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Concentrations and Characteristics of Polybrominated Diphenyl Ethers (PBDEs) in Marine Zooplankton from the Gaoping Waters of Southwestern Taiwan

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Abstract: Bioaccumulation by zooplankton is the outset for persistent organic pollutants that enter the marine food chain. Owing to a full spectrum of anthropogenic activities, the Gaoping waters of southwestern Taiwan are exposed to large quantities of polybrominated diphenyl ethers (PBDEs). However, information on these contaminants in zooplankton in this study area is lacking. In this study, we analyzed 19 PBDE congeners concentrations in 36 zooplankton samples from the Gaoping waters. A high variation in the total PBDE concentrations in zooplankton (from not detected to 1415 ng g^{-1} dry weight) was found, with the highest PBDE levels being recorded near the entrance of the Kaohsiung Harbor (KH). Significantly higher levels were noted for the KH transect than for the Gaoping River estuary (GR) and Fengshan Township (FS) transects, indicating that PBDE inputs originate from the ocean sewage outfalls. BDE-15 (43%) and BDE-209 (16%) were the predominant PBDE congeners in the zooplankton. Our results suggest that anthropogenic activities might predominantly contribute to significantly high PBDE concentrations. The traditional food web may easily transport these higher levels of PBDEs in zooplankton to higher trophic levels of marine organisms, since the Gaoping waters serve as essential nursery and spawning grounds for invertebrates and fishes.

Keywords: mesozooplankton; persistent organic pollutants; bioaccumulation; surface food chain

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1. Introduction

Polybrominated diphenyl ethers (PBDEs), which consist of two oxygen-linked phenyl rings, were listed as persistent organic pollutants (POPs) in the Stockholm Convention in 2009 [1]. They are widely used as additive brominated flame retardants (BFRs) in various consumer products, such as in furniture, wire and cable insulation, electronics, computers, and building materials. Three major commercial PBDE formulations, penta-BDE, octa-BDE, and deca-BDE, are economically produced. Due to their resemblance to polychlorinated biphenyls (PCBs) in their structure, lipophilicity, and persistence, PBDEs were looked upon as potentially toxic for biota—humans included [2–4]. According to Meironyté et al. [5], between the 1970s and 1990s, the concentrations of PBDEs in breast milk have increased significantly. Consequently, the use of PBDEs in all applications has already been terminated in the European Union and in certain states in the United Sates [6,7]. In Taiwan, the limits on penta-BDE and octa-BDE in manufacturing and use were set in 2015, but commercial deca-BDE combinations are still used despite the fact that there are doubts that deca-BDE mixtures (composed of mainly BDE-209) might debrominate to less-brominated congeners in the environment and bring risks on [8].

Large amounts of PBDEs have been released into the global environment during the production, application, and disposal processes [1,2,9–11]. On account of their hydrophobic properties, PBDEs are preferentially absorbed onto particles in the aquatic environments and lipid in aquatic biota [11,12]. Consequently, these anthropogenic contaminants easily pile up in marine plankton and are transferred to higher trophic

levels by means of the food web [9,13,14]. Zooplankton are indispensable in the food chain as secondary producers and provide marine fishes, birds, and mammals with abundant amounts of food [15,16]. Therefore, it is through zooplankton that water-borne POPs gain access to the food web [17,18]. In marine environments, phytoplankton are exposed to contaminants only via water; in contrast, zooplankton accumulate POPs via food or exposure to polluted water. As a result, this makes POP transport and distribution in the marine plankton food chain more complex.

The accumulation of PBDEs in marine fauna has been evidenced in some previous studies [9,13,14,19,20]. For example, analyses of PBDEs in food webs from the Baltic Sea and the northern Atlantic Ocean [19,21] demonstrated the biomagnification potential of less-brominated congeners. Wan et al. [20] found that in comparison with other marine organisms worldwide, the PBDE concentrations in organisms from Bohai Bay were low. Additionally, it was suggested that BDE-47 was the predominant compound in most samples. Zheng et al. [22] also reported the bioaccumulation characteristics of PBDEs in the marine food web of Bohai Bay and suggested that BDE-209 can be biodegraded to BDE-47 through BDE-154 and BDE-99 in marine organisms. Additionally, the study by Kelly et al. [13] exhibited the absence of biomagnification for BDE-209 in the Canadian Arctic marine food web.

Detectable PBDE levels have been determined in several previous studies in Taiwan, such as in coastal sediments [10,23,24], estuarine fishes [25], and stranded cetaceans [26]. However, the knowledge about the concentrations and characteristics of PBDEs in field zooplankton in Taiwan is lacking. The Gaoping waters, close to Kaohsiung City, are considered the key fishing grounds for the benthic trawling fisheries surrounding Taiwan [27,28]. Kaohsiung is the largest industrial city and the second largest densely populated city (population 1.5 million) in Taiwan. The coastal wastewater in Kaohsiung originates from three ocean sewage outfalls (Zuoying, Jhongjhou, and Dalinpu), whose discharges come from industrial parks and the Southern Taiwan Science Park [29]. Accordingly, the Gaoping waters might be directly polluted by diverse and complicated POP inputs. Consequently, it is necessary to determine the PBDEs levels in zooplankton, in that feeding on zooplankton contributes hydrophobic pollutants to fish [30,31]. The objectives of this study were to (1) examine the concentrations and characteristics of PBDEs in zooplankton and (2) analyze their spatial variability and possible sources in this study area.

2. Materials and Methods

2.1. Sample Collection

Field surveys were conducted in August and October 2015 and April 2016 at 12 sampling stations (three transects: Kaohsiung Harbor (KH), Gaoping River estuary (GR), and Fengshan Township (FS)) from the Gaoping waters of southwestern Taiwan (Figure 1). Hydrographic and zooplankton samplings were carried out with the RV *Ocean Researcher III*. At each surveyed station, the temperature and salinity were recorded in situ using a General Oceanic SeaBird CTD system (SEB-911 Plus, Bellevue, Washington, DC, USA) lowered from the surface to 100 m or 5 m above the bottom at shallow stations. In addition, seawater samples at six different depths (0, 3, 10, 25, 50, and 75 m) were collected using Niskin bottles (General Oceanics, Miami, FL, USA). For the chlorophyll *a* analysis, 1 L samples of water were instantaneously filtered using GF/F filters (0.47 μm pore, Whatman, Clifton, NJ, USA), then frozen in the dark as quickly as possible before their analysis in the laboratory. Additionally, 1 L samples of seawater stored in polyethylene bottles were refrigerated at 4 °C for further quantitative filtration and nitrate analyses in the laboratory.

Nets from the Ocean Research Institute (ORI) (mouth diameter of 1.6 m, length of 6 m, and mesh size of 330 μm) were used to collect the zooplankton. The nets were towed horizontally at a speed of 1 m s^{-1} for about 5 min. Flow meters (Hydro-Bios, Kiel, Schleswig-Holstein, Germany) were installed in the mouths of the nets to calculate the volume of water passing through. On board, the zooplankton samples were equally divided into two subsamples using a Folsom plankton splitter (Aquatic Research Instruments, Wellington,

New Zealand). One was used for the PBDE analysis in zooplankton, which was filtered through pre-combusted glass fiber filters (at −450 °C for 4 h) and then stored at –20 °C until the analysis. The other was used for counts and taxonomic identification and was preserved in a 5% buffered formalin–seawater solution.

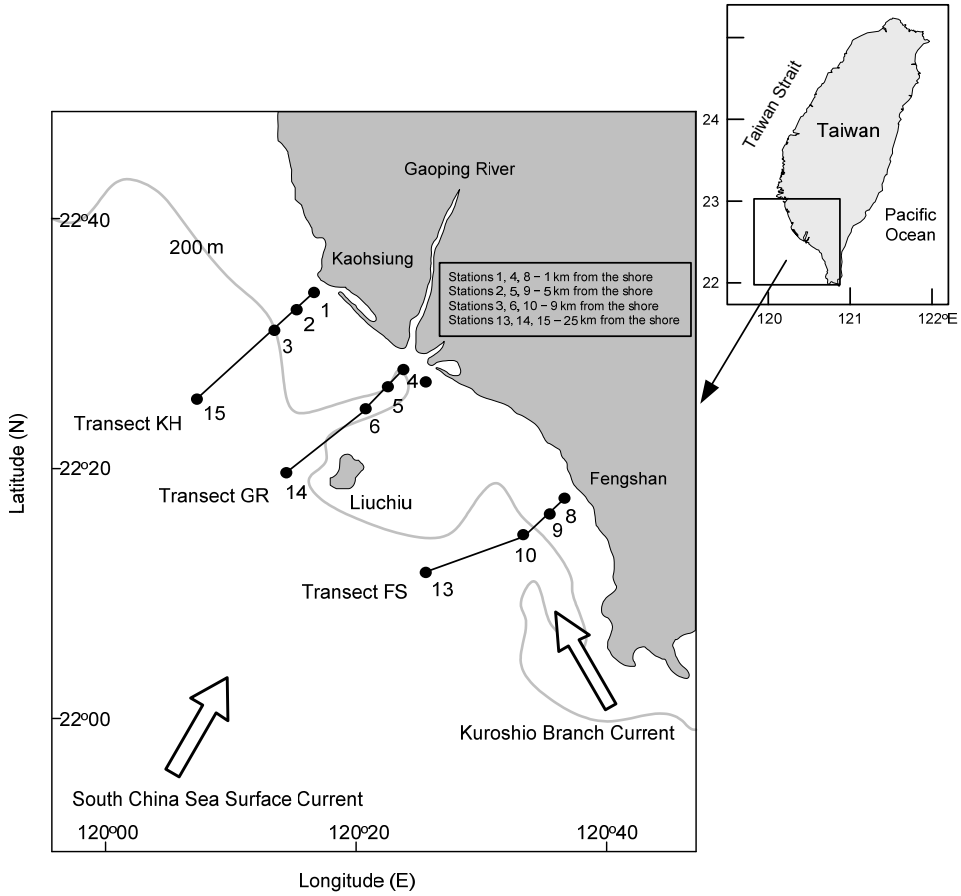

Figure 1. Map of the study area and sampling stations in the Gaoping waters of southwestern Taiwan. KH: Kaohsiung Harbor; GR: Gaoping River estuary; FS: Fengshan Township.

2.2. Measurements of Chlorophyll A and Nitrate

In the laboratory, firstly, the seawater filters collected on board were placed in a 15 mL centrifuge tube with 10 mL of 90% acetone and the pigments were extracted in complete darkness for 20 h after vigorous vortexing [32]. Then, the tubes were centrifuged at 1000× *g* (for 15 min at 4 °C) and the supernatant was transferred to a fluorometer cell. Finally, the chlorophyll *a* concentration in the supernatant was measured using a fluorometer (10-AU; Turner Design, San Jose, CA, USA) based on the method used by Welschmeyer [33]. Additionally, parts of all water samples were filtered through glass fiber filters (GF/F 0.47 µm pore, Whatman, Clifton, NJ, USA) for nitrate measurements. Three replicate measurements were made to be analyzed chemically. A very low nitrate concentration was preconcentrated and determined by the chemiluminescence method [34].

2.3. Zooplankton Identification

The zooplankton subsamples used for counts and taxonomic identification were subdivided repeatedly using a Folsom plankton splitter (Aquatic Research Instruments, Wellington, New Zealand) until the individual number range remaining in the last subsample was 1000–2000. In this way, we calculated the abundance of the zooplankton. The abundance of the zooplankton was presented as the number of individuals per 1 m^3. Going by the classification of zooplankton in the Kuroshio waters, thirty-three taxonomic groups of zooplankton were subsequently identified [35].

2.4. Chemical Analysis of PBDEs

The filtered zooplankton subsamples were analyzed for PBDEs. Prior to the analysis, the whole bodies of zooplankton were oven-dried at 50 °C overnight and the dry weight was measured. The preparation, extraction, and PBDE determination processes were based on standard analytic procedures [36,37]. Briefly, the dried sample was ground with anhydrous sodium sulfate before being extracted. The extraction was performed as accelerated solvent extraction (ASE 300 extractor, Dionex, Sunnyvale, CA, USA). Methylene chloride was used as the extraction solvent, and the other parameters acted according to previous studies [38]. All extracts were thoroughly purified using activated silica gel columns (US EPA method 3630C). The purified fractions were analyzed via gas chromatography (Varian CP-3800) coupled with mass spectrometry (Varian model 320) following the procedure described by Ko et al. [26]. The quantification of each PBDE in the extract was done using the internal standard method. Three $^{13}C_{12}$-labeled BDEs as internal standards, including MBDEs 47, 153, and 209, were used in this study. The congeners in the extracts were determined on the basis of their chromatographic retention times related to the internal standard. We quantified 19 PBDE congeners (BDE 2, 15, 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, 203, 205, 206, and 209) in this study. All concentrations are expressed in terms of dry weight. The matrix (Na_2SO_4) blanks and spikes were analyzed as quality control measurements. Four pre-deuterated PAHs as surrogate standards (d_8-naphalene, d_{10}-fluorene, d_{10}-fluoranthene, and d_{12}-pyrene) were added to each sample (inclusive of blank and spike) before extraction to observe the performance of the analytical procedure on the whole. The average recovery rates of d_8-naphalene, d_{10}-fluorene, d_{10}-fluoranthene, and d_{12}-pyrene were 76 ± 6%, 97 ± 5%, 94 ± 4%, and 109 ± 4%, respectively. To avoid overestimation, we did not correct the concentrations of PBDE congeners for surrogate recovery rates. The recovery rates of individual PBDE congeners in matrix spikes, on average, ranged from 77 ± 6% to 105 ± 3%. The method detection limits (MDLs) were set at three times the amount detected in the procedural blank. The values of MDLs were in the range of 0.01–2.42 ng g^{-1}. In this study, the total PBDE (ΣPBDE) represents the sum of 11 PBDE congeners (2, 15, 17, 28, 71, 99, 100, 190, 203, 205, and 209).

2.5. Statistical Analysis

A one-way analysis of variance (ANOVA) was used to examine the differences in the hydrographic parameters and abundance levels and PBDEs concentration of zooplankton for the sampling times and locations [39]. Statistical significance was determined at $\alpha = 0.05$. Unless indicated otherwise, the data are given as the means ± s.d. In addition, canonical correspondence analysis (CCA) [40] was used to explore the non-linear relationships among the abundance levels (taxa with relative abundance >1%) and 11 PBDE congener concentrations of zooplankton using PC-ORD 6.0 software (MjM Software, Gleneden Beach, OR, USA).

3. Results and Discussion

3.1. Changes in Hydrographic and Biological Variables

The results in terms of the hydrographic variables are shown in Table 1. The surface seawater temperature (3 m depth) showed a clear temporal change (ANOVA, $F = 54.648$, $p < 0.001$). The mean surface seawater temperature was 26.34 ± 0.22 °C in April 2016, compared with 28.63 ± 0.50 °C in August 2015 and 28.88 ± 0.47 °C in October 2015. The seawater temperatures ranged from 25.10 to 29.41 °C, with the spatial variations in April 2016 (25.10–28.05 °C) being much higher than those in August 2015 (27.73–29.30 °C) and October 2015 (27.99–29.41 °C). In general, relatively lower temperatures were recorded for the inshore stations, such as stations 1, 4, and 8, but no significant differences were found among the transects and distances from the shore. According to the previous study [41], the surface water temperatures in this study area were usually below 26 °C in winter and above 29 °C in summer. The transitional period (spring) had a mean surface water temperature of *ca.* 27 °C.

Table 1. Hydrographic variables at the different sampling stations during the study period. KH: Kaohsiung Harbor; GR: Gaoping River estuary; FS: Fengshan Township; –: below minimum detection limit.

Transect	Station	Depth (m)	August 2015				October 2015				April 2016			
			Temperature (°C)	Salinity	NO_3^- (mg L^{-1})	Chl. *a* (ug L^{-1})	Temperature (°C)	Salinity	NO_3^- (mg L^{-1})	Chl. *a* (ug L^{-1})	Temperature (°C)	Salinity	NO_3^- (mg L^{-1})	Chl. *a* (ug L^{-1})
KH	1	12	27.73	33.18	0.010	1.92	29.39	32.00	0.027	1.03	26.18	34.49	0.006	3.26
	2	58	28.29	33.55	0.004	1.86	29.07	33.42	0.006	0.54	26.36	34.54	0.009	0.60
	3	188	28.90	33.48	0.004	1.26	29.02	33.63	0.004	0.34	26.54	34.41	0.012	0.26
	15	582	29.13	33.59	0.031	0.80	28.94	34.07	0.008	0.44	28.05	34.53	0.032	0.22
GR	4	33	28.06	33.71	0.009	0.66	27.99	25.63	0.019	0.03	25.10	33.64	0.061	5.50
	5	294	28.08	33.42	0.005	0.46	28.16	33.20	0.011	0.52	25.16	34.38	0.014	3.24
	6	310	28.50	32.83	0.006	0.57	28.28	32.92	0.016	0.52	25.95	34.48	0.015	2.18
	14	545	28.60	34.02	0.021	0.32	28.95	33.83	0.028	0.10	27.67	34.45	0.024	0.24
FS	8	29	29.02	33.40	0.004	0.31	29.16	33.87	0.005	0.54	26.01	34.49	0.008	0.43
	9	138	29.30	34.05	0.004	0.26	29.02	33.90	0.004	0.26	25.79	34.43	0.011	2.52
	10	557	28.80	33.65	0.013	0.63	29.12	33.98	0.007	0.40	26.05	34.42	0.016	0.83
	13	423	29.10	33.74	0.034	0.22	29.41	34.59	0.016	–	27.17	34.49	0.031	0.22

The surface seawater salinity (3 m depth) values fluctuated from 32.83 to 34.05 in August 2015, from 25.63 to 34.59 in October 2015, and from 33.64 to 34.54 in April 2016 (Table 1). A temporal pattern in salinity was found (ANOVA, $F = 3.359$, $p < 0.05$), with clear higher mean salinity in April 2016 (34.40 ± 0.24). In addition, the spatial variations in August and October 2015 were much bigger than those in April 2016. This phenomenon was similar to that mentioned by Hsieh et al. [41], who reported that apparently lower surface salinity was recorded in summer than in spring and winter in this study area, and a broader range (31–34) was noted in summer. In the present study, relatively lower salinity levels were generally measured at the stations within <5 km from the shore in August and October 2015, having salinity levels <33.5. The lowest salinity value (25.63) was observed at station 4 (near the mouth of the Gaoping River) in October 2015, which was probably the result of the precipitation that occurred in the two weeks before the sampling.

The mean nitrate concentration was slightly higher in April 2016 (0.02 ± 0.02 mg L^{-1}) than in August (0.01 ± 0.01 mg L^{-1}) and October 2015 (0.01 ± 0.01 mg L^{-1}), although the difference did not reach statistical significance (ANOVA, $F = 2.026$, $p = 0.148$). Meanwhile, no significant difference in nitrate concentration was detected between sampling stations, but relatively high nitrate values were found at the stations *ca.* 25 km from the shore (Table 1). Generally speaking, the riverine outflow was responsible for the main source of nutrients in the Gaoping waters located in the south of Taiwan [42,43]. Nevertheless, in addition to the riverine outflow, nutrient-rich water to some areas of this study may have been provided by nutrient upwelling to surface waters via vertical mixing of the water column [41]. In winter and early spring, the upwelling moves more nutrients into the mixed layer, since the northeasterly monsoon weakens the summer thermal stratification. This speculation could be demonstrated by the slightly higher nitrate concentration observed in April 2016.

Significant differences were found in chlorophyll *a* concentrations over time. The surface chlorophyll *a* concentrations ranged between 0 (below minimum detection limit) and 5.50 ug L^{-1} (Table 1), with a higher mean value in April 2016 (1.62 ± 1.71 ug L^{-1}) than in August (0.77 ± 0.59 ug L^{-1}) and October 2015 (0.39 ± 0.28 ug L^{-1}) (ANOVA, $F = 4.254$, $p < 0.05$). The variation in chlorophyll *a* concentrations during the different seasons in this study area was large [41]. Higher phytoplankton production and resource availability rates for grazers (i.e., copepods) would be made possible with bountiful nutrients [43,44]. In this study, the chlorophyll *a* rates were higher at the stations within <1 km from the shore (e.g., stations 1, 4, and 8). In contrast, stations located *ca.* 25 km from the shore had relatively lower chlorophyll *a* concentrations. We speculated that the variations in chlorophyll *a* concentration are likely controlled by nitrate, while the phytoplankton distributions in this study area are patchy and variable. On the onshore side of Kuroshio off of southern Japan, Ichikawa and Hirota [45] and Sassa and Hirota [46] also reported higher chlorophyll *a* concentrations integrated over the 0–200 m water column from January to March when the water column was well vertically mixed.

3.2. The Zooplankton Communities

The overall mean abundance of zooplankton was 326 ± 379 ind. m^{-3}, with the values ranging from 9 ind. m^{-3} at station 1 to 1766 ind. m^{-3} at station 10 in August 2015, from 24 ind. m^{-3} at station 1 to 512 ind. m^{-3} at station 15 in October 2015, and from 69 ind. m^{-3} at station 13 to 415 ind. m^{-3} at station 1 in April 2016. Figure 2 shows the variation in the mean abundance levels of zooplankton among the three transects in each sampling month. A significant temporal difference in zooplankton abundance (ANOVA, $F = 5.782$, $p < 0.01$) was observed in this study, with the highest mean abundance level being recorded in August 2015 and the lowest in October 2015. In contrast, there were no significant spatial differences among the transects (ANOVA, $F = 0.985$, $p = 0.384$) or among the different distances from the shore (ANOVA, $F = 0.456$, $p = 0.715$) in terms of zooplankton abundance. In the marine pelagic ecosystem, an increase in zooplankton biomass is generally coupled with the phytoplankton bloom [43,47], but with a 1–2-month

lag. However, in the present study, no significant correlation between zooplankton and chlorophyll *a* was observed (ANOVA, $F = 0.250$, $p = 0.620$). In contrast to the lower mean values in terms of the chlorophyll *a* concentrations that occurred in August and October 2015, the greatest zooplankton abundance was recorded in August 2015. We thought that the growth of the zooplankton population in spring (April 2016) did not reflect the high chlorophyll *a* concentration.

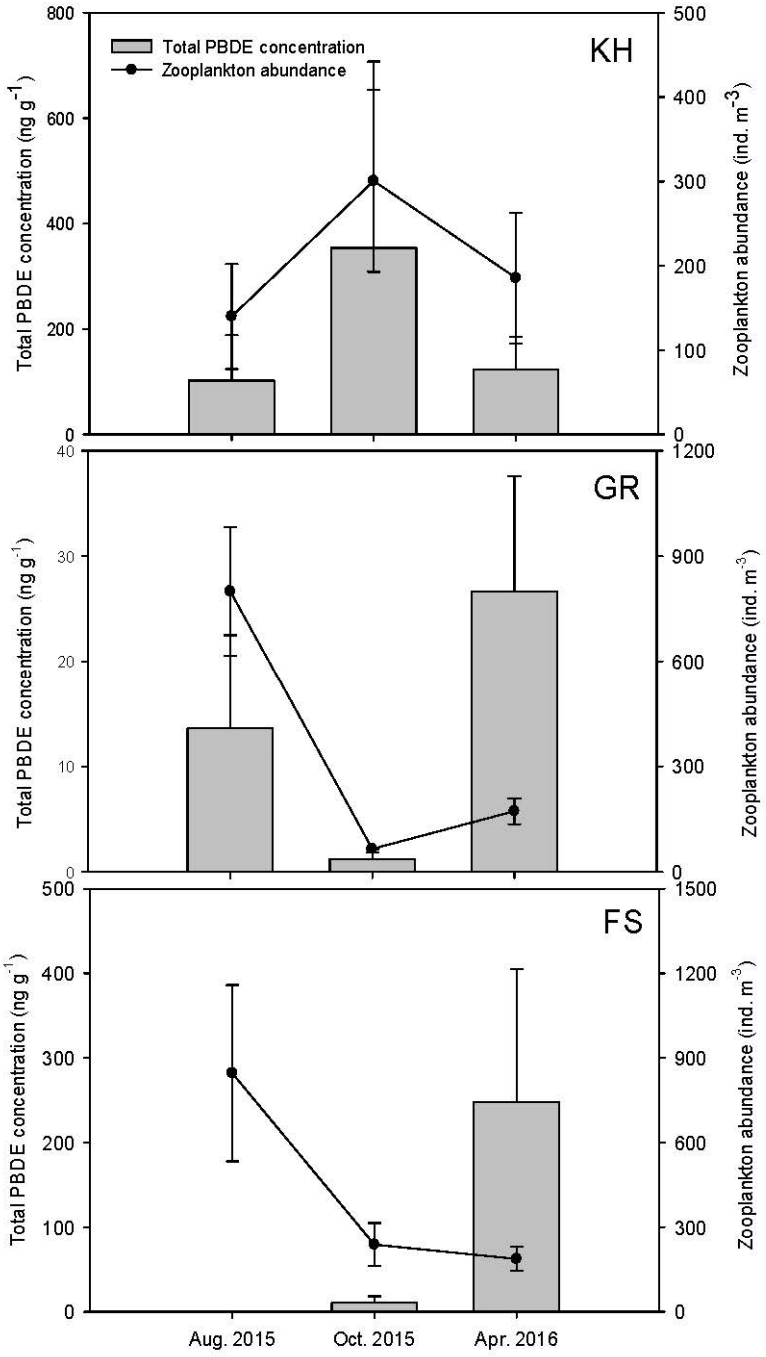

Figure 2. Mean values (±SE) of PBDE concentrations and zooplankton abundance levels in the Gaoping waters during the study period. KH: Kaohsiung Harbor; GR: Gaoping River estuary; FS: Fengshan Township.

The abundance and occurrence levels of different zooplankton taxa are shown in Table 2. Twenty-eight major zooplankton taxa were identified in the present study. Among them, calanoids were the most abundant taxa in all samples, with the relative abundance

level being over 65% at each sampling time. Comparing the total zooplankton catches, the ranking of dominant taxa was as follows: calanoids (233 ± 285 ind. m^{-3}; RA 72%), chaetognaths (27 ± 26 ind. m^{-3}; RA 8%), shrimp larvae (9 ± 17 ind. m^{-3}; RA 3%), cyclopoids (7 ± 7 ind. m^{-3}; RA 2%), heteropods (6 ± 10 ind. m^{-3}; RA 2%), and pteropods (6 ± 13 ind. m^{-3}; RA 2%). The top six dominant taxa comprised 88.64% of the overall zooplankton catch. In most tropical and subtropical oceans around the world, copepods usually contain *ca.* 75% of the total zooplankton catch [48,49]. Copepods prey on phytoplankton and microzooplankton (ciliates or flagellates), and furthermore they are hunted by higher trophic levels, e.g., chaetognaths and fish larvae. Copepods, therefore, are crucial to the transport of materials and energy from primary producers and the microbial loop food web to the conventional food chain [50].

Table 2. Mean abundance (ind. m^{-3}) and total relative abundance (%) levels of zooplankton in the Gaoping waters during the study period. Note: –: no occurrence.

Taxa	August 2015	October 2015	April 2016	RA
Foraminifera	9.13	5.47	1.32	1.63
Radiolaria	0.13	0.36	–	0.05
Polyp	–	–	–	–
Medusa	–	–	0.03	0.003
Obelia	–	–	–	–
Siphonophore	5.83	1.85	1.00	0.89
Ctenophora	0.19	0.03	–	0.02
Polychaeta	2.02	0.19	0.37	0.26
Pteropoda	13.58	2.82	2.36	1.92
Heteropoda	8.88	5.90	4.57	1.98
Amphipoda	0.36	0.47	0.32	0.12
Crab zoea	1.06	1.25	2.15	0.46
Crab megalopa	0.15	0.11	0.01	0.03
Lucifera	3.44	2.94	0.75	0.73
Sergestidae	0.05	–	0.24	0.03
Other Decapoda	–	–	–	–
Cladocera	0.75	0.72	0.56	0.21
Ostracoda	2.53	0.80	0.61	0.40
Copepoda nauplius	–	–	–	–
Calanoida	451.19	129.42	119.83	71.61
Cyclopoida	6.29	6.12	7.40	2.03
Harpacticoida	10.19	0.42	0.16	1.10
Shrimp larva	18.42	6.08	3.86	2.90
Mysidacea	–	–	–	–
Euphausiacea	4.78	0.68	0.28	0.59
Barnacle nauplius	2.12	0.07	9.53	1.20
Echinodermata larva	0.26	–	0.01	0.03
Chaetognatha	35.75	28.91	15.74	8.22
Appendicullaria	10.09	1.96	3.21	1.56
Thaliacea	3.97	2.71	1.44	0.83
Fish eggs	1.94	1.36	4.45	0.79
Fish larva	1.91	0.64	1.21	0.38
Insect larva	–	0.03	0.01	0.004
Others	0.29	0.02	0.15	0.05

3.3. Concentrations, Compositional Profiles, and Possible Resources of PBDEs in Zooplankton

The present study provides information on the concentrations and characteristics of PBDEs in zooplankton from the Gaoping waters. Nineteen PBDE congeners were analyzed in zooplankton samples from the Gaoping waters. The overall mean value of the total PBDE concentrations (sum of 11 PBDE congeners) was 98 ± 265 ng g^{-1} (dry weight basis). The PBDE concentrations varied widely, ranging from not detected to 1415 ng g^{-1}. Two sporadic high concentrations of 1415 ng g^{-1} and 713 ng g^{-1} were measured at station 1 in October 2015 and at station 9 in April 2016, respectively. Comparatively higher total PBDE

concentrations were observed in October 2015 and April 2016, with a lower concentration in August 2015, even though it was not statistically significant (ANOVA, $F = 0.436$, $p = 0.650$). The means for the total PBDE concentrations for the three transects were 193 ± 404 ng g^{-1} (transect KH), 14 ± 24 ng g^{-1} (transect GR), and 86 ± 203 ng g^{-1} (transect FS), respectively (Figure 2). In general, higher levels were noted for transect KH than transects GR and FS, although there was no significant spatial difference among the transects in terms of the total PBDE concentration (ANOVA, $F = 1.426$, $p = 0.255$). Among the sampling stations for transect KH, inshore stations 1–3 (especially station 1 adjacent to the entrance of the Kaohsiung Harbor) usually had significantly higher total PBDE concentrations (Table 3). The less-brominated BDE-2, BDE-15, and BDE-17 were abundant at these stations.

Based on the halogenation of the phenyl rings analyzed in this study, the PBDE concentrations of 11 PBDE congeners in zooplankton were exhibited (Figure 3). In most of the sampling stations, it was clear that mono-BDE, tetra-BDE, and penta-BDE were most abundant, comprising 76% of the total PBDE concentration. Among these less-brominated congeners, BDE-15 constituted 43% of the total PBDE concentration measured throughout the study, being the most dominant compound. BDE-99 (13%), BDE-17 (12%), and BDE-2 (7%) were the next three predominant PBDEs. Tetra- and penta-BDE are the main components of penta-BDE commercial products [51]. According to the previous studies by La Guardia et al. [52], Sellström et al. [53], Lacorte et al. [54], Domínguez et al. [55], and Eljarrat et al. [56], the dominance of less-brominated BDEs could be due to either the past production and extensive use of penta- and octa-BDE mixtures, or a consequence of the natural debromination of highly brominated BDEs due to UV light. In the present study, BDE-209 was another major congener (16%). Its dominance in zooplankton has also been suggested in [9,11,12]. In addition, extensive highly brominated BDEs, such as BDE-203 and BDE-205, were also found, indicating the use of highly brominated BDE-209.

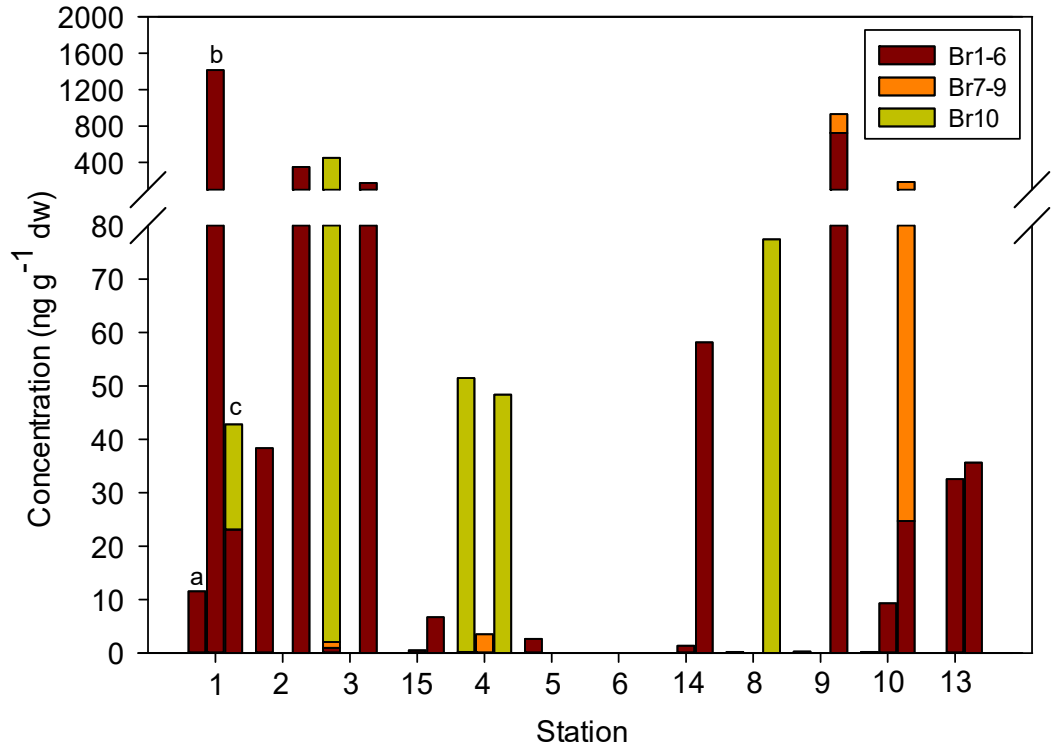

Figure 3. PBDE concentrations in zooplankton samples at each sampling station. Note: a: August 2015; b: October 2015; c: April 2016.

Table 3. PBDE concentrations in zooplankton (ng g^{-1} dw) samples collected at the different sampling stations during the study period. KH: Kaohsiung Harbor; GR: Gaoping River estuary; FS: Fengshan Township; ND: non-detectable concentration; [a] mean (min–max).

Compound	Transect KH				Transect GR					Transect FS		
	1	**2**	**3**	**15**	**4**	**5**	**6**	**14**	**8**	**9**	**10**	**13**
BDE-2	4.66 (0.00–13.97) [a]	54.25 (0.00–133.79)	25.90 (0.00–77.70)	ND	ND	0.50 (0.00–1.49)	ND	ND	ND	ND	ND	ND
BDE-15	424.54 (0.00–1273.61)	3.13 (0.00–9.39)	ND	0.56 (0.00–1.18)	ND	0.31 (0.00–0.94)	ND	19.84 (0.00–58.16)	ND	32.45 (0.00–97.36)	1.40 (0.00–2.30)	20.03 (0.00–31.23)
BDE-17	50.33 (0.00–141.88)	50.67 (0.00–152.00)	25.86 (0.00–77.59)	1.84 (0.00–5.52)	ND	ND	ND	ND	ND	0.78 (0.00–2.34)	9.95 (0.00–22.40)	2.70 (0.00–4.41)
BDE-28	ND	ND	ND	ND	0.07 (0.00–0.21)	0.08 (0.00–0.24)	0.05 (0.00–0.16)	ND	0.07 (0.00–0.20)	0.09 (0.00–0.28)	0.07 (0.00–0.22)	ND
BDE-71	3.85 (0.00–11.54)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BDE-99	ND	ND	0.33 (0.00–0.99)	ND	ND	ND	ND	ND	ND	151.63 (0.00–454.88)	ND	ND
BDE-100	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.62 (0.00–4.85)	ND	ND
BDE-190	ND	ND	0.36 (0.00–1.07)	ND	ND	ND	ND	ND	ND	51.30 (0.00–153.89)	43.66 (0.00–130.97)	ND
BDE-203	ND	ND	ND	ND	1.17 (0.00–3.52)	ND	ND	ND	ND	ND	ND	ND
BDE-205	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.35 (0.00–7.05)	ND
BDE-209	6.57 (0.00–19.71)	ND	119.10 (0.00–357.30)	ND	33.21 (0.00–51.26)	ND	ND	ND	25.82 (0.00–77.45)	ND	ND	ND
ΣPBDE	489.94 (11.54–1415.48)	108.05 (0.00–285.79)	171.55 (0.00–359.37)	2.40 (0.00–6.71)	34.46 (3.52–51.47)	0.89 (0.00–2.68)	0.05 (0.00–0.16)	19.84 (0.00–58.16)	25.88 (0.00–77.45)	237.87 (0.00–713.32)	57.43 (0.22–162.72)	22.73 (0.00–35.64)

The PBDE levels in zooplankton obtained from this work were comparable to the levels found in several areas in Asia and Europe (Table 4). Surprisingly, the concentrations of total PBDEs in zooplankton in this study area were much higher than those found in Bohai Bay (China) [22], Tokyo Bay and Sagami Bay (Japan) [11], and Baiyangdian Lake (China) [57]; and also higher than in the Baltic Sea [12] and Bohai Bay (China) [14,20], measured by lipid contents and wet weight, respectively. Only the PBDE concentrations from Lago Maggiore (Italy; lipid basis) [58] were higher than those recorded in this study. These results are corroborated by the fact that heavy PBDEs polluted the area due to the increasing use of this compound in brominated flame retardants. Despite the fact that both natural and anthropogenic sources give rise to PBDEs in the environment, the major sources of PBDEs are anthropogenic. Local sources were responsible instead of long-range air transportation brought about PBDE contamination in transect KH in particular (Figures 2 and 3). Kaohsiung is a densely populated and highly industrialized (with petrochemical industrial parks included) city. Thus, it is expected that the Gaoping waters will receive direct diverse PBDE inputs through the discharges of industrial wastewater and domestic sewage or atmospheric fallout.

Table 4. PBDE concentrations in zooplankton samples in other marine environments. KH: Kaohsiung Harbor; GR: Gaoping River estuary; FS: Fengshan Township.

Location	PBDE Numbers	PBDEs (ng g^{-1} dw)	Reference
Marine			
Gaoping waters (Taiwan)			Current study
—transect KH	19	0–1415.48	
—transect GR	19	0–58.16	
—transect FS	19	0–713.32	
Bohai Bay (China)	13	0.15–32.8 (ng g^{-1} lw)	Wan et al. (2008) [20]
Baltic Sea (in 2002)	14	2.36–4.87 (ng g^{-1} lw)	Peltonen et al. (2014) [12]
Baltic Sea (in 2010)	14	2.76–10.69 (ng g^{-1} lw)	Peltonen et al. (2014) [12]
Bohai Bay (China)	13	12 ± 1 (ng g^{-1} ww)	Shao et al. (2016) [14]
Bohai Bay (China)	6	0.75–7.29	Zheng et al. (2016) [22]
Tokyo Bay (Japan)	45	0–23.24	Yeo et al. (2020) [11]
Sagami Bay (Japan)	45	7.18–27.09	Yeo et al. (2020) [11]
Freshwater			
Baiyangdian Lake (China)	9	14.3	Hu et al. (2010) [57]
Lago Maggiore (Italy)	15	379–2094 (ng g^{-1} lw)	Poma et al. (2014) [58]

Field studies of the marine food web have shown that zooplankton acquire PBDEs from feeding on phytoplankton, passively from the surrounding waters or from suspended particulate matters [9,11–13]. Zooplankton are sensitive to what are known to be important in determining their abundance and spatiotemporal distribution—any subtle changes in the physical, chemical, and biological properties of the marine environment [59,60]. These hydrographic fluctuations not only affect the abundance of zooplankton, but also change the composition of zooplankton communities [60,61]. The spring bloom is widely acknowledged to mark the beginning of zooplankton production in temperate marine ecosystems [62,63]. The quantity and quality of food are determining factors in the egg production rates of marine copepods [64]. Although no significant relationship between zooplankton abundance and the chlorophyll *a* concentration was found in the present study, the distribution patterns of the two were similar, with higher levels at the stations within <9 km from the shore. However, in our data set, the PBDE concentrations did not increase with the higher zooplankton abundance. The results of the CCA bi-plot (Figure 4) derived from the abundance levels of the 10 most dominant taxa showed that the Pearson correlations between the abundance levels and PBDE concentrations for zooplankton (0.606 with axis I and 0.559 with axis II) were low. The first two canonical axes explained only 19.9% of the constrained variance in the distribution of dominant taxa of zooplankton. The

results pointed out that other processes perhaps mark the bioaccumulation of PBDEs in zooplankton. The variation in PBDE concentrations in zooplankton in our study could not be interpreted via the distribution of the zooplankton, which is in accordance with the finding reported by Kelly et al. [13]. Therefore, further investigations on the potential sources and transport of PBDEs and the impact on the marine ecosystem in detail are necessary given that the Gaoping waters are the main fish nursery and spawning grounds.

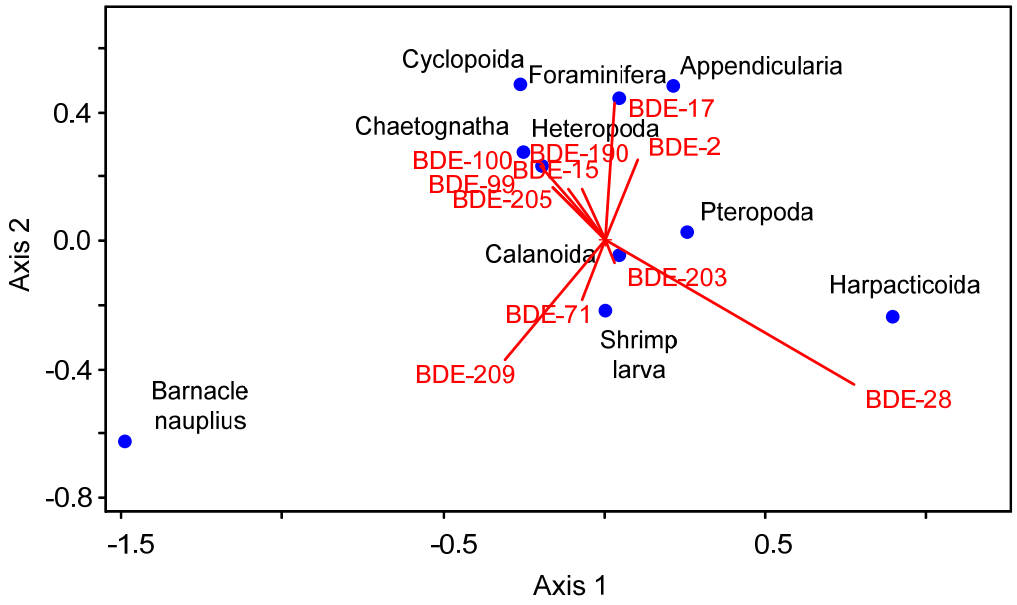

Figure 4. Ordination diagram of the canonical correspondence analysis (CCA) based on the 10 most dominant taxa and 11 PBDE congener concentrations of zooplankton.

4. Conclusions

This is the first investigation to examine the concentrations and characteristics of PBDE congeners in marine zooplankton in Taiwan. Overall, PBDE concentrations ranging from not detected to 1415 ng g^{-1} dry weight were found in all samples collected. Less-brominated congeners and deca-BDE were the predominant compounds. The concentration of PBDEs in the zooplankton in this study area was much higher than in other studies around the world, reflecting the fact that Kaohsiung is a highly industrialized and densely populated city. We believe that the highly PBDE-contaminated zooplankton may lead to increased hazards for higher trophic levels of marine organisms, particularly for fishes spawning and feeding in the Gaoping waters.

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