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CONCENTRATIONS, CHARACTERISTICS, AND CORRELATIONS OF POLYCHLORINATED BIPHENYLS AND POLYBROMINATED DIPHENYL ETHERS IN COASTAL AQUACULTURE ENVIRONMENT SEDIMENTS IN ZHEJIANG PROVINCE, CHINA

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ABSTRACT

The concentrations of 20 polychlorinated biphenyls (PCB) congeners and 39 polybrominated diphenyl ethers (PBDE) congeners in sediments collected from three major coastal aquaculture areas in Zhejiang province, China were analyzed. The concentrations of ∑20 PCB and ∑39 PBDE congeners ranged from nd-43.76 ng/g, and 1.35-26.18 ng/g, respectively. In general, the average homolog composition of PCBs decreased in the following order: penta- > hexa- > tetra- > hepta- > tri- > octa –PCBs. The average homolog composition of PBDEs decreased in the following order: mono- > di- > tri- > tetra- > penta- > hexa- > hepta –BDEs. A statistical analysis using principal component analysis was performed on the 20 PCB and 39 PBDE congener profiles. The first principal component PCB-52, 105, 112, 118, 123, 126, 156, 157, 167, 169, and 189, accounted for 51.17% of the total variance in Taizhou city, making a significant contribution to the local pollution levels. The contribution of BDE-2, 3, 8, 10, 17, 33, 47, 138, and 153 was relatively high in these samples. A significant correlation was observed between the concentrations of CB-105 and CB-123, 126, 156, 157, 167, and 169. There were also positive correlations between some bromine congeners, such as BDE-2 and BDE 3, BDE 8, BDE 10, and BDE 33; BDE-33 and BDE 8 and BDE 10; and BDE-33 and BDE 15, BDE 49, and BDE 77, with the low molecular weight bromine compounds likely to have originated from the decomposition of commercial bromine compounds.

KEYWORDS:
Polychlorinated biphenyls; polybrominated diphenyl ethers; coastal aquaculture environment sediments; concentrations, characteristics; correlations

INTRODUCTION

Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are two contaminants of particular concern because both are persistent, bioaccumulative, and toxic, and have some similarities in terms of molecular and physicochemical properties [1]. They are hydrophobic and tend to occur in the particulate phase during their transport, distribution, and final deposition [2]. These compounds have become ubiquitous in environmental and biological samples worldwide due to their persistence and long-range transport [3]. PCBs have been used in electrical products since the 1930s due to their insulating properties, and their worldwide production during the last 60 years has ranged from 1.2 to 2 million tons [4]. It has been reported that 8000 tons of PCBs were manufactured from the 1960s to 1970s in China [5]. However, it was not until 1966 that PCBs were detected in organisms in the marine environment [6]. In 1968, the Yusho poisoning incident occurred in Japan, in which 1800 people were poisoned by PCB-contaminated rice oil [7]. In recent decades, PCBs have been found in biota globally, causing great concerns due to their recalcitrance and toxicity [8]. Despite the restrictive legislation in effect since the 1970s in the USA and Europe and since 1993 in Russia, PCBs still persist in the environment and PCBs have been implicated in thyroid and estrogenic disturbances [9]. PBDEs are a group of brominated flame retardants that are used as additives in many polymers for the manufacture of consumer products, such as electrical and electronic equipment, textiles, upholstery, and many types of plastics, to reduce their flammability [10]. Three major commercial PBDE products (penta-BDE, octa-BDE, and deca-BDE) have been manufactured since the 1970s and are currently still in use. PBDEs have a similar chemical structure to PCBs, and are presumed to have similar toxicological and environmental properties [11]. Like some other environmental pollutants (e.g., organochlorine compounds)

PBDEs are persistent, lipophilic, and bioaccumulative (World Health Organization, 1997). Among the available commercial mixtures, penta- and octa-BDE have been banned in Europe and since 2004 several companies in the USA have voluntarily phased out PBDE manufacture [12]. The Stockholm Convention in 2009 listed penta- and octa-BDE as persistent organic pollutants and classified them as materials requiring international regulation [13]. The benefits derived from PBDEs are outweighed by their negative impacts on the environment, human health, and wildlife, due to their persistence, potential to bioaccumulate, toxicity, and their capacity for long-range environmental transport [14]. PBDEs can be transported and accumulated in soils, sediments, and organisms through gas absorption/volatilization and dry/wet deposition [15,16]. Sediment is an environmental sink of organic compounds and plays an important role in the distribution and fate of these contaminants in aquatic environments, where organic contaminants can be adsorbed to suspended particles and selectively survive degradative processes during vertical transport and deposition [17].

Zhejiang Province is an important electronic waste (e-waste) recycling base, and a cluster of small villages in the littoral zone has become a flourishing recycling center for e-waste, but this has come at the expense of having thousands of village workers engaged in primitive recycling operations without the use of adequate protective equipment [18]. In recent years, the concentration and distribution of PCBs and PBDEs originating from this e-waste recycling region has been reported to affect the air, soil, and marine organisms [19]. Inshore cultivation in seawater is one of the main agricultural industries in Zhejiang province, and it has a number of advantages including the provision of a natural seawater environment, feed, and growth. Chemical compounds from e-waste recycling are continuously dissolving, attaching to suspended particles, being resuspended due to diagenesis or the shear force of the flowing water on top of the sediments, reacting, diffusing, and advecting with bulk water movement [20]. Therefore, the marine sediments have become contaminated with PCBs and PBDEs, which can harm human health following bio-magnification through the food chain.

The aim of the study was to investigate the distribution of PCBs and PBDEs in offshore aquaculture sediments in Zhejiang province, China. First, the contamination levels of PCBs and PBDEs in sediments from different sampling sites were determined. The concentrations and molecular patterns of the two classes of chemicals in three sampling areas were compared with those reported in previous studies. Then the pollution sources were analyzed, and their variations were considered in relation to the molecular properties. By evaluating the concentrations, characteristics, and correlations of PCBs and PBDEs in the offshore aquaculture sediments of this region we can provide reference values for coastal industries, particularly the e-waste recycling industry, and assist the further development and utilization of offshore resources.

MATERIALS AND METHODS

Study area and sample collection. Based on a careful field survey, a specific sampling programme was conducted in August 2012 (Fig. 1). Sampling occurred at 20 sampling sites in three different offshore aquaculture areas in Zhejiang, China. Stations 1 to 12 were located in Taizhou, where the major industrial enterprises are mold manufacturing, they chemical industry, and e-waste dismantling and recycling. Stations 21 to 24 were located in Xiangshan, where the major industries are mechanical engineering and electronics. Station 31 to 33 were located in Zhoushan, which has an island location and marine aquaculture is the main economic activity. A global positioning system was used to identify the precise location of each station. At each sampling site, about 1000 g of two parallel surface sediments (0–20 cm) were collected using a grab sampler and then placed in pre-cleaned glass containers. All samples were transported to the laboratory within 8 h of collection. The samples were then air-dried, ground, sealed in glass jars, and stored at −20°C for future use.

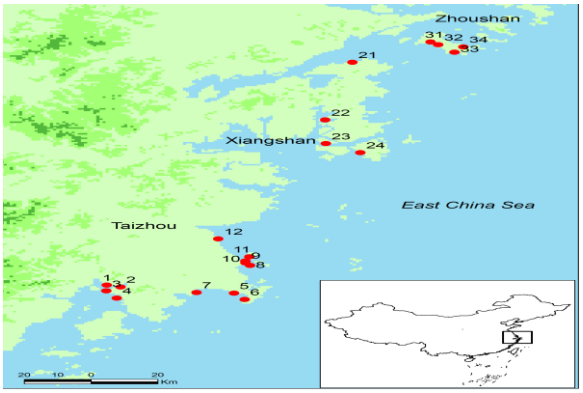

FIGURE 1
The sampling sites in offshore everinment.

Chemicals and instrumentation. A PCB and PBDE analytical standard solution was purchased from Acros Organics (NJ, USA). The standard solution contained CB-28, 52, 77, 81, 101, 105, 112, 114, 118, 123, 126, 138, 153, 156, 157, 167, 169, 180, 189, and 198, and the concentration of

each compound was 1 mg/mL. The standard contained three mono-BDEs (BDE-1, 2, and 3), seven di-BDEs (BDE-7, 8, 10, 11, 12, 13, and 15), eight tri-BDEs (BDE-17, 25, 28, 30, 32, 33, 35, and 37), six tetra-BDEs (BDE-47, 49, 66, 71, 75, and 77), seven penta-BDEs (BDE-85, 99, 100, 105, 116, 119, and 126), five hexa-BDEs (BDE-138, 153, 154, 155, and 166), and three hepta-BDEs (BDE-181, 183, and 190). The concentrations of each compound ranged from 100 ng/mL for the mono-congeners to 250 ng/mL for the hepta-congeners. The standard solution was used to construct a calibration curve and measure the recovery efficiency from spiked samples. Silica gel (100–200 mesh) was pre-cleaned by heating at 450°C for 6 h in a shallow metallic enamel tray. Similarly, anhydrous sodium sulfate was pre-cleaned by heating at 120°C for 6 h in a shallow metallic enamel tray. All organic solvents were of chromatographic grade or equivalent. Milli-Q water (Millipore, Billerica, MA, USA) was used during all experiments.

Extraction and purification. Each sample was processed twice.

PCBs. Sediment samples were extracted by adding 5 g of each sample to a glass flask and then mixing the sample with 2 g of anhydrous sodium sulfate and 0.5 g of powdered copper. Next, 10 ml of hexane:acetone (1:1) was added, followed by ultrasonic extraction for 60 min at 25°C. The sample was then centrifuged at 3000 rpm for 5 min, after which 6 ml of organic extract was eluted with sulfuric acid until the sulfuric acid layer was colorless. The extracts were subsequently eluted with 10 ml of 20% sodium sulfate solution, after which anhydrous sodium sulfate was added to remove any trace amounts of water that remained. The resulting 2 ml of extract was then concentrated using rotary evaporation. Next, the extract was passed through a column packed with 2 g of silica gel (100–200 mesh) and 1 g of anhydrous sodium sulfate. The column was pre-eluted with hexane and then eluted with 20 ml hexane. The sample extracts were then condensed to 0.5 mL and dried with nitrogen. Next, the PCBs in the samples were dissolved in 1 ml of pure n-hexane, after which they were filtered through 0.22 μm pore size filter paper. Finally, the samples were analyzed using gas chromatography–mass spectrometry (GC/MS). Blank samples that were prepared in the same fashion were analyzed concurrently with the actual samples.

PBDEs. Sediment samples were extracted by adding 5 g of each sample to a glass flask and then mixing the sample with 2 g of anhydrous sodium sulfate and 0.5 g of powdered copper. Next, 10 ml of n-hexane/methylene dichloride (1:1) was added, followed by ultrasonic extraction for 60 min at 25°C. The sample was then centrifuged at 3000 rpm for 5 min, after which 6 ml of organic extract was eluted with sulfuric acid until the sulfuric acid layer was colorless. The extract was then eluted with a 20% sodium sulfate solution. Next, anhydrous sodium sulfate was added to remove the trace amounts of water. The extract (2 mL total volume) was then concentrated using a rotary evaporator. The concentrated extract was passed through a glass column (inside diameter: 1 cm) packed (in order, from the base) with 4 cm of alumina, 2 cm of silica gel (100–200 mesh), 3 cm of alkaline silica gel, 2 cm of silica gel, 5 cm of acidic silica gel, and 1 cm of anhydrous sodium sulfate. The glass column was also pre-eluted with hexane and then eluted with 20 mL methylene dichloride/n-hexane (1:1). The sample extracts were then condensed to 0.5 mL and dried with nitrogen. The PBDEs in the samples were dissolved in 1 mL of pure n-hexane and filtered through a 0.22-μm pore size filter paper. The samples and blanks were then analyzed using GC/MS.

Analytical Conditions. GC/MS analyses were performed with a 7890 B gas chromatograph coupled to a 5975C mass spectrometer (Agilent Technologies, Massy, France) with a DB-5MS column (30 m × 0.25 mm × 0.25 μm). Nitrogen was used as the carrier gas at a flow rate of 1.4 ml/min and as the makeup gas for the detector at 60 ml/min. Samples were injected in splitless mode (1 μL, splitless time of 0.75 min). The injector and detector temperatures were maintained at 280 and 300°C, respectively. We used helium (purity: 99.999%) as both the carrier gas (1.0 mL/min) and the makeup gas for the detector (60 mL/min). The injection volume was 1μL. The injection mode was splitless.

The temperature program for the detection of PCBs was initially set at 120°C, and then increased to 230°C at a rate of 20°C/min. Following this, the temperature was increased to 240°C at a rate of 5°C /min, where it was held for 5 min, then increased to 260°C at a rate of 5°C/min, where it was held for 6 min. The temperature program for the detection of PBDEs was initially set at 120°C, then increased to 200°C at a rate of 30°C/min,. Following this, the temperature was increased to 230°C at a rate of 2.5°C /min, then increased to 320°C at a rate of 5°C/min, where it was held for 2 min.

Quality control. For each batch of 10 samples, a solvent and a procedural blank were run to ensure that the samples were free of contamination and the analyses were being conducted correctly. The recovery of the standard PCBs was 71-113%. The method detection limit for

seawater ranged from 0.001 to 0.015 ng/L, while the detection limit for sediment samples and the organisms ranged from 0.005 to 0.02 ng g−1. The recovery efficiency for the PBDEs was between 65 and 112%. The detection limit for animal tissues was between 0.001 and 0.025 ng g−1. The concentration of each congener was quantified using the external calibration method based on a five-point calibration curve for 39 PBDEs.

Statistical analysis. Data analysis (correlation analysis and principal component analysis) was performed using OriginPro 9.0 (OriginLab Corporation) and IBM SPSS Statistics software 20.0 to identify the potential source and correlation of PCB and PBDE congeners in the study area. Differences between samples were evaluated by a one-way analysis of variance (ANOVA).

RESULTS AND DISCUSSION

Twenty PCB and 39 PBDE congeners were analyzed in sediment samples collected from 20 stations located in three major coastal aquaculture areas (12 sampling sites in Taizhou, four in Xiangshan, and four in Zhoushan) in Zhejiang province, China. A total of 20 PCBs, including the tri- to octa–PCBs, and a total of 39 PBDEs, including the mono- to hepta-BDE, were targeted for quantification due to their common occurrence in the environment.

The concentration of PCBs in sediments. The results in Table 1 show the levels of ∑20 PCB congeners in this study. The 20 PCB congeners were detected in all sediment samples, with the exception of some sites at Zhoushan, and ranged from 4.97–43.76 ng/g, with a mean of 19.35 ng/g in Taizhou, and from 7.57–29.18 ng/g with a mean of 20.52 ng/g in Xiangshan, and from nd–2.58 ng/g with a mean of 1.29 ng/g in Zhoushan, respectively. The highest value (43.76 ng/g) was found at Station 9, which was located close to the electronic waste dismantling area in Taizhou. In Zhoushan, of the 20 PCB congeners, only CB-52, 81,101, and 169 were detected in the sediment samples. The samples collected from the Taizhou and Xiangshan sample sites had substantially higher concentrations of PCBs than those collected from Zhoushan. The results suggest that the sources of PBDEs and PCBs in offshore aquaculture environments could be ascribed to the input of industrial pollutants via rivers and atmospheric deposition [21]. Generally, PCB concentrations at stations 6, 9, 12, and 21 were the highest, while stations 33 and 34 were the lowest, demonstrating that the concentration decreased with distance from the coastal industrial zones, especially those involved with the dismantling of waste electrical products. This result is consistent with the results of previous studies, and it is believed that hydrodynamic conditions are the most important factors influencing the distribution of PCBs in surface sediments [22].

The PCB data was compared with other recent studies from estuary and coastal zones around the world (Table 2). The levels of PCBs in surface sediments found in this study indicated a moderate degree of contamination in Taizhou and Xiangshan, and were generally lower in Zhoushan, although it is difficult to compare the PCB concentrations in the sediments from different ecosystem types and regions due to the different modes of expression and individual congeners that were present. For example, the concentration range of PCBs in the surface sediments in Etang de Thau lagoon, France, was reported to be 2528–33,319 ng/g [23], whereas the range was 9.1–266.9 ng/g in the coastline of Marseille, France [21], nd–3908 ng/g in a coastal lagoon in the northern Adriatic region of Italy [24], and 1.91–368 ng/g in the Scheldt Estuary in the Netherlands [25]. PCB concentrations have been reported to be at more moderate levels in surface sediments from other estuaries and bays. For example, 4.97–43.76 ng/g in Taizhou and 7.57–29.18 ng/g in Xiangshan in this study, 5.08 -19.64 ng/g in the Yangtze River Estuary and adjacent East China Sea, China [26], 4.93–108.79 ng/g in Jiaojiang Bay, China [22], 9.33–19.60 ng/g in three separate bays in Zhejiang Province, China [27], and 0.07–24 ng/g in Masan Bay, Korea [28]. PCB concentrations in sediments have also been reported at lower levels, for example in Zhoushan, China (nd–2.58 ng/g) in this study, the northern Atlantic coast of Spain (0.56–4.66 ng/g) [29], the coastal area of southwest Taiwan (0.88–7.13 ng/g) [30], and the aquatic environment near Brunswick, Georgia, USA (0.02–3.84 ng/g) [31].

The concentration of PBDEs in sediments. In this study, the concentrations of 39 mono- to hepta-brominated PBDE congeners in sediments from the 20 sampling sites were determined. Except for BDE-77, 126, 154, and 155, all of the PBDEs were detected at most sampling sites. The concentrations of 18 PBDEs with a high detection frequency and the total PBDE levels (∑39 PBDEs) in sediment samples are listed in Table 3. The concentrations of the ∑39 PBDEs ranged from 3.05 to 26.18 ng/g, with a mean of 14.19 ng/g in sediment in Taizhou, 13.42 to 22.70 ng/g with a mean of 16.10 ng/g in Xiangshan, and 1.35 to 11.73 ng/g with a mean of 5.36 ng/g in Zhoushan. The mean concentration of the ∑39 PBDEs decreased in the following order Xiangshan off shore ≅ Taizhou near shore > Zhoushan coast. As expected, the samples collected from the Taizhou coast, which is

near the e-waste dismantling area, had substantially higher concentrations of PBDEs than those collected from the Zhoushan coast. It has been reported that solid waste dissembling industries in Taizhou could contribute PBDEs to the offshore environment through atmospheric transport and runoff [32,33]. High concentrations of PBDE residues were detected in sediment and soil samples from Taizhou, which receives waste from the electric/electronic appliance recycling industry (e-waste) [34]. However, Zhoushan city is located in the Zhoushan islands in Zhejiang province, off the southeast coast in China, and has fewer sources of industrial pollution.

A comparison of the PBDE concentrations in the coastal sediments with other areas in the world is given in Table 4. Although the PBDE congener numbers and types detected, and the sampling and testing periods were slightly different in these studies, low molecular weight PBDE compounds were found in most study areas. Table 4 shows that the levels of ∑39 PBDE in this study were lower than those in San Francisco Bay (nd–211.8 ng/g) [35], rivers and estuaries of the UK (1.3–1270 ng/g) [36], Osaka Bay, Japan (8–352 ng/g) [37], and Korean coastal waters (2–2253 ng/g) [38]. Levels were similar to the Macao Coast in south China (1.25–19 ng/g)[28], and other coastal areas of China (0.6–41.3 ng/g) [39], but were slightly higher than along a coastal transect in British Columbia (0.7–1.2 ng/g) [1], the coastal area of southwestern Taiwan (0–1.82 ng/g) [40], the Bohai Sea (0.2–0.9 ng/g) [41], Yangtze River Estuary (0–8 ng/g) [42], Xiamen offshore areas (0.3–6.4 ng/g) [43], and Deep Bay in south China (0.7–4.85 ng/g) [44].

TABLE 1
The concentration of the PCBs in sediment from offshore aquaculture environment in Zhejiang (ng/g, dry weight).

Sampling area	No	28	52	81	101	105	114	118	123	126	138	153	156	157	167	169	180	198	∑PCBs
Taizhou	1	0.16	0.03	17.23	0.05	0.19	0.25	0.28	0.04	nd	0.30	0.19	0.12	0.02	0.04	0.04	0.27	0.16	23.99
	2	0.27	0.07	2.88	0.15	0.11	0.03	0.11	0.06	0.05	0.07	0.05	0.11	0.03	0.16	nd	nd	0.02	4.97
	3	0.07	nd	1.91	3.74	1.00	0.20	1.18	0.09	0.22	0.39	nd	0.07	0.03	0.61	0.02	nd	0.03	11.38
	4	0.28	0.18	nd	1.10	2.12	0.27	1.69	1.61	1.79	0.69	nd	1.11	1.52	1.97	1.71	0.80	nd	16.98
	5	1.71	0.71	2.39	1.57	0.06	0.06	2.76	0.03	0.02	2.46	2.03	0.36	0.03	0.84	0.04	0.67	0.22	17.24
	6	0.24	2.47	0.19	1.10	2.93	0.30	2.20	2.25	3.05	1.53	0.76	1.66	1.91	2.96	2.46	0.81	1.34	33.34
	7	nd	nd	0.02	1.19	nd	0.46	nd	nd	1.61	nd	nd	nd	nd	1.79	nd	nd	nd	5.07
	8	0.16	0.03	3.23	0.17	0.46	0.35	0.54	0.46	0.12	0.50	0.33	0.30	0.05	0.88	0.29	0.24	0.16	12.56
	9	1.41	1.63	0.52	3.18	3.78	0.19	4.52	1.90	1.94	8.94	0.88	1.63	1.80	2.13	2.17	2.13	nd	43.76
	10	0.15	0.30	0.08	0.35	1.94	0.08	1.29	1.43	1.69	0.65	0.66	1.18	1.40	1.74	1.69	nd	nd	17.74
	11	0.25	0.20	0.07	1.50	1.94	0.68	1.20	1.43	1.69	0.57	nd	1.04	1.25	1.72	1.77	nd	nd	18.24
	12	2.31	1.89	0.07	1.19	2.96	0.20	1.82	2.22	2.44	1.06	0.98	1.46	2.01	2.57	2.24	nd	nd	26.91
Mean		0.58	0.63	2.38	1.27	1.46	0.26	1.47	0.96	1.22	1.43	0.49	0.75	0.84	1.45	1.04	0.41	0.16	19.35
Xiangshan	21	0.45	0.64	0.37	1.65	2.88	0.10	2.15	2.09	2.16	1.82	1.43	1.59	1.96	2.38	2.80	0.57	nd	29.18
	22	0.08	0.22	0.02	0.21	2.64	0.03	2.04	2.01	2.17	1.30	1.44	1.42	1.89	2.36	2.29	0.44	1.26	26.76
	23	0.19	0.37	0.09	0.57	2.56	nd	1.61	2.00	2.19	nd	nd	1.38	1.83	2.38	2.15	nd	1.23	18.55
	24	nd	nd	3.50	0.30	0.33	0.07	0.07	0.20	0.19	nd	nd	0.17	0.02	0.99	0.31	0.10	0.15	7.57
Mean		0.18	0.31	1.00	0.68	2.10	0.05	1.47	1.58	1.68	0.78	0.72	1.14	1.43	2.03	1.89	0.28	0.66	20.52
Zhoushan	31	0.04	0.09	0.14	0.20	nd	0.04	nd	nd	nd	nd	nd	nd	nd	nd	2.04	nd	nd	2.55
	32	nd	nd	0.04	nd	nd	nd	nd	nd	2.54	nd	nd	nd	nd	nd	nd	nd	nd	2.58
	33	nd	nd	0.02	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.03
	34	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Mean		nd	0.03	0.05	0.05	nd	nd	nd	nd	0.64	nd	nd	nd	nd	nd	0.51	nd	nd	1.29

No: "nd" means no detected.

TABLE 2
The PCBs concentrations (ng/g dry weight) in sediment reported other coastal locations in the world.

Location	Northern Atlantic, Spanish	Marseille, France	Yangtze River Estuary,China	Coastal Lagoon, Italy	Jiaojiang Estuary, China
Sampling year	2006	2010	2007		2008
n[a]	18	7	22	15	20
∑PCB[b] (Mean)	0.56-4.66 (2.49)	9.1- 226.9 (84.3)	5.08 -19.64 (10.15)	n.d.–3,908	4.93 -108.79 (29.08)
Reference	29	21	26	24	22
Location	Zhejiang province,China	Masan Bay, Korea	Brunswick, U.S.A.	Scheldt estuary	Etang de Thau lagoon, France
Sampling year		2004	2009	2010	
n[a]		22		33	
∑PCB[b] (Mean)	9.33–19.60	0.07 -24 (7.2)	0.02 -3.84 (0.64)	1.91–368 (31.5)	2,528–33,319
Reference	27	28	31	26	23

a: Number of PCBs congeners analyzed in sample.
b: The sum of all target PCB congeners except for CB 209.

TABLE 3
The concentration of the PBDEs in sediment from offshore aquaculture environment in Zhejiang (ng/g, dry weight).

Sampling area	BDE-	1	2	3	8	10	17	33	47	49	71	75	99	138	153	183	∑PBDE
Taizhou	1	3.66	0.82	0.05	0.18	1.47	0.08	0.07	nd	0.99	0.91	nd	0.02	nd	nd	nd	9.13
	2	0.45	0.08	0.04	0.12	0.26	0.07	0.04	0.03	0.05	1.52	nd	nd	0.02	nd	nd	4.25
	3	2.27	0.66	0.16	0.12	1.19	0.10	0.09	0.04	nd	0.25	nd	nd	0.02	nd	nd	6.09
	4	0.54	0.03	0.12	0.13	0.56	0.07	0.04	nd	0.56	0.52	nd	0.03	0.02	nd	nd	3.05
	5	1.86	0.22	0.20	0.30	1.07	0.05	0.03	0.03	nd	0.26	nd	nd	nd	nd	nd	4.73
	6	8.18	1.01	0.25	0.52	3.04	0.06	0.14	0.03	4.05	3.70	0.02	0.03	nd	nd	0.02	26.18
	7	5.15	0.21	0.19	0.27	2.37	0.12	0.06	0.02	1.62	1.48	0.02	nd	nd	nd	0.02	13.37
	8	4.47	0.32	0.16	0.36	2.30	0.08	0.06	0.02	0.04	0.69	0.13	0.04	0.02	0.02	0.04	9.79
	9	nd	8.02	5.03	1.33	9.95	0.29	0.16	0.04	0.03	0.80	0.03	0.02	0.02	0.02	0.02	27.71
	10	0.85	5.20	3.24	0.78	5.98	0.18	0.12	0.04	1.65	1.51	0.32	0.02	0.03	nd	0.03	22.63
	11	10.16	2.68	0.23	0.56	4.09	0.16	0.10	nd	0.85	0.75	0.03	0.03	0.02	nd	0.04	21.27
	12	nd	2.78	2.65	0.74	5.98	0.15	0.10	0.06	2.59	2.37	0.16	0.03	0.02	0.02	nd	22.14
Mean		3.13	1.84	1.03	0.45	3.19	0.12	0.08	0.03	1.04	1.23	0.06	0.02	0.02	0.00	0.02	14.19
Xiangshan	21	0.26	3.68	0.44	1.49	11.65	0.29	0.24	0.09	0.12	1.21	nd	0.07	0.03	0.02	nd	22.70
	22	5.77	1.67	1.60	0.39	2.24	0.08	0.09	0.04	nd	0.30	nd	nd	0.03	0.02	0.03	13.42
	23	7.31	1.28	0.14	0.86	3.87	0.39	0.10	0.16	0.03	0.58	0.04	nd	0.03	0.02	0.02	16.05
	24	6.87	0.23	0.15	0.50	2.70	0.13	0.05	0.04	0.06	0.13	nd	0.03	nd	nd	0.02	12.22
Mean		5.05	1.72	0.58	0.81	5.12	0.22	0.12	0.08	0.06	0.56	0.02	0.03	0.03	0.02	0.02	16.10
Zhoushan	31	4.08	0.12	0.21	0.42	2.32	0.11	0.04	nd	1.43	1.31	nd	0.03	nd	nd	nd	11.73
	32	1.44	0.69	0.61	0.37	1.09	0.12	0.09	0.15	0.03	0.77	0.04	0.02	0.03	0.02	nd	6.64
	33	0.37	0.10	0.09	0.09	0.30	0.14	0.06	0.07	0.03	0.05	nd	nd	nd	nd	0.02	1.72
	34	nd	0.56	0.12	nd	nd	0.03	0.03	0.02	0.02	0.23	0.04	0.02	nd	nd	nd	1.35
Mean		1.47	0.37	0.26	0.22	0.93	0.10	0.05	0.07	0.38	0.59	0.03	0.02	0.01	0.01	0.01	5.36

No: “nd” means no detected.

TABLE 4
The PBDEs concentrations (ng/g dry weight) in sediment reported other coastal locations in the world.

Location	San Francisco Bay, USA	Rivers and estuaries,UK	Columbia, British	Osaka Bay, Japan	Coast, China
Sampling year			2006		
n[a]			49		
∑PBDE[b] (Mean)	nd-211.8	1.3-1270	0.7-1.2 (0.7)	8–352	0.6-41.3
Reference	35	36	1	37	53
Location	Southwestern Taiwan	Bohai Sea	Yangtze River Estuary, China	Xiamen, China	Deep Bay, China
Sampling year	2005		2006-2007		2004
n[a]	13	7	7	7	22
∑PBDE[b] (Mean)	0-1.82	0.2-0.9	0-8 (1.6)	0.3-6.4	0.07-4.85 (0.68)
Reference	40	51	42	43	44

a: Number of PBDEs congeners analyzed in sample.
b: The sum of all target PBDE congeners except for BDE 209.

Composition of PCBs and PBDEs. PCB congener profiles. The dominant coplanar congeners of PCBs were CB-77, CB-81, CB-105, CB-118, CB-126, CB-138, CB-167, and CB-169. The horizontal distribution of the total PCBs in the surface sediments in this study revealed that concentrations varied widely between stations. Generally, PCB concentrations at stations 6, 9, 12, and 21 were the highest, while the Zhoushan sampling sites (stations 31, 32, 33, and 34) were the lowest, demonstrating that the concentration decreased with distance from the coastal industrial zones. Surprisingly, in the Zhoushan sampling sites, levels of all of the 20 PCB homologues were close to the detection limit. Among the PCB congeners, tetra-chlorinated biphenyls (tetra-PCB) to penta-PCB were all detected in the sediment samples collected in the offshore aquaculture environment of Taizhou and Xiangshan. The PCB congeners in this study were classified into six groups according to their number of chlorine (Cl) atoms: tri-, tetra-, penta-, hexa-, hepta-, and octa-PCBs. The average percentage composition of PCBs in the Taizhou sampling sites decreased in the following order: penta-PCB (37.73%) > hexa-PCB (28.38%) > tetra-PCB (25.42%) > hepta-PCB (4.87%) > tri-PCB (2.90%) > octa -PCB (0.70%). Similarly, the average homolog composition of the PCBs decreased in the following order: hexa-PCB (35.68%) > penta-PCB (35.18%) > tetra-PCB (16.67%) > hepta-PCB (8.39%) > octa-PCB 3.33%) > tri-PCB (0.75%) in the Xiangshan sampling sites (Fig. 2), and those containing tri-, tetra-, and penta-PCBs were the major components (>90%) in this study area. This was consistent with the results of other studies, for example, the pattern of isomer dominance was penta > hexa > hepta > tetra > tri > di > octa PCBs in Masan Bay sediments, which suggested that the pattern could have arisen from the commercial PCB mixture, Aroclor 1254, which has been historically used for dechlorination and may have weathered over time [28,45]. The relative environmental homolog contribution reported by some authors indicated the removal of PCB congeners containing 3–4 chlorine atoms to the detriment of 5–7 Cl congeners, which are not easily biodegraded [21].

PBDE congener profiles. The PBDE congeners in this study were classified into seven groups according to their number of bromine (Br) atoms: mono-, di-, tri-, tetra-, penta-, hexa-, and hepta-BDEs. The average percentage composition of the 1 to 7 bromine atom compounds was 41.23, 29.47, 5.44, 16.63, 3.95, 0.32, and 0.56% of the total PBDEs, respectively, in the offshore aquaculture sediments from Taizhou. Similarly, in Xiangshan the average percentage composition of the 1 to 7 bromine atom compounds was 45.68, 41.16, 5.76, 4.83, 1.77, 0.42, and 0.39% of the total PBDEs, respectively (Fig. 3). The World Trade Organization has reported that the annual global consumption of PBDEs is about 40,000 tons, with commercial penta-, octa-, and deca-BDE responsible for 10, 15, and 75% of total consumption, respectively [46]. However, in this study, because of the high levels of BDE-1, BDE-2, BDE-10, BDE-49, and BDE-71 in the Taizhou and Xiangshan sampling sites, the mono- and di-BDE were dominant among the groups. In contrast to previous reports, the lower-brominated congeners, BDE-1, BDE-2, and BDE-10 were the most abundant components, despite not being among the three major commercial PBDE products (penta-BDE, octa-BDE, and deca-BDE). This may be because the relatively high levels of lower-brominated BDEs were partly derived from the degradation of higher-brominated BDEs by

microorganisms in the offshore aquaculture environment, and degradation by sunlight during atmospheric transport into the surface water system [47]. This may also be the reason for the low concentration of PBDEs, especially the higher-brominated compounds in Zhoushan. In addition, long-range transport of airborne pollutants is a possible source of PBDEs in the aquatic environment [48]. Previous studies have suggested that in addition to the use of commercial penta- and octa-PBDE products, the debromination of deca-BDE might be an important formation mechanism for lower-brominated BDE congeners [49]. This may imply that higher-brominated BDE congeners have a low bioaccumulation potential in organisms [50]. Further study is needed to explain the relatively high proportions of lower-brominated BDE congeners in the offshore aquaculture environment that were found in this study.

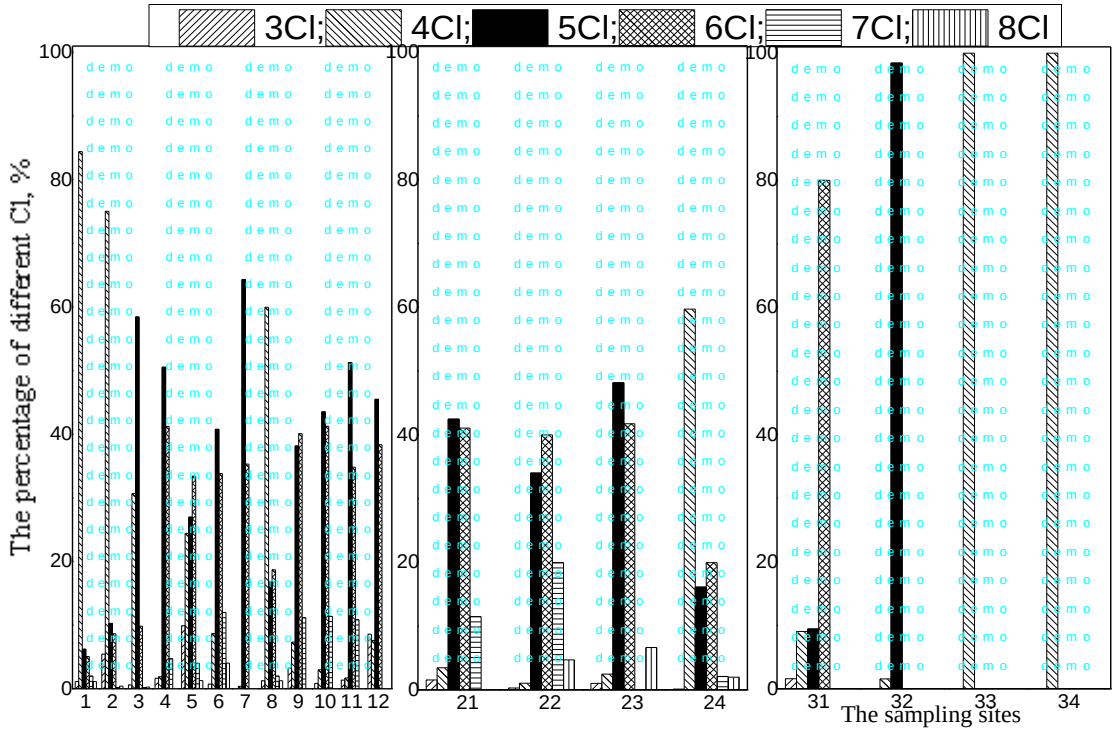

FIGURE 2
The percentage of different chloride condentration in the total concentration of PCBs

Principal component analysis of PCBs and PBDEs. Principal component analysis, a method to describe the variation in a system with the minimum loss of information, is commonly used to identify possible sources of pollution by comparing the composition of sediment samples, and as a multivariate analytical tool to reduce the size of a set of original variables and extract a small number of latent factors (principal components) for analyzing the relationships among the observed variables [51].

Principal component analysis of PCBs. A statistical analysis using PCA was performed on the 20 PCB congener profiles from the 16 stations in Taizhou and Xinagshan, because the chemical components of PCBs were similar and they may therefore be derived from the same pollution sources. The first two principal components explained 74.70% of the total variance (51.17% PC1 and 15.01% PC2) (Fig. 4). The results showed that the first principal component, PCB-52, 105, 112, 118, 123, 126, 156, 157, 167, 169, and 189, accounted for 51.17% of the total variance, making a significant contribution to local environment pollution. The second component, PCB-28, 101, 138, 180, accounted for 15.09%, meaning that the first and second principal components gave a cumulative explanation of 74.70% of the total variance. They are found in electrical capacitors, electrical transformers, vacuum pumps, and are released into offshore aquaculture sediments through atmospheric diffusion and deposition [26]. In addition, sediment resuspension from tidal movement in the estuary may promote chlorination, further masking source concentration

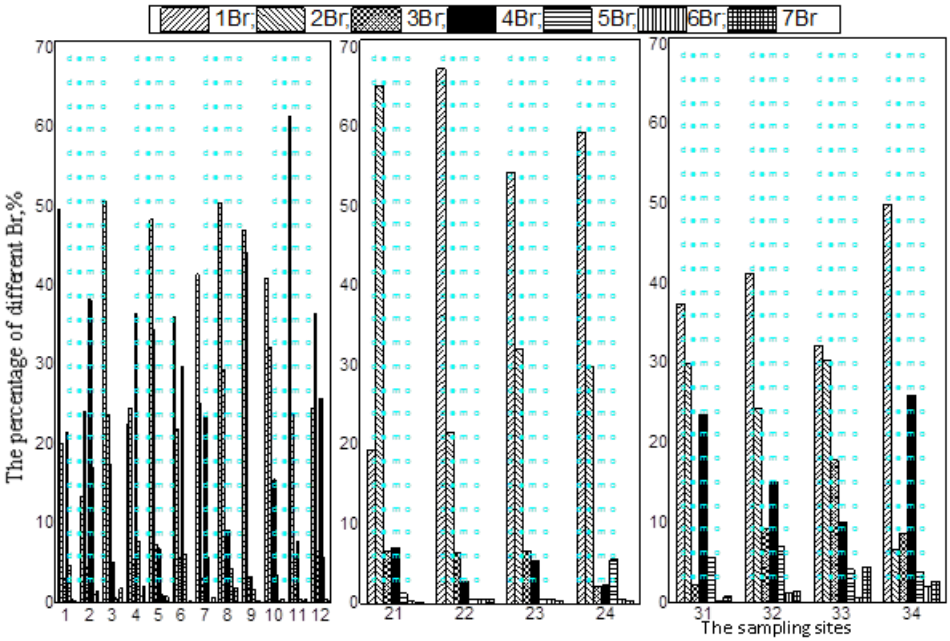

FIGURE 3
The percentage of different bromine condentration in the total concentration of PBDEs

matches [52]. In the four Zhoushan sampling sites, the first principal component explained 86.66%, and the second principal component explained 13.22% of the total variance. The first principal component was PCB-28, 52, 81, 101, and 169, and the second principal component was PCB-126. However, PCB-81 and 126 are rarely present in commercial products, which suggests that these compounds were derived from the natural environment or the degradation of higher-chlorine compounds. It also suggests that the contaminants in the offshore aquaculture environment originated mainly from coastal industrial zones. More attention should be given to determining the exact distribution between the cultural and industrial zones.

Principal component analysis of PBDEs. The 18 PBDE congener patterns among the samples were analyzed using PCA in the Taizhou and Xiangshan offshore aquaculture sediments. The samples from the Zhoushan sampling sites were not analyzed because of their very low concentration. The PCA of the PBDE congener patterns produced two components. As shown from the score plot (Fig. 5), the first principal component accounted for 34.86% of the total variance, whereas the second accounted for 19.43%, which together explains 54.29% of the overall variability. When all the samples from Taizhou and Xiangshan were considered, there were high scores for PC1, which indicates that the contribution of BDE-2, 3, 8, 10, 17, 33, 47, 138, and 153 was relatively high in these samples. These results suggest that mono- and di-BDE were the primary contributors to the overall PBDE contamination in the offshore aquaculture sediments in Taizhou and Xiangshan. The PC2 of the PBDE congener profile showed a cluster of four bromine compounds (BDE-15, 28, 49, 71), and suggested that they may have the same source. However, BDE-99 constituted 50% of the technical penta-BDE mixture, but contributed much less to the total PBDE in this study. The degradation of higher-bromine compounds is a possible source of lower-bromine compounds [53].

Relationships between PBDE congeners, PCB congeners, and between ∑PBDEs and ∑PCBs. A correlation analysis between the concentration of indicator PCB congeners in the sediment samples was conducted. Table 5 summarizes the correlations of the 20 PCBs. A significant correlation was observed between the concentrations of CB-105 and CB-123, 126, 156, 157, 167, and 169 in these sediment samples, while the concentrations of CB-123 and CB-126 were strongly correlated with the concentrations of CB-123, 126, 156, 157, and 167, respectively. However, no significant correlation was observed between the concentrations of low molecular

weight chlorine compounds. The correlation analysis results suggest that these contaminants might have originated from similar sources, with the correlation coefficients for sites without obvious emission sources being higher than at those with significant local emission sources [54].

The relationship between each of the PBDE congeners in the sediments collected from the breeding environment in Taizhou and Xiangshan was analyzed by PCA. Table 6 summarizes the correlations of the 18 PBDE congeners. It can be seen that there was a positive correlation between the small number of bromine congeners, such as between BDE-2 and BDE 3, BDE 8, BDE 10, and BDE 33; between BDE-33 and BDE 8 and BDE 10; and between BDE-33 and BDE 15, BDE 49, and BDE 77, indicating that the low molecular weight bromine compounds might have originated from the decomposition of commercial BDE 49 and BDE 77 [55]. However, there was a weak relationship between the low and high molecular weight bromine congeners, suggesting that the source of the low molecular weight bromine congeners was not the decomposition of congeners with larger numbers of bromine atoms [56]. Combined with the results of previous studies, this suggested that biological degradation was the main source of the low molecular weight bromine congeners in the breeding environment in Taizhou and Xiangshan [57].

The relationships between the concentrations of ∑PBDEs and ∑PCBs were analyzed in three different breeding environment sediments in Zhejiang. Significant correlations were found between the concentrations of ∑PBDEs and ∑PCBs in Taizhou sediment samples (Fig. 6). In consideration with the results of previous studies, the PBDEs and PCBs in the offshore aquaculture environment sediments in Taizhou region may be derived from the electronic waste dismantling industry [58]. A strong correlation was also found between PCBs and PBDEs in sediments from Zhoushan. Although the concentrations were very low, there were similar input pathways to ecosystems for both chemicals, with atmospheric deposition playing a major role. Generally, PBDEs and PCBs were widely distributed in aquatic environments, as a consequence of the impact of long-range atmospheric transport and deposition [59]. However, there was no significant correlation between the concentrations of ∑PBDEs and ∑PCBs in Xiangshan sediment samples. We suggest the PBDEs and PCBs in the Xiangshan breeding environment may originate from other sources. Therefore, further studies with larger numbers of samples are necessary to better understand their sources and accumulation routes and to evaluate their possible impacts on the ecology and environment of coastal areas of China.

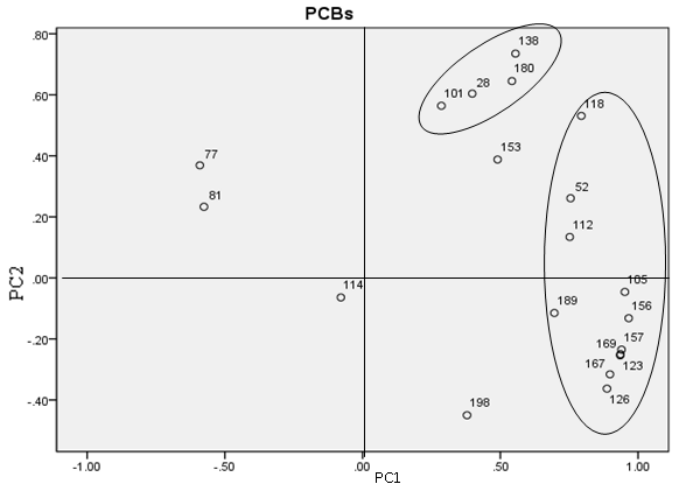

FIGURE 4
Principal component analysis performed with relative abundance of individual PCBs in sediment samples.

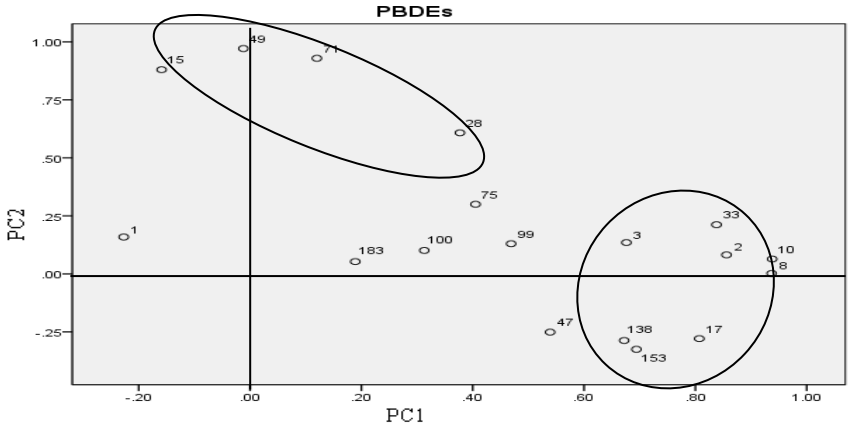

FIGURE 5
Principal component analysis performed with relative abundance of individual PBDEs in sediment samples.

TABLE 5
The correlation between different composition of PCBs

PCB-	28	52	77	81	101	105	112	114	118	123	126	138	153	156	157	167	169	180	189	198
28	1.00																			
52	0.61	1.00																		
77	-0.12	-0.28	1.00																	
81	-0.14	-0.28	0.80	1.00																
101	0.31	0.27	-0.17	-0.30	1.00															
105	0.30	0.65	-0.49	-0.49	0.31	1.00														
112	0.41	0.82	-0.35	-0.32	0.33	0.69	1.00													
114	-0.14	-0.01	0.10	-0.01	0.17	-0.07	0.17	1.00												
118	0.58	0.65	-0.29	-0.37	0.55	0.73	0.53	-0.18	1.00											
123	0.25	0.62	-0.54	-0.51	0.07	0.96	0.66	-0.06	0.60	1.00										
126	0.15	0.63	-0.68	-0.58	0.10	0.85	0.65	0.11	0.48	0.91	1.00									
138	0.51	0.52	-0.04	-0.16	0.55	0.52	0.42	-0.08	0.86	0.32	0.23	1.00								
153	0.58	0.44	-0.16	-0.17	0.10	0.30	0.36	-0.38	0.63	0.31	0.21	0.43	1.00							
156	0.30	0.66	-0.53	-0.49	0.12	0.96	0.70	-0.11	0.71	0.98	0.88	0.44	0.41	1.00						
157	0.26	0.60	-0.58	-0.50	0.10	0.96	0.65	-0.10	0.63	0.99	0.91	0.34	0.33	0.98	1.00					
167	0.21	0.63	-0.68	-0.67	0.12	0.84	0.62	0.05	0.53	0.90	0.97	0.26	0.30	0.88	0.89	1.00				
169	0.21	0.58	-0.57	-0.50	0.09	0.95	0.68	-0.07	0.61	0.99	0.90	0.34	0.34	0.98	0.99	0.89	1.00			
180	0.35	0.51	0.00	-0.10	0.44	0.50	0.34	-0.07	0.82	0.34	0.26	0.92	0.39	0.45	0.35	0.29	0.35	1.00		
189	-0.09	0.36	-0.36	-0.32	0.07	0.64	0.49	-0.05	0.52	0.63	0.60	0.41	0.49	0.68	0.64	0.57	0.68	0.42	1.00	
198	-0.22	0.30	-0.19	-0.14	-0.27	0.33	0.02	-0.27	0.18	0.44	0.45	-0.09	0.18	0.41	0.41	0.46	0.40	0.04	0.46	1.00

TABLE 6
The correlation between different composition.

BDE-	1	2	3	8	10	15	17	28	33	47	49	71	75	99	100	138	153	183
1	1.00																	
2	-0.32	1.00																
3	-0.43	0.89	1.00															
8	-0.18	0.80	0.57	1.00														
10	-0.28	0.84	0.61	0.97	1.00													
15	0.18	-0.15	-0.07	-0.09	-0.08	1.00												
17	-0.02	0.59	0.36	0.81	0.72	-0.28	1.00											
28	0.16	0.37	0.37	0.20	0.24	0.35	0.06	1.00										
33	-0.12	0.69	0.40	0.86	0.89	0.11	0.62	0.38	1.00									
47	0.03	0.17	0.05	0.55	0.40	-0.09	0.81	0.08	0.41	1.00								
49	0.18	0.03	0.10	-0.01	0.04	0.85	-0.21	0.57	0.17	-0.17	1.00							
71	0.02	0.11	0.12	0.14	0.18	0.92	-0.10	0.47	0.33	-0.03	0.91	1.00						
75	-0.24	0.40	0.50	0.21	0.25	-0.03	0.12	0.52	0.11	0.05	0.31	0.25	1.00					
99	-0.08	0.22	-0.03	0.54	0.60	0.03	0.24	0.05	0.63	0.09	0.11	0.21	0.09	1.00				
100	0.33	0.30	0.22	0.26	0.32	-0.06	0.29	0.17	0.14	-0.06	0.12	0.03	0.11	0.07	1.00			
138	-0.21	0.43	0.32	0.48	0.44	-0.37	0.56	0.36	0.47	0.56	-0.31	-0.17	0.37	0.22	0.01	1.00		
153	-0.10	0.44	0.41	0.56	0.55	-0.31	0.60	0.08	0.43	0.51	-0.32	-0.16	0.20	0.27	0.31	0.60	1.00	
183	0.58	0.18	0.12	0.07	0.05	-0.14	0.05	0.29	0.02	-0.15	-0.01	-0.09	0.36	0.09	0.48	0.24	0.27	1.00

CONCLUSIONS

Twenty PCB and 39 PBDE congeners were analyzed in sediment samples collected from 20 stations located in three major coastal aquaculture areas (12 sampling sites in Taizhou, four in Xiangshan, and four in Zhoushan) in Zhejiang province, China. A total of 20 PCBs, including the tri- to octa–PCBs, and a total of 39 PBDEs, including the mono- to hepta-BDEs, were targeted for quantification due to their common occurrence in the environment. The main conclusions were as follows:

The concentration of the ∑20 PCB congeners ranged from 4.97 to 43.76 ng/g, with a mean of 19.35 ng/g in Taizhou; 7.57 to 29.18 ng/g, with a mean of 20.52 ng/g in Xiangshan; and n.d. to 58 ng/g, with a mean of 1.29 ng/g in Zhoushan. The levels of PCBs in surface sediments found in this study indicated a moderate degree of contamination in three major coastal aquaculture areas in Zhejiang province.

The concentrations of the ∑39 PBDEs ranged from 3.05 to 26.18 ng/g, with a mean of 14.19 ng/g in sediment in Taizhou; 13.42 to 22.70 ng/g, with a mean of 16.10 ng/g in Xiangshan; and 1.35 to 11.73 ng/g, with a mean of 5.36 ng/g in Zhoushan. The mean concentration of the ∑39 PBDEs decreased in the following order Xiangshan off shore ≅ Taizhou near shore > Zhoushan coast, and low molecular weight PBDE compounds were found in most study areas.

A statistical analysis using PCA was performed on the 20 PCB and 39 PBDE congener profiles. The dominant coplanar congeners were CB-77, CB-81, CB-105, CB-118, CB-126, CB-138, CB-167, and CB-169. The contribution of BDE-2, 3, 8, 10, 17, 33, 47, 138, and 153 was relatively high in these samples.

A significant correlation was observed between the concentrations of CB-105 and CB-123, 126, 156, 157, 167, and 169 in these sediment samples, while the concentrations of CB-123 and CB-126 were strongly correlated with the concentrations of CB-123, 126, 156, 157, and 167, respectively. There was a positive correlation between the small number of bromine congeners, i.e., between BDE-2 and BDE 3, BDE 8, BDE 10, and BDE 33; between BDE-33 and BDE 8 and BDE 10; and between BDE-33 and BDE 15, BDE 49, and BDE 77.

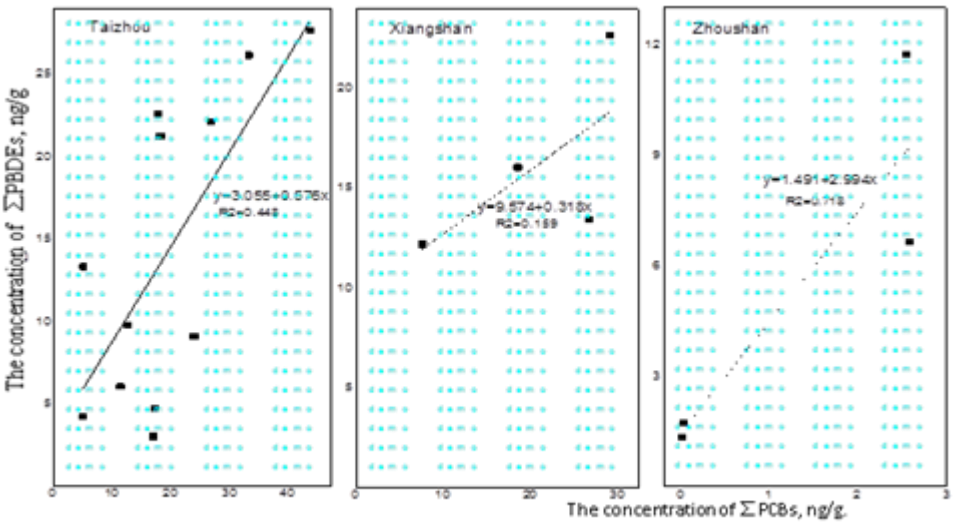

FIGURE 6
The correlation between ∑PCBs and ∑PBDEs

ACKNOWLEDGEMENTS

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