Environmental Science and Pollution Research (2021) 28:33623–33631
https://doi.org/10.1007/s11356-021-13141-z

RESEARCH ARTICLE

Spatiotemporal characteristics and pollution level of brominated flame retardants in bivalves from Fujian southern coastal areas

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Received: 24 September 2020 / Accepted: 22 February 2021 /

Abstract

The concentration and spatiotemporal distribution of brominated flame retardants (BFRs), including hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA), were analyzed in bivalves from Fujian southern coastal areas. The concentrations of HBCD and TBBPA ranged from ND (not detected) to 5.540 ng·g^{-1} (ww) (median of 0.111 ng·g^{-1}) and ND to 0.962 ng·g^{-1} (ww) (median of ND), respectively. In addition, α-HBCD was found as the predominant diastereoisomer in all the studied samples, followed by β-HBCD and γ-HBCD. The spatial distribution of BFRs showed a peak distribution, with the content being higher in the marine environment of Xiamen and Quanzhou, in South Fujian, and lower toward the marine environment of Zhangzhou, and Putian. BFRs contamination level was correlated to the bay geographical location and proximity to local industries. Furthermore, the results of the study showed a seasonal variation pattern: summer > autumn > spring > winter. This study provides base information on the contamination status of these BFRs in the marine environment of southern Fujian.

Keywords Hexabromocyclododecane (HBCD) · Tetrabromobisphenol A (TBBPA) · Bivalves · Spatial distribution · Temporal distribution

Introduction

The southern coastal area of Fujian, one of the major coastal areas in China, is mainly composed of Meizhou Bay, Dagang Bay, Quanzhou Bay, Weitou Bay, Anhai Bay, Xiamen Bay, Jiuzhen Bay, Fotan Bay, Dongshan Bay, and Zhao'an Bay. In recent years, with the settlement of large-scale chemical and industrial projects and the extension of industrial urbanization resulting from the economic development of southern Fujian, large quantities of brominated flame retardants (BFRs) are discharged into the coastal areas, which seriously affects the safety of the marine ecosystems (Cao et al. 2018; Guo et al. 2010). Recognized as the two most widely used BFRs, hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) have been extensively used in textiles, thermal insulation materials, electrical equipment, building materials, and plastic materials for decades. In 2011, the global production of HBCD was approximately 31,000 tons (POPRC 2011, 2012), while in China the estimated domestic production reached 18,000 tons (Li et al. 2016). Commercial HBCD product consists of three stereoisomers: α-HBCD (12%), β-HBCD (6%), and γ-HBCD (82%). Due to its high bioaccumulation, persistence, hepatotoxicity, neurotoxicity, and immunotoxicity (Tomy et al. 2008; Marvin et al. 2011; Zhu et al. 2016; Wang et al. 2016; Zhang et al. 2018), HBCD was explicitly listed as a POP under Annex A of the Stockholm Convention in 2013 (POPRC8.3 2013) and it was recommended to be banned from production and use. TBBPA is mainly used in epoxy resins of printed circuit boards or in various polymers as a reactive or additive flame retardant. The usage of TBBPA increased rapidly from 2004 (Liu et al. 2016), with a rising domestic market demand (Zhang et al. 2014). However, because of its structural similarity to the thyroid hormone thyroxine, TBBPA may act as an endocrine-disruptor chemical. Additionally, previous studies (Samuelsen et al. 2001; Van der Ven et al. 2008; Cunha et al. 2017) have shown that TBBPA exhibits potential cytotoxicity, immunotoxicity, thyroxine, and estrogen interference effects. TBBPA has been listed as a priority control chemical under the Hazardous Substances Strategy.

Responsible Editor: Hongwen Sun

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Marine sediments in coastal areas are commonly enriched in contaminants. A large number of bivalves are widely distributed in marine sediments. Due to their sessile lifestyle and filter-feeding habit, bivalves are prone to absorb and accumulate important amounts of pollutants from their environment. Therefore, they can be used as biological indicators of marine pollution, and the level of pollutants in their bodies can be an indicator of the pollution status of their habitat environment, to a certain extent. The use of bivalves for monitoring and risk assessment of chemical pollutants in the marine environment has become an important method applied in many countries through programs such as the United States' Mussel Watch and the International Mussel Watch. Moreover, studies have shown that HBCD and TBBPA have been detected in various bivalves (Fernandes et al. 2008; La Guardia et al. 2012; Munschy et al. 2013; Munschy et al. 2015; van Leeuwen and de Boer 2008).

The objectives of the present study were to get a better understanding of the recent levels of HBCD and TBBPA pollution in the coastal areas of southern Fujian by analyzing the distribution of such levels in representative bivalve species. Additionally, a spatial and temporal distribution study was conducted using cluster analysis and single factor analysis to provide a basis for the protection of the coastal ecological environment of Fujian.

Materials and methods

Sampling

Based on the abundant bivalve populations present in 10 coastal bays of southern Fujian (Meizhou Bay, Dagang Bay, Quanzhou Bay, Anhai Bay, Weitou Bay, Xiamen Bay, Fotan Bay, Jiuzhen Bay, Dongshan Bay, and Zhao'an Bay), 200 bivalve samples (Table S1), including *Crassostrea gigas*, *Ruditapes philippinarum*, *Arca granosa*, *Sinonovacula constricta*, and *Paphia undulate*, were collected between March 2017 and December 2018 (Fig. 1). We collected the same length of bivalves to avoid age differences. The length of *Crassostrea gigas*, *Ruditapes philippinarum*, *Arca granosa*, *Sinonovacula constricta*, and *Paphia undulate* were 90–100, 40–45, 30–35, 60–65, and 40–45 mm, respectively. The samples were placed in a car refrigerator (0 °C–5 °C) for transportation to the laboratory on the sampling day. In the laboratory, all edible contents of bivalves were taken, homogenized, lyophilized, grinded, and kept at – 20 °C until analysis. Twenty same species individuals of similar size collected from each sampling site were blended into one sample, and a total of 200 samples were obtained.

Chemicals and materials

Standards of α-, β-, and γ-HBCD were purchased from AccuStandard Inc. (New Haven, CT, USA) and TBBPA was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). $^{13}C_{12}$-β-HBCD and $^{13}C_{12}$-TBBPA standards were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). HPLC-grade hexane, dichloromethane, acetone, acetonitrile, and methanol were supplied from Tedia (Fairfield, OH, USA). Sodium sulfate was baked at 500 °C and stored in the sealed containers. Silica gel solid-phase extraction column was obtained from Waters (Milford, MA, USA).

Analytical methods

Approximately 10.0 g of each homogenized sample was spiked with internal standards ($^{13}C_{12}$-β-HBCD and $^{13}C_{12}$-TBBPA). 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 reaction 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;

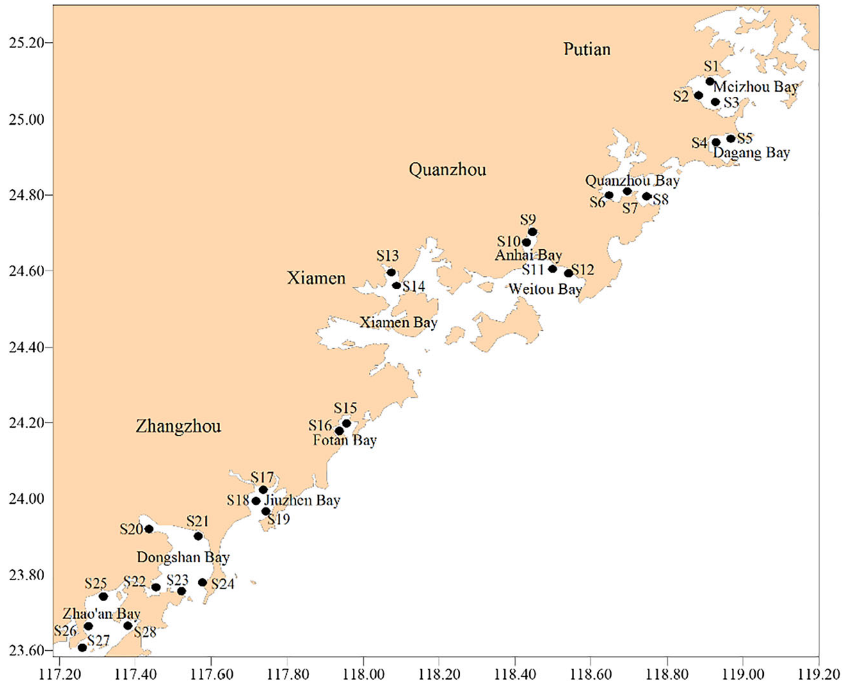

Fig. 1 Geographical location of the sampling sites

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. SRM signals for quantification and confirmation for TBBPA were from *m*/*z* 542.9 to 420.0 and 542.9 to 418.0, respectively. A transition of 652.9 to 81.2 *m*/*z* was applied to quantify $^{13}C_{12}$-β-HBCD, and that of 555.0 to 431.0 for $^{13}C_{12}$-TBBPA.

Quality control (QC)

The identification of BFRs was based on their relative retention time to the corresponding standards. BFR identification based on their relative retention times was also performed according to the corresponding SRMs for each targeted analyte. For compensation of any unexpected effect of the matrix, we preferred the use of isotopically labeled standards for HBCD isomers and TBBPA. Otherwise, we used matrix-matched calibration standards prepared from blank bivalves for quantification. The standard curves for the internal standards (included in a blank matrix sample) were linear over the range of 1 to 100 ng·mL^{-1}, with an $R^2 \geq 0.990$. The limits of detections (LOD) based on a signal-to-noise ratio of 3:1 were 0.05 ng·g^{-1}. One batch of 20 samples was analyzed daily. For each batch of 20 samples, a procedural blank, a spiked blank, five fivefold LOD spiked samples, and a tenfold LOD spiked sample were analyzed. Procedural blanks were performed to check the potential contamination and interferences. Neither HBCD nor TBBPA was detected in the procedural blanks. All recoveries of spiked samples were between 65% and 110%. Inter-day reproducibilities (5*LOQ level) of HBCD and TBBPA (n = 5) were 3.1%–10.9% and 4.7%–9.0%, respectively. Intra-day reproducibilities (10*LOQ level) of HBCD and TBBPA (n = 10) were 8.6%–13.8% and 12.7%, respectively. Results of spiked experiments are shown in the supplementary information (Table S2). HBCD and TBBPA concentrations in samples were calculated using Eq. (1) and expressed on a wet weight (ww) basis (Table 1).

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

where C_i is the concentration of HBCD and TBBPA, in ng·g^{-1} (ww), in the wet sample; C_j is the concentration of HBCD and TBBPA, in ng·g^{-1}, in the lyophilized sample; and ω_{H_2O} is the moisture content of the wet sample, in %, calculated according to Eq. (2).

$$\omega_{H_2O} = \frac{m_w - m}{m_w} \times 100\%, \tag{2}$$

where m_w is the weight of the wet sample, in g, and m is the weight of the lyophilized sample, in g.

Data obtained from of the HBCD and TPPBA tests in marine fishes, organized by the State Oceanic Administration People's Republic of China, were validated by inter-laboratory comparison. Data from our laboratory were found to be within the range of the consensual values.

Statistical analysis

Statistical analyses were performed using SPSS 20.0 (SPSS, Chicago, IL, USA). Concentrations below the LOD were set to half of the LOD. The results were presented with median

Table 1 Concentrations of typical chemical contaminants in bivalves (ww)

	HBCD		TBBPA	
	Mean ± SD Median (range) (ng g^{-1} ww)	Detection rate (%)	Mean ± SD Median (range) (ng g^{-1} ww)	Detection rate (%)
Crassostrea gigas	0.288 ± 0.588 ND(ND–3.954)	43.1	0.111 ± 0.163 ND(ND–0.758)	35.7
Ruditapes philippinarum	0.347 ± 0.683 0.126(ND–4.156)	67.5	0.077 ± 0.170 ND(ND–0.867)	22.5
Arca granosa	0.446 ± 0.515 0.218(ND–1.620)	75.0	0.123 ± 0.164 0.040(ND–0.590)	50.0
Sinonovacula constricta	0.599 ± 1.044 0.131(ND–5.540)	66.0	0.144 ± 0.240 ND(ND–0.962)	40.4
Paphia undulate	0.559 ± 0.952 0.090(ND–4.670)	67.9	0.129 ± 0.206 ND(ND–0.940)	35.7
Bivalve	0.427 ± 0.787 0.111(ND–5.540)	60.0	0.116 ± 0.191 ND(ND–0.962)	37.0

ND not detected, *SD* standard deviation

value, mean value, ± standard deviation, and range. Before performing the statistical analyses, data were tested for normality and homogeneity of variance and processed for logarithm transformation. However, no matter what kind of data processing method was adopted, the data obtained in this study still showed a non-normal distribution. Nonparametric Kruskal-Wallis tests (K-W test) were used to analyze differences among species, seasons, and bays. A significant level of $p < 0.05$ was used. The spatial similarity of HBCD and TBBPA was analyzed by means of a hierarchical cluster analysis.

Results and discussion

Contamination level and compositional characteristics

Although it has been previously reported that the HBCD levels in aquatic products were significantly higher than those observed in other kinds of food products, there are some comprehensive studies on the contamination of HBCD and TBBPA on a large scale with bivalves as research subjects. Van Leeuwen et al. focused on the residues of HBCD and TBBPA in fish and shellfish originated from Dutch marine and fresh waters (van Leeuwen and de Boer 2008). In their study, the detection rate of HBCD in marine fish and shellfish was low (range, ND–7.3 ng·g^{-1} ww) and TBBPA was not detected in all aquatic products. In the study of Fernandes et al. (2008), four kinds of shellfish samples were collected from Scotland; HBCD (range of 0.03–12.1 ng·g^{-1} ww) was detected in all shellfish samples and TBBPA was not detected in any of the species. A French study by Munschy et al. (2013) on the residue of HBCD in marine shellfish showed that the content of HBCD in shellfish was 0.01–0.55 ng·g^{-1} ww from 2008 to 2010. The HBCD concentrations in another study by Munschy et al. (2015) were shown to have increased in shellfish along French coasts from 2011 to 2012. Spatial distribution of HBCD in bivalves from Japanese coastal waters was conducted by Ueno et al. (2010). Concentration ranges of HBCD were 12–5200 ng·g^{-1} lw, and the highest concentration of HBCD was found in the Osaka region. Isobe et al. (2012) investigated the contamination status of HBCD in the coastal waters of Asia using mussels as a bioindicator. The results suggest that environmental pollution level of HBCDs in Japan is ubiquitous. A Chinese study by Hu (2015) showed that the TBBPA concentrations in digestive gland tissue ranged from 14.28 to 37.24 ng·g^{-1} dw in scallops collected offshore from Qingdao.

In the present study, as shown in Table 1, the overall detection rates of HBCD (sum of α-, β-, γ-HBCD) and TBBPA were 60.0% and 37.0%, respectively, and the levels were ND–5.540 and ND–0.962 ng·g^{-1}. Among species, no significant differences were found in the BFR concentrations (K-W test; $p < 0.05$). The HBCD levels detected in the present study were higher than those observed in shellfish originating from the Dutch marine environment (van Leeuwen and de Boer 2008) and collected from French coasts (Munschy et al. 2013; Munschy et al. 2015). Additionally, our result showed a lower level of HBCD in bivalve samples compared with those caught on the Japanese coasts (range, ND–77.3 ng g^{-1} ww; Nakagawa et al. 2010). The TBBPA concentrations in the present study were significantly higher than those in Scottish shellfish (Fernandes et al. 2008) and shellfish collected from the Netherlands (van Leeuwen and de Boer 2008). The levels of TBBPA in this study were also higher than those reported in shellfish from South Korea (Lee et al. 2020).

Table 2 Concentrations of typical chemical contaminants in bivalves from different bays

Sampling regions	Species (*n*)	HBCD		TBBPA	
		Mean ± SD Median (range) (ng g^{-1} ww)	Detection rate (%)	Mean ± SD Median (range) (ng g^{-1} ww)	Detection rate (%)
Meizhou Bay	*Crassostrea gigas* (11) *Sinonovacula constricta* (9)	0.539 ± 0.711 0.217(ND–2.233)	60.0	0.177 ± 0.223 ND(ND–0.761)	45.0
Dagang Bay	*Crassostrea gigas* (4) *Ruditapes philippinarum* (4) *Arca granosa* (4) *Sinonovacula constricta* (4) *Paphia undulata* (4)	0.515 ± 0.742 0.278(ND–3.180)	65.0	0.118 ± 0.208 ND(ND–0.870)	35.0
Quanzhou Bay	*Crassostrea gigas* (6) *Ruditapes philippinarum* (7) *Sinonovacula constricta* (7)	0.149 ± 0.169 0.064(ND–0.476)	55.0	0.054 ± 0.050 ND(ND–0.199)	35.0
Anhai Bay	*Crassostrea gigas* (4) *Ruditapes philippinarum* (4) *Arca granosa* (4) *Sinonovacula constricta* (4) *Paphia undulata* (4)	0.479 ± 0.701 0.253(ND–3.031)	65.0	0.132 ± 0.216 ND(ND–0.820)	40.0
Weitou Bay	*Crassostrea gigas* (4) *Ruditapes philippinarum* (4) *Arca granosa* (4) *Sinonovacula constricta* (4) *Paphia undulata* (4)	0.840 ± 1.333 0.192(ND–4.67)	65.0	0.230 ± 0.308 ND(ND–0.940)	40.0
Xiamen Bay	*Crassostrea gigas* (8) *Sinonovacula constricta* (4) *Paphia undulata* (8)	0.910 ± 1.461 0.207(ND–5.540)	70.0	0.213 ± 0.289 ND(ND–0.962)	45.0
Fotan Bay	*Crassostrea gigas* (8) *Ruditapes philippinarum* (12)	0.226 ± 0.288 0.090(ND–0.934)	60.0	0.049 ± 0.046 ND(ND–0.179)	30.0
Jiuzhen Bay	*Crassostrea gigas* (9) *Sinonovacula constricta* (11)	0.203 ± 0.244 0.047(ND–0.680)	50.0	0.058 ± 0.061 ND(ND–0.232)	30.0
Dongshan Bay	*Crassostrea gigas* (4) *Ruditapes philippinarum* (4) *Arca granosa* (4) *Sinonovacula constricta* (4) *Paphia undulata* (4)	0.219 ± 0.263 0.096(ND–0.915)	55.0	0.055 ± 0.053 ND(ND–0.200)	35.0
Zhao'an Bay	*Crassostrea gigas* (8) *Ruditapes philippinarum* (4) *Arca granosa* (4) *Paphia undulata* (4)	0.189 ± 0.253 0.070(ND–0.867)	45.0	0.072 ± 0.076 ND(ND–0.258)	35.0

ND not detected, *SD* standard deviation

The present work shows that the detection rates of α-, β-, and γ-isomers in all the studied positive samples were 100%, 40%, and 3.33%, respectively, and α-HBCD was found as the predominant diastereoisomer in those positive samples. This phenomenon was consistent with previous studies where the dominance of α-HBCD was observed in the vast majority of aquatic organisms and mammalian species. An underlying reasons could be the slowest metabolic rate of α-HBCD (Law et al. 2006; Eljarrat et al. 2014), compared with β- and γ-HBCD, which are likely metabolized to hydrocarbon analogues rapidly. Moreover, a low degree of elimination rate of α-HBCD in biota, which results in higher adipose tissue deposition of α-HBCD, might be another explanation for these results. The bioconversion from β- and γ-HBCD to α-HBCD was also considered a possible explanation (Zhu et al. 2016; Zheng et al. 2017; Letcher et al. 2015; Su et al. 2018). Besides, the bioavailability of HBCD could affect HBCD diastereoisomer profiles. Water solubility of α-, β-, and γ-HBCD are 48.8, 14.7, and 2.1 μg·L^{-1}, respectively (Hunziker et al. 2004). Although γ-HBCD is the major isomer in the technical mixture, α- and β-HBCD have a relatively higher aqueous solubility than γ-HBCD. This suggests that α- and β-HBCD are more likely to be found in aquatic environments, which can explain their higher bioaccumulation in aquatic organisms compared with γ-HBCD. Moreover, the pollution level of TBBPA in bivalves was relatively lower, namely, lower than that of HBCD. The detection rates of TBBPA were also lower, except for the detection rate of 50% in *Arca granosa*. This finding could be explained by the lower bioaccumulation potential of TBBPA due to its low Kow. In addition, TBBPA is a

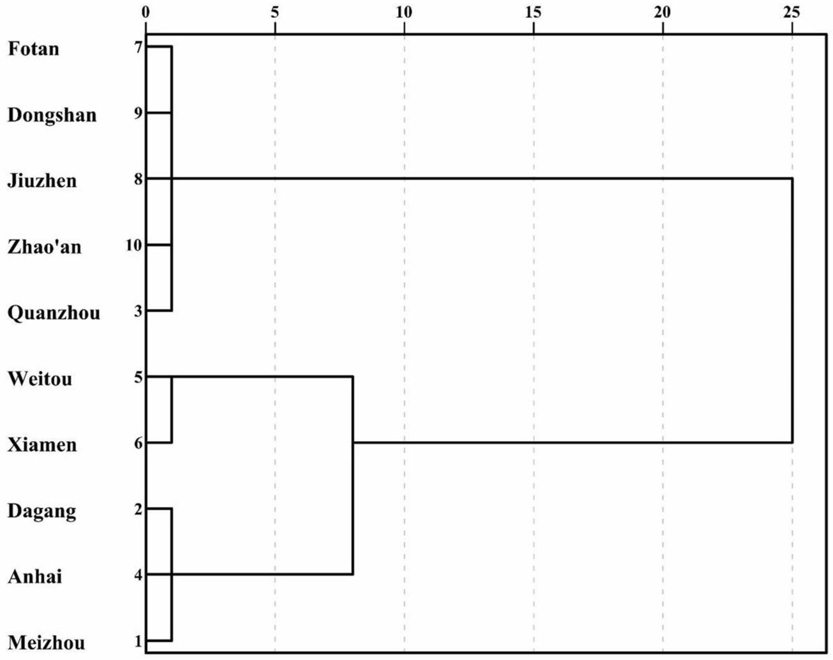

Fig. 2 The dendrogram of 10 bays (Ward clustering method, squared Euclidean distance)

reactive BFRs that is chemically bound into a polymeric matrix, resulting in a limited release rate into the environment. Also, its low biomagnification potential through the aquatic food web might be another explanation (Tao et al. 2016).

Spatial distribution of HBCD and TBBPA

Table 2 listed the levels of HBCD and TBPPA in bivalves collected from 10 major bays in South Fujian. The spatial distribution of the overall level showed a peak distribution, with the content being higher in the marine environment of Xiamen and Quanzhou in South Fujian, and lower toward the marine environment of Zhangzhou, and Putian (Fig. 1). The results of *q*-type system cluster analysis based on each bay mean concentration showed that the 10 bays were divided into three categories: bays in category I included Xiamen Bay and Weitou Bay; bays in category II included Meizhou Bay, Anhai Bay, and Dagang Bay; and the remaining five bays were in category III (Fig. 2). The Kruskal Wallis analysis showed that there was no significant difference ($p < 0.05$) in the content of chemical pollutants in each group, but there were significant differences ($p < 0.05$) in the content of HBCD among the three categories. The overall pollution situation was as follows: Category I bays > Category II bays > Category III bays. These results are closely related to the shape of each bay, dense population, agricultural, and industrial activities.

Weitou Bay is a semi-open bay, along which there are many small- and medium-sized industrial enterprises. It was more densely populated and the discharge of

Table 3 Concentrations of typical chemical contaminants in bivalves from different seasons (ww)

Sampling season	HBCD		TBBPA	
	Mean ± SD Median (range) (ng g^{-1} ww)	Detection rate (%)	Mean ± SD Median (range) (ng g^{-1} ww)	Detection rate (%)
Spring	0.203 ± 0.210 0.128(ND–0.857)	62.0	0.065 ± 0.084 ND(ND–0.422)	32.0
Summer	1.024 ± 1.314 0.650(ND–5.540)	72.0	0.234 ± 0.297 ND(ND–0.962)	48.0
Autumn	0.396 ± 0.448 0.247(ND–1.620)	54.0	0.120 ± 0.170 ND(ND–0.710)	40.0
Winter	0.083 ± 0.103 0.060(ND–0.511)	52.0	0.044 ± 0.040 ND(ND–0.192)	28.0

ND not detected

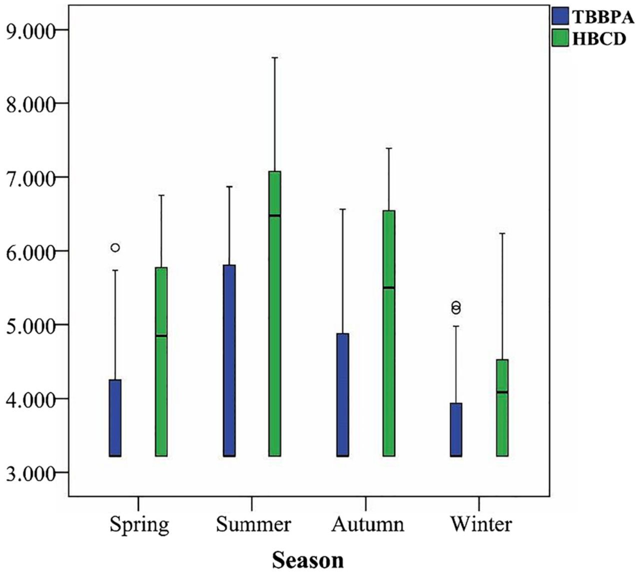

Fig. 3 Seasonal variations of hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA concentrations in 10 coastal bays of southern Fujian

industrial and domestic wastewaters was greater than the self-purification capacity of the port. Similarly, Xiamen Bay is also a semi-enclosed bay. High-value areas with chemical pollutants in Xiamen Bay were mainly located in the interior of Xiamen Bay, with poor hydrodynamic conditions and weak dilution and self-purification capacities of their liquid wastes. In addition, the surrounding areas of Xiamen Bay have relatively developed industry and agriculture sectors, with a larger use of pesticides and fertilizers per unit area, larger ports, and more frequent pollution activities relative to maritime transportation and tourism. Therefore, the discharge of land-based pollutants, such as industrial and agricultural sewage, domestic wastewater, and oily wastewater from ships exceeding the self-purification capacity of the bays, was the main reason for the high accumulation and pollution of HBCD and TBBPA among the bivalves in Weitou Bay and Xiamen Bay. The Category II bays of Meizhou Bay, Anhai Bay, and Dagang Bay are located in the south-central region of Fujian and are adjacent to each other, making them important economic development zones and aquaculture areas in Fujian. Due to the rapid development of the petrochemical and energy industries in the Meizhou Bay in recent years, its development zone has become an important petrochemical base in Fujian province. Therefore, the results showed that the pollution levels of HBCD and TBBPA in Meizhou Bay bivalves were medium among the 10 bays in southern Fujian. HBCD and TBBPA values were lower in Category III bays, which included Quanzhou Bay, Fotan Bay, Jiuzhen Bay, Dongshan Bay, and Zhaoan Bay. Among them, Fotan Bay, Jiuzhen Bay, Dongshan Bay, and Zhaoan Bay belong to the Zhangzhou region, which is a region where agriculture activities still predominate until recent years. As a result, the HBCD and TBBPA pollution levels in Category III bays were about one-half to one-quarter of the pollution levels found in the other two categories.

Seasonal variation

Results from the seasonal variation analysis showed that α-HBCD was present in bivalve samples in spring, summer, autumn, and winter seasons. β-HBCD was found in bivalve samples in spring, summer, and autumn, whereas this compound was detected in only one bivalve sample in winter. Also, γ-HBCD was detected only in summer. As illustrated in Table 3 and Fig. 3, significant differences were found in HBCD and TBBPA concentration among seasons (Tukey HSD, $p < 0.05$), as seen by the obvious higher mean and median concentration values in summer. Furthermore, the highest concentrations of α-HBCD, β-HBCD, γ-HBCD, total HBCD, and TBBPA were measured in summer. The results of this study showed the next seasonal variation pattern: summer > autumn > spring > winter, which was similar to the seasonal variation pattern of HBCD found in Shanghai (Wu et al. 2014; Tang et al. 2015). The seasonal variation may be attributed to a combined effect of several factors, such as HBCD and TBBPA solubility, temperature, and wet deposition. The solubility of HBCD and TBBPA increased with an increase in summer temperature, causing an increased release of HBCD and TBBPA from sediment desorption to water. At the same time, sufficient rainfall in summer could also transfer the fine particles encapsulating the HBCD and TBBPA present in the atmosphere to the ground, increasing, in this way, their accumulation into coastal sediments through the water, and promoting the bioaccumulation of these sediment-bound compounds in the bivalves living in these areas. Otherwise, the seasonal characteristics of bivalves with a higher lipid content in summer and autumn may also have a certain influence on the variation of changes.

Conclusions

This study provides the first data collected on pollution level of HBCD and TBBPA in bivalves from Fujian southern coastal areas. Additionally, a spatial and temporal distribution study was investigated. The results showed that spatiotemporal characteristics were related to the bay geographical location and high anthropogenic pressure of industrial and urban activities. Furthermore, the results of the study showed a seasonal variation pattern: summer > autumn > spring > winter. Further studies are needed to focus on the long-term monitoring of bivalve BFR levels in the coastal areas of southern

Fujian as well as the relationship between BFR emission and urbanization in the future.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11356-021-13141-z.

Acknowledgements We thank Xuelong He for the field work and sample processing.

Author contribution Zhuozhen Qian contributed the central idea, analyzed most of the data, and wrote the initial draft of the paper. Cuiya Xu collected the data. Xiaoyi Dong refined the ideas. Shuifen Tang carried out additional analyses. Shaohong Wei finalized the paper.

Funding This research was supported by the Natural Science Foundation of Fujian Province (No. 2018J01056).

Data availability The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare that they have no competing interests.

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