Science of the Total Environment 579 (2017) 1885–1893

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Bioconcentration of polybrominated diphenyl ethers and organochlorine pesticides in algae is an important contaminant route to higher trophic levels

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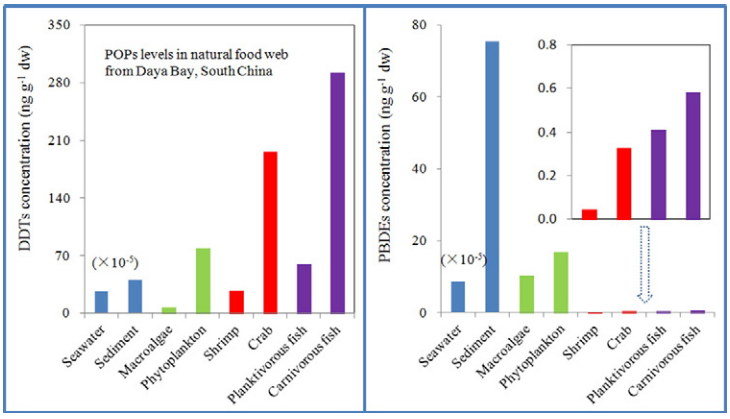
HIGHLIGHTS

- Concentrations of POPs in algae have been studied in subtropical bays of China and similar data around the world are scarce.
- Phytoplankton with larger surface areas have higher uptake efficiency for POPs.
- The BCFs and BAFs of the targeted chemicals are affected by factors such as cell size, nutrients and lipid content.
- Bioconcentration is an important route for transporting DDTs and PBDEs in algae to organisms of higher trophic levels.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 September 2016
Received in revised form 26 November 2016
Accepted 26 November 2016
Available online 8 December 2016

Editor: Adrian Covaci

Keywords:
Polybrominated diphenyl ethers
Organochlorine pesticides
Algae

ABSTRACT

Persistent organic pollutants (POPs) present in water may be bioconcentrated in phytoplankton and further transferred into higher trophic levels. In the present study, seawater, sediment, phytoplankton and macroalgae (*Ulva lactuca* L.) samples were collected from two estuarine bays in South China and analyzed for 24 polybrominated diphenyl ethers (PBDEs) and 22 organochlorine pesticides (OCPs). The concentrations of PBDE congeners except BDE-209 were low in both phytoplankton and *Ulva*. BDE-209 was the predominant congener in phytoplankton and *Ulva*, accounting for 89.5% and 86.6% of the total average concentrations of PBDEs (48.5 and 4.1 ng g^{-1} dw), respectively. The average concentrations of DDTs, HCHs and 1-chloro-2,2-bis(4-chlorophenyl)ethane (*p,p′*-DDMU) in phytoplankton were 398, 241 and 11.3 ng g^{-1} dw, respectively, while those of DDTs and HCHs in *Ulva* were 8.4 and 33.1 ng g^{-1} dw. The levels of both PBDEs and OCPs were an order of magnitude higher in phytoplankton than in *Ulva*, indicating that phytoplankton with larger surface areas have higher uptake efficiency for POPs than *Ulva*. Bioconcentration factors (BCFs) of DDT and PBDE in phytoplankton from the two bays were in the range of 10^5– 10^6, suggesting that bioconcentration

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http://dx.doi.org/10.1016/j.scitotenv.2016.11.192

Bioconcentration
Food web

may be one of the key sources of POPs and algae can be an important route for POPs to move toward higher trophic levels.

1. Introduction

Algae (both phytoplankton and macroalgae) play an important role in the biogeochemical cycles of persistent organic pollutants (POPs) in aquatic ecosystems (Russell et al., 1999). The biological uptake of POPs by marine phytoplankton has been shown to have a strong effect on concentrations of POPs in the water column (Galbán-Malagón et al., 2013). The cellular walls of algae, principally its fibril matrix and intercellular spaces, are enriched with sulphated polysaccharides. Proteins, lipids and nucleic acids may exist on the surface of macroalgae cellular walls, but occur preferentially in cytoplasmatic membranes and in the cytoplasm of the cells. These compounds easily absorb lipophic POPs which attract increasing attention for their widespread occurrence in the environments and their toxic, mutagenic and carcinogenic characteristics. As a result, POPs absorbed in cellular carbon and/or adsorbed to cell surfaces can be efficiently transferred up the food web (Skoglund et al., 1996). Phytoplankton uptake is thought to be a key process in transferring pollutants from water to fish, and impacts the transport of POP in aquatic environments (Del Vento and Dachs, 2002). As algae have a high capacity to bind POPs, they are considered as suitable contaminant biomonitors. The knowledge of POPs concentrations in algae is important for understanding the fate of these contaminants and can alert coastal managers of possible impacts upon the food web which can potentially lead to the bioaccumulation of contaminants in higher trophic level organisms.

Several classes of POPs, including organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs), have been studied intensively for a number of years (e.g., Fowler, 1990; De Wit, 2002; Chen et al., 2012; Zhang et al., 2013; Rigét et al., 2016). Recent studies have primarily focused on organisms of high trophic levels (e.g., shellfish, fish, seal, whale, bear and bird), but comparatively few have paid attention to algae (Fisk et al., 2001; Macdonald et al., 2002; Chiuchiolo et al., 2004; Gerofke et al., 2005; Wan et al., 2008; Nizzetto et al., 2012; Galbán-Malagón et al., 2013; Echeveste et al., 2016). Bioconcentration and bioaccumulation of POPs in algae were relatively widely studied in the last century (Swackhamer and Skoglund, 1991; Rhee and Thompson, 1992; Halling-Sørensen et al., 2000). The fate of POPs in seawater is strongly influenced by algae through adsorption. POPs as well as many trace metals are mostly concentrated in particulate matter including phytoplankton in aquatic ecosystems (Rhee and Thompson, 1992). The uptake of POPs and their bioconcentration are influenced in a complex manner by duration of exposure and cell density, by environmental factors such as pH, the concentration of nutrients and of dissolved and colloidal organic matter, as well as by phytoplankton physiological conditions (Rhee and Thompson, 1992; Halling-Sørensen et al., 2000). Marine algae including phytoplankton and macroalgae are at the base of food webs, and POPs accumulation could greatly affect their trophic transfer and thus the pollutants accumulation at higher trophic levels, including humans.

Rapid economic growth has resulted in severe environmental pollution worldwide. South China, one of the economically fastest growing regions in China, is an important hub for imported e-waste and electronic manufacturing ventures, as well as having the largest amounts of organochlorine pesticides usage in history due to well-developed agriculture and fisheries. High levels of POPs such as PBDEs and OCPs were found in water, sediment and fish in local areas (e.g., Fu et al., 2003; Mai et al., 2005; Meng et al., 2007; Chen et al., 2013; Liu et al., 2014), and levels of DDTs and HCHs did not significantly decline, while concentrations of PBDEs continued to increase in the last few years (Zhang et al., 2013). Abundant data indicated bioaccumulation/biomagnification of POPs and heavy metals in the local marine food chains, with higher concentrations detected in carnivorous fish than in planktivorous fish (Qiu et al., 2009; Qiu, 2015). There are however few data on the occurrence of POPs in algae. The present study was conducted to investigate the occurrence of PBDEs and OCPs in phytoplankton and macroalgae from Hailing Bay and Daya Bay of South China (Fig. 1), to calculate bioconcentation factors (BCFs) and biota-sediment accumulation factor (BSAF) of the targeted pollutants, and to study the variations of the concentrations of DDTs and PBDEs along the natural food chains in Daya Bay.

2. Materials and methods

2.1. Study area

Daya Bay is one of the most important economic development districts and mariculture zones in Guangdong Province, with a coastal line of 92 km and an area of 600 km^2 (Fig. 1). The bay receives inflows from a few small seasonal streams, as well as from a nuclear power plant. Non-reefal coral communities are patchily and sporadically distributed in the bay, with 34 species of hermatypic corals. The average annual values of water color, transparency, turbidity, temperature, salinity, pH and dissolved oxygen in the past two decades were 8.0, 3.0 m, 2.53, 23.81 °C, 31.52‰, 8.23 and 7.06 mg L^{-1}, respectively, based on a long-term monitoring program (Qiu et al., 2005b). Impaired water quality as characterized by frequent occurrence of red tides has resulted in a drastic decline of zooplankton biomass, severely depressing the fish population (Qiu, 2015). On the other hand, Hailing Bay, located in the western Guangdong Province (Fig. 1) where agriculture has traditionally been a dominant economic driving force, is relatively less impaired by industrial activities compared to Daya Bay, and was therefore selected as a reference site (Qiu, 2015).

2.2. Sample collection and processing

Phytoplankton and macroalgae samples were collected from Daya Bay and Hailing Bay in June 2007 and January 2008. Phytoplankton samples were collected in the water column 2 m above the sea floor with a phytoplankton trawl (0.077 mm mesh size) while macroalgae (*Ulva fasciata*; also known as sea lettuce attached in fish cage and coastal rock) samples were collected by hand with gloves. All samples were stored in polyethylene bags with ice immediately after collection and frozen at −20 °C prior to treatment. In addition, seawater and sediment samples were also collected following a previously published procedure (Qiu, 2015). Briefly, 2 L of surface water (at 0.5 m under the air-sea interface) and bottom water (0.5 m above the sea floor) samples were collected. Three sediment samples at each site (triangle sampling method) were collected from the upper 2 cm layer using a box sediment grab sampler and placed in acid-rinsed polypropylene bag. For identification of taxonomic groups, sub-samples of phytoplankton were preserved in lugal solution. The dominant phytoplankton species in Daya Bay were *Nitzschia sp*., *Skeletonema costatum* and *Scrippsiclla trochoidea*, while in Hailing Bay were *Chaetoceros lorenzianus*, *Nitzschia*, *Bacteriastrum hyalinum* and *Thalassionema nitzschioides*.

Analytical procedures generally followed those of Guo et al. (2009). Briefly, algae (phytoplankton and macroalgae) samples were freeze-dried and grounded into fine powder. Upon spiking with surrogate standards, PCB-67, ^{13}C-PCB-141, PCB-209 and ^{13}C-BDE-77, the samples were Soxhlet extracted with an 1:1 (v:v) acetone and hexane mixture for 48 h, and concentrated to 5 mL with a TurboVap II evaporator

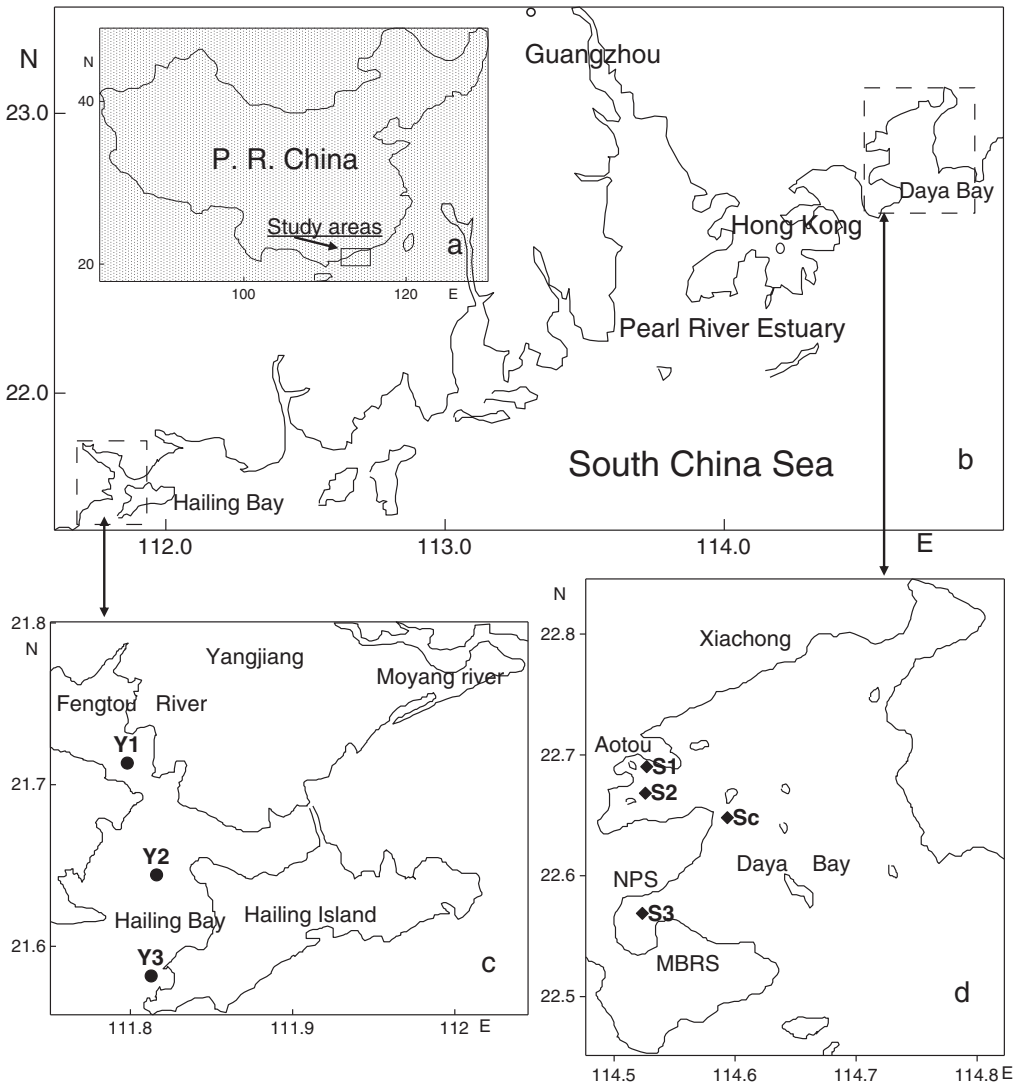


Fig. 1. Sampling locations in Daya Bay and Hailing Bay, South China.

(Zymark, Hopkinton, MA, USA). Twenty percent of the extract was used for lipid content determination with a gravimetric method (Meng et al., 2007) and the remainder was cleaned successively with a gel permeation column and a silica/alumina column. Each sample was concentrated to 100 μL under a gentle stream of N_2. Lastly, internal standards (PCB-82 for OCPs and ^{13}C-PCB-208 for PBDEs) were added to the extract before instrumental analysis. Analytical procedures for processing seawater and sediment samples were reported previously (Yu et al., 2011).

2.3. Instrumental analysis

Concentrations of DDT and its metabolites (*o,p′*- and *p,p′*-DDT, -DDD, and -DDE and *p,p′*-DDMU, sum of which is designated as DDXs and DDXs minus *p,p′*-DDMU is designated as DDTs), as well as HCHs (sum of α-HCH, β-HCH, γ-HCH and δ-HCH), heptachlor, heptachlor epoxide II, aldrin, endosulfan I, endosulfan II, endosulfan sulfate, dieldrin, endrin, endrin aldehyde, endrin ketone and methoxychlor, were determined with a Varian 3800 gas chromatograph interfaced with a Saturn 2000 mass spectrometer in the selective ion monitoring mode. Twenty-four BDE congeners (BDE-15, -17, -25, -28, -35,-47, -49, -66, -85, -99, -100, -116, -118, -119, -126, -138, -153, -154, -181, -183, -190, -196, -206, and -209, sum of which is designated as PBDEs, thereafter) were measured in phytoplankton and macroalgae samples. The procedures for the instrumental analysis of OCPs and PBDEs have been detailed in a previous study (Guo et al., 2009). For OCPs, a fused-silica capillary column (DB-5; 60 m × 0.25 mm inner diameter; 0.25 film thickness, J&W, Agilent) was used for separation. The temperature of the injector was programmed from 60 °C and raised to 280 °C at 200 °C/min (held for 30 min). The oven temperature was programmed from 60 °C (held for 1.0 min), raised to 180 °C at 12 °C/min, increased to 220 °C at 4 °C/min, then increased to 245 °C at 1 °C/min, and finally ramped to 290 °C at 30 °C/min (held at 290 °C for 20 min). To minimize the breakdown of DDTs in the GC injector, *p,p′*-DDT and mixed OCP standard was injected every day to check whether the DDT breakdown occurred, in addition to the use of a temperature program for the injector Guo et al. (2009). For PBDEs, a DB-5 (30 m × 0.25 mm inner diameter, 0.25 μm film thickness, J&W, Agilent) capillary column was used for the measurements from mono- to hepta-BDEs. The column temperature was initiated at 110 °C (held for 1 min) and increased to 180 °C at 8 °C/min (held for 1 min), 240 °C at 2 °C/min (held for 5 min), 280 °C at 2 °C/min (held for 25 min), and 290 °C at 5 °C/min (held for 15 min). For BDE-196, BDE-206, and BDE-209, a DB-5 (15 m × 0.25 mm inner diameter, 0.1 μm film thickness, J&W, Agilent) capillary column was used. The oven temperature was programmed initiated at 110 °C (held for 5 min) and increased to 200 °C at a rate of 20 °C/min (held for 4.5 min) and 310 °C at a rate of 10 °C/min (held for 20 min). The reporting limits (RLs) for DDXs, tri- to octa-BDEs, nona-BDEs and BDE-209 were 1, 0.04, 0.2 and 2 ng g^{-1} for 1 g of

macroalgae or 1 g of phytoplankton on a dry weight basis. In addition, all of the ^{13}C-labeled compounds referenced in the present study were acquired from Cambridge Isotope Laboratories (Andover, MA) and others were acquired from Accustandards (New Haven, CT).

2.4. Quality assurance/quality control

For each batch of 20 samples, a field blank, a procedural blank, a spiked blank, a matrix spiked sample and a matrix spiked sample duplicate were processed. The mean recoveries of the surrogate and spiking standards varied from 58% to 118% and from 58% to 121%, respectively. Detailed QA/QC data are presented in Table S2. The concentrations of BDE-116, -183, -190, -196, -206, and -209 in procedural blanks, which were higher than the reporting limits, were subtracted from the sample measurements. For other BDE congeners and OCPs, concentrations in the procedural and field blank samples were close to or only slightly higher than the reporting limits; therefore blank values were not subtracted out. To ensure minimal degradation of *p,p′*-DDT during instrumental analysis, a standard solution of *p,p′*-DDT was analyzed once for every batch of 10 samples and instrumental analysis could proceed if thermal degradation rate was determined as <20%. Sample analyses were conducted at the State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences.

2.5. Data analysis

Biota-sediment accumulation factor (BSAF) or bioconcentration factor (BCF) is defined as the ratio between the concentrations of a target analyte in biota and in sediment or seawater, which can be calculated by

$$BSAF = C_b/C_s$$

$$BCF = 1000 \times C_b/C_w$$

where C_b (ng g^{-1} dw), C_s (ng g^{-1} dw) and C_w (ng L^{-1}) are the analyte concentrations in biota, sediment and seawater, respectively. Statistical analysis was carried out using SPSS for Windows Release 18.0. Pearson correlation analysis was used to explore the relationship between the variables ($p = 0.05$). *t*-Tests were conducted to check if there was significant difference in the concentrations of the target contaminants between data groups.

3. Results and discussion

3.1. Occurrence of OCPs and PBDEs in algae

Total average concentrations of 22 OCPs (including α-HCH, β-HCH, γ-HCH, δ-HCH, *o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD, *o,p′*-DDT, *p,p′*-DDT, *p,p′*-DDMU, heptachlor, heptachlor epoxide II, aldrin, endosulfan I, endosulfan II, endosulfan sulfate, dieldrin, endrin, endrin aldehyde, endrin ketone and methoxychlor) in both phytoplankton and macroalgae samples from Daya Bay and Hailing Bay are summarized in Table S3. Components of DDT and HCH were detectable in most samples, while other target OCPs were less detectable. The concentrations of DDTs in phytoplankton from Hailing Bay (mean ± SD, hereafter: 844 ± 1054 ng g^{-1} dw) were significantly greater than those from Daya Bay (78.9 ± 46.5 ng g^{-1} dw), while the concentrations of HCHs in phytoplankton from Hailing Bay (202 ± 123 ng g^{-1} dw) were slightly lower than those from Daya Bay (269 ± 375 ng g^{-1} dw). The concentrations of DDTs in macroalgae from Hailing Bay (8.9 ± 6.0 ng g^{-1} dw) were slightly higher than those from Daya Bay (7.0 ± 6.0 ng g^{-1} dw), while the concentrations of HCHs in macroalgae from Hailing Bay (21.5 ± 16.6 ng g^{-1} dw) were significantly lower than those in Daya Bay (67.9 ± 51.8 ng g^{-1} dw). Besides, phytoplankton from Hailing Bay contained higher *p,p′*-DDMU concentrations (16.1 ± 13.0 ng g^{-1} dw) than those (7.9 ± 9.1 ng g^{-1} dw) from Daya Bay. Higher DDT concentrations in both phytoplankton and macroalgae from Hailing Bay than from Daya Bay may be attributed to more intensive agriculture activities and larger amounts of pesticides used around Hailing Bay. This is consistent with our previous results that concentrations of DDTs in water and fish of Hailing Bay (0.5 ng l^{-1} and 159 ng g^{-1} ww) were significantly higher than those in Daya Bay (0.17 ng l^{-1} and 73 ng g^{-1} ww) (Yu et al., 2011). The total average concentration of HCHs in phytoplankton from Hailing Bay and Daya Bay (241 ± 40 ng g^{-1} dw) was much higher than that from the Southern Ocean (1.4 ng g^{-1} dw), which is one of the most pristine environments in the world (Galbán-Malagón et al., 2013).

Concentrations of PBDEs in macroalgae from Hailing Bay (1.0 ± 1.2 ng g^{-1} dw) were lower than those in Daya Bay (10.3 ± 3.2 ng g^{-1} dw), whereas those in phytoplankton from Hailing Bay (90.8 ± 128.7 ng g^{-1} dw) were higher than those in Daya Bay (16.8 ± 43.6 ng g^{-1} dw) (Table S4). The concentrations of PBDE congeners except BDE-209 in both phytoplankton and *Ulva* were low, mostly near the detection limits. BDE-209 was the predominant congener in phytoplankton and *Ulva*, accounting for 89.5% and 86.6% of the total average concentrations of PBDEs (48.5 ng g^{-1} dw and 4.1 ng g^{-1} dw), respectively. By comparison, levels of PBDEs in water and fish from Hailing Bay (mean: 0.16 ng L^{-1} and 4.5 ng g^{-1} ww) were higher than those from Daya Bay (mean: 0.08 ng L^{-1} and 3.6 ng g^{-1} ww; Yu et al., 2011).

Phytoplankton contained significantly higher concentrations of DDTs, HCHs and PBDEs (397.8 ± 748.5, 241.3 ± 289.0 and 48.5 ± 94.0 ng g^{-1} dw) than macroalgae (8.4 ± 5.6, 33.1 ± 32.3 and 4.1 ± 5.1 ng g^{-1} dw) (Table S3), probably because phytoplankton with larger surface area possesses higher uptake efficiency for POPs than macroalgae. As the phytoplankton life cycle is only 2–3 days, these organisms provide a continuous source of suspended particles for biosorption of POPs from water and subsequent deposition onto sediment. For example, vertical distribution of PAHs followed the vertical profile of phytoplankton biomass, and phytoplankton uptake and subsequent transfer to zooplankton drove the sinking fluxes of POPs in the water column (Dachs et al., 1997, 2000). Phytoplankton can passively adsorb and actively assimilate different toxic substances from the aqueous environment (Wilde and Benemann, 1993; Wang and Rainbow, 2008; Smolyakov et al., 2010; Vega-López et al., 2013).

The concentrations of DDTs, HCHs and PBDEs in phytoplankton and macroalgae from Daya Bay were greater in winter than in summer (Fig. 2), as summer is the wet weather season and pollutants in seawater were diluted by flood. In comparison, the concentrations of target chemicals in phytoplankton and macroalgae of Hailing Bay were lower in winter than in summer except for DDTs and PBDEs in macroalgae. Agricultural activities have been quite intensive around Hailing Bay, but sewage treatment capacity is not sufficient in these relatively undeveloped areas (Qiu, 2015). This would result in high pollutant loadings in Hailing Bay due to summer floods draining over these areas. In addition, the nutrients (e.g., N and P) are another important factor for regulating the growth of algae which will affect the pollutant levels in algae.

3.2. Source diagnostics by compositional analysis

The most abundant component of the 22 target OCP in phytoplankton was DDTs (59%), followed by HCHs (36%), while in macroalgae was HCHs (74%), followed by DDTs (19%) (Fig. 3a). *p,p′*-DDMU and heptachlor were detectable in all samples, and other OCPs were detectable in some of the samples only. DDTs were easier to be bio-concentrated in phytoplankton and HCHs tended to be bio-concentrated in macroalgae in the present study, and the results need to be further confirmed. In the environment, DDT may be transformed by microorganisms to DDE and DDD under aerobic and anaerobic conditions, respectively. Although recent work showed that portions of DDE/DDD in sediments were degraded to DDMU and other metabolites

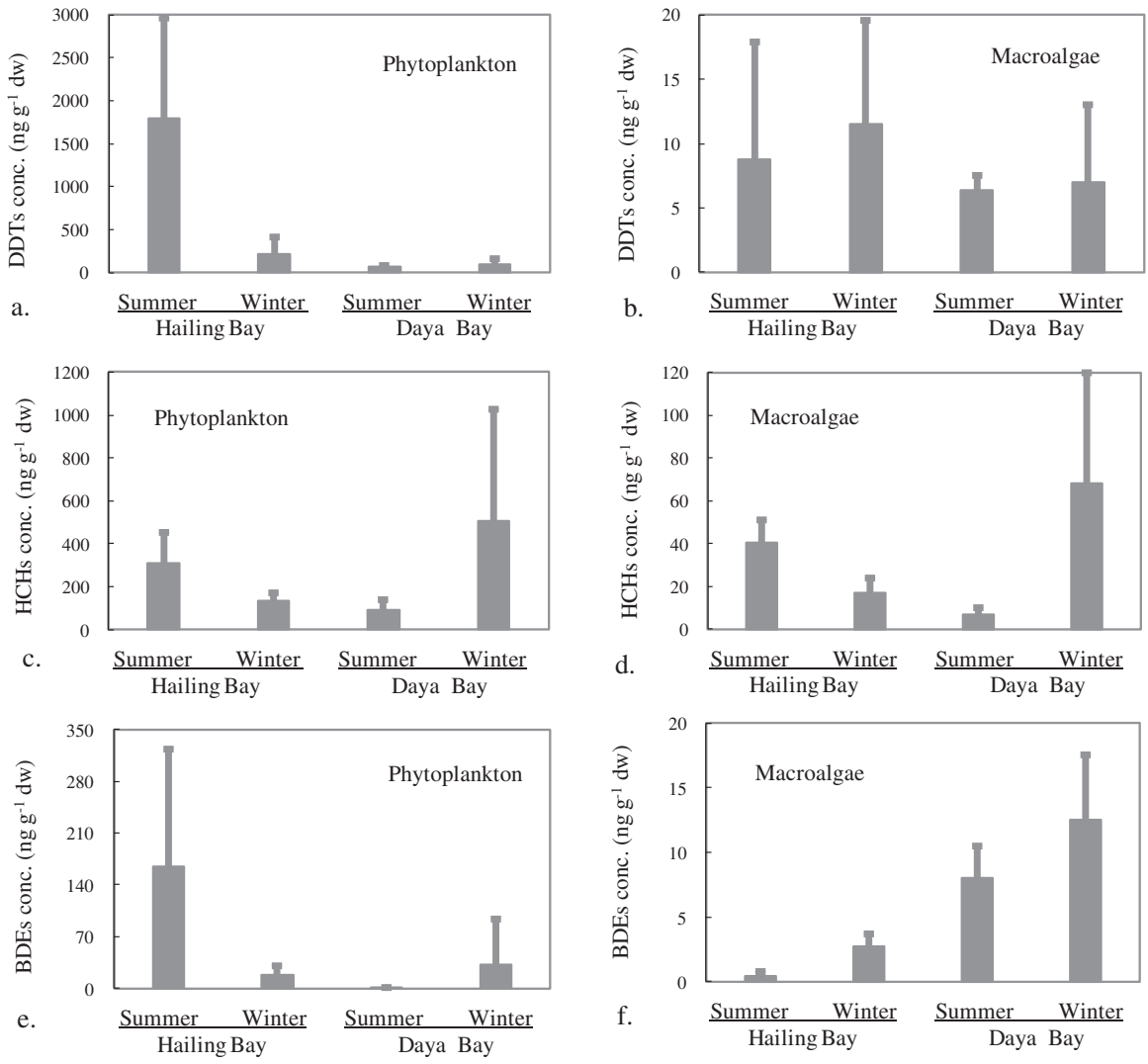


Fig. 2. Seasonal variation of DDT, HCH and PBDE both in phytoplankton and macroalgae from Daya Bay and Hailing Bay of South China.

(Eganhouse and Pontolillo, 2008), the ratio of DDT/(DDE + DDD) which is larger than 1 can still be used to indicate possible new sources (Qiu et al., 2009). In the present study, the mean (±SD) values of DDT/(DDE + DDD) in phytoplankton and macroalgae from Daya Bay were 0.32 ± 0.14 and 0.47 ± 0.10, and were 0.58 ± 0.63 and 0.64 ± 0.15 from Hailing Bay, which were all <1 indicating no obvious fresh inputs of DDTs into the two bays. However, previous studies showed that there were new inputs of DDTs in Daya Bay (Zhou et al., 2001).

Dicofol, an acaricide now widely used in China, was suspected to be a new source of DDTs in the study region (Qiu et al., 2005a). Normally a higher proportion of *o,p′*-DDT than *p,p′*-DDT can be found in dicofol residues. The *o,p′*-DDT/*p,p′*-DDT value was reported as 0.2– 0.26 in technical DDT and ~7.5 in dicofol products (Qiu et al., 2005a). In the present study, the average *o,p′*-/*p,p′*-DDT values in phytoplankton and macroalgae were 0.42 ± 0.24 and 0.36 ± 0.10, respectively, which were much <7.5, but were still higher than that in technical DDT mixture, suggesting that technical DDT was most prominent in algae of the two bays. This was consistent with previous conclusions that ca. 95% of DDTs present in the atmosphere of Chinese cities was from technical DDT with only ca. 5% of dicofol origin (Liu et al., 2009).

Two types of HCHs-related products have been used globally, i.e., technical-HCH (α-HCH/γ-HCH in the range of 3–7) and lindane (γ-HCH > 99%) (Qiu et al., 2009). In the present study, the average values of α-HCH/γ-HCHs in phytoplankton and macroalgae were 0.96 ± 0.81 and 0.50 ± 0.11, respectively, which were lower than those in crop and paddy soils (1.9 and 2.6) in the Pearl River Delta, South China (Li et al., 2006). The relatively lower values of α-HCH/γ-HCH in algae samples than those in technical-HCH implicated lindane as the primary component of HCHs.

Historical mass production and usage of DDT and HCH, as well as the ongoing production and usage of some OCPs and intermediates in China, may have driven the levels of OCP pollution in the study region. Over the past two decades, large-scale transformation of land use has taken place in the study region, mobilizing sequestered contaminants in the process. The fact that the two bays studied are located in subtropical rain-belt would facilitate the release of contaminants from soil. Approximately 2 and 30– 60 tons per year of DDT were introduced to the coastal environment of Guangdong Province from the production of dicofol and anti-fouling paint, respectively (Zhang et al., 2007). Several types of anti-fouling paints used for boat maintenance in the Pearl River Delta were found to contain high levels of *p,p′*-DDT, which may have been another significant source of DDT in the region (Li et al., 2006). Application of DDT for public health issues (e.g., to control mosquitoes that transmit malaria) may have constituted another important source of technical DDT. In addition, domestic sewage and industrial and agricultural discharge are likely to be the source of DDT inputs.

BDE-209 was the most abundant BDE component in both phytoplankton and macroalgae, accounting for 89.5% and 86.8% of the total

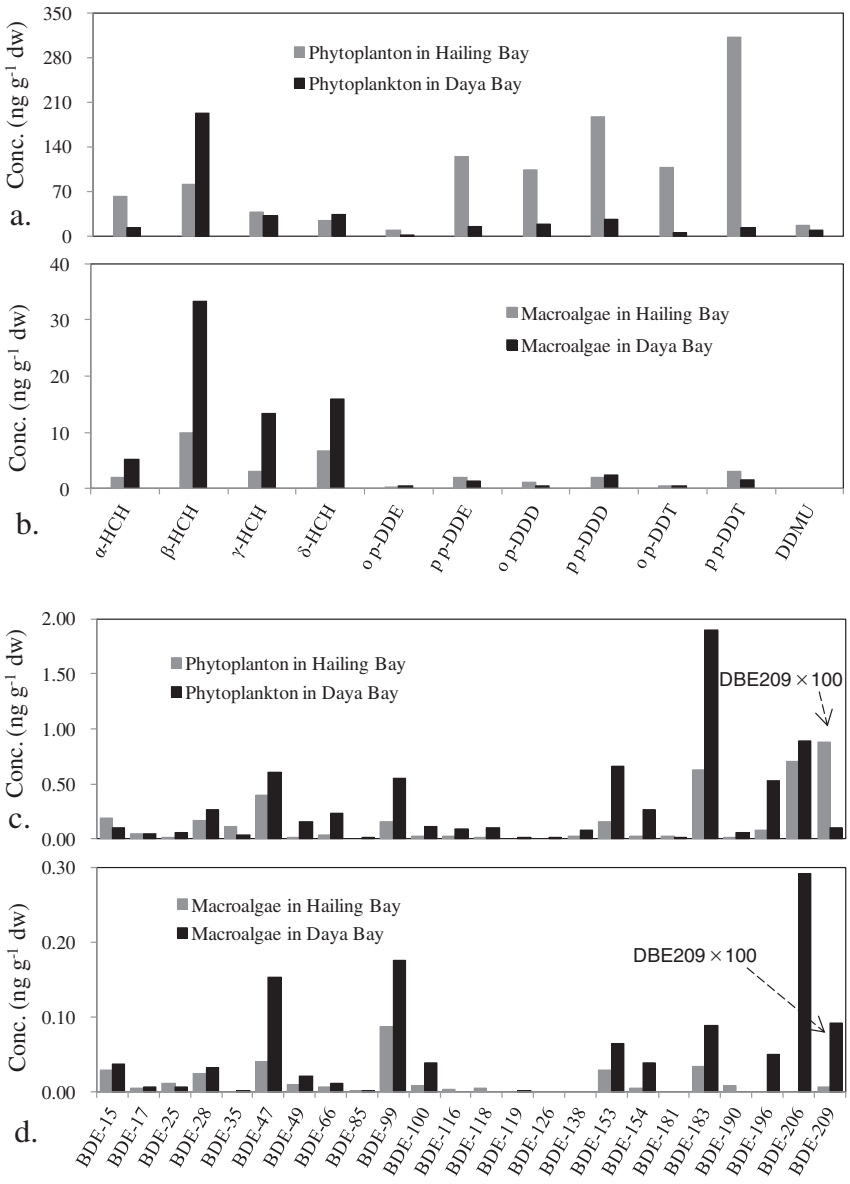


Fig. 3. Composition of DDT, HCH and PBDE both in phytoplankton and macroalgae from Daya Bay and Hailing Bay of South China.

BDE concentrations, respectively (Fig. 3). The top six PBDE congeners were BDE-209 (89.5%), BDE-183 (2.79%), BDE-206 (1.68%), BDE-47 (1.07%), BDE-153 (0.91%) and BDE-99 (0.78%) in phytoplankton, and BDE-209 (86.6%), BDE-99 (2.86%), BDE-206 (2.38%), BDE-47 (1.90%), BDE-183 (1.28%) and BDE-153 (1.00%) in macroalgae. Three major PBDE commercial mixtures are commonly used, i.e., Deca-, Octa- and Penta-BDE, with the amount of Deca-BDE consumed being 30,000 tons in 2005 in China (Zou et al., 2007). A previous study found that BDE congeners in sediments of the Pearl River Delta and adjacent South China Sea were also dominated by BDE-209 (72.6–99.7%; Mai et al., 2005). On the other hand, our previous study showed that BDE-47 was the predominant congener and the BDE-209 concentrations in fish from Daya Bay were relatively low, despite high BDE-209 concentrations in surface sediments (Guo et al., 2008). There were reports that BDE-209 has a low bioaccumulation potential to fishes (Sellström et al., 1998; Boon et al., 2002), though the relatively high levels of BDE-209 in biota were also reported in recent years (Byun et al., 2013; Rochman et al., 2014; Zheng et al., 2016). BDE-209 can be metabolically transformed and degraded to lower brominated congeners, and then be accumulated in organisms at lower trophic levels (Stapleton et al., 2006).

POPs generally enter into algae by absorption, while they enter into fish primarily by assimilating food (Lederman and Rhee, 1982; Wang and Rainbow, 2008). Phytoplankton form the base of virtually all marine food webs, and the total phytoplankton biomass outweighs all marine animals combined (zooplankton, fish and whales). As a consequence of their large surface area and abundant organic carbon content, phytoplankton absorb POPs effectively (Gerofke et al., 2005). Almost all phytoplankton species were significantly affected by POPs (Echeveste et al., 2016). Every species should be its unique strategy to incorporate pollutants. As mentioned above, the composition of the dominant phytoplankton species were different between Hailing Bay and Daya Bay. The present study suggested that algae species may be one of the important factors for regulating PBDE and DDT in algae.

3.3. Assessment of bioaccumulation of POPS in algae BCFs and BSAF

Algae are primary producers in aquatic ecosystems and play a key role in the transport of organic contaminants through the food chain to higher trophic levels. The extent of POP bioaccumulation by algae is related to the characteristics of organic substances, algae species, biomass, lipid content and environmental factors (e.g., Berglund et al.,

2001). In the present study, the average of concentrations in seawater from Hailing Bay and Daya Bay were 0.51 ng L^{-1} and 0.26 ng L^{-1} for DDT, and 0.16 ng L^{-1} and 0.09 ng L^{-1} for PBDEs; while in sediment were 35.9 ng g^{-1} dw and 40.6 ng g^{-1} dw for DDT, and 3.7 ng g^{-1} dw and 75.5 ng g^{-1} dw for PBDEs. The BCFs of DDT and PBDE in phytoplankton and macroalgae from Daya Bay and Hailing Bay are summarized in Table 1. Both BCFs and BSAF of DDT (except for BCFs of *p,p′*-DDMU) in phytoplankton were remarkably higher in Hailing Bay than in Daya Bay. BCFs of both DDT and PBDE congeners in macroalgae were lower in Hailing Bay than in Daya Bay except for a few congeners, while comparable BSAF values in macroalgae from the two bays were observed. The different values of BCFs and BSAF in algae may partly be caused by the different current and historical DDTs and PBDEs pollution status in Hailing Bay and Daya Bay as mentioned above. Similar to the results of bioconcentration of POPs in four species of marine phytoplankton (Gerofke et al., 2005), different composition of phytoplankton species in the two bays would also affect the values of BCFs and BSAF of DDTs and PBDEs in algae. BCFs (10^5– 10^6) of both DDT and PBDE in phytoplankton from the two bays were comparable to those of PCB congeners in phytoplankton from Lake Maggiore of Italian ($10^{5.5}$– $10^{7.6}$, Nizzetto et al., 2012). As the order of magnitude for BCFs of both DDT and PBDE in phytoplankton of the two bays were 10^5–10^6, algae may be the source of these contaminants for organisms in the higher trophic levels. These results suggest that bioconcentration of DDT and PBDE in algae can be an important route for transporting contaminants into organisms of higher trophic levels. Moreover, log BCF of BDEs in algae (phytoplankton and macroalgae) on the whole increased with increasing log K_{OW}.

Phytoplankton cell size is an important parameter determining the absorption sensitivity to POPs (Echeveste et al., 2010). Cell volume has been identified previously as an important factor governing accumulation of POPs in phytoplankton, because small cells have great capability to incorporate chemicals per unit volume (Del Vento and Dachs, 2002). The uptake of POPs first undergoes fast adsorption to the phytoplankton surface and then diffusion into the cell matrix in a partitioning-like fashion (Skoglund et al., 1996; Del Vento and Dachs, 2002). The average BCFs and BSAF of both DDT and PBDE in the two bays were all obviously higher in phytoplankton than in macroalgae (Table 1), further confirming that phytoplankton with larger surface area has higher uptake efficiency for the target analytes than macroalgae.

Table 1
Bioconcentration factors (BCFs) and bioaccumulation factors (BSAF) of DDT and PBDE in phytoplankton and macroalgae from Daya Bay and Hailing Bay of South China.

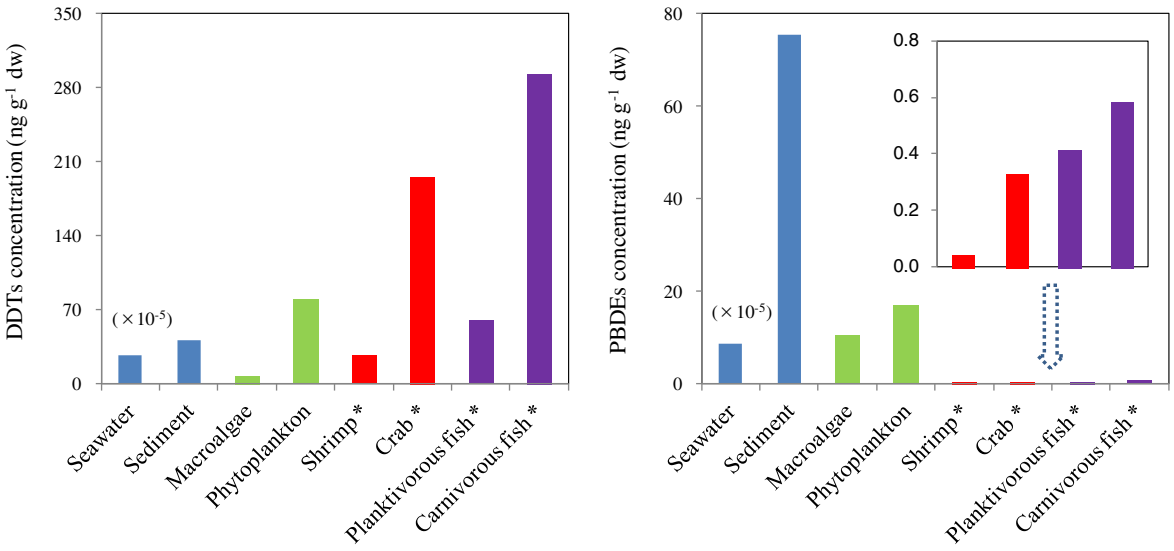
Congener	BCFs in phytoplankton		BCFs in macroalgae		BSAF in phytoplankton		BSAF in macroalgae	
	Hailing ×1000	Daya ×1000	Hailing ×1000	Daya ×1000	Hailing	Daya	Hailing	Daya
o,p′-DDE	1135.6	545.2	21.3	149.4	113.6	4.6	2.1	1.3
p,p′-DDE	1680.7	366.8	27.0	34.5	37.7	4.9	0.61	0.46
o,p′-DDD	3160.0	799.3	36.0	21.8	37.2	6.6	0.42	0.18
p,p′-DDD	1695.5	321.9	17.9	30.3	17.9	2.4	0.19	0.22
o,p′-DDT	1820.7	97.9	9.1	10.3	39.8	1.2	0.20	0.12
p,p′-DDT	1359.5	188.8	13.0	23.0	18.8	0.68	0.18	0.08
DDTs	1642.7	299.2	17.2	26.4	23.5	1.9	0.25	0.17
p,p′-DDMU	204.1	415.8	ND[a]	ND[a]	14.7	5.6	ND[a]	ND[a]
BDE-15	6.8	2.4	1.1	0.87	ND[a]	ND[a]	ND[a]	ND[a]
BDE-28	122.8	137.5	17.5	17.3	45.2	18.7	6.4	2.3
BDE-47	55.9	129.2	5.6	32.5	21.2	17.9	2.1	4.5
BDE-49	ND[a]	ND[a]	ND[a]	ND[a]	2.9	6.3	1.6	0.9
BDE-66	16.8	65.0	2.8	3.1	16.0	86.6	2.7	4.2
BDE-85	<RL[b]	77.0	7.2	17.6	<RL[b]	<RL[b]	1.3	<RL[b]
BDE-99	26.5	98.1	15.3	31.5	16.4	22.0	9.5	7.0
BDE-100	168.4	68.9	58.0	23.2	15.8	17.5	5.4	5.9
BDE-138	19.7	67.8	<RL[b]	<RL[b]	<RL[b]	4.7	<RL[b]	<RL[b]
BDE-153	95.9	438.5	18.2	43.0	6.7	5.1	1.3	0.50
BDE-154	87.6	911.4	19.8	133.5	<RL[b]	85.3	<RL[b]	12.5
BDE-183	56.9	145.9	3.1	6.9	41.7	17.2	2.3	0.81
BDE-196	156.8	675.2	<RL[b]	64.4	33.9	21.3	<RL[b]	2.0
BDE-206	234.9	1104.4	<RL[b]	359.3	<RL[b]	<RL[b]	<RL[b]	<RL[b]
BDE-209	925.9	1209.2	7.0	1117.0	24.4	0.13	0.19	0.12
PBDEs	575.2	191.9	6.0	120.3	24.6	0.22	0.26	0.14

[a] ND: not detected.
[b] <RL: concentration less than the reporting limit (RL) in water or in sediment or in algae.

The effect of growth dilution is another factor regulating the occurrence of chemicals in organisms. Algae growth rate is dependent on various factors, such as nutrient concentrations, temperature and light. Moreover biomass is not only controlled by algae growth, but also by grazed pressure. Higher biomass results in lower concentrations of POPs in phytoplankton, and high phytoplankton growth may also lead to a significant dilution of POP concentrations (Dachs et al., 1999). Red tides, known as harmful algal blooms, have frequently broken out in the coastal waters around the world in the past several decades, and decreased POPs levels in phytoplankton were observed during red tides (e.g., Zhao et al., 2009). In the Southern Ocean, the variability of PCBs concentrations in phytoplankton was significantly correlated with phytoplankton biomass, with lower concentrations in more productive waters (Galbán-Malagón et al., 2013). In the present study, concentrations of nutrients were higher in Hailing Bay than in Daya Bay (Table S1), but did not reach the thresholds normally required to trigger red tides. The BCFs and BSAF of DDTs in phytoplankton were also higher in Hailing Bay than in Daya Bay. This is similar to a previous finding that an increase in ambient nitrogen concentrations considerably enhanced metal uptake by phytoplankton (Wang and Dei, 2001). Under most circumstances the rate of metal uptake increased exponentially with increasing cell growth rate constant. Nutrient enrichment in many coastal waters can considerably affect trace metal uptake in phytoplankton and presumably metal trophic transfer in marine food chains (Wang and Dei, 2001). On the other hand, many studies have reported that nitrogen deficiency induced a significant increase in algal lipid content and enhanced the bioconcentration of POPs (Halling-Sørensen et al., 2000; Zhao et al., 2009; Li et al., 2010; Chai et al., 2013). In the present study, positive correlations between concentrations of POPs (e.g., DDTs, DDMU, HCHs and Σ_{23}PBDE) and lipid contents in phytoplankton were also observed (Fig. S1). As POPs are hydrophobic, they tend to associate with lipids. Positive correlations between concentrations of POPs and lipid contents in organisms have frequently been reported (e.g., Bentzen et al., 1996; Guo et al., 2008; Qiu et al., 2009, 2010). Phytoplankton components other than lipids, particularly abundant organic carbon, are capable of enriching appreciable amounts of POPs (Skoglund et al., 1996).

3.4. DDTs and PBDEs in the natural food chains

The accumulation and transfer of POPs in marine food webs is an important criterion for assessing its ecological risk (Zheng et al., 2016). The cycling of POPs in pelagic systems can be considerably impacted by the interaction of POPs with marine plankton and affected by POPs transfer between marine phytoplankton and zooplankton, which can propagate up to higher trophic levels including humans. When pollutants associated with phytoplankton are ingested by zooplankton, they can be either retained in the organisms, egested as packed fecal pellets or excreted into the dissolved phase, all of which can greatly affect the fate and distribution of pollutants in the marine system (Xu et al., 2001). Marine organisms, such as shellfish and fish, concentrate pollutants by direct absorption from water or uptake through diet. Because of their unique trophic position and importance as food source for humans, they are often chosen as suitable targets for environmental monitoring. Our recent study observed bioaccumulation and trophic transfer of heavy metals (Cu, Pb, Zn, Cd and Hg) in the food web of Daya Bay (Qiu, 2015). Previous results showed that the median concentrations of DDTs, HCHs and PBDEs (sum of BDE-28, 47, 66, 85, 99, 100, 138, 153, 154 and 183) in fish from 11 coastal cities of Guangdong Province were 6.0, 0.50 and 0.15 ng g^{-1} ww (Meng et al., 2007), while those of DDTs, HCHs and Σ_9PBDE (sum of BDE-28, 47, 66, 85, 99, 100, 138, 153



* Data from our previous article (Guo, et al., 2008).

Fig. 4. DDTs and PBDEs levels in the natural food webs from Daya Bay, South China.

and 154) in shellfish were 0.35, 5.3 and 0.11 ng g^{-1} ww (Guo et al., 2007a, 2007b). In the present study, the average concentrations of DDTs, HCHs and PBDEs (excluding BDE-209) were 398, 241 and 5.1 ng g^{-1} dw in phytoplankton and 8.4, 33.1 and 0.54 ng g^{-1} dw in *Ulva*. As water contents in fish and shellfish were approximately 70–80%, concentrations of DDTs, HCHs and PBDEs were actually much greater in algae than in both fish and shellfish. Combined with our previous POPs data in wild organisms from Daya Bay (Guo et al., 2008), concentrations of DDTs and PBDEs in the marine food web from Daya Bay are shown in Fig. 4. The sequence for the concentrations of DDTs was Carnivorous fish > Crab > Phytoplankton > Sediment ≫ Seawater, but it was different pattern for the concentrations of PBDEs: Seawater ≪ Fish and invertebrates (shrimp, crab and fish) < Algae (phytoplankton and macroalgae) < Sediment. Crab is a scavenger in the benthic environment and generally feeds on the carcasses of higher trophic organisms, and shrimp is also a sediment-dwelling predator with similar feeding habits to crab. Fish, on the other hand, primarily live in the pelagic zone feeding on phytoplankton via zooplankton or relatively small fishes. The difference in the concentrations of DDTs and PBDEs between animal species was probably due to the different ecological characteristics of different species such as feeding habits and habitats. The different patterns may also be due to the difference in the physicochemical and biochemical properties of DDTs and PBDEs, wherein PBDEs have higher biodegradability and lower lipophilicity than DDTs.

4. Conclusions

The concentrations of both PBDEs and OCPs were an order of magnitude higher in phytoplankton than in *Ulva*, indicating that phytoplankton with larger surface areas have higher uptake efficiency for POPs than *Ulva*. Seasonal variation of the concentrations of DDT, HCH and PBDE in phytoplankton and macroalgae were different in the two bays, which were greater in winter than in summer from Daya Bay. The BCFs and BSAF of the targeted chemicals were affected by various factors, e.g., cell size, nutrients and lipid content. Concentrations of DDTs in the natural food webs from Daya Bay showed different patterns from those of PBDEs, with the lower DDTs levels in algae than in fish and the higher PBDEs levels in algae than in fish.

Acknowledgments

This work was supported by National Key Basic Research Program of China (No. 2013CB956101) and National Natural Science Foundation of China (No. 41376091, 40573061) to Y.-W. Qiu. We thank Dr. H.-Y. Yu and Dr. Y. Guo for determination of organochlorine pesticides and PBDEs concentrations in algae. Thanks also go to the anonymous reviewers for their kind constructive suggestions on the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.11.192.

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