the surrounding area of the sampling site. Therefore, we suspected that selective HBCD bioaccumulation in *T. ovatus*, carnivorous fish, might be related to the diet of this organism (Van der Oost et al., 2003). It feeds on small fishes, plankton, and crustaceans. Trophic position in food chain might be another underlying reason, since an increasing trend in HBCD concentrations was observed from herbivorous to omnivorous (mean, 0.053 ± 0.136 ng g^{-1} ww) to carnivorous fish species (mean, 0.169 ± 0.371 ng g^{-1} ww). This result was consistent with previous study (Meng et al., 2012; Tomy et al., 2004) that found a strong positive linear relationship between the HBCD concentrations and trophic levels. The different metabolism and elimination capacity in *T. ovatus* were also possible reasons. To some extent, *T. ovatus* could be chosen as a marine biological indicator of HBCD, as it sensitively responds to HBCD exposure and it is widely distributed in the coastal areas of Xiamen all year around.

Regional distribution of HBCD in Xiamen

Table 2 shows the amounts and detection rates of HBCD in fish samples collected from 6 administrative regions (Siming, Huli, Haicang, Jimei, Tong'an, and Xiang'an) of Xiamen. These six regions showed marked geographical differences (KW test, $p < 0.05$; Fig. 4). Siming, where no HBCD was found in fish, is significantly different from Jimei, Haicang, and Xiang'an. The average HBCD level (0.031 ± 0.067 ng g^{-1} ww) and detection rate (21.1%) in fish samples observed in Huli were the lowest among regions. This was consistent with the economic pattern of Siming and Huli, where the government has mainly developed commercial and cultural industries. The reason why pollution level was higher in Huli compared with Siming is serious pollution by sewage outlets in Dailiao as well as north of the Wuyuanwan Bridge (Xiamen Municipal Bureau of Ocean Development, 2017). This might have a serious adverse impact on seawater quality, which needs strict supervision and

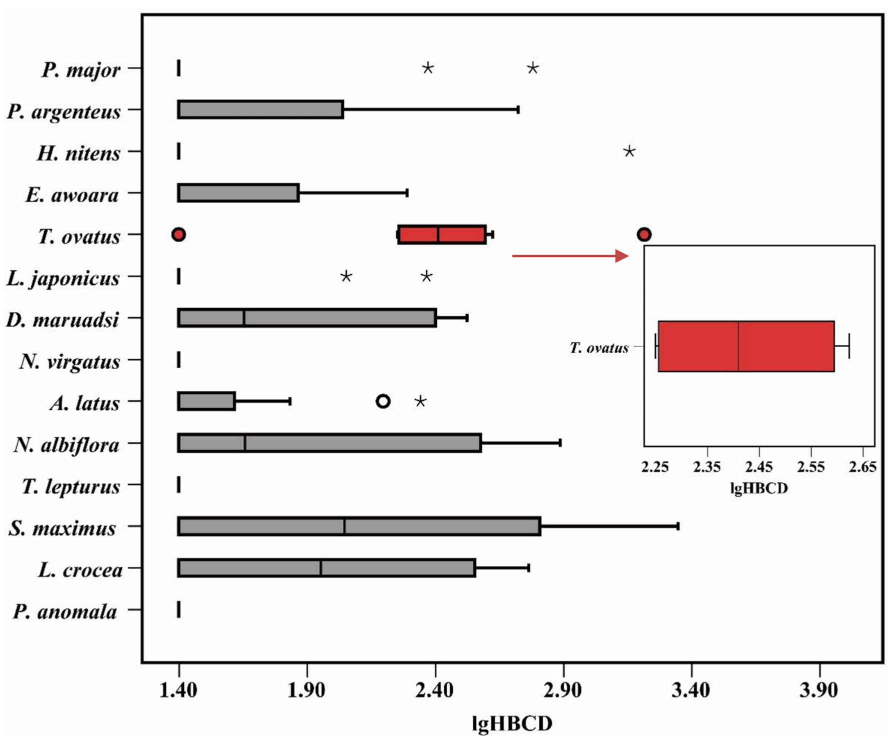

Fig. 3 HBCD concentrations in different fish species

Table 2 Detection rates and levels of HB CD in fish specimens collected in 6 different regions of Xiamen

Sampling Regions	α-HBCD	β-HBCD	γ-HBCD	HBCD	
	Mean ± SD Median (range)	Mean ± SD Median (range)	Mean ± SD Median (range)	Mean ± SD Median (range)	Detection rates (%)
Siming	ND	ND	ND	ND	—
Huli	0.031 ± 0.067 ND (ND–0.215)	ND	ND	0.031 ± 0.067 ND (ND–0.215)	21.1
Haicang	0.221 ± 0.401 ND (ND–1.637)	0.013 ± 0.055 ND (ND–0.239)	ND	0.248 ± 0.407 0.112 (ND–1.637)	42.1
Jimei	0.127 ± 0.181 ND (ND–0.602)	ND	ND	0.127 ± 0.181 ND (ND–0.602)	47.4
Tong'an	0.085 ± 0.168 ND (ND–0.580)	ND	ND	0.085 ± 0.168 ND (ND–0.580)	26.3
Xiang'an	0.283 ± 0.577 ND (ND–2.216)	ND	ND	0.283 ± 0.577 ND (ND–2.216)	47.4

ND not detected, *SD* standard deviation

management. The detection rates of HBCD in fish samples collected in Haicang, Jimei, and Xiang'an were between 40 and 50%. However, the mean concentration of HBCD in Haicang, where industry is developed, was almost 2- and threefold higher than those of Jimei and Tong'an, respectively. These results can be explained in different aspects: (1) Haicang and Jimei are located in the west coast of Xiamen, where water quality is assessed as the fourth level, according to the single factor evaluation method (Xiamen Municipal Bureau of Ocean Development, 2018); (2) Electronics, machinery and biopharmaceutical industries are concentrated in Haicang; (3) as the earliest cultural and educational administrative area of Xiamen, with a dense population, the discharge of domestic sewage in Jimei in the past decades has caused a remarkable damage to the adjacent sea areas. Thus, discharge of land-based pollutants, including industrial sewage and domestic wastewater,

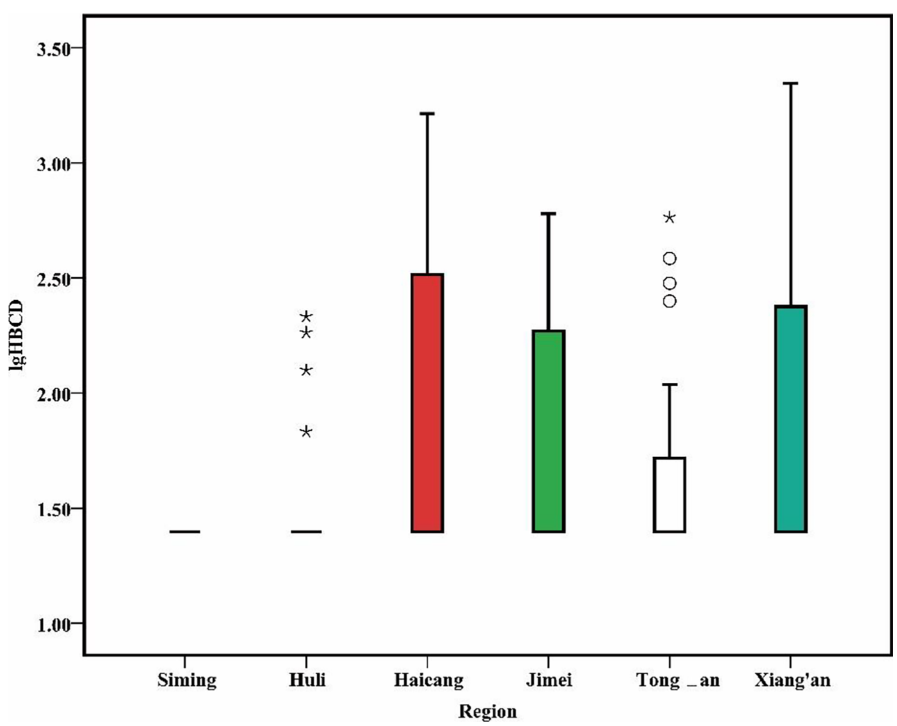

Fig. 4 HBCD concentrations in the 6 administrative regions

beyond the self-purification capacity of bays, represented the major factor promoting accumulation and pollution of HBCD in Haicang and Jimei. Nevertheless, it is noteworthy that the maximum value and detection rate of HBCD was found in Xiang'an, demonstrating that rapid industrial development and urbanization in Xiang'an in recent years may lead to new environmental problems. We suspected that the emerging electrical and electronics industry in Xiang'an might be potential HBCD sources.

EDI of HBCD through fish consumption

HBCD can enter the human body through a variety of ways, including diet, skin contact, and respiration, of which dietary intake is the main pathway. Estimation of daily intake of HBCD was carried out based on seafood consumption (Qian et al., 2017). Values relative to mean bodyweight (70.3 and 57.8 kg for adult males and females, respectively) were obtained from the General Administration of Sport of China. Because HBCD amounts in some specimens were below LOD, values < LOD were considered to be zero ("lower bound" approach, LB), 0.5 × LOD ("medium bound," MB) or equal to LOD ("upper bound," UB). Average intake levels in male Xiamen residents exposed to HBCD were 0.064 ng kg $bw^{-1}d^{-1}$ (LB), 0.073 ng kg $bw^{-1}d^{-1}$ (MB), and 0.081 ng kg $bw^{-1}d^{-1}$ (UB), respectively. Average daily intake levels of HBCD in Xiamen females were 0.078 ng kg $bw^{-1}d^{-1}$ (LB), 0.088 ng kg $bw^{-1}d^{-1}$ (MB), and 0.099 ng kg $bw^{-1}d^{-1}$(UB), respectively, which were slightly higher than in men. These EDI values were elevated in comparison with those reported for residents of South China via fish consumption (12.5–16.0 ng kg $bw^{-1}d^{-1}$) (Meng et al., 2012). EDI values in this study were also elevated than 0.01–1.00 ng kg $bw^{-1}d^{-1}$ and 0.004–0.37 ng kg $bw^{-1}d^{-1}$ found in urban and rural residents of Chinese coastal areas through fish consumption (Xia et al., 2011). Additionally, the present values were lower than those reported for Taiwan China (0.252 ng kg $bw^{-1}d^{-1}$; Lee et al., 2019) and the Yangtze River Delta of China (0.181 ng kg $bw^{-1}d^{-1}$; Zhang et al., 2013), and markedly reduced in comparison with those found in the Netherlands (0.12 ng kg $bw^{-1}d^{-1}$; van Leeuwen & de Boer, 2008), Korea (males: 0.392 ng kg $bw^{-1}d^{-1}$, females: 0.252 ng kg $bw^{-1}d^{-1}$; Barghi et al., 2016), and Japan (1.3–3.7 ng kg $bw^{-1}d^{-1}$; Nakagawa et al., 2010).

A no-observed-adverse-effect level (NOAEL) of 10.2 mg kg $bw^{-1}d^{-1}$) in rats was recommended on the basis of a two-generation reproductive toxicity study (Ema et al., 2008). Considering interspecies extrapolation from animals to humans and potential intraspecies differences in sensitivity among humans, an uncertainty factor (100) was introduced to estimate equivalent effect levels in humans. Thus, our EDIs correspond to 0.064–0.098% of the NOAEL, suggesting low potential health risk to Xiamen residents through fish consumption. On the other hand, the average daily intake of fish by Xiamen residents was 35.5 g d^{-1}, which is much higher than the national aquatic product consumption (14.8 g d^{-1}) reported in the 2017 China Statistical Yearbook (China Statistical Yearbook, 2017). In addition, Shi et al. (2017) demonstrated that the mean HBCD level in aquatic food in China showed an upward trend from 2007 to 2011. HBCD utilization in construction materials is still allowed in China, suggesting HBCD pollution might continue to increase in the future. Therefore, although HBCD amounts in Xiamen fish in this study may not threaten the health of Xiamen residents, it is important to monitor the HBCD concentration trend in fish collected from Xiamen.

Conclusions

This study provided the first data on isomer-specific HBCD levels in a variety of fish in Xiamen. HBCD was detected in > 30% of the examined fish samples, and compared with previous studies, the concentrations of HBCD were in the middle level. α-HBCD was the predominant diastereomer in fish, which is also in accordance with the majority of other studies. Significant differences in the amounts of HBCD were recorded among the species. This study found that *T. ovatus* could be chosen as a marine biological indicator of HBCD. At present, little is known about relationship between the HBCD concentrations and *T. ovatus*. More studies are needed to determine its environmental behavior and its metabolism in *T. ovatus*. Among the regions investigated, the pollution levels of Haicang, Jimei, and Xiang'an were relatively serious. Although the daily intakes in Xiamen from fish were below the proposed thresholds, it is important to monitor the HBCD concentration trend in fish collected from Xiamen due to higher daily intake of fish by Xiamen residents.

Acknowledgements We thank Wenxue Ma for field work and sample processing.

Author contribution Zhuozhen Qian conceived the study, performed data analysis, and drafted the manuscript. Zhiyu Liu provided critical points for discussion. Shuifen Tang and Fangfang Luo carried out additional analyses. Shaohong Wei collected the data.

Funding This research was funded by the Natural Science Foundation of Fujian Province (No. 2018J01056) and the Fujian Province Marine and Fishery Structure Adjustment Project (2021HYJG02).

Availability of data and materials The datasets utilized or analyzed in this study are available from the corresponding author upon reasonable request.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

References

Ashizuka, Y., Nakagawa, R., Hori, T., Yasutake, D., Tobiishi, K., & Sasaki, K. (2008). Determination of brominated flame retardants and brominated dioxins in fish collected from three regions of Japan. *Molecular Nutrition & Food Research, 52*(2), 273–283. https://doi.org/10.1002/mnfr.200700110

Barghi, M., Shin, E. S., Son, M. H., Choi, S. D., Pyo, H., & Chang, Y. S. (2016). Hexabromocyclododecane (HBCD) in the Korean food basket and estimation of dietary exposure. *Environmental Pollution, 213*, 268–277. https://doi.org/10.1016/j.envpol.2016.02.026

China Statistical Yearbook. (2017). Regional consumption of main foodstuffs per head (2016). Retrieved March 7, 2021, from http://www.stats.gov.cn/tjsj/ndsj/2017/indexch.htm

Covaci, A., Gerecke, A. C., Law, R. J., Voorspoels, S., Kohler, M., Heeb, N. V., Leslie, H., Allchin, C. R., & de Boer, J. (2006). Hexabromocyclododecanes (HBCDs) in the environment and humans: A review. *Environmental Science & Technology, 40*(12), 3679–3688. https://doi.org/10.1021/es0602492

Cunha, S. C., Oliveira, C., & Fernandes, J. O. (2017). Development of QuEChERS-based extraction and liquid chromatography-tandem mass spectrometry method for simultaneous quantification of bisphenol A and tetrabromobisphenol A in seafood: Fish, bivalves, and seaweeds. *Analytical and Bioanalytical Chemistry, 409*(1), 151–160. https://doi.org/10.1007/s00216-016-9980-3

Du, M., Lin, L., Yan, C., & Zhang, X. (2012). Diastereoisomer- and enantiomer-specific accumulation, depuration, and bioisomerization of hexabromocyclododecanes in zebrafish (Danio rerio). *Environmental Science & Technology, 46*(20), 11040–11046. https://doi.org/10.1021/es302166p

Eljarrat, E., Gorga, M., Gasser, M., Díaz-Ferrero, J., & Barcelo, D. (2014). Dietary exposure assessment of Spanish citizens to hexabromocyclododecane through the diet. *Journal of Agricultural and Food Chemistry, 62*(12), 2462–2468. https://doi.org/10.1021/jf405007x

Ema, M., Fujii, S., Hirata-Koizumi, M., & Matsumoto, M. (2008). Two-generation reproductive toxicity study of the flame retardant hexabromocyclododecane in rats. *Reproductive Toxicology, 25*(3), 335–351. https://doi.org/10.1016/j.reprotox.2007.12.004

Feng, A. H., Chen, S. J., Chen, M. Y., He, M. J., Luo, X. J., & Mai, B. X. (2012). Hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) in riverine and estuarine sediments of the Pearl River Delta in southern China, with emphasis on spatial variability in diastereoisomer- and enantiomer-specific distribution of HBCD. *Marine Pollution Bulletin, 64*(5), 919–925. https://doi.org/10.1016/j.marpolbul.2012.03.008

Fernandes, A., Dicks, P., Mortimer, D., Gem, M., Smith, F., Driffield, M., White, S., & Rose, M. (2008). Brominated and chlorinated dioxins, PCBs and brominated flame retardants in Scottish shellfish: Methodology, occurrence and human dietary exposure. *Molecular Nutrition & Food Research, 52*(2), 238–249. https://doi.org/10.1002/mnfr.200700135

Gorga, M., Martínez, E., Ginebreda, A., Eljarrat, E., & Barceló, D. (2013). Determination of PBDEs, HBB, PBEB, DBDPE, HBCD, TBBPA and related compounds in sewage sludge from Catalonia (Spain). *Science of the Total Environment, 444*, 51–59. https://doi.org/10.1016/j.scitotenv.2012.11.066

Goscinny, S., Vandevijvere, S., Maleki, M., Overmeire, I. V., Windal, I., Hanot, V., Blaude, M. N., Vleminckx, C., & Loco, J. V. (2011). Dietary intake of hexabromocyclododecane diastereoisomers (α-, β-, and γ-HBCD) in the Belgian adult population. *Chemosphere, 84*(3), 279–288. https://doi.org/10.1016/j.chemosphere.2011.04.048

Hloušková, V., Lanková, D., Kalachová, K., Hrádková, P., Poustka, J., Hajšlová, J., & Pulkrabová, J. (2013). Occurrence of brominated flame retardants and perfluoroalkyl substances in fish from the Czech aquatic ecosystem. *Science of the Total Environment, 461–462*, 88–98. https://doi.org/10.1016/j.scitotenv.2013.04.081

Hunziker, R. W., Gonsior, S., MacGregor, J. A., Desjardins, D., Adriano, D., & Friederich, U. (2004). Fate and effect of hexabromocyclododecane in the environment. *Organohalog Compounds, 66*, 2300–2305.

Kakimoto, K., Nagayoshi, H., Yoshida, J., Akutsu, K., Konishi, Y., Toriba, A., & Hayakawa, K. (2012). Detection of Dechlorane Plus and brominated flame retardants in marketed fish in Japan. *Chemosphere, 89*(4), 416–419. https://doi.org/10.1016/j.chemosphere.2012.05.072

Kim, U. J., & Oh, J. E. (2014). Tetrabromobisphenol A and hexabromocyclododecane flame retardants in infant-mother paired serum samples, and their relationships with thyroid hormones and environmental factors.

Environmental Pollution, 184, 193–200. https://doi.org/10.1016/j.envpol.2013.08.034

Law, K., Palace, V. P., Halldorson, T., Danell, R., Wautier, K., Evans, B., Alaee, M., Marvin, C., & Tomy, G. (2006). Dietary accumulation of hexabromocyclododecane diastereoisomers in juvenile rainbow trout (Oncorhynchus mykiss) I: Bioaccumulation parameters and evidence of bioisomerization. *Environmental Toxicology and Chemistry, 25*(7), 1757–1761. https://doi.org/10.1897/05-445R.1

Lee, C. C., Chang, W. H., & Chen, H. L. (2019). Dietary exposure and risk assessment of exposure to hexabromocyclododecanes in a Taiwan population. *Environmental Pollution, 249*, 728–734. https://doi.org/10.1016/j.envpol.2019.03.040

Liu, K., Li, J., Yan, S. J., Zhang, W., Li, Y. J., & Han, D. (2016). A review of status of tetrabromobisphenol A (TBBPA) in China. *Chemosphere, 148*, 8–20. https://doi.org/10.1016/j.chemosphere.2016.01.023

Luo, X. J., Ruan, W., Zeng, Y. H., Liu, H. Y., Chen, S. J., Wu, J. P., & Mai, B. X. (2013). Trophic dynamics of hexabromocyclododecane diastereomers and enantiomers in fish in a laboratory feeding study. *Environmental Toxicology and Chemistry, 32*, 2565–2570. https://doi.org/10.1002/etc.2337

Marvin, C. H., Tomy, G. T., Armitage, J. M., Arnot, J. A., McCarty, L., Covaci, A., & Palace, V. (2011). Hexabromocyclododecane: Current understanding of chemistry, environmental fate and toxicology and implications for global management. *Environmental Science & Technology, 45*(20), 8613–8623. https://doi.org/10.1021/es201548c

Meng, X. Z., Xiang, N., Duan, Y. P., Chen, L., & Zeng, E. Y. (2012). Hexabromocyclododecane in consumer fish from south China: Implications for human exposure via dietary intake. *Environmental Toxicology and Chemistry, 31*(7), 1424–1431. https://doi.org/10.1002/etc.1826

Munschy, C., Marchand, P., Venisseau, A., Veyrand, B., & Zendong, Z. (2013). Levels and trends of the emerging contaminants HBCDs (hexabromocyclododecanes) and PFCs (perfluorinated compounds) in marine shellfish along French coasts. *Chemosphere, 91*(2), 233–240. https://doi.org/10.1016/j.chemosphere.2012.12.063

Nakagawa, R., Murata, S., Ashizuka, Y., Shintani, Y., Hori, T., & Tsutsumi, T. (2010). Hexabromocyclododecane determination in seafood samples collected from Japanese coastal areas. *Chemosphere, 81*(4), 445–452. https://doi.org/10.1016/j.chemosphere.2010.08.015

National Physique Monitoring Center of China. (2014). Bulletin of China's national physical fitness monitoring in 2014. Retrieved March 7, 2021, from http://www.sport.gov.cn/n315/n329/c216784/content.html

Ni, H. G., & Zeng, H. (2013). HBCD and TBBPA in particulate phase of indoor air in Shenzhen, China. *Science of the Total Environment, 458–460*, 15–19. https://doi.org/10.1016/j.scitotenv.2013.04.003

POPRC.7. (2011). Report of the persistent organic pollutants review committee on the work of its seventh meeting: Risk management evaluation on hexabromocyclododecane (UNEP/POPS/POPRC.7/19/Add.1). Retrieved March 7, 2021, from http://chm.pops.int/TheConvention/POPsReviewCommittee/ReportsandDecisions/tabid/3309/Default.aspx

POPRC.8. (2012). Report of the Persistent organic pollutants review committee on the work of its eighth meeting: Addendum to the risk management evaluation on hexabromocyclododecane (UNEP/POPS/POPRC.8/16/Add.3). Retrieved March 7, 2021, from http://chm.pops.int/TheConvention/POPsReviewCommittee/ReportsandDecisions/tabid/3309/Default.aspx

POPRC8.3. (2013). Hexabromocyclododecane. Retrieved March 7, 2021, from http://chm.pops.int/TheConvention/POPsReviewCommittee/ReportsandDecisions/tabid/3309/Default.aspx

Qian, Z. Z., Luo, F. F., Wu, C. Y., Zhao, R., Cheng, X., & Qin, W. F. (2017). Indicator polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in seafood from Xiamen (China): Levels, distributions, and risk assessment. *Environmental Science and Pollution Research, 24*(11), 10443–10453. https://doi.org/10.1007/s11356-017-8659-4

Qian, Z. Z., Xu, C. Y., Dong, X. Y., Tang, S. F., & Wei, S. H. (2021). Spatiotemporal characteristics and pollution level of brominated flame retardants in bivalves from Fujian southern coastal areas. *Environmental Science and Pollution Research, 28*(25), 33623–33631. https://doi.org/10.1007/s11356-021-13141-z

Samuelsen, M., Olsen, C., Holme, J. A., Meussen-Elholm, E., Bergmann, A., & Hongslo, J. K. (2001). Estrogen-like properties of brominated analogs of bisphenol A in the MCF-7 human breast cancer cell line. *Cell Biology & Toxicology, 17*, 139–151. https://doi.org/10.1023/A:1011974012602

Shi, Z. X., Wu, Y. N., Li, J. G., Zhao, Y. F., & Feng, J. F. (2009). Dietary exposure assessment of Chinese adults and nursing infants to tetrabromobisphenol-A and hexabromocyclododecanes: Occurrence measurements in foods and human milk. *Environmental Science & Technology, 43*(12), 4314–4319. https://doi.org/10.1021/es8035626

Shi, Z. X., Zhang, L., Zhao, Y. F., Sun, Z. W., Zhou, X. Q., Li, J. G., & Wu, Y. N. (2017). Dietary exposure assessment of Chinese population to tetrabromobisphenol-A, hexabromocyclododecane and decabrominated diphenyl ether: Results of the 5th Chinese Total Diet Study. *Environmental Pollution, 229*, 539–547. https://doi.org/10.1016/j.envpol.2017.06.093

Su, G., McGoldrick, D. J., Clark, M. G., Evans, M. S., Gledhill, M., Garron, C., Armelin, A., Backus, S. M., & Letcher, R. J. (2018). Isomer-specific hexabromocyclododecane (HBCDD) levels in top predator fish from across Canada and 36-year temporal trends in Lake Ontario. *Environmental Science & Technology, 52*(11), 6197–6207. https://doi.org/10.1021/acs.est.8b01052

Tang, B., Zeng, Y. H., Luo, X. J., Zheng, X. B., & Mai, B. X. (2015). Bioaccumulative characteristics of tetrabromobisphenol A and hexabromocyclododecanes in multi-tissues of prey and predator fish from an e-waste site, South China. *Environmental Science and Pollution Research, 22*(16), 12011–12017. https://doi.org/10.1007/s11356-015-4463-1

Tao, L., Wu, J. P., Zhi, H., Zhang, Y., Ren, Z. H., Luo, X. J., & Mai, B. X. (2016). Aquatic bioaccumulation and trophic transfer of tetrabromobisphenol-A flame retardant introduced from a typical e-waste recycling site. *Environmental Science and Pollution Research, 23*(14), 14663–14670. https://doi.org/10.1007/s11356-016-6940-6

Tomy, G. T., Budakowski, W., Halldorson, T., Whittle, D. M., Keir, M. J., Marvin, C., Macinnis, G., & Alaee, M. (2004). Biomagnification of α- and γ-hexabromocyclododecane isomers in a Lake Ontario food web. *Environmental Science & Technology, 38*(8), 2298–2303. https://doi.org/10.1021/es034968h

Tomy, G. T., Pleskach, K., Oswald, T., Halldorson, T., Helm, P. A., Macinnis, G., & Marvin, C. H. (2008). Enantioselective bioaccumulation of hexabromocyclododecane and congener-specific accumulation of brominated diphenyl ethers in an eastern Canadian Arctic marine food web. *Environmental Science & Technology, 42*(10), 3634–3639. https://doi.org/10.1021/es703083z

Törnkvist, A., Glynn, A., Aune, M., Darnerud, P. O., & Ankarberg, E. H. (2011). PCDD/F, PCB, PBDE, HBCD and chlorinated pesticides in a Swedish market basket from 2005–Levels and dietary intake estimations. *Chemosphere, 83*(2), 193–199. https://doi.org/10.1016/j.chemosphere.2010.12.042

Van der Oost, R., Beyer, J., & Vermeulen, N. P. E. (2003). Fish bioaccumulation and biomarkers in environmental risk assessment: A review. *Environmental Toxicology and Pharmacology, 13*(2), 57–149. https://doi.org/10.1016/S1382-6689(02)00126-6

Van der Ven, L. T. M., de Kuil, T. V., Verhoef, A., Verwer, C. M., Lilienthal, H., Leonards, P. E. G., Schauer, U. M. D., Canton, R. F., Litens, S., De Jong, F. H., Visser, T. J., Dekant, W., Stern, N., Hakansson, H., Slob, W., Van den Berg, M., Vos, J. G., & Piersma, A. H. (2008). Endocrine effects of tetrabromobisphenol-A (TBBPA) in Wistar rats as tested in a onegeneration reproduction study and a subacute toxicity study. *Toxicology, 245*(1–2), 76–89. https://doi.org/10.1016/j.tox.2007.12.009

van Leeuwen, S. P. J., & de Boer, J. (2008). Brominated flame retardants in fish and shellfish - Levels and contribution of fish consumption to dietary exposure of Dutch citizens to HBCD. *Molecular Nutrition & Food Research, 52*(2), 194–203. https://doi.org/10.1002/mnfr.200700207

Wang, F. D., Zhang, H. J., Geng, N. B., Zhang, B. Q., Ren, X. Q., & Chen, J. P. (2016). New insights into the cytotoxic mechanism of hexabromocyclododecane from a metabolomic approach. *Environmental Science & Technology, 50*(6), 3145–3153. https://doi.org/10.1021/acs.est.5b03678

Wang, Y. F., Huang, M. R., Zhang, S. H., Wang, H., & Shi, Z. X. (2014). Survey on pollution levels of decabrominated dipenyl ethers and hexabromocyclododecane in food of animal origin saled in Beijing's markets. *Journal of Food Safety & Quality, 5*(2), 485–491.

Xia, C. H., Lam, J. C. W., Wu, X. G., Sun, L. G., Xie, Z. Q., & Lam, P. K. S. (2011). Hexabromocyclododecanes (HBCDs) in marine fishes along the Chinese coastline. *Chemosphere, 82*(11), 1662–1668. https://doi.org/10.1016/j.chemosphere.2010.11.012

Xia, W., Wang, J. M., Yang, H., Zhang, H., Yang, B., Zeng, Y. H., Xu, J., Li, Z. G., & Qian, M. R. (2018). Bioaccumulation and distribution of hexabromocyclododecane isomers in duck tissues. *Bulletin of Environmental Contamination and Toxicology, 100*(6), 754–759. https://doi.org/10.1007/s00128-018-2342-4

Xiamen Municipal Bureau of Ocean Development. (2017). Bulletin on marine ecological environment of Xiamen in 2017. Retrieved Feburary 20, 2021, from http://hyj.xm.gov.cn/lszt/hyhjxx/201806/t20180625_1906113.htm

Xiamen Municipal Bureau of Ocean Development. (2018). Bulletin on marine environment quality of Xiamen in August 2018. Retrieved Feburary 20, 2021, from http://hyj.xm.gov.cn/lszt/hyhjxx/201810/t20181023_2146827.htm

Zhang, J., Liu, F., Chen, R. B., Feng, T., Dong, S., & Shen, H. (2012). Levels of polychlorinated biphenyls and organochlorine pesticides in edible shellfish from Xiamen (China) and estimation of human dietary intake. *Food and Chemical Toxicology, 50*(12), 4285–4291. https://doi.org/10.1016/j.fct.2012.08.052

Zhang, Y., Sun, H., Liu, F., Dai, Y., Qin, X., Ruan, Y., Zhao, L., & Gan, Z. (2013). Hexabromocyclododecanes in limnic and marine organisms and terrestrial plants from Tianjin, China: Diastereomer- and enantiomer-specific profiles, biomagnification, and human exposure. *Chemosphere, 93*(8), 1561–1568. https://doi.org/10.1016/j.chemosphere.2013.08.004

Zhang, Y. Q., Lua, Y. L., Wang, P., & Shi, Y. J. (2018). Biomagnification of Hexabromocyclododecane (HBCD) in a coastal ecosystem near a large producer in China: Human exposure implication through food web transfer. *Science of the Total Environment, 624*, 1213–1220. https://doi.org/10.1016/j.scitotenv.2017.12.153

Zhu, H., Sun, H., Zhang, Y., Xu, J., Li, B., & Zhou, Q. (2016). Uptake pathway, translocation, and isomerization of hexabromocyclododecane diastereoisomers by wheat in closed chambers. *Environmental Science & Technology, 50*(5), 2652–2659. https://doi.org/10.1021/acs.est.5b05118